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PFAS – Forever Chemicals

Report EUT-P4-22FS-04

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Management Summary

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic fluorinated compounds. Today more than 4'700 PFAS molecules are known. These chemicals have a high resistance and physical stability. They repel water, dirt, and grease. Due to these properties they are used in a wide range of products, from ski-wax and waterproof textiles to fire extinguishers and food packaging. PFAS are the most persistent synthetic chemicals. They do not occur in nature, and they hardly degrade in nature. Therefore they are called "Forever Chemicals". The number of PFAS detections in the environment and in various organisms worldwide is increasing. The recognition of their bioaccumulative properties, their high mobility and their adverse effects on biological systems has led and is still leading to a regulation of multiple PFAS molecules. The response of the industry was the introduction of other PFAS as substitutes, which are now themselves increasingly detected in the environment. Worrying is that the list of negative health effects from an exposure to PFAS is becoming longer every year.

Methods

This report is based on two main sources of information. The major part was based on an internet search of technical articles and published academic papers. In addition, various interviews were conducted with experts in the field of environmental PFAS detection, management, and remediation.

Results

Increasingly it seems that wherever PFAS have been used, residues can be found in the environment. In Switzerland, PFAS were used to a large extent in electroplating and in fire extinguishing agents. The most significant hotspots of PFAS in Switzerland therefore, can be found at sites where large fires have been extinguished. Other PFAS contaminated sites can be found at companies working with galvanic, chemical or textile products.

Natural processes for PFAS destruction are nonexistent, therefore to combat accumulation, treatment methods need to be developed to efficiently remediate contaminated compartments. While certain methods are already commercially available, they are expensive, require intensive processing and may not function indefinitely.

It is certain, that PFAS have a wide range of impacts on the human health, new effects are being added every year. Studies also suggest a link between PFAS and certain lifestyle diseases such as diabetes and hypertension, although the extent of the impact is not yet clear.

Future Outlook

More possibilities of neutralizing PFAS in the environment need to be studied, many of which are at time of writing still experimental. It can be said though, that there are promising methods to efficiently remediate PFAS contamination.

A working group is currently developing a plan for solutions on how an entry in the register of contaminated sites or a site delimitation for PFAS can be designed, as well as how remediation, waste treatment or disposal must be handled in the future. The methods for measuring and neutralizing PFAS need to be further researched and improved.

Similarly, the health effects and environmental impact of PFAS need to be better understood and researched, as society becomes increasingly aware of the problem of PFAS in the environment. To determine the full extent of the impact of extensive use of PFAS on various ecosystems and human health, more data needs to be collected.

Unfortunately, many of the effects that PFAS have are not yet known and in all aspects of PFAS in the environment it can be said that much more research needs to be done.

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List of abbreviations

Abbrivation	Definition
10:2 FTOH	10:2 fluorotelomer alcohol
6:2 FTS	6:2 fluorotelomersulfonic acid
8:2 FTOH	8:2-Fluortelomer alcohol
AFFF	Aqueous Film Forming Foam
AIX	Anionic exchange
AltlV	Ordinance on the Remediation of Polluted Sites
ATSDR	Agency for Toxic Substances and Disease Registry
AWEL	Office for Waste, Water, Energy and Air, Canton of Zurich
CAC	Colloidal Activated Carbon
CDC	Center for Disease Control and prevention
ORRChem	Chemical Risk Reduction Ordinance
CPS	Catastre of Polluted Sites
DSSTox Database	Distributed Structure-Searchable Toxicity Database
DUW	Department for Environment, Canton of Valais
EFSA	European Food Safety Authority
EPA	U.S. Environmental Protection Agency
EU	European Union
EWG	Environmental Working Group, an U.S. American activist group
FDA	U.S. Food and Drug Administration
FOEN	Federal Office for the Environment
FOPH	Federal Office of Public Health, Switzerland
IBRE	Institute for Biomass and Resource Efficiency
LC-MS/MS	Liquid Chromatography - Tandem Mass Spectrometry
NAQUA	National Groundwater Monitoring

List of abbreviations

N-Et-FOSE	N-ethylperfluorooctanesulfonamidoethanol
N-MeFOSE	N-methylperfluorooctanesulfonamidoethanol
NOAEL	No Observed Adverse Effect Level
OECD	Organisation for Economic Co-operation and Development
PAC	Powdered Activated Carbon
PFAS	Per- and polyfluorinated alkyl substances
PFBS	perfluorobutane sulfonic acid
PFCA	Perfluorocarboxylic acids
PFCs	Perfluorocarbons
PFHxS	perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid (also kwon as C8)
PFOS	Perfluorooctanesulfonic acid
PNEC	Predicted No Effect Concentration
POSF	perfluorooctanesulfonyl fluoride
PTFE	Polytetrafluoroethylene
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RfD	Reference Dose
RO	Reverse Osmosis
SCWO	Supercritical Water Oxidation
SPIN	Substances in Preparations in Nordic Countries
TWI	Tolerable Weekly Intake
UN	United Nations
VASA	Ordinance on the levy for the remediation of contaminated sites

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic fluorinated compounds which characteristically have at least one perfluorinated methylene group (-CF2-) or a perfluorinated methyl group (-CF3), together with a variable number of carbon atoms and fluorination degree. Today more than 4700 PFAS molecules are known. Their molecular structure and composition give them a high chemical resistance and physical stability, which leads to very slow degradation. Due to their desirable properties such as water, dirt, and grease repellency, they are produced and used in large quantities for a wide range of products, from non-stick pans to food packaging materials and waterproof textiles. At the beginning of the 21st century, the number of PFAS detections in the environment and various organisms worldwide was increasing. The recognition of their bioaccumulative and biomagnifying properties, their high mobility, and their adverse effects on biological systems led to the regulation and phase-out of multiple PFAS molecules. The response was the introduction of other PFAS as substitutes, which are now themselves increasingly detected in the environment and in organisms such as animals and humans. This is worrying in that the list of negative health effects of exposure to PFAS is getting longer every year.

Even though they share certain characteristics, PFAS can differ greatly from each other, in their molecular structure as well as in their properties. This makes among other things the detection, classification, and quantification of specific PFAS difficult. Unfortunately, these are exactly the steps needed to assess the extent and consequences of humanity's use of PFAS. The lack of transparency on the part of the industry doesn’t improve the situation either [1], [2].

The goals of this report are as follows:

- Investigation of the production volumes of PFAS and how and where they are applied.
- Identification of the environmental hotspots of PFAS.
- Exploration of the possibilities of PFAS-measurement and its accessibility.
- Description of proper ways to handle and dispose of PFAS-containing waste.
- Giving an overview of the current knowledge about the effects of PFAS exposure on ecosystems and the biology of organisms.

To obtain the necessary information, a series of interviews were conducted with various experts, as well as an internet and literature search. Of particular importance was an interview with Dr. Rolf Kettler, an expert report of Arcadis, an article in the science magazine Environmental Science & Technology *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022)*, [1], and a collective study of the international journal Toxics [2]. Even though this report also contains information on the global situation regarding PFAS, the main focus lies on the situation in Switzerland. Due to limited capacity, this report does not address the chemical properties of PFAS in depth. Neither does it address the development of PFAS, the methods of detection and destruction, the possible alternatives to PFAS nor the explicit costs which exist in connection to the thematic of PFAS.

This report is divided into five chapters. These deal with the subjects of, Global Production Volumes of PFAS, Hotspots, PFAS-Measurement, PFAS Waste and Remediation as well as the Biological Effects of PFAS Exposure.

2 Methodology

The report was prepared as follows. In order to develop the basic principles, a comprehensive literature research was carried out for each chapter in the first phase. Interviews were conducted to obtain supplementary, up-to-date information specific to Switzerland. The interviewees were various experts from remediation companies, laboratories, representatives of environmental agencies of the cantons and the federal government. The project supervisor compiled a list of potentially interesting interview partners from her network and this list was extended over the course of the research.

The scientific document called "Addressing Urgent Questions for PFAS in the 21st Century" [1] served as the base document, and the topics addressed in this document were taken up and researched specifically for Switzerland. The literature research was based on expert reports, scientific studies, collective studies and federal ordinances.

In order to be able to formulate in-depth, technical statements, interviews were conducted. The potential interview partners were contacted in advance by e-mail for willingness to participate in an interview and to answer our questions on this topic. The questions were discussed and formulated in advance with the project coach. After the declaration of willingness, our specific questions were sent in advance to the respective interview partners and a suitable date was arranged. The interviews were conducted with at least two project members and the Interviewee. One project member conducted the interview and asked the questions. A second project member protocols and notes key statements in addition to posing supplemental questions as needed. The interviews were audio recorded, but not transcribed. The recording served as a support to answer the research question.

The information obtained from the research and interviews is linked together and used in the chapters to answer the questions. The content of the interview participants' statements was integrated into the report. Compared to other pollutants, exposure to PFAS is a problem that has not been known for long, thus, some data gaps resulted. In addition, there are only a few pilot studies and measurements are available locally to draw conclusions. However, the report reflects the current situation and problems in the handling of PFAS in Switzerland precisely because of the interviews.

3 Production Volumes of PFAS

This chapter presents an overview of the volume and application of PFAS. In a first step, it is shown in which products PFAS can be found. Subsequently, the production volumes for Switzerland as well as for other countries are shown. Since many products imported into Switzerland may contain PFAS. Following this, three specific product groups will be discussed. This covers product groups that are particularly relevant for Switzerland.

Per- and polyfluorinated alkyl compounds (PFAS) have been used industrially since the 1950s. The extensive use of PFAS, however, did not begin until the 1970s. Several PFAS chemical groups are still being used today in various processes in the industry. Only some bonds of the specific PFAS group have been banned to date [3]. The usage still occurs thanks to their excellent properties, although awareness of the hazardous nature of these chemicals is increasing. An overview of the possible applications as well as an estimation of the manufactured products containing PFAS in Switzerland and in comparison to other countries (especially the USA) are covered in this chapter. However, this proves to be difficult as the production volumes are often poorly documented in publicly available documents. However, more is known about certain processes and applications of PFAS. These groups are analyzed and discussed in more detail in separate sections. In an OECD (Organisation for Economic Co-operation and Development) study from 2006 indicates that no domestic production of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (two of the historically commonly used chemicals from the PFAS group) occurred in Switzerland and that the total volume of PFOS and PFOA were imported [4]. This statement cannot be made for other forms of PFAS chemicals, as no information is available on them.

Table 1 displays an introductory list of applications in which PFAS have been or are still being used [3] [5]. Nevertheless, this list is incomplete, and several other product groups may contain PFAS. The PFAS are used in these products in a mixture that can vary depending on the application. According to a 2020 paper, there are up to 200 different uses for PFAS [6]. Major manufacturers of PFAS and PFAS-containing products are for example 3M / Dyneon, Asahi, Arkema, BASF, Bayer, Ciba, Clariant, Daikin, DuPont and Solvay Solexis [7].

Table 1: List of applications for possible PFAS containing products

Product group	**Example**
Chemical industry	pesticides, inks, varnishes, impregnating agents, textiles
Detergents and cosmetics	lipstick, eyeliner [8]
Fire extinguishing	Fire extinguisher
Galvanic industry	Watch production
High-performance hydraulic fluids	aviation
Non-stick cookware	pans
Paint and varnish production	special wall paints
Paper industry	greaseproof food packaging, baking paper, refined papers
Photo industry	films, photographic papers

Product group	Example
Plastics manufacturing	Emulsifier
Semiconductor industry	electronic circuit boards
Textile industry	waterproof membranes, functional clothing, shoes, carpets, wallpaper, leather furniture
Waxes	ski wax
Various	Adhesive tape, ammunition, climbing ropes, guitar sides, x-ray film, biocides, cables and wiring, solar panel films, medical prosthesis

3.1 Production Volumes

This section first shows which volumes of PFAS are known for Switzerland. Subsequently, the known PFAS volumes for the world are shown. One of the main markets and producers is the USA. Many of the largest manufacturers come from this country. Further sources of information are the Scandinavian countries.

3.1.1 Switzerland

According to a recent study by the Federal Office for the Environment (FOEN) and Arcadis Switzerland AG in 2021 as well as various other publications, there are only selective figures on the imported and used amount of PFAS in Switzerland. For example, in 2007, 0.3 tons of PFOS were used for the production of semiconductors, photolithography and metal coating [3], [9]. According to the same study, 12-15 tons of PFOS were still stored in AFFF (Aqueous Film Forming Foam) in 2007 [3], [9]. AFFF was and still is used in fire extinguishing foams. The amount of PFOA utilized in firefighting foams in Switzerland was estimated to be 77 kg per year in 2007. The imported amount of PFOA for further processing or in products was estimated at only about 15 kg in 2007 [9].

In 2009 the FOEN/ BAFU published the “Substance flow analysis for Switzerland for PFOS and PFOA” [9]. A more recent version of this document is not available. They state: “For Switzerland, a volume of 28 t/year fluoropolymers (…products/mixtures containing PFCA or PFCA-related substances…) was received” [9]. Perfluorocarboxylic acids (PFCA) belong to the group of PFAS, whereas PFOA is in the group of PFCA.

There are no import and export figures for PFOS and PFOA at the Swiss Federal Customs Administration. Figures can only be provided for fluoropolymers. These are listed in the Table 2. However, it can be assumed that a high percentage of these figures are for semi-finished products such as molded parts, rods or sheets. Imports included both dispersions and solid forms such as pellets or powder [9]. Polytetrafluoroethylene (PTFE) are often referred to colloquially as the most common market brand using PTFE, Teflon and Gortex.

Table 2: Import and export to Switzerland of fluorpolymers in 2020 [10]

Description of goods	Import [t/year]	Export [t/year]
Polytetrafluoroethylene in primary forms	1'184'	702
Fluoro-polymers in primary forms, excl. polytetrafluoroethylene	1'165	331

3.1.2 Other Countries

The following section is largely based on the statements in the report “Substance flow analysis for Switzerland” [9]. Historical data on PFOS production are only available for the USA. In 1997, 1,848 t/year of perfluorooctanesulfonyl fluoride (POSF) was manufactured or imported into the United States. In the same year, worldwide POSF production by 3M was approximated to be 3,665 t/year. POSF is used for the production of PFOS [9], [11].

The study mentioned above examined the global production volume of PFAS. To a large extent, figures based on volumes are only available for the USA. Accurate figures on the actual volumes can scarcely be defined. The total global production of POSF is estimated at 96,000 t for the period 1970-2002 [12]. Volumes declined significantly between 2001 and 2002 due to 3M's phase-out of production. By 2003, 3M had ceased production of POSF-based materials. According to the “Substance flow analysis for Switzerland for PFOS and PFOA” report China first began producing POSF-based chemicals in 2003, and from 2005, when the output in Western countries declined, annual production in China increased due to the increasing applications of PFOS and overseas demand. Approximately 100 t/year was exported to the EU, Brazil, and Japan [13]. It is estimated that global production of PFOA ranged from 3,600 to 5,700 t during the period 1951-2004. An estimated total of 72,000 tons of goods were sold in 2004, with 11,250 to 13,500 tons of active fluorotelomer constituents [9], [14].

Product fact sheets are available on the websites of various companies that manufacture or sell PFAS. The problem is that it is often not specified exactly which substances are contained in the products. For the study "An overview of the uses of per- and polyfluoroalkyl substances (PFAS)" dozens of fact sheets and safety data sheets were analyzed. However, no conclusive results could be obtained within a reasonable period of time [6].

The Substances in Preparations in Nordic Countries (SPIN) is a publicly accessible database containing non-confidential information on substances from the product registries of northern European countries Denmark, Finland, Norway and Sweden. In SPIN database, one can find the information on PFAS containing commercial products available on the market. The study from Glüge et al. [6] provides a broad overview of many categories where PFAS substance were utilized. Figure 1 shows the applied amounts of PFAS in different industrial, commercial and other use categories for these Nordic countries in the period between 2000 and 2017. For this report, these results should be interpreted as a comparison and indicator, but these data cannot be applied globally and the information is non-exhaustive. It is important to note that PFAS and fluoropolymers are not produced in the countries who compile data to the SPIN database [6], [15].

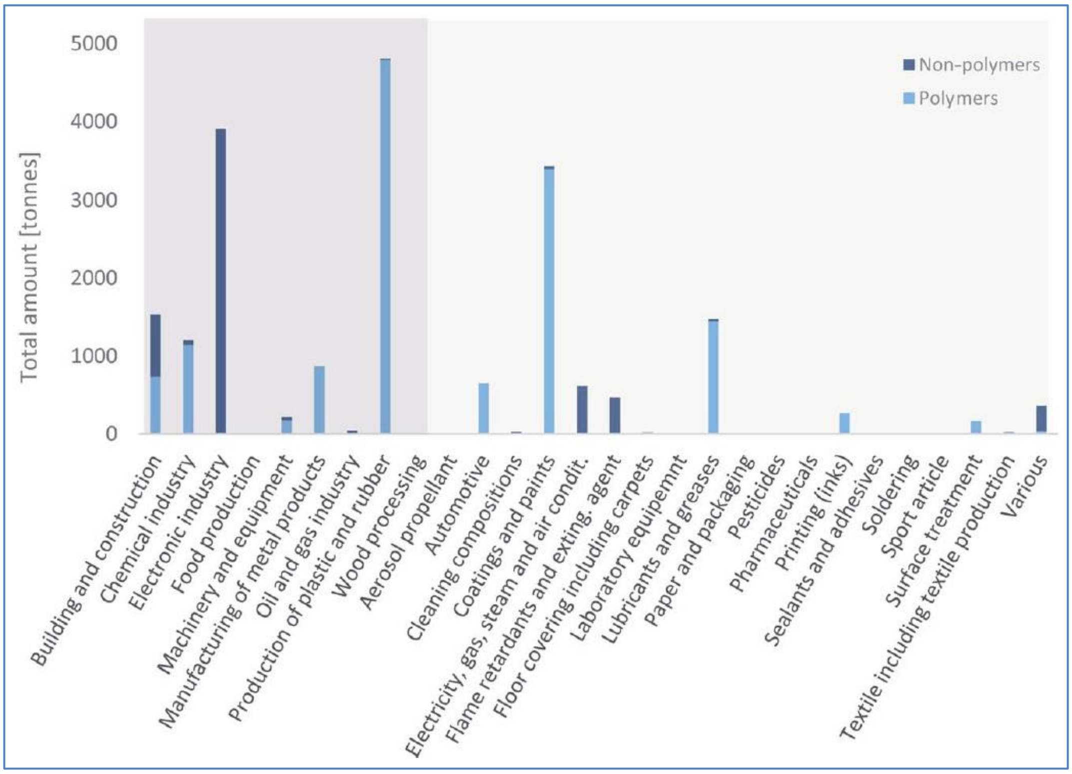


Figure 1: PFAS employed in Sweden, Finland, Norway and Denmark between 2000 and 2017 [6].

The categories "electronic industry", "plastic and rubber" and "coatings and paints" show by far the highest values. Whereby for plastic and rubber approximately 5,000 tons are estimated. According to the study, 6,300 tons of non-polymers were used between 2000 and 2017. At least 13,700 tons of polymers were used in the participating countries during the same period. Of these, 10,000 tons were PTFE. This corresponds to 73% of the polymers used [6]. According to the agcce.com website, 320,000 tons of fluoroplastics were consumed worldwide in 2018. PTFE accounted for an estimated 53% of that total. AGC says it is one of the world's largest producers of fluorochemicals [16].

3.2 Specific product investigations

There are specific products on the market where PFAS was commonly used. These product groups are “firefighting foams", "metal products/electroplating" and "textiles" and are examined in more detail below. These categories were selected because they are all of great importance to Switzerland since all of these products or processes are or were frequently used in this country. In addition, considerably more information is known about these groups than about others. However, the categories are only intended as examples for the products listed in the introduction to this chapter.

3.2.1 Firefighting foams

The use of PFAS in high-performance extinguishing foams has been known since the 1960s. Chemists at the 3M Company developed agents that provided surface tension properties that enable the formation of an aqueous film [9]. In 1985, the U.S. market for AFFF products was 6.8 million liters [9], [17]. It is assumed that PFAS-containing firefighting foams have been used in Switzerland since the 1970s. No production of AFFF has occurred in Switzerland and all the concentrates from which the foam was produced, have been imported. In Switzerland, the production and use of substances with a mass content of 0.005 percent or more of PFOS have been prohibited since 2011 [3]. The environmental impact on PFAS containing firefighting foam is described in greater detail in section 4.1.1. With the ban on PFOS production by manufacturers, mainly short-chain PFAS compounds have been used in firefighting foams in the recent past. In 2005, an estimated 15 - 18 tons of AFFF were stored in Switzerland [18]. The stockpile quantity decreased by 15% to 20% between 2005 and 2007 [9]. Despite this trend, it can be assumed that in Switzerland many fire departments still have PFAS-containing foams in stock and continue to use them. More recent figures on the number of stockpiles in Switzerland have not been found.

The exact composition of AFFF is not known, varies from manufacturer to manufacturer and over time in a product. Although the composition of AFFF is proprietary, several studies provide information on its composition [3], [19].

The following designations are known for AFFF:

AFFF	Aqueous Film Forming Foam
AFFF	(AR)Aqueous Film Forming Foam (Alcohol Resistant)
FP	Fluoro Protein Foam
FP (AR)	Fluoro Protein Foam (Alcohol Resistant)
FFFP	Film Forming Fluoroprotein Foam
FFFP (AR)	Film Forming Fluoroprotein Foam (Alcohol Resistant)

A typical composition of such an extinguishing agent consists of the following components listed in Table 3 [9] [20]. A typical firefighting foam contains only up to 0.45% of the PFAS chemical AFFF. Yet due to the large volume of foam usually employed during firefighting, PFAS is still found extensively at the sights of previous burns or firefighting training facilities (as further discussed in section 4.1.1).

Table 3: Composition of extinguishing foam [9]

Description of goods	**Approximate chemical make up of firefighting foam [%]**
Water	98 – 99 %
AFFF	0.03–0.45 %
Glycol ether	0.50 – 1.10 %
Ethylene glycol	0.34 – 0.60 %
Urea	0.20 – 0.40 %

3.2.2 Metal products / Electroplating

It is well known that PFAS is used in electroplating processes to treat metal or plastic. There is a possibility that PFAS has been or is still being used in the following processes [3], [21]:

Table 4: Electroplating processes containing PFAS [3]

Copper plating	Tin plating
Hard chromium plating	Plastic electroplating
Bright chrome plating	Palladium and rhodium plating
Gold plating	Brass plating
Zinc plating	Galvanizing of polymers such as PTFE on steel

In electroplating, PFAS chemicals are used to reduce surface tension [9], improve the coating of the material being processed, drip off faster, and prevent the mixing of electroplating fluids from different baths [3]. Another important use of PFAS in electroplating is to prevent the formation of toxic chroma aerosols that outgas. In the past, PFOS has been used primarily, but also perfluorobutane sulfonic acid (PFBS) and, to a lesser extent, perfluorohexane sulfonic acid (PFHxS) [3], [21].

The specific substance used in metal plating is the tetraethylammonium salt of PFOS. Imports into Switzerland in 2007 and 2008 combined for this industry are estimated to be at least 560 kg [9]. In comparison, the estimated use of PFOS in the EU for chromium plating in 2007 was 10’000 kg/year [9]. For anodizing and acid pickling, 20-30 kg/year is estimated. This figure corresponds to about 150 kg/year for Switzerland on a per capita basis [9]. Of the three mentioned types of PFAS, PFOS is the longest chained molecule, whereas PFBS is the shortest chained molecule [22], [23], [24].

After the extensive ban of PFOS in 2012, 6:2 fluorotelomersulfonic acid (6:2-FTS) or PFBS were increasingly used. As mentioned PFBS is an explicit shorter chained molecule than PFOS. The 6:2-FTS on the other hand has a similar molecule length as PFOS [25]. However, the two mentioned molecules can only be used for decorative chrome plating [21]. In 2019, at a conference of the Stockholm Convention, the parties decided that the use of PFOS in hard chromium plating should be phased out as soon as possible, but within five years at the latest [26]. The Stockholm Convention is described in more detail in section 3.3. In Switzerland, a significant decrease in the use of PFOS and its substitutes in electroplating has been observed. However, the use of 6:2 FTS has increased [3].

3.2.3 Textiles

Easy-to-clean, waterproof yet breathable textiles are needed for many applications. When textiles are treated with PFAS, fluorotelomer-based polymers, they acquire precisely these properties. In addition, these textiles can be oil repellent and have a higher resistance to mechanical stress and heat. These properties are permanently retained in PFAS-treated products, which makes them very popular. The PFAS that have been and are generally used for textile treatment are N-MeFOSE and N-Et-FOSE [9], [27].

In textile manufacturing, PFAS have been used since the early 1960s for soil- and water-repellent finishing of textiles. These include technical textiles for the automotive industry or the construction industry, such as fleece. During production, the fabrics are coated with layers of PFAS polymers. PFAS are or have been used in the following application areas [3], [21]:

Table 5: areas of application for PFAS containing textiles [3]

Protective clothing for police, firefighters, military	Various textiles in the automotive and aerospace industries
Lifting and carrying belts	Tapes, gaskets, insulation products
Bulletproof vests	Outdoor sun protection textiles
Protective clothing in medicine	Technical textiles and seals in the construction industry
Protective clothing in the chemical industry	Tents
Functional outdoor clothing	Filter media for industrial dust removal
Air and liquid filter materials	Tablecloths with stain protection

In addition, impregnating agents may contain PFAS, in which the chemicals are applied during final product processing or in private use [3]. In Switzerland, textiles may currently still be placed on the market with a PFOS content of a maximum of 1 $\mu g/m^2$ (ChemRRV, Annex 1.16, Number 1.2) [28].

The majority of textiles treated with PFAS are imported from Asia. In 2007, more than 10,000 tons of textile finishing agents containing fluorine were imported into China to treat garments [13]. In the same year, imports of textiles and clothing potentially containing Perfluorocarbons (PFCs) into Switzerland amounted to approximately 16’000 tons and 8’000 tons, respectively, according to statistics from the Swiss Federal Customs Administration [9].

In the “Substance flow analysis for Switzerland”, an overview was provided for the year 2007 as well as for the historical use of selected PFAS in imported textiles and clothing [9]. These can be viewed in Table 6. 8:2 FTOH has by far the highest historical usage. However, according to the Stockholm Convention, this substance is now subject to a ban (See section 3.3). Unfortunately, more recent data are not available for this report. It can be assumed though that the substances used in the textile industry have changed significantly in the meantime, partly due to bans.

Table 6: Imports to Switzerland, estimated amounts in textiles and clothing [9]

Substance	**Use in 2007 [kg/year]**		**Historical use [kg/year]**	
	Best guess	Range	Best guess	Range
PFOS	0.5	0.05 – 8	5	0.5 – 80
PFOA	2	0.2 – 10	20	2 – 100
N-MeFOSE	0.7	0.07 – 7	7	0.7 – 70
N-EtFOSE	0.1	0.01 – 1.5	1	0.1 – 15
8:2 FTOH	200	20 – 2800	200	20 – 2800
10:2 FTOH	9	0.9 - 30	9	0.9 - 30

3.3 Legal restrictions for the use of PFAS

This section will describe the current, various legal restrictions to PFAS usage in the EU, Switzerland and the USA. A majority of the legal work in Europe is based on the Stockholm Convention on Persistent Organic Pollutant. (Stockholm Convention, for short). The Stockholm Convention regulates bans on persistent pollutants under international law. The Convention became effective in 2004 and has been ratified by 185 countries. Among the banned substances are PFOA, its salts and related compounds [26]. Both the EU and Switzerland have implemented the Convention in the below mentioned EU regulation respective in the Swiss ChemRRV.

According to the European Union (EU) Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), the following regulations will apply to PFOA, its salts, and PFOA-related substances/precursors as of July 4, 2020 [29]:

1. “Shall not be manufactured, or placed on the market as substances on their own from 4 July 2020.”
2. “Shall not, from 4 July 2020, be used in the production of, or placed on the market in:

   (a) Another substance, as a constituent;

   (b) A mixture;

   (c) An article in a concentration equal to or above 25 ppb of PFOA including its salts or 1’000 ppb of one or a combination of PFOA-related substances.”

In addition to these two articles, four others clarify the provisions or explain exceptions. As of July 2022, the mentioned compounds are also banned in equipment used to manufacture semiconductors and latex printing inks. As of July 2023, their use is banned in textiles for the protection of workers, membranes intended for use in medical textiles, filtration in water treatment, production processes and effluent treatment, and plasma nanocoatings. The REACH is equally and directly applicable in all states of the EU [29].

In Switzerland, the regulations of the Stockholm Convention are laid down in the Chemical Risk Reduction Regulation (ChemRRV). The ChemRRV is an ordinance which restricts or prohibits the handling of particularly hazardous substances or regulates their handling. It states that the use of PFOA, its salts and precursors are banned for use since June 2021. The production and use of PFOS have been banned since

2011 and similar requirements apply to PFOA. However, there are exemptions for the use of PFOS as well as PFOA. These requirements are regulated in Annex 1.16 Per- and polyfluorinated alkyl compounds of the ChemRRV [28].

In comparison, the U.S. Food and Drug Administration (FDA) reached a voluntary agreement with manufacturers in July 2020 to phase out certain short-chain PFAS in food packaging [30]. Under the 2010/2015 PFOA Stewardship Program, eight global leading chemical producers, such as 3M / Dyneon, DuPont and Asahi along with the United States Environmental Protection Agency (EPA), agreed to remove PFOA and PFOA-related chemicals from their goods and as emissions from their factories [8].

4 Hotspots of PFAS

The usage of PFAS chemicals in various industries and products has left a legacy of PFAS contamination in different environmental compartments. In the following chapter the most important occurrence sites of PFAS in Switzerland are described. Further, how the polluted sites are listed and managed, as well as what can be considered a hotspot in general, and where they can be found is presented. In addition to extensive research, eight interviews were conducted with experts and some cantonal authorities to show the current viewpoint of the PFAS issue at the cantonal and federal levels. The interviews also helped to understand and reflect on the situation in Switzerland.

4.1 Main hotspots in Switzerland

Initially, a definition for a hotspot and its characteristics was outlined. As described in Chapter 3, PFAS are used in a wide variety of products and manufacturing processes. Namely, these compounds are utilized extensively in industrial/manufacturing activities, including the manufacturing of packaging, textiles, firefighting foams, semiconductors, pesticides, and protective non-stick coatings. However, it is not possible to speak of a hotspot for every application or every product, as PFAS can be detected in low concentrations almost worldwide.

Many measurements that have already been made in groundwater or at known contaminated sites are not available to the public. This creates a data gap, making it impossible to assess the exact extent of environmental impacts. In addition, the extent to which these low environmental concentrations impact human health and the environment is not clear, more information about this topic can be found in the chapter 7. For this reason, a “hotspot” was not assessed in this report based on the concentration of a measurement sample. Rather, with the help of the interviewed experts, locations were identified where large amounts of PFAS would likely be found.

4.1.1 PFAS-containing firefighting foam

All eight experts and cantonal authorities interviewed described the sites as the largest or at least the best-known hotspots in Switzerland where firefighting foams containing PFAS were used. This mainly concerns fire extinguishments, fire training areas, fire stations area, and plant fire brigade [3].

The use of PFAS in high-performance extinguishing foams has been well known since 1963. As previously mentioned, from the 1970s, PFAS-containing extinguishing foams were widely used in Switzerland. In general, for fire extinguishing, the PFAS-containing foams (e.g. AFFF-, FFFP-, FP-foams) were predominantly used in liquid fires or melting solids. The application area of these foams was to prevent the rapid spread of the fire and fire gases. The foam is applied to the source of the fire and forms a thermally stable liquid film [3]. This film is applied to the source of the fire and separates it from the surrounding area in an airtight manner. Unfortunately, due to their good extinguishing performance, PFAS-containing foams have been used for more than just liquid fires. Recent incidents have shown that foams have been used for fires where it was not necessary. After extinguishing, there are several ways in which the pollutants can enter the environment. They can run off with the mixed water into the soil, groundwater, sewer leaks or ditches [3].

Fire training areas deserve special mention. On such sites, high PFAS inputs into the soil and groundwater have occurred repeatedly. Many professional and plant fire departments have a fire training ground.

The pollutants seep into the soil or drainage ditches. There, after rainfall or flooding, they can lead to secondary contamination around these sites [3].

M. Voutaz supplemented in the interview that there are numerous sites where firefighting has been frequently simulated. For example, refineries and various chemical industries seem to stand out in this regard. Found on the grounds of most of these industrial facilities are almost always plant fire departments, which regularly practiced firefighting drills for liquid fires on the premises with foam containing PFAS *(M. Voutaz, Research Associate Section Contaminated Sites, Soil and Groundwater, Canton of Valais, Interview, 09.05.2022).*

Other places where AFFF foams are typically used can be found at large plastic processing plants, tire manufacturing, airports, and military airfields. In some instances, automatic release foam extinguishing devices have been installed at large warehouses and handling facilities that operated with explosive goods or liquids. These were sometimes triggered by malfunctions and led to contamination [3].

Some fire departments have been known to have contamination similar to fire training areas. These resulted from cleaning operations and unprofessional handling of chemicals. Known cases have also occurred at locations where no one would have suspected PFAS, such as at sites where foam parties were held at fire department festivals in the 1990s [3].

According to Dr. Rolf Kettler, another problem with firefighting foams is that fire departments do not know precisely what chemical compound the foams contain. The knowledge of such compositions used are often trade secrets. In other words, there is a high probability that in many places there are still foams containing various PFAS compounds *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

Case Studies of Environmental contamination from PFAS containing firefighting foams:

The following is a brief description of two Swiss cases where the contaminated sites have been remediated. Canton Thurgau, city of Egnach, fire at a fruit processing plant:

The following fire case and the resulting problems, B. Schmid summarized as follows. In March 2018, a large fire involving many plastic containers occurred at a fruit processing company in Egnach. Foam containing PFAS was used to extinguish the melted and burning plastic containers. During the emergency response, the runoff water and foam were discharged directly into the sewer system. At one point, the sewage system reached its capacity limit, due to the large quantities of foam utilized to extinguish the plastic fire, and the foam was then directed to an undeveloped property. Most of the foam subsequentially seeped away, into the soil and subsurface or was laterally transported until the next day.

In order to bring this incident under control, many different fire departments of the canton were deployed. Most of them were packed with all available foam reserves. After the event, suspicions quickly arose that older PFAS, and PFOS-containing foams had also been used in the rush. This was despite the fact that PFOS-containing foams are banned under the Stockholm Convention. Subsequent analyses of soil samples showed PFOS levels around 1 milligram per kilogram (mg/kg). To prevent the spread of the pollutants, the canton immediately ordered an evaluation of the extent of the contamination and the remediation of the impacted soil and subsurface materials. Friedlipartner AG was tasked with the environmental investigation and remediation management of this project. In as little as 2 weeks after the fire, it was found that the mobile PFOS could be detected down to a depth of 80 cm. Thus, the contaminated site was excavated to the extent and depths of known PFAS contamination. A portion of the excavated material was treated in a soil washing plant, the remaining portion, as well as the filter cake remnants from soil washing had to be thermally treated in a hazardous waste incineration plant *(B. Schmid, Senior Expert Contaminated Sites / Disposal, Friedlipartner AG, Interview, 21.04.2022).*

Figure 2: Photo shows the extent of the major fire at Tobi Seeobst in Egnach TG [31].

Canton of Wallis, city of Visp, Lonza Group AG chemical production plant:

The second incident concerns a former fire training area of the Lonza Group AG plant fire department. From the 1970s until the 2000s, the extinguishing of chemical fires were regularly practiced on this site by local firefighting departments. Subsequently, about 80,000 tons of soil were contaminated with PFAS [32]. Figure 3 displays the extent of the soil contamination around the training area. This soil is now being removed and cleaned by a specialized company out of Austria. At the same time, groundwater down-gradient from the fire training area will be treated for up to ten years [32]. In Visp, the remediation of the old Lonza fire training area has already begun in 2020 and is one of the first PFAS remediations in Switzerland [33].

Figure 3: Map shows concentrations of the site. PFAS concentrations are displayed in mg/kg [34].

However, this is not an isolated case. The Department of the Environment (de. DUW) of the Canton of Valais, has investigated groundwater downstream of sites that may be contaminated due to the use of PFAS in firefighting foams or industrial processes, and upstream of drinking water wells. These investigations have shown that a total of five sites exceed PFAS limits and require remediation. One additional site is to be monitored. All samples in the inflow from operated drinking water wells are uncontaminated. The sites to be remediated are the industrial sites in Visp, Evionnaz, Monthey and Collombey, and the civil defense training center in Grône. Further investigations have been initiated at the sites and measurements have been requested by DUW [33].

4.1.2 Galvanic industry

In the electrochemical surface treatment of products made of metal or plastic, electroplating for short, the use of products containing PFAS is widely known. The galvanic processes in which PFAS were mainly used can be found in chapter 3. In the treatment process, the PFAS compounds are used to improve the wetting of workpieces or to make the solutions drip off the workpieces faster, as well as to avoid the mixing of the electroplating liquids of the individual baths.

The main points of entry are in the storage of the PFAS-containing agents, in the baths and draining areas, the liquid lines, the process engineering treatment of the electroplating baths and sewers. After switching to fluorine-free wetting agents, PFOS could still be detected in the microgram per liter (µg/l) range after one year because the PFOS strongly adhered to the basin, tank, and pipe walls [35].

In some interviews the question was raised whether it was necessary to investigate the electroplating industries in more detail and how this should be approached. The opinion emerged that it would make sense to investigate these places where there have been known entries. However, the question is how, in which period and with which resources. Dr. Rolf Kettler summarized that the data situation is not yet sufficient to justify systematic action. The individual cantons hosting these industries can consider whether they should carry out measurements. Then it could be determined whether or not there are systematic problems at such sites. As a result, it could be deduced whether there are companies that have used larger amounts of PFAS. The assessment will be made individually from site to site. There is certainly no special measurement program planned for specific branches of industry. The procedure is currently being worked out by the FOEN and multiple cantons, if and how the sites contaminated with PFAS are to be entered in the Cadastre of Polluted Sites (CPS; de. Kataster der belasteten Standorte [KbS]) *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

On behalf of the FOEN, the company Hauser & Walz GmbH wrote a report on the use of fluorosurfactants in the electroplating industry [36]. This is extensive and contains numerous additional detailed information about the products used and areas of application, occurrence and structure of the plants.

4.1.3 Paper and textile industry and other chemical products

As previously stated in the chapter 3, PFAS compound is used in various applications in the paper and textile industries. According to current knowledge, PFAS are used in the paper industry almost exclusively in the production of water-, grease- and dirt-repellent food contact papers, such as packaging or baking papers [3]. For other papers, which do not have to have these or similar characteristics, it can be assumed that no PFAS was used.

Recently, a large-scale contamination was discovered in southern Germany [37], which was a result of pressed sludge from local paper production being applied as a fertilizer amendment to fields. The affected soils show significantly elevated concentrations of various PFCA and PFOS. Interestingly, most of the fluorinated compounds detected in the contaminated soils were precursor compounds. This could be problematic at this site because mobile perfluorinated PFAS are created from these precursor compounds and can lead to significant groundwater contamination. It is presumed that the entry of PFAS at manufacturers of specialty papers can be found in storage and coating, as well as in the process water system [3]. It has not been possible to conclusively clarify whether similar exposures have occurred in Switzerland. The paper industry was less represented in Switzerland than in southern Germany. However, there are or were factories that produced paper. In this respect, it would have to be analyzed in more detail and additional data would have to be collected to determine whether similar exposures occurred in Switzerland.

Other PFAS applications were in the manufacture of paints, printing inks, putties, in paint and varnish production, cleaning and cosmetic products, aviation-specific hydraulic fluids, and in other chemical products such as pesticides, surfactants in petroleum production, as well as in sealants and lubricants. These are described in more detail in the document called Decision Bases for Enforcement at PFAS Contaminated Sites in Switzerland [3].

4.1.4 Monitoring and mapping

The structure and functions of monitoring and mapping will be explained in the following section. This will include addressing how polluted sites should be entered and how already known Cadastre of Polluted Sites (CPS) entries might be handled.

According to Dr. C. Guggenheim, the working group of the FOEN and the involved cantons are currently working on a concept how to list and map the loads with PFAS. Once a concept is defined, the cantons will implement this approach. Depending on the outcome of the working group, the cantons still have some leeway on how they want to record sites polluted with PFAS. So far, the procedure for an entry in the Cadastre of Polluted Sites varies from canton to canton *(Dr. C. Guggenheim, Scientific Officer, Building Directorate Canton of Zurich, Contaminated Sites Section, Interview, 11.05.2022).*

Dr. Rolf Kettler indicated that if the mapping is done through the CPS, the process would be as follows. The monitoring and mapping are part of the contaminated site management, which always works in step-by-step manner. First, a cadastral entry is made, initially without investigation, but on the basis of good indications that there may be contamination of a site. Consequently, the responsible canton must assess whether the site must be investigated. Then two possible scenarios follow. Either the site may have contamination present, but the pollution is determined to be neither requiring remediation or monitoring for the protection of the environment or the legally protected good. An entry is made only that if this site is acquired or built on, that the owner is in the knowledge that there is a burden existing there. This is the most common case that occurs. The other scenario is that a site must be investigated due to its historical usage or of a suspicion of existing contamination. In terms of PFAS, there will certainly be quite a few such sites in the future.

If the canton decides to carry out a more detailed investigation, two results can be obtained. Either nothing further has to be done or the site has to be remediated. However, there are borderline cases as to whether there is a need for remediation or not. In this case, additional measurements are taken to clarify whether a trend in pollutant levels can be identified and how the concentrations change over time. If this occurs, there is a need for monitoring. This need for monitoring does not indicate a need for remediation, it is only a transitional phase to gain additional knowledge. After the transitional phase, the final classification is made.

If a site is in need of remediation, it has a clear negative impact on the environment. When a site needs remediation, it automatically remains also in need of monitoring. If necessary, immediate measures must be taken prior to remediation. For example, in the case of drinking water wells, if it is found that there is or was a PFAS discharge, the water must be treated before it is released. In the worst case, the well must be taken out of operation until the remediation would be completed *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

Consequently, the question arises whether it would make sense to test all contaminated sites for PFAS as well. Dr. Rolf Kettler was convinced that this would not be necessary. This is because many of the sites already registered, such as shooting ranges, are not suspect for PFAS. These may very well have some background contamination, but there is no knowledge that PFAS were used in the bullet traps. Therefore, the exposure to PFAS is not likely to be greater than the rest of the surrounding area. If there is no concrete evidence that PFAS have been used, it can be assumed that no testing for PFAS is necessary. However, if it is known or suspected that, for example, a large company with its own fire department is or was operating on this site, or if there is an oil storage facility or similar, it will be necessary in the future to investigate PFAS in the surroundings of the site. Especially if there is knowledge about accidents or fires, as well as whether exercises have taken place with extinguishing foams *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

A new NAQUA study (de. Nationale Grundwasserbeobachtungsstudie) on national groundwater monitoring is currently underway on behalf of the FOEN. In this, measurements are being carried out in groundwater at over 600 different locations and also tested for over 20 PFAS. The results have not yet been published but can be expected shortly *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

4.2 Approaches of two cantons

The following section contains information on the approaches of two cantons, canton of Zurich, with its active investigative methodology and with the canton of Solothurn, whose approach is rather passive regarding the handling and investigation of PFAS. The two cantons were chosen to show different approaches and not to evaluate or question them. Each canton in Switzerland has some leeway to address the issue. The selected cantons serve as an example, but other cantons could have been compared as well.

In the canton of Zurich, no systematic and periodic measurements in groundwater or solids for PFAS are planned at the moment. However, the canton participated in the new NAQUA study and is waiting for the results. The canton has indeed commissioned initial individual investigation studies. For example, a pilot study with measurements in groundwater was carried out. This pilot study included 9 toxicologically weighted individual substances in 19 investigated sites, which were divided into 5 categories. These are: fire sites (de. Brandfälle), fire training sites (de. BÜP), electroplating sites (de. Galvaniken), other industries from the chemical and textile sectors (de. andere Industrien), and landfill sites (de. Ablagerungsstandorte).

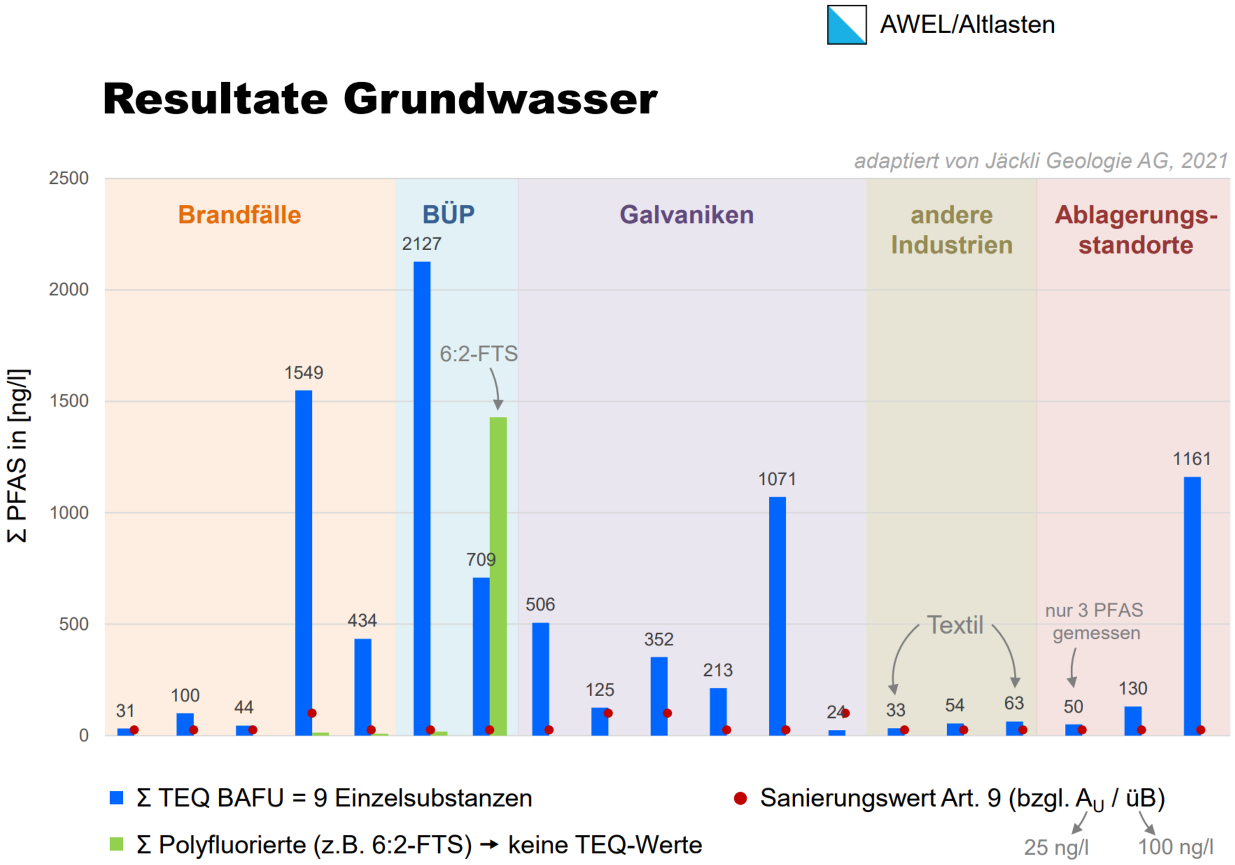


Figure 4: Results of the sum of PFAS in groundwater from the Canton Zurich's pilot PFAS investigation. Results displayed in nanograms per liter (ng/l) [38]

As shown in Figure 4, PFAS were found everywhere at concentrations ranging from 24 to 2127 ng TEQ/l, which is above the remediation level, described in chapter 5.2 in many places. According to Dr. Carole Guggenheim, there is too little knowledge about what the high loads are resulting from, what limits should be observed or about the background load. This lack of knowledge does not allow a definitive assessment of the situation, but serves as a point of reference for the current situation *(Dr. C. Guggenheim, Scientific Officer, Building Directorate Canton of Zurich, Contaminated Sites Section, Interview, 11.05.2022).*

If remediation is carried out, nevertheless, for substances such as PFAS that are not included in Annex 1 of the Contaminated Sites Ordinance, the site-specific and toxicity-weighted limit values must be derived and approved by the FOEN. For the sites that have already been remediated, as well as for those that will follow, it is necessary to approve the limit value. The limit value depends on what kind of material it is. This is different, for example, if it is soil or if it is groundwater. As described in the chapter 4.1.4, there is currently a lack of omit knowledge to know how in the future the polluted sites will be listed and how systematically or not they will be checked. Until the next specifications in the form of a leaflet or an enforcement aid have been developed, the Canton of Zurich can order remediation at sites obviously contaminated with PFAS and have a limit value approved by the FOEN on a site-specific basis *(Dr. C. Guggenheim, Scientific Officer, Building Directorate Canton of Zurich, Contaminated Sites Section, Interview, 11.05.2022).*

The Office for Waste, Water, Energy and Air (de. AWEL) expects expert companies to integrate PFAS into the reprocessing of contaminated sites. The pilot study shows that PFAS has been found at many sites. Based on the available results, this substance class must be included in investigations and monitoring if PFAS are suspected. However, many questions are still open in the assessment, such as how a CPS discharge is designed or how a site boundary is drawn. Other questions arise as to how remediation should be carried out, how waste should be classified, or how waste treatment and disposal should be handled. The AWEL of the Canton of Zurich is currently developing solutions to these problems *(Dr. C. Guggenheim, Scientific Officer, Building Directorate Canton of Zurich, Contaminated Sites Section, Interview, 11.05.2022).*

In the canton of Solothurn, targeted investigations of suspected PFAS sites are not currently planned. The recording and assessment of soil areas and polluted sites contaminated with PFAS are costly. In view of the great toxicological relevance of PFAS, this effort would be justified fundamentally. However, a prerequisite for systematically tackling these tasks is a corresponding legal basis and associated federal enforcement aids. If necessary, cantonal legislation must also be adapted [40, p. 6].

The following statement was confirmed by Cantonal Councilor Ms. Marlene Fischer from Solothurn: As long as the regulatory framework in the form of a leaflet or an enforcement aid has not yet been established, the canton of Solothurn sees no need for action for additional investigations. For cost reasons, the canton takes a defensive stance. First, relevant sites would have to be identified. For this purpose, a pilot study would have to be carried out at sites with a particular suspicion of PFAS before a systematic investigation of sites in the CPS or, for example, at fire training areas could be carried out. The canton is aware that if investigations are ordered, PFAS are likely to occur, and these sites would have to be remediated if the levels are too high. There is an understanding of the position that official federal guidance is awaited first, but it would be desirable that the canton take a more proactive stance and begin to conduct initial investigations *(M. Fischer, Environmental Geologist, Msc ETH, Cantonal Councilor Green Party, Interview, 22.04.2022).*

More detailed insights into the viewpoint of the Canton of Solothurn can be found in the interpellation of Ms. Marlene Fischer, as described in [40, p. 1-7].

4.3 Approaches of the FOEN

There is a suspicion of background contamination in Switzerland, states Dr. Rolf Kettler. Therefore, caution is required when determining a remediation value. It should not be lower than the value of the background pollution. This would lead to problems in various future building projects. If a construction project were to start on a building site that is registered in the CPS but does not require remediation, the contaminant loads would first have to be measured and this time to include measurement of soil, underground and ground and/or surface waters for PFAS. In the case of the remediation value being lower than the background level, a property would thus remediation. This would be despite the fact that no direct PFAS input has occurred on the site, meaning presumably, for example, the same concentration could be measured on the neighboring parcel. This would not be feasible or manageable. For this reason, the FOEN is currently working with the cantons on a concept of how to deal with the problem of a background concentration of PFAS in the future *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

The National Soil Monitoring of Switzerland periodically measures around 114 measuring points on uncontaminated sites such as meadows, fields, parks, green spaces, and forests for a variety of pollutants and records changes. The FOEN had some of these samples analyzed for PFAS. The first results of soil samples taken from the top 20cm suggest a background contamination at which the eluate could already be critical from a toxicological point of view. The specific results have not yet been officially published, but they show the current problem. The assessment is a great challenge for the engineering offices and the cantons. There is a background load of PFAS in various environmental compartments and the FOEN is currently working with the cantons to find a solution for how best to manage this situation. It will not be possible to remediate the background pollution throughout Switzerland. Therefore, special attention is given to the reduction of the input. It can be assumed that already the input is in a critical range, likely caused by atmospheric sources, for instance by precipitation, dust, and wind. Realistically, it must probably be assumed that sites will already have to be remediated before further bans on PFAS substances or a ban on the entire PFAS group come into force. *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

4.4 Financial aspects

The Contaminated Sites Ordinance does not regulate who is responsible for funding contaminated sites. The “polluter-pays” principle anchored in environmental law generally applies. Implementation is however up to the cantons and is therefore regulated differently in Switzerland. The following is an example of how financing is regulated in the Canton of Zurich, described by HEV Schweiz.

In dealing with contaminated sites, there is a duty to act. The Contaminated Sites Ordinance explicitly states that the owner of the contaminated site in need of remediation must in principle take the necessary measures for investigation, monitoring, and remediation (Art. 20 AltlV). This is also connected with the obligation of the owner to make advance payments. In order to ensure that the elimination of the hazard is carried out quickly, the question of the real obligation to perform, i.e., who has to carry out and advance the necessary measures, must be assessed in advance. The responsible office at the canton, in the canton of Zurich, for example the AWEL, can order this by means of a decree, which can be contested by the affected owner. The obligation to bear the costs is regulated in environmental law, where the “polluter-pays” principle applies. The polluter must bear the costs of the necessary measures for the investigation, monitoring, and remediation of polluted sites (Art. 32d USG). The law does not define the “polluter-pays” principle or the term "polluter". In the absence of a definition of the term, case law falls back on the police law "concept of disrupter". According to this, a distinction is made between behavioral and condition disturber [40].

Behavioral disturber: The person who has caused the damage or danger himself - or through the conduct of third parties occurring under his responsibility.

Condition disturber: Whoever has legal or actual power over the thing that causes the disorderly condition.

Thus, the original polluter of the contaminated site (behavioral polluter) and the site owner (condition polluter) are both considered polluters under the Environmental Act. The original polluter (behavioral polluter) is primarily liable for costs, and the owner (condition polluter) is secondarily liable. If more than one polluter is involved, they must bear the costs in proportion to their share of the contamination. The owner of the site must apply in writing to the competent authority, i.e., in the Canton of Zurich to the AWEL, for the apportionment of costs. The AWEL initiates a so-called cost allocation procedure. Since this is very time-consuming and involves high costs, the AWEL attempts to reach an agreement in a negotiation procedure. If no agreement can be reached, the cost allocation procedure is continued, and a cost allocation order is issued. This order can be appealed by the parties concerned. Behavioral disturbers have to pay a higher share of the costs than conditional disturbers, and those who act culpably pay more. Problematic are cases in which it can no longer be determined who originally caused the burden or in which the polluter no longer exists because, for example, he has gone bankrupt or is insolvent.

In the latter two cases, the law stipulates that the responsible community steps in and assumes its share of the costs [40].

The federal government contributes financially to the investigation, monitoring and remediation of contaminated sites as well as to the investigation costs of sites that turn out not to be contaminated. To finance these costs, it has created the Contaminated Sites Fund through the Ordinance on the Levy for the Remediation of Contaminated Sites (de. VASA). This fund is accumulated with the levy on the disposal of waste. The payments are made to the cantons according to the costs incurred and amount to 30 or 40 percent of the chargeable costs. They are only paid if the measures taken are environmentally compatible and economical and correspond to the state of the art. Applications for compensation can only be made by the cantons - not by the landowner concerned [40].

The site owner can only be exempted from bearing the costs if he can prove that he could not have known about the pollution by exercising due diligence. Whether or not due diligence was exercised depends on the individual case. The cadastre of polluted sites must always be checked, especially before acquiring a property [40].

5 PFAS-Measurement

As previously discussed, the extent to which PFAS was and still are being used in various industrial and commercial products as well as the growing awareness of PFAS chemicals being found in the environment means that there is a critical need to further develop analytical instrumentation for an increasing array of PFAS chemicals. As discussed earlier, PFAS occur everywhere. To be able to detect the chemicals everywhere, different measurement techniques are required. The goal is to be able to measure PFAS in various environmental and biological matrices, such as water, animal tissue, food, sewage sludge or solid material. This will enable the regulatory authority to get have a reliable overview of the abundance of PFAS. Thus, in a further step, limit values can be introduced or substitutes for the manufacture of medicines or everyday items can be switched to. The next chapter describes the current situation regarding measurement in Switzerland. It will be shown to what extent the cantons are involved and support the FOEN in the entire measurement topic. Furthermore, chapter 05.2 clarifies whether limits have already been set and to what extent they will potentially be adjusted. In chapter 5.3 the LC-MS/MS method is presented and explained how this works. In chapter 5.4, similarities and differences between the USA and Switzerland are shown. It is explained to what extent these two countries proceed regarding the measurement topic and where they stand.

5.1 Measurement Switzerland

Globally, analytical measurement technology for PFAS is constantly being developed and improved. In Switzerland, the companies Bachema AG and Arcadis Schweiz AG are industry specialists offering commercially available and reliable measurements of PFAS in water and soil material. These two companies are working closely with the FOEN and its new project team to increase progress on PFAS knowledge.

Currently, there is no official measurement authorization in Switzerland. Basically, as soon as the infrastructure is in place, a company can start accepting samples for commercial PFAS measurement. The FOEN is now trying to establish certain regulations in this regard as part of a new project. At the moment, government representatives working on the topic of PFAS analytical technologies are collecting data, although it will likely be a period up to the year 2025 until first representative results can be expected *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

At the moment, the responsibility still lies with the cantons. Some cantons taking a more active approach to the investigation of PFAS in various environmental compartments, such as the canton of Valais and the canton of Zurich, are providing significant support the federal government. However, these cantons finance this themselves, but can draw on knowledge from the FOEN. It makes sense, therefore, that other cantons with a more passive approach, such as the canton of Solothurn are more cautious in their response to the PFAS problem since there is as yet no regulated financial support and no real representative results in Switzerland. Attempts are being made to investigate already known sites and to trace back the effects of PFAS substances accordingly. To speed up the whole process, there is also close cooperation with neighboring countries. The aim is to establish a uniform solution within the EU and thus in Europe. However, as analytical measurement technology is still in a strong development phase, there is increasing competition, which makes cooperation with different companies more difficult *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

The FOEN examined 32 different sites for PFAS in 2019. As already described in chapter 4, the highest concentration is in firefighting foams and in disposal sites. Concentrations in water were analyzed for all sectors and subsequentially compared.

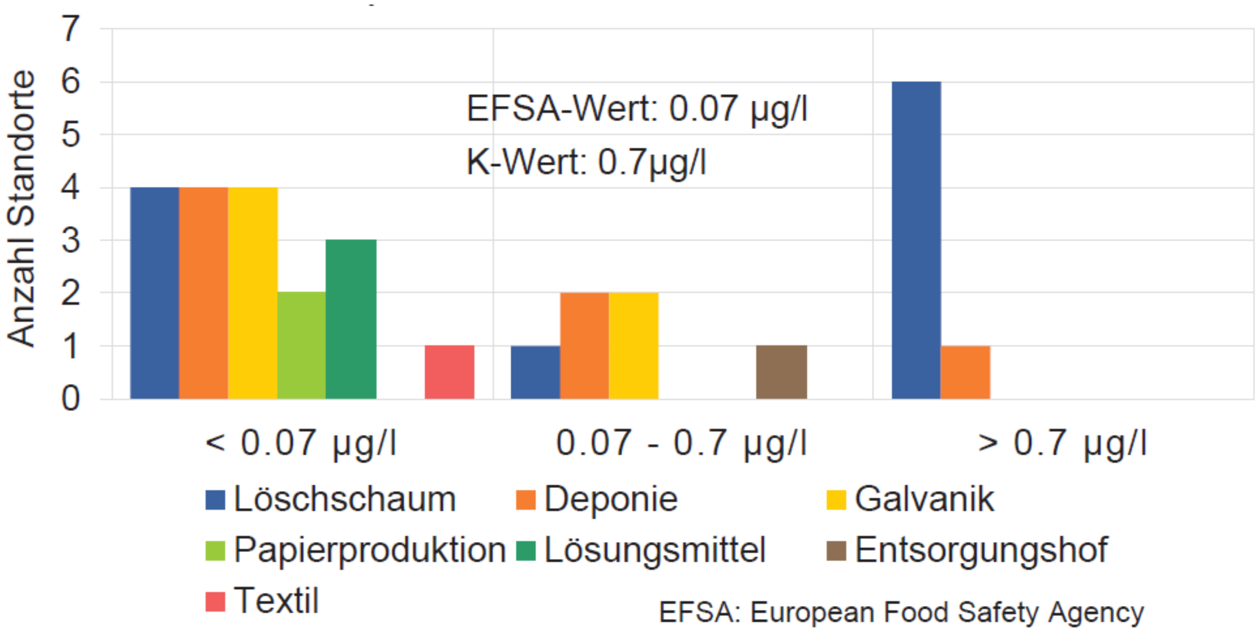


Figure 5: PFAS Project Switzerland: Studies [41]

In Figure 5, at six different sites where firefighting foam was used, a concentration greater than 0.7 micrograms per liter (µg/l) was detected. Only at four such locations were a concentration less than 0.07 µg/l measured. The European Food Safety Authority (EFSA) implemented a limit of 70 nanograms per liter (ng/l). The limits applicable today are discussed further in section 5.2. The K-value describes the limit value according to the Contaminated Sites Ordinance [41], [42].

5.2 Limits of PFAS

In Switzerland, no legal concentration limit values for PFAS in water or soils have been established thus far. However, the FOEN is attempting to evaluate such limits as part of a new project. A team of experts from the FOEN is working with the cantons to develop a concept for setting such legal limits *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

As only about 30 different PFAS substances can be detected by exiting analytical instrumentation, it is difficult to make an accurate statement about the exact concentrations of PFAS substances, as of the majority of PFAS chemicals are not yet measurable. In order to be able to make a statement about the concentration that is as representative as possible, there is a so-called K-value, or an allowable concentration limit of a substance or substance in an environmental matrix such as soil or groundwater. For PFAS, this consists of the sum of nine different PFAS substances (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFHxS, PFOS), with the individual substances weighted according to their toxicity. In Switzerland the K-value is unofficially aet at 50 ng/l. The cantons, which carry out individual investigations, adhere to this value. However, a site-specific permit must currently still be obtained from the FOEN *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022).*

Since 2020, there is a new assessment from the European Food and Safety Authority EFSA that determined group-related tolerable weekly intake (TWI). This is based on the sum of the most important PFAS (PFOA, PFOS, PFNA and PFHxS) and amounts to 4.4 nanograms per kilogram (ng/kg) body weight and week. This value was calculated based on different population groups. According to EFSA, infants and children have the highest exposure. The foods that contribute most to exposure are fish, fruit, and derived products, as well as eggs and egg products. The Figure 6 shows the development of the total

TWI on *(Dr. C. Guggenheim, Scientific Officer, Building Directorate Canton of Zurich, Contaminated Sites Section, Interview, 11.05.2022).*

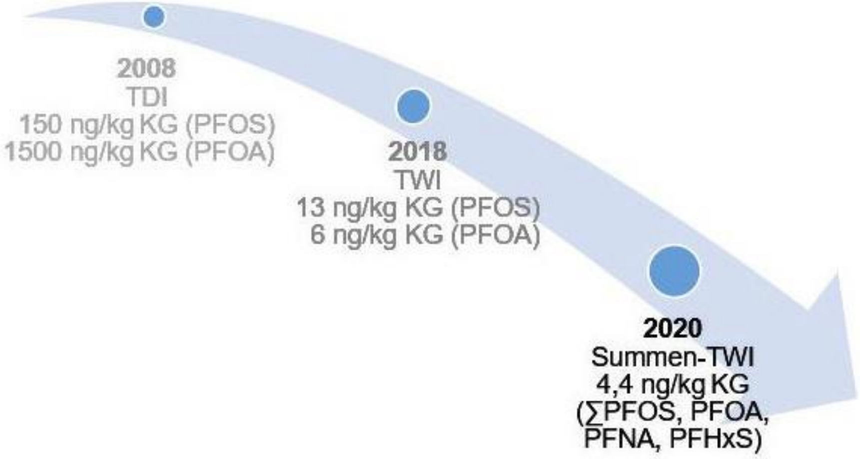


Figure 6: Development of toxicological reference values for PFAS at EU level [43]

5.3 Measuring methods

In Switzerland, there is one established measurement method, LC-MS/MS (liquid chromatography-mass spectrometry/mass spectrometry) as shown in Figure 7. This method has a limit of analytical determination of 1 ng/l in water and 100 ng/kg for solids.

Figure 7: LC-MS/MS measuring instrument of the company Bachema AG

The LC of the designation explains the separation system. This means that mixtures of substances are transported as a liquid over a certain distance. The individual components are transported at various rates and can therefore be separated from each other. PFAS substances are easily transported and remain in the liquid for a longer time. The movement takes place either by means of pressure, capillary force or by applying an electrical voltage. Injection of the sample into the system is automatic, and it is only necessary to inject the sample into the instrument. This is called an autosampler in technical terminology. Subsequently, the substance mixture is separated over a separating pathway. To make it visible when a substance passes a certain part of the chromatography system, physical properties are used, such as absorption of light, fluorescence, light scattering, or thermal conductivity. However, a signal can also be obtained from chemical reactions. An example output signal can be seen in Figure 8. The time at which the different substances pass a certain passage. This generates deflections peaks and the height of the deflection peak determines the concentration of the substance in the sample *(Dr. F. Bühler, General consulting / reports, Bachema AG, Interview, 04.05.2022)*.

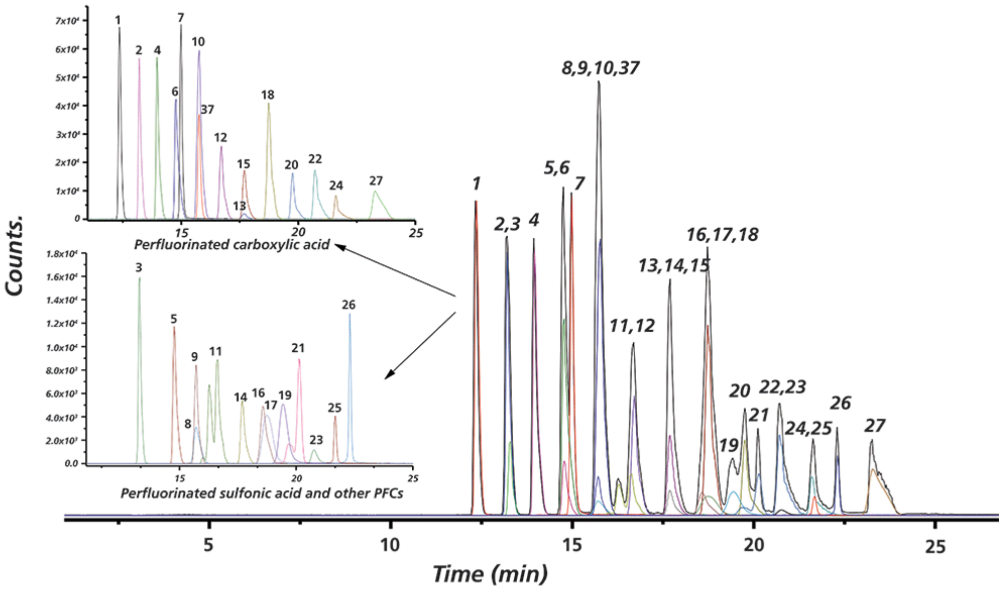


Figure 8: Output signal of a measurement with a LC-MS/MS measuring instrument [44].

Mass Spectrometry (the "MS" in the method acronym) is an analytical technique for analyte measurement over a total mass range and depending on the analyte, one specific atomic mass is selected and separated. The resulting fractions are determined. The second MS in the designation describes this procedure. Based on this fragmentation pattern, a substance can be identified very selectively as shown in Figure 9 *(Dr. F. Bühler, General consulting / reports, Bachema AG, Interview, 04.05.2022)*.

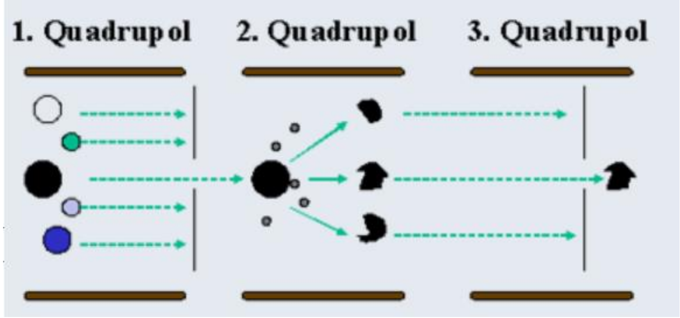


Figure 9: A visual representation of a Triple-Quadrupole mass spectrometer analyzer [45].

Once the sample has been injected into the instrument, the analysis takes place within milliseconds. This allows a company to perform many measurements in a short period of time. However, the method is only suitable for liquids. For solid samples such as soils, the sample is first mixed with ethanol to extract the analytes to be measured. This extraction is then into the instrument and measured. Such analytical instrumentation costs between a quarter and half a million euros. This means that measurements for PFAS will also become expensive *(Dr. F. Bühler, General consulting / reports, Bachema AG, Interview, 04.05.2022)*.

5.4 Differences of PFAS-handling between the US and Switzerland

Both the United States of America and Switzerland currently do not have a legal framework for PFAS. It is the responsibility of the states to conduct measurements in order to discuss a proposal for legislation. In contrast to Switzerland, the USA conducts large-scale measurements for PFAS in various environmental matrices. As a result, the following digital map could be created: *https://www.ewg.org/interactive-maps/pfas_contamination/map/* as shown in Figure 10. EWG is a non-profit organization that compiles these data for public use on this website *(Prof. Dr. C. Higgins, Professor, civil and environmental engineering, Interview, 06.04.2022)*.

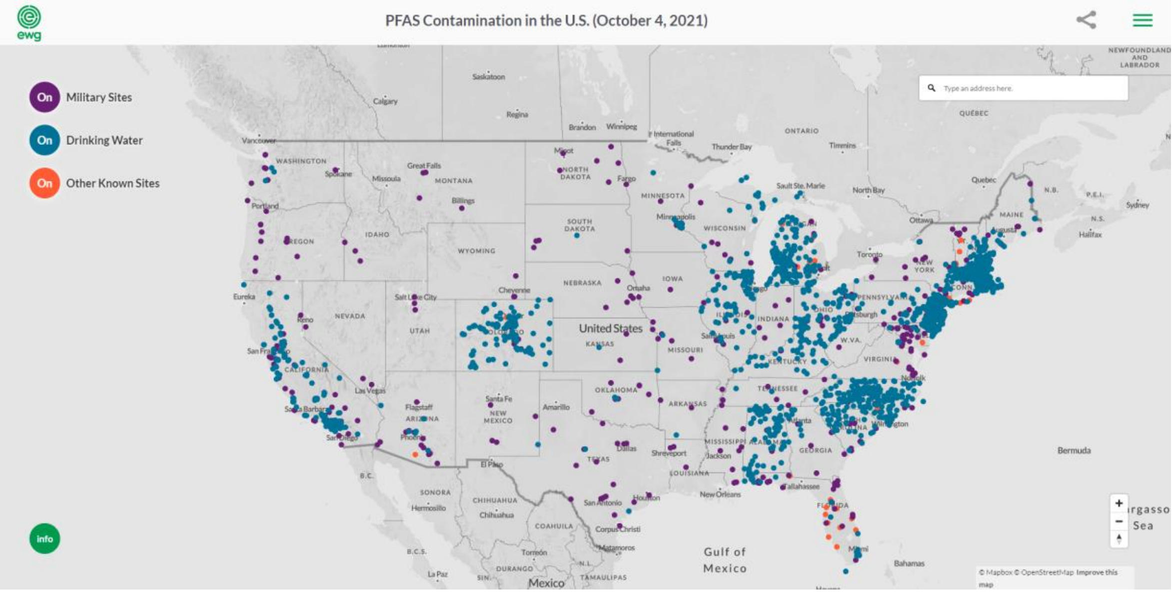


Figure 10: Interactive Map, showing PFAS contamination in drinking water at various military and non-military locations in the U.S. [46].

This interactive map shows different locations where PFAS was detected in groundwater. The map is continuously updated and gives the user an informative overview of the PFAS problem in the USA. Switzerland has a GEO portal where cadasters of contaminated sites can be viewed. However, most of these sites have not been investigated for PFAS and it is not yet foreseeable to what extent this will change. The FOEN does not intend to resurvey the sites entered in the various cantonal cadasters the time and costs involved would be too great. *(Dr. R. Kettler, Research Associate, Federal Office for the Environment FOEN, Interview, 12.05.2022)* Although analytical measurement tools are continuously being improved, it is not known in Switzerland that sites that have already been tested will be measured repeatedly. At this stage, however, it is known that the subject matter surrounding PFAS needs to be significantly expanded. In addition, the countries must cooperate so that legal foundations can be developed in the foreseeable future *(Prof. Dr. C. Higgins, Professor, civil and environmental engineering, Interview, 06.04.2022)*.

6 PFAS Waste and Remediation

The growing awareness of the risks of PFAS-contamination in wildlife and humans coupled with the recalcitrant nature of PFAS compounds has given rise to different treatment methods of contaminated environmental compartments. Thus, PFAS contamination remediation techniques are mainly focused on individual environmental compartments, for example water and soil. Due to their widespread applications and their longevity PFAS can be detected in most environments, hence, different remediation technologies need to be developed on a site-to-site basis. Some remediation technologies will be discussed in this chapter, with a few of those technologies already commercially available whilst others remain in an experimental stage.

6.1 PFAS in environmental compartments

As mentioned, PFAS compounds can be found in most environmental compartments, either due to direct disposal of contaminated material or through natural transportation methods. Figure 11 visualizes the various compartments where PFAS – compounds can be found in. These are the atmosphere (de. Atmosphäre), water (de. Wasser), the biosphere (de. Biota), and soil and sediment (de. Boden/Sediment).

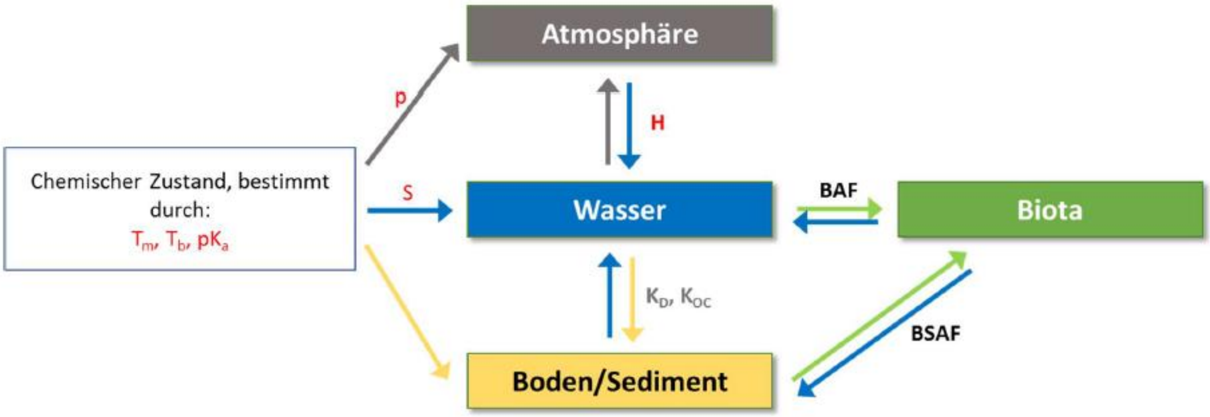


Figure 11: Environmental compartments with PFAS – contamination and respective physical and chemical properties which lead to transportation [47].

This section will mainly focus on PFAS – contamination within water and soil since these are the compartments most often at risk of contamination. Biological accumulation of PFAS will be discussed later in this paper.

Transport of PFAS – compounds in and between soil and water compartments mainly depends on the sorption- and desorption- characteristic of the given compounds. While those characteristics remain a complex subject that are still under investigation, research indicates that, within certain subgroups of compounds the sorption depends on the length of the compound chain and how bifurcated the structures the structure are. Compound with shorter lengths and fewer forks tend to have higher sorption capacities [47].

Desorption of PFAS compounds back into a mobile form is similarly linked to the length and bifurcation of the compounds. Shorter-chained compounds have been shown to elute almost to the same degree as they get absorbed, while longer-chained compounds are irreversibly absorbed.

While Figure 11 differentiates between water and soil as compartments of PFAS-contamination, for the purpose of transportation the two are closely interlinked. Compounds can cross from one compartment into the other due to the sorption-characteristics. Examples include the use of firefighting-foam containing PFAS, which will be washed into soil and transported via groundwater, causing a plume of PFAS-contamination to spread throughout the affected groundwater aquifer. These compounds will then remain underground indefinitely since no natural processes which would destroy these compounds exist.

Compounds which have either not been absorbed by the soil or eluted back into groundwater will be transported further along those paths, accumulating in source water, and drinking water over time. Accordingly, PFAS – compounds have been found in drinking water, with concentrations expected to rise should steps to combat contamination not be undertaken [48].

Atmospheric contamination with PFAS has not been extensively covered within this paper, but thermal treatment of contaminated material, if not done at the required temperature, is projected to lead to compounds escaping into the atmosphere, where they are likely to be caught by rain and subsequently transported back into soil and/or water.

6.2 Methods of remediation

PFAS remediation methods can broadly be divided into three categories: *in-situ, on-site and off-site. In-situ* – methods are considered less expensive to implement, as no large-scale removal of material is required, but rely on the efficacy of those methods to immobilize, wash out or otherwise neutralize contaminants, a factor which is heavily dependent on the characteristics of the individual PFAS - compound (e.g., chain-length and bifurcation).

On-site and off-site methods are virtually identical, only differentiating between the availability of the specific treatment on a given site. These methods require contaminated material to first be excavated from site, increasing associated cost, and raising questions regarding the leftover material after remediation. Once material has been excavated legal hurdles may require material to be at PFAS concentrations below a given limit before it can be reintroduced into the environment. This poses a challenge in respect to cost of treatment, efficacy, and time-investment. Similarly, materials which have been used until now and would be in the process of being discarded (e.g. construction material) can find itself above the limits of contamination *(B. Schmid, Senior Expert Contaminated Sites / Disposal, Friedlipartner AG, Interview, 21.04.2022).*

In both instances, such materials would require treatments to decrease PFAS concentrations to below the given legal limits or will be stored on landfills. The later case can prove detrimental to the environment if storage isn't maintained properly. Contaminants might be released into the environment via washing out in the landfill leachate due to rainwater and subsequentially natural distribution. If landfill – wastewater and leachate isn't carefully monitored and treated, PFAS compounds could leak again into the environment.

6.2.1 Soil-contamination

Soil contamination and subsequent handling of contaminants have the broadest range of treatment and remediation techniques. These treatments are either focused on the *in-situ* stabilization of PFAS compounds or the removal of the contaminants from the subsurface.

Washing out

Washing of contaminated soil relies on the ability of PFAS – compounds to be eluted from soil and transferred via hydrological processes with the intent on capturing the contaminants into the wash water to later remove them via pump and treat processes. To wash out contaminants, the soil needs to not be completely saturated. A viable strategy of washing relies on accurate models, increasing the cost *(B. Schmid, Senior Expert Contaminated Sites / Disposal, Friedlipartner AG, Interview, 21.04.2022).*

Immobilization

Immobilization utilizes the injection of minerals or stabilization agents into contaminated soil to either absorb PFAS or form an impenetrable layer. Examples of such agents include colloidal activated carbon (CAC), powdered activated carbon (PAC) or modified clay, with an efficacy shown in the >80% range in capturing long-chained compounds. Additionally, the likelihood of long-chained compounds to leach back into the environment decreased by up to 99%.

Methods of immobilization are already being used in the U.S. and Canada, for example those described by Carey et al. where they conclude a contamination immobilization longevity on the timescale of decades. [49] In Switzerland however such methods will still require more research before being implemented, as the longevity of these processes still needs to be evaluated *(B. Schmid, Senior Expert Contaminated Sites / Disposal, Friedlipartner AG, Interview, 21.04.2022).*

Foam fractionation

Many PFAS – compounds are naturally inclined to foam, a property which can be used to extract them from contaminated aquifers using a process known as foam fractionation. Figure 12 visualizes the remediation technique of foam fractionation.

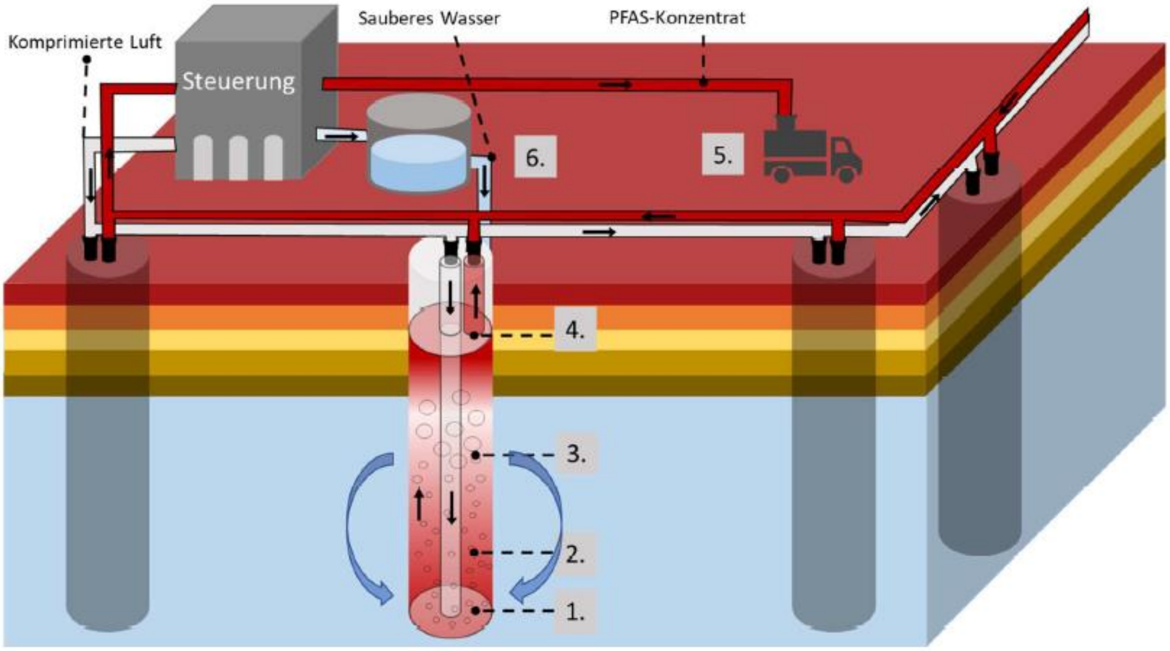


Figure 12: Scheme of foam fractionation. 1: compressed air is transported to the base of the well. 2: PFAS foams out of the groundwater. 3: Air bubbles carry foam to the surface. 4: Foam is retrieved and transported to the plant. 5: PFAS - solution is transported [47].

At time of writing, this process has been developed and applied by OPEC-Systems, which reports efficiency of up to 99% on eleven different compounds that were being measured for.

Biological treatment

As synthetic organic compounds, PFAS have long been recalcitrant to treatment with biological remediation. Recent studies however have identified bacteria and fungi which are capable of inducing degradation of PFOS [2], [50].

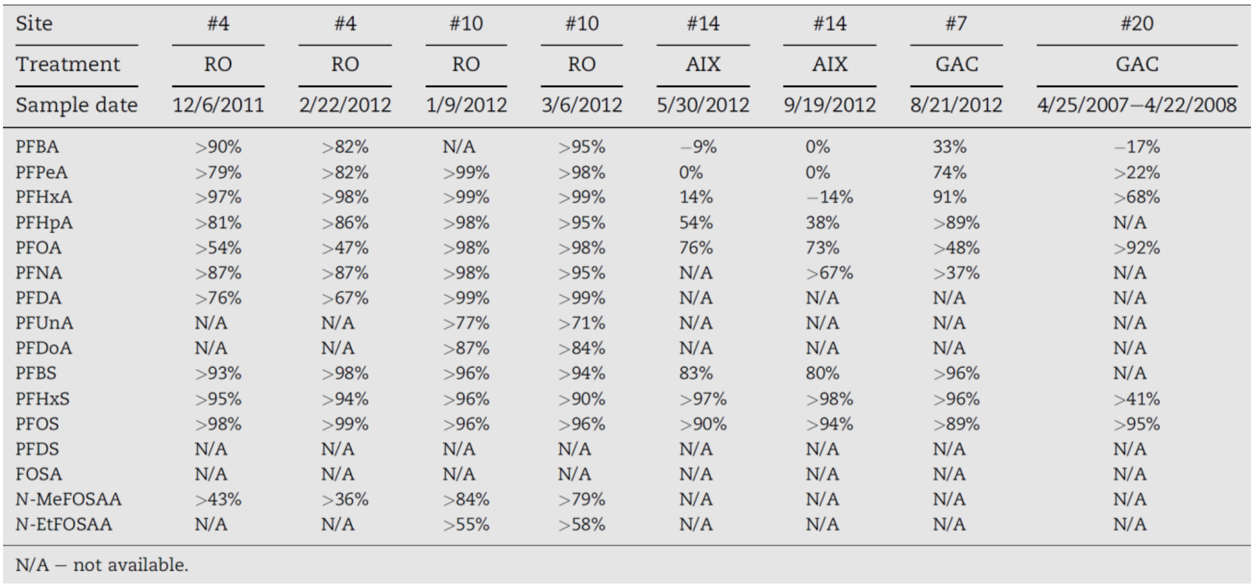
Such treatment is still experimental, and efficiency has thus far underperformed as compared with more traditional methods, with the most bioremediation technique reaching only 67% efficacy [51].

Uptake of contaminants due to bioaccumulation has been studied as well, with Gobelius et al. testing the uptake on a contaminated firefighting-facility. Plants were seeded into contaminated soil and PFAS contamination was measured before and after growth. While the plants being used were able to absorb material, the accumulation rate was deemed too low to have any measurable impact on future remediation plans [52].

6.2.2 Water-contamination

Many PFAS – compounds can be found in wastewater, as a by-product of industrial waste or due to soil-washing processes, in which PFAS contamination in soil gets flushed out with water and are transported away. Many different methods of treating contaminated water have already been developed and are well understood, with more methods under development.

Of the existing technologies three have stood out as being most reliable in their efficiency of contaminant removal: Granular activated carbon (GAC), Anion exchange resin (AIX) and Reverse Osmosis (RO). Each of these treatments can have an efficacy of up to 99% based on the type of compound, as seen in Figure 13:



Site	#4	#4	#10	#10	#14	#14	#7	#20
Treatment	RO	RO	RO	RO	AIX	AIX	GAC	GAC
Sample date	12/6/2011	2/22/2012	1/9/2012	3/6/2012	5/30/2012	9/19/2012	8/21/2012	4/25/2007–4/22/2008
PFBA	>90%	>82%	N/A	>95%	−9%	0%	33%	−17%
PFPeA	>79%	>82%	>99%	>98%	0%	0%	74%	>22%
PFHxA	>97%	>98%	>99%	>99%	14%	−14%	91%	>68%
PFHpA	>81%	>86%	>98%	>95%	54%	38%	>89%	N/A
PFOA	>54%	>47%	>98%	>98%	76%	73%	>48%	>92%
PFNA	>87%	>87%	>98%	>95%	N/A	>67%	>37%	N/A
PFDA	>76%	>67%	>99%	>99%	N/A	N/A	N/A	N/A
PFUnA	N/A	N/A	>77%	>71%	N/A	N/A	N/A	N/A
PFDoA	N/A	N/A	>87%	>84%	N/A	N/A	N/A	N/A
PFBS	>93%	>98%	>96%	>94%	83%	80%	>96%	N/A
PFHxS	>95%	>94%	>96%	>90%	>97%	>98%	>96%	>41%
PFOS	>98%	>99%	>96%	>96%	>90%	>94%	>89%	>95%
PFDS	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
FOSA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N-MeFOSAA	>43%	>36%	>84%	>79%	N/A	N/A	N/A	N/A
N-EtFOSAA	N/A	N/A	>55%	>58%	N/A	N/A	N/A	N/A

N/A – not available.

Figure 13: Percent removal for GAC, AIX and RO treatments of various PFAS compounds [53].

These technologies have various advantages and drawbacks. Reverse osmosis has been shown to be highly efficient, even being able to filter out precursor-compounds. The process of RO involves high pressures and filtration by size exclusion and charge rejection [48]; however, it is both cost and energy intensive and produces a concentrated retentate, or a fluid concentrate containing the PFAS, which must later be disposed (See section 6.2.3).

Anionic exchange resins are effective, rapid and have an increased affinity for short chain PFAS, and increased contaminant sorption capacity as compared to GAC. The resins used are porous substances with high surface areas. Contaminated solutions are pumped through these resins where compounds such as PFAS are trapped onto the resin and filtered out of the solution. They suffer from disturbance of other charged particles in treated water such as sulfate, chloride, or different acids, reducing the treatment efficiency. Furthermore, used resin is difficult to regenerate.

Activated Carbon is most widely used, reported, and evaluated and benefits from being easily and repeatedly regenerable. Due to its large surface area the adsorption capacity is high and organic compound are filtered out. It's efficiency again depends strongly on the type of compound to be removed and on the surface structure of itself along with other contaminants in the treated water [48]. Commercially, GAC offers an effective method of PFAS – removal at low prices.

In addition to these technologies, Ozo-Fractionation, Ultrasound treatment, and Supercritical water oxidation are treatments or technologies that have recently emerged as potential PFAS remediation technologies, which are either still in development or are being used on a smaller scale:

Ozo – fractionation

Ozo – fractionation makes use of the same properties of PFAS, as already been discussed for foam fractionation and *in-situ* treatment, the technique uses the properties of ozone to aid in the oxidation of PFAS, albeit on a smaller scale. Rather than destruction of PFAS – compounds the fractionation allows for concentrated contaminated material to be further processed. An additional benefit is the ability to not only treat groundwater but also wastewater with up to 20% solids, as during the fractionization process, solids and liquids are separated. During development, an efficiency of up to 99.9% was demonstrated and seems to be applicable for large commercial use, because the underlying processes can be upscaled easily. Further independent research is required to verify the efficacy of this technique [47].

Ultrasound-treatment

Ultrasound-treatment has proven to destroy a wide range of PFAS – compounds, utilizing soundwaves to form cavities in which high temperatures cause the compounds to undergo pyrolysis. The technology has been proven on small scales yet remains to be implemented on industrial scales. A long treatment duration makes continuous treatment of groundwater unlikely, although the technology might see use in treating landfill wastewater with PFAS contamination [47].

Supercritical water oxidation (SCWO)

In a recent paper by McDonough et al. the use of supercritical water oxidation has been shown to destroy and remove over 99.999% of the 12 researched PFAS – compounds after two trials, with a graph showing efficiency seen in Figure 14. The technology relies on the reactivity and transport properties of waste streams brought above the supercritical point of water. This point is achieved at 374°C and 218 atm. At this point, oxidation within the waste material occurs. Commercial application of this technology has existed since the 1980s and benefited from increased energy efficiency. While further research needs to be done, the technology has shown potential in destroying PFAS – compounds [54].

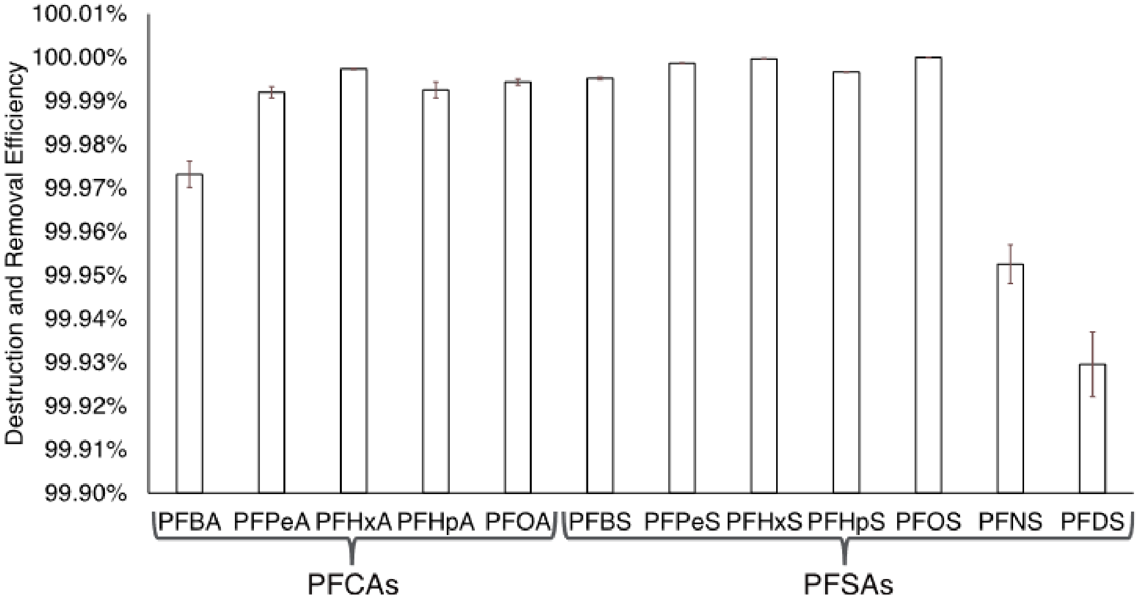


Figure 14: Efficiency of removal from the SCWO technique on different PFAS compounds [54].

6.2.3 Waste-contamination

Most remediation technologies involve filtering PFAS – compounds out of the contaminated compartment without destroying the compounds themselves. Thus, concentrated sludge remains as leftover, which either needs to be treated to destroy the compounds or stored in landfills.

To eliminate PFAS – compounds, there are three processes are currently being used: High-temperature hazardous waste incinerators, thermic desorption and as contribution to cement-production.

High-temperature incinerators destroy PFAS – compounds by heating them up to temperatures of between 1’100 and 1’300 °C, at which point the organic compounds are destroyed. Filters at the end of the incinerators filter out the escaped fumes and thus prevent contamination into the air. Only a small number of incinerators with those capabilities exist, most of which are private property. Thus, the capacity regarding the large volume of various forms of PFAS waste is still lacking. Thus, the contaminated waste will need to be temporarily stored in landfills until high-temperature incinerators are designed to handle the large amount waste.

Thermic desorption involves smaller temperatures in the range of 400 – 800 °C and produces reusable material as opposed to sludge. The resulting materials are however still contaminated, albeit to a lesser extent. Explicit use of thermic desorption to destroy PFAS – contaminated material has thus far only been done as a pilot project which reported efficiency of up to 99.9%, although data on the complete destruction of those compounds is still inconclusive and still needs to be verified by further research.

Mixing contaminated material into cement production is hypothetically possible, although this process would require the same temperatures as in high-temperature incinerators to effectively destroy the PFAS - compounds. Research into this method is still required, with pilot projects underway in Australia [47].

7 Biological effects of PFAS exposure

Since their introduction in the early 1950s, PFAS have found their way into practically every corner of the globe. Figure 15 visualizes the cycling of PFAS through various environmental compartments. They are highly mobile and spread through air as well as water. PFAS can be found in rainwater for example. This alone would be enough for them to spread over great distances. That is why they can reach even the most remote areas on earth, like the Arctic and Antarctica. Even in regions far from any PFAS emitting sources, PFAS can be found in the ground, the water, the plants, and the organisms, including humans. Because of this rapid spread, it is important to know what influence PFAS have on living organisms, in nature as well as in humans [2]. The following chapter gives a general overview of the effects that PFAS have on organisms like plants, animals, and humans. It also covers the different ways of intake and how the bioaccumulative and biomagnifying properties of PFAS play an important role in their transfer from one organism to another. Lastly a study is presented, the results of which might lead to the development of a therapy for people who already have a high PFAS concentration in their body.

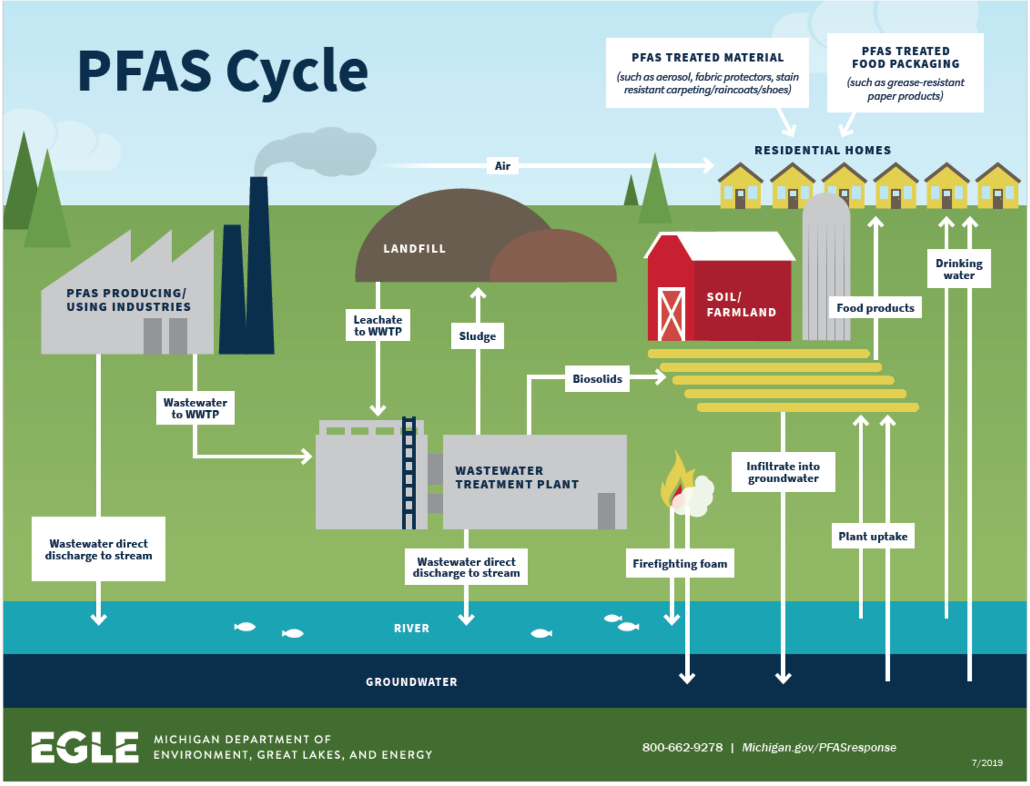


Figure 15: Transportation of PFAS in the environment [55].

7.1 Effects of PFAS-Exposure on the ecosystem

Animals

One reason they are particularly dangerous to the health of natural ecosystems is that they tend to bioaccumulate and thus biomagnify. Figure 16 conceptualizes these processes. In essence, bioaccumulation is the accumulation of certain substances, such as PFAS, but also mercury, polychlorinated biphenyls, and other chemicals, in an organism. This happens, when an organism absorbs a substance faster than it can degrade it or eject it from its body [56]. This also causes a contamination up the food chain in a process known as biomagnification. Here is how it works: Organism 1, which is low on the food chain gets consumed by organism 2, consuming also the bioaccumulative substances inside the body of organism 1. Now not only does organism 2 consume one specimen of organism 1, but multiple. With every organism consumed, the concentration of the specific bioaccumulative substances inside the body of organism 2 is increasing. If now this organism 2 gets consumed by an organism 3, this organism 3 now contains all the bioaccumulative substances of the specimens of the organism 1 and those of the organism 2. This way, the concentration of the substances magnifies up the food chain with the increasing trophic levels. On the one hand, the higher concentration of these substances, in this case PFAS, makes it more likely for them to influence the organism's health and their surrounding ecosystem. On the other hand, it heightens the possibility of the substances finding their way into human bodies, for example through the consumption of animal products like meat, milk, and eggs [55]–[59].

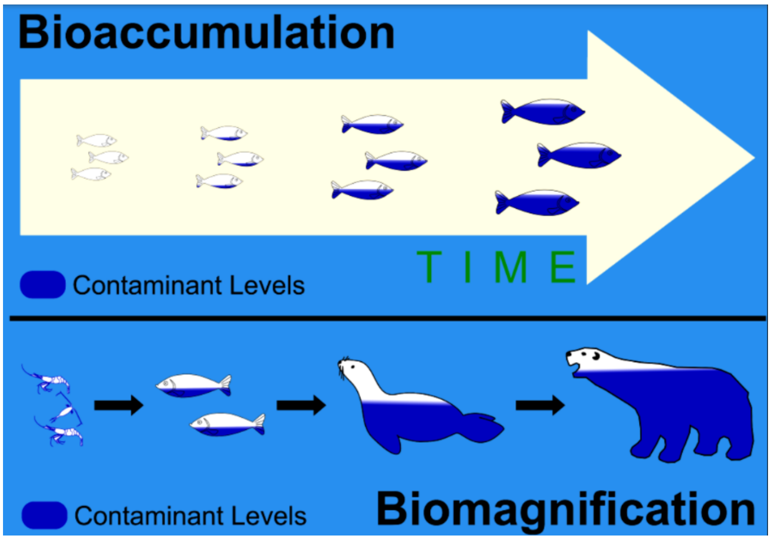


Figure 16: Schematic describing the bioaccumulation and biomagnification process.

Plants

The accumulation of PFAS not only occurs in animals, but also in plants. A recent study revealed that PFOA and PFOS molecules, which can be found in the Nakdong River in South Korea can also be found in six different crops like fruits, rice, and leafy vegetables like lettuce, which are being grown in the region around the Nakdong River. These PFAS in the river are said to have come from the use of biosolids, which came from wastewater treatment plants, from accidental or illegal discharges and from irrigation water. They were also found in the soil, where the above mentioned crops are being grown. The concentration of PFOA and PFOS is attributed partially to the contaminated soil, but also to the river water, which is being used to water the crops. The study concluded that the amount of PFAS found in the crops is not above the from the European Food Safety Authority (EFSA) defined reference dose (RfD). But the author concludes that, in combination with other intake routes like drinking water, the dietary intake poses a relevant factor in the exposure to PFAS [61].

In connection with the absorption of PFAS through plants, a study of plant-soil-water systems revealed, that the macrophyte *Juncus effusus* absorbs PFAS molecules with longer carbon chains more efficiently than shorter ones. Coincidentally, long chained PFAS molecules are said to be generally more toxic than shorter chained molecules [62]. The study also showed that there are differences in the absorption rate of different PFAS molecules, depending on the overall molecular structure. PFSAs were more efficiently absorbed than PFCAs for example. In addition to this investigation, the DNA of the microbial communities associated with these soil-plant-water systems have been studied as well. This way, the authors found out, that the microbial communities associated with the systems contaminated with PFAS at lower concentrations had a larger diversity than those exposed to higher concentrations of PFAS [63].

Similarly for aquatic systems, the available studies about PFOA and PFOS indicate a moderate ecotoxicity of these two molecules for aquatic organisms. The lowest NOAEL (No Observed Adverse Effect Level) for PFOS lies at 2.3 µg/L for the lake fly *Chironmomidae* [64]. Also important for the ecotoxicity is the PNEC (Predicted No Effect Concentration). Beneath this concentration, no negative effects are expected to occur in an ecosystem. For aquatic systems, the PNEC has been set at 0.65 µg/L for PFOS [65] and at 48 ng/L for PFOA [66].

In order to make a conclusive statement about the ecotoxicological effects of PFAS on plants and animals, further studies will be necessary, among other things because of the various influences of environmental conditions and site-specific factors [2].

7.2 Human health

The danger of PFAS exposure to the human health is well recognized today and receives more and more attention from the professional world. But even now, after large amounts of data have already been collected, the general view among experts is that our knowledge of the health effects of PFAS is still very patchy. However, the results of the studies so far clearly show the urgency to act. The information presented in this chapter has been collected through epidemiological studies on humans, through in vitro studies on cells of humans, rats, and mice and through in vivo studies (animal experimentation) on rats and mice.

Human exposure to PFAS

Humans are exposed to PFAS in a variety of ways. PFAS can be absorbed via the lungs by breathing PFAS containing dust or vapor and through the digestive system by ingesting contaminated food, water, soil, and dust. But it can also be absorbed through the skin, for example if PFAS containing cosmetic products are being used.

For the general population, the consumption of drinking water and the dietary intake are the most prevalent forms of exposure. Exposure due to inhalation and dermal contact is more relevant in an occupational context [67], [68]. Currently, PFOS, PFOA, PFNA and PFHxS are believed to be the PFAS molecules, which are contributing the most to human exposure [69]. The topic of the risk of PFAS to the human health came to international awareness at the end of the 1990s, when a high concentration of PFAS was detected in the human population near a facility of the company DuPont. In 2005 a health study was carried out on about 69’000 people from the area around the DuPont facility [70]. This study, which was conducted through interviews, questionnaires and the analysis of blood samples, concluded that a long term exposition to PFOA might cause a heightened cholesterol level, thyroid and chronic inflammatory bowel disease, as well as testicular and kidney cancer [71]–[75].

Various PFAS are associated with several different human health issues, some of which are summarized in Figure 17. Among others, PFAS chemicals can cause alterations in the lipid metabolism, the endocrine system, and alterations in the development. They are also said to have properties such as cancerogenicity, reprotoxicity, hepatotoxicity and immunotoxicity. With the ongoing research, the list of biological functions influenced by PFAS is rapidly getting longer. Health outcomes that consistently reappear are:

- Heightened cholesterol levels
- Increased uric acid levels in the blood
- Reduced kidney function
- Testicular and kidney cancer
- Changes in the immune response
- Altered levels of thyroid hormones and sex hormones
- Thyroid disease
- Reduction of fertility in women
- Later age for the start of menstruation in girls and earlier menopause

The potential impact of PFAS on the human health is depending on a variety of factors such as age, sex, health status, ethnicity, and the genetic predisposition of the person, as well as the duration of the exposure, the concentration of PFAS in the body and the route of exposure [61], [76], [77].

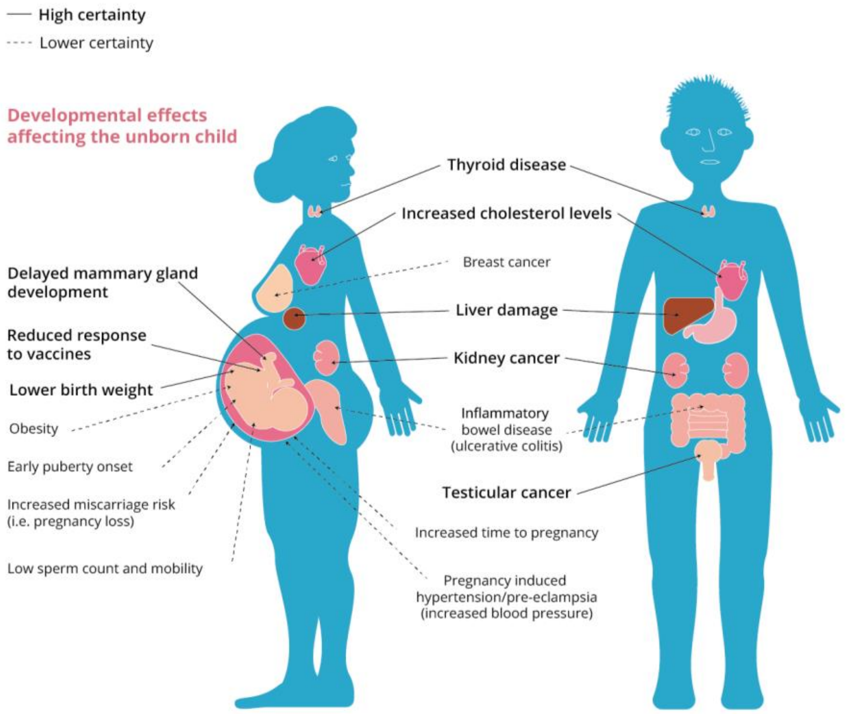


Figure 17: Effects of PFAS on the human body [78].

Some worrying effects are those of PFAS exposure on infants. The exposure to PFAS begins for children already in the womb. An analysis of the umbilical cord blood of newborn children of workers of DuPont revealed that PFAS can pass the placenta barrier. This way, the unborn child is partially exposed to the

PFAS molecules in the blood of the mother. Postnatal exposure occurs mainly through breastfeeding [79], [80]. The effects on the child's health this may lead to are among others:

- abnormal prenatal growth, which often leads to a low birth weight
- greater risk of childhood obesity
- higher vulnerability to infections
- lower immune response to vaccinations

But not only the child's health can be affected. A higher exposure to PFAS during pregnancy heightens the risk for the mother to develop gestational diabetes and a form of high blood pressure called pre-eclampsia [79].

In vitro studies

The majority of the in vitro studies selected by the authors of the collective study "PFAS Molecules: A Major Concern for the Human Health and the Environment" investigated the effects of PFOA and PFOS on thyroid and hepatic cells [5]. These studies have shown that certain PFAS, including PFOA and PFOS have disrupting effects on thyroid cells. Both PFOA and PFOS inhibit the accumulation of iodide through certain thyrocytes acutely, but reversible. PFOS also reduces the concentration of iodide in iodide containing cells. Studies on human liver cells made clear, that all PFAS increase the cellular triglyceride levels, the main constituents of human body fat, but without influencing the cholesterol level directly. Indirectly, the presence of both PFOA and PFOS cause a strong decrease of CYP7A1, a key enzyme in the synthesis which changes cholesterol into bile acids. Thus, PFAS indirectly cause an increase in cholesterol levels [2], [81], [82].

In vivo studies

Most in vivo studies concluded that the exposure of mice and rats to PFAS has negative consequences for their health. One study revealed a link between the exposure to PFOS and a dysregulation of 241 proteins, which are involved in the lipid and xenobiotic metabolism of the liver [83]. According to another study, which was conducted on female mice, PFOS accumulates in the lungs, kidneys, heart, brain, and the spleen as well as the liver [84]. It was also revealed that exposure to PFOA increases hepatic and renal functions and decreases the activity of enzymatic antioxidants in the tissue of the liver and the kidneys [85]. The amount of PFAS these animals were exposed to, mainly by ways of indigestion, was much higher than it would have been in nature. Therefor these results are not representative, neither for what PFAS do to the human body, nor what the results of a naturally occurring exposition would be. But the results give an idea, which body parts might be effected in which way after a long term exposure [2].

Recent developments

In light of the COVID-19 pandemic, the impact of PFAS exposure on the immune response to vaccination is of particular interest. The Agency for Toxic Substances and Disease Registry (ATSDR) lists a decreased vaccine response in children as a possible health outcome of PFAS exposure and is supported in this by the results of multiple studies [2], [86]–[89]. The oldest subjects of this studies were 18 years old. The particular study these subjects were a part of investigated the impact of an exposure to PFAS on the number of antibodies 7 and 13 years after a booster vaccination against diphtheria at the age of 5. The study concluded that the exposure to certain PFAS has a significant impact on the effectiveness of the booster vaccination after this amount of time [88]. A similar negative effect on the number of antibodies has been observed with the vaccination against tetanus and Haemophilus influenza type b [86], [87]. To draw a parallel between the effect of PFAS on the effectiveness on the mentioned vaccinations and the COVID-19 vaccination is difficult. For one because of the fact that they are vaccines against different pathogens but also because of the different ages at the time of the vaccination. The Swiss Federal Office of Public Health (FOPH) recommends the first vaccination against COVID-19 at the age of 12, even though it is possible to be vaccinated at the age of 5 [90]. On the other hand the Centers for Disease Control and Prevention (CDC) recommends the first vaccination against diphtheria and tetanus at the age of 2 months [91]. So far there is only limited evidence for a influence of PFAS on the effectiveness of vaccines in adults [92]. In order to make a conclusive statement about this topic, more research is needed.

Right now, the international focus lies on how to reduce the emission of PFAS in the environment and on identifying the health outcomes an exposure to PFAS causes. A much less prominent aspect is the question of how to help people who already have a high concentration of PFAS in their body. For PFAS to have a negative effect on a person's health, they need to be present in a certain concentration in the body. Because of bioaccumulation, the concentration in a person's body might rise over time so that at some point in their lives, a harmful concentration might be reached. In this context, a question that should be asked is if there is a way to lower the concentration of PFAS in a human body. A study on firefighters investigated this topic and came to a promising conclusion. An analysis of blood samples of 285 firefighters revealed that donating blood and plasma significantly reduces the amount of PFAS in the bloodstream. The implication is that extracting contaminated blood and letting it be replaced naturally by the body might be a way to extract PFAS from a person's body. This revelation might lead to the development of a therapy to reduce the harmful impact of PFAS on strongly exposed people. It also needs to be mentioned that, even if bioaccumulative and long-lived, PFAS do degrade over time. This means that if the PFAS intake of a person is reduced to zero, the concentration of PFAS inside the body will sink naturally over time [93].

8 Conclusions and Future Outlook

This paper set out with the aim of assessing the different questions regarding the problems of PFAS. These questions are regarding the production of PFAS – compounds, their spread into the environment and how contamination can be measured. Additionally, it set out to summarize current knowledge into the techniques with which PFAS contamination can be remediated and what the biological effects of contamination on humans and the biosphere in general are.

Concerning the production and importation of PFAS, much information was difficult to gather. Usage of PFAS started in the 1950s, with over 200 different applications and an unquantifiable number of different products. Large quantities of PFAS were imported into Switzerland in finished products, however, many compounds were used for manufacturing, for example the watchmaker-industry. An extensive ban of PFOS in 2012 caused manufacturers to substitute banned compound with new, shorter-chained alternatives. The Stockholm Convention, where the EU and Switzerland are a part of, regulates ban on persistent pollutants yet due to the number of different compounds, many alternatives with little understanding of their effects remain in use.

Research and interviews have concluded that wherever firefighting foam has been used, contamination is to be expected. Further hotspots can be expected at sites of galvanic processes, although more investigation remains to be done. Sampling of ground- and drinking-water wells have thus far not produced alarming measurements in most cases. Research predicts that there is a widespread, detectable amount of background contamination in Switzerland and present results indicate that in future, an investigation into the pollutants of suspected areas must include measurement of PFAS concentrations. In addition, registration, monitoring, or remediation of contaminated sites must be clarified and standardized.

Measurement techniques of PFAS – contamination are already quite advanced but comparatively expensive. Determination limits are expected to improve in the future, with current limits of quantification deemed not sufficient. Capability of concentration measurement needs improvement as well, as even small amounts of contamination are suspected to endanger humans.

Different technologies to treat PFAS – contamination in various environmental compartments exist or are being developed, yet due to the wide range of compounds further research into the efficiency of technologies is still required. Technologies such as RO, GAC and foam fractionation are efficient but expensive and do not solve the underlying problem of those compounds existing, instead only concentrating them into a smaller volume for future destruction. Methods to destroy compounds which are cost-effective, quick, and applicable on a large-scale need to be further developed.

In both areas, the effect of PFASs on ecosystems and the effects on the human body, further studies are needed to determine the full extent of the consequences of humanities extensive use of PFASs. Clear is that considerable impacts are already noticeable, both in nature and in the human populations. Because of the persistent nature of PFASs, their high mobility and bioaccumulative tendency, PFASs will haunt future generations too, even if they are no longer produced. One property of PFASs is that they can have many different effects on an organism, and the list of health problems and diseases connected to PFASs is growing longer with every year. Studies have shown a connection between the exposure to PFASs and certain diseases of civilisation like diabetes and high blood pressure. The extent of the influence PFASs have on the number of cases of such diseases has yet to be determined. But the information gathered so far makes a significant impact seem plausible.

8 Conclusions and Future Outlook

The problems concerning PFAS are varied and multifaceted, ranging from their ubiquitous uses, the hotspots that have been generated in the environment in the decades since it's usage, their longevity and possible treatment, how to detect and measure them and the effect they have on the biosphere, especially on human beings. Due to the nature of being a large collection of different compounds, data might be easily accessible for certain compounds while others remain shrouded in uncertainty, missing information, or incomplete research.

Knowledge on production of PFAS is limited and guarded by various companies interested in keeping trade secrets. Hotspots are difficult to establish without proper definitions and limits to address. Measurement in itself is dependent on the type of compound that is being measured for and the limits up to which samples need to be measured, for which strict regulations still need to be established. PFAS contamination, treatment and remediation relies heavily on the specific compounds and is expensive, often not destroying compounds but rather concentrating them to be stored in landfills with the possibility of future elimination methods. Methods on destruction also rely on research into compounds with different PFAS – compounds requiring different methods of effective treatment. Biological effects of PFAS – exposure have gained rapid awareness within the last few decades, yet knowledge is still spotty concerning the effect of various alternatives to now banned compounds with alternatives found in shorter chained PFAS-

The longevity of PFAS coupled with the continued production of lesser understood PFAS – alternatives to known compounds and the wide range of different compounds within this family suggest that PFAS will remain an issue for humanity for the foreseeable future. More research into the covered aspects of PFAS needs to be done to understand as much as possible the effects these compounds have on the environment and humanity. Tightening of guidelines and regulations is needed to tackle the hurdles associated with even properly working with contaminated material and research into ways of eliminating PFAS – contamination, both in the environment and humans, is imperative. Based on the data collected in this paper, these steps need to be made to safeguard humanity from the dangers, both potential and still unknown, that PFAS present.

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