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Quick Scan impact of diffuse PFAS contamination on groundwater extraction sites BTO 2024.064 | July 2024

### Colophon

### Quick Scan impact of diffuse PFAS contamination on groundwater extraction sites

### BTO 2024.064 | July 2024

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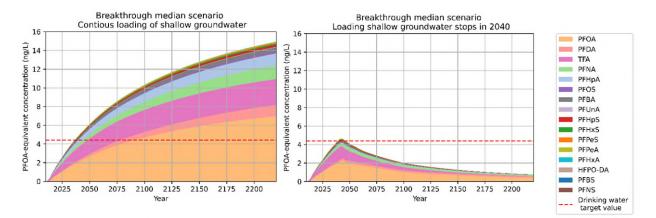
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### **Executive Summary**

### Ban on PFAS is effective for protecting drinking water sources

### Author(s): Bas van der Grift and Onur Köse

The diffuse contamination of the soil with PFAS may threaten groundwater extraction in the Netherlands. A quick scan was performed to identify this threat: indicative calculations were made for vulnerable groundwater extraction into the development of PFAS concentrations in groundwater extracted for drinking water production over the next 200 years. For this purpose, PFAS concentrations that are currently measured in the shallow groundwater and substance-specific adsorption properties of PFAS to soil particles were used. The calculations show that if PFAS concentrations remain the same in the shallow groundwater, the drinking water targe value of 4.4 ng PEQ/L will be exceeded over a period of approximately 20 years. The scenario calculations show that a ban on PFAS is effective, but will probably come too late to completely prevent exceedances. Additional treatment of extracted groundwater is then temporarily necessary. It is, however, uncertain when and for how long this will be needed, which also differs per location. The quick scan shows that this could be the situation within 10 years.



PFAS breakthrough in extracted groundwater as PFOA-equivalent concentration (PEQ) with continuous loading of the shallow groundwater (left) and stopping the load in 2040 as a result of a PFAS ban in 2025

# Importance: providing insight into the impact of diffuse PFAS contamination on groundwater extraction

Due to atmospheric deposition, the use of pesticides and run-off from paved surfaces, the soil in the Netherlands is diffusely contaminated with PFAS. It is important to know whether and to what extent this "PFAS blanket" poses a potential threat to groundwater extraction.

## Approach: AquaPriori modelling of a vulnerable groundwater extraction site for two scenarios

A quick scan was carried out to get a view on the impact of diffuse PFAS contamination on vulnerable

groundwater extractions. The development of PFAS concentrations in groundwater extracted for drinking water production over the next 200 years was calculated using a simple groundwater model. This should provide an indicative insight into whether and when PFAS concentrations will exceed the drinking water guideline value and what effect can be expected from a total ban on PFAS production.

The AquaPriori model was used to calculate the development of PFAS concentrations in extracted groundwater on the basis of a travel time distribution and flow path pattern for a fictitious but realistic vulnerable groundwater extraction site. For this

calculation, PFAS concentrations in shallow groundwater that are currently being measured were used as input. The compound-specific retardation behaviour of PFAS in the soil has also been taken into account. Two scenarios have been calculated. The first is a median scenario, which is indicative of a 'normal' diffuse polluted area and assumes the 50 percentile of measured PFAS concentrations in the shallow groundwater. The second is an upper bound scenario for a high diffuse polluted area, which is based on the 90-percentile values of measured PFAS concentrations. For both scenarios, a variant was calculated with continuous PFAS leaching from the soil and a variant in which the groundwater is contaminated with PFAS leaching from the soil over a period of 30 years (2010-2040), after which this leaching stopped. The idea behind this variant is that if PFAS production stops in the short term, it will take another 15 years before effects on the concentrations in the shallow groundwater become visible.

# Results: drinking water guideline value exceeded at constant concentrations in the shallow groundwa-ter

As a threshold value, we used the drinking water target value of 4.4 ng/L PFOA equivalent (PEQ) derived by the RIVM. This is a sum concentration of PFAS compounds that takes into account the differences in toxicity of the different substances. The results of this quick scan show a number of things:

- As a result of the diffuse PFAS contamination, the shallow groundwater contains currently such a high PFAS concentrations (median: 20 PEQ/L, P90: 99 PEQ/L) that groundwater extracted from a vulnerable groundwater extraction site will exceed the target value (4.4 ng PEQ/L) after approximately 20 years.
- In areas with a high diffuse load, this may be the situation years earlier.
- If PFAS concentrations remain the same in the shallow groundwater, PEQ in the extracted groundwater will be 2 to 10 times higher than the target value in 2100.
- In the scenario in which PFAS leaching to the shallow groundwater stops in 2040, the PFAS concentration in the extracted groundwater will peak around 2045 and then slowly decrease. In the median scenario the drinking water target value of 4.4 ng PEQ/L will be temporarily exceeded around

2045. In the upper bound scenario, this is much more clearly the case.

 The differences in mobility of the different PFAS in the subsurface lead to differences in the breakthrough of PFAS in extracted groundwater. The short-chain PFAS flow towards the extraction well at almost the same rate as the groundwater, PFAS with longer CF chains much slower. PFAS with CF chain lengths longer than 10 have very limited mobility in the subsurface and are therefore unlikely to pose a threat to groundwater for drinking water production in the relatively longer term.

This quick scan assumes that PFAS will reach the groundwater at a constant concentration from 2010 onwards as a result of leaching from the soil. Because PFAS was already produced around 1950, the actual PFAS load on groundwater will likely have started earlier, but the PFAS composition and concentration development are unknown. It is not impossible that concentrations in the shallow groundwater will increase even further in the future, even if PFAS production stops in 2025, because the peak load of PFAS from diffuse sources may still be largely present in the unsaturated zone. On the other hand, the production of PFOA and PFOS has been banned for some time, but it is unknown when this will affect leaching to the shallow groundwater. All this makes it uncertain that the concentration in the shallow groundwater will drop to from 2040 onwards, as assumed in the 'ban on PFAS' scenario. It is not known how long these substances will continue to leach to groundwater when PFAS production in Europe stops completely and what effect degradation of PFAS precursors has on PFAS-20 concentrations.

## Application: PFAS ban is effective, but may be too late to avoid exceeding guideline value

A ban on PFAS is effective, but it will probably come too late to prevent temporal exceeding of the drinking water target value, so that additional treatment of extracted groundwater is necessary. It is uncertain when this treatment will be needed exactly and for how long – that will also differ per location. This moment may come soon.

#### Report

This research is described in the report *Quick Scan effects of the national PFAS blanket on groundwater extraction* (BTO 2024.064).

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Credentials

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Contamination of water by PFAS (Per- and polyfluoroalkyl substances) is currently in the spotlight. Attention is often focused on surface water in which PFAS has been found in elevated concentrations or on PFAS-contaminated sites such as (former) factory sites, firefighting training locations and military basis. In addition to these specific contaminated locations, there is also a PFAS load in the Netherlands which is spread diffusely over larger areas over Dutch soils. Important sources of this diffuse PFAS load are atmospheric deposition, the use of pesticides containing PFAS and urban run-off rainwater contaminated with PFAS. There are many sources behind atmospheric deposition, including factories, waste incineration plants and fluorinated gases from leaking refrigeration/air conditioning systems. The latter mainly concerns very short chains of PFAS that are highly mobile in the subsurface. PFAS are increasingly used in pesticides to improve the effectiveness and stability of the product. In about 50% of new products launched between 2016 and 2022, the active ingredient contains one or more fluorinated components (Jeschke, 2023) and the use of these types of substances is increasing (PAN Europe, 2023). Run-off rainwater from road and paved areas is still a relatively unknown source of diffuse PFAS pollution. A recent study has, however, shown that this may be important. For example, many different types of PFAS are used in vehicles, including lubricants, waxes and coatings. PFAS is released into the environment through run-off from these vehicles (Speijer et al., 2023). This run-off water will mainly end up on road verges where it infiltrates into the soil. Recent research found relatively high PFAS concentrations in the groundwater under road verges (Visser, 2023). Road run-off will not pollute the soil everywhere, but it will be present as line sources in the landscape.

It is important to estimate the future consequences of this diffuse PFAS contamination on groundwater extraction sites for drinking water production because, in contrast to surface water, the contamination of groundwater is a relatively slow process. However, in the long term it can lead to irreparable deterioration of groundwater as a source of drinking water. PFAS can leach into the shallow groundwater with the infiltrating groundwater recharge (precipitation surplus) and then continue to flow towards the groundwater sources (Figure 1.1). Here, it should be borne in mind that the PFAS levels in the soil in diffusely polluted areas are a few micrograms/kg dry matter, while the target value for drinking water derived by RIVM is in nanograms/L. In terms of weight percentages, a factor of 1000 lower than for soil. This creeping risk of groundwater contaminations is also present in other European countries. It is therefore important to obtain an indication of the risk for exceeding of safe values in the extracted groundwater. The purpose of this quick scan was to get an impression of the expected PFAS concentrations over

*AquaPriori-Subsurface* is a web application recently developed by KWR to make initial assessments of the risk of breakthrough of (new) organic micropollutants in groundwater extraction wells (Van der Grift et al., 2024). Based on the hydrological characteristics of a standardized type of drinking water supply well field, AquaPriori calculates a flow path pattern and associated travel time distribution of the extracted groundwater. Subsequently, the retardation and degradation of the organic micropollutants is calculated along these flow paths. The different types of drinking water supply well fields in *AquaPriori-Subsurface* are: a phreatic groundwater extraction, a semi-confined water groundwater extraction, a riverbank filtration extraction and a dune infiltration extraction. The compound properties for transport and removal of substances during transport through the subsurface are retrieved from online database with sorption and degradation parameters or can be specified by the user. To support so, *AquaPriori-Subsurface* generates overviews of known half-lives value of compounds in the subsurface based on field measurements from international scientific literature and from measurements along groundwater monitoring transect in the Netherlands.

*AquaPriori-Subsurface* will be part of the groundwater risk toolbox from RIVM: https://www.risicotoolbox-bodem.nl/grondwater/

the next 200 years in a vulnerable groundwater extraction site and the effectiveness of a total European ban on PFAS production, use, sale and import by using *AquaPriori* modelling (see text box below).

To do this, substantiated assumptions had to be made about the presence of PFAS in the shallow groundwater as a result of atmospheric deposition and the other diffuse sources. Subsequently, the transport of 20 PFAS relevant to the European Drinking Water Directive supplemented with TFA and HFPO-DA (GenX) to the deeper aquifers and groundwater extraction wells is modelled.

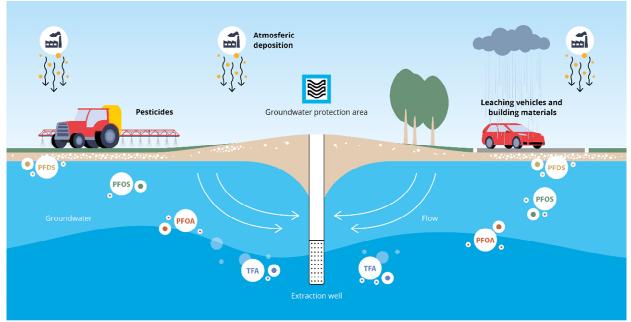


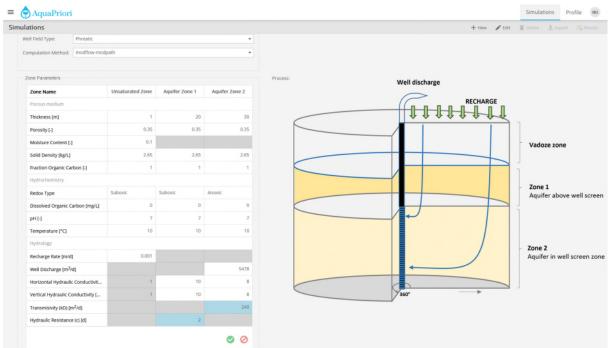
Figure 1.1. PFAS sources that responsible for diffuse PFAS contamination of the topsoil and transport through the subsurface to a drinking water well.

### 2 AquaPriori Mondeling

The AquaPriori web application (see text box in the previous chapter) was used to calculate the breakthrough of various PFAS in a extraction well of a typical phreatic groundwater extraction site. This type of drinking water production locations is not protected by a confined (clay) layer and the extracted groundwater is relatively young. The starting point for the calculations are the PFAS-20 of the new European Drinking Water Directive (DWD), supplemented with TFA and HFPO-DA (GenX). The mobility of these substances in the subsurface determines how quickly these substances breakthrough in extracted groundwater. This mobility is highly compound specific and decreases with increasing CF<sub>2</sub> chain length.

In this quick scan, it was assumed that PFAS will not be degraded during transport through the subsurface. This is a common assumption according to the current scientific knowledge on PFAS behavior in the subsurface. The break-through in the extracted groundwater is therefore only determined by the degree of adsorption of PFAS to soil material. For the modelling of the adsorption, substance specific linear partition coefficients were used, which assume the adsorption of PFAS to organic material, and mineral soil particles (silt and clay fraction), see section below.

The AquaPriori model needs the following input: 1) the travel time distribution of extracted groundwater, 2) contends of reactive soil components that can adsorb PFAS, 3) substance specific partition coefficients for adsorption of different PFAS and 4) input concentration of PFAS in the shallow groundwater.



#### Groundwater extraction site

The groundwater extraction site is schematized with 3 layers: an unsaturated zone, an aquifer above the extraction well and an aquifer at the depth of the extraction well (

Figure 2.1). The groundwater extraction site needs to be parameterized with hydrological parameters such as the depth and flow rate of extraction, geohydrological buildup of the subsurface, precipitation surplus and properties important for substances transport such as organic matter content, silt content and clay content. The groundwater extraction site of this quick scan has been parameterized in AquaPriori in such a way that it is representative for a relatively vulnerable groundwater extraction site in the Netherlands. This concerns a groundwater extraction of 2 million m<sup>3</sup>/year at a depth of 20 to 50 below surface level and a precipitation surplus of 1 mm/day.

According to the flow path pattern and the travel time distribution calculated by AquaPriori as shown in Figure 2.2, 25% of the groundwater extracted is younger than 11.7 years, 50% is younger than 30 years and 75% is younger 66 years. The maximum travel time of the groundwater is about 300 years.

The contents of reactive soil components in the aquifer sand have been assigned on the basis of common geochemical knowledge: organic matter 0.4% (= 0.2% organic carbon), clay 2% and silt 1%.

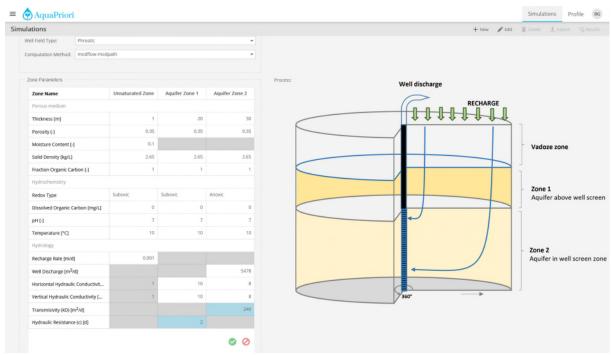


Figure 2.1. Schematization and parameterization of phreatic groundwater extraction site in AquaPriori.

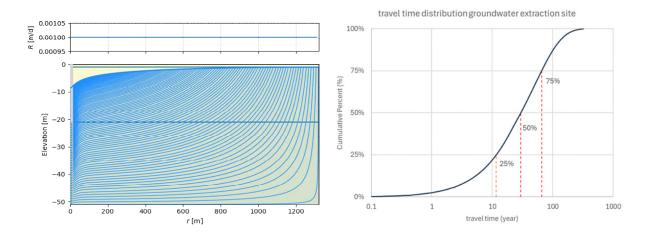


Figure 2.2. Flow path pattern and cumulative travel time distribution of the phreatic groundwater extraction site.

#### Compound specific partition coefficients

The compound specific partition coefficients for the PFAS-20, TFA and HFPO-DA were derived from literature values (Table 2.1), using the method of Fabregat-Palau et al. (2021). In this method, the partition coefficient (K<sub>d</sub>) is calculated based on a distribution coefficient for organic carbon (K<sub>oc</sub>) and a distribution coefficient for mineral soil constituents ( $K_{min}$ ) in combination with the organic matter, clay and silt content of the soil. This is an improved approach compared to the classic concept for the mobility of compounds in soils, where only the adsorption by organic matter is considered. Based on the partition coefficient, the bulk density and the porosity of the aquifer sand, AquaPriori then calculates the retardation factor, the ratio of the solute's distance travelled to the solvent's

distance travelled. PFAS with a calculated retardation factor greater than 50 were not included in the AquaPriori model calculations. These compound will not pose a threat to groundwater extraction site over a period of 200 years.

The mobile PFAS which are included in the model are a series from the (ultra) short chain PFAS to longer chain carboxylic acids: TFA, PFBA, PFBS, PFPeA, PFPeS, PFHxA, PFHxS, PFHpA, PFHpS, HFPO-DA, PFOA, PFOS, PFNA, PFNS, PFDA and PFUnA. TFA is the smallest and most mobile (least retardation) and PFUnA is the longest and least mobile of the PFAS considered.

Table 2.1. PFAS partition coefficients to soil organic carbon and soil mineral constituents in the aquifer sands calculated according to the method of Fabreat-Palau (2021) assuming 0.4% organic matter, 2% clay and 1% silt and the retardation factor based on a bulk density of 1.69 kg/L and a porosity of 0.35.

	Kd organic carbon	Kd mine- ral	- Retardation Kd total factor		Modeled	
PFBS	0.022	0.01	0.04	1.2	yes	
PFPeS	0.045	0.02	0.07	1.3	yes	
PFHxS	0.100	0.04	0.14	1.7	yes	
PFHpS	0.296	0.10	0.40	2.9	yes	
PFOS	PFOS 1.218		1.50	8.2	yes	
PFNS	1.954	0.45	2.41	12.6	yes	
PFDS	9.210	0.95	10.16	50	no	
PFUnDS	12.913	1.98	14.90	73	no	
PFDoDS	33.192	4.14	37.33	181	no	
PFTrDS	85	8.6	94	455	no	
TFA	0.001	0.00	0.00	1.0	yes	
PFBA	0.006	0.01	0.019	1.1	yes	
PFPeA	0.030	0.01	0.04	1.2	yes	
PFHxA	0.030	0.01	0.04	1.2	yes	
PFHpA	0.100	0.05	0.15	1.7	yes	
PFOA	0.214	0.10	0.313	2.5	yes	
PFNA	0.648	0.06	0.71	4.4	yes	
PFDA	1.208	0.42	1.63	8.9	yes	
PFUnA	4.892	0.75	5.64	28.2	yes	
PFDoA	10.742	6.87	17.61	86.0	no	
PFTrA	33.192	4.14	37.33	181.3	no	
HFPO-DA	0.045	0.02	0.07	1.33	yes	

### PFAS concentration in shallow groundwater

The model run starts in 2010 model runs for 200 years. For the quick scan the composition and concentrations of the various PFAS in the shallow groundwater were assumed to be constant over time and the shallow groundwater has furthermore homogeneous composition over the entire catchment area. The composition of the shallow groundwater is based on PFAS concentrations recently measured in the Netherlands. The measurements stems from the phreatic groundwater monitoring network in the province of Utrecht (Vissers, 2023) and from the nation-wide monitoring network of the RIVM (Wintersen et al., 2021) (Table 2.2). For the phreatic monitoring network of the province of Utrecht, median concentration (value where 50% of the measurements have a higher and 50% have a lower concentration) and P90 (90% of the measurements a lower concentration) were calculated from the entire

dataset. From the RIVM data, the P50 and P95 percentile values were taken from the report as the original dataset on which these values are based were not available during the duration of this quick scan.

With these values, two scenarios have been drawn up, in which the P90/P95 scenario can be seen as an upper bound scenario for diffuse pollution and the P50 scenario as a mid-range scenario (Table 2.2).

For a number of substances in both datasets, the median value or even the P90/P95 value is equal to the limit of quantification (LOQ). For the median scenario, it was decided to use half of the lowest LOQ (Utrecht of RIVM) as model input. In the upper bound scenario, the lowest LOQ is used as model input.

Table 2.2. Median and P90/P95 concentration of the PFAS-20, TFA and HFPO-DA of the phreatic groundwater measurements of the province of Utrecht and the RIVM, the AquaPriori model input for PFAS concentration for the median and upper bound scenario and the Relative Potency Factors (RPF) derived by RIVM (RIVM, 2023; Van der Aa et al., 2022).

PFAS-20	P50 Utrecht	P90 Utrecht	P50 RIVM	P95 RIVM	Median scenario	Upper Bound Sce- nario	RPF
	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	
PFBS	2.4	9.9	3.2	20	2.4	9.9	0.001
PFPeS	0.5	0.5	0.3	1.2	0.15	1.2	0.6
PFHxS	0.5	1.5	0.6	7	0.25	1.5	0.6
PFHpS	-	-	0.3	0.3	0.15	0.3	2
PFOS	0.5	0.5	0.3	6.7	0.15	6.7	2
PFNS	-	-	-	-	0.1a <sup>)</sup>	0.1a)	-
PFDS	-	-	-	-	-	-	2
PFUnDS	-	-	-	-	-	-	-
PFDoDS	-	-	-	-	-	-	-
PFTrDS	-	-	-	-	-	-	-
TFA	1410	4910	-	-	1410	4958	0.002
PFBA	9.1	23	5.5	21	9.1	23	0.05
PFPeA	0.5	4.8	1.7	15	1.7	4.8	0.05
PFHxA	1.6	6.5	1.8	15	1.6	6.5	0.01
PFHpA	0.5	3.7	1.4	10	1.4	3.7	1
PFOA	8.7	47	6	43	8.7	47	1
PFNA	0.5	0.5	0.6	1.5	0.25	1.5	10
PFDA	-	-	0.6	0.6	0.3	0.6	10
PFUnA	-	-	-	-	0.1 <sup>a)</sup>	0.1 <sup>a)</sup>	4
PFDoA	-	-	-	-	-	-	3
PFTrA	-	-	-	-	-	-	3
HFPO-DA	0.5	0.5	-	-	0.25	0.5	0.06
ΣPFAS					1437	5065	
ΣPFAS-20 (DWR) <sup>b)</sup>	37	150	22	143	27	107	
PEQ <sup>c)</sup>					20	99	

a) Estimated on the basis of measured concentrations of the other PFAS

b) PFAS-20 according to European Drinking Water Directive, TFA and HFPO-DA are excluded

c) PFOA-equivalent concentration

For PFAS that are included in the model but for which no phreatic groundwater monitoring data is available (PFNS and PFUnA), the concentration has been (conservatively) estimated on the basis of the measured concentrations of the other PFAS.

For the PFAS that are not included in the AquaPriori model due to calculated retardation factor greater than 50 (see Table 2.1), input concentrations were not available.

The median and upper bound scenario was finally constructed according to the following step-by-step approach:

- 1) If measured in phreatic groundwater and > LOQ, the P50 and P90 values of the province of Utrecht were used.
- 2) If P50 Utrecht and P50 RIVM are equal to LOQ, half of the lowest LOQ is used as the input value for the median scenario.
- 3) If P50 Utrecht is equal to the LOQ and P50 RIVM is higher than the LOQ, then the P50 RIVM is used as the input value for the median scenario.
- 4) If P90 Utrecht is equal to the LOQ and P95 RIVM is higher, then the P95 RIVM is used as the input value for the upper bound scenario.

### Threshold value PFAS concentrations

The government determines the quality requirements that drinking water must meet. The legal quality requirements for drinking water are set out in the Drinking Water Directive (DWD). For the sum of the PFAS-20 of the DWD, the legally permitted amount in drinking water is 100 nanograms per liter (ng/L). Table 2.2 makes it clear that the sum of the measured P50 concentrations in the shallow groundwater does not exceed this value, whereas this is the case for the sum of the P90/P95 concentrations.

PFAS are more harmful to human health than previously thought. Therefore, in 2022, the Dutch government set a drinking water target value for PFAS of 4.4 ng/L, expressed as PFOA-equivalents. In the future, this target value will be included as a legal quality requirement in the Drinking Water Directive. (www.rivm.nl/pfas/drinkwater). This drinking water target value was derived by RIVM in 2021 to test a cocktail of PFAS in drinking water to the EFSA-TWI (Tolerable Weekly Intake) of 4.4 ng/kg body weight per week and is based on the principle that drinking water may contribute a maximum of 20% of the EFSA-TWI for PFAS (Van der Aa et al., 2021). This method makes use of knowledge about the toxicity of individual PFAS compared to PFOA, expressed in relative potency factors (RPFs), see Table 2.2. The concentrations of individual PFAS can be expressed in equivalent concentrations of PFOA (PFOA-equivalents, PEQ) with these RPFs. The sum of this PEQ-concentrations can be compared with the drinking water target value of 4.4 ng PEQ/L.

When there is only intake of PFAS through consumption of drinking water, the EFSA-TWI has been calculated by RIVM at 22 ng PEQ/L, or 5 times the drinking water target value, assuming 2 liters per day by an adult person weighing 70 kg (Van der Aa et al., 2022). This value of 22 ng PEQ/L is seen by RIVM as a trigger value whereby in the case of an exceedance in drinking water, it is important that PFAS concentrations decrease in the short term.

The concentrations in the extracted groundwater calculated with AquaPriori have been converted into PFOA equivalents using the RPFs and the sum of the PFOA equivalents has been plotted against time

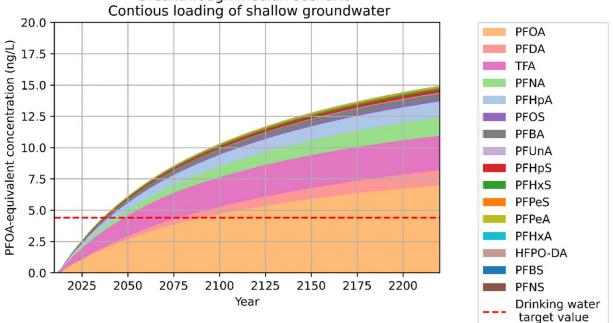
### Effect of ban on PFAS

To gain insight into the effect of an European ban on production, use, sale and import of PFAS, AquaPriori was applied to model a scenario in which the PFAS concentrations in the shallow groundwater are set to zero in 2040, after being are kept constant for a period of 30 years (from 2010 to 2040). The idea behind this scenario is that the diffuse PFAS contamination at the soil surface would have ended well before 2040, but it will take several years before the concentrations in the soil leachate that fed the shallow groundwater will drop.

#### 3 **Results and discussion**

The model results shows that, as a result of the breakthrough of PFAS expressed in PFOA-equivalent concentration, (PEQ) the drinking water target value of 4.4 ng PEQ/L will eventually be exceeded in both the median and upper bound scenarios (Figures 3.1 and 3.2). In 2100 the PEQ-concentration will be slightly more than a factor of two higher than the drinking water target value for the median scenario, while in the upper bound scenario this will be more than a factor of 10. PFOA is the most important component in the PEQ-concentration in both scenarios, followed by PFDA, TFA and PFNA and PFOS. The trigger value of 22 ng PEQ/L calculated by RIVM on the basis of drinking water consumption alone is far exceeded in the upper bound scenario (input shallow groundwater = 99 ng PEQ/L), while this is not the case in the median scenario (input shallow groundwater = 20 ng/L PEQ) (Figures 3.1 and 3.2).

To interpret the calculated breakthrough curves, they can, at an appropriate distance, be compared with PFAS measurement in groundwater extracted for drinking water production. Comparison with measured concentrations is however difficult, because PFAS is logically not (yet) present in the extracted groundwater in many sites, but is on its way to the extraction wells. Based on individual pumping stations in the Netherlands, RIVM has looked at how the PFAS sum concentration in drinking water samples relates to the drinking water target value of 4.4 ng PEQ/L (Van der Aa et al., 2022). When only the EFSA-4 PFAS (PFOA, PFOS, PFNA and PFHxS) are considered in the data from 2015 to February 2021, the drinking water target value is exceeded in 10% of the samples of groundwater extracted for drinking water production. When all PFAS are included, the percentage does not change due to low concentrations of the non-EFSA-4 PFAS. This percentage of 10% is in line with the results of the AquaPriori modelling, whereby the drinking water target value is not exceeded in the median scenario but this is the case in the upper bound scenario, which is based on the P90 value of measured concentrations in the shallow groundwater.



Breakthrough median scenario

Figure 3.1. PFAS breakthrough in extracted groundwater as PFOA-equivalent concentration (PEQ) for the median scenario. The drinking water target value is 4.4 ng PEQ/L.

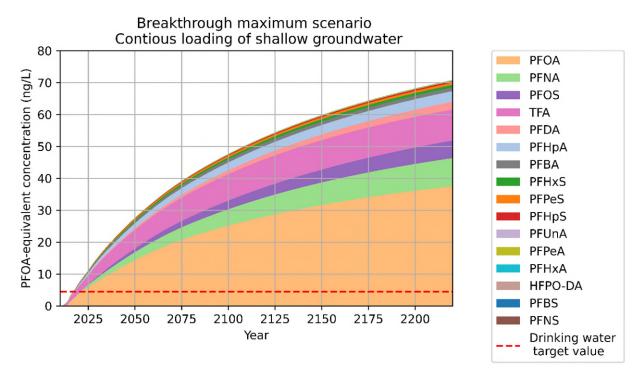


Figure 3.2. PFAS breakthrough in extracted groundwater as PFOA-equivalent concentration (PEQ) for the upper bound scenario. The drinking water target value is 4.4 ng PEQ/L.

### Ban on PFAS scenario

For the scenarios where the PFAS load to the shallow groundwater stops in 2040 as a result of a total ban on PFAS, the PEQ concentration peaks a view years after 2040 and then decreases further (Figure 3.3 and Figure 3.4). In the median bound scenario, the drinking water target value of 4.4 ng PEQ/L is just reached. This is way more pronounced the case for the upper bound scenario and the PEQ concentration will only fall below this target value after 2200. However, due zero leaching to the groundwater from 2040, the PEQ concentration will remain just below the RIVM trigger value of 22 ng/L.

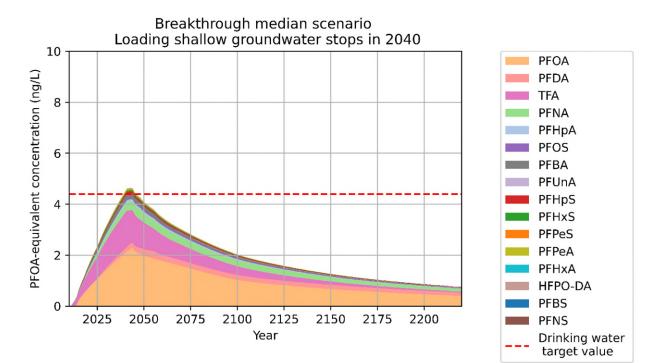


Figure 3.3. PFAS breakthrough in extracted groundwater as PFOA-equivalent concentration (PEQ) for the ban on PFAS median scenario. The drinking water target value is 4.4 ng PEQ/L.

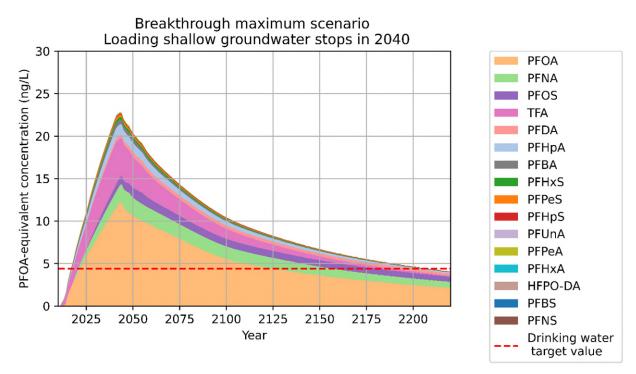


Figure 3.4. PFAS breakthrough in extracted groundwater as PFOA-equivalent concentration (PEQ) for the PFAS ban on PFAS upper bound scenario. The drinking water target value is 4.4 ng PEQ/L.

### 3.1 Assumptions and uncertainties

The results of the AquaPriori model calculations presented in this quick scan give an indication of the extent in with which PFAS concentrations can develop at relatively vulnerable groundwater extractions sites and what the reduction of concentrations in extracted groundwater can be after a total ban on PFAS, which ideally stops the diffuse contamination at soil surface level. Due to limited PFAS measurements in the past and also due the fact that knowledge about PFAS transport in the subsurface is strongly under developing, the presented calculation do contain a large number of assumptions and uncertainties. This results in a strong simplification of the reality, that fits to the purpose of this quick scan.

An important uncertain factor is that the modelling is based on PFAS leaching to the shallow groundwater with constant concentrations from 2010 onwards and then remain constant for 200 years. The assumption that the groundwater does not contain PFAS before 2010 and that the concentrations in the shallow groundwater will not change from 2010 onwards are both inconsistent with reality. The fact is that we don't know what the PFAS concentrations in shallow groundwater were 10-20-30-40 years ago and that we also don't know how they will develop in the future. Is the bulk load of the diffuse PFAS contamination still in the unsaturated zone or has it already been leached out? What we do expect is that the historical leaching to the shallow groundwater will differ per PFAS due to the history in production of different PFAS in combination with the compound specific mobility. In addition we don't know what the possible contribution of degradation of PFAS precursors in the soil to future concentrations of PFAS-20 will be and what other PFAS will be found in groundwater and added to the drinking water target? After all, the PFAS-20 are only a selection. The only thing we know is that the PFAS concentrations that were used as model input have actually been measured in shallow groundwater in recent years. With this in mind, the model results should also evaluated in relation to the actual expected PFAS concentrations in extracted groundwater. As long as the PFAS load at soil surface level does not (completely) stop, it is at least important to get a sufficient insight in the diffuse contaminant loads and the leaching into groundwater.

A second important aspect in the uncertainty of the model calculations is that the knowledge about the sorption mechanisms of PFAS on soil components is still strongly under development. This means that the retardation factors calculated for the various PFAS are still uncertain. The uncertainty about retardation in the unsaturated zone is even higher due to the presence of air and adsorption to the air-water interface. We were able to disregard this aspect by using concentrations measured in the shallow groundwater as model input. An important aspect in the uncertainty of PFAS adsorption during groundwater transport is the extent to which the transport of negatively charged PFAS is affected by anion adsorption. If this would significantly increase retardation, it would take longer for the PFAS to breakthrough at groundwater extractions sites. This will, however, lead to the same peak levels. In addition, it will take longer before a decrease of PFAS pollution at soil surface level will result in sufficient reductions in extracted groundwater will increase even faster, but will also decrease faster when the PFAS load is stopped. In all cases, stopping the PFAS load will reduce peak concentrations and accelerate the removal of PFAS already leached into the groundwater, the sooner the better.

### 4 Conclusions

As a result of atmospheric deposition, the use of pesticides and the run-off from paved surfaces, the soil in the Netherlands is diffusely contaminated with PFAS. This PFAS load may pose a threat to groundwater extraction sites, but the impact is not clear yet. For this reason, the development of PFAS in extracted groundwater of a fictitious but realistic vulnerable groundwater extraction site is calculated this quick scan for the next 200 years, starting in 2010. The results of this quick scan show that with the currently measured PFAS concentrations in shallow groundwater (median concentration = 20 PEQ/L and P90 = 99 PEQ/L) and given the compound specific retardation factors of PFAS, the PFOA equivalent concentration (PEQ) in the extracted groundwater of a vulnerable groundwater extraction site will exceed the indicative drinking water target value of 4.4 ng PEQ/L in a period of approximately 20 years. In areas with a high diffuse load, this may be the situation years earlier. According to the model calculations, which assume that the PFAS concentrations in the shallow groundwater remain constant, the PEQ concentration in the extracted groundwater remain constant, the PEQ concentration in the extracted groundwater remain constant, the PEQ concentration in the shallow groundwater remain constant, the PEQ concentration in the shallow shallow and the stracted groundwater will be 2 to 10 times higher than this target value in 2100.

Next, the calculation in which the load of the shallow groundwater stops in 2040 after 30 years of leaching shows that the PFAS concentration in the extracted groundwater will peak around 2045 and then slowly decrease. In the median scenario, zero-leaching in 2040 would result in a temporary minor exceedance of the indicative drinking water target value of 4.4 ng PEQ/L. In the upper bound scenario, this is exceedance much more pronounced. The RIVM trigger value of 22 ng PEQ/L is not exceeded in this scenario. This shows that a total ban on PFAS is effective for the protection of drinking water sources, but it will probably be too late to prevent a temporary exceedance of the indicative drinking water target value. Additional treatment of the extracted groundwater is then necessary. It is uncertain when this treatment will be necessary and for how long it will be needed. This also differs per location. The quick scan shows that this could be the case within 10 years.

Finally, the quick scan shows that the differences in mobility of the various PFAS in the subsurface lead to a delayed and differentiated breakthrough of PFAS in extracted groundwater. The short-chain PFAS, which are often linked to the deposition of fluorinated gases, flow to the extraction wells at almost the same rate as the groundwater, while PFAS with longer  $CF_2$  chain lengths will be transported much slower. PFAS with  $CF_2$  chain lengths longer than 10 have very limited mobility in the subsurface and are therefore unlikely to pose a threat to groundwater extraction site in the relatively longer term.

The assumption of constant concentrations in the shallow groundwater is a rough approximation in this calculation. Given the start of PFAS production around 1950, the PFAS pollution of groundwater has likely started earlier in reality, but the PFAS composition and concentration development are unknown. It is not impossible that leaching concentrations will increase in the future because the peak load from the diffuse PFAS contamination is probably still largely present in the unsaturated zone. On the other hand, the production of PFOA and PFOS has been banned for some time, but it is not known when this affects leaching concentration to the shallow groundwater. Finally, a part of the atmospheric deposition also originates outside the EU. All this means that the assumed zero-concentration from 2040 onwards in the 'ban on PFAS' scenario are also uncertain. It is unknown how long the legacy of these substances in leaching into the groundwater will be when PFAS production completely stops and what the effect is of the degradation of PFAS precursors on the concentrations of PFAS-20.

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