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PFAS Contamination in Groundwater

Evaluating Factors Influencing the Impact of PFAS Contamination on the Drinking Water Source in a Holistic Approach

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Anna Söderman

Division of Water Resources Engineering
Department of Building and Environmental Technology
Lund University

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By: Anna Söderman

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Division of Water Resources Engineering
Department of Building & Environmental Technology
Lund University
Box 118
221 00 Lund, Sweden

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Author(s):	Anna Söderman
Supervisor:	Dauren Mussabek
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Abstract

Aqueuous Film Forming Foam (AFFF) containing Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) is one of the major sources of groundwater contamination in Sweden. Groundwater contamination caused by the use of AFFF in correlation to fire training events was investigated in Kallinge, Sweden. At the site groundwater was previously used as a drinking water source consequently affecting the inhabitants. In Sweden there are many areas with similar issues. The variation in PFAS concentrations corresponding to an annual emission estimate was studied at two groundwater wells. Factors influencing the estimate as well as how it affects the assessment of a contaminated area were analysed. The emission source and rates were firstly studied followed by an estimate of the transport in soil and groundwater. Three PFAS (PFOS, PFHxS, and FASA) were selected as possible substances in AFFF with a yearly total emission of 280±220 moles. Of the emission source 67 % of the total amount partitioned into soil and 33 % to the groundwater, thus the majority was retained in the soil. The estimated concentration in two of the drinking water wells were a total of 600000±450000 ng/L and 490000±370000 ng/L, with 76% consisting of FASA, 14 % of PFHxS, and 10 % of PFOS. In addition, the removal of water from the drinking water wells showed a reduction in the groundwater concentration by 17 %.

Sammanfattning

Brandskum som innehåller per- och polyfluorerade ämnen (PFAS), på engelska Aqueuous Film Forming Foam (AFFF), är en av de främsta källorna till föroreningarna i Sverige. Grundvattenförorening orsakat av användandet av AFFF under brandövningar har undersökts i Kallinge, Blekinge. I området har grundvattnet använts som råvatten vilket lett till höga halter av PFAS i dricksvattnet. Liknande fall förekommer däremot på andra områden i Sverige. Variationen av PFAS koncentration motsvarande ett årligt utsläpp uppskattades vid två grundvattenbrunnar vilka tidigare använts för dricksvattenförsörjning. Faktorer som påverkar den uppskattade koncentrationen samt hur dessa påverkar bedömningen av ett förorenat område undersöktes och modellerades. Utsläppskällans sammansättning och kvantitet undersöktes först följt av transport i mark och grundvatten. Tre PFAS (PFOS, PFHxS, and FASA) valdes som möjliga ämnen i AFFF med en årlig mängd utsläpp av 280±220 mol. Av dessa fördelades 67% i marken och 33 % i grundvattnet. Koncentrationen vid grundvattenbrunnarna var totalt 600000±450000 ng/L och 490000±370 000 ng/L där 76% bestod av FASA, 14% av PFHxS och 10% av PFOS. Påverkan av uttaget från brunnarna uppskattades minska koncentrationen i grundvattnet med 17%.

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Abbreviations

General

AFFF	Aqueous Film Forming Foam
AWI	Air-Water Interface
CAFS	Compressed Air Foam System
CLP	Classification, Labelling and Packaging of substances and mixtures
EC	European Commission
ECHA	European Chemicals Agency
ECF	Electrochemical Fluorination
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EU	European Union
GC/MS	Gas chromatography-mass spectrometry
HRMS	High Resolution Mass Spectrometry
HPLC	High-Performance Liquid Chromatography
MB	Miljöbalken
MS/MS	Tandem Mass Spectrometry
MSB	Myndigheten för Samhällsskydd och Beredskap
NAFS	Nozzle Aspirated Foam System
NAPL	Non-aqueous Phase Liquid
PFAS	Perfluoroalkyl and Polyfluoroalkyl Substances
PMT	Persistent, Mobile and Toxic
POPs	Persistent and Organic Pollutants
SOC	Soil Organic Carbon
SGI	Statens Geotekniska Institut
SVHC	Substances of Very High Concern

PFAS

PFAAs	Perfluoroalkyl acids				
	PFCAs	Perfluoroalkyl carboxylates			
		PFBA	Perfluorobutanoic acid		
		PFPeA	Perfluoropentanoic acid		

		PFHxA	Perfluorohexanoic acid
		PFHpA	Perfluoroheptanoic acid
		PFOA	Perfluorooctanoic acid
		PFNA	Perfluorononanoic acid
		PFDA	Perfluorodecanoic acid
		PFUnDA	Perfluoroundecanoic acid
		PFDoDA	Perfluorododecanoic acid
		PFTrDA	Perfluorotridecanoic acid
		PFTeDA	Perfluorotetradecanoic acid
		PFHxDA	Perfluorohexadecanoic acid
		PFOcDA	Perfluorooctadecanoic acid
	PFSAs	Perfluoroalkane sulfonic acids	
		PFBS	Perfluorobutanesulfonic acid
		PFPeS	Perfluoropentanesulfonic acid
		PFHxS	Perfluorohexane sulfonate
		PFHpS	Perfluoroheptanesulfonic acid
		PFOS	Perfluorooctane sulfonic acid
		PFNS	Perfluorononanesulfonic acid
		PFDS	Perfluorodecanesulfonic acid
		PFDoDS	Perfluorododecane sulfonic acid
		PFTrDS	Perfluorotridecane sulfonate
	PFSAs	Perfluoroalkane sulfonic acids	
	PFSIAs	Perfluoroalkane sulfinic acids	
	PFPAs	Perfluoroalkyl phosphonic acids	
PASF	Perfluoroalkane sulfonyl fluorides		
FASAs	Perfluoroalkane sulfonamides		
	FOSA	Perfluorooctane sulfonamide	
PAFs	Perfluoroalkanoyl fluorides		
PFAIs	Perfluoroalkyl iodides		
PFALs	Perfluoroalkyl aldehydes		
N-FASAs	N-Alkyl perfluoroalkane sulfonamides		
	MeFOSA	N-methyl perfluorooctane sulfonamide	
	EtFOSA	N-ethyl perfluorooctane sulfonamide	

FASEs	Perfluoroalkane sulfonamidoethanols	
	MeFOSE	N-Methyl perfluorooctane sulfonamidoethanol
	EtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol
FASAAs	Perfluoroalkane sulfonamidoacetic acids	
	FOSAA	Perfluorooctane sulfonamidoacetic acid
	EtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid
	MeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid
SFAs	Semifluorinated n-alkanes	
n:2 FTIs	n:2 Fluorotelomer iodides	
n:2 FTOs	n:2 Fluorotelomer olefins	
n:2 FTOHs	n:2 Fluorotelomer alcohols	
	n:2 FTOH	n:2 Fluorotelomer alcohol
n:2 FTACs	n:2 Fluorotelomer acrylates	
PAPs	n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates	
n:2 FTALs	n:2 Fluorotelomer aldehydes	
n:2 FTCAs	n:2 Fluorotelomer carboxylic acids	
n:3 Acids	n:3 Saturated acids	
n:2 FTSAs	n:2 Fluorotelomer sulfonic acids	
	6:2 FTSA	6:2 Fluorotelomer sulfonate
	8:2 FTSA	8:2 Fluorotelomer sulfonate
	10:2 FTSA	10:2 Fluorotelomer sulfonate
APFO	Ammonium perfluorooctanoate	
HPFO-DA	Hexafluoropropylene oxide-dimer acid (also known as “**GenX**”)	
PFPE	Polymetric perfluoropolyethers	

1. Introduction

Problems with elevated levels of Per- and Poly-fluoroalkyl substances (PFAS) is more of a rule than exception in Swedish watercourses (VISS, n.d.-b). Due to the substances persistence to natural degradation they have been named 'forever chemicals' (Sörengård et al., 2022), which poses a difficult issue to the areas affected. In Sweden, the main historical and current sources of these chemicals in the environment are associated with areas and locations exposed to firefighting foam containing PFAS (Banzhaf et al., 2017; Gobelius et al., 2018). However, many different sources contribute to the release worldwide (Banzhaf et al., 2017).

PFAS are a class of thousands of manmade chemicals containing different fluorinated alkyl moieties and have over the last decade increased in attention worldwide (Banzhaf et al., 2017; Lyu et al., 2022). However, PFAS have been mass-produced and used since the 1940s (Lyu et al., 2022). Applications include textiles, packaging, household products, pesticides, aqueous firefighting foam (AFFF) and much more (Gobelius et al., 2018; Lyu et al., 2022). Studies have shown that PFAS can be toxic for both animals and humans (Banzhaf et al., 2017); where an increased risk of testicular and kidney cancer in human, as well as hormonal imbalances and lowered fertility correlated with PFAS have been reported (Svenskt Vatten, 2021). Due to the substances high persistence, bioaccumulation, and surfactant properties, the substances can remain in soil and other environments for a vast amount of time continuing to leach into aquatic environments (Banzhaf et al., 2017). They can also be highly mobile in water and be classified as Persistent, Mobile and Toxic (PMT) substances (Svenskt Vatten, 2022).

There are several PFAS contamination sources, both diffuse and point sources. The major point sources include wastewater treatment plants, firefighting foam, and landfills (Banzhaf et al., 2017; Gobelius et al., 2018). Diffuse sources include contamination from a range of industrial and urban sources, which can lead to long range transport of the substances from the contaminant source (Banzhaf et al., 2017; Gobelius et al., 2018). The focus in this study will be point sources originating from firefighting foam, though it is important to know that a vast number of other sources exist.

Due to the complexity of groundwater measurements, this medium has not been investigated in the same systematic way as other aquatic environments in Sweden (Banzhaf et al., 2017). Instead, most sampling have been done close to known point sources such as airfields and landfills (Banzhaf et al., 2017). In these known point sources the highest PFAS concentrations have been found, especially from areas where AFFF have been used (Banzhaf et al., 2017). Approximately a fourth of the drinking water in Sweden originates from groundwater sources situated in highly permeable aquifers which are, therefore, vulnerable to contamination (Banzhaf et al., 2017; Krisinformation, 2021). Hence, understanding how PFAS affects these areas is of importance in order to secure current and future drinking water sources as well as to fulfil two of Sweden’s environmental objectives “Good-Quality Groundwater” and “A Non-Toxic Environment”.

1.1 Research Questions

The focus of this master thesis is to investigate groundwater contaminated by PFAS previously used for drinking water in a holistic point of view. Starting from the source and working towards the well water, evaluating each step of the process, and finally linking the findings to the current regulations existing in Sweden today. By working in this way, it can capture the larger picture of PFAS contamination originating from firefighting foam, the effect it has as well as factors which influence it. It is worth to keep in mind that not all aspects can be covered in a master thesis. Thus, this study is limited to a case study based in Kallinge, Blekinge, where the groundwater, used as a drinking water source, has been contaminated by the use of firefighting foam. Though, there are many similarities with this case study and other PFAS polluted areas in Sweden as well as the rest of the world.

The research questions to be answered can be seen below.

- What is the PFAS emission source and how can it be estimated?

- What is the distribution and composition of PFAS in soil and groundwater at the study site?
- What is the concentration of PFAS in the drinking water wells at the study site?
- How can estimations be improved and what are the limitations?
- What regulations are there on PFAS and how do they correspond to the estimated values?

2. Background and Theory

2.1 PFAS Background

2.1.1 Physical and Chemical Properties

PFAS is a group of manmade chemicals consisting of thousands of different substances, each containing a fluorine-carbon alkyl chain with varying length (Banzhaf et al., 2017; Lyu et al., 2022). Due to the large variety of substances, each with different structure, the transport pattern of a specific substance can vary greatly. Thus, it is important to understand the physical and chemical properties of PFAS for the prediction of their fate and transport in the environment (ITRC, 2022).

2.1.2 Definition and Classification

There is, as to today, no universally accepted definition or classification of PFAS. The most used is defined by Buck et al. (2011) and is the definition that will be used in this study. It defines PFAS as; "PFASs are aliphatic substances containing one or more C atoms on which all the H substituents present in the nonfluorinated analogues from which they are notionally derived have been replaced by F atoms, in such a manner that PFASs contain the perfluoroalkyl moiety $C_nF_{2n+1}^{-}$".

PFAS can further be divided into two main classes: polymers and non-polymers, as seen in Figure 1. The definition from Buck et al. (2011) will also be used for polymers which defines them as "all polymers for which one or more of the monomers units contains the element F, in the backbone and/or in the side chain". In addition, PFAS polymers can be divided into three subclasses; fluoropolymers, polymeric perfluoropolyethers (PFPE) and side-chain fluorinated polymers (Buck et al., 2011). Polymers are larger molecules than non-polymers and are formed by combining many identical smaller molecules, or monomers, in a repeating pattern (ITRC, 2022). The different subclasses of polymers have different characteristics. Fluoropolymers contain a carbon-only polymer backbone with fluorine attached to it. They have higher molecular weight and are extremely stable, which makes them less bioavailable than other PFAS (ITRC, 2022). Polymetric PFPE contains a carbon and oxygen polymer backbone with fluorine attached to it, however not a lot is known about these substances in the environment (ITRC, 2022). Side-chain fluorinated polymers contain a nonfluorinated polymer backbone, from which fluorinated side chains branch. It is the non-polymers which will be the focus of this study, though it is important to keep in mind that polymer PFAS exist and can have the ability to transform into non-polymer PFAS (ITRC, 2022).

Non-polymer PFAS can be divided into two subclasses: perfluoroalkyl substances and polyfluoroalkyl substances, as seen in Figure 1, where the difference between per- and polyfluoroalkyl substances is the degree of saturation of fluorine. The definition from Buck et al. (2011) will also be used to define the non-polymers, which states; “In perfluoroalkyl substances all the H atoms have been replaced whereas in polyfluoroalkyl substances at least one has been replaced”. The main difference is that polyfluoroalkyl substances have the potential to be transformed into perfluoroalkyl substances, whereas perfluoroalkyl substances are more recalcitrant (Buck et al., 2011). Non-polymer PFAS are the most studied class of PFAS in the environment. The most studied group of substances in non-polymer PFAS is perfluorinated alkyl acids (PFAAs). They are highly recalcitrant and other PFAS have the potential to transform into this group. They are sometimes referred to as “terminal PFAS” due to this (Buck et al., 2011). Another way of classifying PFAS is by their functional group which includes carboxylates, sulfonates, sulfates, phosphates, amines, and others. It is mainly these functional groups that govern many fate and transport properties of PFAS (ITRC, 2022).

The classification of PFAS can be seen in Figure 1, and are derived from Buck et al. (2011) and is the classification further used in the study.

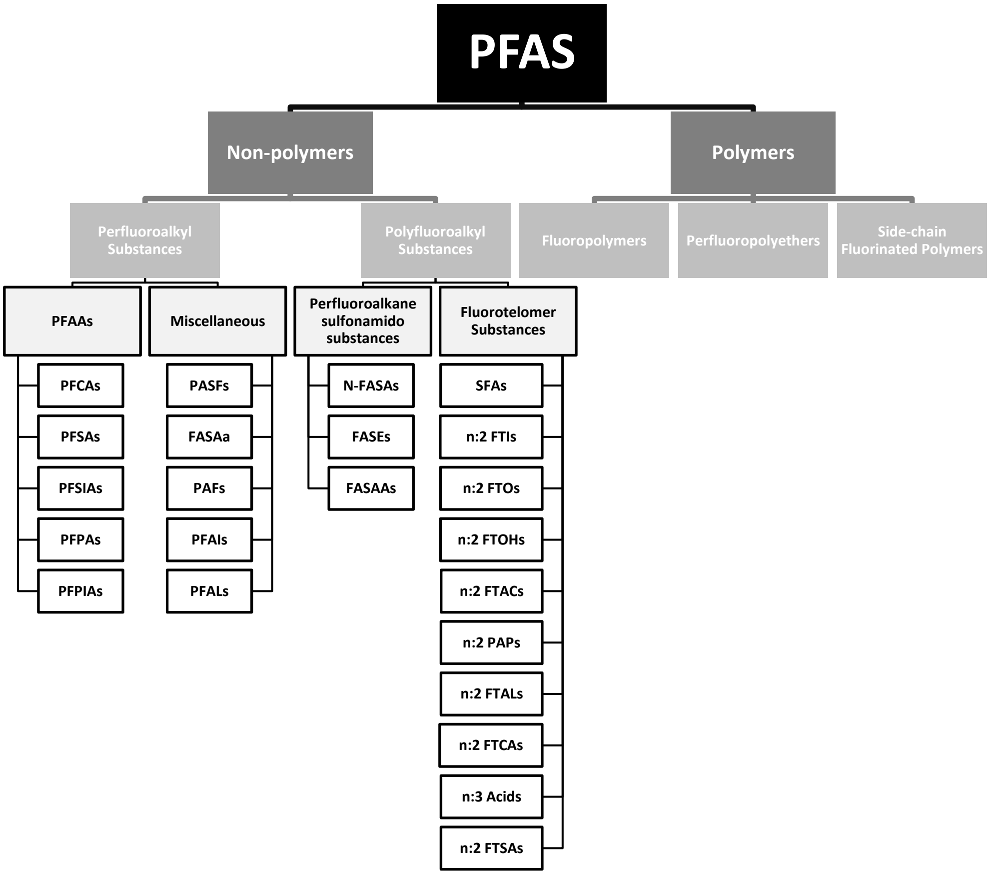

Figure 1 – Classification of PFAS used in the study.

2.1.3 Perfluoroalkyl-moity

The common structure of PFAS is their perfluoroalkyl moity, consisting of one or multiple carbon-fluorine bonds. Fluorine is the most electronegative element which induces a polarisation in the bond. In addition, the overlap between the 2s and 2p electron orbitals of the fluorine and the orbitals of the carbons makes the bond extremely polarized. It is, therefore, the strongest of known covalent bonds (Lyu et al., 2022). It is also this moity which makes PFAS more thermally and chemically stable than similar hydrocarbon analogues (Lyu et al., 2022). The fluorine is, therefore, held tightly due to the high electronegativity and are reluctant to get involved in resonance or interact as hydrogen bonding acceptors (O'Hagan, 2008).

The carbon-fluorine bond also provides the hydrophobic and oleophobic properties as well as stability of the substances, which has also led to their widespread usage (Savvaides et al., 2021). The strength of the bond also prevents significant degradation of the substances and their high resistance to environmental transformation (Lyu et al., 2022; Savvaides et al., 2021).

2.1.4 Branched and Linear

Depending on the manufacturing method of PFAS, the substances can be either of branched or linear isomers. Branched isomers are more polar than linear, and is therefore suggested to be more prone to partition to water than linear (Schulz et al., 2020). Linear isomers have on the other hand been suggested to be more likely to sorb to soil and sediments (Gobelius et al., 2018). Studies have also shown that the percentage of branched isomers increases which depth, which corresponds to the sorption capacities of the isomers, where the branched isomers are more mobile than the linear (Lyu et al., 2022).

2.1.5 Chain Length

PFAS are often classified as “long-chain” or “short-chain”. The definition is mostly applied to perfluoroalkyl carboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs), which are subgroups of PFAAs, as seen in Figure 1 (Buck et al., 2011; ITRC, 2022). Long-chain PFCAs are defined as consisting of 8 or more carbons whereas long-chain PFSAs are defined as consisting of 6 or more carbons. Furthermore, short chain PFCAs are defined as consisting of 7 or less carbons and PFSAs as 5 or less carbons (Buck et al., 2011; ITRC, 2022). Within this study a simplified adaptation of this definition will be used, where long-chain PFAS is defined as consisting of 7 or more carbons in its carbon chain, and short-chain PFAS as consisting of 6 or less carbons in its carbon chain.

The chain length is suggested to affect the sorption mechanisms of the substances. Longer chain lengths have higher hydrophobicity than shorter chain lengths leading to increased sorption (Adamson et al., 2022; Gobelius et al., 2018).

2.1.6 Surfactants

Generally, PFAS have a surfactant like nature with a hydrophilic (polar) head and hydrophobic tail (Buck et al., 2011). Surfactants lower the surface tension of a liquid and can decrease the interfacial tension between two liquids or between a liquid and a solid (Buck et al., 2011). PFAS are generally more surface active than hydrocarbon surfactants and only a low concentration of PFAS is therefore needed to reduce a liquids surface tension (Lyu et al., 2022).

Due to the surfactant properties, PFAS have high sorption capacities which have been suggested to be correlated with the organic carbon fraction in soil (Higgins & Luthy, 2006). Since the material properties of PFAS vary, such as the molecular weight and carbon chain length, the surfactant capacity among the substances consequently varies as well. The extent of fluorination and location of the F atoms highly affects this (Buck et al., 2011). Studies have also shown that PFAS are prone to micellization at low concentrations, hence below the critical micelle concentration (CMC), however more studies have to be conducted in this area (ITRC, 2022).

2.1.7 Interactions

PFAS can interact in several ways in the environment where the main interactions include electrostatic interactions, hydrophobic interactions, hydrogen bonding, and ligand exchange (Lyu et al., 2022). The two main interactions to control transport in the environment, with regards to PFAS, is considered to be electrostatic and hydrophobic interactions (Lyu et al., 2022). However, the research within this field is still developing and these findings should be taken with some precaution.

Electrostatic interactions depend on the charge of a substance polar head, i.e., if it is anionic, cationic, zwitterionic or non-ionic. Thus, the charged polar head will either be repelled or attracted to charged surfaces, such as soil particles (Lyu et al., 2022). Hydrophobic interactions, on the other hand, occurs at the fluorinated tail of the substances and between other hydrophobic surfaces such as organic carbon. Typically long-chain PFAS, thus more hydrophobic, substances have greater hydrophobic interactions than short chained PFAS (Lyu et al., 2022).

In addition, hydrogen bonding is an electrostatic attraction which occurs between hydrogen and another more electronegative atom (Lyu et al., 2022), which occurs at the polar head. Furthermore, ligand exchange can occur through exchange of a surface's functional group with the polar head of the PFAS (Lyu et al., 2022). However, it is uncertain to which degree these two mechanisms affect the transport and sorption of PFAS.

2.1.8 Charge – Anionic, Cationic, Zwitterionic and non-ionic

PFAS are often strong acids or bases and therefore dissociates in water resulting in ionization (Lyu et al., 2022). The ionization of compounds is highly dependent on the acidity/alkalinity of the compound as well as the pH of the medium (Lyu et al., 2022). Generally uncharged substances are less water soluble, hence less mobile, due to their ability to not act as a hydrogen donor or acceptor.

Historically, mainly anionic PFAS have been studied, such as PFAAs. Over the last years more PFAS have been identified where the majority of the newly identified have been zwitterionic and non-ionic PFAS (Lyu et al., 2022). Consequently, less is known of the fate and transport behaviour of cationic, zwitterionic and non-ionic PFAS. Some studies suggest a larger sorption affinity for zwitterionic and cationic PFAS than for anionic due to enhanced electrostatic interactions (Adamson et al., 2022).

2.1.9 Environmental Factors - Partitioning

The transport of PFAS is highly affected by both microscopic and macroscopic conditions as well as intrinsic properties of the medium. Due to the variance in properties of PFAS, as discussed above, the hydrophobic and electrostatic interactions which occurs in different medium will vary depending on the composition of PFAS.

2.1.9.1 Soil Parameters

Soil consists of a variety of different materials which vary greatly spatially. Thus, the properties of soil will vary, and must be carefully determined to get an accurate picture of the transport mechanisms occurring in the medium. These properties includes surface charge, soil organic carbon (SOC), as well as cation exchange capacity (CEC) (Lyu et al., 2022). Natural soils often carry a negative surface charge which can lead to attractive or negative interactions leading to either sorption or repelling respectively (Lyu et al., 2022) mainly via electrostatic interactions (ITRC, 2022; Lyu et al., 2022). Thus, anionic PFAS would be more likely repelled and cationic adsorbed. It is also possible that the soil contains minerals which are of positive charge which would then lead to the opposite sorption pattern (Lyu et al., 2022).

The organic carbon fraction of soil are often small but can lead to strong adsorption of PFAS through their carbon-fluorine tail by hydrophobic interactions (Lyu et al., 2022). This is mostly present with long chain PFAS whereas short chain PFAS do not have as strong hydrophobic interactions (Lyu et al., 2022). Moreover, the hydrophobic interactions are highly dependent on the hydrophobicity of a substance, thus the polar head and its molecular size also influence the sorption ability. This leads to, for example, that sulfonate moieties sorbs more than carboxylate moieties (Lyu et al., 2022). Some studies have also shown indications of hysteresis under certain conditions, leading to a slower desorption of PFAS than adsorption (ITRC, 2022).

In groundwater the same interactions occur as in soil. However, due to the saturation of water, the substances are more likely to be subject of mass transfer with advective groundwater flow (ITRC, 2022).

2.1.9.2 Solution Chemistry

The solution chemistry is another factor influencing the transport of PFAS. One of the most important aspects is the pH, which can alter the charge of the substances as well as soil grains. In higher pH both SOC as well as clay minerals become more negatively charged, causing increased electronic repulsion for anionic PFAS and attraction for cationic PFAS (Lyu et al., 2022).

Whereas in low pH the SOC can become protonated which can cause increased sorption for anionic PFAS and increased mobility for cationic PFAS (Lyu et al., 2022).

In addition, the cation concentration in the solution can decrease the negative charge sites in the soil, which leads to a decrease of electrostatic interactions for cationic PFAS and an increase of electrostatic interactions for anionic PFAS (ITRC, 2022; Lyu et al., 2022).

2.1.9.3 Air-Water Interface

One major interaction mechanism for PFAS is the partitioning into the air-water interface (AWI). The AWI is important in the vadose zone where the unsaturated conditions provide significant air-water areas, which the hydrophobic tail partitions to (Lyu et al., 2022). The AWI, therefore, has the potential for increased retention (ITRC, 2022; Lyu et al., 2022).

2.1.9.4 Non-Aqueous Phase Liquid Interface

In certain areas there can be co-contaminants present such as non-aqueous phase liquids (NAPLs) originating from hydrocarbon fuels (ITRC, 2022). The PFAS may, therefore, partition into the NAPL and accumulate along the NAPL/water interface (ITRC, 2022). It has been suggested that these processes may result in an increase of the retardation as well as persistence of PFAS (ITRC, 2022; Lyu et al., 2022).

2.1.10 Transformation and Degradation

Due to the strong carbon-fluorine bond present in PFAS, biodegradation and transformation is often limited to regions of the molecules that are not fully fluorinated, such as polyfluoroalkyl substances and polymetric substances (Lyu et al., 2022). Thus, these may transform into more recalcitrant PFAS, such as PFAAs and short chain PFAS (Lyu et al., 2022). However, the pathways of the transformation and degradation is still not well understood, and more research must be done to establish these.

2.1.11 Remediation Efforts

There are, as to today, no clear remediation strategy for PFAS. In Sweden the current remediation strategy towards groundwater has been by using ‘pump and treat’. However, soil extraction and collection of runoff water have also been done (Banzhaf et al., 2017).

2.2 Aqueous Film Forming Foam

There are many kinds of firefighting foams used to extinguish fires, each being used at different classes of fires. The major classes are class A and class B. Class A foam is intended to be used in fibrous material such as wood and do not typically contain PFAS. Class B foam is intended to be used to extinguish liquid fires as for example oil, diesel, plastic and alcohol (KEMI et al., 2016). Within class B there are various kinds of foams such as alcohol-resistant film-forming foam (AR-AFFF), Film-forming fluoroprotein foam (FFFP), Alcohol-resistant film-forming fluoroprotein foam (AR-FFFP), Fluoroprotein foam (FP), Alcohol-resistant fluoroprotein foam (FPAR) and Aqueous Film Forming Foam (AFFF) (ITRC, 2022). Most of the AFFFs have been produced by using fluorinated surfactants (PFAS) and is the foam that is in focus of this report (ITRC, 2022). The type of foam used depends on the standards and specifications required for their use in different systems (Rupert et al., 2005). It is worth to keep in mind that due to the properties of firefighting foam needed to extinguish fires all foams impact the environment in one way or the other (Rupert et al., 2005).

AFFF have been used to extinguish fires since the early 1960s, with a variety of different production techniques and composition (Lyu et al., 2022). It has greater surface lowering properties than hydrocarbon based foams and by creating a film around the fire it is more effective in extinguishing fires than other analogues (Place & Field, 2012). AFFF have been the most widely used and available class B foam (ITRC, 2022). Its repeated use, especially at military sites, has contaminated the surrounding soil and groundwater (Moody & Field, 2000).

There are several methods to manufacture AFFF, each which leads to different composition in the product. In addition, the raw materials used as well as the manufacturing efficiency will affect the end-product, and consequently also the PFAS composition in the soil and groundwater. Since it has been produced for a long period of time, there is a large uncertainty on how these compositions look like. Thus, it is of importance to analyse the compositions to get an understanding of the following contamination in the environment.

2.2.1 General Composition

Commercial AFFF formulations vary among manufacturers. The major components include a solvent, surfactants (e.g.: hydrocarbon or/and fluorocarbon), stabilizing agents and water (Moody & Field, 2000). Most of the foam (in its stock solution) consists of water with about 60 % of the total mass (ITRC, 2022; Moody & Field, 2000). Moreover, around 20% is made up out of solvents and around 18 % of surfactants with a small fraction consisting of PFAS (ITRC, 2022). The percentage of PFAS vary between different brands of foam. Even though the concentration of PFAS is in overall low, when mixed with water the resulting solution achieves the interfacial tension characteristics needed to extinguish heavier fires (ITRC, 2022). The AFFF then forms a film on the surface consisting of two mixed monolayers of surfactants (Moody & Field, 2000).

2.2.2 Manufacturing Processes

There are two main surfactant manufacturing processes used to produce AFFF, which results in a difference in composition of PFAS. These processes are electrochemical fluorination (ECF) and flourotelomerization.

2.2.2.1 Electrochemical Fluorination

The first commercial production process to synthesize PFAS was ECF (Korzeniowski et al., 2018), which started to be used in the industry from the late 1960s (ITRC, 2022). In ECF organic raw materials undergo electrolysis in anhydrous HF which replaces all the hydrogen atoms with fluorine, leading to perfluorinated substances (Moody & Field, 2000). It has a free radical nature which leads to carbon chain arrangements and breakage. This results in a mixture of linear and branched isomers (Buck et al., 2011; ITRC, 2022). The ratio of linear and branched isomers is approximately 70:30% (ITRC, 2022; Korzeniowski et al., 2018). The main subgroups of PFAS in ECF derived AFFF are perfluoroalkane sulfonic acids (PFSAs), perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonamides (FASAs) and perfluoroalkane sulfonamide amino carboxylates (Korzeniowski et al., 2018). The PFAS results in both even and odd carbon chain lengths and can include many side products (ITRC, 2022; Moody & Field, 2000). ECF have been economically attractive due to the relatively low cost of electricity and hydrogen fluoride reagent (Moody & Field, 2000).

The main and first manufacturer of ECF AFFF was 3M which produced an AFFF called *Light Water* (ITRC, 2022). The composition of the foam has changed throughout the years used and do, therefore, vary in PFAS composition. The main component present in many formulations were, however, perfluoroalkyl sulfonates and its salts, as seen in Table 1. These were mainly C6-C8 such as perfluorohexanesulfonic acid (PFHxS) and perfluorooctane sulfonic acid (PFOS) (Place & Field, 2012). In addition, 3M AFFF was composed of various zwitterionic PFAS, named amphoteric fluorialkylamide derivatives (Place & Field, 2012), as seen in Table 1. Although the foam is not reported to consist of PFCAs, they contain polyfluorinated substances that have shown to degrade into PFCAs in the environment (ITRC, 2022). In the early 2000s 3M withdrew from long chain PFAS, such as PFOS, and transitioned to short chain PFAS instead (Korzeniowski et al., 2018). The AFFF containing short chain PFAS are not today in use since these did not meet required firefighting specifications (Korzeniowski et al., 2018). Instead, there were a shift in the early 2000s towards fluorotelomerized AFFF.

Table 1 - 3M lightwater composition, an ECF AFFF (3M, 2005; Moody & Field, 2000).

Components	**% by weight**
Water	69-71
Diethylene glucol butyl ether	20
Amphoteric fluoroalkylamide derivative	1-5
Perfluoroalkyl sulfonate salts	0.5-1.5
Alkyl sulfate salts	1-5
Triethanolamine	0.5-1.5
Residual organic fluorochemicals	Not known

2.2.2.2Fluorotelomerization

In fluorotelomerization a raw product, for example perfluoroalkyl iodide (PFAI), reacts with two or more unsaturated molecules (Buck et al., 2011; Moody & Field, 2000). This produces various fluorotelomer based PFAS which are all with an even carbon chain length and mainly linear (Buck et al., 2011; ITRC, 2022; Korzeniowski et al., 2018; Moody & Field, 2000). Fluorotelomerization mainly produces polyfluorinated alkyl substances and polymers, although they can contain trace quantities of perfluorinated alkyl substances such as PFAAs (ITRC, 2022).

These fluorotelomer foams have been in use since the 1970s but became more frequently used in the beginning of 2000s (ITRC, 2022). Historical fluorotelomer based AFFF mainly contained long chain PFAS whereas modern production mainly produce short chain PFAS (Korzeniowski et al., 2018).

2.2.3 Foam Utilization

Firefighting foam can be used in several different ways. These, in most of the cases, depends on the protocol and the type of hazard and will govern the use of class A and/or class B foam. Furthermore, the type of equipment plays a big role in how firefighting foam is utilized. The fire suppression protocols, and the type of the equipment can vary both locally and internationally. In Sweden, the aggregation of the foam is primarily achieved by means of the two systems: nozzle aspirated foam system (NAFS) and compressed air foam system (CAFS). However, the use of a particular system and/or firefighting foam is inconsistent between regions and stations. In either of the scenarios the foam must be mixed with water and air. Thousands litres of foam solution may be applied during a given event (ITRC, 2022). Thus, if not constrained sufficiently the foam could contaminate a large surface area.

2.3 Analytical Methods

One of the major historical challenges when it comes to PFAS analysis has been the technical aspect, where there has been a lack of analytical standards and liquid chromatography–mass spectrometry (LC-MS/MS) instruments that have not had desired accuracy or sensitivity (Banzhaf et al., 2017). This has led to a limited range of PFAS that have been identified, which could have given a reduced understanding of the large spectra of substances. Historically mainly PFAAs have been identified and analysed (Lyu et al., 2022). Over the last years numerous isotopically labelled standards have been developed and the detection limits have been significantly lowered, which have led to new discoveries of multiple PFAS (Banzhaf et al., 2017). Understanding the difference between the various analysis methods are, therefore, of importance since the detection vary greatly, and could consequently affect the assessment of a contaminated area.

The major analysis methods relevant for this paper will hereby be taken up. Note that the field of analytical chemistry is vast and there are more analytical methods than being covered by this report. The exact procedure will not be discussed either, instead the focus is to highlight the difference between methods to understand the impact it can have on the assessment of a sample.

2.3.1 Targeted Analysis

Most methods used in PFAS analysis are targeted, which means that they are applicable to a set of known analytes (U.S. EPA, 2023). These are often what is referred to when discussing PFAS 4, PFAS 11 etc, where the number is the number of target analytes in the analysis.

Currently most methods use LC/MS/MS for the analysis of PFAS (ITRC, 2022). LC/MS/MS are especially suited for analysis of ionic compounds such as PFAAs. For non-ionic compounds gas chromatography-mass spectrometry

(GC/MS) can also be used, such as FTOHs, although it is not used in the same extent as LC/MS/MS (ITRC, 2022).

2.3.1.1TOP Assay

Since PFAS consist of a large spectrum of substances the target analysis may not be able to identify all the substances existing in a sample. Thus, additional techniques have recently been developed to be able to identify these. The main technique used today is the TOP assay (or TOPA), which transforms PFAS to PFAAs though oxidative digestion before the target analysis (ITRC, 2022). The oxidized PFAS can, therefore, be identified though LC/MS/MS in the same matter as in regular analysis since PFAAs are often included in the target analyte list. Not all PFAS is likely to be subject to oxidation, and the analysis may, therefore, not be able to capture all the substances in the samples or quantify the original PFAS concentration (ITRC, 2022). However, the results often identify much larger concentrations than regular analysis.

2.3.2 Non-targeted Analysis

In contrast to targeted analysis, there are also methods to analyse PFAS in a non-targeted way (screening), which aims at identifying a wider spectrum of substances. When identifying substances present in a sample this would theoretically be more ideal since it can identify all the known as well as unknown analytes in a sample (U.S. EPA, 2023). This is often done in high-resolution mass spectrometry (HRMS) (ITRC, 2022). It is, however, more time demanding and can be subjective. In addition, there is no standard protocol for PFAS yet, and further research would therefore have to be conducted.

2.4 Legislations and Regulations

Currently there are several different regulations for PFAS both on international and national level which were developed in the last couple of years. Since the U.S. was the first country to start to manufacture PFAS it is not surprising that the first regulations came from the country, as a response to an increase of awareness of the impact of the substances (Bock & Laird, 2022). However, other regulatory bodies have to date responded and is continuing to develop ways to regulate the substances. There are currently no regulations on PFAS as a group, instead the existing regulations focus on individual substances.

It is important to understand and know how and why the regulations have been implemented to understand the difficulties with managing PFAS and how it affects contaminated sites.

2.4.1 Early Regulations

The first regulation with regards to PFAS occurred in 2000, when the company 3M phased out PFOS. This was a response to the increased awareness of the negative impacts on the environment as well as humans of PFAS (Bock & Laird, 2022). In correlation to the phaseout of PFOS, the company also ceased the production of PFOA which was, at the time, the main polymerisation aid used to produce fluoropolymers (Bock & Laird, 2022). During the same time U.S. Environmental Protection Agency (EPA) created a voluntary global stewardship program on PFOA, (2010/2015 PFOA Stewardship Program), in which 8 companies joined. In order to meet the program goals most companies stopped manufacturing as well as importing long-chain PFAS and consequently transitioned towards other substances (U.S. EPA, 2022). To complement the PFOA Stewardship Program, the U.S. EPA issued another set of regulations, “significant new use rules”, which requires manufacturers and processors of these chemicals to notify the EPA of new uses of these chemicals before they are commercialised (Bock & Laird, 2022).

2.4.2 Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (POPs) is an international environmental treaty signed in 2001 and entered into force in 2004. It aims towards protecting the environment from POPs (Stockholm Convention, n.d.-a) and is signed by 152 states. It is built up upon three annexes: Annex A, Annex B, and Annex C. Where in simple terms Annex A aims towards prohibition and/or elimination, Annex B towards restriction and Annex C towards reduction (Stockholm Convention, n.d.-a).

Currently there are three groups of compounds that are covered by the convention, these are PFOS, PFOA, and PFHxA. PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) was added to Annex B of the convention in 2009 (Decision SC-4/17) (Stockholm Convention, n.d.-b), which corresponds to hundreds of substances (Kemikalieinspektionen, 2022c). In 2019, the Conference of the Parties listed PFOA, its salts and PFOA-related compounds in Annex A of the Convention (Decision SC-9/12) (Stockholm Convention, n.d.-b), which corresponds to around 800 substances (Kemikalieinspektionen, 2022c). In 2022, the Conference of the Parties listed PFHxS, its salts and PFHxS-related compounds in Annex A to the Convention (Decision SC-10/13) (Stockholm Convention, n.d.-b). Though, an indicative list of the substances covered is yet to be made (Stockholm Convention, n.d.-b). In addition, the POPs Review Committee is currently reviewing long-chain PFCAs, their salts and related compounds, proposed for listing in Annexes A, B and/or C to the Stockholm Convention (Stockholm Convention, n.d.-b).

The Stockholm Convention on Persistent and Organic Pollutants have been incorporated into the EU through the POPs legislation (EU 2019/1021).

2.4.3 REACH

REACH (EC 1907/2006) is an EU wide regulation which regulates the supply and use of substances. This is done by the four processes of REACH, namely the registration, evaluation, authorisation, and restriction of chemicals. The Regulation also calls for the progressive substitution of the most dangerous chemicals (referred to as "substances of very high concern" (SVHC)) when suitable alternatives have been identified (European Commission, n.d.). There are currently 9 PFAS on the candidate list for SVHC as seen in Table 2. When substances are listed as SVHC certain legal obligations for the importers, producers as well as suppliers are needed (ECHA, n.d.).

Currently there are no substances under Annex XIV of REACH which are under permit requirements (Kemikalieinspektionen, 2022c). However, long chain (C9 – C14) PFCAs are included in Annex XVII of the REACH regulation (EU 2021/1297) and are therefore restricted. This includes around 200 substances and is in effect since February 2023 (Kemikalieinspektionen, 2022c). Thus, after this time long chain PFCAs cannot be manufactured or be released on the market. This includes PFCAs related substances that can transform or degrade into PFCAs. Though there are exemptions if the concentration in the substance, the mixture, or the article is below 25 ppb for the sum of C9-C14 PFCAs and their salts or 260 ppb for the sum of C9-C14 PFCA-related substances.

2.4.4 EU Classification, Labelling and Packaging

The classification, labelling and packaging (CLP) directive is EUs adaption of UN global harmonized system (GHS) (MSB, 2020). It complements the REACH regulation and ensures that the hazards of chemicals are clearly communicated to workers and consumers through pictograms and standard statements on labels and safety data sheets (Your Europe, 2022). Currently there are only five PFAS which have been classified by CLP. These are PFOS, PFOA, PFNA, PFDA and APFO. However, PFHpA and 6:2 FTOH are under evaluation (Kemikalieinspektionen, 2022c).

Table 2 – Current (to date) main regulations and legislation on PFAS.

PFAS	**Sthlm Convention**	**CLP**	**REACH Annex XVII**	**REACH Candidate List of SVHC**
PFOS, its salts and similar substances	Annex B 2009			
PFOA and its derivates	Annex A 2019			
PFHxS and its salts	Annex A 2022			
APFO			X	X
PFNA and its ammonium and sodium salts (C9 PFCA)	Candidate		2023	X

PFDA and its ammonium and sodium salts (C10 PFCA)	Candidate		2023	X
PFUnDA (C11 PFCA)	Candidate		2023	X
PFTeDA (C12 PFCA)	Candidate		2023	X
PFTrDA (C13 PFCA)	Candidate		2023	X
PFDoDA (C14 PFCA)	Candidate		2023	X
HPFO-DA (GenX)				X
PFBS and its salts				X
PFHpA		Proposed		
6:2 FTOH		Proposed		

2.4.5 Overall Restriction on PFAS

In February of 2023 a proposed restriction of around 10000 PFAS was made to the EU by 5 member countries, including Sweden (ECHA, 2023). The aim is to restrict PFAS as a group instead of individual substances with the aim of inhibiting “false substitution” and consequently decrease the amount released into the environment (Kemikalieinspektionen, 2022b; Svenskt Vatten, 2022). The proposal is still under evaluation and would enter into force in 2025 at the earliest (Kemikalieinspektionen, 2022b).

2.4.6 Chemical Agency (Kemikalieinspektionen)

Swedish law states that PFAS that are added consciously in products should be disclosed to the product register of the Chemical Agency (Kemikalieinspektionen) (KIFS 2017:7 14 § 12a). This includes all molecules which have a perfluorinated carbon cain with a minimum of 2 carbons as well as a bond to an arbitrary atom or group of atoms (Kemikalieinspektionen, 2022a).

2.4.7 Firefighting Foam

Currently there is no overall regulation of PFAS in firefighting foam, except the individual substances listed in Table 2. There are however exceptions for firefighting foam in the newly added long-chain PFCAs in the Annex XVII of REACH. The substances are, therefore, allowed to be used until 2025 in already installed in systems but cannot be used for training purposes or testing unless all releases are contained.

In parallel, the European Chemicals Agency (ECHA) have brought forward a proposal for an EU-wide restriction on all PFAS in firefighting foams (ECHA, 2022a). The restriction would prevent further groundwater and soil contamination and, therefore, protect drinking water sources (ECHA, 2022c). The proposal was made due to a concern that the restricted PFCAs will be replaced by other PFAS instead of changing to PFAS-free foam (Ivarsson, 2020). The proposal was made in February 2022 and is currently under evaluation (ECHA, 2022b).

In Sweden the firefighting foam containing PFAS has been removed from fire departments. This occurred during 2022 where The Swedish Civil Contingencies Agency (Myndigheten för samhällsskydd och beredskap (MSB)) was given, by the government, the task to remove PFAS from the fire departments (MSB, 2022). Instead PFAS-free foam will be used. Thus, there has been an ongoing project at the local fire departments to collect and exchange the firefighting foams. Each fire department regulates which foam to use themselves. Moreover, the current tanks should, according to MSB, be cleaned before entering PFAS free foam to avoid cross-contamination (MSB, 2022). How this should be done is not to date regulated.

2.4.8 Drinking Water

Before 2021 there were no legally binding limit for PFAS in drinking water in Sweden or the EU (Livsmedelsverket et al., 2021). However, in Sweden an ‘action threshold’ value has been in place since 2014 for PFAS in drinking water. The threshold value was set to 90 ng/L. Initially from 2014 to 2016 this included 7 different substances but was in 2016 extended to 11 substances, as seen in Table 3. If drinking water producers exceeded this threshold, actions were recommended to be done. An upper threshold of 900 ng/L was also implemented at which the water was recommended not be consumed (Livsmedelsverket et al., 2021).

In the revised EU drinking water directive (EU 2020/2184) PFAS have been included as regulating substances in drinking water. It is a minimum directive, where each country can choose to have a stronger regulation. The new directive includes 20 different PFAS, as seen in Table 3, with a limit of 100 ng/L, as well as a limit value of 500 ng/L for the total PFAS concentration (Livsmedelsverket et al., 2021). The limit value of 500 ng/L will only be applied once a method for measuring the total PFAS concentration is available. The member states should have taken measures to align with these values until 2026.

Sweden have implemented the directive by adding two threshold values: one with four PFAS (PFAS 4) and one with 21 PFAS (PFAS 21). PFAS 21 includes the 20 substances in the EU regulation as well as 6:2 FTS, as seen in Table 3, and has a threshold value of 100 ng/L, in line with the EU regulation. In addition, PFAS 4 has a threshold value of 4 ng/L, seen in Table 3. The idea behind this additional threshold value is to in parallel decrease the PFAS 21 concentrations. This is since the treatment techniques adapted to lower the PFAS 4 will consequently also lower PFAS 21 (Livsmedelsverket, 2022). The limit of 4 ng/L was based on European Food Safety Authority’s (EFSA) safety threshold of tolerable weekly intake (EFSA, 2020; Livsmedelsverket, 2023).

Table 3 – Current and previous threshold concentrations for PFAS in the drinking water, in Sweden.

<table>
<tr><th>PFAS 4</th><th>PFAS 7</th><th>PFAS 11</th><th>PFAS 20/21</th></tr>
<tr><td>PFOA
PFOS
PFHxS
PFNA</td><td colspan="3" rowspan="2">PFOA
PFOS
PFHxS
PFBS
PFPeA
PFHxA
PFHpA</td></tr>
<tr><td>4 ng/L</td></tr>
<tr><td></td><td>90 ng/L</td><td colspan="2">PFNA
6:2 FTOH
PFBA
PFDA</td></tr>
<tr><td></td><td></td><td>90 ng/L</td><td>PFUnDA
PFDoDA
PFTrDA
PFPeS
PFHpS
PFNS
PFDS
PFDoDS
PFTrDS</td></tr>
<tr><td></td><td></td><td></td><td>6:2 FTS</td></tr>
<tr><td></td><td></td><td></td><td>100 ng/L</td></tr>
</table>

In a survey conducted by Livsmedelsverket et al. (2021) detectable limits of PFAS was discovered at 74 of 154 waterworks in Sweden. Furthermore, in 15 of these, which supplies water to 2.2 million people, the PFAS 7/11 concentration had exceeded 10 ng/L on at least one occasion.

2.4.9 Environmental Quality Standards

Currently there are no environmental quality standards for PFAS in groundwater on higher institutional levels. With that said, a proposal to the EU (Directive 2000/60/EC) has been made to include 24 PFAS in the standards for groundwater. In Sweden environmental quality standards in the groundwater have, however, been available. These align with the previous drinking water regulations of 90 ng/L for PFAS 11 (Vattenmyndigheterna & Länsstyrelserna, 2018). Groundwater reservoirs exceeding this are classified as "bad status" and an action program should be made which ensures that the environmental quality standards are met (Kemikalieinspektionen, n.d.).

In addition, there are also guidelines for PFAS in groundwater and soils which are not legally binding, set by Statens Geotekniska Institute (SGI). These are currently set to 2 ng/L for PFAS 4 in groundwater. In soils these are set to 0.25 and 1.2 µg/kg TS for sensitive land use and less sensitive land use respectively (SGI, 2022).

2.4.10 Water Protection Areas in Sweden

The Swedish environmental code (Miljöbalken (MB)), hold most of the environmental laws in the country. It, therefore, also includes the regulations on water protection area and contaminated sites. A water protection area can be put in place according to 7 kap. 21 § MB to protect a water resource which is currently used or planning to be used (HaV, 2021). It has a preventive function for water resources with low turnover times and where the area is difficult to remediate in retrospect (HaV, 2021). In a water protection area special regulations exists with regards to chemical use (Naturvårdsverket, 2016). A study conducted by Naturvårdsverket (2016) reported that 21 water protection areas in Sweden lies within a 500 meters distance away from possible PFAS contamination sources, such as fire training facilities or airports.

3. Materials and Methods

3.1 Study Area

The study area is situated in the middle of the province Blekinge, just west of the town Kallinge inhabiting around 4500 people. Just south of the town Kallinge the larger city Ronneby is situated. The main activity in the area is the F17 military airfield, which has been in use since 1944. The airfield is restricted and used by both civil and military air traffic (Mussabek et al., 2022). In addition to the airfield, there is also a water plant situated in the area called Brantafors, which has supplied drinking water for the town Kallinge and parts of the larger city Ronneby (Ronneby Kommun, 2021). It has been in use since the 1970s and extracted groundwater from four different wells in the area. This can be seen in Figure 2 where the locations mentioned are shown, except for the drinking water wells where approximate locations are shown (mentioned GW1, GW2, GW3 and GW4).

In, 2013 Brantafors waterworks was shut down due to the detection of high amounts of PFAS in the water (Ronneby Kommun, 2021). It was later discovered that the source of the contaminant was the F17 airfield which had released firefighting foam in connection to fire training activities. The location of the main fire training activities is just east of Klintebäcken, seen in Figure 2, hereby mentioned as the fire training facility (FTF). However, there are additional sites in the area where PFAS could have been released in smaller quantities (Mussabek et al., 2022). These will not be discussed further but is worth to keep in mind. The shutdown of the waterworks in Brantafors got media attention and significant public concern arose (Banzhaf et al., 2017).

After the shutdown the inhabitants instead receive water from a source further south (Ronneby Kommun, 2021). In addition, after the contamination was discovered an association which consists of members of affected citizens was formed called “PFAS-föreningen”. In 2016 they sued the local water company *Ronneby miljö och Teknik AB* due to the high PFAS concentrations. In the first instance, Blekinge tingsrätt, the water company was held accountable and had to compensate the members of the association of their physical injuries

(Svenskt Vatten, 2021). However, in the second instance, hovrätten, the sentence changed, and the water company is no longer held accountable. The association responded by appealing to the highest instance, högsta domstolen, where the case now lies (SVT, 2023). This is one of the first cases in Sweden regarding PFAS contamination which have made it up in court.

The study area was from 1975 classified as a water protection area by Swedish environmental law (MB 7 kap. 21 §), but was in 2017 repealed (Eriksson, 2018). The study area is still covered by the 7th article of The EU Framework Directive (2000/60/EG) which states that water resources that are being used for extraction of certain quantity or are reserved for future extraction should be protected in order to guarantee the access of water with good quality (VISS, n.d.-a).

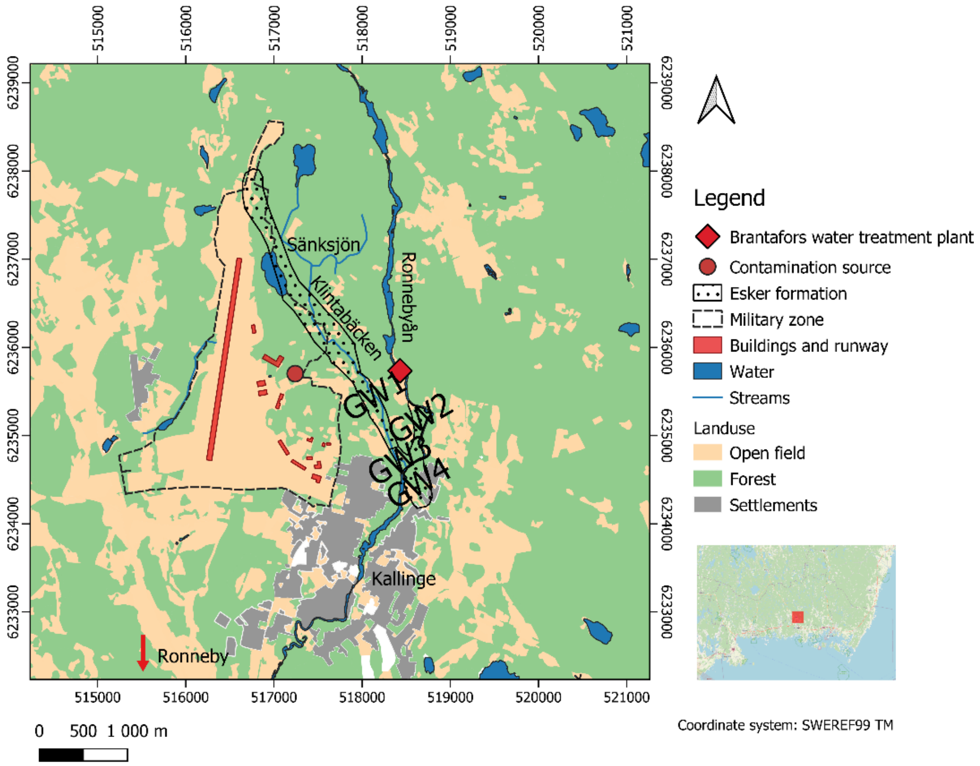

Figure 2 – Overview map over the study area. GSD-Terrängkartan, vector, scale interval 1:50 000 © Lantmäteriet (2020); Background map © OpenStreetMap.

3.1.1 Geology and Geomorphology

The study area is located in one of the largest delta formations in South-eastern Sweden; Bredåkradeltat, which was formed during the withdrawal of the last ice age (Möller, 1980). The area is mainly covered by glaciofluvial material consisting of sand and silt. An esker formation is also present, called Bredåkraåsen, which runs from north of the airfield to the city of Kallinge, as seen in Figure 2, and mainly consists of sand, gravel, and rocks (Möller, 1980). It is located directly on the bedrock and is partially covered by mixed glaciofluvial material. The esker formation is confined by the bedrock to the west and east forming a channel like structure. The contamination source, FTF, is just west of Klintabäcken, which runs along the esker formation, see Figure 2 and Figure 3.

The general soil structure can be seen in Figure 3, where the esker formation is marked in yellow, and the mixed glacial deposits is marked in grey. It is a simplified conceptual model based on field measurements conducted by Mark & Vatten (1992) and may not be used for exact location or geology. The geological properties of the area are divided into two separate areas, based on the conceptual model. The esker formation is consisting mostly of sandy gravel and gravelly sand and the mixed glacial deposits are consisting of layers of finer sand and silt.

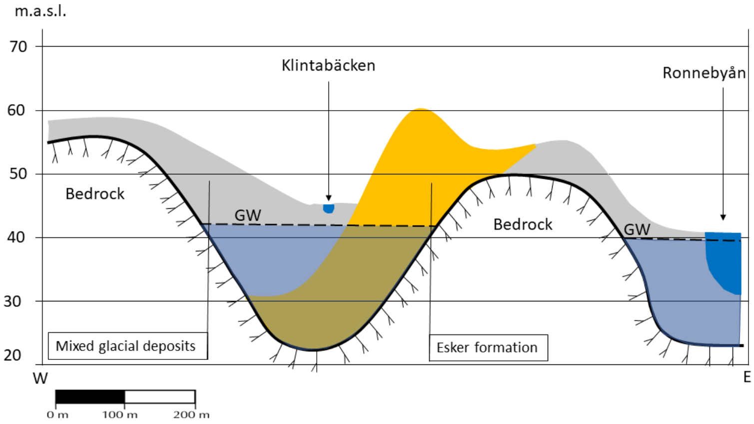

Figure 3 – General soil structure of the study area. Conceptualized through information by Mark & Vatten (1992).

The bedrock is primarily represented by Karshamngranit (a granite) consisting of quarts, feldspar, and mica and the bedrock surface is characterised by deep and long fractures in direction from north to south.

3.1.2 Hydrology and Hydrogeology

There are several surface water bodies in the study area, including the Hasselstadsbäcken creek, the Klintabäcken creek, the river Ronnebyån, and the lake Sänksjön, as seen in Figure 2. The study area is located within the larger main catchment area of the river Ronnebyån. Furthermore, the area is divided into two sub-catchment areas which are divided straight through the F17 airfield, where the FTF is within the klintabäcken catchment area. Hasselstadsbäcken originates in the wetland area south-west of Sänksjön and eventually discharges into Sörbybäcken creek, a tributary to Ronnebyån. Klintabäcken originates from the wetland areas in north and east of Sänksjön and discharges into Ronnebyån. Ronnebyån flows in a south direction and discharges into the Ronnebyfjärden Bay of the Baltic Sea. Lake Sänksjön is a kettle lake (formed by the retrieving glacier) and primarily fed by groundwater and surface runoff (Möller, 1980).

The area contains a groundwater reservoir that is represented by the esker formation and the mixed glaciofluvial material, seen in Figure 3. It is mainly an unconfined aquifer, however local confined conditions can occur due to fine glaciofluvial materials (Möller, 1980). The aquifer contains local subsystems, and a fluctuating groundwater divide which runs along the airfield to the west. To the east the reservoir runs towards Ronnebyån where it is bounded by the bedrock which is close to the surface at this area. The mixed glaciofluvial material contains a lower groundwater extraction potential of 1-5 L/s whereas the esker formation contains a higher potential of 5 – 25 L/s. Close to Ronnebyån the potential is even higher due to the added infiltration from the river. The primary groundwater flow direction is southeast following the flow of Klintabäcken. The groundwater system can be seen in Figure 4, as well as its relation in location to the contamination source.

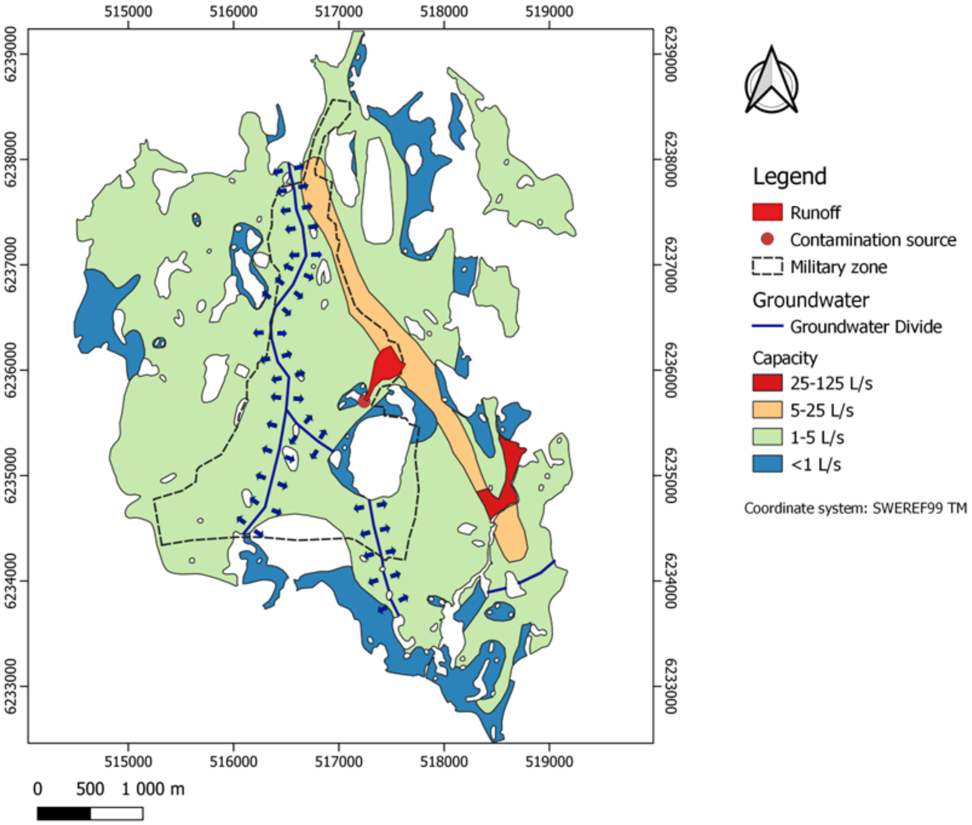

Figure 4 – Groundwater system of the study area. Grundvattenmagasin 1:50 000 © SGU (2015).

3.1.3 Fire Training Activities

The source of the PFAS contamination in the area was, as noted, the fire training activities at the FTF where AFFF was used. Information of the training activities was received by previous studies conducted by Mussabek et al. (2022), however is limited due to confidential reason. The FTF is located just west of the F17 airfield and is paved with concrete. At the FTF the release of AFFF was primarily connected to aircraft rescue operation training. However, the exact training protocol prior to 2004 have not been clarified due to several reasons including confidential. After the detection of the PFAS contamination the training activities were ceased. According to former military personnel the training was designed for fire safety and rescue missions from the aircrafts, where the main training objective was rapid fire suppression and crew rescue in the event of a crash. The rescue training was carried out during specified training periods where several sessions could occur in one day. These kinds of training were conducted on several occasions a year.

3.1.4 Contamination Levels

PFAS concentrations were measured in previous studies at the study site (Mussabek et al., 2022). The study addressed the PFAS concentrations in the wells downstream of the fire training area and analysed 29 PFAS in total, using LC/MS/MS, seen in Table 4. It consists of five perfluoroalkane sulfonates (PFSAs), thirteen perfluoroalkyl carboxylates (PFCAs), three perfluorooctane sulfonamides (FASAs), two perfluorosulfonamidoethanols (N-FASAs), three perfluorooctane sulfonamidoacetic acids (FOSAAs), and three fluorotelomer sulfonates (n:2 FTSAs).

Table 4 – List of measured PFAS in previous studies (Mussabek et al., 2022).

PFSA	PFCAs	FASAs	N-FASAs	FOSAAs	n:2 FTSAs
PFBS (C4)	PFBA (C3)	FOSA	MeFOSE	FOSAA	6:2 FTSA
PFHxS (C6)	PFPeA (C4)	MeFOSA	EtFOSE	MeFOSAA	8:2 FTSA
PFHpS (C7)	PFHxA (C5)	EtFOSA		EtFOSAA	10:2 FTSA
PFOS (C8)	PFHpA (C6)				
PFDS (C10)	PFOA (C7)				
	PFNA (C8)				
	PFDA (C9)				
	PFUnDA (C10)				
	PFDoDA (C11)				
	PFTriDA (C12)				
	PFTeDA (C13)				
	PFHxDA (C15)				
	PFOcDA (C17)				

The results of the analysis can be seen in Table 5, where the percentages as well as the concentrations at the different drinking water wells can be seen. The approximate location of the wells can be seen in Figure 2, where GW1 is the most upstream and closest to the FTF and GW 3 is more downstream just north of Ronnebyån.

Table 5 – Distribution and concentration of PFAS in the wells of the study area (Mussabek et al., 2022).

	PFOS	PFHxS	FOSA	PFHxA	PFOA	PFBS	C [ng/L]
Well 1	72%	19%	-	-	-	-	20000±40
Well 3	48%	33%	-	6%	6%	5%	4200±40

3.2 Estimation of Concentration

To be able to estimate the impact of PFAS it is important to establish the quantities as well as the distribution in the environment. Therefore, an estimation of the concentration at two drinking water wells was conducted. The wells in question are GW 1 and GW 3 since these are located downstream of the contaminated source in the esker formation. The contamination outside this esker formation will be neglected in this study to keep the scope of the thesis down. The analyses were performed using Microsoft Excel (Microsoft, proprietary), Argo (Booz Allen Argo, open source) software, QGIS 3.16 (Open-Source Geospatial Foundation Project), EPI Suite™ (U.S. EPA), HENRYWIN™ (U.S. EPA), KOCWIN™ (U.S. EPA), BIOWIN™ (U.S. EPA), and FEFLOW 8.0 (DHI Global Europe LTD).

The estimation was conducted in 6 steps, as seen in Figure 5. Firstly, the qualification of the foam was analysed with respect to PFAS. Secondly, a simulation of the fire training events was conducted, thus a distribution of the quantity of foam released was estimated followed by qualification and quantification of the transport of PFAS in the environment. The vadose zone (unsaturated zone) was modelled using a general fugacity model. This was followed by the determination of the groundwater flow. The contaminant transport was calculated analytically using the groundwater flow as well as the output from the fugacity model. Lastly, the PFAS mass balance was estimated; this is to indicate the PFAS remained in the groundwater, as well as fraction of the PFAS mass transferred due to raw water extraction by treatment plant. These steps are further discussed below.

The transport model is built to follow one years’ worth of training events. To get a more accurate picture of the events in Kallinge one could duplicate the procedure for the years of active fire training in the area. However, this was not done to keep the scope of the thesis down.

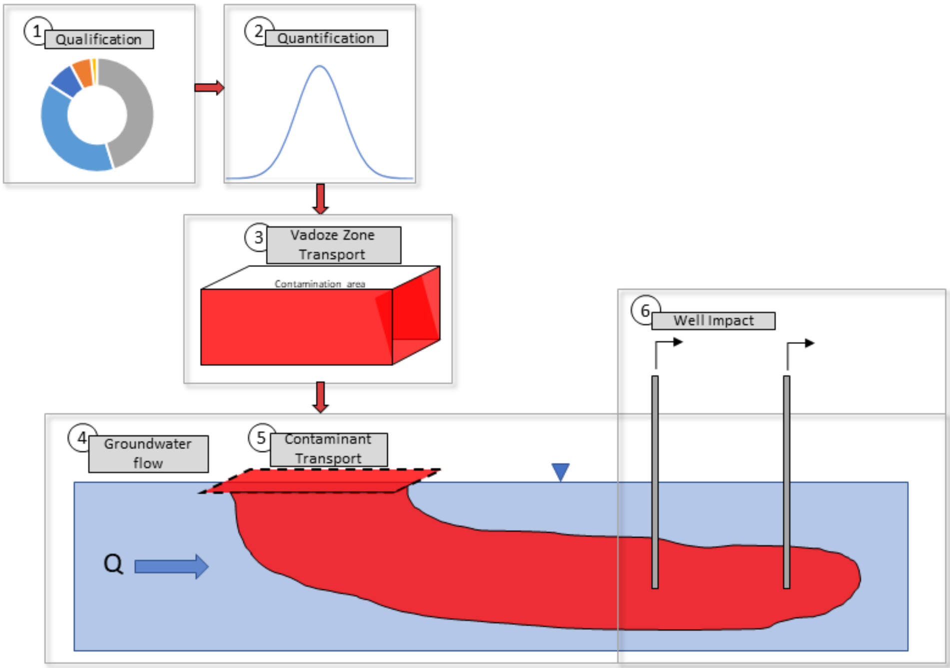

Figure 5 – Conceptualization of the steps conducted to estimate the PFAS concentrations.

3.2.1 Qualification

Throughout the thesis process, field investigations were conducted at fire stations in Stockholm, Lund, Klippan, and Svedala, where the technical aspects of the firefighting foam utilization and handling were studied. Furthermore, various foam formulations were sampled for analysis. This was conducted as a part of the project on firefighting foam and PFAS in Sweden by LTH and MSB (MSB, 2023). Due to the time span of the main project, the analysis schedule did not coincide with the thesis study. Nevertheless, besides the analysis, there was relevant data and important observations gathered.

In the context of this thesis, the composition of the foam used was estimated by analysing previously measured PFAS concentrations at the study site in the groundwater. Only one type of AFFF was considered in this report. However, a variety of foam types is suggested to have been used in the study area. By analysing the groundwater samples in the study area, seen in Table 5, all consisted of high amounts of sulfonate based PFAS, such as PFOS. In addition, indications of ECF based foam existed (Mussabek et al., 2022). By combining these finding it was assumed that 3M lightwater most likely had been used at the site and was the foam used for further analysis. It consists of the regulated PFOS and has, therefore, not been used in later years. However, before that it had previous been widely used all over the world.

The PFAS present in 3M lightwater was mentioned in section 2.2.2.1 Electrochemical Fluorination and the composition of 3M lightwater can be seen in Table 1. It consists of perfluoroalkyl sulfonate salts and amphoteric fluoroalkylamide derivatives. To represent the perfluoroalkyl sulfonate salts, PFOS as well as PFHxS was used which also corresponds to the substances identified in the groundwater samples, as seen in Table 5. The substances included in the amphoteric (zwitterionic) fluoroalkylamide derivatives are not reported. However, in a study conducted by Place and Field (2012) C4−C6 perfluoroalkyl sulfonamides (FASA) containing carboxylic acid and tertiary amine functionalities was suggested to be one of these substances. Thus, C6 of this substance was used to represent this class of compounds, hereby named FASA for simplification.

3.2.2 Quantification

There is, as noted, limited historical information available on the use of AFFF at the study site as well as confidential limitations. Hence, there is a large uncertainty on the quantity of foam released. In order to capture this uncertainty a distribution of the quantity was conduced using monte carlo simulations with iterations of 20000. This was conduced in similar way as the doctoral thesis by Mussabek (2021).

In the first simulation the percentage of PFAS in the foam (based on indentified the PFAS in section 3.2.1 Qualification) was determined. As noted, PFOS and PFHxS belongs to the perfluoroalkyl sulfonate salts and FASA to the ampoteric fluoroalkylamide derivatives. The weigth percentage for the two PFAS groups (perfluoroalkyl sulfonate salts and ampoteric fluoroalkylamide derivatives) was based on the composition of the foam, as seen in Table 1. Moreover, the range of percentages for the three substances of the two groups was assumed as seen in Table 6. Furthermore a gaussian distribution was assumed and a monte carlo simulation was conducted for the two groups as well as the three substances.

Table 6 – PFAS composition of the selected AFFF.

	%
Perfluoroalkyl sulfonate salts	0.5-1.5
PFOS	20-40
PFHxS	20-40
Amphoteric fluoroalkylamide derivative	1-5
FASA	30-50

The results where thereafter converted into concentrations by multiplying the percentages with the density and dividing by the molar mass. Since the two PFAS groups (perfluoroalkyl sulfonate salts and amphoteric fluoroalkylamide derivative) do not have a singular material property, such as for the three substances, a distribution of these values was used in order to convert these to concentrations. Thus, monte carlo simulations of the density and molar mass were conduced in order to determine these, again a gaussian distribution was assumed with 20000 iterations. The minimum, maximum and mean values were received by tabular values of substances within each group ranging from 4 to 6 carbons.

Additional factors influencing the quantificiation was indentified to be the dilution factor i.e. the amount of water added to the formulation, utilization i.e. the amount of foam used each event, and how many times these events occurred per day, week and year. This information was based on staff information conducted in a previous study by Mussabek et al. (2022). Each factor was monte carlo simulated using different ranges as well as distributions. These factors where therafter multiplied with the recieved concentrations, resulting in a range of masses in moles for the three substances (PFOS, PFHxS and FASA), as well as the two groups (perfluoroalkyl sulfonate salts and amphoteric fluoroalkylamide derivative). In addition, the amount of water added was estimated in the same manner and later converted into volume.

3.2.3 Vadoze zone

Moving forward only the three substances identified (PFOS, PFHxS, and FASA) were used in the calculations for simplicity and the two PFAS groups (perfluoroalkyl sulfonate salts and amphoteric fluoroalkylamide derivative) were neglected. Since the two groups do not hold substance specific data these would have to be assumed or simulated in each of the following steps and were therefore neglected in further calculations.

The transport of contaminants through the vadose zone is highly complex due to presence of many biological, chemical, and physical activities. It depends, as discussed, on a variety of different factors and a lot is still unknown about how different PFAS acts in the medium. A simplified model of the transport was set up based on the fugacity approach with the aim to quantifying the amount of PFAS retained in the soil. Theoretically fugacity is defined as the chemical activity of a gas and expresses the escaping tendency from a compartment. It is expressed as

$$C = z \times f$$

where C is the concentration [mol/m^3],
z the fugacity capacity [$mol/m^3/Pa$],
f is the fugacity [Pa].

3.2.3.1 Model Structure

The model was built up by three compartments: foam, soil, and groundwater. Each compartment is built up by three materials: water, air, and solids. The foam consists of air and water, the soil of solids, water, and air, and the groundwater of solids and water. The foam compartment is not a compartment which exist but acts as a way of simulating the foam spread on the surface. It can be seen as a very shallow pond on top of the soil.

The geometry of the compartment was estimated based on the previous studies at the study site conducted by Mark & Vatten (1992), as well as analyses of geographical maps provided by SGU and Lantmäteriet. The area represents the surface area of the fire training activities. This can be seen in Table 7.

Table 7 – Geometry of the compartment used in the fugacity model.

	Foam	Soil	Groundwater
Height [m]	0.5	3.0	15
Area [m^2]	1400	1400	1400
Volume [m^3]	680	4100	20000

3.2.3.2 Processes

The processes included in this model are degradation, advection, and the emission. Firstly the emission was added to the foam compartment. The foam compartment is then linked to the soil compartment via advective flux. Moreover, the soil compartment is subject to degradation. Thereafter the soil compartment is linked to the groundwater compartment via advective flux as well. In the groundwater degradation is the only process included. The groundwater compartment is not subject to advective flux within this model in order to capture the concentration of PFAS.

3.2.3.3 Partitioning Coefficients

The partitioning coefficients were estimated by EPI Suite™ which is a based suite of physical/chemical property and environmental fate estimation programs. This was determined to be used since there are a limited number of measured values available for PFAS. Within EPI Suite™ there are various of estimation programs for different partitioning coefficients, used for the model were K_{AW} and K_{OC}. HENRYWIN™ was used to calculate K_{AW} where the bond contribution method was used. KOCWIN™ was used to calculate K_{OC} where the traditional method based on log K_{OW} was used. These values can be seen in Table 8.

Table 8 - Partitioning coefficients, Koc and Kaw, for the three substances.

Partitioning coefficient	PFOS	PFHxS	FASA
K_{OC} [L/kg]	2600	470	17
K_{AW} [unitless]	4.5E-1	1.6E-2	2.8E-4

Furthermore, the solid-water partitioning coefficient, K_{SW}, was based on the fraction of organic carbon, the density of the solids, and the organic carbon-water partitioning coefficient. This is expressed as

$$K_{SW} = K_{OC} \times F_{OC} \times \varphi_{solids}$$

where K_{SW} is the solid-water partitioning coefficient [unitless],
K_{OC} is the octanol water partitioning coefficient [L/kg],
F_{oc} is the fraction of organic carbon in the soil [%],
φ_{solids} is the density of solids [kg/L].

The values used for the calculations can be seen in Table 9. The fraction of organic carbon of the soil in the area was derived from Jones R.J.A. (2005). For the fraction of organic carbon in the groundwater it was assumed to be significantly less than in soil and therefore a tenth of the value for soil. The solid particle density was retrieved from Blake (2008) where the value for quartz was used.

Table 9 - Values used to calculate the soil-water partitioning coefficient.

Foc [%]	10
$\varphi_{solids,soil}$ [kg/L]	2.7
$\varphi_{solids,GW}$ [kg/L]	$\varphi_{solids,soil}/10$

3.2.3.4 Fugacity capacities for material

The fugacity capacity, z, was thereafter determined for each material. Firstly, the air was determined, which is based on the ideal gas law and the expression of fugacity mentioned above. At dilute concentration f=P, and the fugacity capacity for air can therefore be converted into

$$PV = nRT \leftrightarrow \frac{n}{V} = \frac{P}{RT} \leftrightarrow C = f \times \frac{1}{RT}$$

$$z_{air} = \frac{1}{RT}$$

where z_{air} is the fugacity capacity in air [mol/m^{3}Pa],
R is the ideal gas constant [J/(mol*K)],
T is the temperature [K].

The fugacity capacities, z, for water and solids can be determined based on the expression for partitioning coefficients. This is expressed as

$$K_{AW} = \frac{z_{air}}{z_{water}} \leftrightarrow z_{water} = \frac{z_{air}}{K_{AW}}$$

$$K_{SW} = \frac{z_{solids}}{z_{water}} \leftrightarrow z_{solids} = K_{SW} \times z_{water}$$

where z_{water} is the fugacity capacity for water [mol/m^3/Pa],
K_{AW} is the air-water partitioning coefficient [unitless],
z_{solids} is the fugacity capacity for solids [mol/m^3/Pa],
K_{SW} is the solid-water partitioning coefficient [unitless].

3.2.3.5 Fraction of Material in Compartments

Since each compartment consists of multiple materials, the fraction, F, of each material for each compartment was calculated. Starting with the soil compartment. The fraction of solids in the soil ($F_{solids,soil}$) was calculated based on the total porosity of the soil (n_{tot}). Assuming that all void space is filled with either air or water, and the rest is therefore solids.

$$F_{solids,soil} = 1 - n_{tot}$$

Furthermore, the fraction of water in the soil ($F_{water,soil}$) was calculated by taking the effective porosity (n_e) multiplied with the field capacity (θ_{fc}). The field capacity represents the water held in the soil after gravity has drained most of the water. This is an assumtion since the water content in the soil will, in reality, vary thoughout the year.

$$F_{water,soil} = n_e \times \theta_{fc}$$

Lastly the fraction of air in the soil ($F_{air,soil}$) was calculated, which, therefore is the part of the void space not occupied by water.

$$F_{air,soil} = n_{tot} - F_{water}$$

The groundwater compartment consists of water and solids. It is, therefore, assumed that the entire void space is filled up with water. Thus, the same method as for the soil compartment was used to calculate the groundwater compartment.

$$F_{water.GW} = n_{tot}$$

$$F_{solids,GW} = 1 - n_{tot}$$

The foam compartment is based on the the foam itself, and consist of air and water. Thus, a rough estimate of the ratio was made where the foam compartment consist of 90% water and 10% air. The values used for the calculations can be seen in Table 10.

Table 10 - Values used to determine the fraction of material in each compartment.

n_{tot} [%]	36
n_e [%]	≈30
θ_{fc} [%]	≈23
C_u	3.1

The total porosity was determined by an emphiral relationship received by Wang et al. (2017) which is based on the uniformity coefficient C_u. Since C_u was measured in the area in previous studies by Mark & Vatten (1992), it was assumed to give a better estimate than tabular values. Thus by taking an average value of the C_u measured in the area the porosity cold be estimated. It is expressed as

$$n_{tot} = 0.2(1 + 0.93^{C_u})$$

where C_u is the uniformity coefficient.

Moreover, the effective porosity was derived from tablular values of sand from Stephens et al. (1998) Tabular values for the field capacity was also used for sand, recived from Fetter (2014).

The fugacity capacities for each compartment, consisting of the materials, could therefore be calculated, as seen below.

$$z_{foam} = F_{water,foam} \times z_{water} + F_{air,foam} \times z_{air}$$
$$z_{soil} = F_{solids,soil} \times z_{solids} + F_{water,soil} \times z_{water} + F_{air,soil} \times z_{air}$$
$$z_{GW} = F_{solids,GW} \times z_{solids} + F_{water,GW} \times z_{water}$$

3.2.3.6 D-values

The D-values can be described as the ‘molar flux’ of the compounds. It is expressed as

$$D = k \times V \times z$$

where D is the 'molar flux' [mol/Pa/yr],
k is the process rate [yr^{-1}],
V is the volume [m^3],
z is the fugacity capacity [$mol/m^3/Pa$].

The processes included in the model were calculated as D-values, as seen below.

3.2.3.6.1 Degradation

The D-value for degradation was based on the half-lives of the substances included in the model which were determined by using estimations from EPI Suite™. The tool used was BIOWIN™ using the BIOWIN3 model which quantitatively estimates biodegradation in water under aerobic conditions. According to Boethling et al. (1995) one can approximate that the half-life in water is the same as in soil. The BIOWIN3 models the ultimate biodegradation based on the fragments of the substance and will give a score, which then must be converted into half-lives. This was done by using a conversion scheme by Aronson et al. (2006). Since the BIOWIN3 scores of the substances all where low, the conversion in this study was done by fitting an exponential equation to the conversion scheme. This is expressed as

$$t_{1/2} = 13509 \times e^{-2.153 \times BIOWIN3}$$

where BIOWIN3 is the score from BIOWIN3.

The process rate, k, for degradation could thereafter be calculated as

$$k = \ln(2)\,/t_{1/2}$$

where $t_{1/2}$ is the half-life [yr].

The BIOWIN3 scores as well as the half-lives can be seen in Table 11 below.

Table 11 - Half-life estimates and BIOWIN3 scores for the three substances.

	PFOS	**PFHxS**	**FASA**
BIOWIN 3	0.29	0.93	0.50
$t_{1/2}$ [yrs]	20	5.0	12

3.2.3.6.2 Advection

The advection was based on the flow of water through the compartments. The two advection pathways included are from the foam compartment to the soil compartment and from the soil compartment to the groundwater compartment. It is expressed as

$$D_{advection} = k_{advection} \times V_{compartment} \times z_{compartment} = Q \times z_{compartment}$$

where Q is the advective flux of the water [m^3/yr],
z is the fugacity capacity in for each compartment [mol/m^3/Pa].

The advective flux from the foam compartment to the soil compartment consists of two fluxes, one from the fire training activity and one from precipitation. The flux from the fire training activities was received by the results from the quantification step (section 3.2.2 Quantification). Moreover, the flux for the precipitation was received by the yearly average precipitation in the area. From the soil compartment to the groundwater compartment 40 % of the water from the original flux was used. This was based on Devillers et al. (1995) due to leaching.

3.2.3.6.3 Emission

The quantity of the three substances received by the results in the quantification step (section 3.2.2 Quantification) was used as the emission source. These were inserted into the foam compartment.

3.2.3.7 Mass Balance – Solution

The model was solved using a Level II model where one assumes equilibrium between the compartments as well as steady state. This is expressed as

$$E_{tot} - f \times (\Sigma\ D) = 0$$

where E is the emission in [mol/yr],
f is the fugacity for each substance [Pa],
D is the sum of all the D-values [mol/Pa/s].

The amount of moles, n, in each compartment can thereafter be calculated by multiplying the fugacity with the z-value for each compartment as well as the volume. This is expressed as

$$n = f \times z_x \times V_x$$

where n is the amount of mole [mole],
f is the fugacity [Pa],
z is the fugacity capacity for x compartment[mol/m^3/Pa],
V is the volume for x compartment [m^3].

The percentage of partitioning to each compartment could thereafter be determined for each substance. These percentages were thereafter multiplied with the masses received in section 3.2.2 Quantification for a yearly estimate. The concentrations could be received by multiplying the masses with the molar mass for each substance and dividing it with the compartment volumes. This resulted in concentrations in soil and groundwater.

3.2.4 Groundwater Flow

The groundwater hydraulics in the study area were based on measured well data. These where received by two sources; a previous study by Mark & Vatten (1992) and data received from SGU (Brunnar © SGU 2015). As seen in Figure 6, there is good coverage over the area downstream of the contaminated site. In addition, local boundary conditions such as Ronnebyån, Sänksjön and the groundwater divide were used for the geographical extension of the calculations. To receive the hydraulic gradient, the entire aquifer system was used, as seen in Figure 4, since the measured well data and local boundaries somewhat were located outside the esker formation. After receiving the hydraulic gradient, the rest of the calculations were focused within the esker formation.

The area was simplified into four different areas based on the extraction potential, received from SGU (Grundvattenmagasin © SGU 2015) and background geological information (section 3.1.1 Geology and Geomorphology), seen in Figure 6. Two areas were determined in the eskers formation, one with higher groundwater potential (red) (A) and one with lower potential (orange) (B). It was assumed that these have similar geological properties based on the geological information and the added extraction potential was suggested to come from the infiltration from Ronnebyån, seen in Figure 2 and Figure 4. Furthermore, the area with an extraction potential of 1-5 L/s (green) was all assumed to be of similar geological properties and consistent of a mixed glacial deposit consisting of gravelly sand (C), see Figure 3. The last area is on the top right (D), with a similar extraction potential as the esker. Minor background information was existing in this area; thus, it was assumed to have similar geological properties as the esker formation. These are hereby mentioned as A, B, C and D.

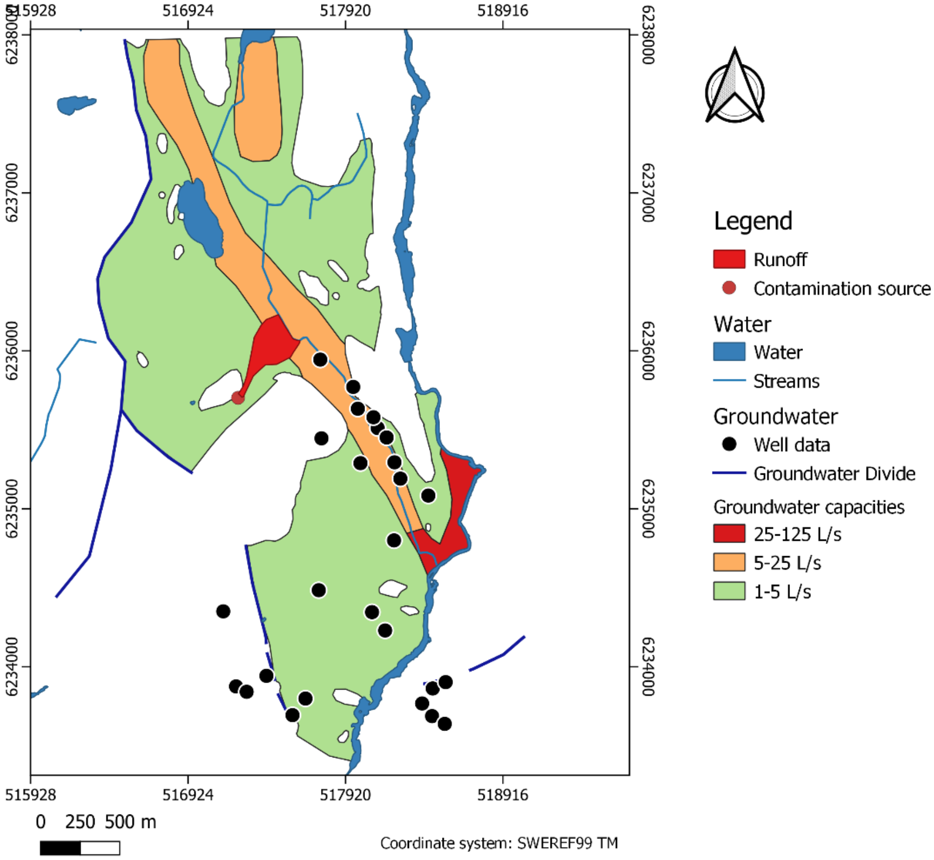

Figure 6 – Data used for the groundwater model.

The geographical extension in addition to the well data were then inserted into FEFLOW for further calculations. The well data of the groundwater levels were added as boundary conditions, 1st kind, as well as the river (Ronnebyån), the groundwater divide, and the two lakes. The model properties where set to steady state and unconfined aquifer conditions.

Lastly, the material properties values were set and can be seen in Table 12. The specific yield was received based on the geological information and table values received from (Fetter, 2014). Area A, B and D were given table values for gravelly sand and area C for course fine sand. The hydraulic conductivity was based on previous studies in the area conducted by Mark & Vatten (1992), where hydraulic conductivity within the esker formation had been measured. The measurements were conducted in relation to depth, however this was not considered within this study. Therefore, the measurement values were monte carlo simulated using a gaussian distribution and 20000 iterations. A distribution of the hydraulic conductivity could, therefore, be received. Furthermore, the bottom and top elevations were received by analysing topographical maps and soil depth data received from Lantmäteriet (Jorddjupsmodell © Lantmäteriet 2017, GSD-Höjddata © Lantmäteriet 2019). The rest was set to standard values.

Table 12 - Material properties used for calculations in FEFLOW.

	A	**B**	**C**	**D**
Specific Yield	0.25	0.25	0.21	0.25
Bottom elevation [m]	29	36	41	43
Top elevation [m]	42	50	52	55

After executing the model, the hydraulic head values at the nodes were extracted and inserted into QGIS. The values where thereafter interpolated to create a surface area of head values. By extracting a cross section along the esker formation, point values every 100m were extracted to receive the hydraulic gradient along the esker.

The velocity downstream of the contamination were thereafter determined by using Darcy's law, which is expressed as

$$v = -\frac{K}{n_e}\frac{\Delta H}{\Delta L}$$

where v is the groundwater velocity [m/yr]
K is the hydraulic conductivity [m/yr],
n_e is the effective porosity [%],
$\Delta H/\Delta L$ is the hydraulic gradient.

It assumes uniform and horizontal flow within any vertical cross section. The effective porosity used was the same as in section 3.2.3 Vadoze zone (Table 10). Furthermore, the hydraulic conductivity used was the same as used in the FEFLOW material properties input. Velocities every 100 m along the esker could, therefore, be extracted. However, only the part downstream of the contaminant source was used. A monte carlo simulation was thereafter conducted on the velocity values assuming gaussian distribution and 20000 iterations. Resulting in a distribution of velocities.

3.2.5 Contaminant Transport

The contaminant transport was calculated with the assumption that the contamination occurred at the esker formation, thus the distance from the FTF to the esker formation was not included in the calculations. This was a simplification due to the variance in geological material at the site. However, the runoff does eventually reach the esker formation, as well do the groundwater transport.

The concentration at an arbitrary point at a distance L downstream of the source at concentration C_0 can be calculated as (Fetter, 2014)

$$C = \frac{C_0}{2}[erfc\left(\frac{L - v_x t}{2\sqrt{D_L t}}\right) + \exp\left(\frac{v_x}{D_L}\right) erfc\left(\frac{L + v_x t}{2\sqrt{D_L t}}\right)]$$

where C is the solute concentration [ng/L],
C_0 is the initial solute concentration [ng/L],
L is the flow path length [m],
v_x is the average linear groundwater velocity [m/yr],
D_L is the longitudinal coefficient of hydrodynamic dispersion [m^2/yr].

The erfc is the complementary error function which is expressed as seen below (Fetter, 2014).

$$erfc(x) = 1 - \mathrm{erf}(x)$$

$$erfc(-x) = 1 + \mathrm{erf}\,(x)$$

$$\mathrm{erf}(x) = \sqrt{1 - \exp\left(\frac{-4x^2}{\pi}\right)}$$

The initial concentrations, C_0, were received from the results in section 3.2.3 Vadoze zone, where the concentrations in groundwater were used. The flow path length, L, was determined by the distance to the two wells from the closest point at the esker from the contamination source. This was approximately 800 and 1600 m for well 1 and 3, respectively. The average linear groundwater velocity was derived though the groundwater model step (section 3.2.4 Groundwater Flow). The time was set to 1 year. Furthermore, the longitudinal dispersion coefficient was determined by the expression below (Fetter, 2014)

$$D_L = a_L v + D^*$$

where D_L is the longitudinal coefficient of hydrodynamic dispersion [m^2/yr],
a_L is the dynamic dispersivity [m],
v is the groundwater velocity [m/yr].
D^* is the molecular diffusion [m^2/yr].

The molecular diffusion was estimated by Fetter (2014) and set to 0.032 m^2/yr. Furthermore, the dynamic dispersivity can be determined by the equation below (Fetter, 2014)

$$a_L = 0.83(log(L))^{2.414}$$

where a_L is the apparent longitudinal dynamic dispersivity [m],
L is the length of the flow path [m].

Hence, the concentration at the two wells downstream of the contaminant source could be determined, hereby mentioned as C_1 and C_3 where 1 is the one closer to the contaminant source and 3 is more downstream, corresponding to GW1 and GW3 seen in Figure 2.

3.2.6 Impact of Pumping

To be able to analyse the impact of the drinking water wells (GW 1 and GW 3) a simple mass balance was set up by assuming steady state. The mass balance can be expressed as

$$\frac{dC}{dt}V = Q_{in} \times C_0 - Q_W \times C_W - Q_{out} \times C = 0$$
$$C = \frac{Q_{in} \times C_0 - Q_W \times C_W}{Q_{out}}$$

where Q is the groundwater flow [m^3/yr],
C_0 is the initial concentration [ng/L],
Q_W is the sum of the pumping of the wells [m^3/yr],
C_W is the average concentration at the two wells [ng/L],
C is the concentration in the groundwater [mg/L].

The initial concentration, C_0, was assumed to be zero. Furthermore, for C_w the average concentrations at well 1 and well 3 was used derived in section 3.2.5 Contaminant Transport. Moreover, the pumping from the wells, Q_W, was assumed to be approximately 1000000 m^3 per year. The groundwater flow was established from the groundwater velocities derived in section 3.2.4 Groundwater Flow and can be expressed as

$$Q = v \times A \times n_e$$

where v is the groundwater velocity [m/yr],
A is the cross-sectional area [m^2],
n_e is the effective porosity [%].

The cross-sectional area was established by taking the average soil depth over the esker formation (A), seen in Table 12, as well as the average length (approximately 180 m).

4. Results

4.1 Qualification

The composition of the chosen foam formulation was determined as seen in section 3.2.1 Qualification. This resulted in the three PFAS analysed; PFOS, PFHxS and FASA originating from the perfluoroalkyl sulfonate salts and amphoteric fluoroalkylamide derivatives group.

4.2 Quantification

The results of the quantification can be seen in Table 13, where the mean value as well as one standard deviation are shown. The largest quantity originated from the amphoterical fluoroalkylamide derivatives which was almost three times larger than the perfluoroalkyl sulfonate salts.

Table 13 - Result of quantification.

	Amount [mole]
Amphoterical fluoroalkylamide	130±130
FASA	43±36
Perfluoroalkyl sulfonate salts	50±39
PFOS	10±7.8
PFHxS	18±14
Total	280±220

Of the three substances identified FASA had the largest quantity followed by PFHxS and lastly PFOS. Consequently, the substances range followed the same pattern. This can be seen in Figure 7.

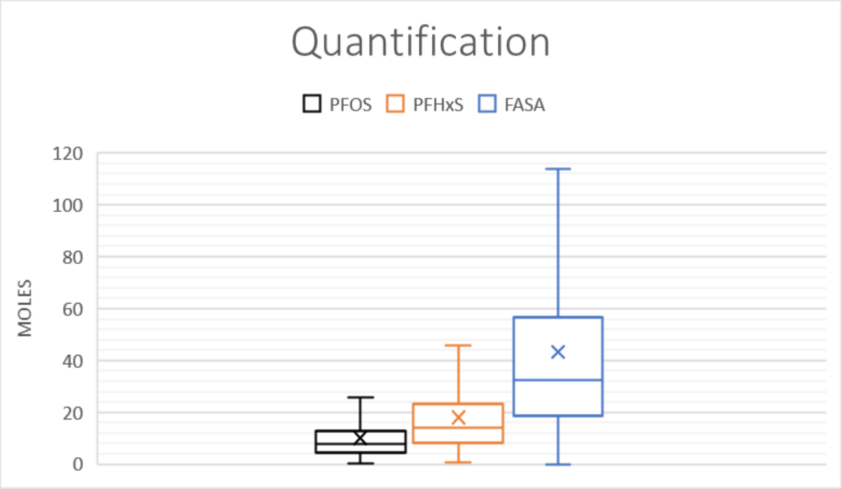

Figure 7 - Quantification of the three substances.

In addition, the amount of water added to the foam during the training events was estimated to be 480000±320000 L (one standard deviation).

4.2 Vadose Zone

The percentage of partitioning to each compartment for the three PFAS all showed similar results, as seen in Figure 8. About two thirds of the mass partitioned into the soil and one third partitioned into the groundwater.

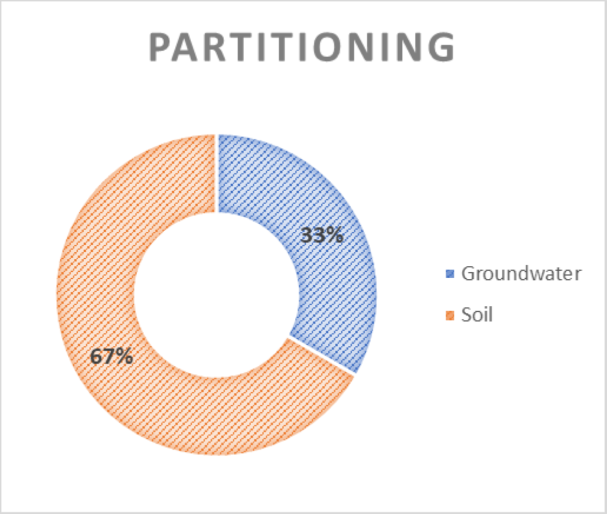

Figure 8 – Percent of mass partitioning to the different compartments.

With a closer look there are some minor differences in the partitioning between the substances, as seen in Table 14. The partitioning to the foam compartment was negligible for all three substances. Moreover, PFOS partitioned the highest to the soil compartment, followed by FASA, and lastly PFHxS. Consequently, PFHxS partitioned the highest to the groundwater compartment, followed by FASA and lastly PFOS.

Table 14 – Partitioning to the different compartments for the three substances.

	PFOS	**PFHxS**	**FASA**
Foam [%]	8.636E-6	1.653E-3	3.006E-4
Soil [%]	66.67	66.54	66.64
Groundwater [%]	33.33	33.46	33.36

The concentration of the different substances in the soil and groundwater can be seen in Figure 9 and Figure 10 respectively. As seen the concentration in the soil compartment was a magnitude 10 higher than that of groundwater. Both do, however, follow the same distribution since it is only the percentages differing mathematically between them.

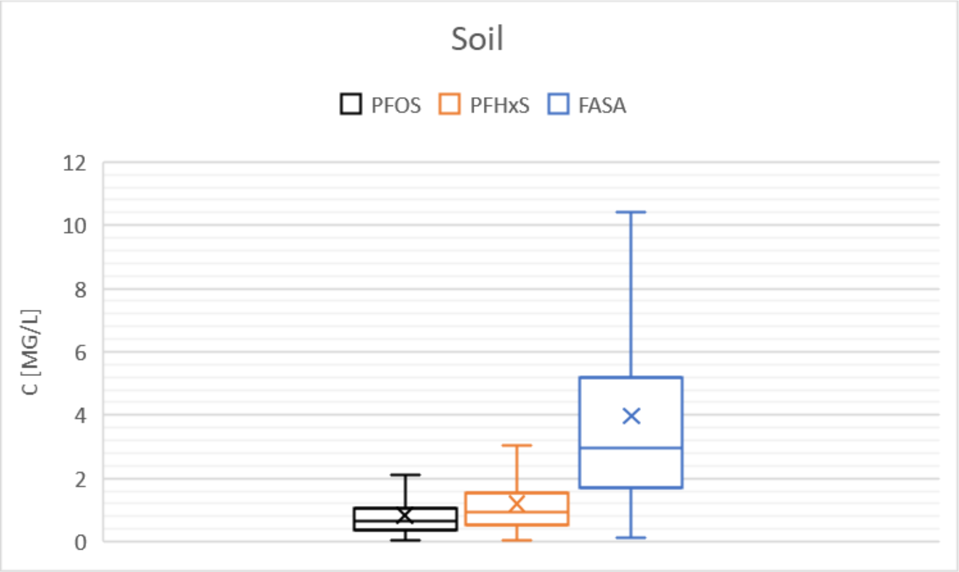

Figure 9 – Concentration for the three substances in the soil compartment.

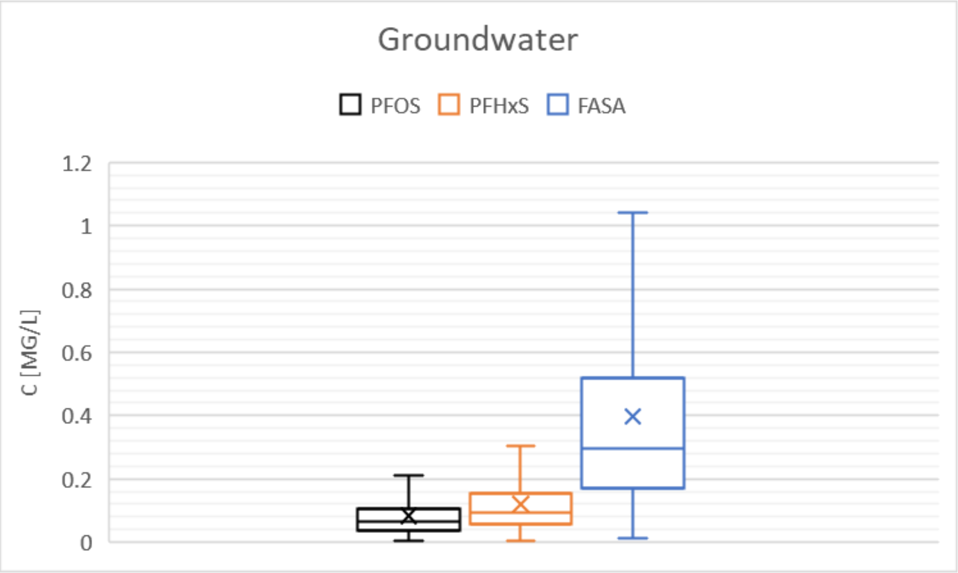

Figure 10 - Concentration for the three substances in the groundwater compartment.

The mean value as well as one standard deviation can be seen in Table 15. The concentrations for the groundwater compartment were the values used for further calculations.

Table 15 - Concentration of PFOS, PFHxS, and FASA in soil and groundwater.

	Soil	**Groundwater**
PFOS [ng/L]	830 000±650 000	83 000±65 000
PFHxS [ng/L]	1 200 000±930 000	120 000±94 000
FASA [ng/L]	4 000 000±3 000 000	400 000±330 000

4.3 Groundwater Flow

The results of the groundwater hydraulics can be seen in Table 16, for the conductivity and groundwater velocity. Note that this is only valid within the esker formation.

Table 16 - Estimates of conductivity and groundwater velocity in the esker formation.

Conductivity[m/yr]	**Velocity [m/yr]**
100 000±16 000	1 600±320

4.4 Contamination Transport

The concentration in the two wells had the same distribution of the substances, as seen in Figure 11. As seen the percentage of FASA with 66 % was the largest, followed by PFHxS with 20 % and lastly PFOS with 14 %.

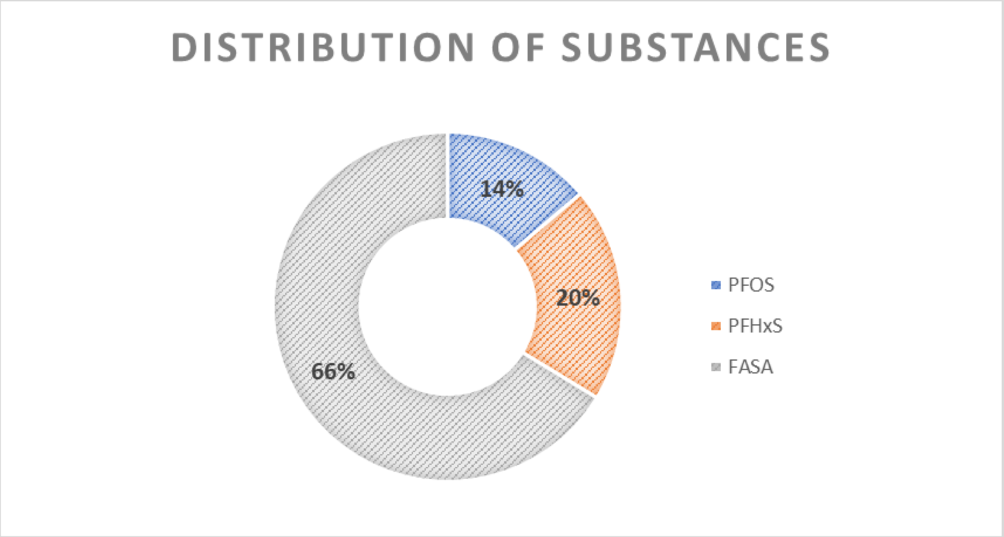

Figure 11 - Percentage distribution of the three substances at well 1 and well 3.

The concentrations did, however, vary. At well 1 the total average concentration was 600000 ng/L whereas at well 3 the concentration was 490000 ng/L. This can be seen in Table 17, as well as the concentration and distribution for each individual substance.

Table 17 – Estimated concentration at well 1 and well 3.

	Well 1	**Well 3**
PFOS [ng/L]	82 000±65 000	67 000±52 000
PFHxS [ng/L]	120 000±94 000	97 000±76 000
FASA [ng/L]	390 000±330 000	320 000±270 000
Sum [ng/L]	**600 000±450 000**	**490 000±370 000**

In Figure 12 below the total concentration for the sum of all three substances are illustrated at the two wells.

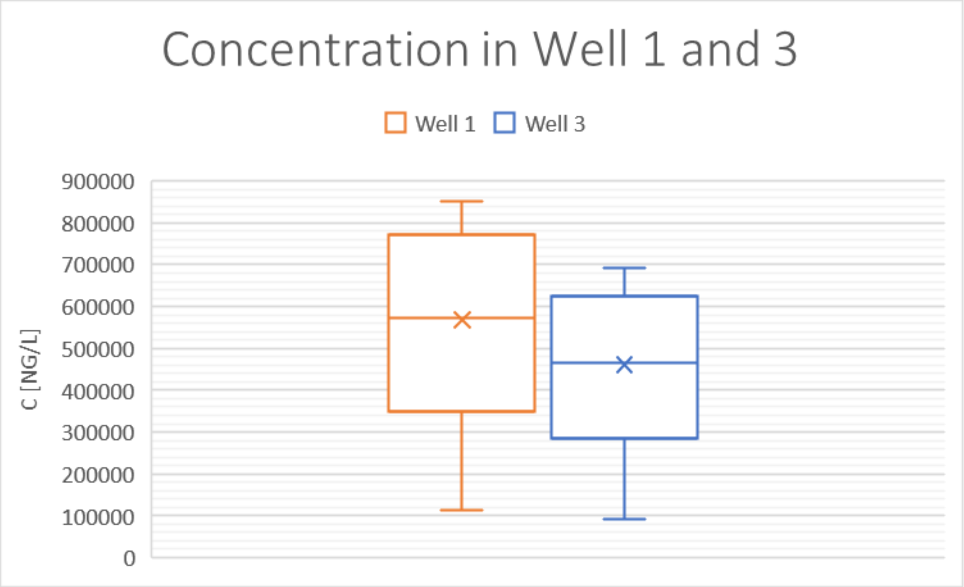

Figure 12 – Total estimated concentration of the three PFAS at well 1 and well 3.

4.5 Impact of Pumping

The mass balance resulted in a concentration, C, of -60000 ng/L, meaning that the concentration in the groundwater would decrease with this amount. This would correspond to a decrease of concentration in the aquifer by 17 %. Thus, the estimated values after the pumping can be seen in Table 18.

Table 18 – Estimated concentration after pumping.

	Well 1	**Well 3**
PFOS [ng/L]	68 000±54 000	56 000±44 000
PFHxS[ng/L]	100 000±78 000	80 000±63 000
FASA [ng/L]	330 000±28 000	270 000±220 000
Sum [ng/L]	**500 000±380 000**	**400 000±310 000**

5. Discussion

As noted during the thesis process the issues surrounding PFAS are complex. By following the same methodology as in section 3.2 Estimation of Concentration, hopefully the larger picture of the issues of PFAS related to firefighting foam can be captured and the research questions answered.

5.1 Estimation of Concentrations

5.1.1 Qualification

The foam used at a specific affected site will determine which type of PFAS that enters the environment. The substances included in this study were based on reported properties of the 3M lightwater foam. However, it is likely that a variety of different foam formulations have been used at the site. Thus, the substances included in this report does not fully represent the emission source at the site, which would have led to a broader spectrum of substances. This can be confirmed by the measured groundwater concentrations at the wells from previous studies, as seen in Table 5, which detected additional substances. Furthermore, the foam analysed is most likely composed of substances that were not identified or selected in this study. This is also the reason for not representing the three substances (PFOS, PFHxS, and FASA) as the entire percentage of perfluoroalkyl sulfonate salts and amphoteric fluoroalkylamide derivatives, since it would not be realistic that these PFAS represented the entire mass, as seen in Table 6. Thus, basing the substances through literature may neglect a large portion of the PFAS present in the foam and consequently also released. In addition, since an ECF based foam was used in this study it is assumed to contain branched isomers. This was not included in the estimate but could be included for a more accurate estimate.

As the composition of PFAS in the foam has varied over the years so has the composition in the environment. In earlier years ECF based foams were used, consisting of more branched isomers, as well as longer chain lengths. Both properties were suggested by literature to have an increased capacity for retention in soils. Thus, by shifting away from these kinds of foams it is possible that the mobility of PFAS that have entered the environment in the last couple of years have higher mobility in soil and groundwater. Other interactions, such as electrostatic, have also shown to affect the mobility of PFAS. Therefore, other properties such as the charge of PFAS must also be evaluated to draw a definite conclusion. However, it shows the importance to identify which substances that have been released to be able to analyse the impact they might have.

To identify the substances in AFFF proper analytical methods are needed. As noted previously the TOP analysis could be a step forward to quantify the overall mass of PFAS in foam formulations. However, it cannot identify the substances which are being oxidized. Thus, more research must be done to qualify the different PFAS present. This can be seen in the results of the estimate connected with the zwitterionic PFAS, "FASA", which is not commonly used as representative for PFAS but did contain a larger mass than PFOS and PFHxS. Thus, neglecting it might have a large impact of the assessment of an area.

5.1.2 Quantification

The quantification of foam will impact the amount of PFAS released into the environment. Due to the large uncertainty of the amount of foam used at the study site the distribution of foam estimated should be able to capture this uncertainty and be able to represent the actual training events at the study site. With that said, by receiving additional information about the protocol used would most likely decrease this range, and result in a more accurate estimate.

It can be noted by the ranges from the results of mass released over a year, seen in Figure 8, that small changes in the amount of foam used can lead to a large difference in the amount of PFAS released, which is reasonable. Thus, it is obvious that preventing release into the environment is the most important step to manage the contamination. However, since regulations regarding PFAS came in relative recent years the risk is that a large quantity of foam already have been released. The current regulations on PFAS are limited to substance specific PFAS. However, the overall restriction proposed to the EU could reduce the emissions by avoiding false substitution if to be accepted. In addition, the restriction proposal on PFAS in firefighting foams would also mitigate a large emission source of PFAS since this have been determined to be one of the main point sources of PFAS. Additional regulations, such as REACH, will reduce the releases of the substance specific PFAS. However, with the risk of substituting one PFAS with another.

Even with regulations of PFAS there is always the risk of unintentional emissions. By increasing awareness to consumers of the risk of PFAS, such as by pictograms linked to CLP, it is possible that it will be handled with more cautiousness. In addition, cross-contamination of PFAS is possible when PFAS-AFFF is removed and exchanged with PFAS free foam. Guidelines must therefore be clear to reduce cross-contamination as well as unintentional emissions. The PFAS-free AFFF must also be sufficiently tested so that one harmful chemical is not exchanged with another.

5.1.3 Vadose Zone

Even though the three substances analysed had differences in partitioning coefficients, such as K_{OC}, the percentage of mass partitioning to the soil compartment was still more or less the same for all three substances, seen in Figure 8. It is unclear why this occurred; however, it seems likely that the fluxes controlled the partitioning more than the coefficients. Thus, by developing the model further, making it potentially not at steady-state and at non-equilibrium, and by adding more partitioning processes it would be interesting to see how the results would change. Although, this would be very time demanding. The overall partitioning behaviour for the three substances did however correspond to the literature review conducted, which showed an enhanced retention of PFAS in the unsaturated zone. Due to the enhanced retention as well as the fact that PFAS is highly recalcitrant, PFAS can stay in the soil for a very long time after the emission continuing to leach into the groundwater.

There were minor changes in percentage for the three substances, as seen in Table 14. PFOS partitioned the largest percentage to the soil, followed by FASA and lastly PFHxS. This do seem reasonable with aspect to the literature study conducted. PFOS which is defined as long-chain PFAS was proposed to have an increased adsorption capability through hydrophobic interactions. Moreover, PFHxS which is defined as short-chain PFAS was proposed to be more mobile. In addition, the substance represented by FASA is zwitterionic which in studies are proposed to have increased adsorption capabilities through both electrostatic and hydrophobic interactions. The only soil mechanism affecting the partitioning in this study was the fraction of organic carbon, which is linked to hydrophobic interactions, thus the impact of electrostatic interactions was not included. The impact is, therefore, most likely linked to the chain length. With that said, the changes are minor, and no definite conclusions can be drawn.

The understanding on how different PFAS behaves in the vadose zone is still low, due to the complexity of soil as well as the lack of knowledge of PFAS interactions. The current estimates were only based on the air-water as well as the solid-water partitioning coefficients, which were based on the fraction of organic carbon. Although, the literature review did identify certain partitioning processes linked to PFAS which were not included in this study, such as partitioning to the AWI and NAPL interface as well as electrostatic interactions. The estimate was also based on a variety of assumptions and tabular values, as seen in section 3.2.3 Vadoze zone, which would induce uncertainties in the results. The model in the vadose zone would therefore have to be further developed to capture the processes occurring in the medium and to get more reliable results.

5.1.4 Groundwater Transport

As noted, the focus of this report was to capture an overview of the issues surrounding PFAS. Thus, to limit the scope of the thesis a simplified groundwater model was conducted. The groundwater model was based on measured values which had good coverage over the downstream area of the contaminant source, as seen Figure 6, and should therefore capture the hydraulic gradient well. The range of velocities within the esker formation, as seen in Table 16, are therefore believed to be reliable. However, the model could be expanded further to capture the geological structure better which would have had an impact on the hydraulics. In this study the esker formation was simplified to an underground channel and the geological material was only set to two different ones. Since the FTF was located outside of the esker formation the hydraulics from this point to the esker formation was neglected. Thus, if expanded this transport could be included which would have had an impact of the concentrations downstream. It is, therefore, preferred to expand the groundwater model.

5.1.5 Contamination Transport

The concentration in well 1 and well 3 was 600000±450000 ng/L and 490000±370000 ng/L, respectively, as seen in Table 17, which is much higher than the concentration measured at the site, as seen in Table 5. These were around 20000 ng/L and 4200 ng/L, respectively. Thus, the estimated concentration does overestimate the concentration measured. However, the analysis of the groundwater samples conducted in the area only included 29 PFAS, as seen in Table 4. Within the target analysis PFOS as well as PFHxS were included, however FASA was not, which consisted of 67 % of the total mass in the estimated concentration. These results can, therefore, not be comparable. However, it shows the impact that additional PFAS can have on the concentration and can, therefore, not be excluded from analysis or calculations. These zwitterionic PFAS did consist of a large mass of the 3M lightwater AFFF and it would be reasonable to find these in large quantities in affected areas.

The concentration from the estimation of PFOS at well 1 was 82000±65000 ng/L and for PFHxS 120000±94000 ng/L, as seen in Table 17. Moreover, the measured concentration at well 1 was 20,000 ng/L where 72% of the mass consisted of PFOS and 19% of PFHxS, resulting in a concentration of 14000 ng/L and 3800 ng/L respectively. Hence, even the lowest value of the estimated concentration is still larger than the measured. Moreover, the concentration from the estimation of PFOS at well 3 was 67000±52000 ng/L and for PFHxS 97000±63000 ng/L, as seen in Table 17. Moreover, the measured concentration at well 3 was 4200 ng/L where 48% of the mass consisted of PFOS and 33% of PFHxS, resulting in a concentration of 2000 ng/L and 1400 ng/L respectively. Hence, the estimated concentration is still larger than the measured at well 3. Although the measured and estimated concentrations may not be entirely comparable. The measured values do only cover one time instance whereas the estimated concentrations cover the annual dynamics of the PFAS distribution. Furthermore, local geological and hydrological conditions can vary greatly locally. They do, however, show indications on the accuracy of the estimate, and it can be concluded that the estimated concentrations are likely to be too high. Therefore, each step of the presented model (as in other modelling approaches) needs to be thoroughly validated and calibrated. Not least, a sensitivity analysis needs to be conducted to see the model structure and the impacts of the parameter variabilities.

Even though the estimated concentrations were high, the measured groundwater concentrations are still above the existing regulations. This includes the environmental quality standards in Sweden which are set to 90 ng/L. The area is, therefore, classified as “bad status” accordingly. In addition, the concentrations are also higher than the current regulation on drinking water for EU as well as Sweden. Only looking at PFOS from the PFAS4, it itself exceeds the limit, as well as the PFAS20/21. It is suspected that similar areas where AFFF have been used are similarly impacted. This poses a great challenge for the drinking water suppliers in impacted areas to decrease their levels via treatment for them to meet the new requirements. In addition, the estimated concentration of FASA had the highest concentration of the three substances. Since the substance is not included in any of the regulations as a target substance its mass will not be represented in the concentrations. Thus, the analysis to be chosen for the PFAS total in the EU drinking water directive will be of interest for the assessment of drinking water quality.

5.1.6 Impact of Pumping

The extraction of water in the drinking water wells in the area resulted in a decrease in PFAS concentration by approximately 17%. Thus, the resulting concentrations decreases as seen in Table 18. Even though the concentration decreased they are all were still higher than the measured concentrations. Over a larger time period a large amount of PFAS would have been removed from the area and entered the drinking water. The drinking water pumps in the area, therefore, have at the same time as they have polluted the drinking water in the area also removed PFAS from the groundwater. As the contamination was discovered the pumping ceased. This would consequently increase the concentration of PFAS in the groundwater and could lead to increased transportation of the contaminants. Thus, pump and treat might be a variable to considerer in similarly affected sites. However, the water treatment processes can be a crucial aspect.

5.1.7 Overall Comments on Estimation

The estimated concentration can demonstrate how fire training events using AFFF over a year impacts the downstream area of a highly permeable groundwater reservoir. The estimated concentration did overestimate the concentration when comparing it to previously measured values. Keeping in mind that these might not be entirely comparable due to local variables, different time aspects as well as pumping which have extracted PFAS from the concentration. With that said, the model would have to be expanded, calibrated, and validated further for it to retrieve more reliable results. The model does incorporate a lot of aspects, looking at the issue in a holistic view, which is of importance when discussing these substances. Thus, if expanded, this could be a good method of estimating the concentrations.

5.2 Study Site

Both the concentrations measured as well as estimated showed significantly higher concentrations than the regulatory standards. Even though the area is not covered by a water protection area it is still covered by the 7th article of The EU Framework Directive (2000/60/EG) which states that water resources that are being used for extraction of certain quantity or are reserved for future extraction should be protected to guarantee the access of water with good quality. At the time of release these substances were not under any regulations and the knowledge of the impact of PFAS was low. Thus, of time of release the PFAS were not considered a contaminant by legal standards and the awareness of the practitioner can be assumed to have been low. However, the PFAS have still affected the environment as well as the inhabitants at the study site. Thus, it is of importance to put in effective measures at the site as well as similar sites to prevent further spreading to secure current and future water sources.

6. Conclusion

PFAS are substances which poses challenges in numerous aspects for the environment as well as the society. It is, therefore, important to analyse these aspects in a holistic point of view to properly grasp the extent of the contamination in order to put in proper measures. If one aspect is overlooked, it could have large impacts on the outcome.

The concentrations estimated in the study attempted towards implementing many aspects as well as identifying limitations and possible improvements. Even though the estimated concentrations exceeded the measured values, if expanded it could be a good method to estimate the concentrations. Most importantly it shows the importance to look at the entire picture and the impact each factor has on the results. Such can be seen in the outcome of the FASA included which had significantly higher concentration compared to PFOS and PFHxS. These compounds are currently not under regulations such as the drinking water limits, REACH or POPs. In addition, the transport of PFAS through the vadose zone can often be overlooked in studies due to the large complexity of the medium and uncertainty of PFAS interactions. The addition of this step in the estimated concentration showed the impact the vadose zone has on the overall transport by retaining 66 % of the PFAS. It can therefore not be neglected and should be further studied.

Thus, identifying more substances, quantifying them properly, and analysing the transport in both soil and groundwater could give a better picture of the overall extent of PFAS. Measures, such as regulations, could therefore be more properly established.

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