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## Forever legacies? Profiling historical PFAS contamination and current influence on groundwater used for drinking water

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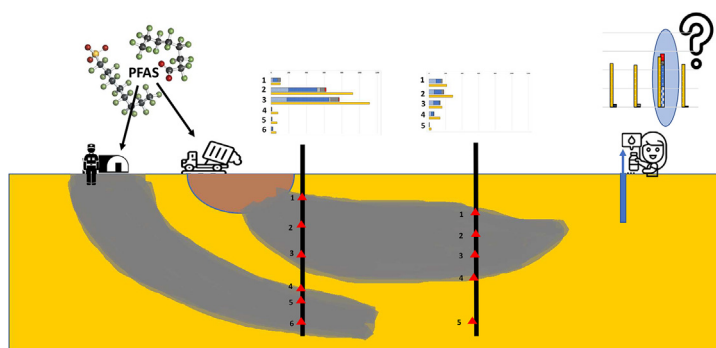
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### HIGHLIGHTS

- Historical PFAS contamination was followed in a drinking water aquifer.
- In a decade time PFAS migrated by increase with depth and distance.
- PFAS profile and isomer pattern were used as source indicators.
- Landfill and military camp were confirmed as contamination sources for groundwater.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A wide range of PFAS residues were studied in an aquifer used for drinking water production which was affected by historical PFAS contamination from a landfill and military camp. Samples were taken at three monitoring and four pumping wells at different depths ranging from 33 to 147 m below the land surface and analysed for a series of 53 PFAS (C2-C14) and PFAS precursors (C4-C24). A comparison of results to earlier research from 2013, with a more limited range of PFAS, showed decreasing concentrations and migration of PFAS with increasing depth and distance from the contamination source.

The PFAS profile and branched/linear isomer ratio are used as source characterization tools. The landfill was confirmed to contaminate the groundwater in both monitoring wells, while the military camp was indicated as a probable source for PFAS observed in the deep sampling points of one of the monitoring wells. Pumping wells used to produce drinking water are not yet affected by these two PFAS sources. In one of the four sampled pumping wells, a different PFAS profile and isomer pattern was observed, which indicated a different but yet unknown source.

This work shows the necessity of implementing regular screening to identify potential (historical) PFAS sources to be able to prevent future contaminant migration nearby and towards drinking water abstraction wells.

### 1. Introduction

Groundwater represents 30 % of the world's freshwater volume and represents a third of human freshwater consumption, while in some parts of the globe, it is the only source of drinking water (Bierkens and Wada,

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2019). Groundwater typically has a more stable composition and lower microbial and chemical contamination as compared to surface water. Therefore, in comparison to surface water sources, groundwater often requires limited treatment to be suitable for human consumption, depending on factors such as anthropogenic pressures and hydrology (Jurado et al., 2022). However, groundwater can also be contaminated via municipal, commercial, industrial, and agricultural activities (Kiefer et al., 2021). Some chemical and microbiological contaminants can be removed as groundwater infiltrates through soils (Narain-Ford et al., 2022). After contamination, remediation by natural processes such as biodegradation, and chemical reactions (redox, hydrolysis) can take decades or even longer (Albergamo et al., 2019). Active remediation of contaminated groundwater is expensive, and mostly applied only at hotspots of chemical contamination (Bolan et al., 2021).

Groundwater contamination is a major concern, particularly with persistent and mobile chemicals (Pitt et al., 1999). One such group is per- and poly-fluoroalkyl substances (PFAS), which are a diverse group of persistent and mobile chemicals with a wide range of applications, including paper coatings, food packaging, textiles, industrial surfactants, insecticides, and aqueous film-forming foams (AFFF) (Buck et al., 2011; Glüge et al., 2020). They have been widely detected in various environmental matrices (Baabish et al., 2019; Cousins et al., 2022; Fiedler et al., 2022b; Fiedler et al., 2022a; Fiedler and Sadia, 2021; Kaiser et al., 2021; Lauria et al., 2022). Still relatively limited information is available about their toxicity, and (proposed) environmental and human health thresholds are highly variable (US EPA, 2022; WHO, 2022). However, there is an increasing concern about potential adverse human health effects (Panieri et al., 2022).

PFAS have been manufactured for over 70 years, mainly via electrochemical fluorination or telomerization reactions. The telomerization process produces substances consisting of only linear alkyl chains, whereas electrochemical fluorination (ECF) produces a mixture of branched and linear isomers (Buck et al., 2011). The physical-chemical properties of linear and branched isomers differ slightly which leads to differences in sorption behavior, and subsequently their relative distribution and fate in environmental compartments (Sadia et al., 2023; Schulz et al., 2020). The linear and branched isomer profile has been implemented as a source-tracking tool to distinguish contamination sources in the environment (Benskin et al., 2010). Since about 2000, the compositions of different commercial PFAS mixtures have changed due to innovations in the production processes, as well as regulations and restrictions on their production and use. Consequently, the profiles of emitted PFAS in the environment have shifted for example resulting in an increased contribution of shorter-chain PFAS (Cookson and Detwiler, 2022).

The fate of PFAS in groundwater and surface water is strongly affected by the carbon chain length (short-chain <C6, and long-chain  $\geq$  C6) and functional group (carboxylates  $\text{COO}^-$ , and sulfonates  $\text{SO}_3^-$ ). The anionic group in perfluoroalkyl carboxylic acid (PFCA) and perfluoroalkyl sulfonic acid (PFSA) renders PFAS water-soluble, whereas sorption to soil and sediment is generally determined by the chain length and branching. The short-chain PFAS are more frequently detected in groundwater as compared to the long-chain PFAS (Joerss et al., 2022; Sadia et al., 2023). Despite several studies on the presence of PFAS in the environment, information on PFAS such as hexafluoropropylene oxide-dimer acid (HFPO-DA) and chlorinated polyfluoroalkyl ether sulfonic acid (PFESA) in groundwater is still relatively scarce (Xu et al., 2021).

Drinking water can be a significant source of PFAS exposure, especially when drinking water sources are impacted by PFAS contamination such as industrial discharges from fluorochemical production, firefighting training locations, landfills, or municipal wastewater treatment plant effluents (Domingo and Nadal, 2019). It is essential to know the origin of the contamination observed in (sources of) drinking water, to be able to protect sources for drinking water being either groundwater or surface water. Industrial and municipal wastewaters are considered as main sources of PFAS contamination of surface water (Bach et al., 2017). Atmospheric deposition is relevant for both surface water and groundwater (Schroeder et al., 2021). In addition, groundwater may face PFAS contamination

from landfills (Hepburn et al., 2019), firefighting training activities (Hatton et al., 2018), surface runoff (Murakami et al., 2009), surface water infiltration, and other activities where PFAS containing products are applied and emitted.

A better understanding of the sources and behavior of different PFAS in contaminated areas can help to protect groundwater. Fate and transport of PFAS in aquifers have been investigated e.g. (Sharifan et al., 2021; Söregård et al., 2022), however knowledge gaps remain. For example regarding PFAS concentrations and composition in surface, vadose, and saturated zones (Rovero et al., 2021), transformation and precursor biodegradation (Harding-Marjanovic et al., 2015), partitioning behavior such as the partitioning to air in the vadose zone, sorption to soil constituents (Sharifan et al., 2021), and the role of hydrology and geochemistry with regards to infiltration, flow direction and the impact of different redox conditions (Weber et al., 2017).

In 2013, PFAS contamination in a Dutch drinking water abstraction area was studied, where a landfill and military camp were identified as sources of PFAS contamination in groundwater (Eschauzier et al., 2013). In this study at the time 16 PFAS (C4-C12 PFCA, C4-C10 PFSA, and FOSA) were investigated, of which seven were encountered above the limit of detection at the time (0.02–0.45 ng/L). An elevated level of PFAS was observed in the shallow groundwater below and near the landfill, and a lower concentration was observed in deeper groundwater and further downstream from the landfill. A breakthrough of the landfill-contaminated water in the water abstraction area for the production of drinking water was subsequently predicted by 2026 (Eschauzier et al., 2013; Vergouwen et al., 2015).

One decade later, we aim to profile the current situation of this historical PFAS contamination in this same groundwater abstraction area for drinking water. Improved analytical methods currently allow to study a wider range of PFAS and precursors at lower concentrations, including ultrashort-chain PFAS (C2-C3), a variety of precursors (C4-C24), various short to long-chain (C4-C14) PFCA and PFSA and branched isomers of 8 different PFAS. We studied the PFAS composition at different depths at different locations nearby the abstraction area. This analysis and comparison with earlier data can improve predictions of how historical contamination will impact (abstracted) groundwater in future.

## 2. Material and methods

### 2.1. Standard and chemicals

Native and isotopic mass labeled standards were purchased from Wellington Laboratories (Guelph, Canada), except *n*-deuteriomethylperfluoro-1-*n*-octanesulfonamidoacetic acid- $d_3$  (N-MeFOSAA- $d_3$ , >99 %) and *n*-ethylperfluoro-1-*n*-octanesulfonamidoacetic acid- $d_5$  (N-EtFOSAA- $d_5$ , >99 %) that were purchased from Chiron (Trondheim, Norway), trifluoroacetic acid (TFA, >99 %) and perfluoropropanoic acid (PFPrA, >97 %) that were purchased from Sigma-Aldrich (Darmstadt, Germany), perfluoroethane sulfonic acid (PFETs, > 98 %) that was purchased from Kanto Chemical (Japan), and *n*-methylperfluorobutanesulfonamide (MeFBSA, >97 %) that was purchased from Apollo Scientific (Manchester, United Kingdom). Further details are provided in Table S1. Milli-Q water was used throughout the experiments. LC-MS grade methanol and acetonitrile were acquired from Biosolve Chimie (Dieuze, France). Ammonium acetate ( $\geq$ 99 %) and glacial acetic acid ( $\geq$ 99 %) were purchased from Sigma-Aldrich, ammonia solution (25 %, analytical reagent grade) was acquired from Fisher Scientific (Massachusetts, United States).

### 2.2. Study area

The study area is located in the central part of The Netherlands, on the edges of the Utrechtse Heuvelrug in a wooded and partly urban area (Fig. 1). The abstraction area for drinking water supply was constructed in the years 1881 to 1883, and covers 25 pumping wells from which water is regularly extracted. Different wells are used for extraction at

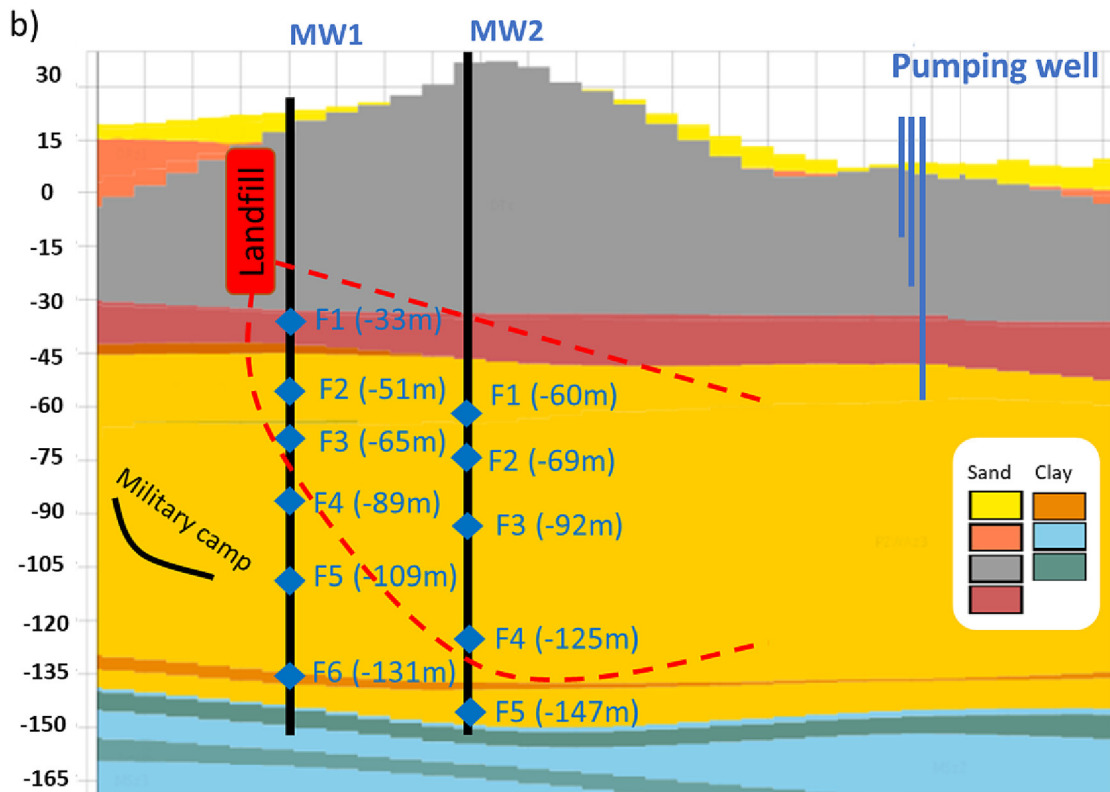
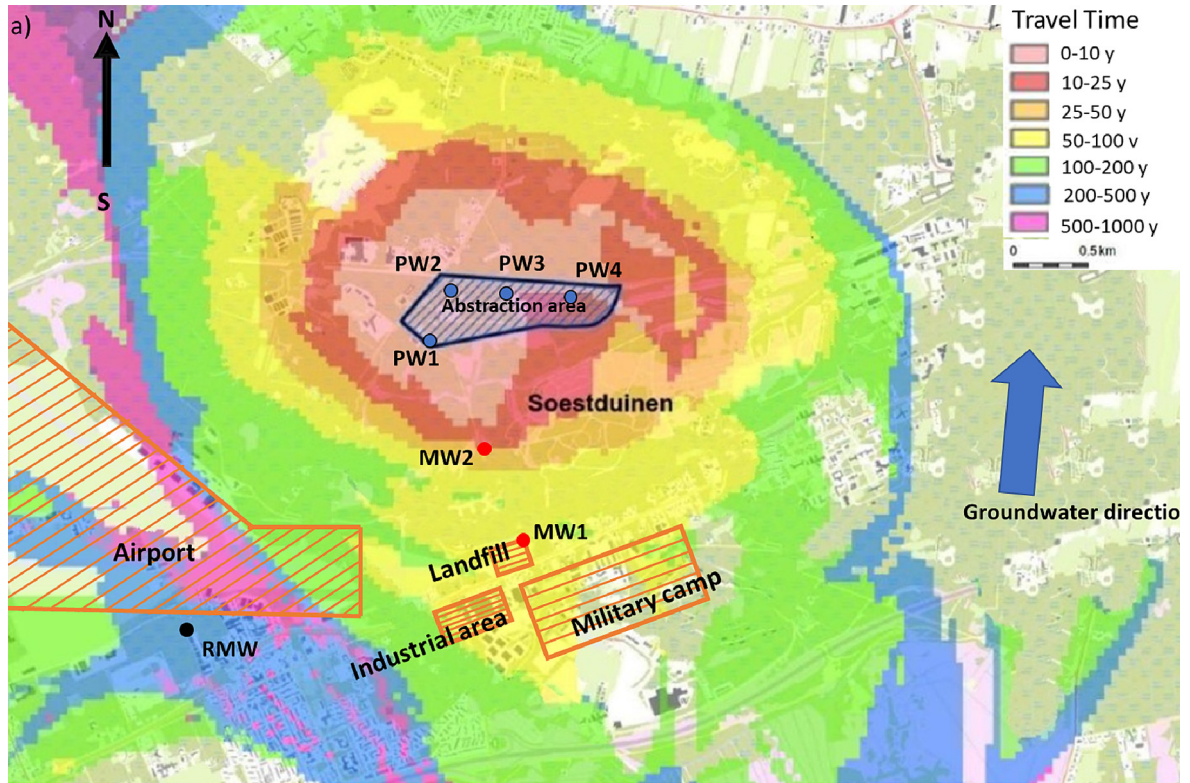


Fig. 1. Overview of the studied area, a) Travel time in years of the groundwater in the studied area towards drinking water abstraction area defining the potential contamination sources and the sampling location for the monitoring wells (MW), reference monitoring well (RMW), and pumping wells (PW) as a red, black, and blue colored circle, respectively, source: (HYDROMEDAH model calculations, adopted from Engel et al. (2021); b) Geohydrological profile for the studied area with the sampling location of the monitoring well at different depths below land surface, with the earlier defined contamination plume from landfill and military camp. The different colors of sand and clay represent their distinct origins. Source: (TNO, Geological Survey of the Netherlands, 2017, adopted from Engel et al. (2021)).

different times, resulting in a variable source water quality. The geohydrological profile of the study area (Fig. 1b) shows a vulnerable phreatic aquifer consisting of soil with medium-coarse sand, interspersed with clay, silt, and loam layers. The maximum thickness of the clay and silt layers is two meters (Sjerp et al., 2013). The groundwater level varies between 0.5 and 1.0 m below surface.

The land-use in the area is a forest, a former landfill which was used in the years 1972–1995, a former military airport which was in service from 1913 to 2009, a military camp, and a small active commercial and industrial area situated south of the landfill (Fig. 1). It was not possible to characterize the PFAS composition at the source by sampling directly below the landfill or military camp due to the absence of a leachate collection system and no permission, respectively. Hydrological details of the study site are described in detail elsewhere (Engel et al., 2021; Eschauzier et al., 2013). Road runoff might be an additional diffuse source as a result of wide use of PFAS. Sewage water from a small village (north of the abstraction area, < 1 km) was collected in cesspits until 1987, from which leaching was possible. All houses and enterprises were connected to the sewage network and sewage treatment plant since 1987. Groundwater for drinking water production is abstracted in the abstraction area from a depth of 7 to 57 m and subsequently treated by intensive aeration. The groundwater flow is dominated by pumping activities (9 Mm<sup>3</sup> abstraction per year) and the natural groundwater recharge has been altered due to urbanization and forest management. The spatial distribution of residence times for the groundwater abstraction wells is shown in Fig. 1a. The hydrological traveling time of the landfill and military camp to the abstraction area is estimated 50–100 years while it is 100–200 years for the military airport (Engel et al., 2021).

### 2.3. Sample collection

HDPE sampling bottles (2 L) were pre-cleaned with water and methanol in the laboratory of the University of Amsterdam (UvA). Water samples were collected by the drinking water company Vitens on the same day in October 2021. After sampling, the bottles were shipped to the UvA laboratory and stored at 4 °C within 8 h, and analysed within 2 weeks. In total two monitoring wells were sampled, MW1 (closest to the landfill) was sampled at six different depths between 33 and 131 m below land surface and MW2 (second close to the landfill) was sampled at five different depths between 66 and 147 m below land surface (Fig. 1). One monitoring well that is not influenced by the known PFAS sources served as a reference monitoring well (RMW) and was sampled at two different depths 59 and 101 m below land surface. Four pumping wells, of which PW1 was closest to the two PFAS sources, and PW2, PW3, and PW4 were located further away, were sampled from pumping water extracted at a depth of 7 to 57 m below land surface. Finally, two samples were taken from the mixed raw water (from all pumping wells) that is used to produce drinking water (RW1 and RW2), and one sample was taken from the produced drinking water (DW). All samples were taken as grab samples. Table S3 and Fig. 1 present the sampling location and detailed information about the exact depths and interval depth of the samples in the monitoring, pumping and reference wells.

### 2.4. Sample extraction and quantification

All samples were extracted in duplicate using solid phase extraction (SPE). Extraction and quantification procedures were reported in detail elsewhere (Sadia et al., 2023). Briefly, the samples were sonicated for 10 min in their original HDPE bottle, then 500 mL was weighed into new and pre-cleaned HDPE containers. Mass-labeled extraction standards (10 µL; 0.1–0.2 ng/µL) were added and pH was adjusted to 4 using acetic acid. The samples were loaded on preconditioned weak anion exchange Waters Oasis® WAX-SPE cartridges (3 mL, 60 mg, 30 µm; Waters Corporation Milford, USA). The cartridges were preconditioned by subsequently 3 mL of 0.1 % ammonium hydroxide in methanol, 3 mL of methanol, and finally 3 mL of Milli-Q water. After loading the sample, the cartridges

were washed with 3 mL ammonium acetate buffer solution with a pH 4, then dried for 20 min under vacuum. Elution was performed with 3 mL 0.1 % ammonium hydroxide in methanol. The extracts were evaporated under nitrogen to 65 µL, then 175 µL 0.05 % acetic acid in water, and a mass-labeled injection standard solution (10 µL; 0.1 ng/µL) were added. The 250 µL extract was vortex-mixed, centrifuged (5 min at 4000 rpm), and then transferred to LC vial for further chemical analysis.

Quantification was performed with a Nexera UHPLC system (Shimadzu, Kyoto, Japan) coupled to a Bruker Maxis 4 G high-resolution q-TOF-HRMS, equipped with an Ion Booster Electro Spray Ionization (IB-ESI) source. Aliquots of 5 µL were injected into an Acquity UPLC CSH C18 column (130 Å, 2.1 × 150 mm, 1.7 µm). The mobile phase consisted of 0.05 % acetic acid in water (A) and 0.05 % acetic acid in acetonitrile (B). Details of mobile phase gradient and instrument parameters are described elsewhere (Sadia et al., 2023). Internal mass calibration for each analysis by infusing a 2 mM sodium acetate solution in water:methanol mixture (1:1, v:v), with a loop injection of 40 µL at the beginning of the analysis (0.1–0.5 min) was performed. For the analyte HPFO-DA (known as Gen-X) the HPLC system (Shimadzu, Kyoto, Japan) was connected to a tandem mass spectrometer (4000 QTrap, Applied Biosystems, Toronto, Canada) operating in the negative ionization mode with scheduled MRM was used.

The identification of the 57 targeted PFAS (Table S1; 4 ultrashort chain PFAS, 14 PFCA, 10 PFSA, and 29 precursors) was performed using the accurate mass, retention time, and fragment ions (Sadia et al., 2023). Quantification of the targeted analytes was based on a 10 point calibration curve consisting of a series of concentrations ranging from 50 pg/mL to 6000 pg/mL (R > 0.99). The branched isomers for PFOS, PFHxS, EtFOSAA, and MeFOSAA were quantified using the branched isomer standard, while PFOA, PFHpA, PFHpS and PFNA were semi-quantified using their linear counterparts. No branched isomers were detected for other PFAS.

For each batch of samples, two procedural blanks (Milli-Q water) and one quality control (Milli-Q water spiked with native standards) were extracted simultaneously and analysed to assess background contamination, and investigate any systematic errors. Internal validation of the analytical method showed a <20 % relative standard deviation of the analysis results of the quality control sample. Methanol injections were carried out before and after the standard injection to assess any carryover or contamination in the LC system. The calculation of the limit of quantification and recoveries are reported in Table S1, Table S2, and described in detail together with the method validation elsewhere (Sadia et al., 2023). Blank concentrations were typically below limit of quantification except for TFA (6 ng/L), PFPrA (0.46 ng/L), and PFBA (0.14 ng/L) and were not subtracted from the samples.

It was not possible to conduct statistical analysis of either the full profiles or individual PFAS since the sampling was not repeated over time with only one sampling time a decade ago. Therefore, the profiles observed should be considered indicative.

## 3. Results and discussion

### 3.1. Changes in PFAS profile over time

The distribution and concentration levels of PFAS changed over time, as compared to work done in the same aquifer a decade ago (Eschauzier et al., 2013), sampling took place in 2011). PFAS were transported over time with decrease in PFAS concentration near the landfill MW1, and an increase in PFAS concentration farther away from the landfill MW2. At that time (2011), 16 PFAS (Σ16-PFAS; namely: C4-C12 PFCA, C4-C10 PFSA, and FOSA) were investigated, without differentiation between linear and branched isomers.

The highest PFAS concentrations in 2011 were observed at –65 m in MW1 (4400 ng/L) and at –69 m in MW2 (219 ng/L). A decade later these Σ16-PFAS traveled towards MW2 (Fig. 2) and showed a significant decrease in MW1–33 and –65 m, while deeper in MW1 PFAS concentrations did not change, corresponding to the distant contamination sources (military camp). This lowering of concentration of PFAS in the upper

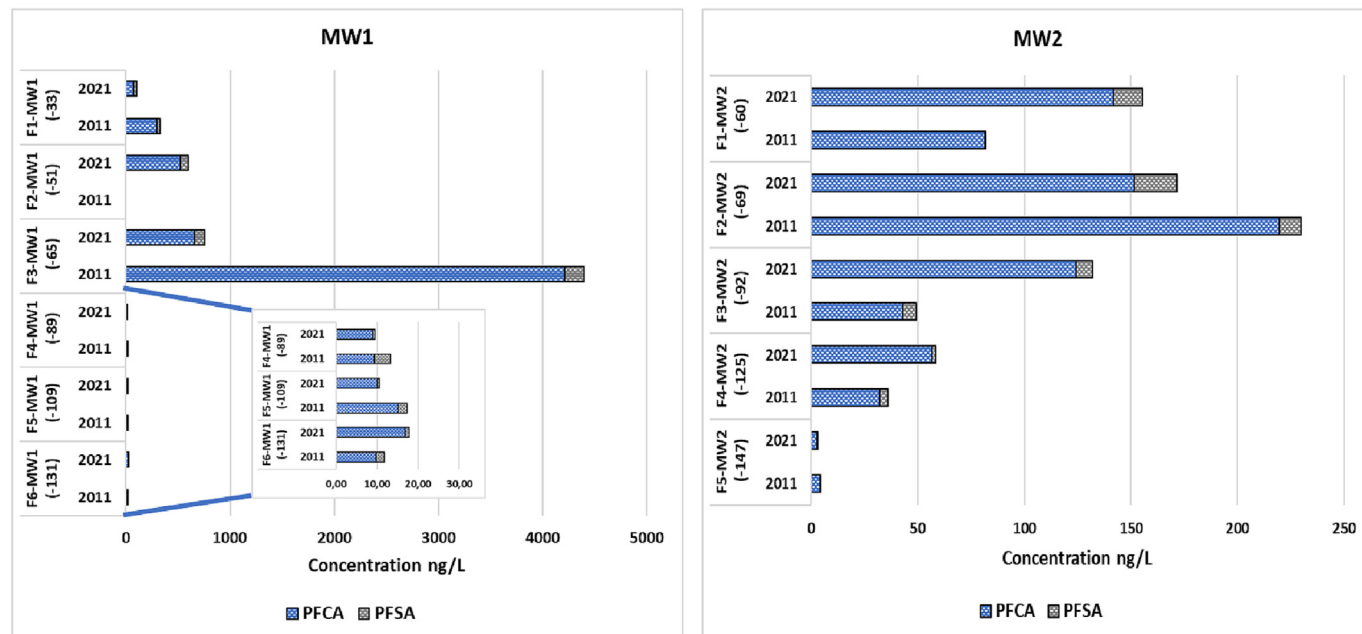


Fig. 2. Concentration (ng/L) of the 16-PFAS (PFCA and PFSA) studied now and a decade ago (Eschauzier et al., 2013) in monitoring well MW1 and MW2 at different depths.

samples of MW1 compared to 2011 could be attributed to migration of the peak and the initiation of measures at the landfill. Specifically, the functioning of the run-off ditch (granulate ditch) and the drainage pipes, which have been in place since 2014, likely contributed to a reduction in the impact of landfill leachate.

For MW2 however, elevated concentrations were observed at  $-60$ ,  $-92$  and  $-125$  m, reflecting the PFAS plume transport. At depth  $-69$  m the concentration decreased, perhaps due to that at 2011 the main PFAS peak was at depth  $-69$  m and over time the plume is being transferred more with depth and towards the abstraction area. Because only 7 PFAS were detected a decade ago, no conclusion regarding the full profiles could be drawn.

### 3.2. Distribution of PFAS in space and depth

The use of an improved analytical method has allowed for the investigation of a higher number of PFAS (57 PFAS), including ultrashort chain PFAS and branched isomers. Out of the 57 investigated PFAS and precursors, 25 PFAS were detected above limits of quantification near the landfill (MW1) at depth of 33–65 m while lower numbers of PFAS were detected in deeper water (at MW2) and at larger distances from the landfill (MW2). Legacy PFSA (PFBS, PFPeS, Br-/L-PFHxS, Br-/L-PFHpS, Br-/L-PFOS), PFCA (PFBA, PFPeA, PFHxA, Br-/L-PFHpA, Br-/L-PFOA, Br-/L-PFNA, PFDA), and three PFAS alternatives (Br-/L-EtFOSAA, 6:2FTS, PFECHS) were detected in MW1 (Table S4). Next to the legacy PFAS, ultrashort chain (C2-C3) PFAS (TFA, PFPrA, PFPrS) were detected with TFA showing the highest concentrations. High  $\Sigma$ PFAS concentration is found near the landfill (MW1, 80–1900 ng/L), and somewhat lower  $\Sigma$ PFAS concentration further downstream (MW 2, 30–460 ng/L) (Fig. 4, Table S4).

$\Sigma$ PFAS concentration in MW1 increases at  $-51$  and  $-65$  m to 1900 ng/L and then decreases to around 86 ng/L at  $-89$  m and lower. For PFCA a decrease in the relative contribution of PFPeA and PFHxA at deeper sampling points and an increase in the shorter and longer chain lengths (PFBA and PFOA) was observed (Fig. 3a). However, for PFSA the relative contribution of PFHxS and PFPeS increased with depth (Fig. 3a).

Based on different sorption behavior for different chain lengths, an increased relative contribution of shorter PFAS was expected in the deeper sampling points (Gobelius et al., 2018; Newell et al., 2021; Sharifan et al., 2021). However, this was not observed in the present study, which might be explained by the presence of the two different historical contamination

sources and different travel times from those sources. South of the landfill, also the military camp is a potential source of PFAS contamination, which was identified previously by (Eschauzier et al., 2013). In the deeper groundwater indeed a different PFAS profile was observed (Fig. 3a) with the domination of specific PFAS (e.g. PFOA, PFOS, PFHxS) that were reported earlier in groundwater contaminated due to military activity (Moody et al., 2003; Reinikainen et al., 2022). Similarly, Eschauzier et al. reported earlier that the former military camp was a potential source of the deeper groundwater in the MW1 (Eschauzier et al., 2013) based on organic fingerprints (such as methane, and total organic carbon level) as well as inorganic fingerprints such as chloride/bromide ratio, and nitrate contents.

In the deep sample MW1  $-131$  m, the PFAS profile exhibited an increased relative contribution of long chain PFOA and PFNA, as well as the short chain PFBS, compared to the upper samples in MW1, F4- and F5-MW1 ( $-89$  m and  $-109$  m, respectively). The PFAS profiles of these three deeper PFAS samples differ from the upper three samples in MW1 ( $-33$  m to  $-65$  m). It is possible that these discrepancies in PFAS profile in the deeper three samples could be attributed to the slow impact of a distant military camp plume, which could potentially be confirmed by conducting sampling at the main plume of the military camp.

The highest  $\Sigma$ PFAS concentration in MW2 was observed at  $-69$  m (470 ng/L) and the  $\Sigma$ PFAS concentration decreased with further depth. All except the deepest  $-147$  m sample in MW2 share a similar profile (clearly for PFSA, Fig. 3b) to the first three samples in MW1 ( $-33$  m to  $-65$  m). This indicates that the landfill is the main PFAS source here and the groundwater doesn't seem to be significantly affected by the military camp (Fig. 3b). The last sample in F5-MW2 ( $-147$  m) shows a low level of  $\Sigma$ PFAS with a similar range and profile to the reference well RMW (Fig. 3, Fig. S1).

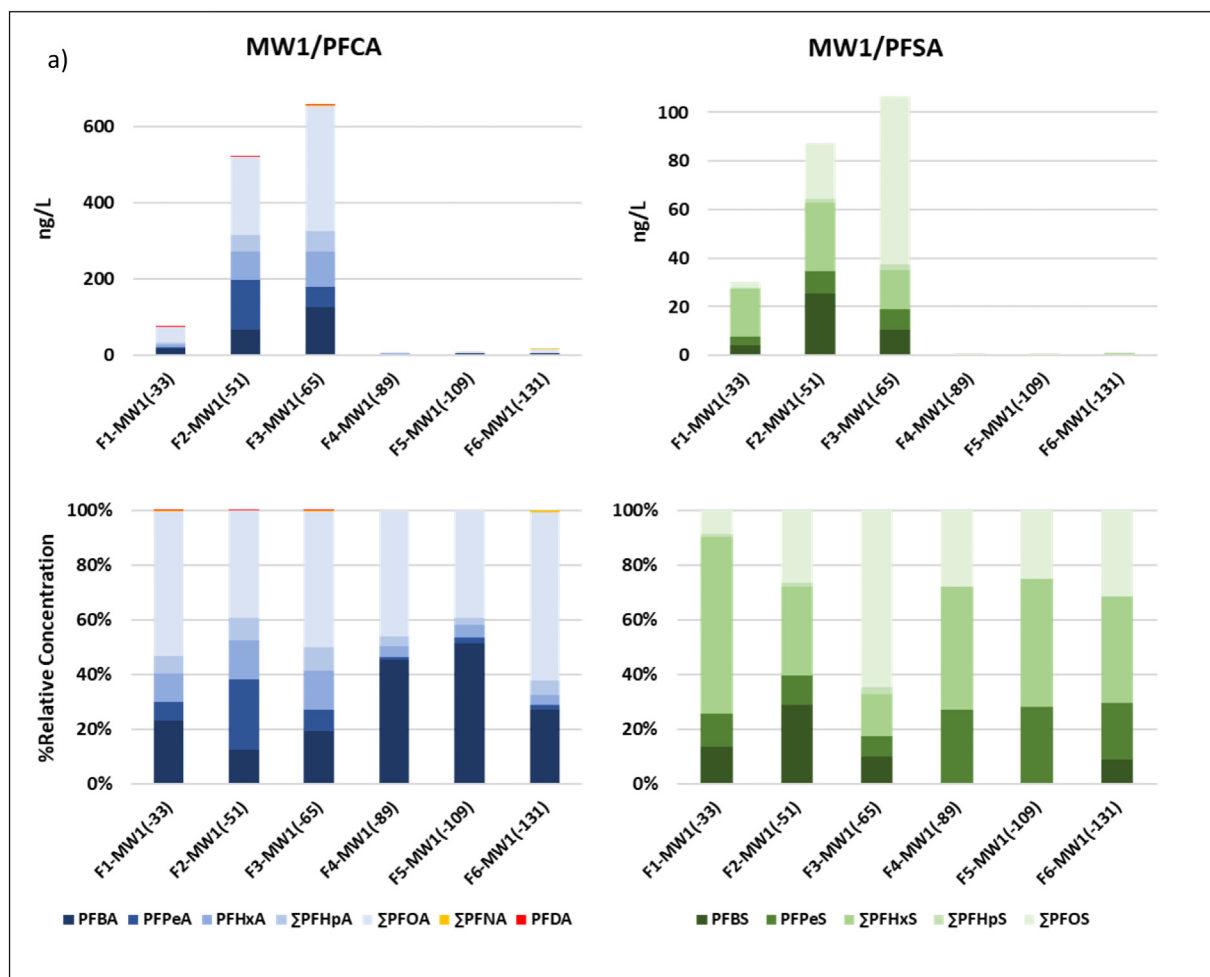
Only three PFAS alternatives (EtFOSAA, 6:2 FTS, and PFECHS) were detected in the monitoring well. EtFOSAA was detected only in MW1 at two depths  $-33$  m (0.62 ng/L) and  $-51$  m (4.54 ng/L). Sorption and biodegradation processes are anticipated to take place in the subsurface for both EtFOSAA and 6:2 FTS, whereas the persistent PFECHS is not expected to undergo such processes (Liu et al., 2021; Mejía Avendaño and Liu, 2015; Wang et al., 2011). 6:2 FTS was detected in all samples in both monitoring wells with a range of 0.20 to 2.43 ng/L, with low concentration in MW2 and the deep water of MW1. 6:2 FTS is expected to be associated with landfill leachate and the activity in the military camp as it was used as a main product in the aqueous film forming foam (AFFF). PFECHS was detected in the

– 33 to – 65 m samples in MW1 (F1-F3) with a range of 1.1 to 8.2 ng/L and in lower concentrations in the first four samples (– 60 to – 125 m) of the MW2 ranging from 0.2 to 2.7 ng/L. PFECHS was not detected in the three deepest samples (– 89 m to – 131 m) in the MW1. The geochemical retention via sorption/desorption occurred in the subsurface, resulting in the decrease in PFECHS concentration with increase distance from the source in the MW2, while no detection of this compound was observed with increasing depth in the deep sample MW1. This might be considered extra evidence of the military camp as contamination source as PFECHS is a persistent chemical and is not expected to degrade. PFECHS is an 8-carbon cyclic PFAS, produced in the late 1940s. It is used in many different industrial applications, and considered as an alternative for PFOS in many applications (de Solla et al., 2012; PubChem, n.d.) and is commonly detected in landfill leachate and surface waters (Sadia et al., 2023).

The ultrashort PFAS, dominated by TFA, showed a higher concentration as compared with other PFAS classes (Table S4, Fig. 4). TFA is known as a widespread PFAS. It is introduced to groundwater via different pathways, such as transformation of pharmaceutical and agricultural products (Scheurer et al., 2017) and hydrofluorocarbon refrigerants in atmospheric deposition (Ellis and Mabury, 2000). The concentration pattern of TFA is following the pattern for the other PFAS in MW1 and MW2 (Fig. 4), indicating that the landfill is also the main source of this PFAS. The TFA concentration in RMW was in the same order of magnitude as in the deeper samples in both MW1 and MW2, PW, RW, and DW ranging between 25 and 70 ng/L (Fig. 4, Table S4) and in similar level of TFA in the groundwater as reported earlier in The Netherlands (Sadia et al., 2023). This suggest that besides the leaching of TFA from the landfill, the lower background TFA concentrations (in the range of 25 to 70 ng/L) might be from atmospheric deposition.

### 3.3. Concentration in pumping wells and drinking water

The pumping wells extract water from the shallow aquifer (7 to 57 m) and the contamination sources are located at long traveling times, i.e. 50–100 year for the landfill and military camp that started in 1972 (Fig. 1), and breakthrough of the landfill-contaminated water in the abstraction area was predicted by 2026 (Eschauzier et al., 2013; Vergouwen et al., 2015). PFAS concentrations and profiles in PW currently do not show the PFAS composition that points to landfill leachate or military camp influence yet (Fig. 3, Fig. S1). Nevertheless, PFAS were found in all pumping wells (up to 111 ng/L for  $\Sigma$ PFAS). The PFAS profiles of PW1, PW3 and PW4 were dominated by ultrashort chain PFAS (mainly TFA), and similar to the RMW samples. This is a profile that is typically associated with atmospheric deposition (Bjørnsdotter et al., 2022). Surprisingly, a different PFAS profile regarding PFCA (domination of PFPeA and PFHxA) was observed in PW2, further away from the contamination sources (dominated by PFBA and PFOA in MW1 and MW2) (Fig. 3, Fig. S1). This observation might reflect a different, unknown, source of contamination other than the landfill or military camp. The relatively high concentration level of 6:2 fluorotelomer sulfonate 6:2 FTS (7.19 ng/L) in PW2 as compared to other monitoring wells (highest in MW1 2.4 ng/L) also points to an additional unknown potential contamination source. 6:2 FTS is the predominant breakdown product of C6 fluorosurfactants in fluorotelomer-based AFFF (Field and Seow, 2017). Such contaminants are commonly observed at different types of facilities and industries such as electric power plants, compositing facilities, oil refineries (Munoz et al., 2017), and also regularly detected in wastewater treatment plant influents (Field and Seow, 2017). Although AFFF is frequently used for training purposes at airports, which



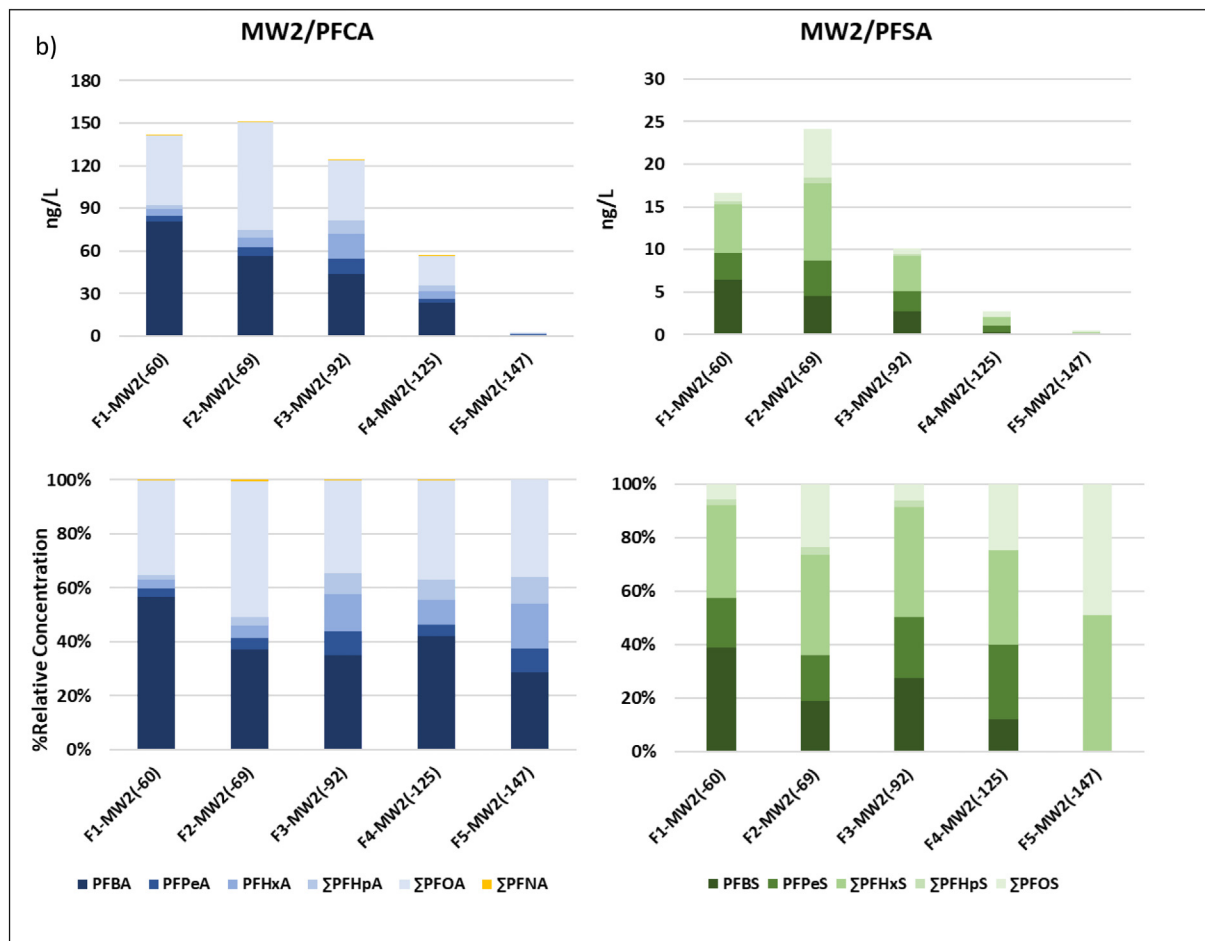


Fig. 3. Concentration in (ng/L) and relative concentration of individual perfluoroalkyl-carboxylic-acids (PFCA) and perfluoroalkyl-sulfonic-acid (PFSA) in both monitoring well (MW1, MW2) at different depths excluding the ultrashort chain PFAS.

might be a potential source as shown in Fig. 1. Further research should be carried out to investigate the source of this contamination, in order to protect the drinking water abstraction area.

The untreated drinking water samples (RW1, RW2) are composed of water from multiple pumping wells. The contribution of the pumping wells to the mixed raw water varies in time, and is not documented at the time of sampling. RW2 showed a lower PFAS level as compared with RW1, with a  $\Sigma$ PFAS without ultrashort of 2.98 ng/L and 9.00 ng/L, respectively. The higher concentration in RW1 seems affected by a higher contribution of PW2, as both the RW1 and PW2 share the same PFAS profile albeit at a different concentration level (Fig. S1). The PFAS concentrations did not change during the drinking water treatment (conventional treatment with intensive aeration), as the DW produced from a mixture of RW1 and RW2 showed a  $\Sigma$ PFAS level without ultrashort PFAS of 5.52 ng/L that fell in between the levels of RW1 and RW2 and shared a similar profile (Fig. 2).

Both the recommendation of the European Food Safety Authority of the total weekly intake for the sum of four PFAS [ $\Sigma$ 4-PFAS: PFOS, PFHxS, PFOA, and PFNA] of 4.4 ng/kg body weight per week (Schrenk et al., 2020) -would translate into a safe level in drinking water of 3.7 ng/L for the sum of these four PFAS using an allocation factor of 20 %, intake of 2 L/d, and 60 kg body weight (WHO, 2017)- and the standard of the safe drinking water based on drinking water directive (European Union, 2020) were used to evaluate the safety of the drinking water. The drinking water produced from this location ( $\Sigma$ 4-PFAS = 1.89 ng/L) would be considered safe, similarly to drinking water produced from groundwater reported earlier in The Netherlands (Sadia et al., 2023).

PFAS are widely considered as a problematic chemical group with a very wide range of applications and usage, leading to a large number of diverse sources and challenges in source identification. Recently, tens of thousands of potential point sources of PFAS contamination across the USA were identified (Andrews et al., 2021). Nevertheless, further screening for potential PFAS sources and evaluation of the fate of PFAS in aquifers is relevant in the Netherlands and Europe in order to find potential sources and ensure groundwater aquifer protection and the safety of future drinking water.

### 3.4. Isomer patterns

The branched isomers for 6 out of all investigated PFAS (namely: PFHpA, PFOA, PFNA, PFHpS, PFHxS, and PFOS) were detected in the monitoring wells, whereas in the pumping wells only 3 branched PFAS (PFOA, PFHxS, and PFOS) were detected. Since the main contamination source (landfill) in the area was active until 1995 and the ECF process used in 80–90 % of total PFAS produced before 2002 (Kempisty et al., 2018), it can be assumed that the majority of PFAS was produced by ECF, and thus a mixture of linear and branched isomers will be present. ECF yields only 20–30 % branched form for PFOS, 15–20 % for PFOA, and ~5 % for PFHxS (Lindstrom et al., 2011; Schulz et al., 2020). As reference materials for technical ECF manufacturing standards are not available for other PFAS, the percentages of the branched isomers for other PFAS are unknown.

A disproportional large contribution of branched isomers, as compared to the original ECF production mixture was observed for both investigated PFSA (PFHxS and PFOS), and PFCA (PFHpA, and PFOA) in the monitoring



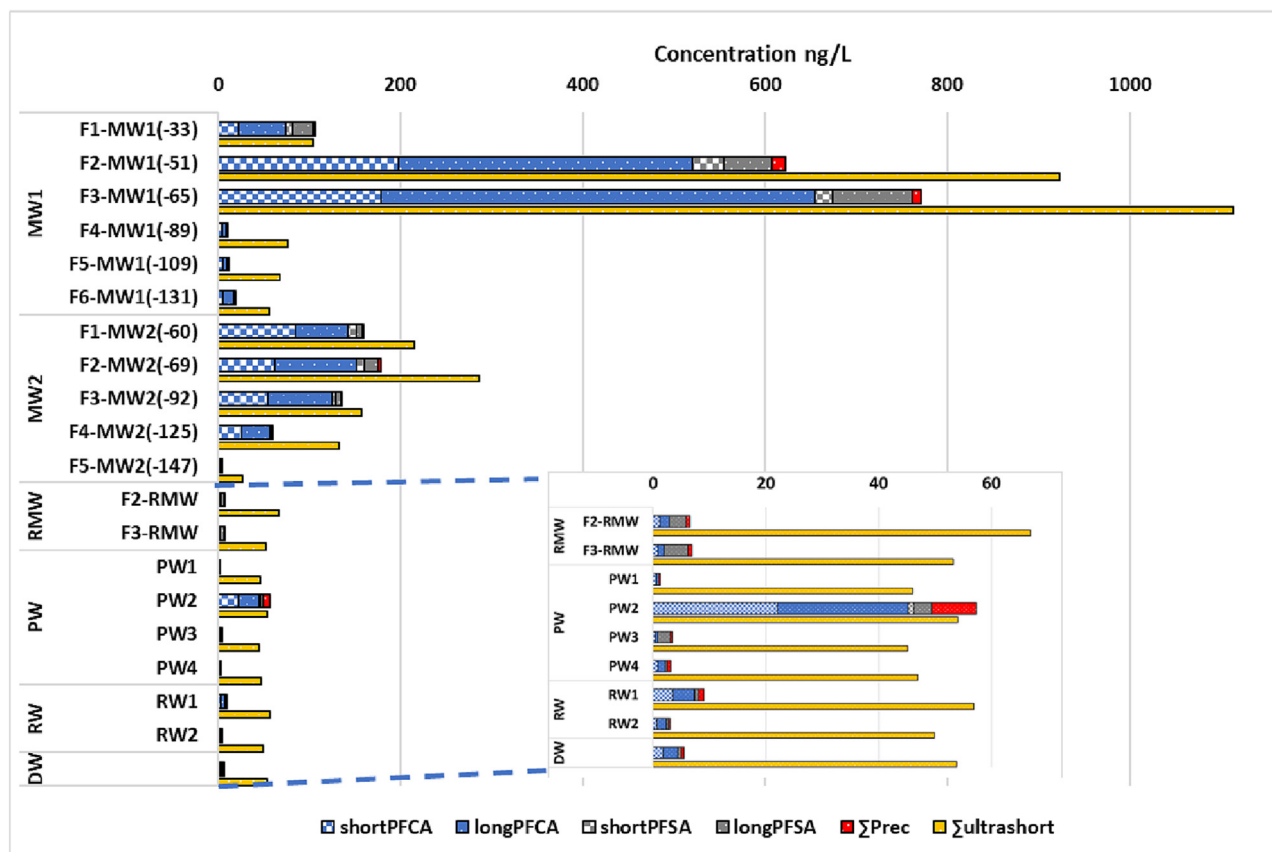


Fig. 4. Concentration (ng/L) of different PFAS classes in both monitoring wells (MW1, MW2), and reference monitoring well (RMW) at different depths, and in pumping well (PW), raw water (RW), and drinking water (DW). PFAS class: ultrashort chain PFAS (C2-C3), PFCA: perfluoro-carboxylic acids (C4-C14) PFSA: perfluoro-sulfonic acids (C4-C10), Prec: variety of precursors (C4-C24).

and pumping wells. Enrichment of branched PFAS can be a result of differences in the sorption behavior of more mobile branched vs linear isomers, but deviations can also reflect different sources. The branched isomer is enriched in both monitoring well by increase with depth and distance as compared with the original ECF mixture (Fig. 5). The findings for the isomer pattern are in line with the findings on the PFAS profiles (Section 3.2) suggesting the presence of two different sources of contamination. The branched isomers are enriched in depth for MW1, with a different pattern between the first (F1-F3) and the last three samples (F4-F6). The last three samples (F4-F6) in MW1 showed a higher contribution of branched isomer of PFOS (40–57 %) and PFHxS (32–42 %), as compared with the upper samples (F1-F3) with the contribution of branched isomer of PFOS (36–43 %) and PFHxS (13 %) (Fig. 5). The investigated PFCA branched isomer showed a slightly higher contribution compared to the ECF production mixture in the first three samples of MW1 for PFOA (12–14 %) and PFHpA (8–11 %). Furthermore, the contribution of the branched isomer increased in the deep groundwater in the last three samples (F4-F6) of MW1, with a contribution of PFOA (19–24 %) and PFHpA (23 %). This branched enrichment between the upper sample (F1-F3) and the deep sample (F4-F6) might be a reflection of the sorption behavior by enrichment of the branched due to increase with depth, but the large difference in the branched contribution especially for PFOA and PFHxS between the depth at –65 m and at –89 m could again refer to a different contamination source in the deep groundwater, which is in agreement with a previous observation (Section 3.1).

MW2 showed a higher branched isomer contribution as compared to MW1 for investigated PFSA and PFCA (Fig. 5). This might be attributed to the higher mobility of branched isomers, as MW2 is further from the contamination source than MW1 (Benskin et al., 2007; Gao et al., 2019). The pumping well showed enrichment in branched isomer contribution as

compared with the original ECF mixture (Fig. 5). A different branched isomer contribution pattern was observed in PW2 (especially for PFHxS and PFOA) as compared with other pumping well, reflecting a different source of PFAS contamination in PW2. Consistent with this, other studies (Kärman et al., 2011; Gebbink et al., 2016; Langberg et al., 2021), have demonstrated that the isomer pattern can serve as a source indicator in PFAS contamination, with enrichment of branched isomer contribution increasing with distance from the contamination sources.

In the subsurface, the use of both PFAS profiles and isomer patterns can be a valuable tool for trace contamination detection. Eschauzier et al. employed low-cost analyses, such as total organic carbon levels and chloride/bromide ratios, to track contamination from landfills. Their approach was effective in differentiating between two plumes in the deep and shallow water in MW1. Incorporating the PFAS profile and isomer pattern as presented in this study can serve as an additional tool for confirmation and be highly useful in more complex subsurface systems that present numerous potential sources to the same location. Furthermore, the knowledge on environmental behavior of different PFAS present in the area, including, newly produced PFAS and the ratio of branched to linear, can also track the age of the contamination.

#### 4. Conclusion

This study demonstrates the use of PFAS profiles and isomer patterns as a tool to better understand the sources, migration, and transport of PFAS in the subsurface system. In this study, two known contamination sources in the area were identified using organic and the inorganic fingerprints a decade ago, i.e. a landfill and a military camp, and the earlier data is used to track contamination transport over the past decade. By studying PFAS profiles and isomer patterns at different depths, the sources could be

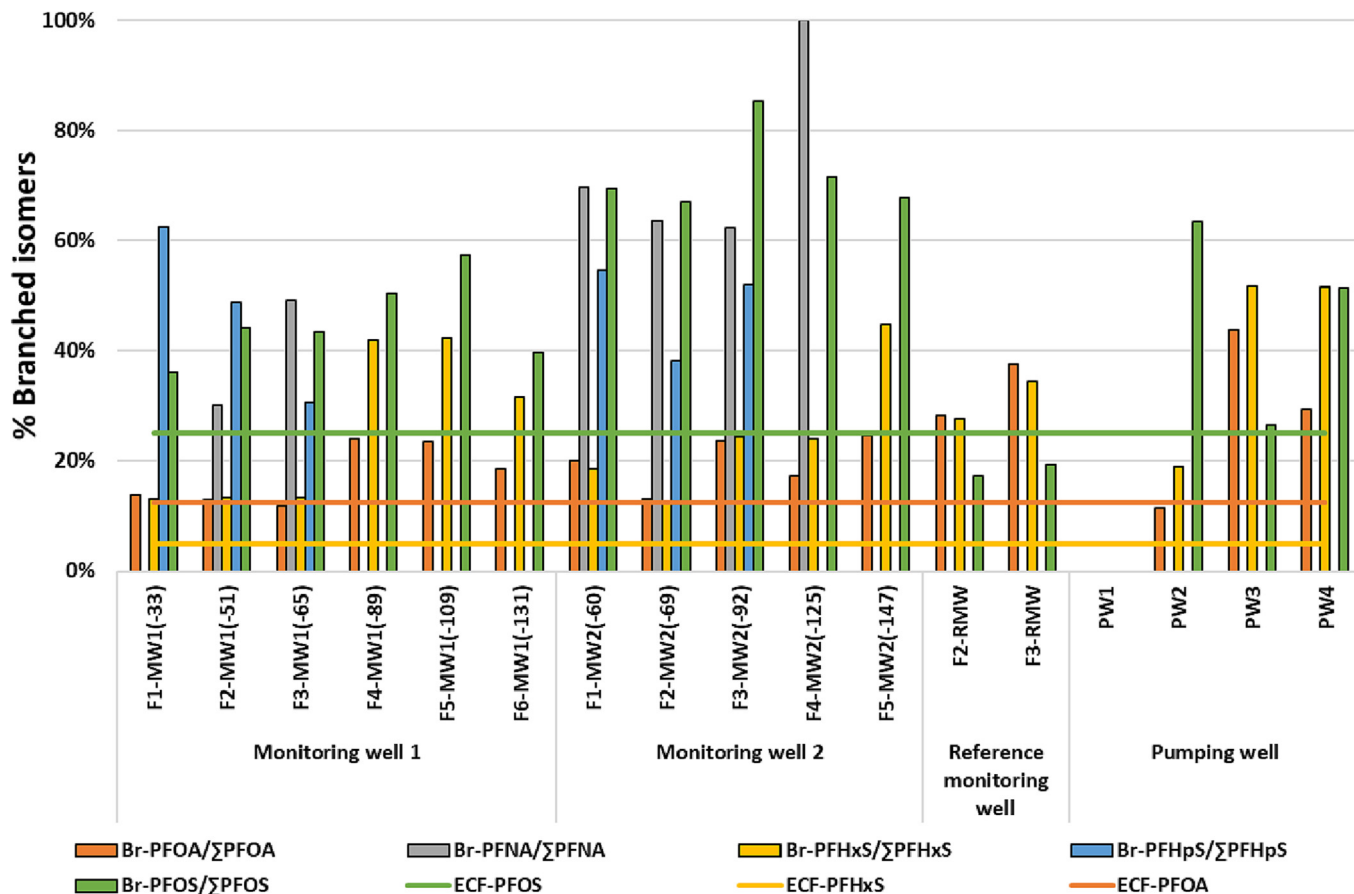


Fig. 5. The relative contribution of the branched isomers (Br) for selected PFAS in the monitoring well (MW) at different depths, reference monitoring well (RMW), pumping well (PW), raw water (RW), and drinking water. The horizontal line represents the original mixture of the electrochemical fluorination (ECF) production process.

discriminated in the deeper aquifer. This study provides evidence on an additional yet unknown contamination source in the drinking water abstraction area, which needs further investigation.

Over the past decade, PFAS clearly migrated towards the drinking water abstraction area and future risk to the drinking water is expected. Source identification combined with hydrological information helps to predict the potential impact of the contamination on the quality of the future drinking water and also enables mitigation measures. This work showed the value of local screening to identify potential sources of PFAS beyond manufacturing facilities. Such information is very valuable for designing mitigation strategies to prevent migration of PFAS contamination into groundwater. Thereby this study supports the protection of groundwater sources for drinking water from these persistent mobile chemicals and the safety of drinking water for future generations.

#### CRediT authorship contribution statement

**Mohammad Sadia:** Conceptualization, Data curation, Methodology, Formal analysis, Visualization, Writing - original draft. **Marlene Kunz:** Formal analysis. **Thomas ter Laak:** Methodology, Supervision, Writing - review & editing. **Martin De Jonge and Merijn Schriks:** Methodology, Sample collection, Writing - review & editing. **Annemarie P. van Wezel:** Funding acquisition, Conceptualization, Project administration, Supervision, Writing - review & editing.

#### Data availability

No data was used for the research described in the article.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.164420>.

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