A network diagram consisting of various-sized light blue circles connected by thin white lines, set against a solid blue background. The circles are scattered across the page, with some larger and some smaller, creating a complex web of connections.

Joint Research Programme  
KWRW 2025.027 | March 2025

**Trifluoroacetic acid  
(and other ultrashort-  
chain PFAS) in  
abstracted  
groundwater for  
drinking water  
production**

Joint Research Programme

**KWR**

Bridging Science to Practice



# Colophon

## Trifluoroacetic acid (and other ultrashort-chain PFAS) in abstracted groundwater for drinking water production

KWRW 2025.027 | March 2025

This research is part of the Joint Research Programme of KWR, the water utilities and Vewin.

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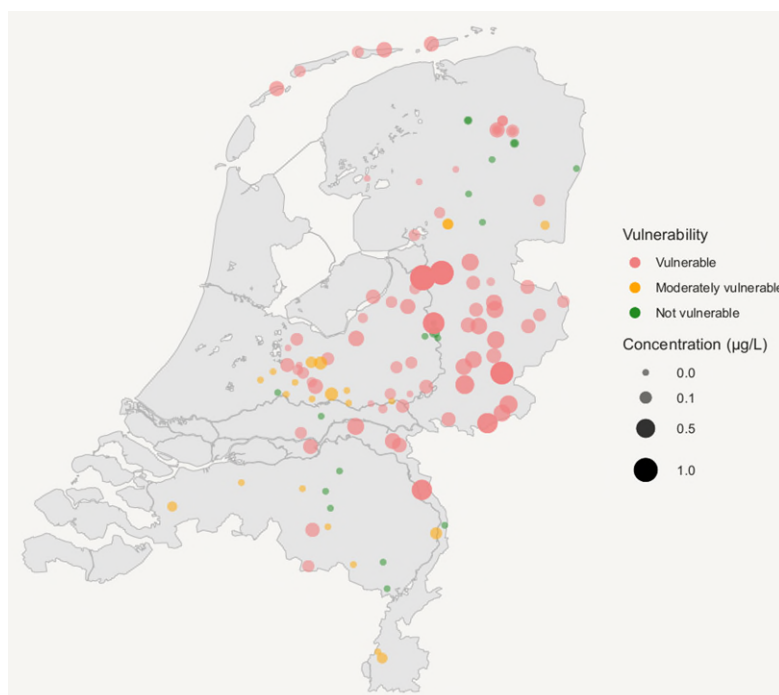
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# Managementsamenvatting

## TFA en andere ultrakorte PFAS vormen een risico voor de grondwaterkwaliteit

**Authors** Elvio Amato, Dennis Vughs, Sanah Majid Shaikh, Johan van Leeuwen.

TFA is een zeer mobiele en persistente polygefluoreerde stof die deel uitmaakt van de per- en polyfluoralkylstoffen (PFAS). TFA komt in ruw grondwater vaak voor in concentraties die ordes van grootte hoger zijn dan die van andere PFAS en wordt ook steeds vaker in drinkwater gemeten. Er was nog weinig bekend over het voorkomen van TFA en andere ultrakorte PFAS in het Nederlandse grondwater. In dit onderzoek werd uit bestaande en nieuwe monitoringgegevens het voorkomen van TFA onderzocht en informatie verzameld over hun bronnen en toxiciteit uit de wetenschappelijke literatuur. TFA werd aangetroffen in respectievelijk 89, 41 en 15% van de grondwaterwinningen uit watervoerende pakketten die die waren gecategoriseerd als 'kwetsbaar', 'matig kwetsbaar' en 'niet kwetsbaar'. Zes andere PFAS met ultrakorte ketens werden consequent onder de kwantificeringslimiet aangetroffen (0,0005 - 0,002 µg/L), maar PFPrA en TFMS werden juist respectievelijk in 17 en 13% van de monsters aangetroffen. Van deze verbindingen zijn weinig toxicologische gegevens beschikbaar, wat de noodzaak van verder onderzoek onderstreept. Er is een correlatie gevonden tussen het percentage water jonger dan 25 of 50 jaar in grondwaterbronnen van Vitens en de concentratie TFA in het onttrokken grondwater ( $r = 0,77$ , met uitzondering van enkele uitbijters), wat duidt op input uit diffuse bronnen met een piek in de jaren 1975-2000. De hoogste concentraties zijn aangetroffen in winningen met een groot aandeel geïnfiltreerd oppervlaktewater. De concentratie van TFA in onttrokken grondwater lag altijd onder de door het RIVM aanbevolen grenswaarde van 2,2 µg/L voor drinkwater. De bijdrage van TFA (en van de andere PFAS met ultrakorte keten) aan de gewogen toxicologische impact als onderdeel van een mengsel van allerlei PFAS moet verder worden onderzocht, omdat TFA en andere ultrakorte PFAS een risico vormen voor de grondwaterkwaliteit.



*TFA-concentraties in onttrokken grondwater. Elk meetpunt vertegenwoordigt een andere drinkwaterwinning. De grootte van de cirkel geeft het concentratieniveau weer. De kleuren verwijzen naar de kwetsbaarheidsklasse van de winning.*

### **Belang: TFA en andere ultrakorte PFAS een potentieel risico voor in grondwaterkwaliteit**

TFA en andere ultrakorte PFAS vormen een potentieel risico voor drinkwater door hun hoge mobiliteit, slechte afbraak in het milieu en door hun breed gebruik met name in landbouw. TFA wordt steeds vaker gemonitord, maar er is nog te weinig bekend over het voorkomen van TFA en andere ultrakorte PFAS in grondwater.

### **Aanpak: beknopt literatuuronderzoek, methodevalidatie en beoordeling van grondwater**

Informatie over de bronnen, het gedrag (in bodem en waterbehandeling) en de toxiciteit van TFA en andere ultrakorte PFAS is verzameld. Vervolgens is een KWR methode gevalideerd voor de bepaling van zeven ultrakorte PFAS. Deze methode is toegepast op 35 grondwatermonsters uit 4 provincies, onttrokken voor drinkwaterproductie uit watervoerende pakketten met een verschillende mate van kwetsbaarheid. Onderzocht is of de mate van kwetsbaarheid invloed heeft op de PFAS concentraties, ook al verschillen de criteria voor de kwetsbaarheidsclassificatie per waterbedrijf. Na aanvulling met gegevens van Vitens werden 115 locaties onderzocht (73 'kwetsbare', 22 'matig kwetsbare' en 20 'niet kwetsbare') verspreid over 8 provincies (Friesland, Groningen, Drenthe, Overijssel, Gelderland, Utrecht, Noord-Brabant en Limburg).

### **Resultaten: TFA alomtegenwoordig in grondwater**

TFA is een zeer mobiele en persistente verbinding die makkelijk in grondwater terechtkomt. TFA wordt alleen effectief uit water verwijderd door omgekeerde osmose. Ozonbehandeling kan juist leiden tot de vorming van TFA door afbraak van C-CF<sub>3</sub>-bevattende verbindingen als geneesmiddelen en pesticiden. TFA kan worden gevormd uit fluor-koolwaterstofgassen voor koeling, resten fluor-polymeren, grotere PFAS en C-CF<sub>3</sub>-bevattende verbindingen als geneesmiddelen en pesticiden. Andere PFAS met een ultrakorte keten, zoals PFPrA, TFMS, PFEtS en PFPrS, worden ook gerelateerd aan fluorkoolwaterstofgassen voor koeling en grotere PFAS, maar ook met PFAS uit lithium-ionbatterijen.

Hoewel TFA minder toxisch is dan PFAS met langere koolstofketens als PFOA en PFOS, is de Relatieve

Potentie Factor (RPF) van TFA vergelijkbaar met andere ultrakorte PFAS. Gegevens over de toxiciteit van ultrakorte PFAS (met uitzonderlijk voor TFA) zijn echter schaars of ontbreken.

TFA werd gedetecteerd in respectievelijk 89, 41 en 15% van de grondwaterwinningen uit watervoerende pakketten die waren gecategoriseerd als 'kwetsbaar', 'matig kwetsbaar' en 'niet kwetsbaar'. Het percentage water jonger dan 25 jaar gaf met uitzondering van enkele uitbijters goede correlatie met TFA-concentraties in grondwater ( $r = 0,77$ ), wat duidt op input uit diffuse bronnen met een piek in de jaren 1975-2000. Wanneer meer dan 30% van het grondwater water jonger is dan 25 jaar, is de TFA concentratie groter dan 0,1 µg/L. Wanneer het onttrokken grondwater in het geheel ouder is dan 50 jaar, werd geen TFA boven de rapportagegrens aangetroffen. TFA is mogelijk nog onderweg naar deze winningen.

Zeven andere ultrakorte PFAS werden niet aangetroffen boven de rapportagegrens, maar TFMS en PFPrA werden wel aangetroffen: uitsluitend in onttrokken grondwater uit 'kwetsbare' (< 0,060 µg/L) en 'matig kwetsbare' (< 0,025 µg/L) watervoerende pakketten. Hoewel TFA alomtegenwoordig bleek in met name kwetsbare grondwaterwinningen, bleef de concentratie consequent onder de indicatieve drinkwater-richtlijnwaarde 2,2 µg/L (aanbevolen door het RIVM) en < 0,3 ng PEQ/L (PFOA-equivalenten) op basis van de mediaanwaarden.

### **Toepassing: Ultrakorte PFAS in routinemonitoring**

De door KWR ontwikkelde methode kan worden toegepast in routinemonitoring. De leeftijd van het grondwater lijkt geschikt om de aanwezigheid en mogelijk ook het concentratieniveau van TFA te beschrijven. Drinkwaterbedrijven kunnen hun monitoringsprogramma's, ruwwaterprognoses en eventueel waterbehandelingen hierop aanpassen. De waargenomen diffuse aanwezigheid van TFA in de grondwaterbronnen laat zien dat het nodig is PFAS-bronnen voortvarend aan te pakken.

### **Het Rapport**

Dit onderzoek is beschreven in het rapport *Trifluoroacetic acid in abstracted groundwater for drinking water production* (KWRW 2025.027).

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# 1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of chemicals of great concern for human health and the environment (Wang et al., 2021). Due to their high environmental persistence and toxicity, some of these compounds, such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), have been phased out (Zheng et al., 2023). As a response, alternative PFAS characterized by shorter aliphatic chains (e.g.,  $C < 8$ ) have been introduced, as these compounds are considered less bioaccumulative and toxic than long-chain PFAS (Li et al., 2020; Liang et al., 2023). However, short-chain PFAS retain the same high stability and persistency of long-chain PFAS. As a consequence, this shift has resulted in increasing environmental concentrations of short-chain PFAS, raising concerns over their potential adverse effects on human health and the environment (Brendel et al., 2018; Zhen et al., 2023). In addition, ultrashort-chain PFAS ( $C < 4$ ) have emerged as a significant concern alongside short and long-chain PFAS.

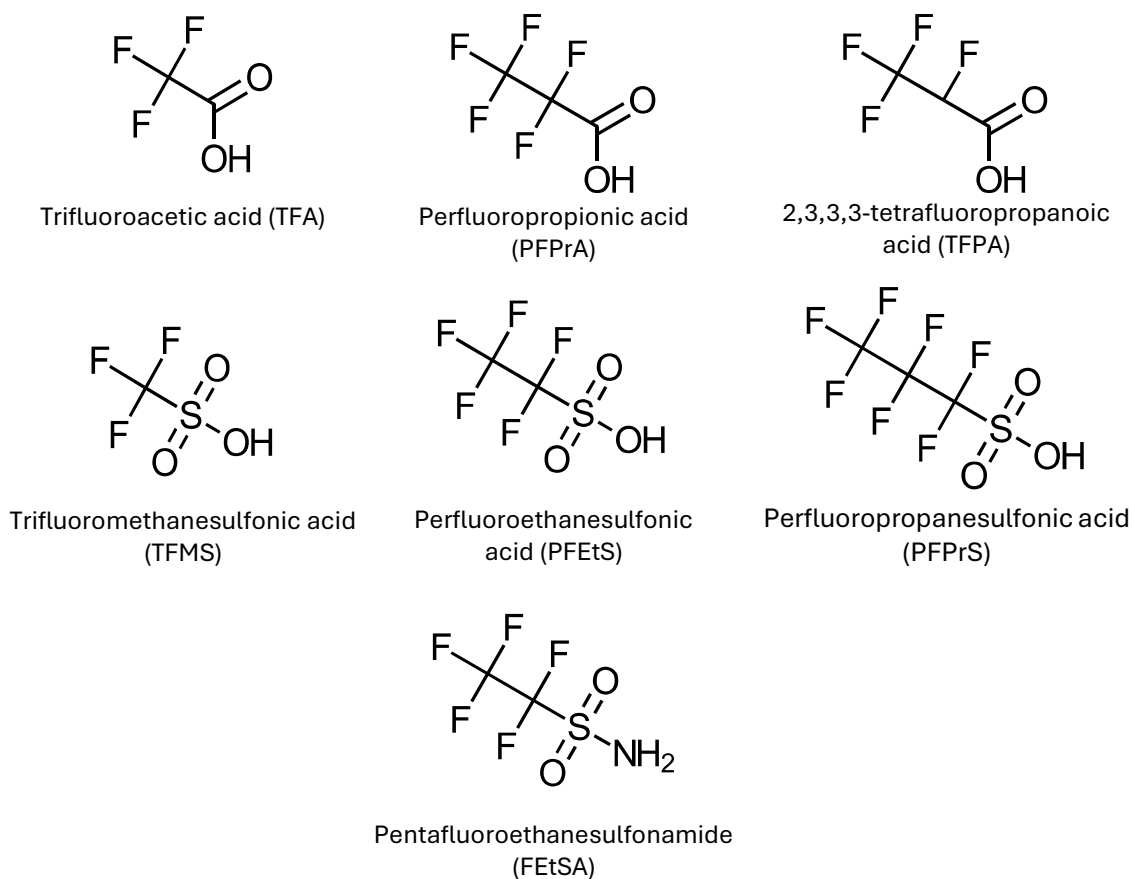
These compounds often occur as impurities or degradation products, and are manufactured for different purposes than other PFAS (Liang et al., 2023). Trifluoroacetic acid (TFA) is one of the most reported and investigated ultrashort-chain PFAS. It is used in various applications including organic synthesis, catalytic processes and environmental analysis (ECHA, 2023; López and Salazar, 2013; Norris, 2015). TFA is recognized as an environmentally persistent compound and is frequently detected in water samples.

TFA is a perfluoroalkyl acid containing a fully fluorinated carbon atom and a carboxylic group (Figure 1). It is fully miscible in water, where it exists in its ionised form. Due to the presence of a fluorinated methyl group, this compound can be classified as PFAS (Wang et al., 2021). With a carbon chain of only two atoms (C2), TFA is often associated with ultrashort-chain PFAS. This terminology is increasingly used to refer to highly hydrophilic PFAS with a backbone of  $< 4$  carbon atoms. Other common ultrashort-chain PFAS include perfluoropropanoic acid (PFPrA) (C3), trifluoromethane sulfonic acid (TFMS) (C1), perfluoroethane sulfonic acid (PFEtS) (C2), perfluoropropane sulfonic acid (PFPrS) (3) (Ateia et al., 2019; Björnsdotter et al., 2019).

TFA has emerged as a significant environmental concern due to its widespread presence in various environmental compartments and potential implications for both ecosystems and human health. With a  $pK_a$  of 0.23, TFA is completely ionized at all environmentally relevant pHs and is thus highly mobile in aquatic environments (Scheurer et al., 2017). Due to its high stability in water, TFA is expected to accumulate in water bodies (Russell et al., 2012) and potentially contaminate sources of drinking water (Björnsdotter et al., 2022). However, measurements of the octanol/water partition coefficient ( $\log K_{ow} = -4.1$ ) indicate a low potential for accumulation in animal tissues or plants (Franklin, 1993). By 2050, the average TFA concentrations in seawater are projected to increase by 4-6 ng/L due to atmospheric deposition ([www.fluorocarbons.org](http://www.fluorocarbons.org)).

Due to their surfactant properties, some PFAS have been shown to transfer from seawater to air via formation of sea-spray aerosols (SSA) (Sha et al., 2022, 2021), potentially affecting coastal areas following SSA deposition (DPWE 2024); however, TFA does not have surfactant properties, and its transfer from seawater to land via SSA formation is not expected to be significant (Clegg, 2023).

TFA and its potassium salt are registered in the European Union under the REACH at a substance quantity of 100–1,000,000 kg/yr (ECHA, 2023), indicating a significant industrial usage. It is commonly employed as a base material or solvent in various synthesis processes, and also finds applications in industrial-scale surface treatment of glass, and as a laboratory chemical. While TFA is manufactured for industrial use, it can also be produced as a result of degradation of TFA precursors in the environment, such as refrigerants (hydrofluorocarbon (HFC)), biocides, and pharmaceuticals.



**Figure 1.** Chemical structure of TFA and other ultrashort-chain PFAS.

In principle, all chemicals that contain a C-CF<sub>3</sub> group may be susceptible to form TFA as a degradation product. Although atmospheric deposition is considered a major source of TFA, several additional sources, such as pesticides, pharmaceuticals, fluorinated hydrocarbons, plastic foams and sprays, have been identified which may potentially contribute to increasing concentrations of TFA in the environment; these are briefly summarized and discussed in Chapter 2.

The present study aims to provide insight into the occurrence, origin and behavior of short-chain PFAS, including TFA, in soil and groundwater. A brief literature study focusing on these topics is followed by the monitoring of TFA and other ultrashort-chain PFAS in groundwater in several locations in the Netherlands. The assessment will include groundwater characterized by different vulnerability and investigate whether TFA and other ultrashort-chain PFAS also occur in less vulnerable groundwater. This will lead to a better understanding of potential risks to groundwater and drinking water posed by these compounds.

## 2 Sources, occurrence, behaviour and toxicity of TFA

### 2.1 TFA sources

#### 2.1.1 Formation of TFA from other fluorinated compounds

Compounds containing at least one carbon-bound trifluoromethyl moiety (C–CF<sub>3</sub>) are potential precursors of TFA (Freeling and Blörnsdotter 2023). Current known sources for TFA from other fluorinated compounds are pharmaceuticals, pesticides, fluorinated hydrocarbons, plastic foams and sprays (Arp et al., 2024; Behringer et al., 2021; Boutonnet et al., 1999; Freeling and Björnsdotter, 2023; UBA, 2022).

##### 2.1.1.1 Degradation of hydrofluorocarbons (HFC)

Due to the implementation of European bans and restrictions on fully halogenated chlorofluorocarbons (CFC) that are harmful for the ozone layer, there has been a shift to partially halogenated gases that have a shorter lifespan in the atmosphere. Hydrofluorocarbons (HFC) compounds have been used as alternatives to fully halogenated CFC in applications such as refrigeration, air conditioning, and blowing agents. These gases are emitted to varying extents during manufacturing, application and disposal. Fluorinated refrigerants and blowing agents escape into the atmosphere from refrigeration and air conditioning systems, plastic foams and sprays, among other sources. Some of these halogenated gases, such as 1,1,1,2-tetrafluoroethane (HFC-134a), have been shown to degrade in the atmosphere to form TFA. Subsequently, TFA is incorporated into clouds and transported into soils and waters through precipitation (Arp et al., 2024; Franklin, 1993). An even less stable TFA precursor, such as HFC-1234yf, has been used as a replacement for HFC-134a (Henne et al., 2012). Besides HFC-134a and HFC-1234yf, TFA can be formed from HCFC-124 (CF<sub>3</sub>CHFCI) and HCFC-123 (CF<sub>3</sub>CHCl<sub>2</sub>) (Boutonnet et al., 1999) and hydrofluoroolefins (HFO).

According to recent studies conducted by the German Environmental Agency (UBA, 2022), nearly 8,000 t of halogenated gases were used in Germany in 2018, and the quantity of refrigerants and blowing agents that may potentially form TFA was estimated to about 5,800 t. Future projections indicate that the use of these gases may largely increase in the coming decades. TFA produced by degradation of HFC may contaminate groundwater via rainwater precipitation. Although responsible for the widespread distribution of TFA in the environment, HFCs have been shown to be insufficient to account for observed TFA environmental concentrations (Jordan and Frank, 1999).

##### 2.1.1.2 Per- and poly fluoroalkyl substance (PFAS)

PFAS comprise a very large group of compounds used in many consumer products and industrial applications (Buck et al., 2011). According to the latest definition from the Organization for Economic Co-operation and Development (OECD), compounds containing a CF<sub>3</sub> or a CF<sub>2</sub> moiety – thus also including TFA – can be classified as PFAS (Wang et al., 2021). Many of these compounds contain a CF<sub>3</sub> moiety, and as a result, PFAS have a great potential for formation of TFA upon undergoing degradation. In PubChem – a large chemistry database containing millions of substances – approximately 5.7 million compounds contain a CF<sub>3</sub> moiety (Schymanski et al., 2023). Although not all of these compounds may be produced at environmentally relevant levels (or not be produced at all), the potential for formation of TFA from PFAS remains significant. TFA may be generated as a result of biotransformation of PFAS precursors in municipal wastewater (Wu et al., 2022), as well as thermolysis of fluoropolymers in rainwater (Ellis et al., 2001) and degradation of fluorotelomer alcohols in the atmosphere (Ellis et al., 2004). In addition, biodegradation of PFAS resulting in the formation of TFA has also been reported in soil and sediment (Zhang et al., 2017; Zhao et al., 2021). Many biocides and pharmaceuticals fall within the definition of PFAS, however, these are discussed separately in the sections below.

### 2.1.1.3 Biocides and plant protection products

Plant protection products are a subset of biocides specifically designed for protecting plants and crops from pests and diseases in agricultural settings. At the EU level, 45 active substances containing a C-CF<sub>3</sub> group are approved for use as plant protection. In general, about 16% of the agrochemicals available in the market contain fluorine, and approximately 40% of these contain a C-CF<sub>3</sub> group (Ogawa et al., 2020). From 2015 to 2021, approximately 5 to 10 million kilograms of biocides have been sold each year in the Netherlands, and ~365 million kilograms in the European Union (CBS, 2023); as a result, degradation of biocides containing a C-CF<sub>3</sub> group may be an important source of TFA, which can potentially contaminate soil, groundwater and surface water.

Fluorination enhances the effectiveness and stability of the pesticide, and allows to achieve a more even and uniform coating when the pesticide is applied. Studies performed as part of the approval process indicated that TFA may be potentially formed following degradation of these substances. The German Environmental Agency estimated a maximum of 504 t of TFA per year may be emitted following the use of plant protection products in Germany (UBA, 2022), and among these flufenacet was identified as one of the products with the highest potential for emissions of TFA across Germany. Flufenacet is one of the few substances for which the formation of TFA has been proven in laboratory studies (UBA, 2022). Furthermore, in a recent groundwater survey conducted throughout the Province of Utrecht, PFAS were detected in all locations ( $n = 82$ ), and TFA was found at concentrations up to 3 orders of magnitude higher than other PFAS (Bakker, 2023). In addition, it was concluded that there was a high correlation between TFA and agricultural land use, suggesting pesticides as the main source for TFA in the phreatic groundwater.

### 2.1.1.4 Pharmaceuticals

The inclusion of a C-CF<sub>3</sub> group in bioactive molecules such as pharmaceuticals may provide a range of benefit including improved selectivity and efficacy. Pharmaceuticals containing C-CF<sub>3</sub> groups that are used for human consumption include anesthetics (isoflurane, sevoflurane and desflurane), diabetes medications (sitagliptin), analgesics (celecoxib), heart medications (flecainide), cancer medications (bicalutamide), HIV medication (efavirenz), and antidepressants (fluoxetine). According to the German Environmental Agency, the use of anesthetic gases alone may result in the formation of about 7,000 kg/yr of TFA (UBA, 2022), whereas the contribution of all pharmaceuticals was estimated to a maximum of 29,000 kg/yr in Germany. While some of these pharmaceuticals are emitted in the atmosphere, the majority of these chemicals is expected to enter the environment via wastewater treatment plant (WWTP) effluents. In addition, prescribed pharmaceuticals that are discarded unused may also enter the environment via municipal waste incinerators or landfills (Tischler et al., 2013).

Several veterinary pharmaceuticals containing a C-CF<sub>3</sub> group exist, including flunixin and its meglumine salt (analgesic), isoflurane (inhalational anesthetic), fipronil, pyriprole, metaflumizone (no longer authorised), fluralaner and esafloxolaner (antiparasitics). Pharmaceuticals with a high vapour pressure that are administered via inhalation can be introduced in the environment directly through air, whereas other pharmaceuticals are mostly introduced after excretion by animals and application of their manure on pasture or crop land.

### 2.1.2 Fluorochemical manufacturing

A few studies have reported manufacturing processes of fluorochemicals as a source of TFA. Chen et al. (2018) found TFA concentrations in the air, water and leaves surrounding a fluoropolymer manufacturing plants up to 1-2 orders of magnitude higher than those commonly measured in the environment. Similarly, Scheurer et al. (2017) linked elevated levels of TFA in surface water to industrial discharges.

### 2.1.3 Waste disposal facilities

TFA, together with perfluoropropionic acid (PFPrA), has been found in leachates from municipal waste, landfills and incineration plants in China (Wang et al., 2020). PFPrA contains one fluorinated carbon more than TFA and is the second shortest PFAS in the perfluoroalkyl carboxylic acids sub-class. Both TFA and PFPrA precursors were identified in leachates by Wang et al. (2020), suggesting that these precursors could potentially contribute to the formation of

TFA and PFPrA in the environment. In the Netherlands there are at least 4000 – 8000 closed landfills and most likely more ([www.bodemplus.nl](http://www.bodemplus.nl)), which may be potential sources for PFAS. Furthermore, also WWTP influents may potentially contribute to the formation of TFA when appropriate CF<sub>3</sub>-containing precursors are present. This was supported by biological degradation and ozonation experiments conducted using chemicals from various classes (including flurtamone, fluopyram, tembotrione, flufenacet, fluoxetine, sitagliptine, and 4:2 fluorotelomer sulfonate), which indicated that TFA may be generated by multiple sources (Scheurer et al., 2017). These findings highlight the importance of addressing these sources and pathways in future studies.

#### 2.1.4 Natural sources

It has long been propagated that TFA is also naturally produced. TFA has been found in pre-industrial fresh water samples, suggesting the presence of natural sources of TFA (Nielsen et al., 2001). Similarly, Scott et al. (2005) found TFA in marine water dated 1000 years old, and suggested that deep-sea hydrothermal vents may be a source of TFA in seawater. However, to date, there seems to be insufficient evidence supporting the existence of natural sources of TFA (Joudan et al., 2021).

## 2.2 Sources of other ultrashort-chain PFAS

### 2.2.1 PFPrA

PFPrA may form via atmospheric degradation of HFC and hydrochlorofluorocarbon (HCFC) (Burkholder et al., 2015), thermolysis of fluoropolymers (Ellis et al., 2001), and oxidation of n:2 fluorotelomer hydroxids (FTOH) and perfluorobutane sulfonamide (FBSA) (Buck et al., 2011). It has been detected in municipal wastewater (Zhang et al., 2013), surface water (Björnsdotter et al., 2022), groundwater (Janda et al., 2019), and bottled water (Chow et al., 2021).

### 2.2.2 TFMS

TFMS is used in organic synthesis (Kazakova and Vasilyev, 2017) and in lithium-ion batteries (Aravindan et al., 2011; Rensmo et al., 2023). It has been reported in surface water and groundwater in association with contamination from firefighting training sites (Björnsdotter et al., 2019), and also in atmospheric deposition samples (Björnsdotter et al., 2022) and drinking water (Liang et al., 2023).

### 2.2.3 PFEtS and PFPrS

PFEtS and PFPrS have been detected in aqueous film-forming foams (AFFF) (Barzen-Hanson and Field, 2015) and AFFF-contaminated surface water (Björnsdotter et al., 2019) and groundwater (Barzen-Hanson and Field, 2015). Both compounds have also been reported in municipal wastewater (Zhang et al., 2013), surface water streams (Björnsdotter et al., 2022), and drinking water (Cappelli et al., 2024; Chow et al., 2021).

## 2.3 Occurrence of TFA in groundwater

Due to low potential for bioaccumulation and acute toxicity, TFA has not received particular regulatory attention, however, increasing levels of TFA measured in the environment, including drinking water sources, are raising concerns over the potential effect of this compound on biota and human health. Except for air, data on the occurrence of TFA in the environmental samples is relatively scarce. Measurements conducted in the mid 90's by Jordan and Frank (1999) found levels of TFA in German young spring waters (< 4 years old) in the same range as those measured in surface waters (70-320 ng/L), indicating poor degradation and high mobility of TFA. Concentrations in old groundwater were generally below the detection limit (10 ng/L). However, two locations containing 10 and 15% of younger water showed levels of 13 and 23 ng/L, respectively. More recent studies reported concentrations of TFA up to 2200 ng/L in German groundwater (Janda et al., 2019).

In Switzerland, TFA was consistently found in groundwater samples from areas used for agricultural purposes at concentrations of approximately 2000 ng/L (Schorr et al., 2023). In a study conducted in the Netherlands, similar concentrations of TFA were found in groundwater and surface water used for the production of drinking water, and ranging between 30 and 1100 ng/L (Sadia et al., 2023). These results are consistent with more recent semiquantitative data obtained from monitoring of surface water, groundwater and drinking water in the Netherlands, which also reported detectable amounts of TFMS and PFPrA in some of these samples (Amato et al., 2023b). In a monitoring study conducted by the Danish Environmental Protection Agency in 2021, TFA was found in 89% of the groundwater wells in Denmark (Freeling and Björnsdotter, 2023).

In The Netherlands TFA was analysed in the groundwater of the province of Noord-Brabant and Limburg. TFA was detected in 90% of the shallow groundwater samples (5-10 meter below ground surface). It was concluded that TFA should be included in future surveys throughout the country to acquire a full overview of TFA (Arcadis, 2023).

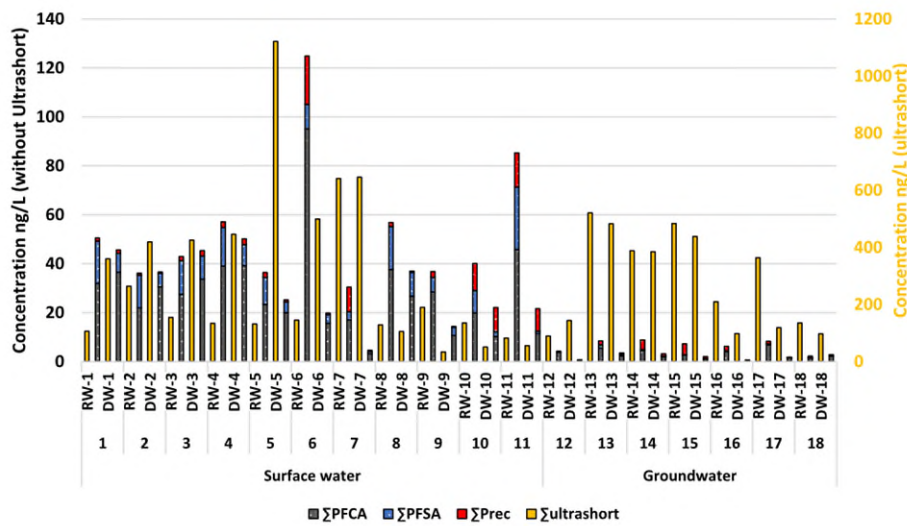


Figure 2. PFAS concentrations in raw water (RW) and produced drinking water (DW) in samples from the Netherlands (Sadia et al., 2023). PFAS are reported as sum of carboxylic acids (ΣPFCA), sulfonic acids (ΣPFSA), precursors (ΣPrec) and ultrashort-chain compounds (Σultrashort).

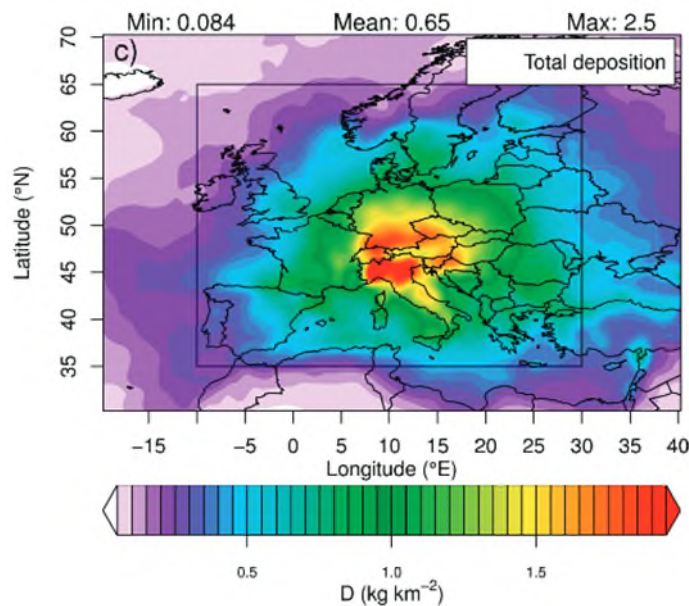


Figure 3. Simulated TFA annual deposition rates (dry and wet) (Henne et al., 2012).

TFA levels found in surface water from Europe are similar to those found in the United States, where concentrations ranging from 21 to 2800 ng/L have been measured in Northern California and Alaska (Cahill, 2022). On average, a 6-fold increase in TFA concentrations was observed in samples from the same area over a period of 23 years. Transport models suggest that the area most impacted by TFA deposition is central Europe, more specifically northern Italy, Switzerland, and south Germany (Henne et al., 2012). As a result, soil and groundwater in these regions may be impacted the most. Globally, TFA levels in various environmental media (including drinking water) have been rising over the past decade and may further increase in the coming decades if this trend persists (Arp et al., 2024).

## 2.4 Fate of TFA in soil and groundwater

TFA may enter the soil and groundwater via both diffuse contamination and local sources. Diffuse contamination of TFA is linked to atmospheric deposition and agrochemicals use, whereas local emissions of TFA include compounds locally applied that may degrade into TFA, such as pharmaceuticals, biocides, and other TFA precursors, that are introduced in soil by livestock, agricultural application of contaminated material (e.g., sewage sludge as fertilizer and wastewater irrigation), or landfills.

PFAS behaviour in the subsurface is influenced by sorption to soil particles. This affects their retardation time and mobility through soil. PFAS with longer carbon chains, such as PFOA and PFOS, are also retarded by air water interface (AWI) sorption which affects transport in the vadose zone before reaching the water saturated subsurface. This AWI sorption is relatively low for TFA due to its hydrophilic properties (Figure 4, 5). While TFA is largely hydrophilic due to the presence of a carboxylic group (-COOH) in its molecular structure (Figure 1), it still contains a hydrophobic moiety (CF<sub>3</sub>) alike other PFAS. These combined properties enable both hydrophobic and electrostatic sorption. A soil retention study in the USA confirmed that detectable TFA was retained by 34 of 54 tested soils (Richey et al., 1997). Retention varied from 25 to 260  $\mu\text{mol kg}^{-1}$  (Table 1). Most soils retain TFA weakly, but soils that contain high organic matter and some minerals such as iron and aluminium exhibit stronger sorption and therefore more retention.

Although retention of TFA was proven, a recent modelling study on Dutch soils (van den Berg, 2023) indicated that TFA retention in soil is relatively low compared to longer chain PFAS (Figure 5). In general, it can be expected that the shorter the PFAS molecule, the faster the leaching from the vadose zone towards the saturated subsurface. In the saturated subsurface TFA is also likely to be the PFAS with the least retardation and the fastest breakthrough in any type of soil. As a result, TFA is expected to be the first PFAS to reach a receptor such as a drinking water production well.

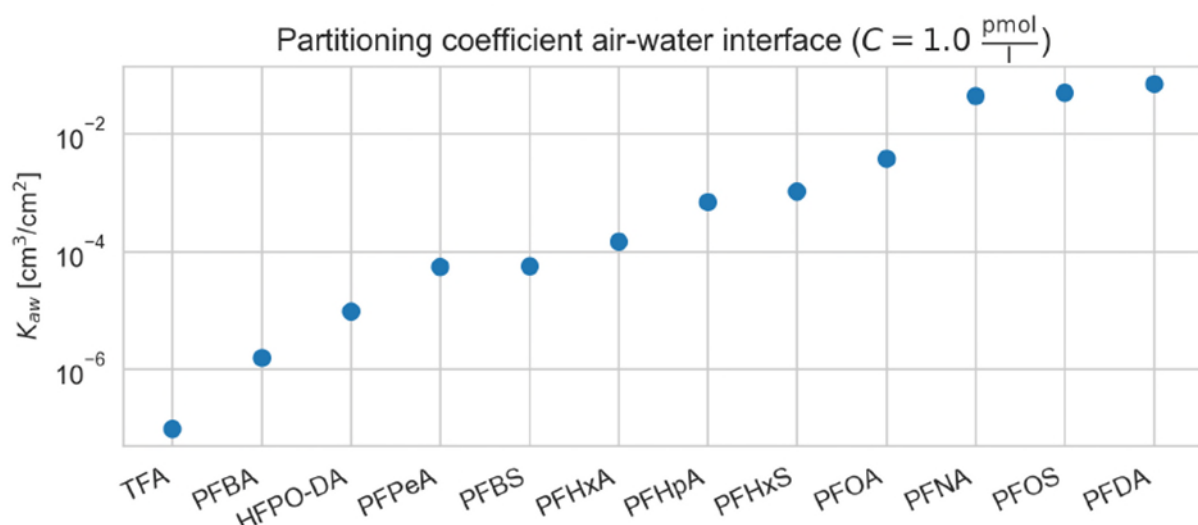
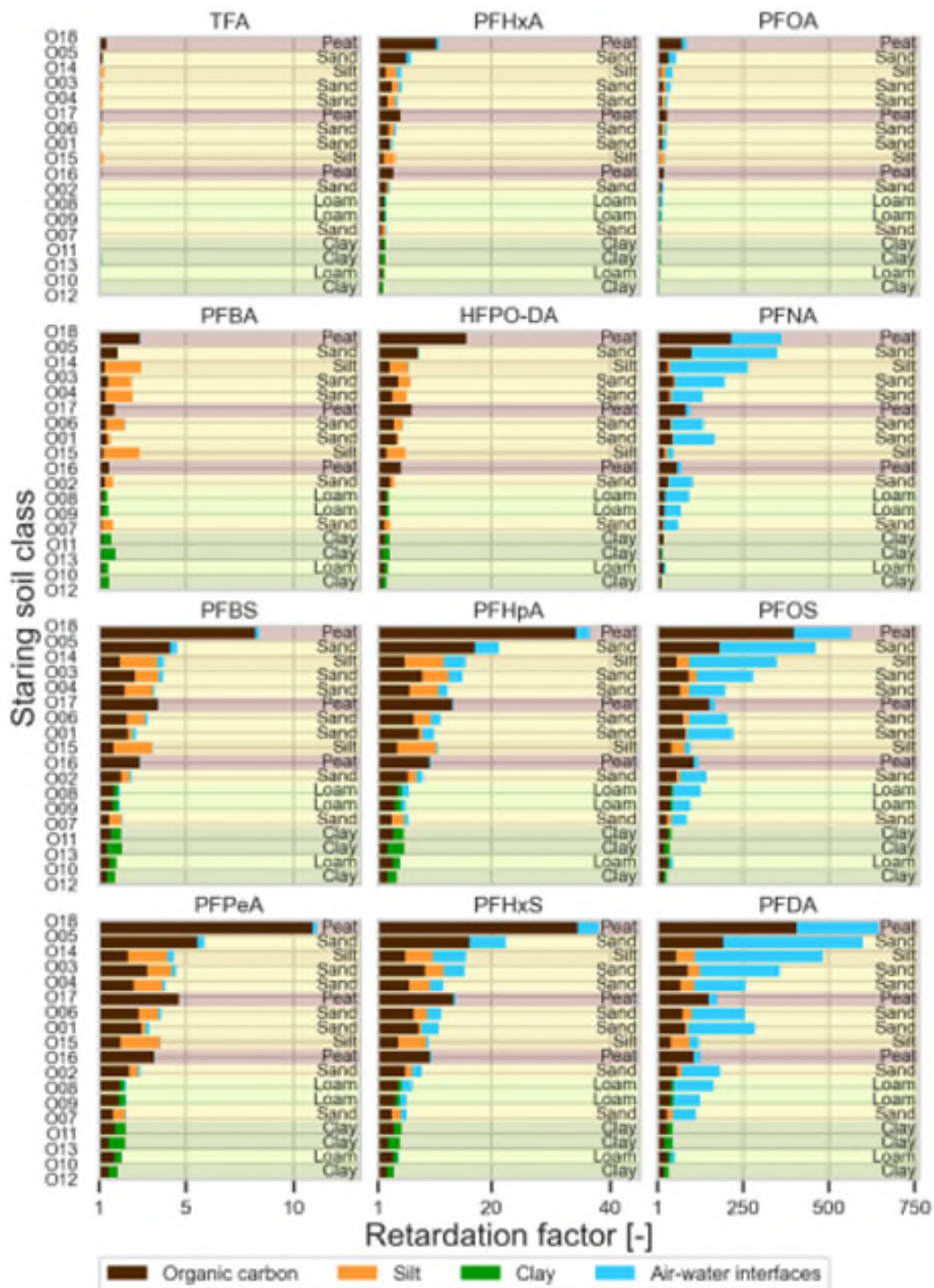


Figure 4: Distribution of the air-water partitioning coefficients ( $K_{ow}$ ) for 12 PFAS compounds (van den Berg, 2023).



**Figure 5:** Retardation of 12 PFAS compounds, from TFA to PFDA, for 18 soil types in The Netherlands, at the average saturation for an infiltration factor  $q = 300 \text{ mm/yr}$  (van den Berg, 2023). Each bar shows the retardation factor in a given soil, with colors representing the cause of retardation. The plots for the different PFAS are sorted in columns by the mean retardation of that PFAS (note the different horizontal scales for each column), and the soils within the plot are sorted by the mean retardation for PFOA. The colors of the background represent the soil class, which is labelled on the right.

**Table 1.** Characteristics and TFA adsorption parameters for US soils (Richey et al., 1997).

location/soil class	soil	pH (0.01M CaCl <sub>2</sub> )	organic matter (%)	clay (%)	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	X <sub>t</sub> (μmol kg <sup>-1</sup> )	K <sub>d</sub> (L kg <sup>-1</sup> )
Bonanza Creek, AK	organic horizon	5.30	82.5	3	63.6	245	11
Inceptisol	mineral horizon	4.61	30.3	5	12.1	10	0.86
Coweeta, NC	A horizon (mesic)	4.16	9.4	3	2.1	26	1.5
Oxisol	AB horizon (mesic)	4.20	6.2	9	1.4	47	0.68
	A horizon (frigid)	4.12	24.8	7	5.4	76	1.2
Lysina, Czech Republic	Oa horizon	2.76	38.5	5	20.6	32	0.71
Spodosol	E horizon	3.11	2.9	2	4.0	27	0.30
	Bs1 horizon	3.34	7.9	6	11.6	30	0.54
	Bs2 horizon	3.81	7.1	7	7.3	45	0.53
	C horizon	4.05	4.0	1	3.7	60	0.60
Hubbard Brook, NH	Oa horizon	3.04	79.5	8	17.2	54	3.9
Spodosol	E horizon	3.18	1.4	2	1.0	19	0.34
	Bh horizon	3.58	17	4	12.5	21	0.68
	Bs1 horizon	4.01	8.1	6	2.3	18	0.42
	Bs2 horizon	4.70	0.5	3	0.05	13	0.17
	wetland	5.04	75.2	2	17.7	180	5.8
Lake Agassiz, MN	peat core	3.22	93.3	1	17	260	20
Histosol							
Konza Prairie, KS	surface soil	5.85	10.1	27	23.1	28	1.5
Mollisol							
Niwot Ridge, CO	organic horizon	4.33	18.6	2	5.5	17	0.19
Inceptisol	mineral horizon	4.71	6.1	11	10.4	4	0.32

In addition to direct emissions, also subsurface biological processes may contribute to TFA contamination in soil. For instance, Sun et al. (2020) reported the formation of TFA following degradation of 4:2 FTOH and 6:2 FTOH in soil bacterial cultures. In contrast, no formation of TFA was observed from degradation of the biocides acrinathrin and trifluralin. 6:2 FTS, a common component of aqueous firefighting foams (AFFF), has been shown to produce TFA upon biotransformation by earthworms (Zhao et al., 2021). Similarly to other legacy PFAS such as PFOA and PFOS (i.e., common perfluoroalkyl acids (PFAs)), TFA is not expected to rapidly degrade in soil (Benesch et al., 2002), although TFA degradation has been observed in sediments under both oxic and anoxic conditions (Oremland et al., 1995; Visscher et al., 1994). In general, TFA appears to be more stable than other PFAS; laboratory experiments have shown that TFA is resistant to photochemical degradation, whereas other perfluoroalkyl carboxylic acids (PFCA) were decomposed to compounds with shorter carbon chains (Qu et al., 2016). In the soil, TFA (and other ultrashort-chain PFAS such as PFPrA) is taken up by plants via roots, at a faster rate compared to longer-chain PFAS in wheat (Zhang et al., 2019). Since it is unlikely to be metabolised by plants, TFA is reintroduced into soil via plant litter, or transported elsewhere in the case of uptake by crops or cattle.

Due to its hydrophilic behaviour, TFA largely partitions to the aqueous phase, and may potentially contaminate groundwater by leaching through the vadose zone. Previous studies have shown that TFA is not strongly retained by most types of soils, except for those with a high organic matter content (Berger et al., 1997). As a result, TFA transport through relatively permeable and aerobic soils is expected to be greater than that of organic soils and clays. TFA retardation has been shown to be very similar to that of bromide (Berger et al., 1997; Richey et al., 1997), which is used as tracer in soil due to its ability to move with the water flow without undergoing significant retardation or transformation. Most of the TFA is expected to occur in the aqueous phase, until it is taken up by plants or removed from the soil via drainage water. Plant uptake of TFA (and other ultrashort-chain PFAS such as PFPrA) via roots has been documented and shown to occur at a faster rate compared to longer-chain PFAS in wheat (Zhang et al., 2019).

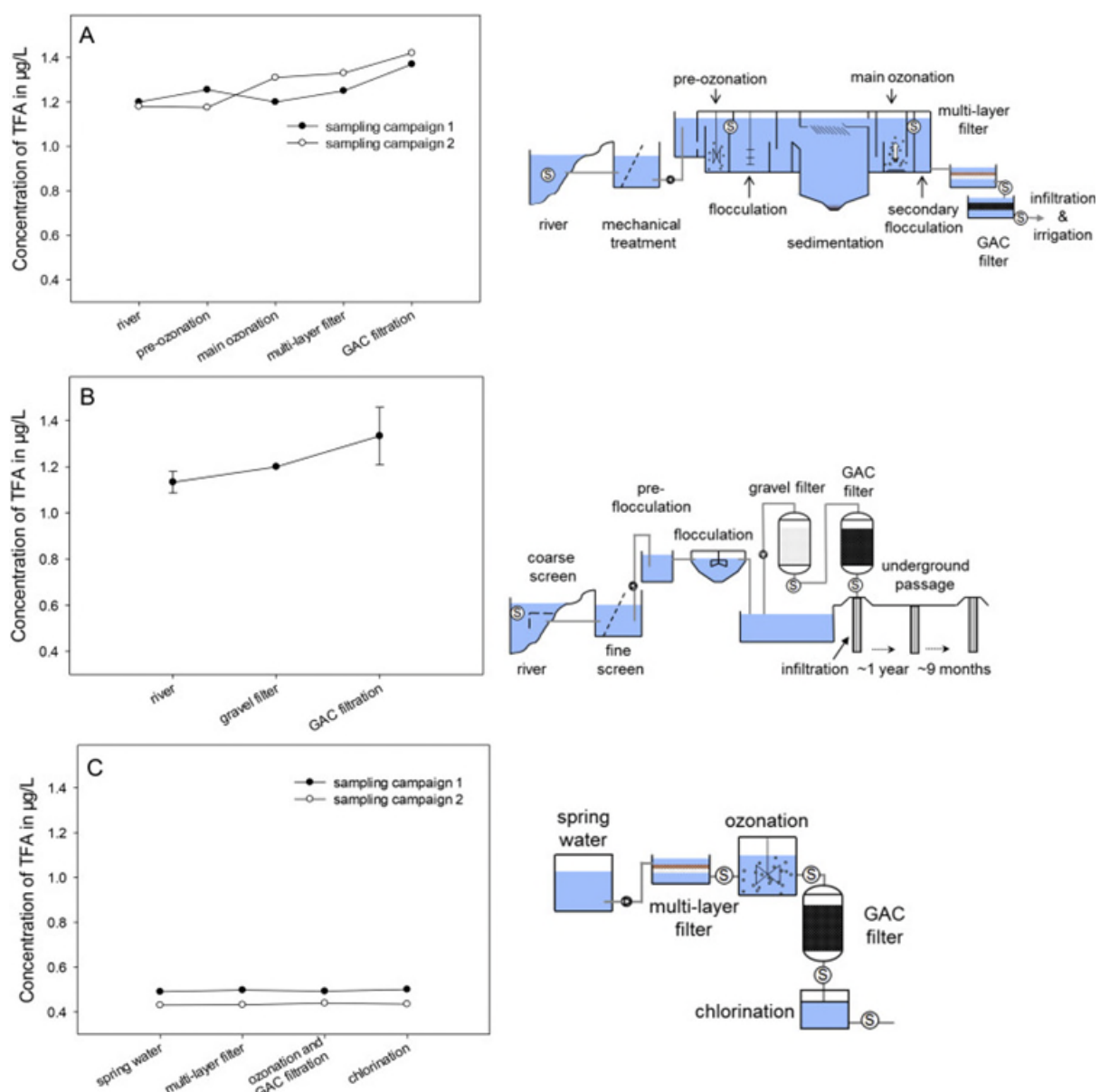
## 2.5 Removal of PFAS in water treatment processes

Due to its physicochemical properties, the removal of TFA is not feasible using conventional techniques, particularly for drinking water treatment (UBA, 2021). This is consistent with poor removal observed for short-chain PFAS (Hofman-Caris, 2024; Veggel and Hofman-Caris, 2024). Scheurer et al. (2017) investigated TFA removal in using laboratory batch tests, pilot- and full-scale set-ups. In ozonation and chlorination batch experiments, no reduction in the TFA concentration in tap water was observed for all oxidant contact times and concentrations considered. This

can be explained by the strength of the carbon–fluorine bond which leads to a high stability of the trifluoromethyl group against oxidizing conditions. The concentrations applied in the laboratory batch tests used exaggerated concentrations, which are not applied in practice. Therefore, it can be concluded that neither ozonation nor chlorination are capable to remove TFA in full-scale treatment plants if present in raw waters used for drinking water production (Figure 1 and Figure 6).

Activated carbon exhibited poor retention and a rapid breakthrough of TFA, and no removal of TFA was observed after a treatment cycle of 18 h using ion exchangers. Effective removal by ion exchange was predicted for a shorted operation time (6 h), but such a short cycle was not deemed feasible due to increased costs.

Recently, it has been shown that surface defunctionalized activated carbon felt (DeACF) carrying anion exchange sites exhibits an outstanding adsorption efficiency for TFA thanks to introduced electrostatic attraction and enhanced interactions between hydrophobic carbon surface and  $\text{CF}_3$  moieties ( $q_{\text{max}} = 30 \text{ mg/g}$ ,  $K_d = (840 \pm 80) \text{ L/kg}$  at a concentration of  $3.4 \text{ mg/L}$  in tap water) (Zhou et al., 2022).



**Figure 6:** TFA concentrations along the treatment train of three waterworks and schemes of the investigated treatment plants (Scheurer et al., 2017).

Among the treatments tested, reverse osmosis provided the best removal efficiency, consistently reducing TFA levels in permeates below detection limits. However, the generated concentrates still constitutes waste that needs to be managed (Hofman-Caris et al., 2024).

Measurements conducted in 3 full-scale waterworks showed no removal of TFA (Figure 6), while increasing levels in effluents were observed in 2 sites potentially due to formation of TFA in bioactive treatments. Ozonation applied to spring water used for drinking water production did not seem to contribute to increasing levels of TFA, however, this was potentially due to the relatively clean matrix that lacked significant amounts of precursors. In contrast, batch experiments showed that formation of TFA may result from degradation of fuoxetine (pharmaceutical), flurtamone (herbicides) and fluopyram (fungicide) following ozonation treatment. The authors concluded that the  $\text{CF}_3$  moiety attached to a benzene ring yielded most TFA. This was consistent with the results of Hermes et al. (2020), who reported minor formation of TFA from the ozonation of the antidiabetic drug sitagliptin which contains a  $\text{CF}_3$  moiety that is not bound to a benzene ring. In contrast, TFA concentrations moderate increase was observed after activated sludge treatment in 4 WWTP.

## 2.6 Short- and ultrashort-chain PFAS toxicity and guidelines

### 2.6.1 Toxicological information

The toxicity of PFAS has been extensively evaluated both in humans and laboratory animals and has been associated with a range of adverse health effects, including altered immune and thyroid function, liver and kidney disease, lipid and insulin dysregulation, reproductive and developmental toxicity, and cancer (Brase et al., 2021; Fenton et al., 2021). However, the bulk of existing toxicity data primarily focuses on relatively few extensively studied legacy PFAS such as PFOA, PFOS, PFBS and a few others (O'Rourke et al., 2024; Post, 2021; Radke et al., 2022). As a result, most PFAS listed in databases such as EPA's CompTox Chemicals Dashboard and Chemical Hazards Database (OpenFoodTox) from the European Food Safety Authority (EFSA) lack sufficient toxicity data, impeding the comprehensive assessment of potential hazards to human health (Shirke et al., 2024).

Although less toxic than long-chain PFAS (e.g., PFOS and PFOA) (Affourtit and Janssen, 2023), short-chain PFAS, such as perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS), are known to pose significant risks to human health including increased incidence of tumors, disruption of endocrine functions, impaired neurodevelopment, and reproductive toxicity (Gonsioroski et al., 2020; Neuwald et al., 2022; Nian et al., 2020). In contrast, our understanding of the toxicity of most ultrashort-chain PFAS remains limited. This is primarily due to limited toxicological data, owing to analytical challenges associated with determining these compounds and the limited availability of detection methods (Björnsdotter et al., 2022). It is important to close this knowledge gap as emerging evidence has shown the presence of short-chain and ultrashort-chain PFAS in various human body fluids, including blood, breast milk and urine (Calafat et al., 2019; Criswell et al., 2023; Jain, 2018; Pennoyer et al., 2023; Xu et al., 2020; Zheng et al., 2023).

Recently, TFA has attracted significant scientific and regulatory attention due to its environmental persistence, high environmental concentrations, and potential implications on human health (Björnsdotter et al., 2020; Freeling and Björnsdotter, 2023). TFA has been shown to incorporate into proteins and other biomolecules of aquatic organisms (Arp et al., 2024). This may explain higher total organic fluorine (TOF) levels than expected based on conventional PFAS analysis in human blood (REFs) and have potential implications for human health. According to the information sourced from the European Chemical Agency (ECHA), TFA is rapidly absorbed by oral route, inhalation route and dermal contact at noncorrosive/irritant concentrations (ECHA, 2023).

In 2014, EFSA conducted an assessment of TFA as the environmental metabolite of the herbicide saflufenacil (EFSA, 2014). The toxicological dossier for TFA included acute, short-term, and semi-chronic oral studies in rats, *in vitro* genotoxicity studies, and a developmental toxicity study in rats, although the latter was incompletely reported according to RIVM (Affourtit and Janssen, 2023). EFSA concluded that TFA (specifically the sodium salt form) is not

genotoxic and does not adversely affect fetal development based on the available data, however, liver effects in repeated exposure studies, such as increased liver weight, hepatocellular hypertrophy, and liver damage, have been reported (Affourtit and Janssen, 2023). In a recent study by Dekant and Dekant (2023), the liver was identified as a target organ showing mild hypertrophy after repeated oral administration. However, these effects were categorised as minor, as mild changes in liver enzymes and minimal to mild liver hypertrophy (even at daily doses above 1000 mg/kg body weight in the 90-day oral study) were observed. In addition, it has been reported that the effect of TFA on the liver is mediated by the proliferation of peroxisomes. This mode of action is considered irrelevant for humans because, unlike rodents, the human liver does not respond to the proliferative effects of peroxisome proliferator-activated receptor- $\alpha$  agonists (Yang et al., 2008).

Similar to TFA, perfluoropropanoic acid (PFPrA) has emerged as another ultrashort-chain PFAS extensively detected in various environmental compartments including surface water, ground water, and soil (Amato et al., 2023b; Sadia et al., 2023; Zheng et al., 2023). The U.S. Environmental Protection Agency (USEPA) recently established a noncancer chronic reference dose (RfD) for PFPrA (0.0005 mg/kg/day), based on the available toxicity data (Lambert et al., 2023). While evidence from human epidemiological studies on health effects of PFPrA is limited, the USEPA emphasised that the absence of observed effects in the available human studies does not necessarily imply lack of effects; rather, this could be due to the limited sensitivity of these types of studies. A chronic noncancer RfD of 0.0005 mg/kg/day for oral exposure was derived, representing an estimate of oral exposure to the human population that includes susceptible subgroups and life stages, and is unlikely to pose a significant risk of adverse health effects over a lifetime. As reported by USEPA, the available database on the hazards and dose-response relationship of PFPrA is based on studies conducted via the oral route of exposure. There are only a few known studies on inhalation or dermal uptake. Importantly, studies on the potential carcinogenic effects of PFPrA and the underlying mechanisms are limited and characterised by a lack of conclusive evidence.

Given the uncertainties surrounding the toxicological profile of PFPrA and its detection in environmental compartments, it is advisable to consider evaluating whether a relative potency factor (see section 2.6.2) should be developed, similar to the approach taken for TFA. This may require additional toxicity studies to provide a more robust and mechanistic understanding of its toxicity, and should also be extended to other frequently detected ultrashort-chain PFAS such as TFMS (Amato et al., 2023b).

### 2.6.2 Drinking-water guidelines

In the European Union, the revised Drinking Water Directive recommends limits of 100 ng/L (0.1  $\mu$ g/L) as “sum of PFAS” for 20 PFAS (long and short-chain, i.e., from C4 to C13), including PFOA and PFOS, and also an alternative parameter “PFAS total” of 500 ng/L (0.5  $\mu$ g/L) for all PFAS (EU Commission, 2020). Ultra short-chain PFAS (C < 4), such as the commonly occurring TFA and PFPrA, are currently excluded from the list. To our knowledge, only a few countries, including the Netherlands, Germany, and Denmark, have established guideline values for TFA in drinking water. In 2017, the Dutch National Institute for Public Health and the Environment (RIVM) derived a drinking water guideline value of 0.35 mg/L for TFA (Janssen, 2017), which was reassessed in 2023 (Affourtit and Janssen, 2023). The reassessment incorporated more recent scientific findings and recognised the toxicity of TFA as comparable to other PFAS, particularly with respect to liver effects.

The approach suggested by RIVM aims to consider the cumulative exposure of PFAS, and adapt the drinking water legislation to the health risk limit indicated by EFSA, which is based on Tolerable Weekly Intake (TWI) of 4 PFAS (PFOA, PFOS, perfluorononanoic acid (PFNA) and perfluorohexane sulfonic acid (PFHxS)) (Schrenk et al., 2020). A relative potency factor (RPF) approach is adopted where the toxic potencies of individual PFAS are expressed in relation to the potency of PFOA; according to this approach, the concentration of a given PFAS is divided by its RPF to give a corresponding RPF-adjusted concentration ( $[PFAS]_{RPF}$ ). The sum of all the RPF-adjusted concentrations (i.e.,  $\sum [PFAS]_{RPF}$ ) is referred to as PFOA equivalents (PEQ). Based on the TWI indicated by EFSA, a health-based risk limit for drinking water of 4.4 ng PEQ/L is derived (van der Aa and te Biesebeek, 2021). The RPF of TFA (0.002) is relatively

low, but comparable to that of other PFAS. RIVM proposes that when TFA occurs in water alone, an indicative drinking water guideline value ( $i\text{-GLV}_{\text{DW}}$ ) of 2,200 ng/L, obtained by dividing the PEQ-based limit value (4.4 ng/L) by the RPF of TFA (0.002), could be used (Affourtit and Janssen, 2023). When TFA occurs in a mixture, the contribution of all other PFAS present for which RPFs is available should be included in the PEQ calculation. However, evidence suggest that TFA is unlikely to occur alone in drinking water (Amato et al., 2023b; Sadia et al., 2023). While the  $i\text{-GLV}_{\text{DW}}$  of 2,200 ng/L is recommend by the RIVM, TFA and other PFAS that are not listed in the EU Drinking Water Directive fall under the group 'other anthropogenic substances' in the Dutch Drinking Water Decree, for which a standard of 1  $\mu\text{g/L}$  applies.

In 2020, the German Federal Environment Agency (UBA) issued a revised guidance value for TFA in drinking water based on recent scientific studies, and provided a drinking water guideline value of 60  $\mu\text{g/L}$  (60,000 ng/L), and a target value of 10  $\mu\text{g/L}$  (10,000 ng/L) (UBA, 2020). The  $i\text{-GLV}_{\text{DW}}$  derived by RIVM for TFA is far below the value derived by UBA. This is because RIVM did not use the data used by UBA and questioned the choice of elevated alanine aminotransferase (ALT) as a critical effect, which formed the basis for the no observed adverse effect level (NOAEL) of 1.8 mg/kg bw per day. RIVM argued that the selection of elevated ALT as point-of-departure could not be substantiated through their dose-response analysis which led to reservations about considering elevated ALT as a reliable critical effect for deriving the NOAEL. In the absence of direct immunotoxicity studies for TFA, RIVM derived its  $i\text{-GLV}_{\text{DW}}$  by extrapolation from the immunological effects observed for other PFAS substances, such as PFOA and PFOS, due to the similarities in their chemical structures and toxicological profiles. Furthermore, given the dose-response curves of different PFAS, which indicate similar effects but varying potencies, RIVM assumed TFA would have comparable immunotoxic effects. The  $i\text{-GLV}_{\text{DW}}$  for TFA was adjusted for its lower potency relative to PFOA, with safety factors applied to account for the uncertainty in the absence of direct data.

A recent KWR report (Amato et al., 2023b) indicated that TFA was frequently detected in drinking water, at levels typically ranging from 94 to 375 ng/L, and reaching 705 ng/L in one drinking water sample. While the detected levels fall well below the indicative drinking water guideline value set by RIVM (2,200 ng/L), a previous study indicated that TFA accounted for 21% and 53% of PFAS exposure in Dutch drinking water produced from surface water and groundwater, respectively, based on PEQ calculations from 20 compounds (Schepens et al., 2023). Due to the limited number of groundwater samples analysed ( $n = 5$ ), the authors recommended more extensive monitoring of TFA in groundwater.

## 3 Materials and methods

### 3.1 Raw water sampling

Sampling was performed at different drinking water production sites located in several Dutch provinces, including Friesland, Groningen, Drenthe, Overijssel, Gelderland, Utrecht, South Holland, North Brabant and Limburg (Appendix I.I). Samples consisted of raw water obtained from abstracted groundwater characterised by different estimated vulnerability. Sampling was performed in 2024, except for Vitens which provided data from May 2017 until January 2024 (but excluding 2018). In total, 10 locations were sampled for Brabant Water, 10 for WBG, 9 for WMD, and 7 for WML. Vitens provided data for 80 locations.

### 3.2 Groundwater vulnerability

Groundwater vulnerability is a measure of how rapidly pollutants can reach groundwater. The more vulnerable the groundwater is, the more likely it is to be contaminated by pollutants. Different criteria can be used to define groundwater vulnerability; these are reported for each drinking water company in Table 2.

**Table 2.** Criteria used for the assessment of groundwater vulnerability.

Drinking water company	Method
Brabant Water	<ul style="list-style-type: none"> <li>• Not vulnerable               <ul style="list-style-type: none"> <li>○ &gt; 50 years of hydraulic resistance above the extraction wells;</li> <li>○ No history of anthropogenic contamination and no negative trend in water quality within 25 years travel time to extraction.</li> </ul> </li> <li>• Moderately vulnerable               <ul style="list-style-type: none"> <li>○ Hydraulic resistance above extraction wells between 5 and 50 years;</li> <li>○ Significantly increasing trend of anthropogenic influence in groundwater within 10 years travel time to extraction.</li> </ul> </li> <li>• Vulnerable               <ul style="list-style-type: none"> <li>○ Less than 5 years hydraulic resistance above extraction wells;</li> <li>○ Exceedance of drinking water standard in aquifer.</li> </ul> </li> </ul>
Vitens	<ul style="list-style-type: none"> <li>• Not vulnerable               <ul style="list-style-type: none"> <li>○ No more than 5% of extracted water is less than 100 years old;</li> </ul> </li> <li>• Moderately vulnerable               <ul style="list-style-type: none"> <li>○ Maximum 5% of extracted water is less than 25 years old, minimum 5% of extracted water is less than 100 years old;</li> </ul> </li> <li>• Vulnerable</li> </ul>

	o At least 5% of the extracted water is less than 25 years old.																																																			
WBG and WMD	<p>REFLECT method (Zaadnoordijk et al., 2024). Groundwater is scored based on soil type, thickness of the non-permeable layer and travel time:</p> <ul style="list-style-type: none"> <li>• &lt; 4 is not vulnerable</li> <li>• 4-7 is possibly vulnerable</li> <li>• &gt; 7 is vulnerable</li> </ul>																																																			
WML	<p>ABIKOU model (Stuyfzand and Bannink, 2003):</p> <ul style="list-style-type: none"> <li>• Type A: phreatic groundwater from sandy aquifers (upper aquifer) (vulnerable);</li> <li>• Type B: (semi)tensile water from sandy aquifers and limestone (sandstone) aquifers (deeper aquifer) (B moderately vulnerable; B2 not vulnerable);</li> <li>• Type I: artificially or naturally infiltrated surface water, possibly after a pre-treatment. This may be area-specific surface water or from the Rhine and Meuse (vulnerable);</li> <li>• Type K: phreatic groundwater from limestone or marl (K1 vulnerable; K2 moderately vulnerable);</li> <li>• Type O: directly purified surface water, mainly from the Rhine and Meuse after residence in a reservoir (vulnerable);</li> <li>• Type U: bank filtrate or bank groundwater (vulnerable).</li> </ul> <table border="1"> <thead> <tr> <th rowspan="2">TYPE</th> <th colspan="2">Ondiep, Freatisch Grondw ater</th> <th colspan="2">Diep, Spannings Grondw ater</th> <th colspan="2">Infiltraat (kunstmatig)</th> <th colspan="2">Kalksteen Grondw ater</th> <th colspan="2">Oppervlaktew ater</th> <th colspan="2">Oever-grondw ater</th> </tr> <tr> <th>A</th> <th>A2</th> <th>B</th> <th>B2</th> <th>I</th> <th>I2</th> <th>K</th> <th>K2</th> <th>O</th> <th>O2</th> <th>U</th> <th>U2</th> </tr> </thead> <tbody> <tr> <td>Kenmerken</td> <td>C<sub>SDP</sub> &lt; 250 d</td> <td>C<sub>SDP</sub> &gt; 250 d</td> <td>C<sub>SDP</sub> &lt; 2500 d</td> <td>C<sub>SDP</sub> &gt; 2500 d</td> <td>Gesloten terugwinning</td> <td>Open terugwinning</td> <td>C<sub>SDP</sub> &lt; 250 d</td> <td>C<sub>SDP</sub> &gt; 2500 d</td> <td>Direct ingenomen oppervlaktewater</td> <td>Oppervlaktewater na verblijf in spaarbekken</td> <td>C<sub>SDP</sub> &lt; 250 d</td> <td>C<sub>SDP</sub> &gt; 250 d</td> </tr> <tr> <td>Leeftijd w ater (jaar)</td> <td colspan="2">2 - 200</td> <td colspan="2">20 - 25000</td> <td colspan="2">0,1 - 10</td> <td colspan="2">2 - 200</td> <td colspan="2">0 - 1</td> <td colspan="2">1 - 50</td> </tr> </tbody> </table>	TYPE	Ondiep, Freatisch Grondw ater		Diep, Spannings Grondw ater		Infiltraat (kunstmatig)		Kalksteen Grondw ater		Oppervlaktew ater		Oever-grondw ater		A	A2	B	B2	I	I2	K	K2	O	O2	U	U2	Kenmerken	C <sub>SDP</sub> < 250 d	C <sub>SDP</sub> > 250 d	C <sub>SDP</sub> < 2500 d	C <sub>SDP</sub> > 2500 d	Gesloten terugwinning	Open terugwinning	C <sub>SDP</sub> < 250 d	C <sub>SDP</sub> > 2500 d	Direct ingenomen oppervlaktewater	Oppervlaktewater na verblijf in spaarbekken	C <sub>SDP</sub> < 250 d	C <sub>SDP</sub> > 250 d	Leeftijd w ater (jaar)	2 - 200		20 - 25000		0,1 - 10		2 - 200		0 - 1		1 - 50	
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c = water travel time.

### 3.3 Sample preparation

Ultra-short chain PFAS were extracted by means of solid phase extraction (SPE). The water samples were stored in 500 mL PP bottles in the freezer (-20°C). The samples were allowed to defrost overnight before extraction. Procedural laboratory blank consisting of ultrapure water were included in the extraction batch. The following internal standards were added to each sample: <sup>13</sup>C<sub>2</sub>TFA (40 ng/L), <sup>13</sup>C<sub>3</sub>PFPrA (8 ng/L), <sup>13</sup>C<sub>3</sub>PFBA (4 ng/L), <sup>13</sup>C<sub>3</sub>PFBS (4 ng/L). Next, the samples were acidified to a pH of 4-5 using HCl (diluted working solution). The SPE was carried out using Oasis-WAX SPE cartridges (150 mg, 30 µm, 6cc, Oasis®). The extraction procedure included a precleaning step which was performed using a polypropylene cartridge containing 3 grams of sea sand placed on top of the Oasis-WAX cartridge using an adapter. Before extraction, both cartridges were conditioned using two times 5 mL 0.25% ammonium

hydroxide in MeOH followed by two times 5 mL ultrapure water (LC-MS grade). To extract the water samples, they were passed over the SPE column at a rate of one drop per second using a nylon tube. After extraction, rinse the original sample bottle twice with 10 mL of ultrapure water and add this to the respective sand filter on the SPE column. Sand cartridges and adapters were removed and 5 mL of 25 mM ammonium acetate pH 4 was added to the WAX SPE cartridges for cleaning. SPE cartridges were covered with aluminium foil and left to dry for circa 1 hours under vacuum.

The empty bottles were allowed to dry and rinsed using 10 mL of MeOH. The rinsing solution was transferred to a clean glass tube. The same tube was then used to collect the eluate from the corresponding SPE cartridges. Cartridges were eluted using 5 mL 0.25% ammonium hydroxide in MeOH. Eluates (i.e., 15 mL in total) were reduced to a volume of 500  $\mu$ L under a gentle stream of nitrogen (Barkey, 67°C). After evaporation, samples were made up to a final volume of 1 mL (MeOH:ultrapure water 1:1 v/v %) spiked with an injection standard (IS) PFAS mixture ( $^{13}\text{C}_2\text{PFOA}$  and  $^{13}\text{C}_4\text{PFOS}$  (2  $\mu\text{g/L}$ )), resulting in a concentration factor of 500x. Samples were then filtered (0.45  $\mu\text{m}$ , regenerated cellulose, Phenex filters) and stored in the freezer (-20 °C) until analysis. Procedural blanks were prepared using the same bottles used for sample collection (i.e., from the same batch), filled with ultrapure water and extracted using the procedure described above.

### 3.4 Method validation

The LOD of ultra-short chain PFAS was determined by spiking reference standards in drinking water (tap water KWR) and in surface water (Lekkanaal) at concentrations of 0.5, 1.0, 2.0 and 5 ng/L ( $n = 5$ ) (concentrations TFA were 10x higher). The LOD is defined by using the standard deviation of the repeatability for the lowest concentration that was detected, and taking into account a confidence interval of 99% with one-side probability. The limit of quantitation (LOQ) for each compound was then determined by using the LOD multiplied by 3. The LOD was used to determine the Reporting Limit (RL), and was set above the LOD to a fixed reporting limit for target analyses purposes. The repeatability and recovery were determined by spiking drinking water and surface water ( $n = 5$ ) with ultra-short chain PFAS at a level of 10 ng/L (100 ng/L for TFA), which were analysed together with the corresponding drinking and surface water blanks. Recoveries were calculated by comparing the concentrations obtained from external standard calibration with the initial spiking level, after subtraction of the corresponding blank sample.

### 3.5 Instrumental analysis

A Tribrid Orbitrap Fusion mass spectrometer (ThermoFisher Scientific, Bremen, Germany) equipped with a heated electrospray ionization source was interfaced to a Vanquish HPLC system (ThermoFisher Scientific). For chromatographic separation, a Trinity P1 mixed-mode column (50 mm  $\times$  2.1 mm I.D., particle size 3  $\mu\text{m}$ , ThermoFisher) preceded by a Krudkatcher ultra HPLC In-line filter (Phenomenex, 0.5  $\mu\text{m}$ ) was used. The Trinity P1 column was kept at 35°C during analysis. Eluent A consisted of ultrapure water with 2 mM ammonium acetate at a pH of 4.5. Eluent B consisted of 80% acetonitrile and 20% ultrapure water (v/v) with 40 mM ammonium acetate at a pH of 4.5. The gradient started constant with 10% B for 1 min. Then increased linear to 60% B in 4 min, and then increased to 100% B in 7 min and stayed at 100% B for 7 min. The injection volume and the flow rate were 5  $\mu\text{L}$  and 0.30 mL/min for both methods, respectively.

Mass spectrometric detection was performed in negative ionization mode. The Vaporizer and capillary temperature were both set to 300 °C. Sheath, auxiliary and sweep gas were set to arbitrary units of 40, 10 and 5. The source voltage was set to - 2.5 kV in negative mode. The RF lens was set to 30%. Full scan high resolution mass spectra were recorded from  $m/z$  80–350, with a resolution of 120,000 FWHM. Quadrupole isolation was used for acquisition with a 5 ppm mass window. The AGC target was set to 400,000 and maximum injection time was set to 100 ms. MS/MS spectra were recorded using a mass table list with a resolution of 15,000 FWHM. Optimal HCD collision energy was

selected for each individual PFAS. With every batch run, mass calibration was performed using a Pierce FlexMix calibration solution to obtain a mass error of < 2 ppm.

Calibration standards for both methods were prepared in 50:50 MeOH:H<sub>2</sub>O (v/v%) at concentration levels of 0, 0.10, 0.25, 0.50, 1.0, 2.5, 10, 25, 50 µg/L while concentrations for TFA were 10× higher. Every batch a control standard was analyzed for quality assurance. The calibration curve was analysed before the sample sequence, and blank runs were collected before and after calibration sequences and in between samples (set of 10 samples).

### 3.6 QA/QC

Blanks consisting of water bottles filled with ultrapure water were included in the analytical protocol ( $n = 3$ ) to assess PFAS background levels and potential contamination. The limits of quantification (LOQ) of the measurements provided by Vitens were 0.1 and 0.01 µg/L for TFA and TFMS, respectively. The LOQ of the method developed by KWR are shown in section 4.1.

### 3.7 Data analysis

Relationships between percentage of water of a given age and the concentration of TFA in groundwater were assessed using linear regression. The Pearson's correlation coefficient was used to evaluate the correlations between variables. Outliers were identified using the interquartile range (IQR). The IQR is the range between the first quartile (Q1, 25th percentile) and the third quartile (Q3, 75th percentile) (i.e.,  $IQR = Q3 - Q1$ ). Outliers are data points that fall outside the following boundaries:

- **Lower boundary:**  $Q1 - (1.5 \times IQR)$
- **Upper boundary:**  $Q3 + (1.5 \times IQR)$

Data points below the lower boundary or above the upper boundary are considered outliers.

## 4 Results and discussion

### 4.1 Method validation (KWR)

The results of method validation for ultra-short PFAS in drinking and surface water are shown in the Table 3 and 4. Satisfactory LOD and RL results were obtained for all ultra-short chain PFAS in drinking- and surface water. The reporting limit ranged from 0.5 ng/L for FEtSA to 10 ng/L for TFA. Recoveries in drinking- and surface water are between 62.3 and 115 % and are satisfactory. The repeatability is lower than 8.8% in both matrices for all compounds and is satisfactory.

**Table 3.** Method performance characteristics in drinking water.

Compound	LOD (ng/L)	Reporting limit (ng/L)	Repeatability (10 ng/L) (%)	Recovery (10 ng/L) (%)
FEtSA	0.056	0.50	7.0	98.6
TFA	0.236	10	3.1*	94.5*
PFPrA	0.062	2.0	1.5	99.2
2,3,3,3-TFPA	0.346	2.0	3.3	98.9
TFMS	0.076	1.0	8.3	73.5
PFEtS	0.165	1.0	3.5	100
PFPrS	0.136	1.0	5.1	99.0

\*Repeatability and recovery for TFA were determined at 100 ng/L.

**Table 4.** Method performance characteristics in surface water.

Compound	LOD (ng/L)	Reporting limit (ng/L)	Repeatability (10 ng/L) (%)	Recovery (10 ng/L) (%)
FEtSA	0.152	0.50	5.8	100
TFA	n.d.	10 <sup>#</sup>	1.3*	95.8*
PFPrA	0.471	2.0	4.6	97.3
2,3,3,3-TFPA	0.271	2.0	8.8	62.3
TFMS	n.d.	1.0 <sup>#</sup>	4.8	92.0
PFEtS	0.221	1.0	3.5	115
PFPrS	0.217	1.0	5.7	107

n.d.: not determined.

\*Repeatability and recovery for TFA were determined at 100 ng/L.

<sup>#</sup> The concentrations of TFA and TFMS in surface water (lekkanaal) are too high to establish a reporting limit for them. Therefore, the reporting limit for drinking water is applied to TFA and TFMS.

## 4.2 TFA and other ultrashort-chain PFAS in abstracted groundwater

### 4.2.1 TFA

#### 4.2.1.1 General overview of TFA concentrations by groundwater vulnerability

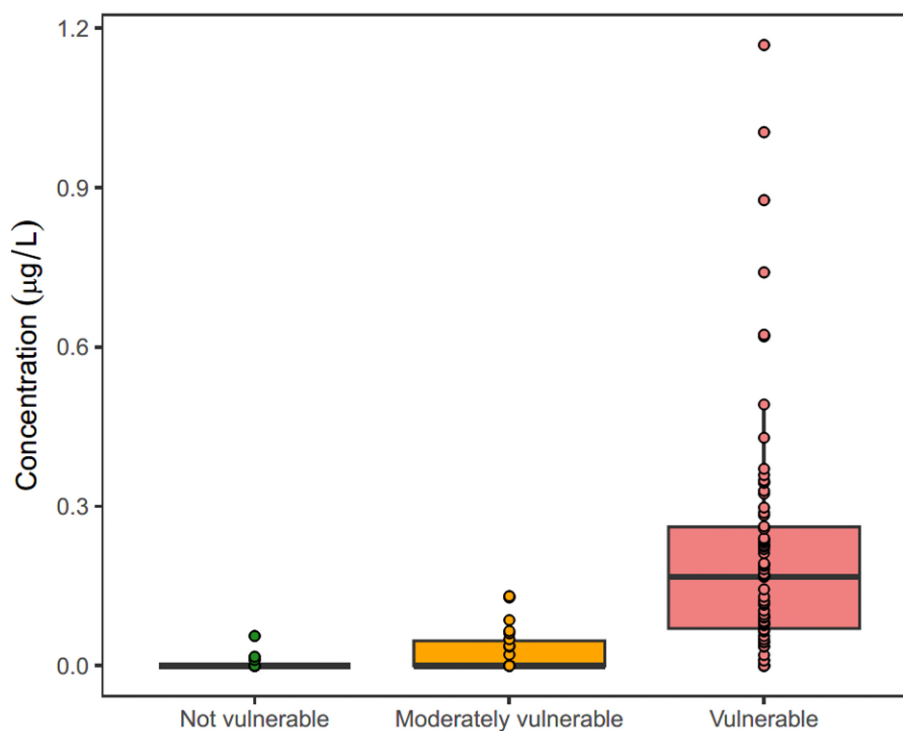
TFA levels varied considerably across different types of abstracted groundwater defined according to three vulnerability classes (Table 5). In ‘not vulnerable’ abstracted groundwater, the maximum average concentration was 0.056 µg/L (V10). A total of 17 out of 20 samples were below the limit of quantification (LOQ), resulting in a detection frequency of 15% (Table 5). In ‘moderately vulnerable’ abstracted groundwater, the maximum average concentration was  $0.13 \pm 0.06$  µg/L ( $n = 3$ ), with a higher detection frequency of 41%, but many samples (13 out of 22) below the LOQ. Due to the low detection frequencies, median concentrations remained < LOQ for both ‘not vulnerable’ and ‘moderately vulnerable’ groundwater. Contamination levels did not seem to largely differ between ‘not vulnerable’ (< 0.06 µg/L) and ‘moderately vulnerable’ (< 0.13 µg/L) groundwater (Figure 7), although levels are likely to increase in these types of groundwater as younger water progressively reaches the aquifer. In ‘not vulnerable’ groundwater, locations exceeding the LOQ included V10 (0.056 µg/L) and WMD6 (0.017 µg/L). In ‘moderately vulnerable’ groundwater, the LOQ was exceeded in V40 ( $0.13 \pm 0.06$  µg/L,  $n = 3$ ), V2 ( $0.13 \pm 0.04$  µg/L,  $n = 3$ ), WML5 (0.07 µg/L), V60 (0.07 µg/L), WMD9 (0.06 µg/L), WML7 (0.05 µg/L), WMD8 (0.04 µg/L), BW10 (0.04 µg/L) and WMD3 (0.02 µg/L) (Figure 8). All remaining ‘non vulnerable’ and ‘moderately vulnerable’ groundwaters had concentrations < LOQ.

In ‘vulnerable’ abstracted groundwater, the highest average concentration was  $1.17 \pm 0.60$  µg/L ( $n = 57$ ), the detection frequency was 89% (i.e., 66 out of 74), and the median concentration was 0.17 µg/L, respectively. The highest TFA concentrations measured in ‘vulnerable’ abstracted groundwater were found in V20 ( $1.17 \pm 0.60$  µg/L,  $n = 57$ ), V67 ( $1.00 \pm 0.30$  µg/L,  $n = 37$ ), V50 ( $0.88 \pm 0.35$  µg/L,  $n = 16$ ), V80 ( $0.74 \pm 0.10$  µg/L,  $n = 6$ ), V15 ( $0.62 \pm 0.07$  µg/L,  $n = 6$ ), and WML4 (0.62 µg/L). These locations differed significantly from other observations in the ‘vulnerable’ groundwater dataset and were thus identified as outliers (Figure 7). Only 8 out of 74 ‘vulnerable’ groundwaters contained < LOQ. Overall, average concentrations were always below the drinking water limit recommended by the RIVM (i.e., 2.2 µg/L). Outliers were also detected in ‘moderately vulnerable’ and ‘not vulnerable’ groundwater. However, due to the large number of samples reported < LOQ, which artificially reduce variability, the analysis was considered ineffective.

**Table 5.** Summary of TFA concentrations in different types of groundwater.

Vulnerability	Max. Conc. (µg/L)	Min. Conc. (µg/L)	Median Conc. (µg/L)	Num. Observations	Obs. < LOQ	Detection frequency (%)
Not vulnerable	0.06	0	0	20	17	15
Moderately vulnerable	0.13	0	0	22	13	41
Vulnerable	1.17	0	0.17	74	8	89

Max. = maximum; min. = minimum; Conc. = concentration; Num. = number; Obs. = observations; Detection frequency =  $[(\text{Num. Observations} - \text{Obs. < LOQ}) / (\text{Num. Observations})] \times 100$ .



**Figure 7:** TFA concentrations in different types of groundwater. Data points indicate individual measurements. The central rectangular part of the plot, which represents the interquartile range (IQR). This is the range between the first quartile (Q1) and the third quartile (Q3), corresponding to the 25th and 75th percentiles of the data, respectively. The line inside the box represents the median. Whiskers extend to the minimum and maximum values within 1.5 times the IQR, beyond which data are considered outliers. The number of observations for each type of groundwater is shown in Table 5. Values < LOQ are set to zero.

#### 4.2.1.2 Interpretation of TFA concentrations by province

The interpretation of TFA groundwater concentrations was conducted at the provincial level because vulnerability assessments were conducted differently for each drinking water company and corresponding province/s (see Section 3.2).

##### *Friesland (Vitens)*

Concentrations in the Friesian islands (i.e., V9, V58, V62 and V70) ranged between 0.08 and 0.26 µg/L (Figure 8 and 9). These islands have a relatively small local population and small urban centers, although the population sharply increases during high tourism seasons. All groundwaters from these locations were categorized as 'vulnerable'. TFA sources in these islands may include plant protection products, which may cause the release of TFA via biotic degradation (section 2.1.1.3), and atmospheric deposition (Wang et al., 2014) (section 2.1.1.1), including potential contributions from sea-spray aerosols (Amato et al., 2023a; Amato and van der Grift, 2024; Sha et al., 2022). However, the absence of agricultural activities in Vlieland, and the fact that agriculture on the other islands is dominated by livestock farming and pasture land, suggests that atmospheric deposition may be a more relevant source of TFA in these islands. This might also hold for other coastal areas. PFAS levels on these islands are likely influenced by sea-spray deposition, however, direct links between TFA and sea-spray aerosols, including evidence of TFA transfer from seawater to sea-spray aerosols, have not been established yet. Laboratory studies have shown that enrichment factors from seawater to sea-spray aerosols decrease with decreasing PFAS chain length (Sha et al., 2024, 2021), thus, moderate transfer of TFA from seawater to sea-spray aerosols is expected. Nevertheless, significant contributions from sea-spray aerosols should not be excluded.

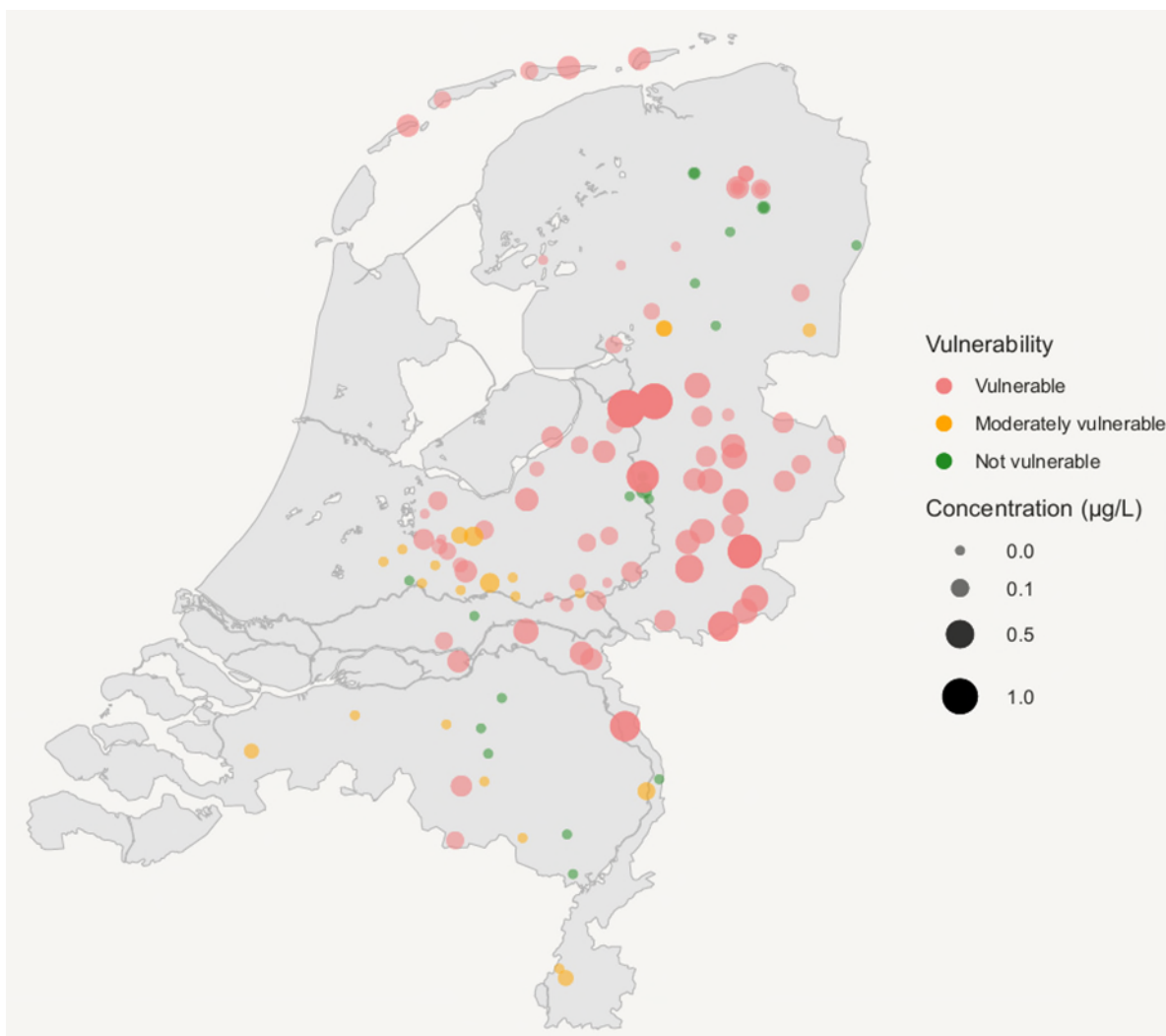
In the Friesian mainland (V51, V61 and V63), TFA levels were consistently < 0.1 µg/L, despite groundwaters were classified as 'vulnerable' (Figure 8 and 9). Higher levels of TFA in the Friesian Islands compared to those measured at

these sites – located between ~20 and ~50 km from the North Sea coast – suggest that deposition of sea-spray aerosols may be an important source of TFA at these islands (and coastal areas in general). In contrast, broader atmospheric deposition did not seem to result in TFA levels > 0.1 µg/L at these vulnerable locations.

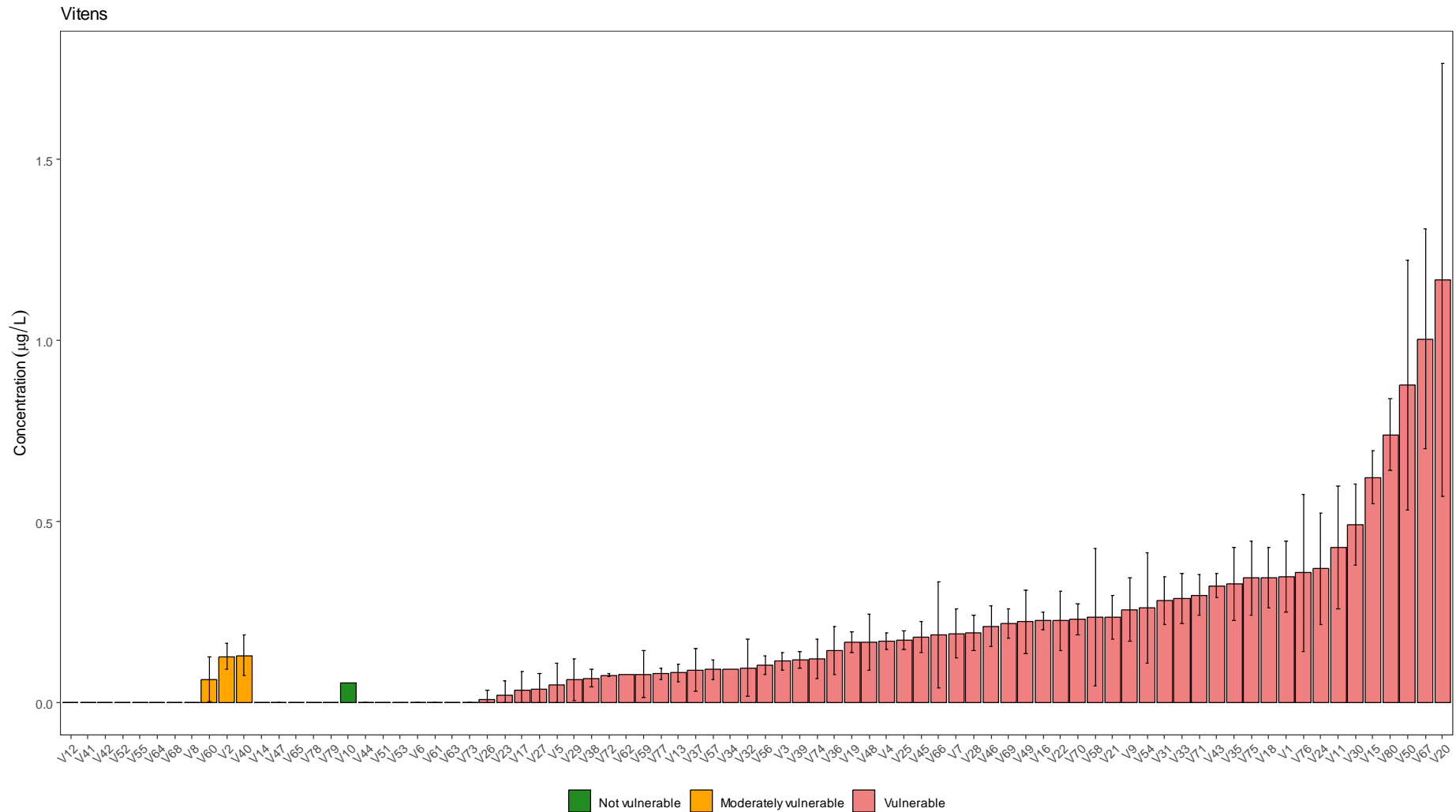
#### *Overijssel, Flevoland, Gelderland, Utrecht (Vitens)*

The Overijssel, Flevoland, and Gelderland regions were characterized by predominantly ‘vulnerable’ groundwater, and relatively high TFA levels (from ~0.3 to ~1 µg/L; Figure 8 and 9). Five ‘vulnerable’ locations, i.e., V20, V67, V50, V80, and V15, were identified as outliers due to their exceptionally high TFA concentrations. In V50 high levels of TFA are likely due to the active infiltration of surface water that typically contains higher levels of TFA. Similarly, relatively high concentrations in V20 and V67 can be explained due to the influence of riverbank filtrate. The higher concentrations of TFA at V15 and V80 cannot be explained at present and require further investigation. ‘Not vulnerable’ groundwaters (V10, V65, and V79) showed relatively low concentrations (< 0.1 µg/L).

In the Utrecht province, groundwater concentrations were low (< 0.3 µg/L) and consistent with the predominantly ‘moderately vulnerable’ groundwater present in this province, although some ‘vulnerable’ groundwaters were also sampled in this province (Figure 8 and 9).



**Figure 8:** Map of TFA concentrations in different types of abstracted groundwater. Each data point represents a different location, with the size of the points reflecting its concentration levels. Colours refer to different abstracted groundwater vulnerability. LOQ = 0.010 µg/L (except for Vitens' locations for which LOQ = 0.1 µg/L).



**Figure 9:** TFA concentrations measured in groundwater in Vitens' sites, which are located in Friesland, Overijssel, Flevoland, Gelderland and Utrecht. Data are reported as means ± standard deviation (n varied from 1 to 57). Values < LOQ (0.01 µg/L) are set to zero.

*Groningen (WBG)*

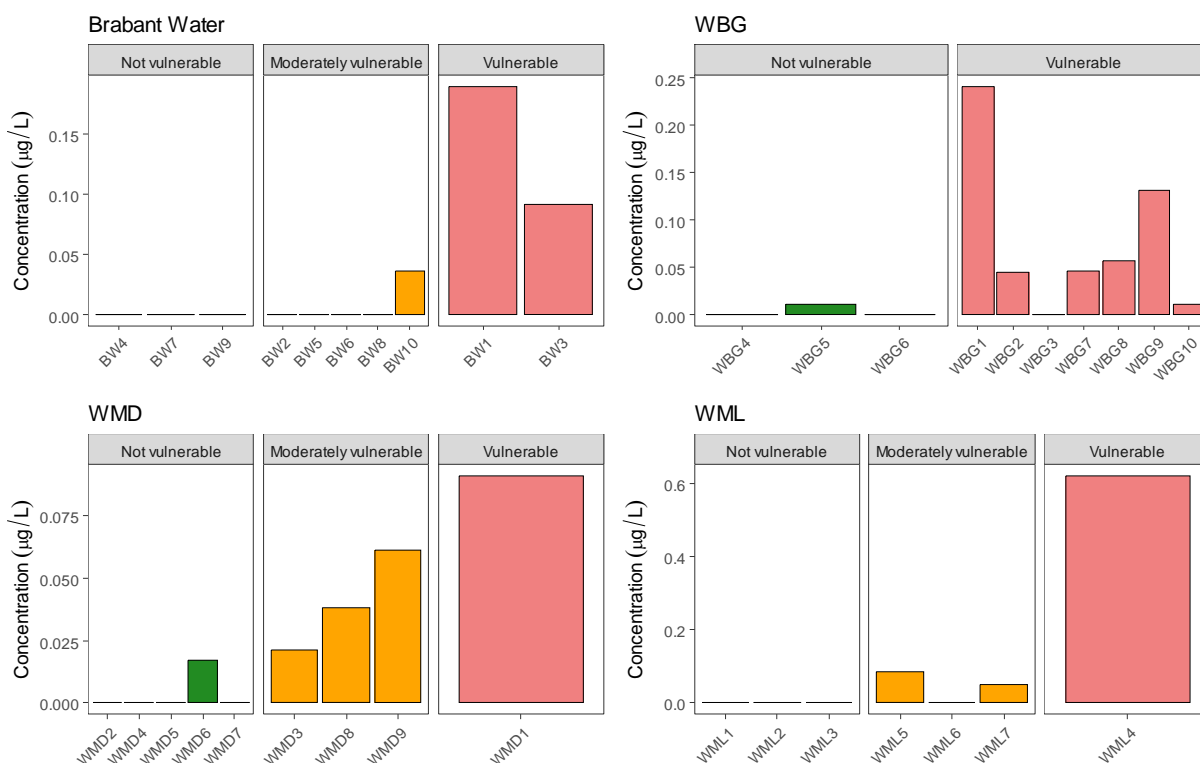
In Groningen, concentrations in ‘not vulnerable’ groundwater were consistently < LOQ (Figure 10). No samples of ‘moderately vulnerable’ groundwater was analysed from this province. Detectable levels were found in ‘vulnerable groundwater’, with concentrations up to 0.130 and 0.240 µg/L measured in WBG9 and WBG1, respectively (Figure 10). WBG1 is influenced by the Drentsche Aa (surface water) via bank filtration, where concentrations up to 1.8 µg/L have been measured. WBG9 also has some influence from surface water, from a marsh area.

*Drenthe (WMD)*

In Drenthe, concentrations in ‘non vulnerable’ groundwater were always < LOQ, except for WMD6, where a concentration of 0.017 µg/L was measured. Levels in ‘moderately vulnerable’ groundwater were < 0.061. Moderately higher levels were found in ‘vulnerable groundwater’, with a concentration of 0.091 µg/L measured in WMD1. Agricultural activities in the area could be potential sources of TFA.

*North Brabant (Brabant Water)*

TFA levels in ‘non vulnerable’ and ‘moderately vulnerable’ groundwater from North Brabant were always < LOQ, except for the ‘moderately vulnerable’ location BW10 (0.036 µg/L) (Figure 10). Levels in ‘vulnerable’ groundwater were also relatively low, with concentrations of 0.092 and 0.190 µg/L measured in BW3 and BW1, respectively. BW10 is characterized by a limited thickness of the sealing layer. The age of the extracted water is relatively young (70% between ≤ 1000 years). BW10 is located in an agricultural (floriculture) area; thus, potential sources of TFA may also include plant protection products. BW3 is a medium-deep extraction without sealing layers. The age of the extracted water is considered young ( 75% < 1000 years). BW1 is a shallow extraction without a contiguous capping layer (the top of the extraction wells is about 25 m below surface). The age of the extracted water is considered young (60% < 100 years). The area is subject to agricultural activities, which may have an impact on groundwater due to the leaching sensitivity of the soil.



**Figure 10:** TFA concentrations measured in groundwater by drinking water supplier (Brabant Water, Vitens, WBG, WMD and WML) and groundwater vulnerability. Values < LOQ (0.010 µg/L) are set to zero.

Limburg (WML)

In Limburg, concentrations in ‘non vulnerable’ and ‘moderately vulnerable’ groundwaters were < LOQ and < 0.086 µg/L, respectively. In WML4, the only ‘vulnerable’ location sampled in this province, a concentration of 0.620 µg/L was measured (Figure 10).

4.2.2 Other ultrashort-chain PFAS

Additional ultrashort-chain PFAS were measured in samples from Drenthe, Groningen, North Brabant, and Limburg. In the provinces supplied by Vitens (Friesland, Overijssel, Flevoland, Gelderland and Utrecht), only TFMS was measured.

PFPrA and TFMS were the only ultrashort-chain compounds detected in groundwater. PFPrA was found at least once in each province in which it was measured, and in 6 locations in total (Figure 11). These included WMD9 (0.0023 µg/L, Drenthe), WML5 (0.0033 µg/L, Limburg), WBG1 (0.0035 µg/L, Groningen), BW3 (0.0066 µg/L, North Brabant), WML4 (0.0130 µg/L, Limburg), and BW1 (0.0250 µg/L, North Brabant). PFPrA was detected in four ‘vulnerable’ locations (WML4, WBG1, BW3, BW1), two ‘moderately vulnerable’ locations (WML5 and WMD9), and none of the ‘not vulnerable’ locations, respectively.

TFMS was detected in WML4, at a concentration of 0.0013 µg/L (Figure 11), and in 14 locations in the provinces supplied by Vitens, at average concentrations < 0.031 µg/L (Figure 12). All locations were categorized as ‘vulnerable’, except for V14 (0.008 ± 0.006 µg/L, n = 9), V40 (0.0003 ± 0.001 µg/L, n = 3), and V60 (0.0001 ± 0.0003, n = 10), which were categorized as ‘non vulnerable’, ‘moderately vulnerable’, and ‘moderately vulnerable’, respectively (Figure 12). It should be noted that TFMS average concentrations were frequently below LOQ (0.01 µg/L). This occurred because averages included concentrations both below the LOQ (set to zero) and above the LOQ.

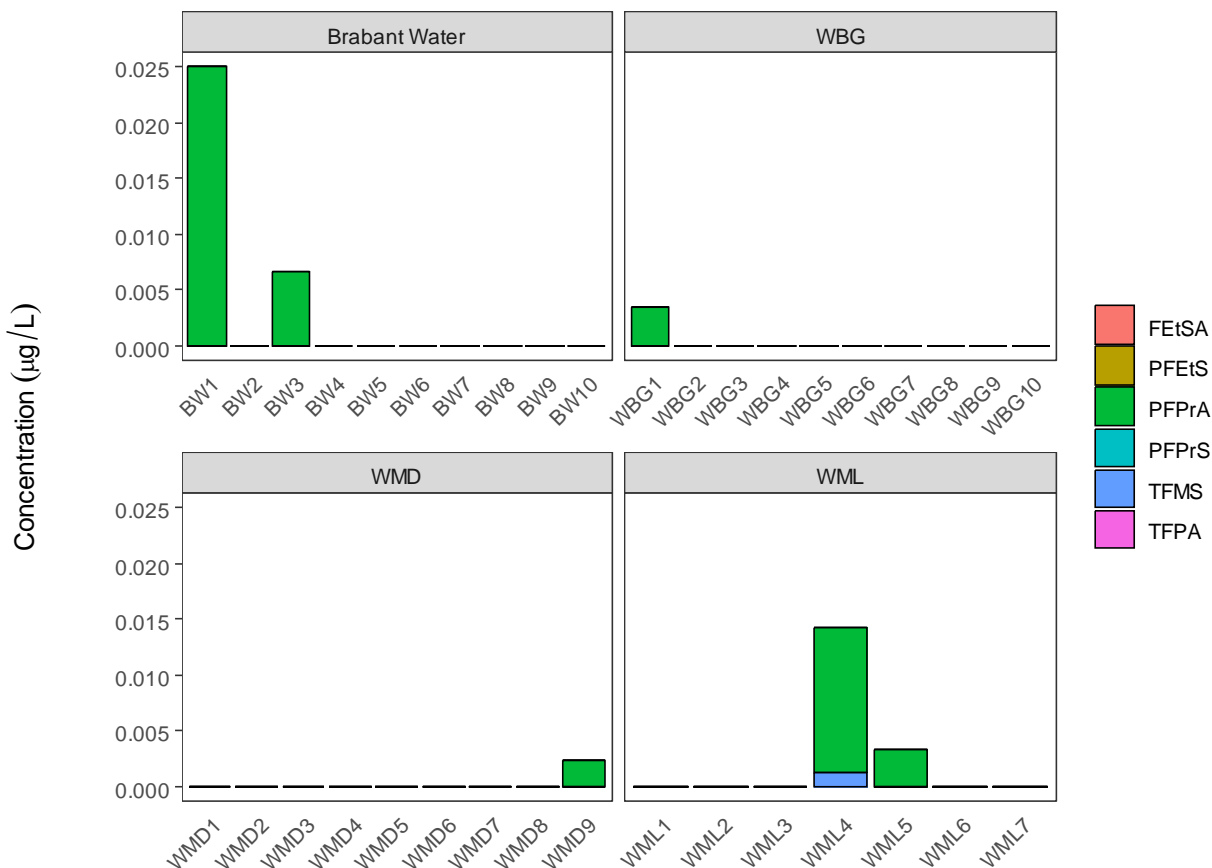


Figure 11: Ultrashort-chain PFAS concentrations in groundwater by drinking water supplier.



### 4.3 Predictions of TFA concentrations based on groundwater age

The dataset provided by Vitens included a classification of groundwater vulnerability based on travel time distributions obtained from hydrological model calculations (Table 2; Appendix I.II). This allows to test if higher percentages of young water in the abstracted groundwater correlate with TFA concentrations in it. This hypothesis was tested by quantifying the correlations between percentage of groundwater of a certain age and TFA concentrations in abstracted water (Figure 13). The percentage of groundwater younger than 10, 25, and 50 years showed the strongest correlations with TFA concentrations ( $r = 0.55$ ,  $0.62$  and  $0.64$ , respectively), whereas groundwaters younger than 10 and older than 50 years exhibited progressively weaker correlations (Appendix I.III).

Concentrations of TFA were truncated at the LOQ of the applied analytical method. All data  $<$  LOQ were set at zero. This resulted in the linear regression containing 0% of water under a certain age and concentrations that were artificially set at 0. If the LOQ would be lowered, the regressions might be improved, especially for groundwaters with a relatively low share of young water and presumably very low TFA concentrations. For this analysis, no data were excluded for not reaching LOQ levels or not having water younger than a certain age class. This might be refined in future.

The dataset included 5 outliers, corresponding to V20, V67, V50, V80, and V15 (Appendix I.IV). These well fields were characterized by unique conditions such as the presence of infiltrated surface water and riverbank filtration, resulting in significantly higher levels of TFA. By excluding these locations, correlations between groundwater age and TFA concentrations improved (Appendix I.III; Appendix I.V), with the strongest predictions of TFA concentrations provided by the percentage of groundwater younger than 25 and 50 years (Appendix I.III; Figure 14). As a result, the percentage of water younger than 25 (or 50) years present in abstracted groundwater could be used to predict its TFA concentration. This also suggests that the general TFA contamination is linked to inputs from diffuse sources rather than local sources, which is consistent with a recent study showing similar TFA aerosol concentrations in two distant locations in the Netherlands (Amato et al., 2024).

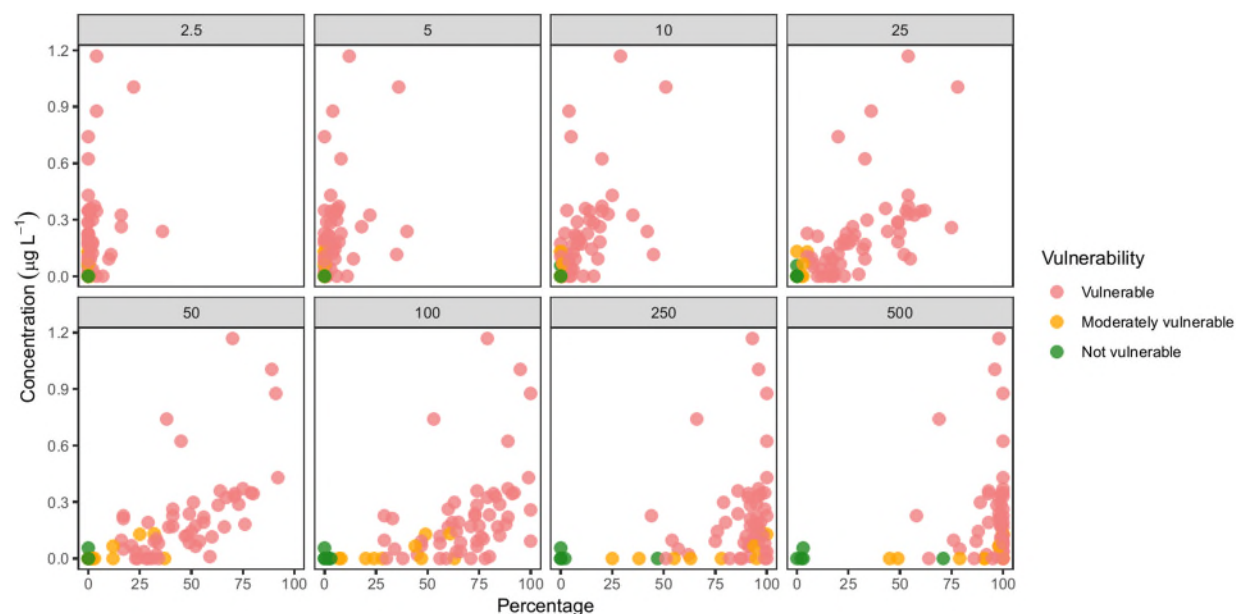
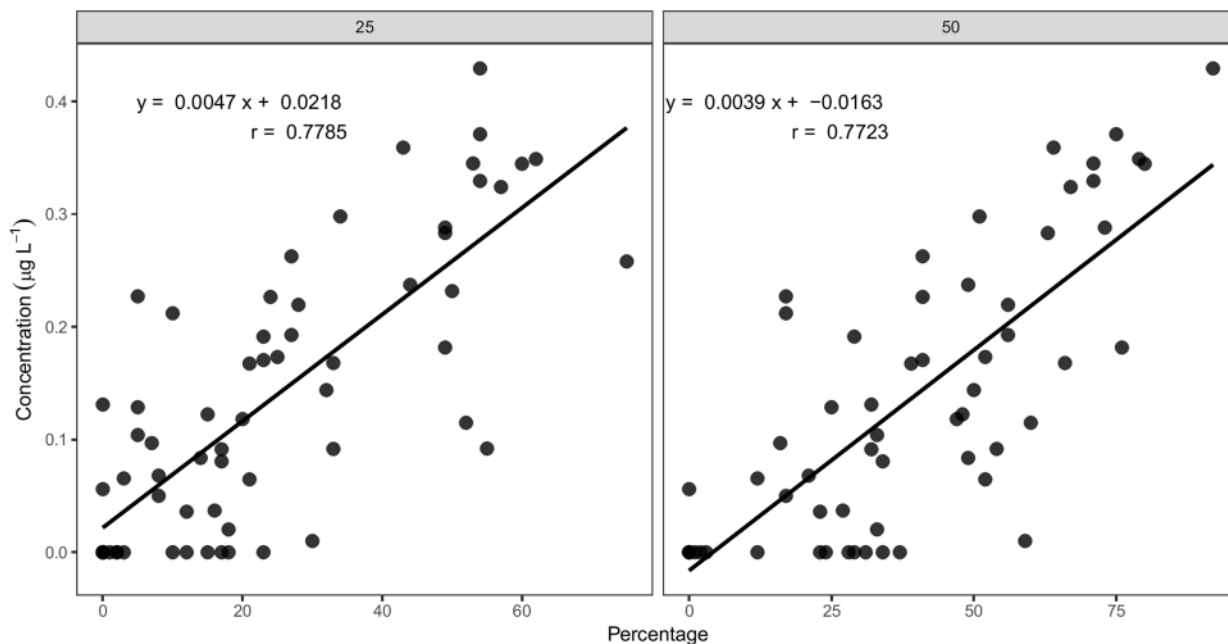


Figure 13: Correlations between the percentage of groundwater of a specific age range (from 2.5 to 500 years old) and its TFA concentration.



**Figure 14:** Linear regression between percentage of groundwater samples younger than 25 (left) or 50 (right) years and TFA concentrations. For instance, if the percentage of groundwater younger than 25 years is 60%, a concentration of 0.3  $\mu\text{g/L}$  of TFA can be expected in groundwater.

In general, groundwaters older than 50 years (i.e., containing 0% of water younger than 50 years) did not contain detectable amounts of TFA, except for V10 (0.056  $\mu\text{g/L}$ ). Since the concentration measured at this location was < LOQ (0.1  $\mu\text{g/L}$ ), and no replicate measurements were available, additional measurements using more sensitive analytical methods are needed to confirm this result. Groundwater older than 10 years (i.e., containing 0% of water younger than 10 years) contained on average < 0.13  $\mu\text{g/L}$  (excluding V14).

Based on the linear model used to predict TFA concentrations as a function of water age, TFA was always above the LOQ when the percentage of groundwater younger than 25 years was greater or equal to 30% (Figure 14). Similarly, when the percentage of groundwater younger than 50 years was greater or equal to 59%, TFA was always found (Figure 14).

## 5 Conclusions

The results of the literature review indicated that TFA has a high potential to penetrate in groundwater due to weak interactions and poor degradation in soil. As a consequence, the occurrence of TFA in groundwater is expected to be closely associated with water travel times, as demonstrated in this study.

TFA is considerably less toxic than other PFAS such as PFOA, PFOS, PFNA and PFHxS. However, its estimated potency (RPF = 0.002) is comparable to that of some short-chain PFAS (i.e., RPF = 0.001 and 0.05 for PFBS and PFBA, respectively). Toxicological data of other ultrashort-chain PFAS is currently lacking, although some of these compounds (i.e., TFMS and PFPrA) have been previously detected in drinking water in the Netherlands, and should be further investigated.

During water treatment processes, TFA is effectively removed only by reversed-osmosis. Ozonation may contribute to the formation of TFA due to degradation of pharmaceuticals, herbicides and fungicide. These compounds contain C-CF<sub>3</sub> moieties, which have been shown to convert to TFA and are thus potential sources of TFA.

In addition to pharmaceuticals and plant protection products, other relevant sources of TFA may include hydrofluorocarbons, fluorochemical manufacturing, waste disposal facilities, and PFAS precursors. Additional ultrashort-chain PFAS (i.e., PFPrA, TFMS, PFEtS and PFPrS) have been associated with hydrofluorocarbons, lithium-ion batteries, PFAS precursors and aqueous film-forming foams. The literature review concluded that TFA is relevant for the drinking water sector and groundwater protection, and the relative contribution of its varying sources should be further investigated. Due to similar properties, additional ultrashort-chain PFAS should also be monitored.

An SPE method was developed and validated, enabling the detection of TFA at levels 10 times lower than those achieved with conventional direct injection (i.e., from 0.1 to 0.010 µg/L). Other ultrashort-chain PFAS (C < 4) were also included in the method, with quantification limits ranging from 0.0005 and 0.002 µg/L. The method was applied to abstracted groundwaters collected from several Dutch provinces, and in combination with existing data provided by Vitens, allowed to perform a national survey covering 8 provinces in the Netherlands (i.e., Friesland, Groningen, Drenthe, Overijssel, Gelderland, Utrecht, North Brabant and Limburg).

TFA was found in 89% of groundwater categorised as 'vulnerable', 41% of groundwater categorised as 'moderately vulnerable', and 15% of groundwater categorised as 'not vulnerable', respectively. The analysis of a subset of the data, corresponding to measurements provided by Vitens (LOQ = 0.1 µg/L), indicated that the percentage of water younger than 25 or 50 years are good predictors of the concentration of TFA in groundwater ( $r = 0.77$ , outliers excluded). Elevated levels of TFA in groundwater were typically associated with surface water influence, either through active infiltration or riverbank filtration. However, in some cases, high TFA levels could not be explained and further investigation is required. The analysis also showed that concentrations > 0.1 µg/L are expected in groundwater containing a percentage of water younger than 25 years equal or greater than 30%. In contrast, TFA was never found above the LOQ (0.1 µg/L) in groundwater older than 50 years (i.e., containing 0% water younger than 50 years). However, with a more sensitive method, it is likely that trace levels of TFA may also be found in water between 50 and 100 years old because TFA precursors (i.e., CFCs) were introduced in the late 1920s.

In Friesland, higher levels of TFA were measured on the Wadden islands compared to sites from the mainland, suggesting that proximity to the sea may be a factor causing higher contamination. This is potentially due to the deposition of sea-spray aerosols and seems to suggest that its contribution may potentially be greater than that of broader atmospheric deposition (which includes precipitations and dry deposition), however, differences in soil properties between the islands and main land areas where samples were taken should also be evaluated.

TFA was always below the indicative drinking water guideline value ( $i\text{-GLV}_{\text{DW}}$ ) of 2,200 ng/L provided by the RIVM, and contributed to a maximum of 2.3 ng/L of PFOA equivalents (PEQ). Based on median values, TFA contributions were 0.3, < 0.2 and < 0.2 ng PEQ/L for 'vulnerable', 'moderately vulnerable' and 'not vulnerable' groundwaters, respectively.

The ultrashort-chain PFAS investigated, other than TFA, included carboxylic acids (PFPrA (C3), TFPA (C3)), sulfonic acids (TFMS (C1), PFETs (C2), PFPrS (C3)), and one sulfonamide (FETSA (C2)). Results indicated that TFPA, PFETs, PFPrS and FETSA occurred at concentrations < LOQ, irrespective of the vulnerability of the groundwater. TFMS was detected in 15 samples at levels < 0.060 µg/L, and PFPrA in 6 samples at levels < 0.025 µg/L, respectively. Both TFMS and PFPrA occurred only in 'vulnerable' and 'moderately vulnerable' groundwaters.

Overall, particularly high levels of TFA in abstracted groundwater were predominantly associated with infiltration of surface water. Local TFA sources may be relevant to explain data variability on the local scale, however, the general trend seems to be consistent with inputs from diffuse sources, such as atmospheric deposition, rather than local sources.

Based on the results of this study we recommend the following:

- investigate the behaviour of PFPrA and TFMS during water treatment processes, as these compounds are expected to behave similarly to TFA;
- evaluate potential toxic effects of PFPrA and TFMS, including the estimation of RPF for mixture toxicity assessment;
- use more sensitive analytical methods to assess TFA concentrations in both groundwater and drinking water, providing a better understanding of the occurrence and fate of TFA;
- raise awareness among water management authorities about the threats TFA and other ultra short PFAS pose to groundwater quality and urge them to design and implement source oriented approaches to minimise PFAS emissions to the environment.

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# Appendix

## I.I TFA concentrations sorted by location, vulnerability and drinking water company

Location	Concentration (µg/L)	SD	n	Vulnerability	Drinking water company
BW1	0.19	na	1	Vulnerable	Brabant Water
BW2	< 0.010	na	1	Moderately vulnerable	Brabant Water
BW3	0.092	na	1	Vulnerable	Brabant Water
BW4	< 0.010	na	1	Not vulnerable	Brabant Water
BW5	< 0.010	na	1	Moderately vulnerable	Brabant Water
BW6	< 0.010	na	1	Moderately vulnerable	Brabant Water
BW7	< 0.010	na	1	Not vulnerable	Brabant Water
BW8	< 0.010	na	1	Moderately vulnerable	Brabant Water
BW9	< 0.010	na	1	Not vulnerable	Brabant Water
BW10	0.036	na	1	Moderately vulnerable	Brabant Water
V1	0.349	0.097	10	Vulnerable	Vitens
V2	0.129	0.037	3	Moderately vulnerable	Vitens
V3	0.115	0.025	8	Vulnerable	Vitens
V4	0.171	0.024	8	Vulnerable	Vitens
V5	0.050	0.059	2	Vulnerable	Vitens
V6	<0.1	0.000	2	Vulnerable	Vitens
V7	0.191	0.068	7	Vulnerable	Vitens
V8	<0.1	na	1	Moderately vulnerable	Vitens
V9	0.258	0.086	3	Vulnerable	Vitens
V10	0.056	na	1	Not vulnerable	Vitens
V11	0.429	0.169	10	Vulnerable	Vitens
V12	0.000	na	1	Moderately vulnerable	Vitens
V13	0.084	0.024	3	Vulnerable	Vitens
V14	< 0.1	na	3	Not vulnerable	Vitens
V15	0.623	0.073	6	Vulnerable	Vitens
V16	0.227	0.026	4	Vulnerable	Vitens
V17	0.036	0.051	2	Vulnerable	Vitens
V18	0.345	0.084	10	Vulnerable	Vitens
V19	0.167	0.029	8	Vulnerable	Vitens
V20	1.168	0.597	57	Vulnerable	Vitens
V21	0.237	0.060	4	Vulnerable	Vitens
V22	0.227	0.081	4	Vulnerable	Vitens
V23	0.020	0.041	4	Vulnerable	Vitens
V24	0.371	0.154	17	Vulnerable	Vitens
V25	0.173	0.027	4	Vulnerable	Vitens
V26	0.010	0.024	6	Vulnerable	Vitens
V27	0.037	0.043	4	Vulnerable	Vitens

V28	0.193	0.049	4	Vulnerable	Vitens
V29	0.065	0.058	3	Vulnerable	Vitens
V30	0.492	0.112	16	Vulnerable	Vitens
V31	0.283	0.066	6	Vulnerable	Vitens
V32	0.097	0.078	6	Vulnerable	Vitens
V33	0.288	0.068	9	Vulnerable	Vitens
V34	0.092	na	1	Vulnerable	Vitens
V35	0.329	0.101	5	Vulnerable	Vitens
V36	0.144	0.066	8	Vulnerable	Vitens
V37	0.091	0.060	3	Vulnerable	Vitens
V38	0.068	0.025	2	Vulnerable	Vitens
V39	0.118	0.023	7	Vulnerable	Vitens
V40	0.131	0.056	3	Moderately vulnerable	Vitens
V41	<0.1	na	1	Moderately vulnerable	Vitens
V42	<0.1	na	1	Moderately vulnerable	Vitens
V43	0.324	0.033	5	Vulnerable	Vitens
V44	0.000	0.000	2	Vulnerable	Vitens
V45	0.182	0.042	8	Vulnerable	Vitens
V46	0.212	0.057	4	Vulnerable	Vitens
V47	<0.1	0.000	2	Not vulnerable	Vitens
V48	0.168	0.077	7	Vulnerable	Vitens
V49	0.224	0.088	8	Vulnerable	Vitens
V50	0.876	0.345	16	Vulnerable	Vitens
V51	<0.1	na	1	Vulnerable	Vitens
V52	<0.1	na	1	Moderately vulnerable	Vitens
V53	<0.1	na	1	Vulnerable	Vitens
V54	0.263	0.151	8	Vulnerable	Vitens
V55	<0.1	na	1	Moderately vulnerable	Vitens
V56	0.104	0.025	2	Vulnerable	Vitens
V57	0.092	0.028	3	Vulnerable	Vitens
V58	0.235	0.190	4	Vulnerable	Vitens
V59	0.080	0.064	4	Vulnerable	Vitens
V60	0.066	0.061	10	Moderately vulnerable	Vitens
V61	<0.1	0.000	3	Vulnerable	Vitens
V62	0.078	na	1	Vulnerable	Vitens
V63	<0.1	na	1	Vulnerable	Vitens
V64	<0.1	na	1	Moderately vulnerable	Vitens
V65	<0.1	na	1	Not vulnerable	Vitens
V66	0.188	0.147	12	Vulnerable	Vitens
V67	1.004	0.303	37	Vulnerable	Vitens
V68	<0.1	na	1	Moderately vulnerable	Vitens
V69	0.220	0.040	4	Vulnerable	Vitens
V70	0.232	0.043	3	Vulnerable	Vitens
V71	0.298	0.056	15	Vulnerable	Vitens

V72	0.077	0.005	2	Vulnerable	Vitens
V73	<0.1	0.000	2	Vulnerable	Vitens
V74	0.122	0.055	3	Vulnerable	Vitens
V75	0.345	0.102	14	Vulnerable	Vitens
V76	0.359	0.218	34	Vulnerable	Vitens
V77	0.081	0.016	4	Vulnerable	Vitens
V78	<0.1	na	1	Not vulnerable	Vitens
V79	<0.1	na	1	Not vulnerable	Vitens
V80	0.741	0.099	6	Vulnerable	Vitens
WBG1	0.240	na	1	Vulnerable	WBG
WBG2	0.044	na	1	Vulnerable	WBG
WBG3	< 0.010	na	1	Vulnerable	WBG
WBG4	< 0.010	na	1	Not vulnerable	WBG
WBG5	0.011	na	1	Not vulnerable	WBG
WBG6	< 0.010	na	1	Not vulnerable	WBG
WBG7	0.045	na	1	Vulnerable	WBG
WBG8	0.056	na	1	Vulnerable	WBG
WBG9	0.130	na	1	Vulnerable	WBG
WBG10	0.010	na	1	Vulnerable	WBG
WMD1	0.091	na	1	Vulnerable	WMD
WMD2	< 0.010	na	1	Not vulnerable	WMD
WMD3	0.021	na	1	Moderately vulnerable	WMD
WMD4	< 0.010	na	1	Not vulnerable	WMD
WMD5	< 0.010	na	1	Not vulnerable	WMD
WMD6	0.017	na	1	Not vulnerable	WMD
WMD7	< 0.010	na	1	Not vulnerable	WMD
WMD8	0.038	na	1	Moderately vulnerable	WMD
WMD9	0.061	na	1	Moderately vulnerable	WMD
WML1	< 0.010	na	1	Not vulnerable	WML
WML2	< 0.010	na	1	Not vulnerable	WML
WML3	< 0.010	na	1	Not vulnerable	WML
WML4	0.620	na	1	Vulnerable	WML
WML5	0.086	na	1	Moderately vulnerable	WML
WML6	< 0.010	na	1	Moderately vulnerable	WML
WML7	0.05	na	1	Moderately vulnerable	WML

SD = standard deviation.

n = number of observations.

na = not available.

**I.II Percentage of water younger than a specific age in Vitens' abstraction points**

Location	0.16	0.33	0.66	1	2.5	5	10	25	50	100	250	500	1,000	2,500	5,000	100,000
V1	0%	0%	0%	0%	0%	0%	3%	62%	79%	92%	99%	100%	100%	100%	100%	100%
V2	0%	0%	0%	0%	0%	0%	0%	5%	25%	49%	100%	100%	100%	100%	100%	100%
V3	1%	2%	2%	3%	11%	35%	45%	52%	60%	76%	94%	99%	100%	100%	100%	100%
V4	0%	0%	0%	0%	2%	5%	10%	23%	41%	71%	94%	99%	100%	100%	100%	100%
V5	0%	0%	0%	0%	0%	1%	3%	8%	17%	34%	57%	79%	95%	100%	100%	100%
V6	0%	0%	0%	0%	0%	0%	1%	10%	29%	56%	100%	100%	100%	100%	100%	100%
V7	0%	0%	0%	0%	0%	0%	9%	23%	29%	62%	80%	93%	95%	99%	100%	100%
V8	1%	1%	1%	1%	1%	1%	1%	3%	12%	28%	55%	79%	91%	100%	100%	100%
V9								75%		100%						
V10	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	3%	11%	73%	86%	100%
V11	0%	0%	0%	0%	0%	3%	25%	54%	92%	99%	100%	100%	100%	100%	100%	100%
V12	0%	0%	0%	0%	0%	0%	0%	2%	37%	63%	78%	91%	96%	100%	100%	100%
V13	0%	0%	0%	0%	0%	0%	1%	14%	49%	66%	89%	99%	100%	100%	100%	100%
V14	0%	0%	0%	0%	0%	0%	0%	0%	1%	2%	2%	3%	32%	84%	95%	100%
V15	0%	0%	0%	0%	0%	8%	20%	33%	45%	89%	100%	100%	100%	100%	100%	100%
V16	0%	0%	0%	0%	0%	8%	13%	24%	41%	73%	100%	100%	100%	100%	100%	100%
V17	0%	0%	0%	0%	0%	0%	5%	12%	23%	64%	100%	100%	100%	100%	100%	100%
V18	0%	0%	0%	0%	4%	6%	20%	53%	71%	82%	91%	93%	95%	98%	100%	100%
V19	0%	0%	0%	0%	0%	3%	8%	21%	39%	60%	95%	100%	100%	100%	100%	100%
V20	0%	0%	0%	1%	4%	12%	29%	54%	70%	79%	93%	98%	99%	100%	100%	100%
V21	0%	3%	10%	16%	36%	40%	42%	44%	49%	73%	86%	98%	100%	100%	100%	100%
V22	0%	0%	0%	0%	0%	0%	2%	5%	17%	29%	44%	58%	79%	94%	100%	100%
V23	0%	0%	0%	0%	0%	0%	2%	18%	33%	45%	62%	92%	97%	99%	99%	100%
V24	0%	0%	0%	0%	3%	7%	20%	54%	75%	89%	96%	100%	100%	100%	100%	100%
V25	0%	0%	0%	0%	0%	0%	0%	25%	52%	75%	92%	99%	100%	100%	100%	100%
V26	0%	0%	0%	0%	0%	0%	2%	30%	59%	80%	92%	97%	99%	100%	100%	100%
V27	0%	0%	0%	0%	2%	3%	6%	16%	27%	66%	99%	100%	100%	100%	100%	100%
V28	0%	0%	0%	0%	0%	0%	9%	27%	56%	65%	97%	100%	100%	100%	100%	100%
V29	0%	0%	0%	0%	0%	1%	4%	21%	52%	74%	91%	98%	100%	100%	100%	100%
V31	0%	0%	0%	0%	0%	3%	16%	49%	63%	74%	92%	97%	98%	100%	100%	100%
V32	0%	0%	0%	0%	0%	0%	2%	7%	16%	29%	54%	76%	95%	100%	100%	100%
V33	0%	0%	0%	0%	0%	1%	8%	49%	73%	85%	95%	99%	100%	100%	100%	100%
V34								55%		100%						
V35	0%	0%	0%	0%	1%	5%	23%	54%	71%	83%	96%	100%	100%	100%	100%	100%
V37	0%	0%	0%	0%	1%	5%	7%	17%	32%	47%	75%	87%	96%	100%	100%	100%
V39	0%	0%	0%	0%	0%	1%	3%	20%	47%	56%	90%	100%	100%	100%	100%	100%
V40	0%	0%	0%	0%	0%	0%	0%	0%	32%	61%	98%	100%	100%	100%	100%	100%
V41	0%	0%	0%	0%	0%	0%	0%	0%	2%	24%	63%	91%	99%	100%	100%	100%
V42	0%	0%	0%	0%	0%	0%	0%	1%	3%	8%	25%	45%	66%	83%	94%	100%
V43	0%	2%	5%	9%	16%	22%	35%	57%	67%	79%	91%	98%	100%	100%	100%	100%
V44	0%	0%	0%	0%	7%	11%	16%	23%	28%	38%	87%	100%	100%	100%	100%	100%
V45	0%	0%	0%	0%	2%	7%	19%	49%	76%	88%	95%	99%	100%	100%	100%	100%
V46	0%	0%	0%	0%	0%	2%	8%	10%	17%	33%	92%	98%	98%	100%	100%	100%

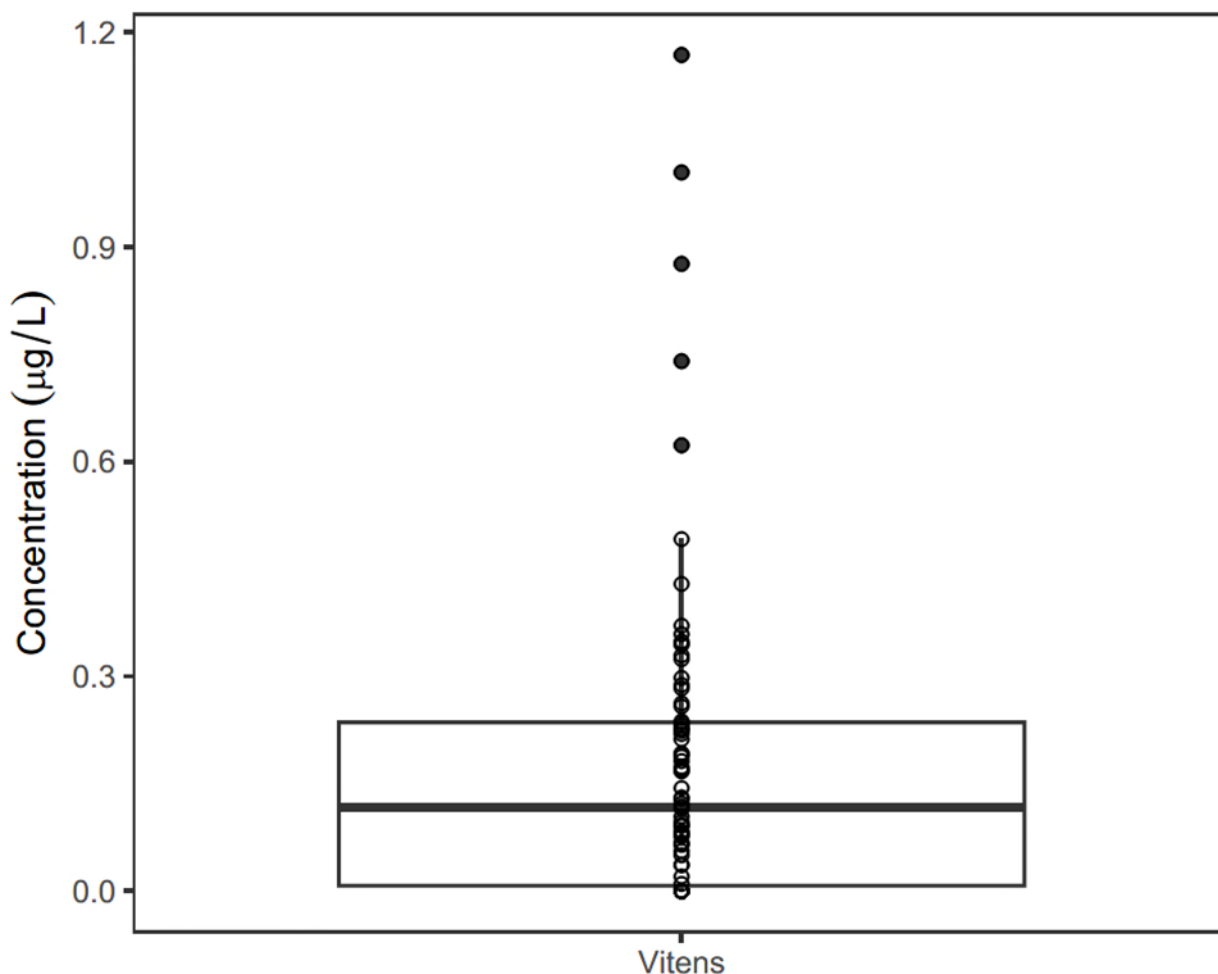
V47	0%	0%	0%	0%	0%	0%	0%	0%	0%	2%	47%	71%	87%	94%	99%	100%
V48	0%	0%	0%	0%	0%	2%	6%	33%	66%	84%	96%	99%	100%	100%	100%	100%
V51	0%	0%	0%	0%	0%	0%	1%	15%	34%	59%	82%	86%	91%	98%	100%	100%
V50	0%	0%	0%	3%	4%	4%	4%	36%	91%	100%	100%	100%	100%	100%	100%	100%
V52	0%	0%	0%	0%	0%	0%	0%	0%	0%	7%	95%	100%	100%	100%	100%	100%
V53	0%	0%	0%	0%	0%	1%	4%	12%	24%	78%	99%	100%	100%	100%	100%	100%
V54	2%	3%	5%	8%	16%	18%	19%	27%	41%	60%	99%	100%	100%	100%	100%	100%
V55								2%		47%						
V56	0%	0%	0%	0%	0%	0%	0%	5%	33%	77%	94%	99%	100%	100%	100%	100%
V57	1%	2%	3%	7%	10%	14%	18%	33%	54%	74%	96%	100%	100%	100%	100%	100%
V60	0%	0%	0%	0%	0%	0%	1%	3%	12%	44%	94%	98%	100%	100%	100%	100%
V61	0%	0%	1%	2%	4%	6%	11%	17%	23%	30%	51%	64%	79%	89%	92%	100%
V62																
V63	0%	0%	0%	0%	0%	1%	5%	18%	31%	71%	88%	95%	99%	100%	100%	100%
V65	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	13%	97%	99%	100%
V67	0%	0%	2%	6%	22%	36%	51%	78%	89%	95%	96%	96%	96%	99%	100%	100%
V68	0%	0%	0%	0%	0%	0%	0%	0%	0%	20%	38%	49%	89%	100%	100%	100%
V69	0%	0%	0%	0%	0%	2%	7%	28%	56%	89%	95%	99%	100%	100%	100%	100%
V70								50%		80%						
V71	0%	0%	0%	0%	2%	6%	14%	34%	51%	63%	79%	89%	97%	100%	100%	100%
V74	0%	0%	0%	0%	2%	4%	6%	15%	48%	85%	98%	100%	100%	100%	100%	100%
V75	0%	0%	0%	0%	0%	3%	14%	60%	80%	91%	97%	99%	100%	100%	100%	100%
V76	0%	0%	0%	0%	1%	6%	12%	43%	64%	74%	86%	93%	97%	99%	100%	100%
V77	0%	0%	0%	0%	0%	0%	4%	17%	34%	56%	99%	100%	100%	100%	100%	100%
V78								0%		3%						
V79	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	2%	15%	58%	87%	100%
V80	0%	0%	0%	0%	0%	0%	5%	20%	38%	53%	66%	69%	69%	89%	96%	100%

**I.III Pearson’s correlation coefficients of linear regressions between the percentage of water of a specific age in abstracted groundwater and TFA concentrations.**

Age	Correlation Coefficient	Correlation Coefficient witout outliers
0.16	-0.043119016	0.028644032
0.33	0.010019708	0.165062645
0.66	0.09707057	0.188674586
1	0.218218512	0.186909463
2.5	0.288313157	0.215395479
5	0.385032991	0.291016009
10	0.553759499	0.570945259
25	0.624056871	0.778482914
50	0.640713799	0.772339547
100	0.509963357	0.62920901
250	0.312150336	0.428375458
500	0.239498287	0.365201163
1,000	0.175223918	0.312005337
2,500	0.137000011	0.262820805
5,000	0.150360659	0.277481439
100,000	na	na

na = not available (because SD = 0).

**I.IV TFA concentrations measured in raw water from Vitens' abstraction points.**



Data points indicate individual measurements. The central rectangular part of the plot represents the interquartile range (IQR). This is the range between the first quartile (Q1) and the third quartile (Q3), corresponding to the 25th and 75th percentiles of the data, respectively. The line inside the box represents the median. Whiskers extend to the minimum and maximum values within 1.5 times the IQR, beyond which data are considered outliers. The number of observations for each type of groundwater is shown in Table 3. Values < LOQ are set to zero.

**I.V Relationships between the percentage of groundwater of a certain age (from 2.5 to 500 years old) and TFA concentrations (excluding outliers).**

