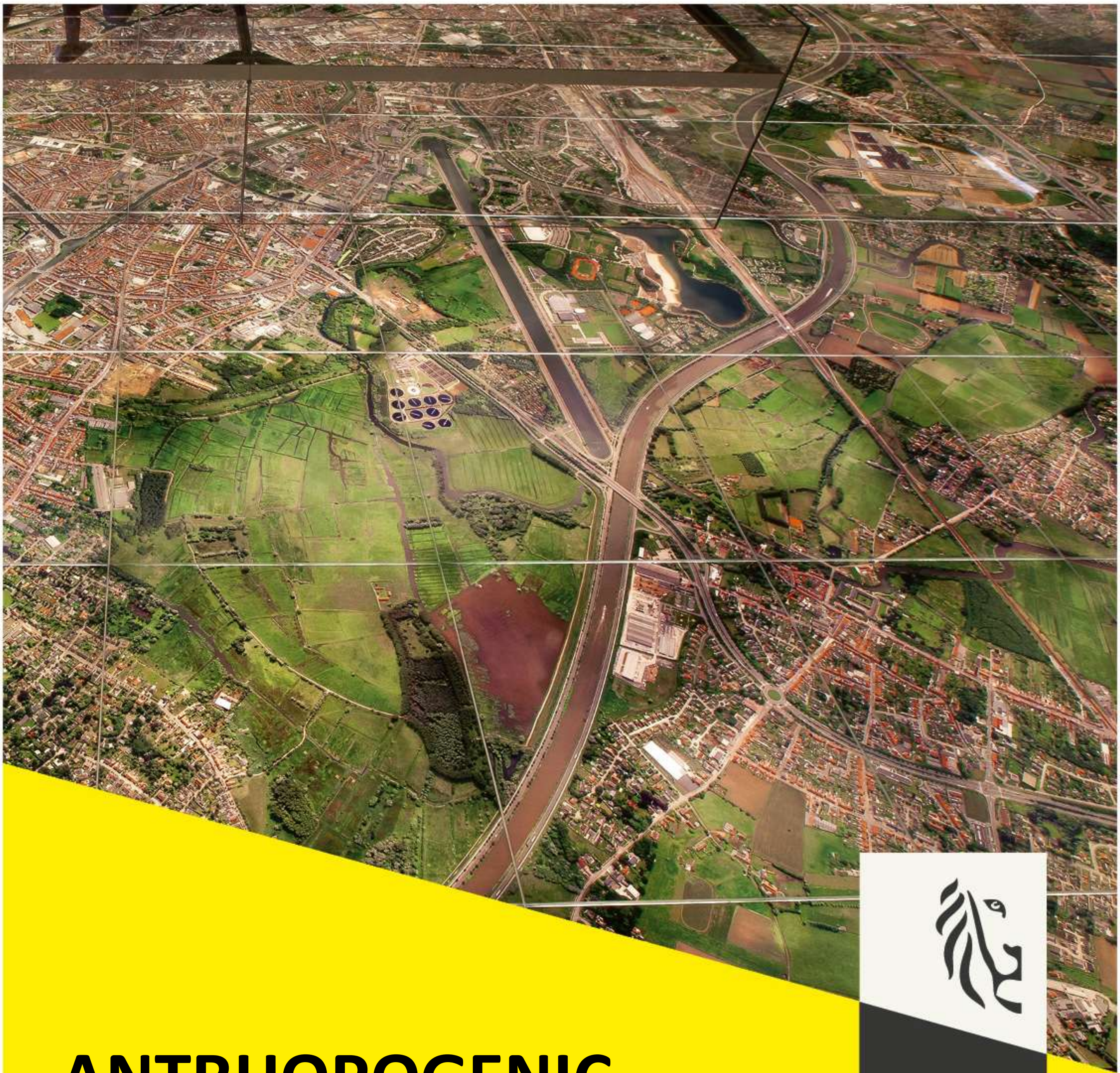


ANTRHOPOGENIC BACKGROUND CONCENTRATIONS FOR PFAS IN SOIL AND GROUNDWATER

Flanders
State of the Art

WE MAKE TOMORROW BEAUTIFUL
OVAM

OVAM.VLAANDEREN.BE

//

ANTHROPOGENIC BACKGROUND CONCENTRATIONS FOR PFAS IN SOIL AND GROUNDWATER.

Publication date / 2.06.2024

//

This work was carried out in the framework of the European Partnership for the Assessment of Risks from Chemicals (PARC) and has received funding from the European Union's Horizon Europe research and innovation programme under Grant Agreement No 101057014. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the Health and Digital Executive Agency. Neither the European Union nor the granting authority can be held responsible for them

DOCUMENT DESCRIPTION

1 *Publication title:*
DETERMINING ANTHROPOGENIC BACKGROUND CONCENTRATIONS FOR PFAS IN SOIL AND GROUNDWATER

2 *Responsible Publisher:*
OVAM

3 *Legal Deposit Number: D/2024/5024/38*

4 *Keywords:*
anthropogenic background concentration, PFAS, groundwater, soil

5 *Summary*:
This report includes a study conducted to determine diffuse anthropogenic presence of PFAS in groundwater in Flanders. For this purpose, groundwater and soil samples were collected at unsuspected locations throughout Flanders. This means that sampling locations were selected where no known PFAS-contaminated sources are present or have been in the past.

6 *Number of pages: 131*

7 *Number of tables and figures: /*

8 *Date of publication:*
2024

9 *Price*: /*

10 *Guidance group and/or author:*
Authors: Dorien Gorteman (Arcadis), Karen Van Geert (Arcadis), Sigrid Willems (Witteveen+Bos), Joachim Jacobs (Witteveen+Bos).
Guidance group: OVAM, VMM

11 *Contacts:*
Griet Van Gestel (OVAM) , Laetitia Six (OVAM)

12 *Other titles on this topic: /*

Table of Content

Overview tables

Overview figures

DEFINITIONS

Anthropogenic background concentrations	The background values for non - naturally occurring substances, set equal to the 90-percentile upper limit of the available data.
Reporting limit (RL)	The value below which a component is reported as not quantifiable ('<'). The reporting limit is the minimum concentration of a contaminant that a laboratory needs to be able to officially report, as agreed in specific analysis protocols
Limit of detection (LOD)	The output signal or concentration above which it can be stated with a specified confidence level, that a sample differs from a blank sample containing no relevant analyte to be quantified.
limit of quantification LOQ)	The limit of quantification (LOQ) is the lowest analyte concentration that can be quantitatively detected with a stated accuracy and precision. The limit of quantification can be calculated using a suitable standard or sample and can be obtained from the lowest calibration point on the calibration curve, excluding the blank. The limits of quantification for the analyses performed as part of this study are given in Annex 3.
Sum PFAS quantitative	Sum of individual PFAS that can be quantitatively determined according to the CMA (Compendium for sampling & analysis for soil) or the WAC (compendium for sampling & analysis for groundwater). In performing the analyses as part of the present study, these components were as follows: **Soil**: PFBA, PFPeA, PFHxA, PFHPA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFOSA, MePFOSA, EtPFOSA, MePFOSAA, EtPFOSAA, 4:2 FTS, 6:2 FTS, 8:2 FTS, 8:2 diPAP, HFPO-DA, DONA, PFECHS, PFBSA, MePFBSA, PFHxSA **Groundwater:** PFBA, PFPeA, PFHxA, PFHPA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, PFHxDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFOSA, MePFOSA, EtPFOSA, MePFOSAA, EtPFOSAA, 4:2 FTS, 6:2 FTS, 8:2 FTS, 8:2 diPAP, HFPO-DA, DONA, PFECHS, PFBSA, MePFBSA, MePFBSAA, PFHxSA
Sum PFAS indicative	Sum of individual PFAS that can be determined indicatively according to the CMA (for soil) or the WAC (groundwater). The components

	involved in the execution of the analyses for the present study are as follows: **Soil:** PFODA, PFDoDS, 6:2 diPAP, 6:2/8:2 diPAP, 10:2 FTS, MePFBSAA **Groundwater:** PFTrDA, PFODA, PFDoDS, PFUnDS, PFTrDS, 10:2 FTS, 6:2 diPAP, 6:2/8:2 diPAP
Sum of PFAS total	Sum of quantitative and indicative PFAS as defined above.
Sum of PFAS (EU DWD 20).	Sum of 20 individual PFAS components in groundwater included in the EU Drinking Water Directive (EU DWD): PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUnDS, PFDoDS, PFTrDS
Sum PFAS EFSA-4	Sum of PFOS, PFOA, PFNA and PFHxS

SUMMARY

This study aims to determine background concentrations of PFAS in soil and groundwater in Flanders. As defined in the Flemish Soil Decree, “background concentrations” represent the level of contaminants found as background in non-contaminated soils, including groundwater. Since PFAS are not naturally occurring, the background concentrations will in this case reflect the diffuse anthropogenic presence of PFAS in soil and groundwater.

To derive these anthropogenic background levels, soil and groundwater were collected at unsuspected locations across Flanders. Sampling locations were selected by excluding areas potentially impacted by PFAS contamination.

To achieve this, spatial data from various sources were compiled into a single map

1) Known and presumed PFAS sources :
   - “No regret measures” zones (PFAS explorer DOV[1]) – These denote areas with suspected past or present PFAS activity where precautionary measures were put in place by the Government (Department of Care) to avoid exposure to PFAS
   - Fire fighting training sites and historical fire incidents (PFAS explorer DOV)
   - Previously reported PFAS detections in groundwater (groundwater results layer in PFAS explorer DOV)
   - Known landfills in Flanders (OVAM data layer)
   - Waste water treatment plants (Geopunt layer)
   - Locations with suspected PFAS activities based on the ‘land information register’ (OVAM)

2) Excluding additional contaminant interference (as they can impact reporting limits for PFAS) :
   - Sediment pollution risk areas identified in "Identifying hotspots of sediment pollution linked to risk activities" (OVAM.be) - This list was expanded to include activities linked to brominated flame retardants and PFAS.
   - Locations with prior soil investigations (defined by OVAM dossier number)

By excluding these areas, the study aimed to collect samples from locations with minimal background PFAS influence, allowing for a more accurate representation of the diffuse anthropogenic PFAS presence in Flanders' soil and groundwater.

A comprehensive area coverage was achieved by selecting 147 monitoring wells with filters in the phreatic groundwater from the VMM monitoring network across Flanders. Soil samples were also collected at 73 of these locations. Sampling and analysis were conducted between February and June 2023. Additionally, 240

[1] https://www.dov.vlaanderen.be/portaal/?module=pfasverkenner

monitoring wells from the groundwater monitoring network were sampled and analyzed for PFAS by VMM (Flemish Environmental Agency) simultaneously with the sampling commissioned by OVAM.

Groundwater

Groundwater samples from 387 locations were analyzed for 42 PFAS according to the WAC/IV/A/025 (version 12/2022, Official Journal 6/7/2023). In 341 of these wells, at least 1 PFAS compound is measured above its limit of quantification.

Table A lists the key indicators of the four most common PFAS compounds detected in the 387 monitoring wells. PFBA and PFBS are detected in more than 50% of samples. PFOA is detected in 49% of samples and PFOS in 34% of samples. The remaining PFAS compounds were detected in less than 33% of the samples.

Table A: Summary of results of the four most common PFAS detected in groundwater.

	Key indicators including results below limit of quantification					Key indicators from results above limit of quantification (ng/L)			
component	Number of measurements	%>LOQ	median (P50) (ng/L)	P90 (ng/L)	P95 (ng/L)	Min of concentrations above LOQ	Maximum measured value	average	median (P50)
PFBA	370	59%	3,0	21,1	34,5	1,0	201,0	13,4	6,8
PFBS	385	57%	2,0	9,5	13,8	1,0	74,0	6,2	3,9
PFOA Total	387	49%	< KL	8,1	13,2	1,0	112,9	6,5	3,0
PFOS Total	387	34%	< KL	5,0	8,0	1,0	26,0	3,2	2,0

Anthropogenic background concentration derivation

To determine anthropogenic background concentrations for the four most common PFAS compounds in non-suspicious areas, the P90 value (90th percentile) was calculated. Outlier checks were performed, and adjustments were made as needed.

For PFAS compounds detected in less than half of the samples, insufficient data exists to statistically derive Annex background value.

Given their widespread occurrence, anthropogenic background concentrations are proposed for PFBA, PFBS, and PFOA in groundwater. PFOA approaches this value (49%). While PFOS is often analyzed in soil investigations and has a soil anthropogenic background concentration in Flanders, its lower detection frequency in groundwater (34%) limits its inclusion in this study. However, the P90 value for PFOS in groundwater is provided in Table B for reference.

Table B: Proposed anthropogenic background concentrations for PFBA, PFBS and $PFOA_{total}$ in groundwater and indicative P90 value for $PFOS_{total}$ in groundwater

	P90 in ng/L
PFBA	21,0
PFBS	9,4
$PFOA_{total}$	8,0
*$PFOS_{total}$**	*5,0*

*For PFOS, the P90 is given for information only, it is not proposed as an anthropogenic background value.

Additionally, the P90 value was also calculated for the following sum parameters:

- PFAS sum quantitative: the sum of all quantifiable PFAS compounds
- PFAS sum 20: The sum of the 20 PFAS included in the European Drinking Water Directive (DWD)
- PFAS total: the sum of all detected PFAS compounds, including those that are measured indicatively

These concentrations are presented in Table C. It's important to note that PFAS compounds below the limits of quantification are not included in the sums (lower bound principle).

Table C: Calculated P90 value for the Sum Parameters.

	P90 in ng/L
Sum PFAS quantitative	48,0
Sum of PFAS (EU DWD20).	47,0
Sum of PFAS total	48,4

Comparison with existing standards and regulations

The current EU Drinking Water Directive limit for the sum of 20 PFAS compounds (PFAS sum EU DWD 20) is 100 ng/L. A significant portion is covered by the anthropogenic background concentration of PFBA alone, namely 21%.

The proposed anthropogenic background concentration for PBFA also exceeds the discharge standard in Flanders (i.e. 20 ng PFAS/L).

The European Commission has proposed an environmental quality standard for groundwater and surface water of 4.4 ng/L PFAS-24 expressed as PFOA equivalents using the relative potency factor. This sums 24 components using relative toxicity factors, where PFOA has a factor of 1 and PFOS has a factor of 2. Notably, the proposed anthropogenic background concentrations (P90) for PFOA and PFOS individually already exceed this value (4.4 ng/L). Although 3 of the 24 PFAS compounds were not analyzed in the current study, the proposed environmental quality standard of 4.4 ng/L is already exceeded in 37% of sampled locations in non-suspicious areas.

Soil

In this study, a total of 73 soil samples were analyzed for PFAS. Additionally, data from 50 soil samples taken in a previous study (OVAM, 2021) was incorporated to derive PFAS anthropogenic background concentrations for soil.

Table D: summary results PFAS in groundwater - Switzerland lists the key indicators of the three most common PFAS compounds detected in the 123 soil samples. Only PFOS is detected in more than 50% of samples. PFOA is detected in 43% of samples and PFBA in 49% of samples.

Table D: Summary of results of the four most common PFAS detected in soil.

	Key indicators including results below limit of quantification					Key indicators of results above limit of quantification (µg/kg dm)			
Component	Number of measurements	%>LOQ	P50 (µg/kg dm)	P90 (µg/kg dm)	P95 (µg/kg dm)	Min of concentrations above LOQ	Maximum measured value	average	Median (P50)
PFBA	123	49%	0,5	0,9	1,1	0,4	2,6	0,8	0,7
$PFOA_{total}$	123	43%	0,5	0,8	0,9	0,2	2,2	0,6	0,5
$PFOS_{total}$	123	72%	0,6	1,5	1,7	0,2	2,6	0,9	0,8

Anthropogenic background concentration derivation

Outlier checks were performed, and adjustments were made as needed. The 90 percentile of the analyzed samples in the present and previous study yield a value of 1.4 µg/kg dw for $PFOS_{total}$ and 0.8 µg/kg dw for $PFOA_{total}$. Given the limited differences between the current published anthropogenic background concentrations for PFOS and PFOA (OVAM, 2021) and the 90-percentile values calculated in this study, it is recommended to maintain the existing values.

Insufficient data is available above the limit of quantification to statistically derive a representative anthropogenic background concentration for the other PFAS compounds.

Recommendations for further investigation

The samples in the present study were taken mainly from agricultural or natural areas and may not necessarily be representative of urban or industrial areas. Given the widespread use of PFAS in various applications, an increased diffuse presence of PFAS also be expected in urban and industrial areas. Further research in these areas can provide valuable insights into the extent and impact of anthropogenic diffuse PFAS contamination.

The derived anthropogenic background concentrations for PFOA, PFBA, and PFBS in groundwater can be effectively used in soil investigations to interpret obtained results. These concentrations can help distinguish between background levels of PFAS and contamination associated with specific sources. By utilizing these anthropogenic background concentrations, environmental consultants can more accurately assess the extent of contamination.

The results from the present study and more specifically the derived anthropogenic background concentrations (PFOA, PFBA and PFBS) can be used when interpreting results in a soil investigation. The anthropogenic background concentrations already take up a significant portion of the value currently used to delimit a contaminant (100 ng/L for sum PFAS EU DWD 20). A recognized soil experts can utilize the results from the present study to interpret contamination delimitation. The values can be used as motivation to demonstrate the extent to which contamination can likely be attributed to the investigated source.

1 INTRODUCTION

The purpose of this study is to determine background values for PFAS in groundwater and to collect additional data to update the previously determined background target values of PFAS in soil.

'background values' as defined in the Soil Decree are "levels of contaminants found as background in unpolluted soils" where, according to the Soil Decree, groundwater is also part of soil. Because PFAS do not occur naturally in the environment, this refers to the diffuse anthropogenic presence of PFAS in the soil and in groundwater.

Delineating PFAS contamination in groundwater from a particular source does not appear to be easy in practice. On the one hand, PFAS contamination plumes can be very extensive. On the other hand, it is suspected that the groundwater is diffusely contaminated with PFAS making it very difficult in practice to determine the extent of the contamination plume.

The purpose of the present study is to determine whether PFAS is commonly found in phreatic groundwater in Flanders, and how these data can be used in the assessment of exploratory soil investigations conducted at locations where PFAS is considered a suspect substance or is detected. A distinction must be made between the groundwater plume originating from a source and any other (regional) increase. Distinguishing contamination related to a source versus diffuse contamination is crucial in the legal-administrative context of the Soil Decree, where investigation and remediation obligations are assigned to operators, owners, users or other parties linked to the source site.

Anthropogenic background concentrations in soil have already been derived for PFOA and PFOS on a limited dataset of 50 soil samples (OVAM, 2021). Through additional soil measurements, this present study aims to verify or adjust the previously derived anthropogenic background concentrations.

<u>Reading Guide</u>
Chapter 2 provides a brief overview of possible sources and uses of PFAS, as well as an overview of PFAS analysis methods. Additionally, a summary of available international information regarding the diffuse presence of PFAS is provided. Based on the insights in Chapter 2, a methodology for the selection of PFAS unsuspected sites and a sampling plan is prepared in Chapter 3. Chapter 4 presents the sampling and analytical results. In Chapter 5 and 6 anthropogenic background concentrations for groundwater and soil are derived by statistical evaluation. In Chapter 7 and 8 additional observations are reported regarding the combined occurrence of PFAS compounds and more specific TOP analyses. Finally, Chapter 9 includes the conclusion and recommendations.

2 BRIEF LITERATURE REVIEW

This chapter provides a brief overview of potential sources and uses of PFAS. Based on these insights, a methodology is then developed for the **selection of PFAS unsuspected** sites. Additionally, an overview of **PFAS analysis methods** is compiled. For comparison purposes, a summary of **available international information** regarding the diffuse presence of PFAS is gathered.

2.1 MAIN PFAS USES

Use of fluorinated firefighting foam

Fluorinated firefighting foams are found in Class B foams used for liquid fires. From the 1960s-1970s, PFOS compounds were used in these foams. The addition of PFOS to foam was banned in 2011, initially transitioning to the addition of PFOA, and subsequently shifting to short chain PFAS (C6 chains instead of C8 chains; for example, PFHxS, PFHxA, 6:2 FTS, etc.). From 2022 onwards, PFOA may not be used if the foam cannot be captured after use. By 2025, PFOA-containing foams will be completely phased out. A proposal to phase out all PFAS in fire-fighting foams is currently being evaluated at the EU level.

PFAS-based firefighting foams for extinguishing flammable liquids (liquid hydrocarbons) may have been used in incidents at airports, military training sites/airports, refineries, and bulk chemical storage and firefighting training areas. (OVAM, 2022)

Galvanization

In galvanization or electroplating, PFOS is primarily used to reduce employees' exposure to chromium-VI during chromium plating. PFOS is used to lower the surface tension of the chromic acid bath, which reduces the size of bubbles and leads to fewer bubbles burst at the interface, resulting in less airborne chromium VI (i.e., mist suppressant) (OVAM, 2022).

Water- and stain-repellent application

PFAS are used to make products such as clothing, shoes, tents, umbrellas, carpets, and furniture water- and stain-repellent. Often, PFAS polymers are applied. These polymers may contain PFAS residues from the production process or they break down into fluorochemical telomers like FTOHs, as well as perfluorinated carboxylic acids such as PFOA and perfluorohexanoic acid (PFHxA) (OVAM, 2022).

Paper industry

PFAS are used in the production of grease- and water-repellent paper commonly used for food packaging. During production, mainly polyfluoroalkyl phosphoric acids (PAPs and diPAPs) are used. Other PFAS are or were also used in the paper industry (OVAM, 2022).

Cosmetics

PFAS are used in the cosmetics industry for various purposes. They can be present in sunscreens and body lotions to make them water-resistant. PFAS are also used in cosmetics as anti-caking agents, antistatic agents, stabilizers, emulsifiers, surfactants, film formers, viscosity regulators and solvents (OVAM, 2022).

Household products and items

PFAS can be present in hydraulic fluids, insecticides, cleaning products, lubricants, paints and varnishers, as well as waxes for floors, cars, planes, and snowboards. Non-stick pans and cookware can also contain PFAS (Teflon) (OVAM, 2022).

Photographic Industry

In the photographic industry, PFAS products were used as solvents, pigments and developing fluids. (OVAM, 2022)

Landfills and wastewater treatment plants

Landfills can be a source of PFAS due to the degradation of PFAS-containing materials such as carpets, furniture, clothing, and waterproofing agents.

Wastewater treatment plants receive waste streams from processing industries, residues from firefighting activities, and household wastewater enriched by PFAS-containing household products (OVAM, 2022).

Soil recycling centers, sludge processing and waste incineration

Soil recycling centers , temporary storage sites for soils , sludge processing and waste incinerators can also be suspected sources of PFAS when processing soils, sludge, or waste originating from PFAS-suspect activities (OVAM, 2022).

2.2 KNOWN PRODUCTION SITES IN FLANDERS

3M production site at Zwijndrecht

PFAS production before 2001 was mainly dominated by 3M's electrochemical fluorination process, which formed 30-45% perfluorooctane sulfonfluoride (PFOS) as the main product, along with other PFCAs and PFSAs. This process was applied at the 3M site in Zwijndrecht. Since 2001, the production of PFAS by electrochemical fluorination has been strongly reduced due to concerns about the environmental impact of PFOS and telomerization became the main method of PFAS production. In this telomerization process, no PFOS or precursors of PFOS are formed (OVAM, 2018).

DuPont (de Nemours) in Mechelen

DuPont's activities in Mechelen were started in 1958, focusing initially on the production of resins, coatings, and plastics. Since 1966, this location has also been involved in the production of Teflon coatings. In the production of Teflon (PTFE), PFOA is used as an additive.

In mid-2015, DuPont split off its Performance Chemicals division (high-performance chemicals) into a separate company, The Chemours Company. The Mechelen site (and Dordrecht, among others) is responsible for the development and production of fluoroproducts within Chemours Company.

2.3 ANALYTICAL METHODS FOR PFAS IN SOIL AND GROUNDWATER

This section provides an overview of both target and non-target analyses for PFAS in soil and in groundwater.

2.3.1 Analytical methods in Flanders (WAC and CMA) - target analyses.

The current standard method for PFAS in groundwater in Flanders is a target analysis described in the WAC/IV/A/025 (ISO 25101:2009) (https://reflabos.vito.be/2021/WAC_IV_A_025.pdf).

The current standard method for PFAS in soil in Flanders is a target analysis described in the CMA/3/D. (https://reflabos.vito.be/2023/CMA_3_D.pdf).

2.3.2 Alternative analytic methods

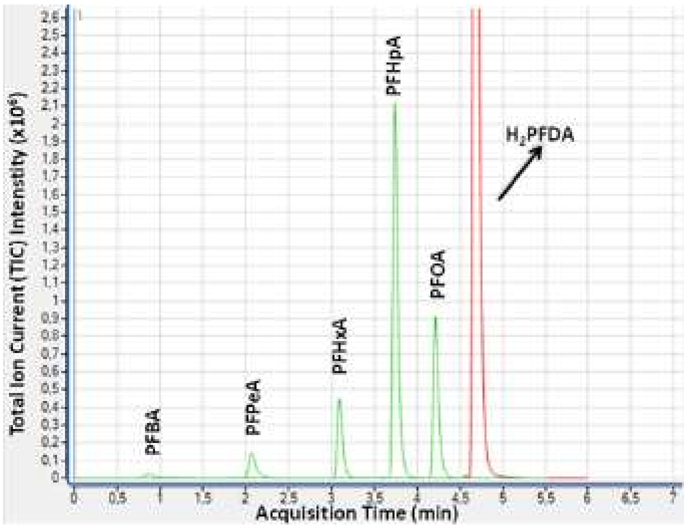
With current analytical methods used in Flanders, it is possible to quantify 34 different PFAS components in groundwater and in soil. six other components in soil and eight other components in groundwater can be measured indicatively, with a higher LOQ. (see definitions "sum PFAS quantitative" and "sum PFAS indicative").

However, there are many other PFAS components that cannot be detected by this method. The use of EOF (Extractable OrganoFluor) and AOF (Adsorbable OrganoFluor) techniques can help determine the total amount of fluorine in a sample as a proxy for the total PFAS amount. Furthermore, PFAS precursors can also be converted to persistent perfluorocarbons. The presence of these precursors can be demonstrated by TOP (Total Oxidizable Precursors) analysis.

TOP (Total Oxidizable Precursor) assays (also called TOPA, Total Oxidizable Precursor Assay)

TOP analysis uses hydroxyl radical-based oxidation reactions, converting precursors to perfluoroalkyl acids (PFAAs) that can be detected in a target analysis.

In the example below, several PFAS precursors were added to water. The concentrations were measured before and after TOP analysis. It can be clearly seen how the precursors are converted into measurable end products. Via TOP analysis, it cannot be shown which precursor is present, only that they are present (Eurofins, 2023).



Red line: Water with precursor H_2 PFDA **for** TOP assay

Green line: Water with precursor H_2 PFDA **after** TOP assay: PFBA, PFPeA, PFHxA, PFHpA and PFOA are detected, H_2 PFDA not.

EOF (Extractable OrganoFluor) and AOF (Adsorbable OrganoFluor) Analysis.

EOF or AOF analysis can be used to estimate the amount of PFAS precursors and PFAS compounds in a sample based on measured fluorine. This includes fluorine from PFAS compounds not analyzed by the current target CMA/WAC method.

With EOF analysis , the fluorine compounds are extracted and the extract is combusted at high temperatures. The total amount of released fluorine can be determined in this process. AOF (Adsorbable OrganoFluor) involves burning the adsorbent used to capture the fluorine compounds. Both EOF and AOF utilize combustion ion chromatography (Combustion IC). This allows for the estimation of the total amount of PFAS components in a sample without determining the molecular structures and properties. Therefore, it is also referred to as a 'non-target analysis'. Additionally, no distinction is made between inorganic and organically bound fluorine. Thorough sample preparation is very important in this case. (Aro, et al., 2022)

2.3.3 Summary comparison of analytical methods and application in the present study

Both TOP and EOF/AOF offer some advantages and disadvantages compared to current CMA/WAC target analyses. Table A provides a brief summary.

In the present study, in addition to the conventional WAC/CMA target analysis, the TOP assay will be used because this technique has a relatively high sensitivity (low limit of quantification) which is important to determine target values, since the expected concentrations are low in PFAS-unsuspected areas.

Table A: Comparison of methods (adapted from (Environment Agency - UK, 2021))

EDF/AOF		TOPA		Target Analysis	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**	**Advantages**	**Disadvantages**
Generates ΣPFAS value.	Non-target analysis method - no uniform interpretation of results	Estimation of PFAS precursors	No uniform interpretation of results due to high variability in oxidized end products	Standardized method	Measures only specific predetermined PFAS components based on an "internal standard per component"
Relatively low cost compared to target analysis (CMA/WAC)	Interference from 'non PFAS' such as drugs and pesticides possible	Provides indicative data on the chain length of PFAS present, which can help in source identification.	Does not consider non-PFAA precursors and next-generation PFAS (e.g., Gen-X).	Accurate and sensitive	No indications on possible precursors
Proper general screening of PFAS contamination present	Lack of standardized methods leads to variable results between labs.	Sensitive (0.1 - 1ng/L)			
/	Possibly not sensitive enough (0.1-0.5 µg/L)	/	Exactly which precursor is oxidized cannot be ascertained		
/	EOF - all matrices AOF - aqueous samples only	/	Variation possible due to difference in steel preparation		

2.4 AVAILABLE NATIONAL AND INTERNATIONAL INFORMATION REGARDING DIFFUSE PFAS CONTAMINATION

2.4.1 International survey

A brief international survey was conducted to gather information on available data and research related to diffuse PFAS contamination in groundwater. The survey was sent to various international contacts in Europe.

The survey inquired about relevant information concerning diffuse PFAS contamination in groundwater:

- Is the presence of diffuse PFAS contamination in groundwater being investigated? Or will it be in the future?
- What measures are currently taken?
- What data are available? Are regional/national/European data available?
- Have specific background values been determined?
- Is a distinction made between suspected and unsuspected sites?
- Is a distinction made between land use types and/or soil types?
- Which PFAS are primarily found in diffuse contaminations?
- What are the insights regarding the distribution of PFAS in groundwater?
- Are non-target analyses such as TOP, AOF, EOF used?

Responses were received from the Netherlands, France, United Kingdom, Denmark, Germany and Italy. The responses indicate that there is little international data regarding background concentrations or diffuse occurrence of PFAS in groundwater. A brief summary of the responses obtained is attached in Annex 11.

The relevant studies regarding available data will be further explained in the following section.

2.4.2 International studies and data

A review of available studies on the presence of PFAS in groundwater reveals that PFAS is found worldwide in water and wastewater (Kurwadkar, et al., 2022). This shows that PFAS is detected in different continents independent of the level of industrial development. The presence of PFAS far from potential sources suggests that long-range atmospheric transport is an important pathway and may determine the diffuse anthropogenic background concentration in soil . PFAS in soil can then also enter groundwater through leaching, leading to diffuse groundwater contamination. Reuse of wastewater in irrigation can also lead to diffuse PFAS contamination in soil and groundwater. PFAS contaminations in groundwater linked to specific sources can also form large plume areas, contributing to diffuse contamination.

Sweden

In Sweden, a study was conducted that investigated the presence of PFAS in 502 of water samples taken from Swedish groundwater, surface water and wastewater treatment plants ((Swedish University of Agricultural Sciences, 2016).

The aim of this study was to establish reference values of PFAS in the aquatic environment and to use these values as a basis for evaluating potential sources. The study mainly focused on regions crucial for drinking water supply. The concentration of the total PFAS (26 components) averaged 49 ng/L in groundwater with a median of 0.4 ng/L. These 26 components are also the main components in the analysis package used in Flanders, 9 of them can be considered precursors (see Table B).

Table B: PFAS analyzed in study (Swedish University of Agricultural Sciences, 2016).

PFBA	PFUnDA	PFHxS	MeFOSA*
PFPeA	PFDoDA	PFOS	MeFOSE*
PFhxA	PFTrDA	PFDS	EtFOSA*
PFHpA	PFTeDA	FOSAA*	6:2 FTSA*
PFOA	PFHxDA	MeFOSAA*	EtFOSE*
PFNA	PFOcDA	EtFOSAA*	
PFDA	PFBS	FOSA*	

*considered a precursors in this study

The high average value can be related to some outliers. In addition, surface water concentrations were also determined in some lakes where the anthropogenic impact is low. The concentrations measured here are presumably caused by atmospheric deposition. A mean concentration of total PFAS of 3.4 ng/L was found in 10 samples. The composition of sum PFAS in groundwater showed contributions from both PFSAs, PFCAs and PFAS precursors. In surface water, the sum PFAS was largely determined by short-chain PFAS. In contrast, a significant ratio of PFHxS to PFOS was generally observed in groundwater while in surface water the concentrations were in the same order of magnitude. This could be due to the stronger sorption of PFOS to soil particles compared to PFHxS which could lead to an increasing fraction of PFHxS in groundwater due to sorption of PFOS to soil particles during the leaching process.

Denmark

In Denmark, analyses of PFAS in groundwater are stored in a national database 'JUPITER' (Geological survey of Denmark and Greenland, 2023), similar to DOV in Flanders. Exceedances of the drinking water standard (0.1 µg/L) are mainly observed in urban areas. Almost no concentrations above the drinking water standard are found in agricultural areas or more remote regions. Research on diffuse PFAS contamination is still ongoing and more information is being collected on the possible sources and pathways. Concrete conclusions cannot yet be drawn on this matter.

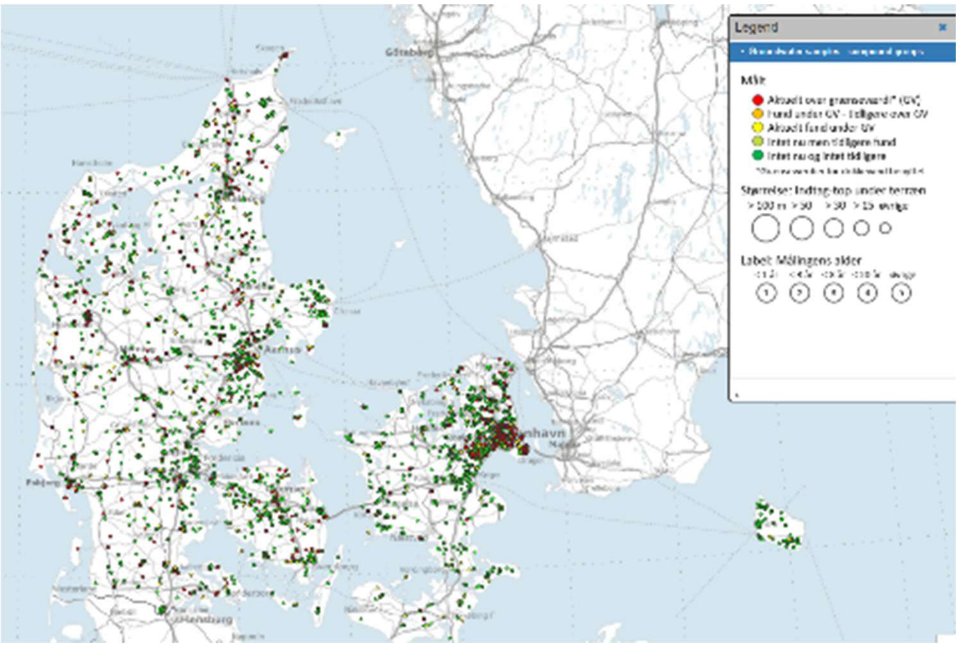


Figure 1 Overview of PFAS results in Denmark. (Geological survey of Denmark and Greenland, 2023)

Netherlands

In the Netherlands, a study was published in 2021 with analytical results for PFAS in groundwater. The results were divided into phreatic (< 10 m-below ground level (bgl)) and medium to deep groundwater (10-25 m-bgl). (RIVM, 2021). The Dutch study did not investigate the proximity of the sampling locations to potential PFAS sources. The samples from the phreatic groundwater originated from urban or industrial areas. Higher values were measured in the phreatic groundwater compared to deeper groundwater. Furthermore, fewer different substances were found at deeper levels. This aligns with the current understanding of PFAS compounds, where a portion of them is mobile and spreads in groundwater, while another part is less mobile due to easier binding to the soil. The results for the phreatic groundwater are summarized in the table below.

Table C: Statistics of detected (>reporting limit, >RG) PFAS in phreatic groundwater in ng/L. A total of 16 of the 30 PFAS analyzed were detected. Substances in bold were not detected in deeper groundwater. (RIVM, 2021)

ID	PFAS	PFAS code	CAS-nummer	n	% <RG	RG [ng/l]	Metingen [ng/l] min	P50 [1]	P95 [1]	m
1	6:2.FTS.(6:2.fluortelomeer.sulfonzuur)	6:2.FTS	27619-97-2	101	87	0,3	0,3	0,3	1,2	6,
2	**8:2.DiPAP.(8:2.fluortelomeer.fosfaat .diester)**	8:2.DiPAP	678-41-1	101	99	2,0	2,0	2,0	2,0	14
3	PFBA.(perfluorbutaanzuur)	PFBA	375-22-4	101	15	0,6	0,6	5,5	21,0	23
4	PFBS.(perfluorbutaansulfonzuur)	PFBS	375-73-5	101	11	0,3	0,3	3,2	20,0	48
5	**PFDA.(perfluordecaanzuur)**	PFDA	335-76-2	101	95	0,6	0,6	0,6	0,6	2,
6	PFHpA.(perfluorheptaanzuur)	PFHpA	375-85-9	101	25	0,3	0,3	1,4	10,0	16
7	**PFHpS.(perfluorheptaansulfonzuur)**	PFHpS	375-92-8	101	94	0,3	0,3	0,3	0,3	12
8	PFHxA.(perfluorhexaanzuur)	PFHxA	307-24-4	101	24	0,3	0,3	1,8	15,0	99
9	PFHxS.(perfluorhexaansulfonzuur)	PFHxS	355-46-4	101	39	0,3	0,3	0,6	7,0	30
10	PFNA.(perfluornonaanzuur)	PFNA	375-95-1	101	80	0,6	0,6	0,6	1,5	3,
11	PFOA.lineair.(perfluoroctaanzuur)	PFOA.lineair	335-67-1	101	11	0,3	0,3	6,0	35,0	63
12	PFOA.vertakt.(perfluoroctaanzuur)	PFOA.vertakt	-	101	18	0,3	0,3	1,6	8,1	22
13	PFOS.lineair.(perfluoroctaansulfonzuur)	PFOS.lineair	1763-23-1	101	44	0,2	0,2	0,3	6,7	96
14	PFOS.vertakt.(perfluoroctaansulfonzuur)	PFOS.vertakt	-	101	36	0,2	0,2	0,7	13,0	82
15	PFPeA.(perfluorpentaanzuur)	PFPeA	2706-90-3	101	37	0,6 – 6,0	0,6	1,7	15,0	11
16	PFPeS.(perfluorpentaansulfonzuur)	PFPeS	2706-91-4	101	60	0,3	0,3	0,3	1,2	32

1) 50 en 95 percentielwaarde van de metingen

United Kingdom

In the United Kingdom, groundwater is also currently being monitored for PFAS. The quantitative data are available on an online platform ((Environment Agency - UK).A first summary study (Environment Agency - UK, 2021) concludes that PFAS are widely distributed in UK ground and surface waters. Short-chain PFAS (PFBS and PFHxS) are found in up to 39% of samples. PFOS and PFOA in 26% and 29% of samples, respectively. The presence of PFOS in freshwater fauna and accumulation in marine animals (fish, otters) indicates a diffuse PFAS contamination in water. Further monitoring should provide a clearer picture on this.

PFAS are monitored in a nationwide groundwater monitoring network. Each point is sampled triennially. Since PFAS has not been included in the program for a long time, only 1 result is available for most points. Until now, groundwater samples have only been analyzed using a semi-quantitative method, so no concentrations are provided in the report.

Switzerland

Switzerland also published data on PFAS in groundwater across the country (Federal Office for the Environment (FOEN, Switzerland), 2023). These are 519 results from the groundwater monitoring network. The report indicates at how many of the sites a PFAS component above the limit of quantification, 1 ng/L, 10ng/L or 100 ng/L was found. 26 components were analyzed.

In 25% of the samples, the value of 10 ng/L was exceeded for the sum of these compounds. 2% of the samples exceeded a value of 100 ng/L, for the same percentage of sites (2%) 100 ng/L was also exceeded when the sum of the 20 components from the EU Drinking Water Directive was taken. The value of 4.4 ng/L for the weighted sum of 24 PFAS, proposed as a new environmental quality standard, was exceeded in 25% of the sites.

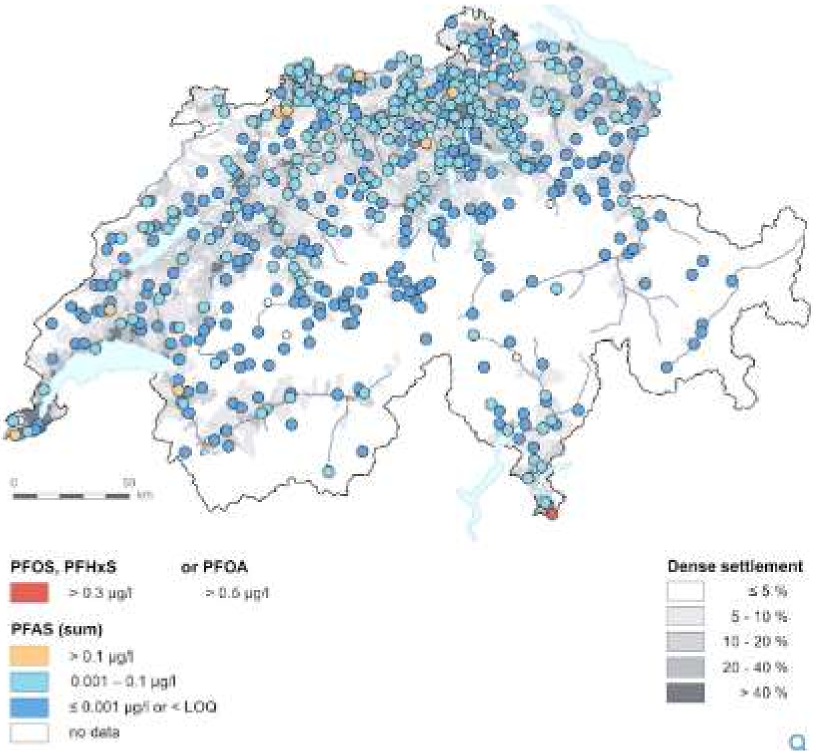


Figure 2: Overview of PFAS in groundwater - Switzerland (Federal Office for the Environment (FOEN, Switzerland), 2023)

Table D: summary results PFAS in groundwater - Switzerland (Federal Office for the Environment (FOEN, Switzerland), 2023)

National Groundwater Monitoring NAQUA

hydrogeologie@bafu.admin.ch

PFAS in groundwater

Period of time 2021

Monitoring site Module SPEZ and TREND

Statistics Maximum value per monitoring site

Substance		Monitoring sites [number]					Monitoring sites [%]
			Concentration				Concentration
		sampled	≥LOQ	>0.001 µg/l	>0.01 µg/l	>0.1 µg/l	>0.1 µg
Perfluorinated carboxylic acids							
PFBA	Perfluorbutansäure	519	145	145	18	-	
PFPeA	Perfluorpentansäure	519	101	101	10	-	
PFHxA	Perfluorhexansäure	519	148	123	12	-	
PFHpA	Perfluorheptansäure	519	121	80	2	-	
PFOA	Perfluoroctansäure	519	163	133	7	-	
PFNA	Perfluornonansäure	519	13	4	-	-	
PFDA	Perfluordecansäure	519	1	1	-	-	
PFUnDA	Perfluorundecansäure	519	-	-	-	-	
PFDoDA	Perfluordodecansäure	519	-	-	-	-	
PFTrDA	Perfluortridecansäure	100	-	-	-	-	
PFTeDA	Perfluortetradecansäure	3	-	-	-	-	
Perfluorinated sulfonic acids							
PFBS	Perfluorbutansulfonsäure	519	161	160	9	-	
PFPeS	Perfluorpentansulfonsäure	519	18	18	2	-	
PFHxS (linear + branched isomers)	Perfluorhexansulfonsäure	519	137	137	19	2	0.
PFHpS	Perfluorheptansulfonsäure	519	9	9	1	-	
PFOS (linear + branched isomers)	Perfluoroctansulfonsäure	519	128	128	29	3	0.
PFNS	Perfluornonansulfonsäure	519	-	-	-	-	
PFDS	Perfluordecansulfonsäure	519	-	-	-	-	
PFUnDS	Perfluordecansulfonsäure	100	-	-	-	-	
PFDoDS	Perfluordodecansulfonsäure	100	-	-	-	-	
PFTrDS	Perfluortridecansulfonsäure	100	-	-	-	-	
Polyfluorinated substances							
4:2-FTS	4:2-Fluortelomersulfonsäure	519	-	-	-	-	
6:2-FTS	6:2-Fluortelomersulfonsäure	519	21	9	1	-	
8:2-FTS	8:2-Fluortelomersulfonsäure	519	-	-	-	-	
PFPrOPrA	Perfluor-2-propoxypropansäure	519	-	-	-	-	
6:2-Cl-PFESA	9-Chlorhexadecafluor-3-oxanonan-1-sulfonsäure	519	-	-	-	-	
DONA	Perfluor-4,8-dioxa-3H-nonansäure	519	-	-	-	-	
PFOSA	Perfluoroctansulfonamid	3	2	2	-	-	

LOQ limit of quantification

* lack of statistical reliable data at the national scale

2.4.3 Available PFAS data in the Walloon and Brussels Capital Region

The Brussels Capital Region conducted three monitoring campaigns for PFAS. The first campaign was an indicative campaign where the surveyed sites were selected based on environmental permits. In the second monitoring campaign, the sites were determined based on suspected risk activities related to PFAS. In the third monitoring campaign, locations were included without suspected risk activities related to PFAS. The third measurement campaign ended in November 2023. Consequently, no results are available yet (PFAS in het Brussel Hoofdstelijk Gewest Update over de recente situatie , 2023).

Since the results of these investigations are mainly focused on risk locations, no conclusion can be drawn for a background value in the Brussels Capital Region.

In the Walloon Region, there are some ongoing studies by ISSeP that have relations to PFAS such as IMP PFAS, which aims to make optimal use of data on PFAS (concentrations and frequency of occurrence) from BIODIEN, PPB-WAL and ôDiSuPer projects, as well as from ESU and Biotes monitoring networks.

The ôDiSuPer project aims to expand the available knowledge regarding the presence of compounds belonging to the PFAS family in surface water and in Walloon tap water.

The PPB-Wal project assesses the presence and impact of certain perfluorinated compounds, phthalates and bisphenol A in water (L'Institut Scientifique de Service Public, 2019).

Only the final report of the BIODIEN project is available. This project involves research on endocrine-disrupting and other emerging substances in water for the protection of public health and the environment. As part of this study, approximately 250 samples were analyzed, with a quarter consisting of groundwater samples. Of the 250 samples, 122 were analyzed for 5 perfluorinated compounds (PFOA, PFOS, PFHxA, PFHpA and PFHxS) with a limit of quantification of 0.5 ng/L.

The 5 perfluorinated compounds were detected above the limit of quantification in at least 35% of groundwater samples in Wallonia. In the Brussels Capital Region, only PFOS was detected in 13% of groundwater samples. The other 4 perfluorinated compounds were detected in 35 to 45% of groundwater samples.

It is concluded in this study that if one of the 5 perfluorinated compounds is detected, the 4 others are generally also detected. Most sampling points are characterized by concentrations less than 5 ng/L. Only a few monitoring sites have concentrations "sum of the 5 perfluorinated compounds" higher than 50 ng/L. The conclusion of this study with limited sampling campaign is that perfluorinated compounds are commonly found, but at concentrations less than 10 ng/L. Locally, PFAS concentrations may be higher, but they do not exceed the 100 ng/L limit at any of the measurement sites in this study (Frippiat, 2018).

3 ACTION PLAN : COLLECTING & SELECTING DATA SETS

Data collection for the determination of anthropogenic background concentrations in groundwater and soil consists of the following sub aspects:

- Developing a sampling strategy for collecting a new dataset in groundwater and soil at unsuspected sites (dataset 1, §3.1)
- selecting representative data from VMM's available groundwater dataset, specifically selection of results of PFAS in groundwater located in PFAS unsuspected zones (dataset 2, § 3.2.1)
- selection of representative data from the available dataset of VITO for the soil, specifically selecting PFAS results in the soil located in PFAS unsuspected zones (dataset 2, §3.2.2)

3.1 SAMPLING PLAN FOR COLLECTING NEW DATA (DATASET 1)

The aim of this study is to determine anthropogenic background concentrations for PFAS in groundwater and to collect additional data to update already determined anthropogenic background concentrations for soil. For this purpose, it is necessary to have analytical results of PFAS from unsuspected zones, meaning areas where no PFAS suspected sources are present or were present in the past.

To select sampling locations , spatial insight into the location of (potential) risk sites is essential. The following spatial data were collected and merged as different map layers into 1 map image:

- Known areas with “no regret measures” (see PFAS explorer DOV)
- Inventory of known fire training sites and incidents (see PFAS explorer DOV)
- known analytical results for PFAS from the PFAS explorer (layer “results groundwater” DOV)
- PFAS results in wastewater (see PFAS explorer DOV).
- Known landfills in Flanders (OVAM data layer).
- Lands where PFAS suspicious activities were conducted based on the land information register

For setting anthropogenic background concentrations, it is also important to avoid contamination with other substances. Other contaminants can potentially impact detection limits for PFAS. Therefore, the following map layers were also added:

- Map layer with all locations where an activity is or has been performed that can result in an increased risk of sediment pollution as used in the study "identifying hotspots of sediment pollution linked to risk activities" (OVAM.be). This list of risk activities was recently expanded to include activities linked to brominated flame retardants and PFAS.
- Map layer of lands with an OVAM file number.
- Location of wastewater treatment plants.

To make the sampling plan as spatially complementary as possible with data from other studies, the following map layers were also added:

- Location of samples used to determine the anthropogenic background concentrations for PFAS in the soil (VITO study, see also § 3.2.2)
- Database of 194 monitoring points from VMM's groundwater monitoring network that were sampled for PFAS in spring 2022.
- Database of 400 monitoring points from VMM's groundwater monitoring network that were sampled for PFAS in spring 2023
- Existing groundwater monitoring networks (including primary and phreatic monitoring network VMM) as available on DOV.

An attempt was made to make maximum use of existing monitoring wells from the VMM's phreatic groundwater monitoring network for the new sampling campaign (dataset 1). The location and technical information of the monitoring wells from the phreatic network was also added as a map layer to the above map image.

To evaluate land use, the regional plan, a land cover map, a land use map and several aerial photographs were also visualized.

A 10 km x 10 km grid was then added to the map image.

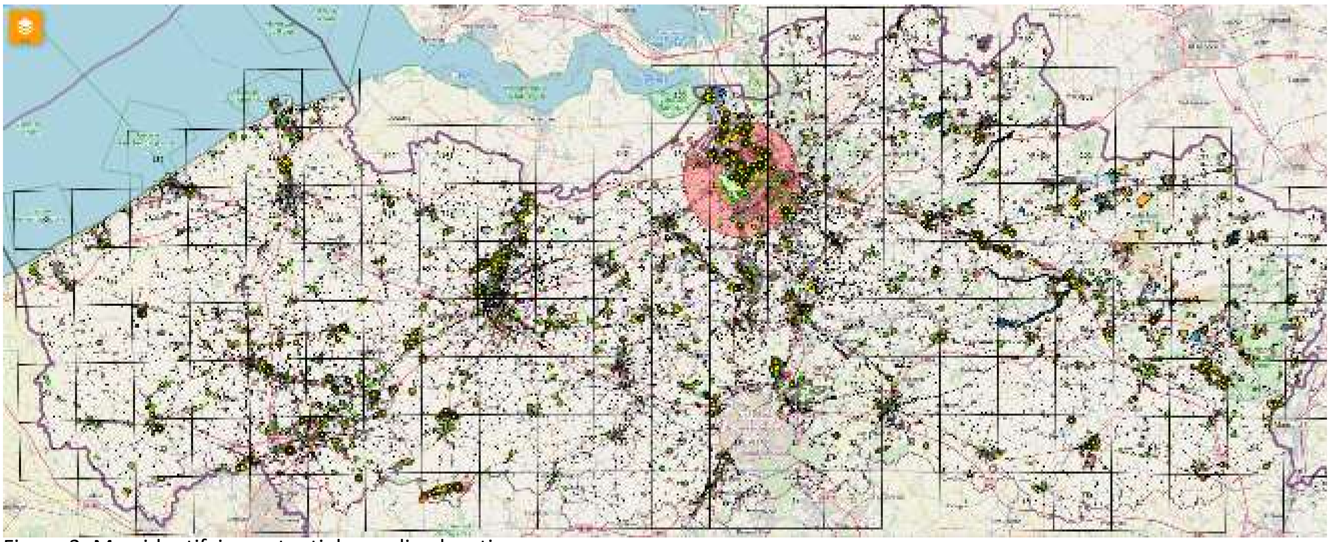


Figure 3: Map identifying potential sampling locations.

To achieve an area-wide survey, a monitoring well was selected from VMM's phreatic monitoring network for 149 of the 168 sections in the grid that met the following conditions:

- Filter in the phreatic groundwater
- Not included in the PFAS analysis campaign conducted by VMM in spring 2022 and 2023 (except for 13 monitoring wells for comparison low and high flow sampling, see section 6.2.1)

- Not located in a no regret zone and at a distance of at least 100 m from land with a known OVAM file number, landfills, soils with activities related to PFAS, potential hotspot soils for water bottom, sewage treatment plants and known discharges of wastewater containing PFAS.

This way, 149 monitoring points were selected spread across Flanders. Monitoring wells that have been recently and regularly sampled and have not been regularly dry in recent years were chosen.

At half of these measuring points, samples were also taken from the soil. When selecting the location of these 75 soil samples, locations were chosen from compartments in the grid where no sample was yet analyzed in the context of determining the current anthropogenic background concentrations in soil (dataset VITO, see paragraph 3.2.2).

Figure 4: Selection of sampling location soil and groundwater

For each selected location, the following data were entered into the database:

- Grid cell number
- Monitoring well ID
- Filter number of the monitoring well (often nested monitoring wells)
- Sampled by VMM in 2023 (yes/no)
- If yes-number of sampled filter by VMM
- Depth of the base of the filter
- Filter length
- Tubed borehole (yes/no)
- Type of area (agriculture, nature, forest)
- Link to well information sheet on DOV
- Status of well: Active/not active
- Year of last gauge measurement according to DOV
- Lithological description of soil layer at the level of the filter
- Main soil type (based on lithological description)
- Coordinates in Lambert and longitude and latitude
- Description of location monitoring well for field work crew as recorded in DOV

The majority of the selected monitoring points are located in agricultural areas (127), 18 in natural areas, 3 in recreation or park areas, 1 in residential expansion areas.

A check was performed to determine whether map elements from the "PFAS suspect layers" as defined above were located within 100 m and 200 m of the selected monitoring points.

Two monitoring points are within 100 m of a PFAS suspect site, 7 within 200 m of a PFAS suspect site. The results of these points were additionally evaluated, based on this evaluation it was decided to keep the monitoring points in the selection.

A total of 149 monitoring sites spread across Flanders were included in the sampling plan (= dataset 1).

Table E: Sampling locations dataset 1 within 100 and 200 m of a PFAS suspect site

Monitoring points at < 100 m PFAS suspect site	Monitoring points at < 200 m PFAS suspect site	Soil sampled	Evaluation
	461/73/1	No	Near file no. 67531 -OBO only - point retained
	343/32/1	No	Near OVAM file no. 83407- OBO - point retained
	112/73/1	No	Near OVAM file nos. 96390, 22712 (OBO) and 76460 (BBO) and potential hot spot location sediment - point retained
	561/64/11	No	Near file nos. 95346, 18384, 1498 (OBO) and 34518 (BBO) - point preserved

842/62/1		Yes	Within no regret zone 3M 5-10 km - keep point and evaluate afterwards - no alternative available
	560/64/7	No	Near file no. 30897 (OBO) - point retained
835/00/1		No	Within no regret zone 3M, 5-10 km, close to dredge dump - point retained - retrospective evaluation - no alternative available

3.2 ADDITIONAL AVAILABLE MEASUREMENT DATA PFAS IN FLANDERS (DATASET 2)

Additional available measurement data of PFAS in the soil and groundwater in Flanders were evaluated to assess their suitability to derive anthropogenic background concentrations. The following data were reviewed:

- PFAS- data in the OVAM database (available in the PFAS Explorer (DOV)). OVAM data are collected from sites where PFAS were investigated as a suspect parameter in a soil investigation. These sites are therefore not suitable for determining anthropogenic background concentrations
- VMM data - see below
- Data in DOV: this is the same data as the OVAM data and data and VMM
- VITO data for calculating anthropogenic background concentrations in the soil.

This analysis shows that mainly the data collected by VMM in the phreatic groundwater and the data collected by VITO concerning PFAS in the soil are relevant for this study. The remaining data are always from sites where PFAS was considered a suspect parameter because it was used at the site.

3.2.1 Available data VMM (dataset 2- groundwater).

In the spring of 2023, VMM sampled monitoring wells across Flanders for PFAS. Results from monitoring wells from phreatic groundwater were included in this study. The data includes::

- 301 sites: 57 from the primary monitoring network and 244 from the phreatic monitoring network
- At 75 of these locations, monitoring wells were sampled at 2 depths at the same point, only the results of most shallow filter were included in the present study.
- To verify the usefulness of these results for setting anthropogenic background concentrations, it was checked which of these points are less than 100 m and less than 200 m from PFAS suspect sites, based on the map layers included in Section 3.1.
  - Of the 301 sites, 13 sites are located within 100 m of a potential PFAS source – these sampling point were not included to calculate anthropogenic background concentrations
  - 46 sites are between 100 and 200 m from a potential PFAS source (Table F). These sites were additionally evaluated for inclusion in the analysis to determine anthropogenic background concentrations. 11 sites were withheld.
- 13 sites were sampled both by VMM and in the present study (see also section 6.2.1). Only the result from the present study (dataset 1) was included.
- This results in **240 additional sampling points** that are considered in section 1 for determining anthropogenic background concentrations in groundwater. These results are referred to as dataset 2 for groundwater.
- Only results for components from the WAC were included in the further evaluation.

Table F: Monitoring wells from VMM dataset less than 100 and between 100 and 200 m from a potential PFAS source

<100 m	Evaluation	Decision
081/21/7	Near sites where OBO (recovery site agricultural vehicles) and a BBO (greenhouse - nickel in GW) has been implemented	Not selected
1-0264	Near site where only a OBO was conducted. textile recycling	Not selected
1-1114b	Within OVAM file - metallurgy	Not selected
133/21/5a	Near site with CAB - sales material ornamental cultivation	Not selected
156/33/10	Near landfill	Not selected
2-0777	Near several PFAS files and remediation files	Not selected
221/32/18	Near site with an OBO (organic farm with blacksmith shop) and a BBO (garage/body shop)	Not selected
4-0243	Within no regret zone fire station	Not selected
422/74/8	Near landfill	Not selected
471/21/3	Near site with OBO - production of traffic signalization n road markings	Not selected
7-0556	Next to remediated site - activities unclear	Not selected
822/21/4	Near remediation file watercourse (asbestos) - watercourse borders some no regret zones	Not selected
932/22/2	Single OBO nearby - livestock farm with garage workshop	Not selected
100-200 m		
016/74/8	only OBO nearby	Selected
1-0159	Near landfill	Not selected
1-0321	In village center - near no regret zone and several sites with studies and remediation	Not selected
1-0478	Next to airport	Not selected
1-0489	Near OBO - farm with garage workshop	Not selected
1-1085	Near site with OBO and BBO (garage workshop)	Not selected
1-1105	Near remediation - asbestos	Selected
115/21/9	Near landfill	Not selected
135/35/5	Near OBO - garden center	Selected
2-0424b	Near OBO - former campground	Selected
3-0061	Near landfill	Not selected
312/21/12	Near airport	Not selected
320/21/6	Near ongoing PFAS research	Not selected
342/32/3	Near site with OBO - horticultural company	Selected
343/74/8	Near sites with OBOs (small gasoline tank and small landscaping company)	Selected
350/21/11	Between garage workshop - former landfill and former waste processor	Not selected
422/74/6	Near OBO - gas release station	Selected
423/21/4	Between 2 landfills	Not selected
474/74/7	Near OBO (florist shop) and remediation (research facility - leaking oil tank)	Selected
480/73/9a	Near no regret zone fire	Not selected
521/63/8	OBO - farm with repair shop	Not selected
522/64/1a	Near landfill	Not selected
530/52/15a	Near several ongoing PFAS studies	Not selected
531/51/3	Near WWTP	Not selected
532/62/15	Near remediation project body shop	Not selected
540/51/5	Near remediation project watercourse ‘de grote Calie”	Not selected
552/63/12	Near sites with BBO (wellness center) and OBO (farm)	Selected
610/77/1	Near landfill	Not selected
662/63/4a	Near site with OBO (garage and body shop)	Not selected
700/75/6	Near landfill	Not selected
7-0350	Near large landfill	Not selected
704/73/6	Near landfill	Not selected
7-0546c	Near site with OBO/damage case - golf club with leak in diesel tank - fairly large distance from tank	Selected
7-0550	Near landfill	Not selected
720/21/2	Near site that is part of a remediation	Not selected
802/35/1	Near site with OBO (garage and body shop)	Not selected
810/21/5	Between sites with several soil investigations and sites with ongoing PFAS investigations	Not selected
831/63/1	Near several sites with OBO (greenhouse farm, hazardous materials storage)	Not selected
840/64/4a	Near landfill, several sites with soil testing and remediation and no regret zones	Not selected
841/35/1	Near no regret zone	Not selected
841/62/5	Near several sites with OBO (mostly garage workshops and body shops) and no regret zone	Not selected
922/22/34	Near WWTP	Not selected
931/22/3	Near no regret zone fire department site	Not selected
940/40/20	Near no regret zone fire department site	Not selected
N/21/16	Near industrial park with several investigations, remediation and PFAS suspected sites	Not selected
N/74h/2r	1 small sites with BBO nearby. Survey from 2000	Selected.

3.2.2 Available data VITO to determine anthropogenic background PFAS in the soil (dataset 2-soil)

In 2021, anthropogenic background concentrations were already determined for the soil (OVAM, 2021). For this 50 samples from the soil were analyzed in March 2020,

The locations of these monitoring sites were re-evaluated in the present study using the map layers of potential PFAS sources as mentioned in section 3.1.

The 14 measurement points included in Table G are within 100 or 200 m of a potential PFAS source:

- Monitoring points more than 100 m from a suspected site were retained for recalculating the anthropogenic background concentration in the soil (see section 6.2.1 and 6.2.2).
- The monitoring points less than 100 m from a suspected site are provisionally retained and anthropogenic background concentration calculations are performed with and without these results, additionally a statistical outlier evaluation is done (see section 6.2.2)

Table G: Sampling locations dataset 2 VDA less than 100 m and 200 m from a PFAS suspect site

Monitoring points at < 100 m PFAS suspect site	Monitoring points at < 200 m PFAS suspect site	Evaluation
	S26 (no. 6)	selected measuring point [1]
	S49 (no. 7)	selected measuring point [1]
	S48 (no. 13)	selected measuring point [1]
S17 (No. 17)		Measurement point within no regret zone 3 M (5-10 km) [2]
	S15 (no. 20)	selected measuring point[1]
	S14 (no. 21)	selected measuring point [1]
S3 (no. 26)		Monitoring point just next to no regret zone Merksem, lots of PFAS suspected sites, soil tests etc nearby [2]
S4 (no. 27)		Monitoring point near potential hot spots of water bottom - 2.3.6.c landfill. [2]
S34 (no. 29)		Measurement point within no regret zone - Torhout fire station -. [2]
	S27 (no. 30)	selected measuring point[1]
	S33 (No. 33)	Monitoring point near site with PFAS suspected activities - file no. 2785 -point retained [1]
S35 (no. 36)		Monitoring point thv potential hotspot water bottom (soil id 2749954) - 2.2.1.c.1 since 1989 - storage and sorting non-hazardous waste - no ovam file no. - [2]
	S29 (no39)	selected measuring point[1]
S47 (No. 55)		Monitoring point adjacent to OVAM file no. 22465 (OBO only) - Aquafin - reed beds - no BBO necessary [2]

Legend:

[1] measurement point retained given this sampling point is further than 100 meters away from a suspected source

[2] measuring point less than 100 m from a suspected site: measuring point is retained for the time being and anthropogenic background concentration calculations are performed with and without these results see section 6.2.2 (statistical outlier evaluation)

4 SAMPLING AND ANALYSIS (DATASET 1)

A sampling campaign was conducted to collect a new dataset. Groundwater samples were taken at selected sites and at some locations, samples of the soil were also collected. The results from this from this campaign form dataset 1.

Sampling and analysis were carried out in accordance with:

- Compendium for Sampling and Analysis for the implementation of the Waste Decree and Soil Remediation Decree (CMA) (http://www.ovam.be/code-van-goede-praktijk)
- The applicable requirements for sampling and analysis are followed, as described in the "PFAS Survey Directive"(OVAM, 2022 link: https://ovam.vlaanderen.be/pfas)
- Groundwater will be analyzed for PFAS according to WAC/IV/A/025 (draft 12/2022).
- Samples from the soil were sampled and analyzed according to CMA/3/D (draft 07/2022).

4.1.1 Sampling (dataset 1)

The sampling campaign was conducted between February and June 2023. An overview of the sites sampled is included in Annex 4.

Measures to avoid cross-contamination

Given the study's objective of determining anthropogenic background concentrations, special attention was paid to avoiding cross-contamination. During fieldwork, extra measures regarding PFAS sampling were taken into account. This included ensuring that the clothing and personal protective equipment worn by fieldworkers were made of material that would not interfere with the PFAS analysis. The use of cosmetics and creams on the day of sampling was not allowed. Additionally, the fieldwork equipment and sample containers had to be made of the appropriate materials. The checklist included in the annex of the OVAM guideline for PFAS research (05/03/2021) was used for this purpose.

Groundwater sampling

The groundwater samples were taken in accordance with the CMA specifically using the low-flow method. The groundwater samples were taken by the groundwater samplers from Eurofins.

These groundwater samplers already sampled a first series of phreatic monitoring wells commissioned by VMM in 2022 and were also used by VMM for the VMM campaign in 2023. For uniformity, it was decided to work with these samplers for the execution of the new groundwater sampling campaign on behalf of OVAM (dataset 1).

Arcadis/Witteveen+Bos performed quality control of the groundwater sampling: prior to the start of fieldwork, a kick-off meeting was held to go over the key aspects of sampling and the purpose of this study. Throughout the project, random field inspections were carried out to verify the proper execution of the groundwater sampling. Some of the 149 selected piezometers were found to be no longer accessible for sampling. Where possible, alternatives were sought Ultimately, a total of 147 groundwater samples were taken (124 in agricultural areas, 18 in natural areas, 3 in recreational areas, 2 in residential expansion areas or residential areas) (Annex 4).

Soil sampling

The sampling of the soil was carried out by the Witteveen+Bos fieldwork team. The sampling was carried out following the method used by VITO to determine the anthropogenic background concentrations for the soil (VITO, 2021): a composite sample of 3 samples from the upper 20 cm over 1 m² of non-anthropogenically manipulated soil was taken at each sampling location. A total of 73 soil samples were analyzed.

4.1.2 Laboratory analyses (dataset 1)

Laboratory analyses were conducted at Eurofins, an OVAM-approved laboratory, between February and June 2023.

Analyses in accordance with CMA and WAC

The groundwater was analyzed for PFAS according to WAC/IV/A/025 (version 12/2022, Official Gazette 6/7/2023), i.e. 34 quantitative PFAS and 8 indicative PFAS. The limits of quantification used in this study, are listed in Annex 3. It is lower for most components than the maximum reporting limit mentioned in the WAC, namely (see also Annex 3):

- 4 ng/L for EtFOSA total (10 ng/L in the WAC)
- 2 ng/L for MeFOSA linear and total, PFBSA and PFODA (10, 10 and 50 ng/L in the WAC, respectively)
- 10 ng/L for MePFBSA, MePFBSAA, PFHxSA, 6:2 diPAP, and 6:2/8:2 diPAP(10,10,10, 50 and 50 ng/L in the WAC, respectively)
- 1 ng/L for the other PFAS components.

The soil was analyzed for PFAS according to the applicable CMA (version 07/2022, Official Gazette 22/09/2023). The reported limit of quantification for the samples of the soil soilis equal to the maximum reporting limit mentioned in the CMA i.e. 0.5 µg/kg dm for the quantitative components. For the indicative PFAS, the limit of quantification is 1µg/kg ds.

Margin of error

Table H shows the margins of error applicable to Eurofins laboratory analyses *(source: communication with Eurofins).*

Table H: Margins of error on laboratory analyses (Eurofins).

Groundwater				Soil			
PFAS	Margin of error (%)	Component	Margin of error (%)	Component	Margin of error (%)	Component	Margin of error (%)
4:2 FTS	21	**PFDoDA**	9	**4:2 FTS**	27	**PFNA**	9
6:2 FTS	12	**PFTeDA**	14	**6:2 FTS**	13	**PFNS**	10
8:2 diPAP	23	**PFHxDA**	14	**8:2 diPAP**	14	**PFOA lin**	9
8:2 FTS	16	**EtFOSA**	25	**8:2 FTS**	18	**PFOA sum**	9
DONA	25	**EtFOSAA**	21	**DONA**	29	**PFOS lin**	9
PFBA	17	**GenX**	17	**EtPFOSA lin**	29	**PFOS sum**	9
PFBS	12	**MeFBSA**	61	**EtPFOSA sum**	29	**PFOSA lin**	8
PFPeA	14	**MeFBSAA**	44	**EtPFOSAA**	17	**PFOSA (lin+ vert)**	8
PFPeS	13	**MeFOSA**	13	**HFPO-DA**	31	**PFPeA**	10
PFHxA	11	6:2/8:2 diPAP	64	**MePFOSA lin**	28	**PFPeS**	13
PFHxS	15	6:2 diPAP	22	**MePFOSA sum**	28	**PFTeDA**	9
PFHpA	15	10:2 FTS	17	**MePFOSAA**	20	**PFUnDA**	21
PFHpS	12	PFTrDS	49	**PFBA**	21	**10:2 FTS**	18
PFOA	12	PFDoDS	42	**PFBS**	8	**PFTrDS**	11
PFOS	15	PFTrDA	20	**PFDA**	7	**PFUnDS**	7
PFNA	14	PFODA	38	**PFDoDA**	9	**MePFBSA**	44
PFNS	12	PFUnDS	25	**PFDS**	9	**PFBSA**	6
PFDA	8			**PFECHS**	7	**PFHxSA**	10
PFDS	16			**PFHpA**	9	PFODA	59
PFUnDA	16			**PFHpS**	8	6:2/8:2 diPAP	49
PFBSA	31			**PFHxA**	11	6:2 diPAP	57
PFECHS	13			**PFHxDA**	9	PFDoDS	14
PFHxSA	17			**PFHxS lin**	12	10:2 FTS	18
PFOSA	12			**PFHxS sum**	12	MePFBSAA	65
MeFOSAA	22			**PFTrDA**	13		

Legend: quantitative PFAS are indicated **in bold**

For most quantitative PFAS, these error rates are within the margins recorded by VITO in the context of the ring tests, specifically 10-25%.

TOP Analysis

To get an idea of the presence of precursors, a TOP analysis was performed on 8 selected samples from the soil and 12 groundwater samples. A TOP analysis uses hydroxyl radical-based oxidation reactions, converting precursors to perfluoroalkyl acids (PFAAs) that can be detected.

The selection of the samples for TOP analysis was done after the results of the classical anthropogenic background analyses (CMA and WAC) were known in order to make a anthropogenic backgrounded selection based on the measured concentrations. Samples were chosen where PFAS were measured above the limit of quantification, where many different PFAS components were measured, and an attempt was made to spread the samples spatially over Flanders.

5 METHODOLOGY DETERMINING ANTHROPOGENIC BACKGROUND CONCENTRATIONS

Based on the publication "Basic information for risk assessments: methodology for setting soil remediation standards and assessment values, guide values and background concentrations" (OVAM, 2016) the background value for naturally occurring substances, corresponds to the normal background in unpolluted conditions. It is determined at the 90-percentile upper limit of the available data (OVAM, 2016).

The background value for non-naturally occurring substances is set equal to the limit of detection, both for soil and groundwater (OVAM, 2016).

Since PFAS do not occur naturally, the background value should in principle be set equal to the limit of detection. However previous research (OVAM, 2021), shows that PFAS are widespread, and target background have already been established for some PFAS components in soil. This is not a natural background value but an anthropogenic background value.

To determine this anthropogenic background concentration of PFAS in soil, similar to the approach for naturally occurring substances, the 90-percentile of the available data was chosen (OVAM, 2021).
The present report uses the same approach for determining anthropogenic background concentrations in groundwater.

A prerequisite for choosing the 90-percentile is that sufficient data are available. If a component is measured only sporadically above the limit of quantification, this indicates that it is not widespread and there is no generally elevated anthropogenic background value.

In the present report, a anthropogenic background concentration is proposed for components that exceed the limit of quantification in more than 50% of the monitoring points. This evaluation is made for different datasets (as mentioned in chapter 1), specifically

- dataset 1 groundwater (new sampling campaign commissioned by OVAM) (see section 6.1)
- expanded dataset: dataset 1 expanded with data VMM (see section 6.2)
- data set 1 soil (new sampling campaign commissioned by OVAM) (section 7.1).
- Expanded dataset: dataset 1 expanded with results VITO (section 7.2)

For the components that occur in less than 50% of the sampling points above the limit of quantification, there are insufficient data to derive anthropogenic background concentrations. If a component is found in less than half of the sampling locations, it can be concluded that no general elevated anthropogenic background is present.

6 EVALUATION OF PFAS IN GROUNDWATER AND DERIVATION OF ANTHROPOGENIC BACKGROUND CONCENTRATIONS.

The evaluation and derivation of anthropogenic background concentrations in groundwater and the mapping of results was performed in several steps as different datasets were collected.

Initially, we work with the newly collected dataset (dataset 1, § 6.1) because these samplings and analyses were highly focused, uniform and done according to low flow sampling (CMA compliant).

In a second step, the calculations are extended with a dataset of available analyses from VMM measurement campaigns (dataset 2), these samplings were done via high flow principle. The combined dataset consists of dataset 1 and dataset 2 (§ 6.2).

By performing the anthropogenic background concentration calculations with both dataset 1 and the combined dataset, insight can be gained into

- possible variability/sensitivity analysis of the calculated anthropogenic background concentrations
- influence of sampling method (high flow versus low flow)

An overarching evaluation is then made and a proposal of anthropogenic background groundwater values (§6.3).

The ProUCL software package was used for statistical processing.

6.1 GROUNDWATER RESULTS - DATASET 1

This section includes the evaluation based on the new dataset sampled as part of the present study, specifically dataset 1.

6.1.1 Statistical key indicators individual PFAS components in groundwater

A total of 147 groundwater samples were analyzed. The summary key indicators for all components that were measured at least once above the quantitation limit are shown in Table I. These statistical key indicators include:

- percentile values P50, P90, P95 based on all results
- mean, median and standard deviation based on all results above limit of quantification
- minimum and maximum measured concentration.

From the statistical key indicators, the following can be summarized:

- In 141 of 147 monitoring wells, at least 1 component was detected above the limit of quantification.
- The majority of the analytical results are below the limit of quantification.

- Only for PFBA, $PFOS_{total}$, $PFOA_{total}$ and PFBS were values measured above limit of quantification in more than 50% of the samples:
  - PFBA is measured above the limit of quantification of 1 ng/L in 63% of the samples.
  - $PFOS_{total\ l}$, $PFOA_{total}$ and PFBS are measured above the limit of quantification of 1 ng/L in 52%, 56% and 58% of the samples, respectively.

For the components PFOA, PFOS, PFBA and PFBS, the distribution of results was examined in more detail. The distribution of results for these 4 components does not conform to a normal distribution, lognormal distribution or gamma distribution. This indicates that there is a wide dispersion in concentrations. This dispersion is also confirmed by the high standard deviations.

Components not included in Table I were never found above the limit of quantification. These include DONA, PFNA, PFUnDA, PFBSA, 10:2 FTS, 6:2 diPAP, 6:2/8:2 diPAP, MeFBSA, MeFBSAA, PFBSA and PFHxSA

Table I: Summary analytical results groundwater (ng/L) - dataset 1 . PFAS components were ranked according to % of samples with results above the limit of quantification. PFAS components that were measured in more than 50% of samples are indicated in green.

		Key indicators including results below limit of quantification								Key figures of the results equal to or above limit of quantification				
							ng/L			ng/L				
component	LOQ (ng/L)	Number of measurements	#>LOQ	#<LOQ	% >LOQ	% <LOQ	P50 (median)	P90	P95	Min of values above LOQ	Max of values above LOQ	average	P50 (median)	SD
PFBA	1	147	92	55	63%	37%	2,3	23,5	42,6	1,07	201,0	16,1	6,5	28,8
PFBS	1	147	86	61	58%	42%	1,2	7,8	11,5	1,01	48,4	5,1	2,8	6,9
PFOA $_{total}$	1	147	82	65	56%	44%	1,2	6,5	9,6	1,02	112,9	5,7	2,5	13,1
PFOS $_{total}$	1	147	77	70	52%	48%	1,0	4,7	7,1	1,03	18,4	3,2	1,8	3,2
PFOA lin	1	147	56	91	38%	62%	<KL	4,2	7,9	1,02	99,5	6,1	2,7	13,7
PFHxA	1	147	53	94	36%	64%	<KL	3,1	4,0	1,04	15,7	2,6	1,8	2,3
PFHxS total	1	147	49	98	33%	67%	<KL	2,8	3,6	1,05	38,7	3,5	1,9	5,9
PFHxS lin	1	147	42	105	29%	71%	<KL	2,4	3,4	1,05	36,6	3,4	2,2	5,7
PFHpA	1	147	40	107	27%	73%	<KL	2,0	3,0	1,01	16,9	2,6	1,7	2,8
PFOS lin	1	147	38	109	26%	74%	<KL	2,2	3,7	1,00	13,3	2,7	1,6	2,5
PFPeA	1	147	29	118	20%	80%	<KL	2,0	2,3	1,01	12,3	2,7	2,0	2,6
GEN X	1	147	29	118	20%	80%	<KL	1,4	1,8	1,00	3,3	1,6	1,4	0,6
etFOSAA	1	147	27	120	18%	82%	<KL	2,0	3,1	1,27	7,2	2,5	2,1	1,3
6:2FTS	1	147	23	124	16%	84%	<KL	1,3	1,9	1,00	7,9	2,3	1,6	1,9
8:2 FTS	1	147	23	124	16%	84%	<KL	1,4	1,5	1,04	2,0	1,4	1,5	0,2
PFOSA lin	1	147	17	130	12%	88%	<KL	1,1	1,3	1,02	3,0	1,4	1,3	0,5
PFOSA total	1	147	17	130	12%	88%	<KL	1,1	1,3	1,02	3,4	1,5	1,3	0,7
meFOSAA	1	147	18	129	12%	88%	<KL	1,2	2,6	1,01	4,7	2,7	2,3	1,3
PFTrDS	1	147	16	131	11%	89%	<KL	<KL	1,4	1,05	7,8	2,2	1,3	2,0
PFPeS	1	147	15	132	10%	90%	<KL	<KL	1,3	1,08	8,1	2,2	1,3	2,0
PFDoDS	1	147	11	136	7%	93%	<KL	<KL	1,1	1,00	1,4	1,2	1,2	0,1
MeFOSA total	2	147	11	136	7%	93%	<KL	<KL	2,9	2,32	7,6	3,8	3,2	1,7
8:2 diPAP	1	147	10	137	7%	93%	<KL	<KL	1,2	1,04	3,0	1,6	1,4	0,7
MeFOSA lin	2	147	9	138	6%	94%	<KL	<KL	2,3	2,14	3,9	2,9	3,0	0,7
4:2 FTS	1	147	7	140	6%	95%	<KL	<KL	<KL	1,01	1,5	1,3	1,3	0,2
PFHpS	1	147	7	140	5%	95%	<KL	<KL	<KL	1,02	2,7	1,4	1,2	0,6
PFTrDA	1	147	7	140	5%	95%	<KL	<KL	<KL	1,01	1,4	1,2	1,2	0,1
PFHxDA	1	147	7	140	5%	95%	<KL	<KL	<KL	1,02	1,2	1,1	1,1	0,0
PFunDS	1	147	4	143	3%	97%	<KL	<KL	<KL	1,87	3,5	2,4	2,2	0,7

		Key indicators including results below limit of quantification								Key figures of the results equal to or above limit of quantification				
							ng/L			ng/L				
component	LOQ (ng/L)	Number of measurements	#>LOQ	#<LOQ	% >LOQ	% <LOQ	P50 (median)	P90	P95	Min of values above LOQ	Max of values above LOQ	average	P50 (median)	SD
PFECHS	1	147	3	144	2%	98%	<KL	<KL	<KL	1,1	2,6	1,6	1,1	0,9
PFNS	1	147	2	145	1%	99%	<KL	<KL	<KL	1,1	1,2	1,1	1,1	0,1
PFDA	1	147	2	145	1%	99%	<KL	<KL	<KL	1,1	1,3	1,2	1,2	0,2
EtFOSAlin	4	147	2	145	1%	99%	<KL	<KL	<KL	4,2	12,9	8,5	8,5	6,2
EtFOSAt	4	147	2	145	1%	99%	<KL	<KL	<KL	5,7	16,0	10,8	10,8	7,3
PFDoDA	1	147	1	146	1%	99%	<KL	<KL	<KL	1,1	1,1	1,1	1,141	/
PFTeDA	1	147	1	146	1%	99%	<KL	<KL	<KL	1,5	1,5	1,5	1,474	/
PFDS	1	147	1	146	1%	99%	<KL	<KL	<KL	2,3	2,3	2,3	2,3	/

LOQ =Limit of quantification
SD =standard deviation
P50 = 50-percentile
P90 = 90 - percentile
P95 = 95 - percentile

6.1.2 Statistical key indicators "Sum PFAS"

The "sum PFAS" was calculated in 2 ways:

- b
- ased on the reporting limits for the individual components as included in the WAC (https://reflabos.vito.be/2023/WAC_IV_A_025.pdf). Components below these limits are not counted in the sum (set equal to 0).
- based on the limits of quantification used in this study (Annex 3), which are lower than the maximum reporting limits from the WAC. Components below these limits are not counted in the sum (set equal to 0).

The statistical key indicators "sum PFAS" were reported as soon as one of the components exceeds its respective limit of quantification or reporting limit from the WAC.

The key indicators of the resulting "sum PFAS" are summarized in Table J and include:

- percentile values P50, P90, P95 based on all results
- mean, median and standard deviation based on all results above limit of quantification
- minimum and maximum measured concentration.

From these statistical key indicators, the following can be summarized:

- When the reported limits of quantification of the individual components are lower than the maximum reporting limits of the WAC, "sum PFAS" can be calculated for more sampling points (141 versus 38 measurements "sum PFAS"). This is because individual concentrations smaller than 10 ng/L can also be quantified and thus reported and summed. This leads to more sum results when the individual components are measured in the lower concentration intervals (and thus not equated to 0).
- When the reporting limit from WAC is used for the individual components, the results for the sums are often higher than in the calculation option with the limit of quantification. This is because only values above 10 ng/L (WAC) are counted in the "sum PFAS," which means that a sum can only be calculated for samples with higher concentrations.
- Figure 5 and Figure 6 show the histograms of "sum PFAS" based on both calculation methods: considering respectively all components above reporting limit from WAC and all components above reported limit of quantification.
- When using the reporting limits for the individual components as included in the WAC, "sum PFAS" cannot be calculated for 109 of the 147 monitoring points, because for all individual components in that monitoring point the concentration is below the reporting limit (74% of the samples). "Sum PFAS" is reported as "below reporting limit" in that case.
- When a limit of quantification per individual parameter is used that is lower than the maximum reporting limit, the highest measured sum in the dataset is also higher than when reporting limits per individual parameter are used, because individual components between 1-10 ng/L are included in the "sum PFAS." For the same reason, the P90 and P95 are also higher. For this dataset, this means that

when using the lower limits of quantification from this study, the P90 for the sum PFAS would be about 50% higher than when using the reporting limits from the WAC.

- There is little /no difference in P90 between "sum PFAS quantitative", "sum PFAS EU DWD20" and "sum PFAS total". That is, most of the components that were detected belong to the group of 20 PFAS included in "sum PFAS EU DWD20" and thus also determine the P90 of "sum PFAS".

Table J: Summary sum PFAS groundwater (ng/L) - dataset 1

			Key indicators including results underreporting limit							Key indicators of results as of reporting limit				
	component	Number of measurements	# with min. 1 PFAS>RL	# with all PFAS <RL	% with min 1 PFAS >RG	% with all PFAS <RL	Median (P50)	P90	P95	Min of values above RG	Max of values above RL	Mean	Median (P50)	SD
Sum PFAS with RL from WAC (1)	Sum PFAS quantitative	147	38	109	26%	74%	<RG	35,8	67,7	10,4	236,9	48,3	24,2	53,6
	Sum of PFAS (EU DWD20).	147	37	110	25%	75%	<RG	35,8	67,7	10,4	236,9	49,2	24,4	54,0
	Sum of PFAS total	147	38	109	26%	74%	<RG	35,8	67,7	10,4	236,9	48,3	24,2	53,6

			Key indicators including results below limit of quantification							Key indicators of results as of limit of quantification				
	component	Number of measurements	# with minus 1 PFAS>LOQ	# with all PFAS<KL	% with min 1 PFAS >LOQ	% with all PFAS <LOQ	P50	P90	P95	Min of values above LOQ	Max of values above LOQ	average	median	SD
Sum PFAS with LOQ from Annex 3 (2)	Sum PFAS quantitative	147	140	7	95%	5%	10,1	58,0	92,8	1,1	265,8	25,4	12,3	39,7
	SUM PFAS (EU DWD 20)	147	132	15	90%	10%	8,8	57,4	89,1	1,0	262,1	24,4	10,6	39,8
	SOM PFAS total	147	141	6	96%	4%	11,7	58,5	92,8	1,1	265,8	25,7	12,3	39,5

SD	Standard deviation
LOQ	Limit of quantification
RL	Reporting limit from WAC
P50	= 50-percentile
P90	= 90 - percentile
P95	= 95 - percentile
(1)	taking into account WAC reporting limits (10 or 50 ng/L) - components below these limits are not counted in the sum (https://reflabos.vito.be/2023/WAC_IV_A_025.pdf)
(2)	taking into account quantitation limits lower than the maximum reporting limits (1 ng/L for most components), components below these limits are not counted in the sum

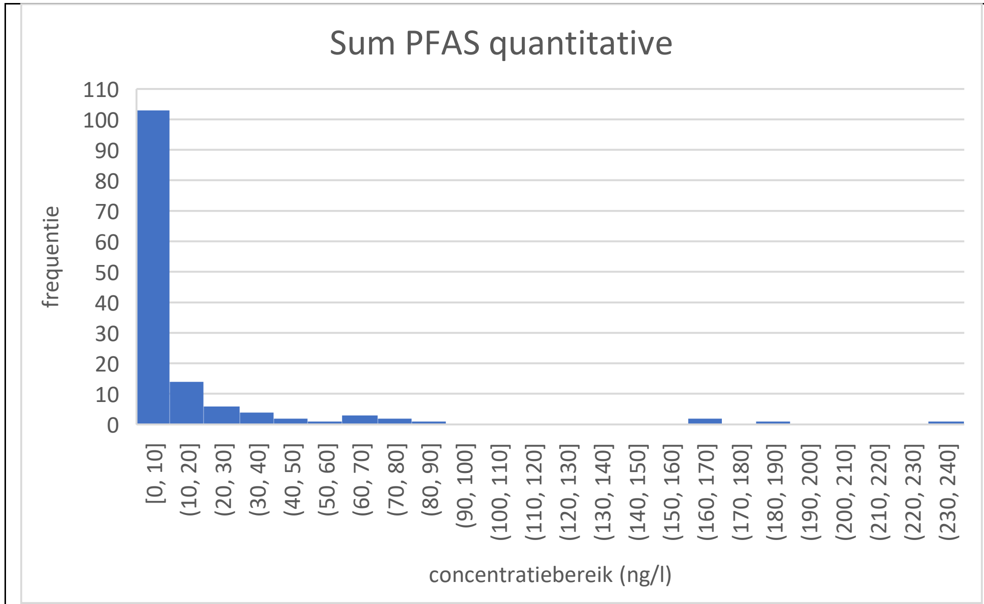


Figure 5: Histogram - sum of quantitative PFAS - based on reporting limits from WAC

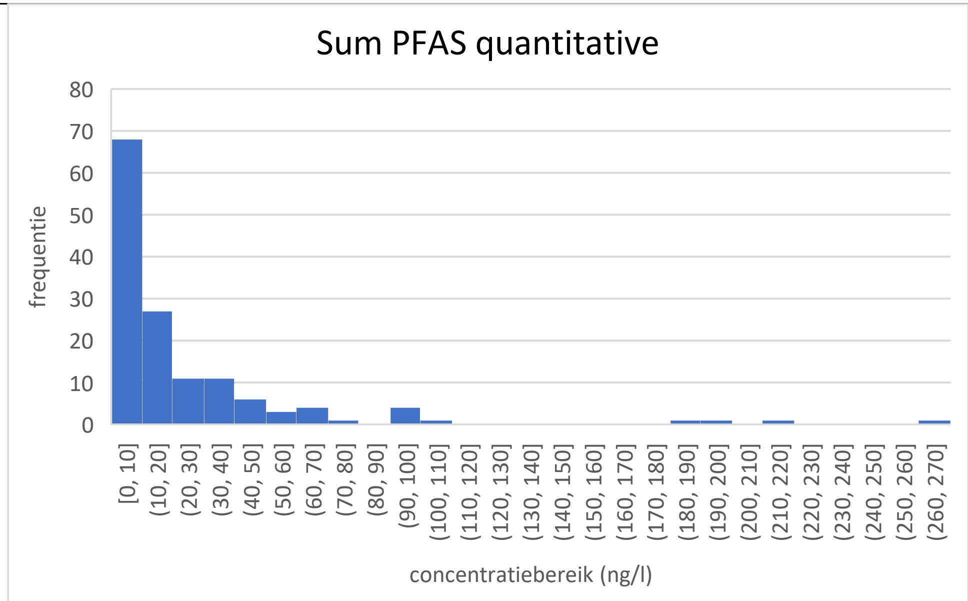


Figure 6: Histogram - sum of quantitative PFAS - based on limit of quantifications from Annex 3

6.1.3 Cartographic representation

The results for $PFOS_{total}$, $PFOA_{total}$, PFBA and PFBS are shown on Figure 7 through Figure 10 and in Annex 5.

The highest concentrations of these 4 components are not necessarily observed at the same locations:

- PFOS occurs throughout Flanders in fairly similar concentrations.
- For PFOA, we see 1 location with higher concentration on the coast. Furthermore, the higher concentrations seem to occur mainly northeast of Antwerp
- For PFBA, highest concentrations are observed between Antwerp, Brussels and Hasselt, and north of Antwerp
- PFBS shows a similar picture to PFBA, albeit at lower concentrations.

Figure 7: PFOS $_{total}$ in groundwater - dataset 1

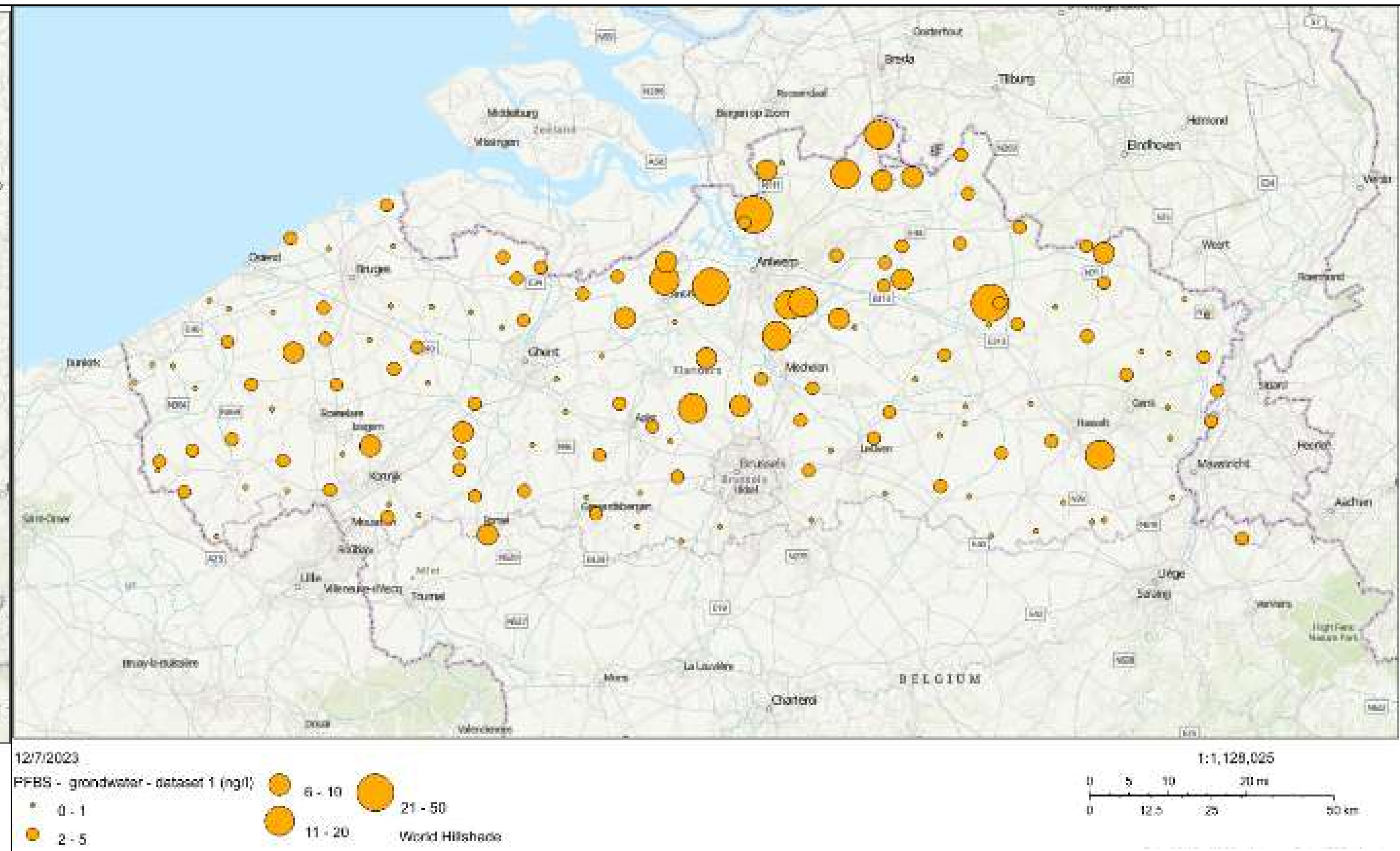


Figure 8: PFBS in groundwater (ng/L) - dataset 1

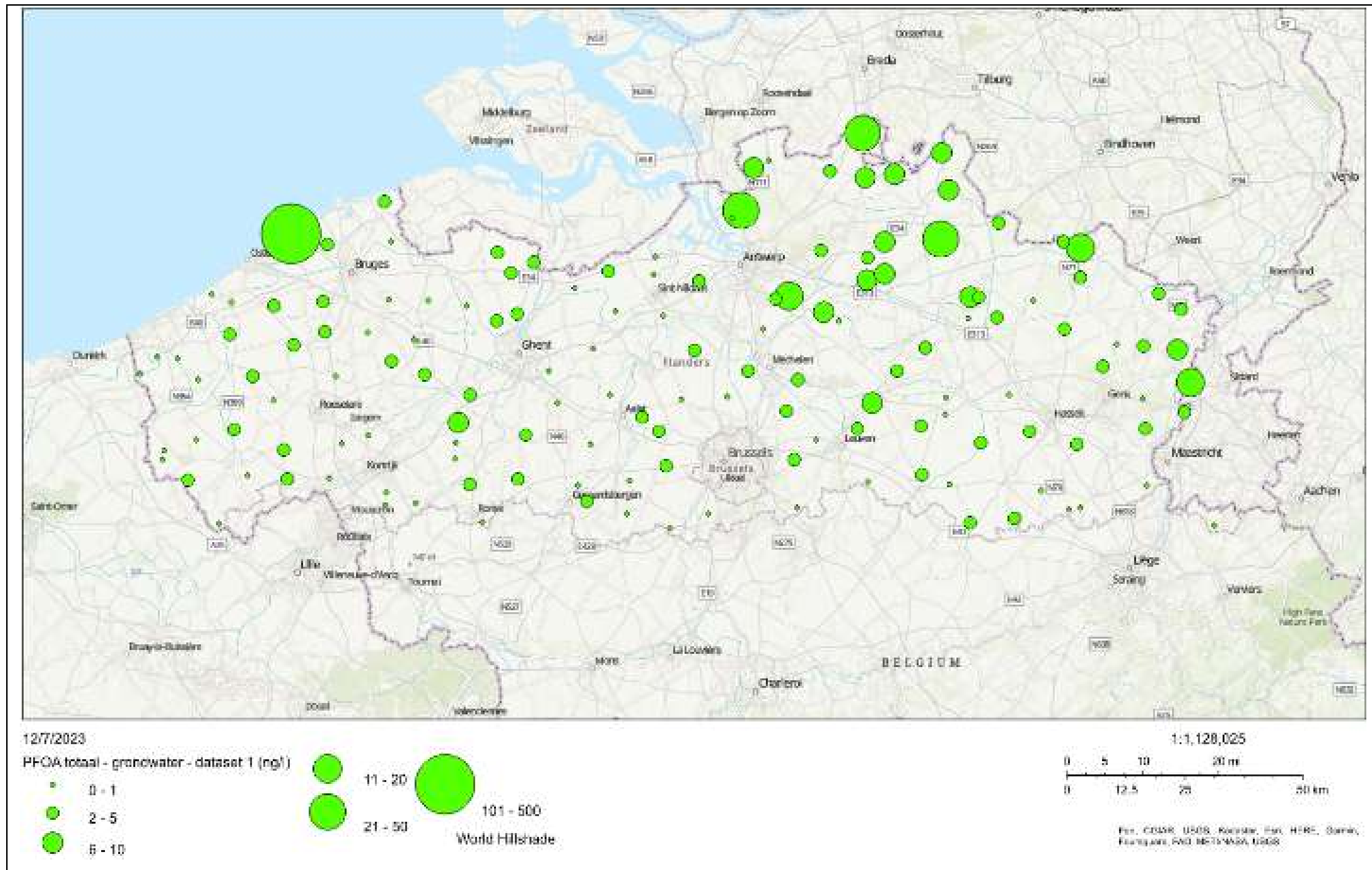


Figure 9: PFOA $_{total}$ in groundwater (ng/L) - dataset 1

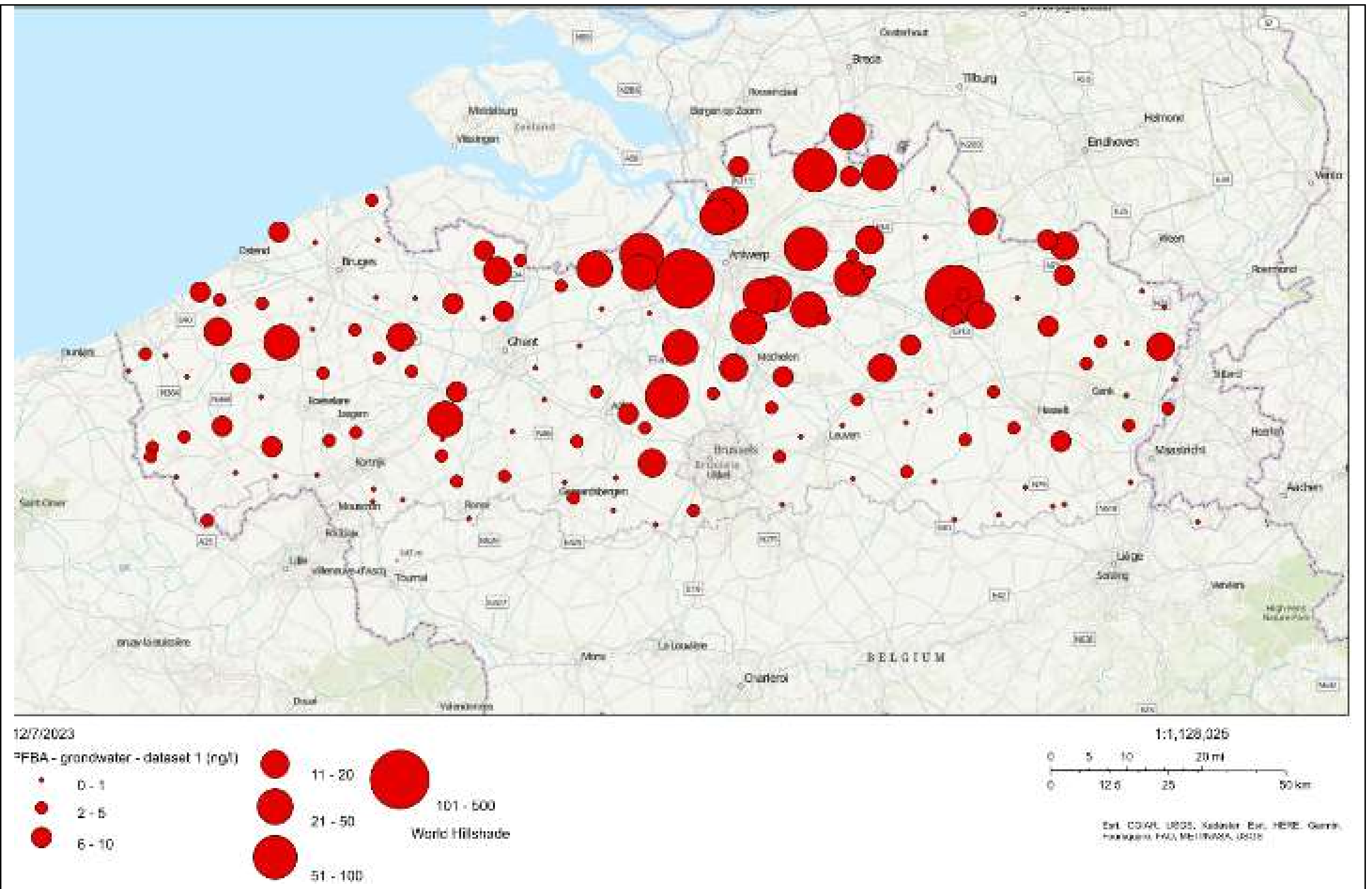


Figure 10: PFBA in groundwater (ng/L) - dataset 1

6.1.4 Outlier analysis

Outlier analysis was performed for PFOA, PFOS, PFBA and PFBS using Rosner's outlier test.
Based on the outlier test, 1 outlier was identified for each of these 4 components, in a different monitoring well. The location of these monitoring wells was considered in more detail (Table K and Figure 11) to determine if this outlier could be explained.

Subsequently, boxplot and histograms were also prepared (Figure 12 through Figure 17). Based on this evaluation, the value for PFBA in monitoring well 842/62/1 was also considered an outlier.

Not all outliers can be explained by the presence of PFAS suspect activities in the neighborhood.

The groundwater flow direction and the presence of known contaminants in the wider environment were not taken into account when selecting locations. Despite the careful selection of measurement points, it can never be completely excluded that some measurements were still influenced by a point source.

Therefore, when calculating the anthropogenic background concentrations, several scenarios will be calculated, namely with and without outliers and their impact on the calculated anthropogenic background concentration will be considered.

Table K: Outliers groundwater dataset 1

Component	Outlier measurement value (ng/L)	Monitoring well	Location
PFBA	201,0	502/62/2	Agricultural area, no known PFAS sources nearby – a few small landfills over 1 km away
	132	842/62/1	Based on boxplot and histogram. Near 3M - also outlier for PFBS
PFBS	48,4	842/62/1	Between Beveren and Kruibeke - near 3M
PFOAtot	112,9	N/10/3	Natural area/dunes
PFOSto	18,35	623/72/1	400 m from a zone with no regret measures - fire training area

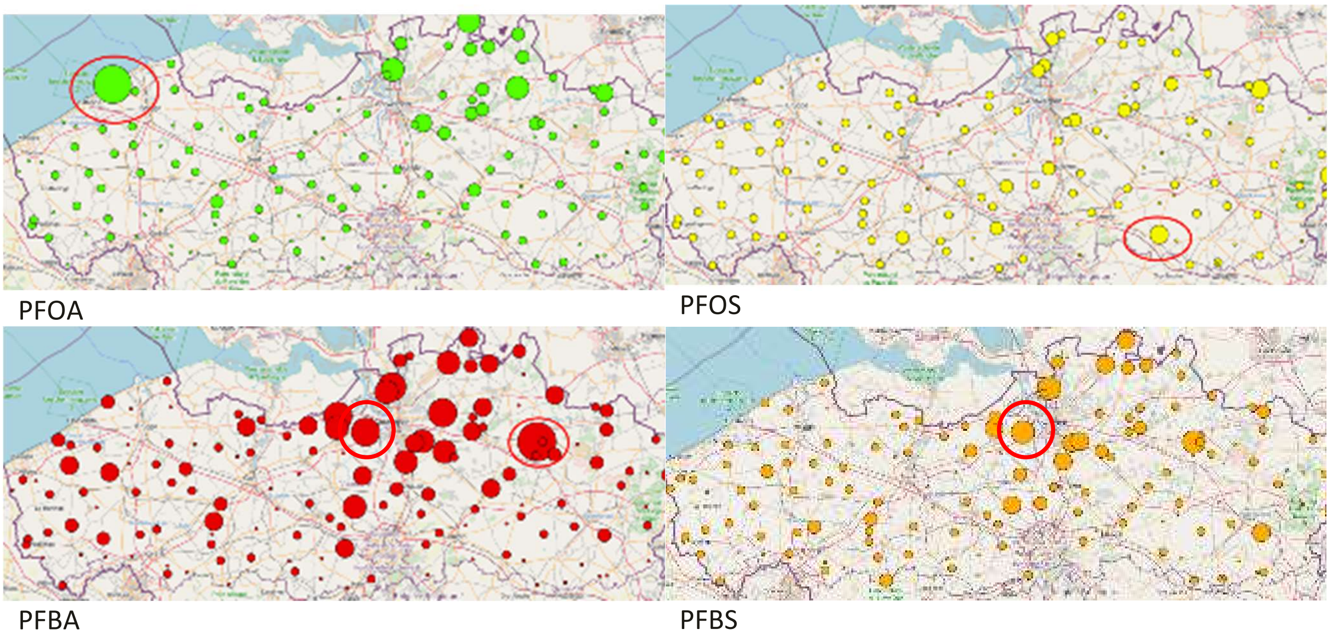


Figure 11: Location outliers groundwater

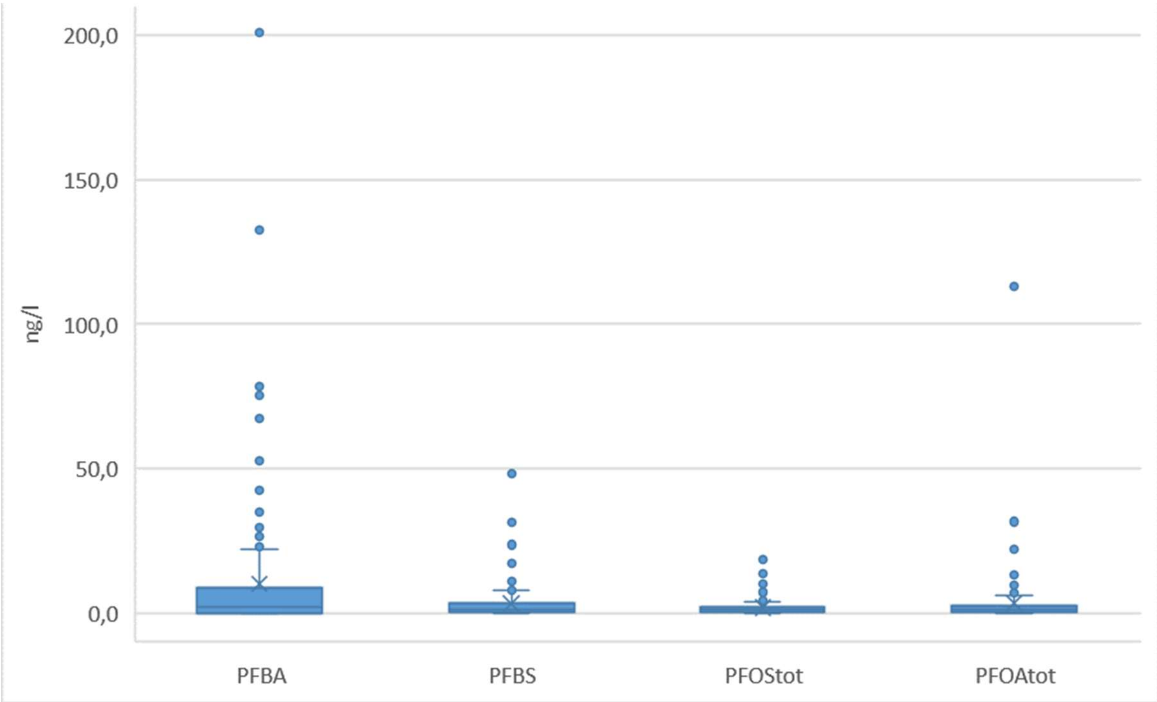


Figure 12: Boxplot results dataset 1, including values below limit of quantification . (x: mean value, - quartiles)

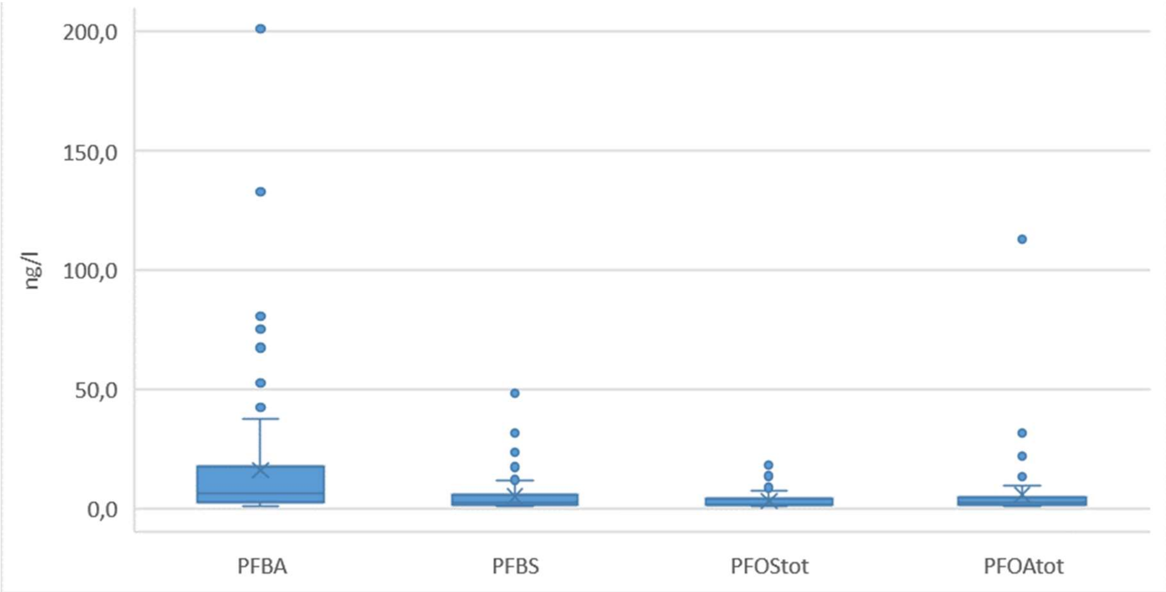


Figure 13: Boxplot results dataset 1, only for values above the limit of quantification. (x: mean value, - quartiles)

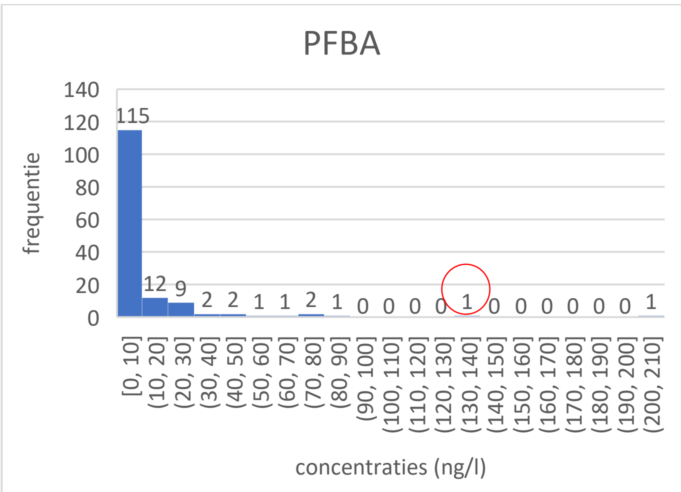


Figure 14: Histogram results PFBA - including results below limit of quantification

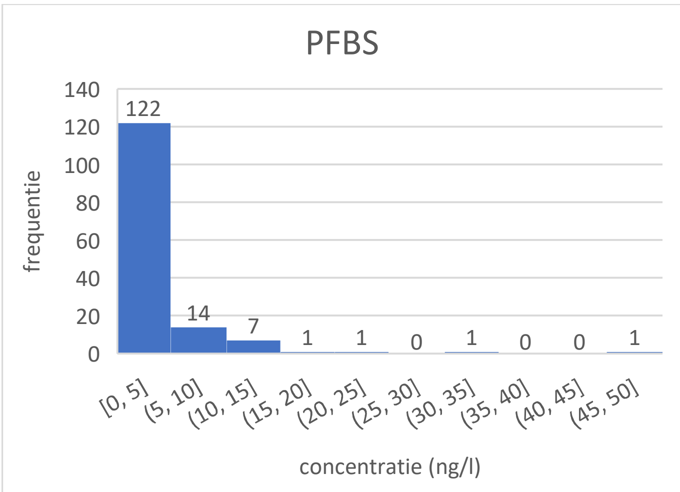


Figure 15: Histogram results PFBS - including results below limit of quantification

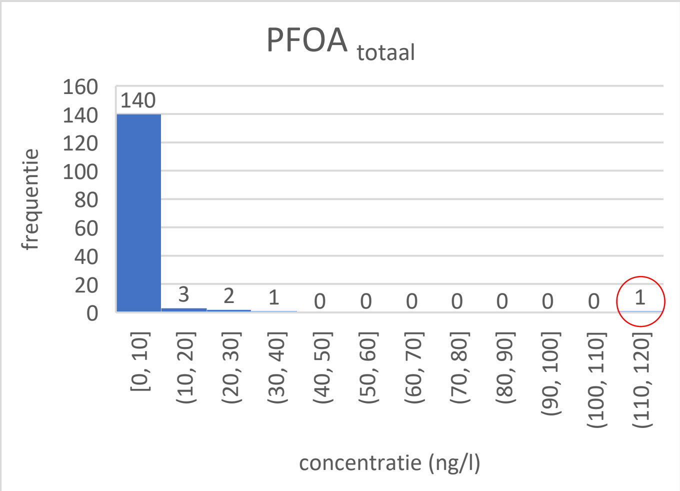


Figure 16: Histogram of results PFOA $_{total}$ - including results below limit of quantification

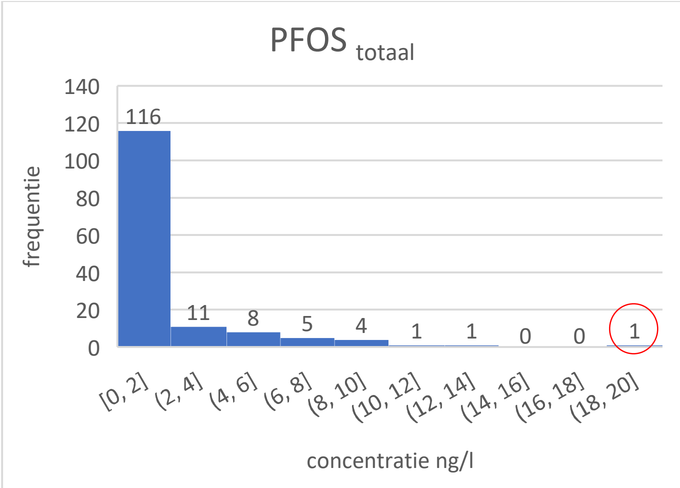


Figure 17: Histogram results PFOS $_{total}$ - including results below limit of quantification

6.1.5 Calculation of 90 percentiles based on dataset 1 and outlier analysis

The 90 percentile was calculated for:

- all results from the measurement campaign,
- all results from the measurement campaign except outliers,
- all results of the measurement campaign excluding outliers and excluding the results of the 2 monitoring wells closer than 100 m to a suspected site (see Table E, §3.2).
- The sum of PFAS, respectively taking into account a reporting limit of the individual components as included in the WAC and limits of quantification as included in Annex 3. All results from the monitoring wells with outliers were excluded in the calculations for the sum PFAS without outliers.

In Table L the 95-percentile is also calculated for comparison.

Table L: Percentiles based on data set 1

ng/L	All results measurement campaign	Without outliers	Without outliers and without monitoring wells 861/62/1 and 835/00/1
90 percentile			
PFBA	23,5	22.9 (1 outlier) 22.5 (2 outliers)	22 (1 outlier) 21.6 (2 outliers)
PFBS	7,8	7,5	7,1
PFOA$_{total}$	6,5	6,2	6,2

ng/L	All results measurement campaign	Without outliers	Without outliers and without monitoring wells 861/62/1 and 835/00/1
$PFOS_{total}$	4,7	4,5	4,4
Sum PFAS quantitative	35,8* 58,0**	25,8* 53,0**	24,0* 46,1**
Sum PFAS (EU20).	35,8* 57,4**	25,8* 49,7**	24,0* 42,9**
Sum PFAS total (quantitative + indicative).	35,8* 58,5**	25,8* 54,6**	24,0* 46,1**
95 percentile			
PFBA	42,6	41.1 (1 outlier) 36.9 (2 outliers)	34.2 (1 outlier) 29.4 (2 outliers)
PFBS	11,5	10,9	10,4
$PFOA_{total}$	9,6	9	9,1
$PFOS_{total}$	7,1	6,8	6,8
Sum PFAS quantitative	67,7* 92,8**	52,9* 69,0**	41,3* 69,5**
Sum PFAS (EU20).	67,7* 89,1**	52,9* 65,6**	41,3* 66,0**
Sum of PFAS total	67,7* 92,8**	52,9* 69,0**	41,3* 69,5**

*using reporting limit WAC. Concentrations of a PFAS component smaller than reporting limit were set to 0 equal in the sum.
** using limit of quantification (Annex 3). Concentrations of a PFAS component less than the limit of quantification were set equal to 0 in the sum.

The variation within the different calculated scenarios with and without outliers is limited. These variations between the different calculations are smaller than the margins of error for these components in the laboratory. The P90 value varies

- for PFBA from 21.6 to 23.5 ng/L (8% variation)
- for PFBS from 7.1 to 7.8 ng/L (9% variation)
- for PFOA total of 6.2 to 6.5 ng/L (variation 5%)
- for PFOS total from 4.4 to 4.7 ng/L (6% variation)

6.2 GROUNDWATER: COMBINED DATASET RESULTS (DATASET 1+ 2)

In this section, the results from dataset 1 are expanded with a dataset of available analyses from VMM's measurement campaigns (dataset 2). Thus, the combined dataset consists of dataset 1 and dataset 2.

6.2.1 Comparison results high flow -low flow sampling

The sampling of groundwater from the analyses from dataset 2 (dataset made available by VMM) was done via high flow principle, in contrast to those from dataset 1 (low flow, CMA compliant). In order to evaluate the possible variability, 13 monitoring wells were sampled via both *high flow* and *low flow*.

These 13 monitoring wells were sampled on the same day first by the *low flow* and then by the *high flow* method.

The results are shown in Figure 18 through Figure 20.

Based on these results, the following can be summarized:

- In 1 monitoring well, none of the components were measured above the limit of quantification.
- In 10 of the 12 remaining groundwater samples, the *low flow* method gives a higher result for the total measured concentration of PFAS, than the *high flow* method (Figure 19).
- For the individual PFAS components, higher values are measured for one component and lower values for another when using a different sampling method. No trend can be observed here. The greatest variation can be seen in the results for PFBA, although no clear trend can be observed here either. The measured concentrations of PFBA are higher for one monitoring well using the *low flow* method and higher for another well using the *high flow* method.
- The PFAS fingerprinting (proportion of PFAS component on total and composition PFAS per monitoring well) varies: different components are measured in some monitoring wells depending on the sampling method used.

Given that there is no unambiguous difference between low flow sampling and high flow sampling and since no components are systematically higher or lower depending on the sampling method, it was concluded that the merging of datasets 1 and 2 is justified in the context of determining anthropogenic background PFAS values.

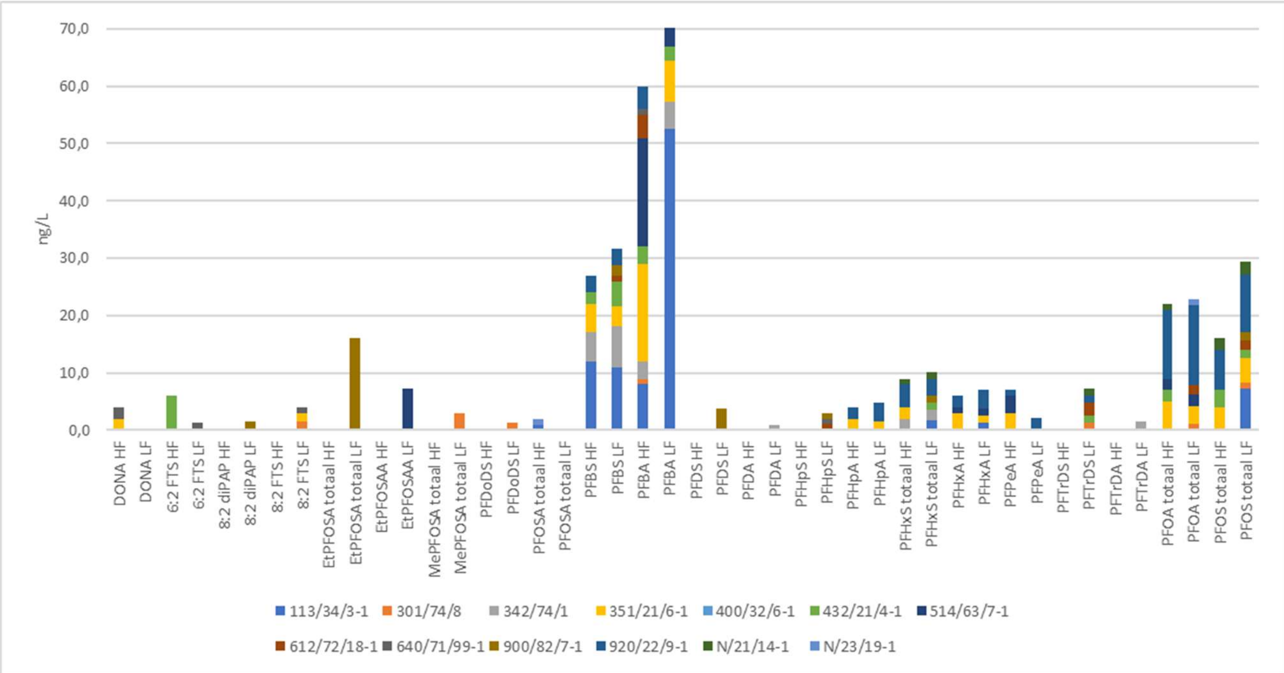


Figure 18: Comparison of PFAS concentrations in groundwater measured after high flow (HF) vs. low flow (LF) sampling - by component summed over 13 monitoring wells.

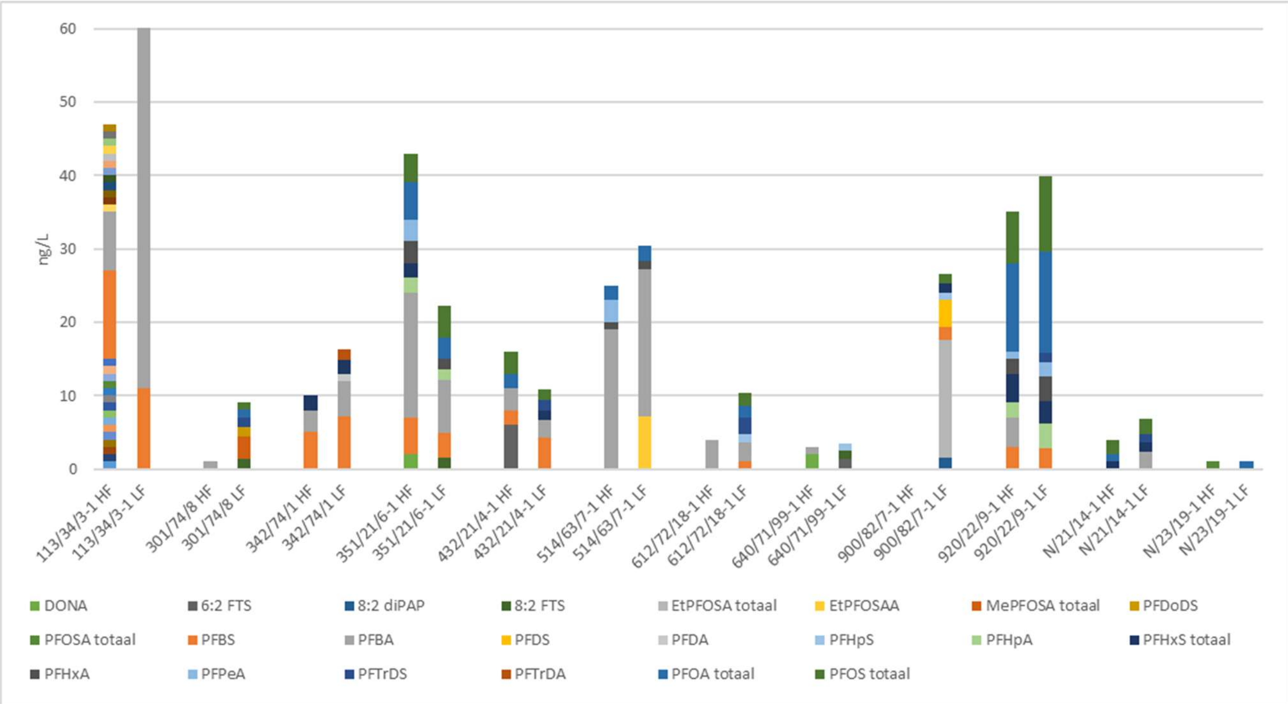


Figure 19: Comparison of PFAS concentrations in groundwater measured after high flow (HF) vs low flow (LF) sampling - per monitoring well

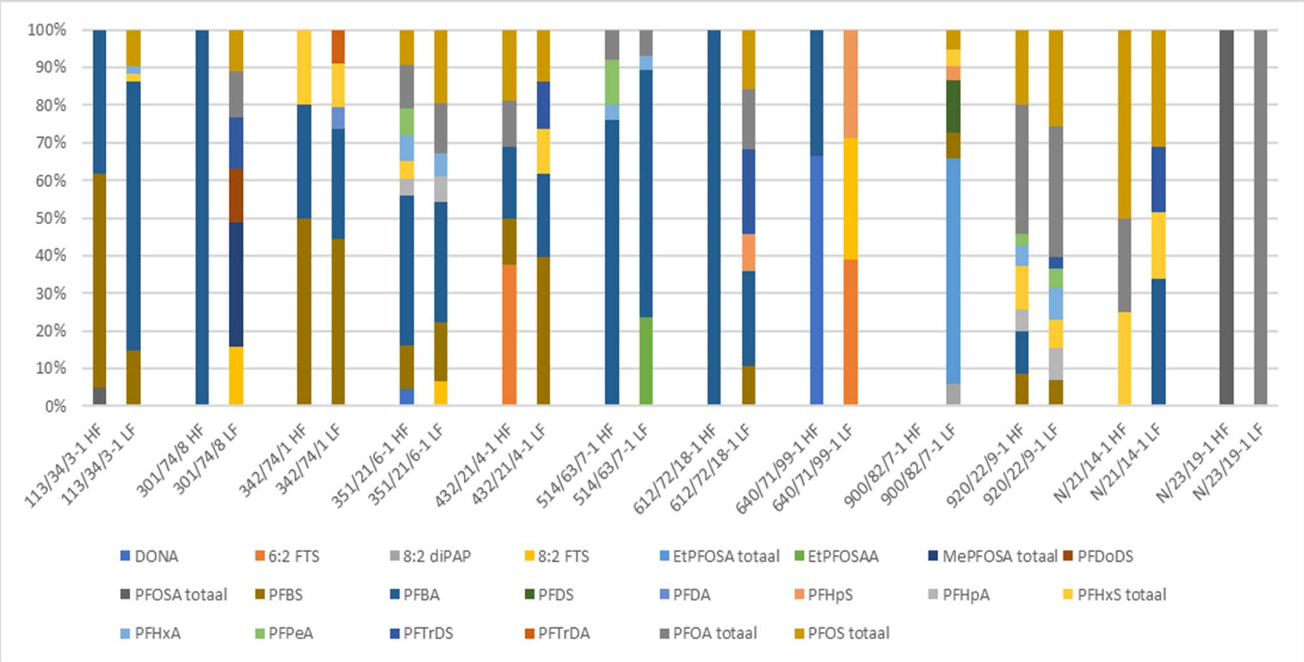


Figure 20: Comparison of PFAS fingerprints in groundwater after high flow (HF) vs. low flow (LF) sampling - relative proportion of each component per monitoring well

6.2.2 Statistical key figures individual PFAS components in groundwater

The combined dataset contains 387 sampling locations: 147 from dataset 1 from OVAM and 240 from dataset 2 from VMM.

The dataset 2 (VMM) was further adjusted as follows:

- If a result from both high flow and low flow sampling is available, the low flow result was included in database
- For some results from dataset 2 (VMM), the laboratory indicated that there was uncertainty in the reported values. These values were not included in the database. As a result, not the same number of results are available for each substance.
- For the branched form of PFOA, PFOS, PFHxS and PFOSA, results are only available in dataset 2 (VMM).

Table M shows the key figures for all components where at least 1 result above the limit of quantification was measured. Components from the WAC that are not included in this table were never found above the limit of quantification.

The results confirm these from dataset 1 (§6.1). From the statistical key figures, the following can be summarized:

- in 341 of 387 monitoring wells, at least 1 PFAS component is measured above limit of quantification at non-suspected sites.
- The majority of the analytical results are below the limit of quantification.
- The top 4 most abundant PFAS in the 387 monitoring wells are PBBA, PFBS, PFOS and PFOA. PFBA and PFBS are analyzed above the limit of quantification in 59% and 57% of samples, respectively. PFOA is reported above the limit of quantification in 49% of samples and PFOS in 34% of samples. The remaining PFAS components are analyzed above limit of quantification in less than 33% of the samples.
- Thus, only for PFBA, $PFOA_{total}$ and PFBS are there sufficient data to perform further statistical analyses and calculate a representative anthropogenic background value. Since $PFOS_{total}$ is a frequently occurring component in soil studies and a anthropogenic background concentration in soil was also determined for this component, PFOS is also included in the further calculations.

Analogous to dataset 1, mapping and outlier analysis is performed for these 4 substances only.

Table M: summary statistical key indicators combined dataset

		Key indicators including results below limit of quantification							Key indicators from results above limit of quantification				
component	Number of measurements	#>LOQ	#<LOQ	%>LOQ	% <LOQ	median (P50) (ng/L)	P90 (ng/L)	P95 (ng/L)	Min of values from LOQ	Maximum measured value	average	median (P50)	SD
PFBA	370	220	150	59%	41%	3,0	21,1	34,5	1,0	201,0	13,4	6,8	21,4
PFBS	385	220	165	57%	43%	2,0	9,5	13,8	1,0	74,0	6,2	3,9	8,2
PFOA Total	387	191	196	49%	51%	< KL	8,1	13,2	1,0	112,9	6,5	3,0	12,0
PFOA lin	387	157	230	41%	59%	< KL	8,0	12,0	1,0	99,5	6,2	2,8	12,0
PFOS Total	387	132	255	34%	66%	< KL	5,0	8,0	1,0	26,0	3,2	2,0	3,5
PFHxA	387	128	259	33%	67%	< KL	4,2	7,0	1,0	19,0	3,1	2,0	3,0
PFHxS Total	387	118	269	30%	70%	< KL	4,0	7,0	1,0	38,7	3,3	2,0	4,8
PFPA	385	112	273	29%	71%	< KL	5,0	8,0	1,0	20,0	3,6	2,1	3,3
PFHxS Lin	387	100	287	26%	74%	< KL	3,0	7,0	1,0	36,6	3,0	2,0	4,5
PFHPA	387	88	299	23%	77%	< KL	3,0	7,0	1,0	18,0	3,0	1,8	3,5
PFOA far	240	51	189	21%	79%	< KL	1,1	2,0	1,0	10,0	1,8	1,0	1,5
PFOS far	240	48	192	20%	80%	< KL	2,0	3,0	1,0	23,0	2,8	2,0	3,4
PFOS lin	387	53	334	14%	86%	< KL	2,0	6,7	1,0	13,3	2,7	1,6	2,4
PFHxS far	240	32	208	13%	87%	< KL	< KL	2,0	1,0	6,0	1,7	1,0	1,1
PFOSA tot	386	50	336	13%	87%	< KL	2,0	7,0	1,0	50,0	4,3	1,5	8,5
PFOSA lin	387	43	344	11%	89%	< KL	1,4	7,0	1,0	45,0	4,1	1,5	8,1
6:2 FTS	387	38	349	10%	90%	< KL	1,3	5,0	1,0	39,0	3,3	1,6	6,2
PFPS	387	33	354	9%	91%	< KL	1,7	4,0	1,0	8,1	2,2	1,6	1,7
GENX	387	32	355	8%	92%	< KL	1,3	3,0	1,0	4,0	1,7	1,4	0,7
ETFOSAA	384	29	355	8%	92%	< KL	1,5	3,2	1,3	7,2	2,5	2,1	1,3
8:2 FTS	387	24	363	6%	94%	< KL	1,1	1,7	1,0	3,0	1,5	1,5	0,4
PFOSA far	240	14	226	6%	94%	< KL	< KL	< KL	1,0	5,0	1,6	1,0	1,2
PFHXDA	387	21	366	5%	95%	< KL	1,1	5,0	1,0	8,0	3,1	2,0	2,3
ADONA	384	19	365	5%	95%	< KL	< KL	5,0	1,0	33,0	5,5	3,0	7,5
MEFOSAA	384	18	366	5%	95%	< KL	< KL	3,0	1,0	4,7	2,7	2,3	1,3
PFTrDS	386	16	370	4%	96%	< KL	< KL	7,0	1,0	7,8	2,2	1,3	2,0
PFNA	387	13	374	3%	97%	< KL	< KL	4,0	1,0	91,0	10,0	2,0	24,5
8:2 diPAP	387	12	375	3%	97%	< KL	< KL	1,6	1,0	16,0	3,5	1,5	4,6
PFDA	387	12	375	3%	97%	< KL	< KL	3,7	1,0	28,0	5,5	3,0	7,6
PFTrDA	387	12	375	3%	97%	< KL	< KL	2,0	1,0	7,0	2,3	1,4	1,9
MEFOSA Total	371	11	360	3%	97%	< KL	< KL	< KL	2,3	7,6	3,8	3,2	1,7
PFDoDS	387	11	376	3%	97%	< KL	< KL	1,3	1,0	1,4	1,2	1,2	0,1
PFUnDA	387	10	377	3%	97%	< KL	< KL	3,0	1,0	14,0	5,0	3,0	4,5
PFDoDA	387	10	377	3%	97%	< KL	< KL	2,0	1,0	10,0	3,8	2,0	3,2
MEFOSA lin	372	9	363	2%	98%	< KL	< KL	2,0	2,1	3,9	2,9	3,0	0,7
4:2 FTS	387	7	380	2%	98%	< KL	< KL	1,3	1,0	1,5	1,3	1,3	0,2

		Key indicators including results below limit of quantification							Key indicators from results above limit of quantification				
component	Number of measurements	#>LOQ	#<LOQ	%>LOQ	% <LOQ	median (P50) (ng/L)	P90 (ng/L)	P95 (ng/L)	Min of values from LOQ	Maximum measured value	average	median (P50)	SD
PFHpS	387	7	380	2%	98%	< KL	< KL	1,3	1,0	2,7	1,4	1,2	0,6
PFTeDA	387	7	380	2%	98%	< KL	< KL	2,5	1,0	6,0	2,8	1,5	2,3
PFUnDS	387	4	383	1%	99%	< KL	< KL	2,0	1,9	3,5	2,4	2,2	0,7
PFECHS	387	3	384	1%	99%	< KL	< KL	< KL	1,1	2,6	1,6	1,1	0,9
ETFOSA lin	371	2	369	1%	99%	< KL	< KL	< KL	4,2	12,9	8,5	8,5	6,2
ETFOSA Total	368	2	366	1%	99%	< KL	< KL	< KL	5,7	16,0	10,8	10,8	7,3
PFNS	387	2	385	1%	99%	< KL	< KL	< KL	1,1	1,2	1,1	1,1	0,1
PFODA	387	2	385	1%	99%	< KL	< KL	< KL	4,0	6,0	5,0	5,0	1,4
PFBSA	384	2	382	1%	99%	< KL	< KL	< KL	2,0	3,0	2,5	2,5	0,7
PFDS	387	1	386	0%	100%	< KL	< KL	< KL	2,3	2,3	2,3	2,3	N/A

LOQ = limit of quantification

SD = standard deviation

P50 = 50-percentile

P90 = 90 - percentile

P95 = 95 - percentile

6.2.3 Statistical key indicators "sum PFAS"

The "sum PFAS" was calculated in 2 ways:

- based on the reporting limits for the individual components as contained in the WAC (https://reflabos.vito.be/2023/WAC_IV_A_025.pdf). Components below these limits are not counted in the sum (set equal to 0).
- based on the limits of quantification that are lower than the maximum reporting limits for the individual components used in this study (Annex 3), components below these limits are not counted in the sum (set equal to 0)

The statistical key indicator "sum PFAS" were reported as soon as one of the components exceeds its respective limit of quantification or reporting limit from the WAC, i.e. from 10 ng/L or 1 ng/L, respectively.

The key indicators of the resulting "sum PFAS" are summarized in Table N and include:

- percentile values P50, P90, P95 based on all results
- mean, median and standard deviation based on all results above limit of quantification
- minimum and maximum measured concentration.

The dataset 2 (VMM) was further adjusted as follows:-.

- For calculating the sum PFAS, all measurement data from monitoring wells where at least 1 result with uncertainty was reported by the lab were removed from the dataset (17 sampling points).

The results confirm these from dataset 1 (§6.1.2):

- When the reported limits of quantification of the individual components are lower than the maximum reporting limits of the WAC, "sum PFAS" can be reported for more sites. This is because individual concentrations smaller than 10 ng/L can also be quantified and thus reported and summed. This thus leads to more sum results when the individual components are measured in the lower concentration intervals (and thus not equated to 0).
- When the reporting limit from WAC is used for the individual components, the results for the sums are often higher than in the calculation option with the limit of quantification. This is because only values above 10 ng/L (WAC) are counted in the "sum PFAS," which means that a sum can only be calculated for samples with higher concentrations.
- When using the reporting limits for the individual components as included in the ASC, no "sum PFAS total" can be calculated in 269 of the 370 monitoring points because for all individual components in that monitoring point the concentration is below the reporting limit (74% of the samples). "Sum PFAS" is reported as "below reporting limit" in that case.
- When a limit of quantification per individual parameter is used that is lower than the maximum reporting limit, the highest measured sum in the dataset is also higher than in the case with reporting limits per individual parameter, because in that case individual components between 1-10 ng/L are counted in the "sum PFAS." For the same reason, the P90 and P95 are also higher. For this dataset, this

means that when using the lower limits of quantification from this study, the P90 for the sum PFAS would be about 50% higher than when using the reporting limits from the WAC.

- There is little /no difference in P90 between "sum PFAS quantitative", "sum PFAS EU DWD20" and "sum PFAS total". That is, most of the components that were measured belon tot the group of 20 PFAS included in "sum PFAS EU DWD20" and also determine the P90 of "sum PFAS".

Table N: Summary sum parameters groundwater (ng/L) - combined dataset

			Key indicators including results below reporting limit							Key indicators of results as of reporting limit				
	component	Number of measurements	# with min. 1 PFAS>RL	# with all PFAS <RL	% with min 1 PFAS >RL	% with all PFAS <RL	Median (P50)	P90	P95	Min of values above RL	Max of values above RL	averag e	Media n (P50)	SD
Sum PFAS with RG from WAC (1)	Sum PFAS quantitative	370	101	269	27%	73%	<RG	33,0	63,8	10,0	239,0	40,6	24,4	45,3
	Sum of PFAS (EU DWD20).	370	97	273	26%	74%	<RG	31,1	63,8	10,0	239,0	40,0	24,0	45,1
	Sum of PFAS total	370	101	269	27%	73%	<RG	33,0	63,8	10,0	239,0	40,6	24,4	45,3

			Key indicators including results below limit of quantification							Key indicators of results as of limit of quantification				
	component	Number of measurements	# with minus 1 PFAS>LOQ	# with all PFAS<LOQ	% with min 1 PFAS >LOQ	% with all PFAS <LOQ	P50	P90	P95	Min of values above LOQ	Max of values above LOQ	averag e	media n	SD
Sum PFAS with KL from Annex 3 (2)	Sum PFAS quantitative	370	323	47	87%	13%	9,0	49,2	81,0	1,0	265,8	24,4	12,0	36,07
	SUM PFAS (EU DWD 20)	370	304	66	82%	18%	9,0	49,2	81,6	1,0	262,1	23,4	11,0	35,39
	SOM PFAS total	370	324	46	87%	12%	9,1	51,2	81,0	1,0	265,8	24,7	12,0	36,11

SD Standard deviation

LOQ limit of quantification

RG Reporting limit from WAC

P50 = 50-percentile

P90 = 90 - percentile

P95 = 95 - percentile

(1) taking into account WAC reporting limits (10 or 50 ng/L) - components below these limits are not counted in the sum (https://reflabos.vito.be/2023/WAC_IV_A_025.pdf)

(2) taking into account quantitation limits below the maximum reporting limits (1 ng/L for most components), components below these limits are not counted in the sum

6.2.4 Cartographic representation

The results for PFOS $_{total}$, PFOA $_{total}$, PFBA and PFBS are shown on Figure 21 through Figure 24 and in Annex 5.

Concentrations from dataset 2 below the limit of quantification are indicated by a dot and a sphere. For these points, the size of the sphere indicates the height of the limit of quantification - as it was increased for a number of sampling points.

Higher concentrations of PFBS, PFOA and PFBA are found mainly around, north and northeast of Antwerp. PFOS occurs in more even concentrations scattered throughout Flanders.

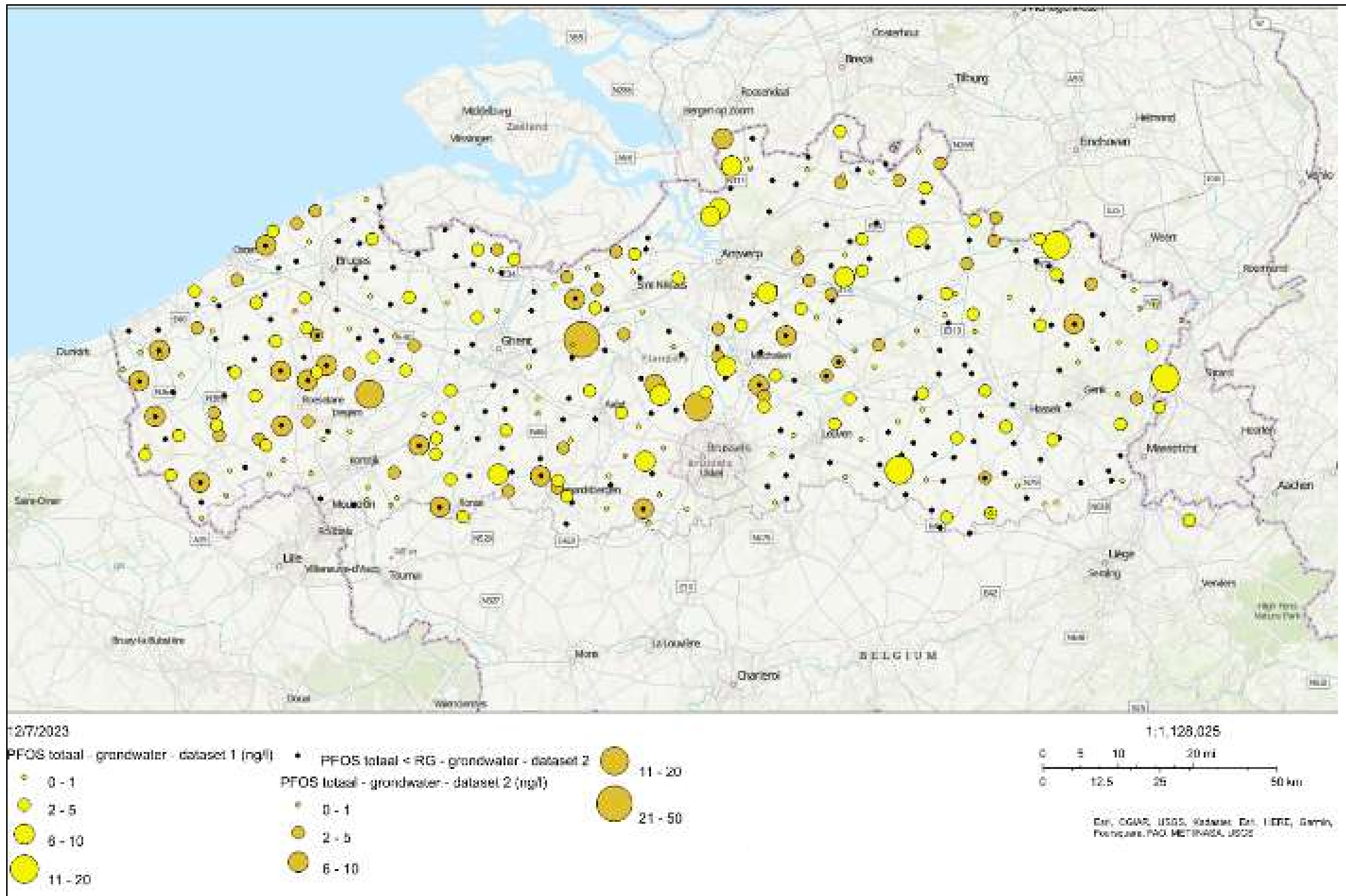


Figure 21: PFOS total in groundwater - data sets 1and 2

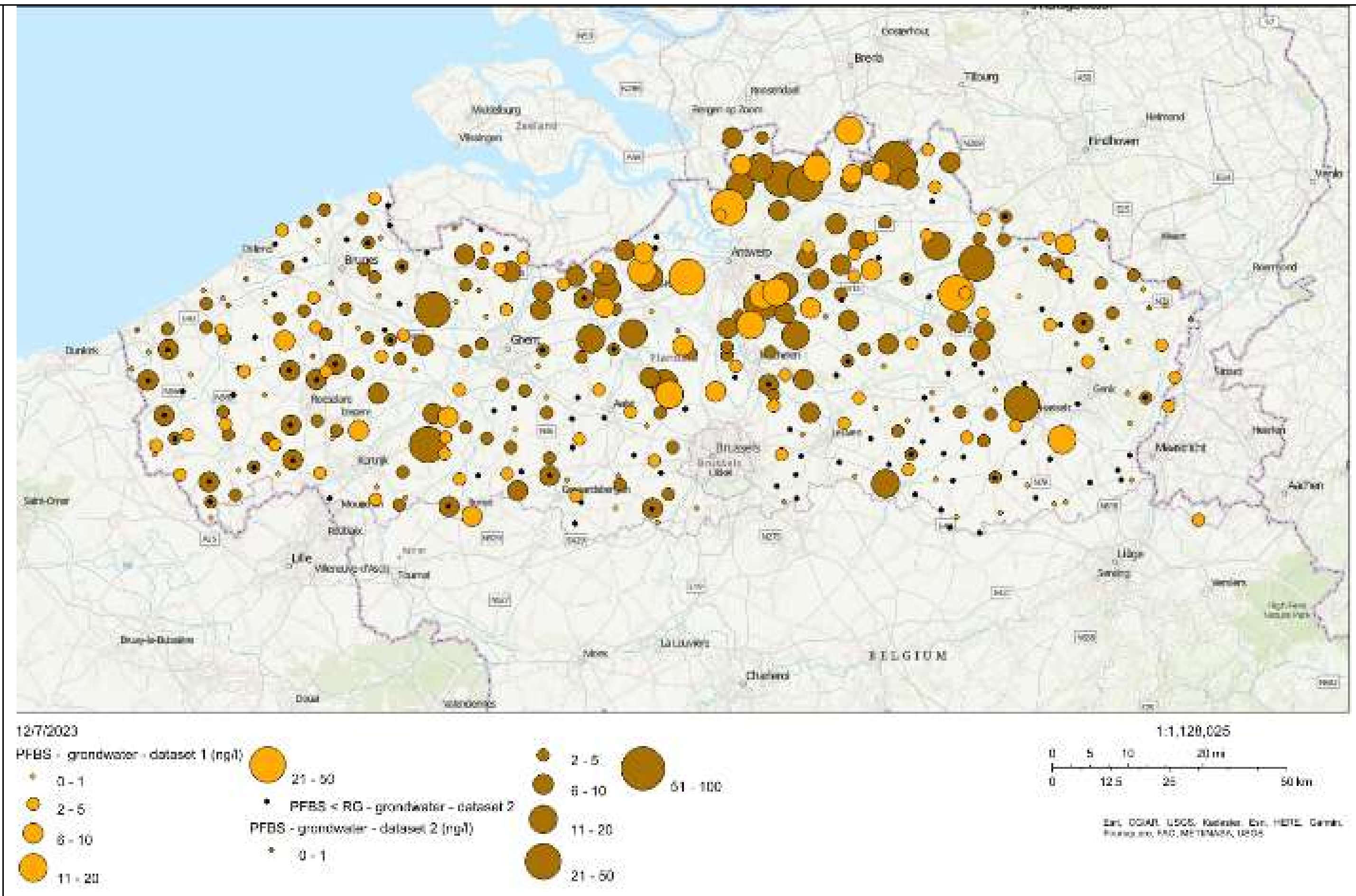


Figure 22: PFBS in groundwater (ng/L) - dataset 1 and 2

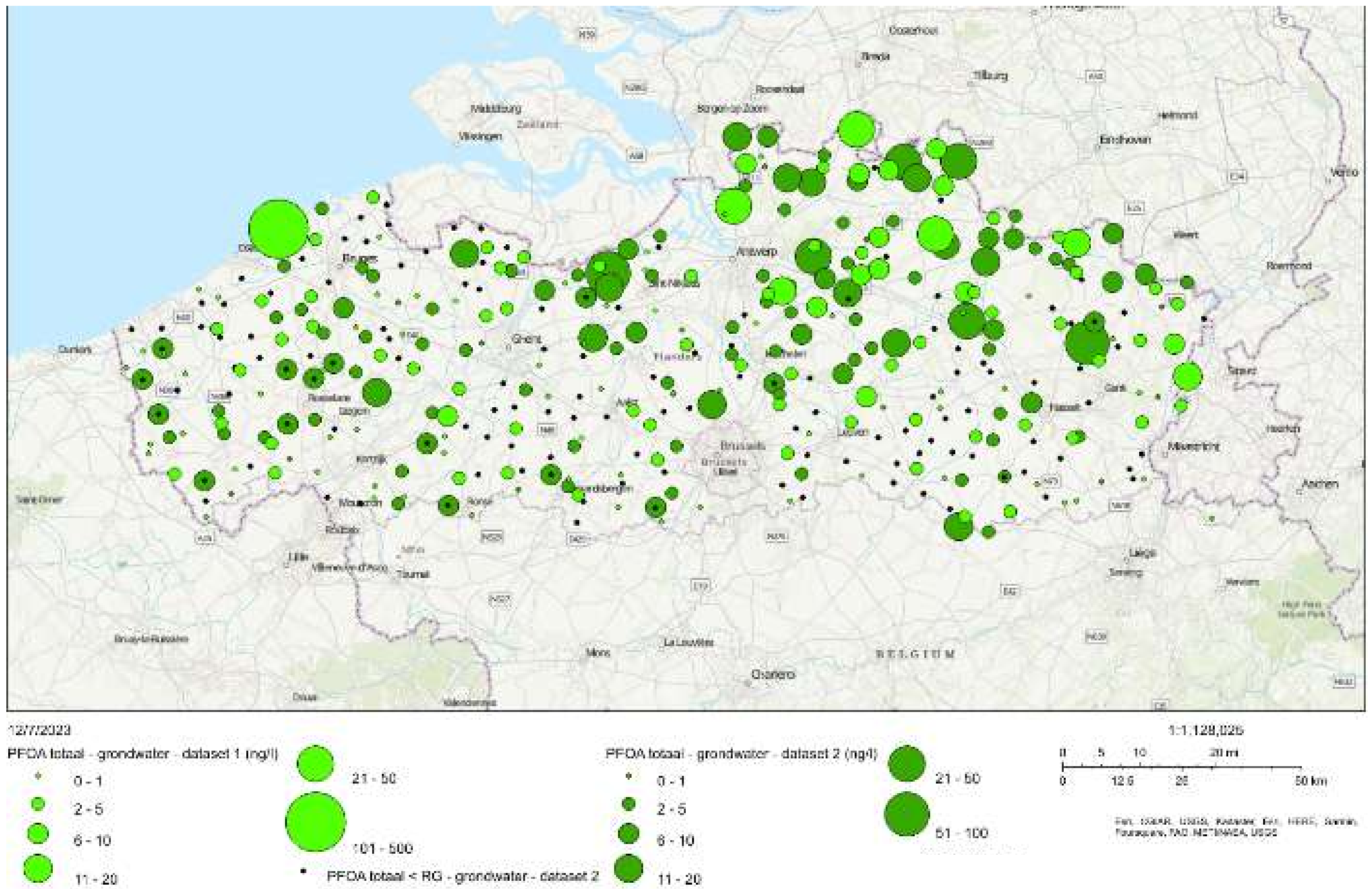


Figure 23: PFOA total in groundwater (ng/L) - dataset 1 and 2

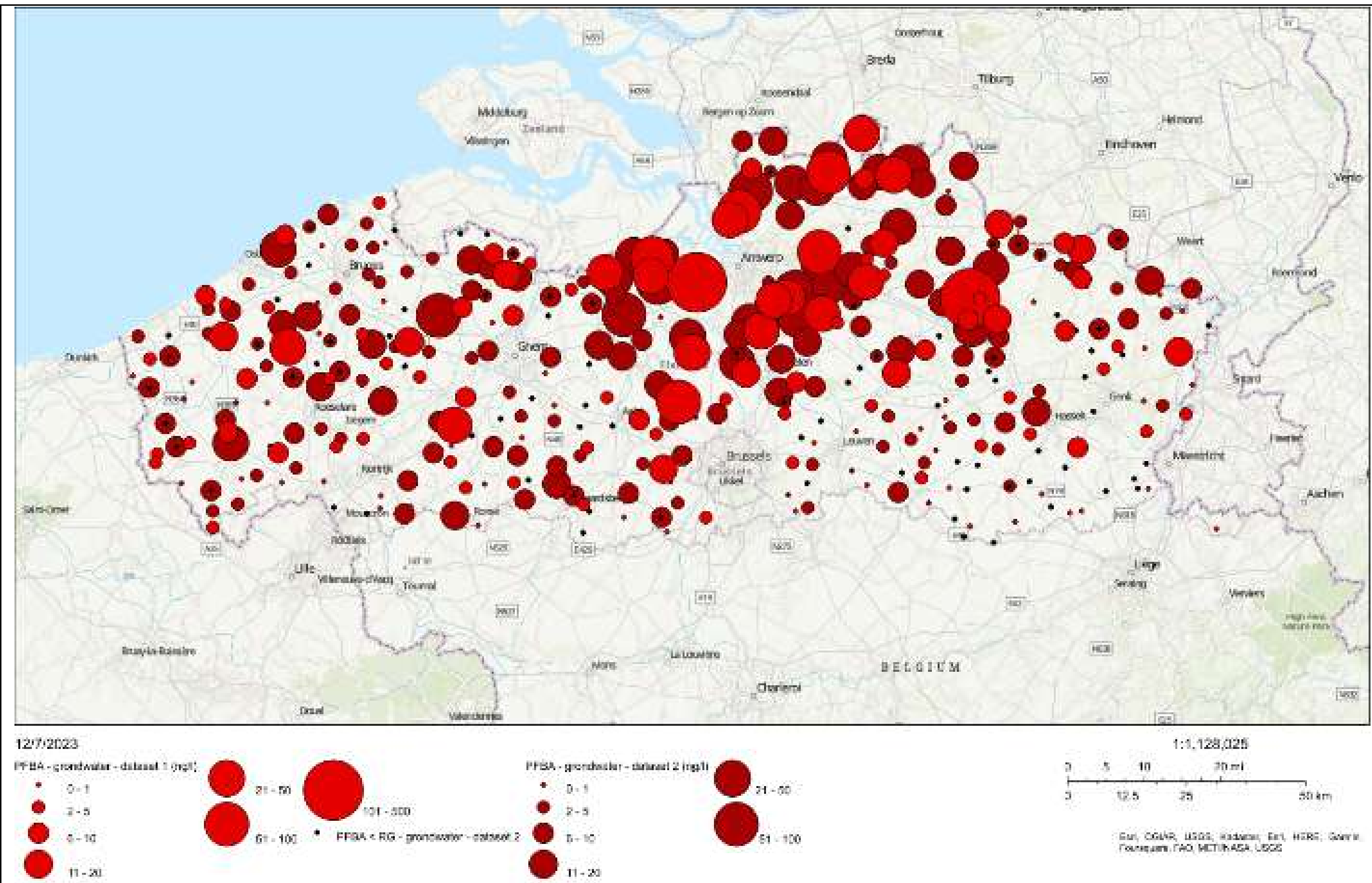


Figure 24: PFBA in groundwater (ng/L) - data sets 1and 2

6.2.5 Outlier analysis

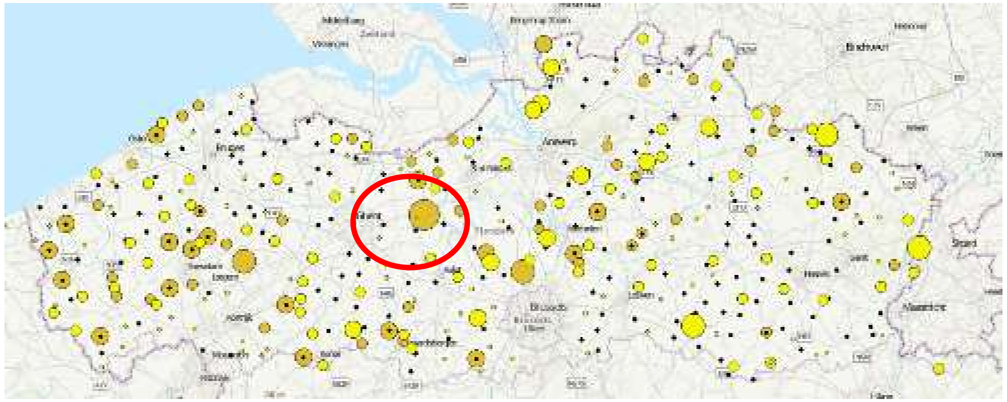
Outlier analysis was performed for PFOS $_{total}$, PFOA $_{total}$, PFBA and PFBS using Rosner's outlier test. Based on this test, 1 outlier was identified for each of these components, each in a different monitoring well. The location of these monitoring wells was examined in more detail (Table O and Figure 25) to see if this outlier could be explained.

A boxplot and histograms were then also prepared (Figure 26 through Figure 30). Based on this evaluation, the value for PFBA at monitoring well 842/62/1 and the value for PFOA at monitoring well 936/23/1 were also considered an outlier.

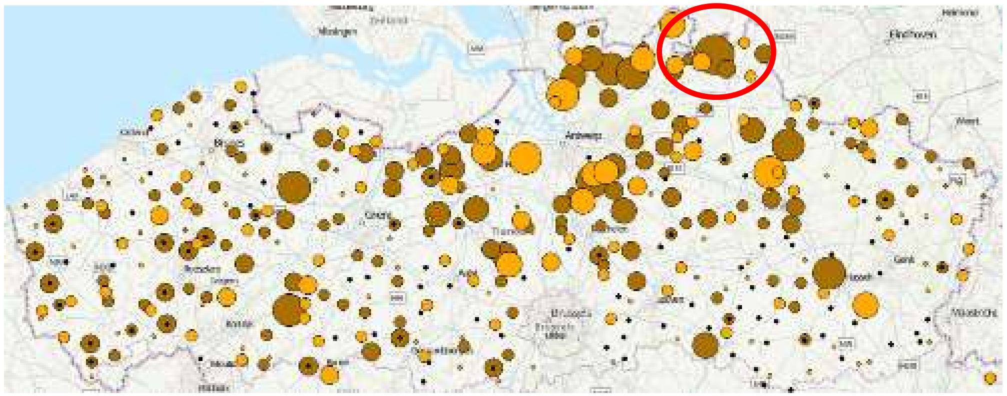
Not all outliers can be explained by the presence of PFAS suspect activities in the neighborhood. Therefore, when calculating the anthropogenic background concentrations, multiple scenarios will be calculated, namely with and without outliers.
Groundwater flow direction and the presence of known contaminants in the wider vicinity were not taken into account when selecting sites. Despite the careful selection of measurement points, it can never be completely excluded that some measurements were still influenced by a point source.

Table O: Outliers groundwater combined dataset

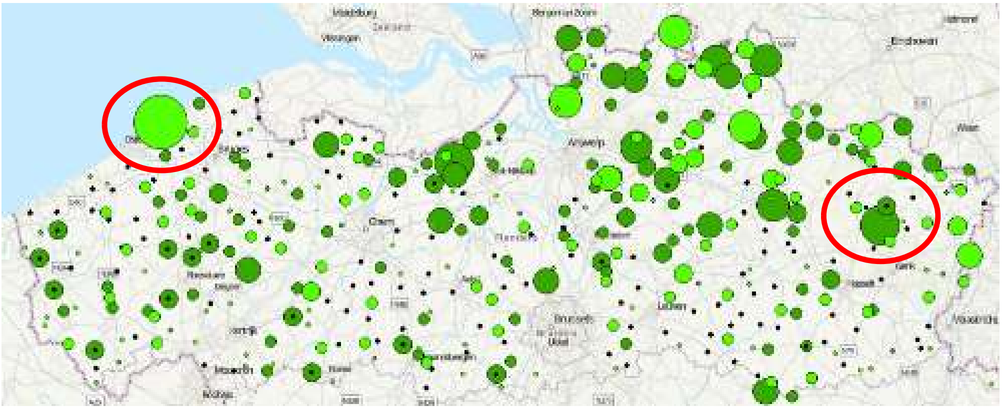
component	Outlier measurement value (ng/L)	monitoring well	Location
PFBA	201,0	502/62/2	Agricultural area, no springs nearby - few small land fills over 1 km away
	132	842/62/1	Based on boxplot and histogram. Near 3M
PFBS	74	941/40/29a	On border with the Netherlands, in Baarle-Hertog - about 700 from a fire station with preventive no regret zone - (PFBA also 84 ng/L, but uncertain result according to lab).
PFOAtot	112,9	N/10/3	Natural area/dunes
	88	935/23/1	Houthalen-Helchteren/Peer, near military domain, approx. 300 m from site where a OBO was carried out - storage of cattle feed, storage area for cars and tractors, manure storage, car wash for agricultural vehicles. Storage tanks diesel. Small workshop metalworking, fermentation plant.
PFOSto	26	801/21/9	Berlare, along E17, Near Industrial Park Lokeren (approx. 400 m - chocolate factory, printing shop etc)



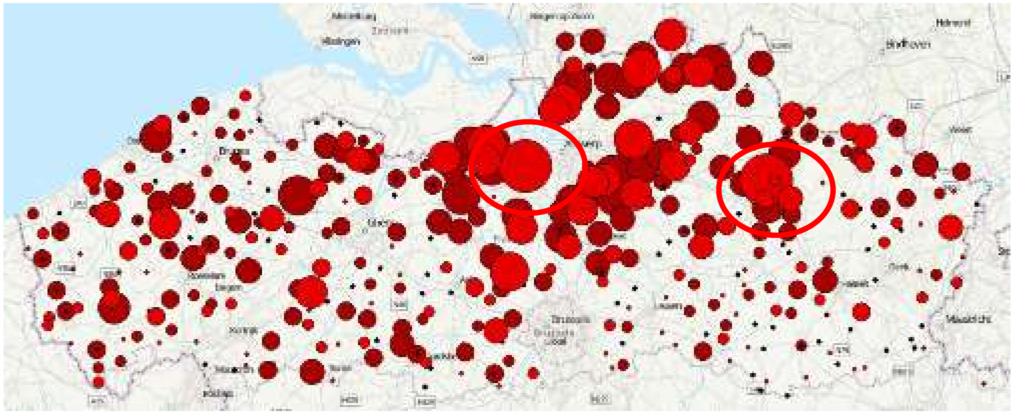
PFOS



PFBS



PFOA



PFBA

Figure 25: Location of outliers combined dataset

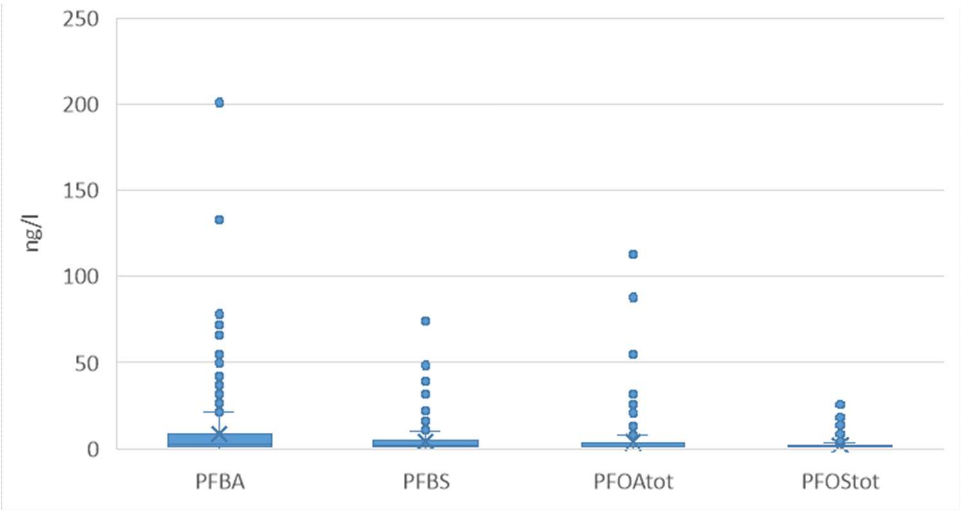


Figure 26: Boxplot results combined dataset, including values below limit of quantification. (x: mean value, - quartiles)

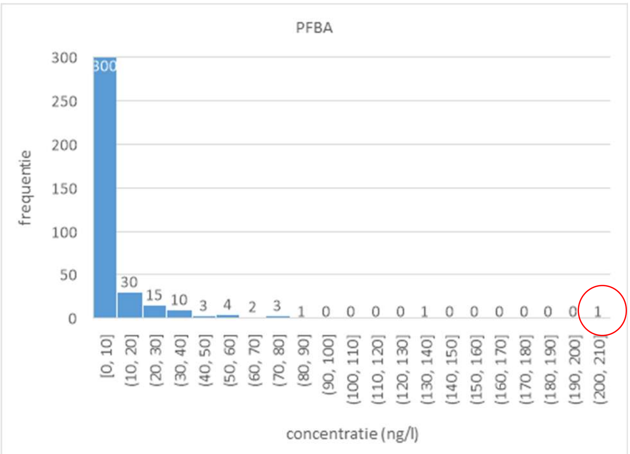


Figure 27: Histogram results PFBA - including results below limit of quantification. (x: mean value, -quartiles)

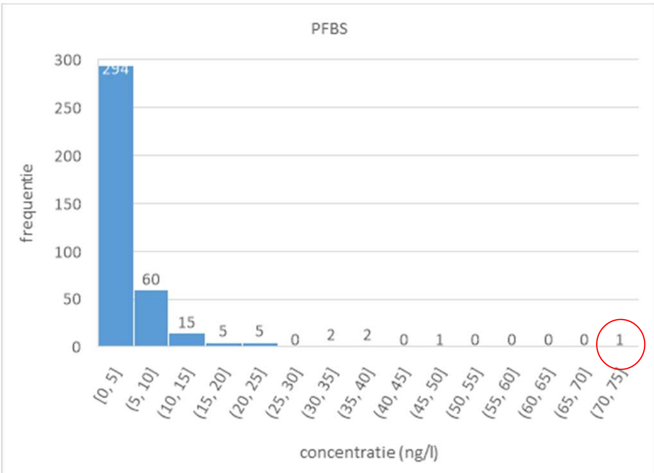


Figure 28: Histogram results PFBS - including results below limit of quantification. (x: mean value, - quartiles)

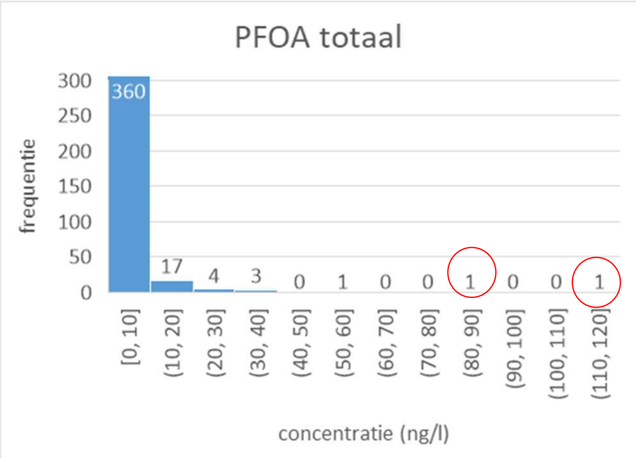


Figure 29: histogram results PFOA total - including results below limit of quantification . (x: mean value, quartiles)

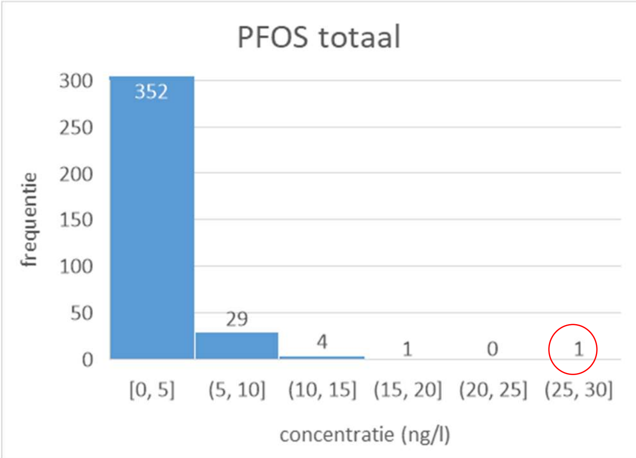


Figure 30: histogram results PFOS total - including results below limit of quantification. (x: mean value, -quartiles)

6.2.6 Calculation P90 groundwater based on combined database

The 90 percentile was calculated for:

- All results from the combined dataset,
- All results from the measurement campaign except outliers,
- all results from the combined dataset excluding outliers and excluding the results from the 2 monitoring wells from dataset 1 that are closer than 100 m to a suspected site (see Table E, §3.2).
- The sum of PFAS, respectively taking into account a reporting limit of the individual components as included in the WAC and limits of quantification as included in Annex 3. All results from the monitoring wells with outliers were not included in the calculations for the sum PFAS without outliers.

The 95 percentile was also calculated for comparison, as were the results based on dataset 1.

Table P: Percentiles based on the combined data set

ng/L	All results combined dataset	Combined dataset without 6 outliers	All results Dataset 1	Dataset 1 without outliers	Dataset 1 without outliers and without 861/62/1 and 835/00/1
90 percentile					
PFBA	21,1	21,0	23,5	22.9 (1 outlier) 22.5 (2 outliers)	22 (1 outlier) 21.6 (2 outliers)
PFBS	9,5	9,4	7,8	7,5	7,1
PFOAtot	8,1	8,0	6,5	6,2	6,2
PFOSto	5,0	5,0	4,7	4,5	4,4

ng/L	All results combined dataset	Combined dataset without 6 outliers	All results Dataset 1	Dataset 1 without outliers	Dataset 1 without outliers and without 861/62/1 and 835/00/1
Sum PFAS quantitative	33,0* 49,2**	30,5* 48,0**	35,8* 58,0**	25,8* 53,0**	24,0* 46,1**
Sum PFAS (EU20).	31,1* 49,2**	27,0* 47, 0**	35,8* 57,4**	25,8* 49,7**	24,0* 42,9**
Sum of PFAS total	33,0* 51,2**	30, 5* 48,4**	35,8* 58,5**	25,8* 54,6**	24,0* 46,1**
95 percentile					
PFBA	34,5	33,0	42,6	41.1 (1 outlier) 36.9 (2 outliers)	34.2 (1 outlier) 29.4 (2 outliers)
PFBS	13,8	13,1	11,5	10,9	10,4
PFOAtot	13,2	13,0	9,6	9	9,1
PFOStot	8,0	8,0	7,1	6,8	6,8
Sum PFAS quantitative	63,8* 81,0**	51,8* 72,1**	67,7* 92,8**	52,9* 69,0**	41,3* 69,5**
Sum PFAS (EU20).	63,8* 81,6**	44* 71,2**	67,7* 89,1**	52,9* 65,6**	41,3* 66,0**
Sum of PFAS total	63,8* 81,0**	51,8* 72,1**	67,7* 92,8**	52,9* 69,0**	41,3* 69,5**

*based on reporting limit WAC
** based on limit of quantification (Annex 3) lower than reporting limit WAC

The variation within the different calculated scenarios with and without outliers is limited. These variations between the different calculations are smaller than the margins of error for these components in the laboratory.

6.3 PROPOSED GROUNDWATER ANTHROPOGENIC BACKGROUND CONCENTRATIONS AND EVALUATION

This section compares the P90 values of all previous calculated scenarios and proposes anthropogenic background concentrations for PFBA, PFBS and PFOA. Only these 3 components have concentrations above limit of quantification in (order of magnitude) half the number of measurements.

No anthropogenic background concentration was derived for the components occurring in less than half of the cases. However, the P90 values for PFOS are included in the tables, since a anthropogenic background concentration in soil is also available for this parameter and this is a common parameter in soil studies at PFAS-suspected sites.

Next, these proposed anthropogenic background concentrations are placed in perspective and compared with available assessment frameworks in Flanders and internationally on the one hand and with the European Groundwater Environmental Quality Standard (WFD) proposal on the other hand.

6.3.1 Proposal anthropogenic background concentrations

In Table Q is an overview of the calculated P90 values considering the different databases and taking into account outliers. In this way, an insight into the variation in P90 value due to size of dataset and to the presence or absence of outliers in the dataset is obtained.

Table Q: Summary of calculated P90 values in ng/L (dataset 1 and combined dataset, with or without outliers)

ng/L	All results measurement campaign dataset 1 (# 147)	All results combined dataset (dataset 1 + 2) (# 370-385)	Results dataset 1- Without outliers (# 145-146)	Results dataset 1 without outliers and without monitoring wells 861/62/1 and 835/00/1 (# 143-144)	Results combined dataset without 6 outliers (# 368-384)
PFBA	23,5	21,1	22.9 (1 outlier) 22.5 (2 outliers)	22 (1 outlier) 21.6 (2 outliers)	21,0
PFBS	7,8	9,5	7,5	7,1	9,4
PFOAtot	6,5	8,1	6,2	6,2	8,0
PFOStot (1)	*4,7*	*5,0*	*4,5*	*4,4*	*5,0*

(1) For PFOS, the P90 is given for information only, PFOS was detected above detection limit in less than 50% of groundwater analyses.

The following can be deduced from the various calculated scenarios:

- Compared to the results from dataset 1, the P90 value of the combined dataset (dataset 1+2) is marginally higher for PFBS, PFOA and PFOS. The P90 of PFBA is marginally lower in the combined dataset.
- The variation of P90 value calculated in groundwater based on the different datasets and with or without outliers, is limited
  - For PFBA between 21.0 and 23.5 ng/L (variation 11%)
  - For PFBS between 7.1 and 9.4 ng/L (variation 24%)
  - For PFOA between 6.2 and 8.1 ng/L (variation 23%)
  - For PFOS between 4.4 and 5.0 ng/L (variation 12%)

These variations between the different calculations are smaller than the allowable margins of error for these components in the laboratory, specifically between 10-25% (ring tests VITO).

Given that the larger data set is more representative of all of Flanders, the values in Table R are presented as anthropogenic background concentrations.

Table R: Proposed anthropogenic background groundwater values for PFBA, PFBS and PFOAtotal and indicative P90 value for PFOS

compound	ng/L
PFBA	21,0
PFBS	9,4
PFOAtot	8,0
PFOStot (1)	*5,0*

(1) For PFOS, the P90 is given for information only, PFOS was detected above detection limit in less than 50% of groundwater analyses.

For PFBS and $PFOA_{total}$, the proposed anthropogenic background concentrations are below the WAC reporting limits.

6.3.2 Anthropogenic background concentrations compared to existing frameworks and international studies

Soil remediation standards and discharge standards.
In Flanders, the soil remediation standards for groundwater are currently equal to 100 ng/L for sum EU DWD20 ((OVAM, 2022) and the discharge standard is 20 ng/L for each individual quantitative component (Vlaanderen.be/PFAS-vervuiling).

For PFBA a relatively high value is obtained for the 90 percentile and proposal anthropogenic background concentration namely 21.0 ng/L. This already fills a significant part of the soil remediation standard for the sum of the EU DWD20 PFAS (100 ng/L). Moreover, the proposed anthropogenic background PFBA is above the proposed discharge standard of 20 ng/L.

Anthropogenic background concentrations the Netherlands and Switzerland
In the Netherlands, a study was published in 2021 with analytical results for PFAS in groundwater. The results were divided into phreatic (< 10 m-mv) and intermediate-deep to deep groundwater (10-25 m-mv). (RIVM, 2021)

This study reports P50 and P95 percentiles. These are included for comparison in Table S along with the P95 percentiles calculated for the combined dataset without outliers in the present study. The Dutch study did not investigate to what extent the sampling locations are close to potential PFAS sources. The samples from the phreatic groundwater did originate from urban or industrial areas.

The P95 for phreatic groundwater in the Netherlands is higher for PFOA (35 ng/L) and PFBS (20 ng/L) than in Flanders and lower for PFOS (6.7 ng/L) and PFBA (21 ng/L).

Switzerland also published data on PFAS in groundwater distributed throughout its territory (Federal Office for the Environment (FOEN, Switzerland), 2023). It concerns 519 results from a groundwater monitoring network. The published data indicates at how many of the sites a PFAS component was found above the limit of quantification, 1 ng/L, 10ng/L or 100 ng/L. Based on this information, Table S estimates in which interval the P90 is located.

In Switzerland, both the P90 and P95 range between 1 and 10 ng/L for PFOA, PFBS and PFBA. For PFOS, the P90 percentile ranges between 1-10 ng/L and the P95 between 10-100 ng/L.
The concentrations in Switzerland are lower than the Flemish values for PFBA, PFBS (P95) and PFOA (P95). The P95 for PFOS in Flanders is lower compared to the Swiss data.

Table S: Comparison P90 and 95 percentiles for Flanders with Dutch and Swiss data

ng/L	PFOS		PFOA		PFBS		PFBA	
	P90	**P95**	**P90**	**P95**	**P90**	**P95**	**P90**	**P95**
Flanders	5,0	8,0	8,0	13,0	9,4	13,1	21,0	33,0
The Netherlands -Phreatic	/	6.7 (lin)	/	35 (lin)	/	20,0	/	21,0
The Netherlands - Shallow (10 m-mv) and mid-depth (25 m-mv).	/	0.22 (lin)	/	15.05 (lin)	/	3,71	/	7,52
Switzerland	1-10	10-100	1-10	1-10	1-10	1-10	1-10	1-10

6.4 COMPARISON WITH PROPOSED EUROPEAN ENVIRONMENTAL QUALITY STANDARD FOR GROUND AND SURFACE WATER

The European Commission proposed new priority substances for ground and surface water in October 2022 (Proposal amending Water Directives - European Commission (europa.eu)).

The proposal also included a proposed environmental quality standard for PFAS. This proposed standard is 4.4 ng/L for the sum of 24 PFAS components, expressed as PFOA equivalents. The equivalent method uses "relative potency factors" (RPF) which expresses the effects of the components relative to PFOA. The 24 PFAS components and their RPF are listed in Table T.

Table T: PFAS components and their RPF used for testing against the proposed environmental quality standard

Component	RPF	Component	RPF
PFBA	0,05	PFPeS	0,3005
PFPeA	0,03	PFHxS total	0,6
PFHxA	0,01	PFHpS	1,3
PFHpA	0,505	PFOS total	2
PFOA total	1	PFDS	2
PFNA	10	GenX	0,06

Component	RPF	Component	RPF
PFDA	7	ADONA	0,03
PFUnDA	4	PFTrDA	1,65
PFDoDA	3	PFODA	0,02
PFTeDA	0,3	(6:2 PHTHOH) (CAS 647-42-7, EU 211-477-1)	0,02
PFHxDA	0,02	(8:2 PHTHOH) (CAS 678-39-7, EU 211-648-0)	0,04
PFBS	0,001	2,2-difluoro-2-((2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl)oxy) acetic acid - (C6O4) (CAS 1190931-41-9)	0,06

3 of the 24 components were not analyzed in the datasets used in the present study:

- (6:2 PHTHOH) (CAS 647-42-7, EU 211-477-1) (RPF 0.02),
- (8:2 PHTHOH) (CAS 678-39-7, EU 211-648-0) (RPF 0.04)
- 2,2-difluoro-2-((2,2,4,5-tetrafluoro-5- (trifluoromethoxy)-1,3-dioxolan-4-yl)oxy) acetic acid - (C6O4) (CAS 1190931-41-9)) (RPF 0.06)

The sum of the remaining 21 components, corrected by their RPF, was calculated for all monitoring wells from the combined dataset without outliers where all results are available with good reliability (366 sampling points).

The results are shown in Table U.

When compared to the European Commission's proposed environmental quality standard for groundwater and surface water of 4.4 ng/L (https://environment.ec.europa.eu/publications/proposal-amending-waterdirectives_en), where 24 components are summed using a relative toxicity factor as PFOA equivalents, we find that:

- The proposed anthropogenic background concentrations (P90) of PFOA and PFOS already individually exceed this value of 4.4 ng/L.
- Although 3 of the 24 components in this sum were not analyzed in the present study, the proposed quality standard of 4.4 ng/L is already exceeded at 37% of sampled locations in unsuspected areas.

- The highest total concentrations are measured at locations where PFNA, PFDA, and PFUnDA are detected, the components with high RPFs (10, 7, and 4 respectively). The maximum concentration in the entire combined dataset, for example, is 1286 ng/L PFOA equivalents (based on the dataset including outliers). This is largely due to a measurement of 91 ng/L PFNA, which with an RPF of 10 contributes 910 ng/L to the total. In the other piezometers with the highest totals, there is always a contribution from PFNA, PFDA, or

PFUnDA. Note that PFNA was only detected above the limit of quantification in 13 of the 387 piezometers (PFUnDA and PFDA in 10 and 12 of the 387 locations respectively). A minority of piezometers with these components can have a significant influence on the percentiles of the weighted sum.

Table U: Calculation Sum 24 PFAS, compared to proposed environmental quality standard

	Key figures including results below limit of quantification				Numbers of sums > 0				
					ng/L				
component	Number of measurements	# with sum >0	# with sum = 0	# > 4.4 ng/L	Min values >0	Max value	average	Median (P50)	SD
Sum 24 (EQS - without 6 outliers).	366	300 (82%)	66 (18%)	134 (37%)	0,001	203,1	9,8	4,0	22,19

Sum parameters with LOQ Annex 3

EQS = proposed environmental quality standard

LOQ = limit of quantification

SD =standard deviation

* Number of measurements where the sum = 0, i.e., each individual component from the sum is smaller than the limit of quantification

7 EVALUATION OF PFAS IN SOIL AND DERIVATION OF ANTHROPOGENIC BACKGROUND CONCENTRATIONS

The evaluation and derivation of anthropogenic background concentrations in the soil and the mapping of the results was performed in different steps as different datasets were collected.
Initially, we work with the newly collected dataset (dataset 1, § 7.1) because this sampling and analysis was very anthropogenic backgrounded and uniform.

In a second step, the calculations are extended with a dataset of available analyses from VITO's measurement campaigns from the initial study where anthropogenic background concentrations for the soil for PFOS and PFOA were already derived (dataset 2). The combined dataset consists of dataset 1 and dataset 2 (§ 7.2).

The calculated anthropogenic background concentrations based on the new dataset are compared with the current anthropogenic background concentrations of PFOA and PFOS. An overarching evaluation is made and a proposal for anthropogenic background concentrations for the soil is presented (§7.3).

The ProUCL software package was used for statistical processing.

7.1 RESULTS SOIL - DATASET 1

7.1.1 Statistical key indicators individual PFAS components in soil

A total of 73 new samples of the soil were analyzed.

The summary key indicators for all components that were measured at least once above the limit of quantification are included in Table V. Components not included in the table were not found above the quantitation limit in any sample.
For the soil samples, the limit of quantification in the present study is equal to the reporting limit of the CMA.

These key indicators include:

- percentile values P50, P90, P95 based on all results
- mean, median and standard deviation based on all results above limit of quantification
- minimum and maximum measured concentration.

From the statistical key figures, the following can be summarized:

- The majority of the analytical results are below the limit of quantification.
- For PFOS , a value above limit of quantification was measured in 58% of the samples

Only for PFOS there are sufficient data to conduct further statistical analyses and calculate a representative anthropogenic background value.

For PFOS total, the distribution of results was examined. These results follow a lognormal distribution.

Outlier analyses were also performed for $PFOS_{total}$.

Table V: Summary analytical results soil (µg/kg ds) - dataset 1

component	LOQ	Number of measurements	#>LOQ	#<LOQ	%>LOQ	% <LOQ	Median (P50)	P90	P95	Min of values above LOQ	Max of values above LOQ	average	Median (P50)	SD
			Key indicators including results below limit of quantification							Key indicators of the results as of limit of quantification				
PFOS total	0,5	73	42	31	58%	42%	0,6	1,4	1,8	0,5	2,6	1,1	1,0	0,5
PFOS linear	0,5	73	36	37	49%	51%	<KL	1,2	1,5	0,5	2,0	0,9	0,9	0,4
PFOA linear	0,5	73	14	59	29%	81%	<KL	0,7	0,9	0,5	1,9	0,8	0,7	0,4
PFOA total	0,5	73	14	59	29%	81%	<KL	0,6	0,9	0,5	1,9	0,8	0,7	0,4
PFBA	0,5	73	10	63	14%	86%	<KL	0,6	0,7	0,5	1,3	0,7	0,7	0,2
6:2 diPAP	1	73	3	70	4%	96%	<KL	<KL	<KL	1,1	4,2	2,6	2,4	1,6
etFOSAA	0,5	73	1	72	1%	99%	<KL	<KL	<KL	1,4	1,4	1,4	1,4	N/A
PFHxS linear	0,5	73	1	72	1%	99%	<KL	<KL	<KL	1,1	1,1	1,1	1,1	N/A
PFHxS total	0,5	73	1	72	1%	99%	<KL	<KL	<KL	1,3	1,3	1,3	1,3	N/A
PFHxSA	0,5	73	1	72	1%	99%	<KL	<KL	<KL	0,8	0,8	0,8	0,8	N/A
PFHpA	0,5	73	1	72	1%	99%	<KL	<KL	<KL	0,5	0.5	0.5	0.5	N/A
meFOSAA	0,5	73	1	72	1%	99%	<KL	<KL	<KL	0.7	0.7	0.7	0.7	N/A

LOQ = limit of quantification

SD = standard deviation

P50 = 50-percentile

P90 = 90 - percentile

P95 = 95 - percentile

7.1.2 Statistical key indicators "sum PFAS"

The "sum PFAS" was calculated based on the reported limits of quantification. These are equal to reporting limits as included in the CMA, so unlike the calculation for groundwater, only one calculation is necessary. Components below these limits are not included in the sum (https://reflabos.vito.be/2023/WAC_IV_A_025.pdf).

From the statistical key indicators, the following can be summarized:

- The majority of the analytical results are lower than limit of quantification.
- For sum PFAS and sum PFAS EFSA 4, a value was calculated in more than 50% of the samples. This is only possible if at least 1 of the individual components exceeds the limit of quantification. This is mainly determined by PFOS.

Table W: Summary analytical results soil (µg/kg ds) - dataset 1

component			Key indicators including results below limit of quantification							Key indicators of the results as of limit of quantification				
	KL	Number of measurements (#)	#>with min 1 PFAS > LOQ	# with all PFAS < LOQ	% with at least 1 PFAS >LOQ	% with all PFAS < LOQ	P50	P90	P95	Min of values above LOQ	Max of values above LOQ	mean	median	SD
Sum PFAS quantitative	0,5	73	43	30	59%	41%	0,6	2,6	3,2	0,5	6,3	1,6	1,1	1,2
Sum PFAS efsa-4	0,5	73	42	31	58%	42%	0,6	2,0	2,6	0,5	4,5	1,4	1,0	0,9
PFAS (sum indicative)	1	73	3	70	4%	96%	1,0	1,0	1,0	1,1	4,2	2,6	2,4	1,6

LOQ Limit of quantification

SD =standard deviation

P50 = 50-percentile

P90 = 90 - percentile

P95 = 95 - percentile

7.1.3 Cartographic representation

The results for PFOS total, PFOA total and PFBA (above the limit of quantification) are shown on Figure 31 through Figure 33 and in Annex 5.

Figure 31: PFOS total in the soil - dataset 1

Figure 32: PFOA in the soil - dataset 1

Figure 33: PFBA in the soil - data set 1

PFOS is found scattered over Flanders in low concentrations in the soil. PFOA and PFBA are much less widespread in the soil and were mainly measured at the coast, at the border with the Netherlands and around Kortrijk.

7.1.4 Outlier analysis

An outlier analysis was performed for $PFOS_{total}$ using Rosner's outlier test. 1 outlier was identified. The location of this data point was examined in more detail.

The outlier cannot be explained by the presence of PFAS suspect activities in the vicinity. Therefore, multiple scenarios will be calculated when calculating the anthropogenic background value, with and without an outlier.

Table X: Outliers soil

component	Outlier measurement value (µg/kg ds)	Sample taken at monitoring well	Location
PFOS total	2,6	131/21/2	North of Ghent Harbor - no suspected sites within 600 m

Figure 34: Location outlier soil

7.1.5 Calculation P90 based on dataset 1

The 90-percentile was calculated from:

- all results from the measurement campaign,
- without the outlier

- without the outlier and without the sample near monitoring well 835/00/1. This sample was within the no regret zone of 3M and close to a landfill site for dredged materials (see Table A).

The 95 percentile was also calculated for comparison:

Table Y: percentiles soil based on dataset 1

µg/kg ds	$PFOS_{total}$ 90-percentile	$PFOS_{total}$ 95-percentile
All results measurement campaign	1,4	1,8
Without outlier	1,4	1,5
Without outlier and without 835/00/1	1,4	1,6

There is no variation within the different calculated scenarios with and without outliers at the P90. The 90th percentile is determined in the different scenarios by the 66^{th}/73 result, the 66^{th}/72 result and 64^{th} /71 result, respectively. Considering there are 3 sites where the concentration of PFOS is equal to 1.4 µg/kg dm (result 64-66 when ranking the results from small to large), the P90 percentile does not change in the three scenarios.

The variation within the different scenarios calculated with and without outliers at P95 is limited.

These variations between calculations are smaller than the margins of error for these components in the laboratory.

7.2 RESULTS SOIL COMBINED DATASET

7.2.1 Statistical key figures individual PFAS components--dataset 2 (VITO)

In 2020, 50 samples from the soil have already been analyzed for PFAS for setting anthropogenic background concentrations (see report "deriving anthropogenic background concentrations for perfluorinated compounds and some other 'emerging contaminants' - part 2: deriving anthropogenic background concentrations for perfluorinated compounds." (OVAM, 2021)).

In this report, anthropogenic background concentrations were derived for $PFOS_{total}$ and $PFOA_{total}$.

The analytical results from this report are summarized in Figure 35.

Parameter	# > KL	Min.	Max.	Gem.	Geom. gem.	Parameter	# > KL	Parameter	# > KL
PFBA	50	0.35	2.60	0.762	0.688	PFDoA	0	10:2 FTS	0
PFOS	47	0.21	2.10	0.775	0.641	PFTrDA	0	FOSA	0
PFOA	36	0.19	2.20	0.558	0.469	PFTeDA	0	MeFOSA	0
6:2 FTS	27	0.21	1.00	0.407	0.377	PFHxDA	0	EtFOSA	0
PFPeA	11	0.20	0.36	0.265	0.260	PFODA	0	FOSAA	0
PFHpA	5	0.21	0.27	0.238	0.237	PFPeS	0	MeFOSAA	0
6:2 PAP	5	0.31	1.60	0.942	0.833	PFHxS	0	EtFOSAA	0
PFHxA	2	0.26	0.39	0.325	0.318	PFHpS	0	8:2 PAP	0
PFBS	2	0.20	0.30	0.250	0.245	PFNS	0	6:2 diPAP	0
PFNA	1	0.24	0.24	0.240	0.240	PFDS	0	6:2/8:2diPAP	0
PFDA	1	0.21	0.21	0.210	0.210	PFDoS	0	HFPO-DA	0
8:2 diPAP	1	0.70	0.70	0.700	0.700	4:2 FTS	0	ADONA	0
PFUdA	0	0	0			8:2 FTS	0	PFECHS	0

Figure 35: Summary results soil -dataset 2 - (KL= limit of quantification)

The previous study used a limit of quantification of 0.2 µg/kg dm (vs. 0.5 µg/kg dm in this study). PFBA was detected above the limit of quantification in 50 samples. PFOS and PFOA were detected in 47 and 36 samples, respectively.

Note that in dataset 2 PFBA was found above the limit of quantification in all samples, while in dataset 1 this is the case for only 10 out of 73 samples. 38 out of 50 samples from dataset 2 are above or equal to 0.5 µg/kg dm (compared to 10 out of 73 samples from dataset 1). 6:2 FTS was observed above or equal to 0.2 µg/kg dm in 27 of the 50 samples in dataset 2 and above or equal to 0.5 µg/kg dm in 6 of the 50 samples. In dataset 1, 6:2 FTS was not detected above or equal to 0.5 µg/kg ds.

From the data of dataset 2, the following percentiles were calculated in the previous report:

Table Z: Percentiles soil based on dataset 2

µg/kg ds	90-percentile	95-percentile
PFBA	1,25	1,5
PFOA	0,96	1,4
PFOS	1,50	1,7

7.2.2 Statistical key figures combined dataset (dataset 1 and 2)

The results of the 50 samples from dataset 2 soil were merged with the 73 samples from the present study (dataset 1). The resulting database includes 123 samples.

The results of the combined database are summarized in the table below. These key figures were calculated for the substances PFBA, $PFOS_{total}$ and $PFOA_{total}$:

- for the full dataset
- complete dataset in which all points less than 100 m from a PFAS suspect site were excluded (see also Table AA).

Only for $PFOS_{tota}$ a concentration above the limit of quantification (being 0.5 µg/kg dm for dataset 1 and 0.2 µg/kg dm for dataset 2) was measured in more than half of the samples of the combined dataset.

Table AA: Summary results soil dataset 1+2 (µg/kg ds)

		Key indicators including results below limit of quantification								Key indicators of results above limit of quantification				
Scenario	Component	Number of measurements	#>LOQ	#<LOQ	%>LOQ	% <LOQ	P50	P90	P95	Min of values above LOQ	Maximum measured value	average	Median (P50)	SD
Dataset 1+2	PFBA	123	60	63	49%	51%	0,5	0,9	1,1	0,4	2,6	0,8	0,7	0,4
	$PFOA_{total}$	123	50	73	43%	59%	0,5	0,8	0,9	0,2	2,2	0,6	0,5	0,4
	$PFOS_{total}$	123	89	34	72%	28%	0,6	1,5	1,7	0,2	2,6	0,9	0,8	0,5
Dataset excl. points < 100 m risk location	PFBA	116	53	63	46%	54%	0,5	0,9	1,0	0,4	1,7	0,7	0,6	0,3
	$PFOA_{total}$	116	44	72	38%	62%	0,5	0,8	1,0	0,2	2,2	0,6	0,5	0,4
	$PFOS_{total}$	116	82	34	71%	29%	0,6	1,4	1,7	0,2	2,6	0,9	0,8	0,5

LOQ = limit of quantification
SD = standard deviation
P50 = 50-percentile
P90 = 90 - percentile
P95 = 95 - percentile

7.2.3 Cartographic representation

The results of the combined dataset for $PFOS_{total}$, $PFOA_{total}$ and PFBA are shown in Figure 36 through Figure 38.

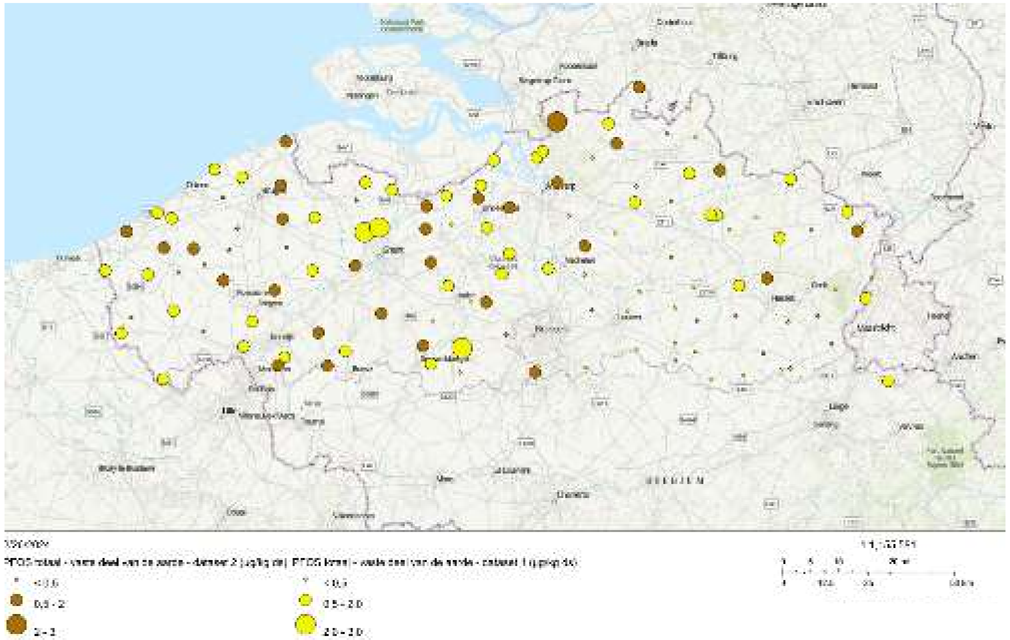


Figure 36: PFOS total in the soil - dataset 1 and 2 . Results from dataset 2 between 0.2 and 0.5 µg/kg dm are shown as < 0.5 µg/kg ds.

Figure 37: PFOA in the soil - dataset 1 and 2 . Results from dataset 2 between 0.2 and 0.5 µg/kg dm are shown as < 0.5 µg/kg ds.

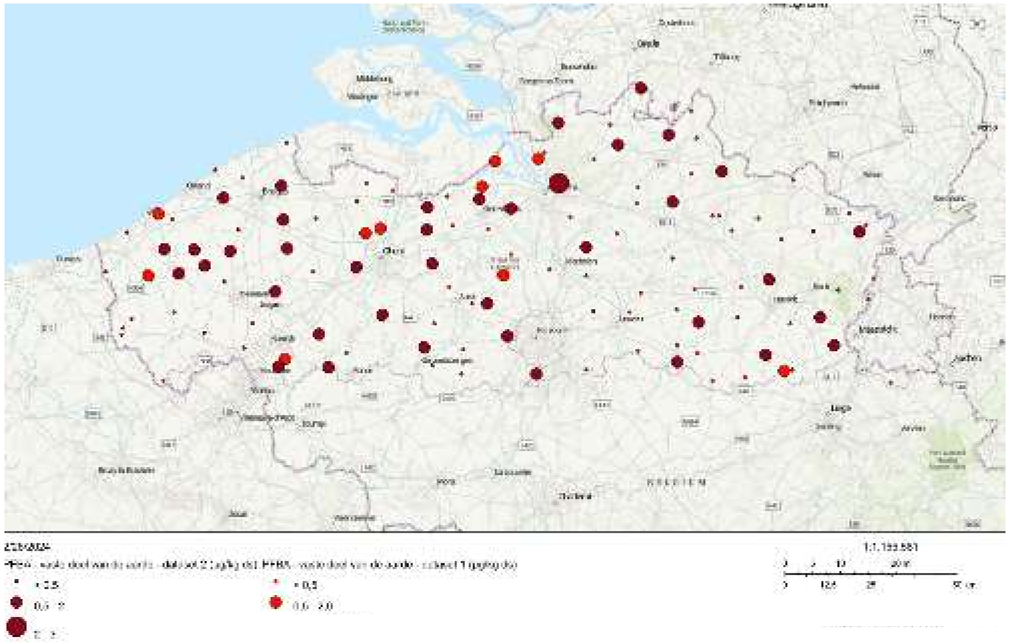


Figure 38: PFBA in the soil - dataset 1 and 2. Results from dataset 2 between 0.2 and 0.5 µg/kg dm are shown as < 0.5 µg/kg ds.

The results of the combined dataset show a fairly even distribution across Flanders for PFBA and PFOS in the soil. PFOA is found in the soil in the combined dataset mainly along the coast and border with the Netherlands.

7.2.4 Outlier analysis

Outlier analysis was performed for $PFOS_{total}$, $PFOA_{total}$ and PFBA using Rosner's outlier test. 1 outlier was identified for each component. The location of these points was considered in more detail (Table BB). Based on the Boxplot (Figure 39), the value for PFOA at 131/21/2 and PFOS at 132/21/5 is also considered an outlier.

Table BB: outliers combined dataset soil

component	Concentration (µg/kg dm)	sampling point	Evaluation
PFBA	2,6	200318-0004	Merksem/Schoten - within no regret zone 3 M, within other no regret zones, near PFAS suspect site
PFOA	2.2	200318-0007	Meerle - in nearest monitoring well also quite high PFOA (31 ng/L 3 km away)
	1.9	131/21/2	Based on. boxplot - North of Ghent harbor
PFOS	2,6	131/21/2	North of Ghent port
	2,5	132/21/5	Based on boxplot - North of Ghent harbor

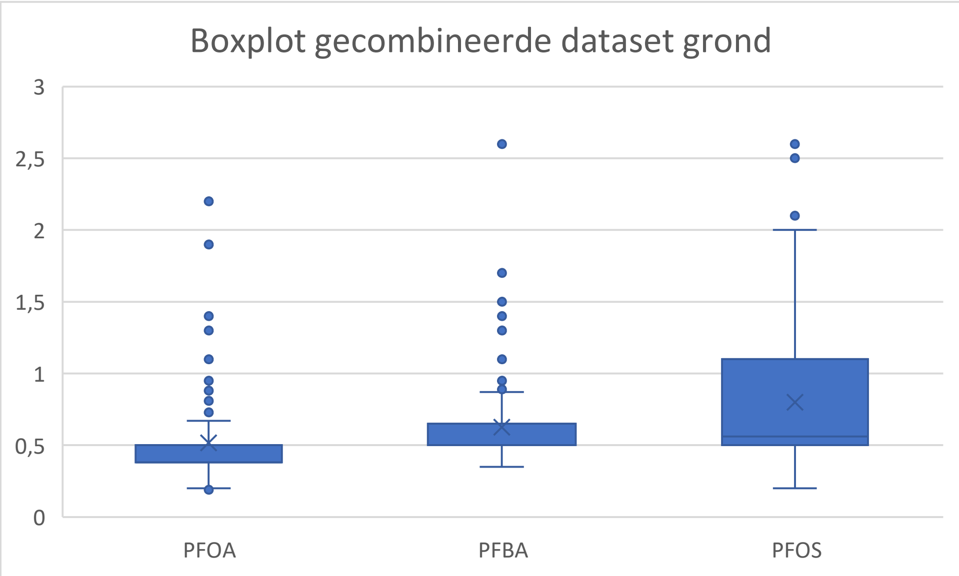
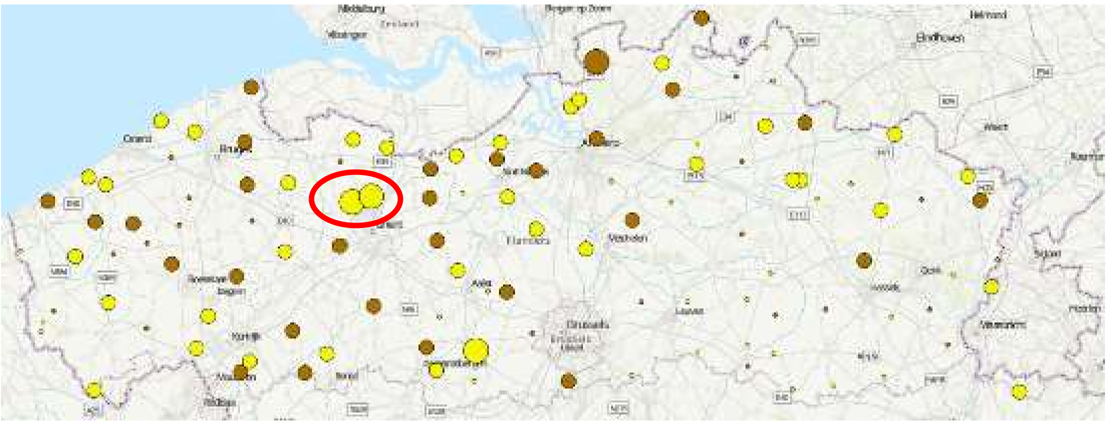


Figure 39: Boxplot PFOA, PFOS and PFBA in the soil - combined dataset



PFOS total

PFOA total

PFBA

Figure 40: location of outliers soil - combined dataset

7.2.5 Calculation P90 based on combined dataset 1 + 2

The 90-percentile was calculated from:

- all results from the measurement campaign,
- without the outliers
- without the outlier and without the sample near monitoring well 835/00/1. This sample was within 3M's no regret zone and close to a land fill for dredged sediment (see Table E in section 3.1).

The 95 percentile was also calculated for comparison.

Table CC: Percentiles soil based on combined dataset

µg/kg dm	$PFBA_{(1)}$	$PFOA_{total\ (1)}$	$PFOS_{total}$	$PFBA_{(1)}$	$PFOA_{total(1)}$	$PFOS_{total}$
	90-percentile			95-percentile		
Dataset 1+2 (OVAM+VITO).	0,9	0,8	1,5	1,1	0,9	1,7
Dataset 1+2 - without locations < 100 m	0,9	0,8	1,4	1,0	1,0	1,7
Dataset 1+2 - without outliers	0,9	0,8	1,4	1,1	0,9	1,6
Dataset 1+2 - without outliers and without locations < 100 m	0,9	0,8	1,4	0,9	0,9	1,4

(1) The number of sites where PFOA and PFBA were measured above the limit of quantification is less than half of the sampling locations. Their Percentiles are provided for information.

There is little to no variation in the P90 within the different scenarios calculated with and without outliers. The variation within the different calculated scenarios with and without outliers at P95 is limited. These variations between the different calculations are smaller than the margins of error for these components in the laboratory.

7.3 EVALUATION ANTHROPOGENIC BACKGROUND CONCENTRATIONS SOIL

The different calculated percentiles for soil are summarized in Table DD for PFBA, $PFOS_{total}$ and $PFOA_{total}$.

Table DD: Summary percentiles soil

µg/kg dm	$PFBA_{(1)}$	$PFOA_{total\ (1)}$	$PFOS_{total}$	$PFBA_{(1)}$	$PFOA_{total\ (1)}$	$PFOS_{total}$
	90-percentile			95-percentile		
Dataset 1- OVAM	0,6	0,6	1,4	0,7	0,9	1,8
Dataset 1- OVAM without outlier PFOS	/	/	1,4	/	/	1,6
Dataset 2- VITO ((OVAM, 2021))	1,25	0,96	1,5	1,5	1,4	1,7
Dataset 1+2 (OVAM+VITO).	0,9	0,8	1,5	1,1	0,9	1,7
Dataset 1+2 - without locations < 100 m	0,9	0,8	1,4	1,0	1,0	1,7
Dataset 1+2 - without outliers	0,9	0,8	1,4	1,1	0,9	1,6
Dataset 1+2 - without outliers and without locations < 100 m	0,9	0,8	1,4	0,9	0,9	1,4

(1) The number of sites where PFOA and PFBA were measured above the limit of quantification is less than half of the sampling locations. Their Percentiles are provided for information.

Currently, anthropogenic background concentrations of 1.5 µg/kg dw and 1.0 µg/kg dw for total PFOS and total PFOA, respectively, are used in Flanders.

The values for the 90th percentile in this study indicate a background value of 1.4 µg/kg dw for total PFOS. This is of the same order of magnitude as the current anthropogenic background concentration (1.5 µg/kg dw). An adjustment of the current value is not necessary. This value is also in line with the background value in the Netherlands (1.4 µg/kg dw).

For total PFOA, lower values are found in this study for the 90th percentile than the current anthropogenic background concentration of 1.0 µg/kg dw. Based on dataset 1 and the combined datasets, a background value of 0.6 to 0.8 µg/kg dw is measured. The total number of measurement locations where the limit of quantification was exceeded is less than half. The percentiles are provided for informational purposes because this parameter often occurs in soil studies and a anthropogenic background concentration for PFOA was also calculated in previous studies. In the Netherlands, a higher background value for PFOA of 1.9 µg/kg dm is used. This difference is probably explained by the fact that the known production sites in the Netherlands mainly produced or processed PFOA.

Given the limited differences with between the current anthropogenic background concentrations for PFOS and PFOA and the 90-percentile values calculated in this study, it is advised to retain the existing values.

For PFBA, there are significant differences between both datasets regarding the number of samples in which a concentration above the limit of quantification was detected. It is therefore not appropriate to set anthropogenic background concentrations based on this data. The P90 of the combined dataset is 0.9 µg/kg dm

Table EE: proposed anthropogenic background concentrations PFOS and PFOA in the soil

Parameter	Proposed anthropogenic background concentration
$PFOS_{total}$	1.5 µg/kg dm
$PFOA_{total}$	1 µg/kg dm

8 EVALUATION CORRELATIONS PFAS COMPONENTS

To ascertain the extent to which the most common components do or do not occur simultaneously in the same monitoring well and/or occur simultaneously in the soil and groundwater, statistical correlations between the components are examined.

For the analytical results in groundwater, a correlation analysis was performed between the components PFOA total, PFOS total, PFBA and PFBS.

For the 73 sampling locations where both a soil and groundwater sample were analyzed, the correlation of these 4 components in the groundwater with the measured concentrations of PFOS in the soil was also considered.

These correlations are indicative, as mainly low concentrations are present in this dataset. A determination of correlations on a dataset with a wider concentration range may lead to a different picture.

The correlation was evaluated based on the "r" value (correlation coefficient)

- $0<r<0.3$ or $-0.3 <r <0$: little or no correlation
- $0.3<r<0.5$ or $-0.5<r<-0.3$: weak correlation
- $0.5 <r<0.7$ or $-0.7<r<-0.5$: moderate correlation
- $0.7 <r<0.9$ or $-0.9<r<-0.7$: strong correlation
- $0.9 <r<1.0$ or $-1.0<r<-0.9$: very strong correlation

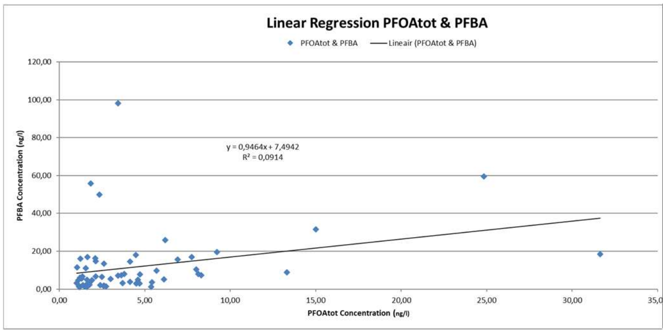
Table FF summarizes the correlation coefficients. The following can be summarized from the correlation analysis:

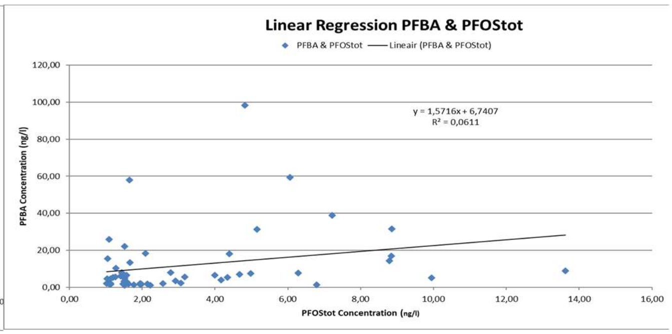
- A moderate positive correlation was found between PFBS and PFOA in groundwater ($r=0.511$) and between PFBS and PFBA in groundwater ($r=0.605$). These components can sometimes occur simultaneously, but this is certainly not systematic given the somewhat "weak" correlation.
- no or weak correlations are observed between the other combinations of components in the groundwater and between the combination soil/groundwater. Therefore, it is not the case that when PFOS is measured in the soil, the PFOS concentrations in the groundwater are also elevated (and vice versa).

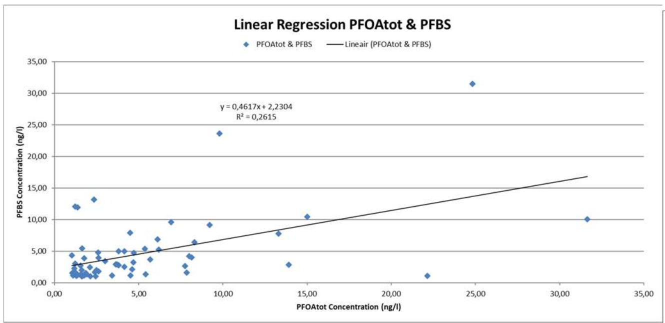
Table FF: Summary correlation coefficients for groundwater and soil - no correlation, weak and moderate correlation are indicated in red, yellow and green, respectively)

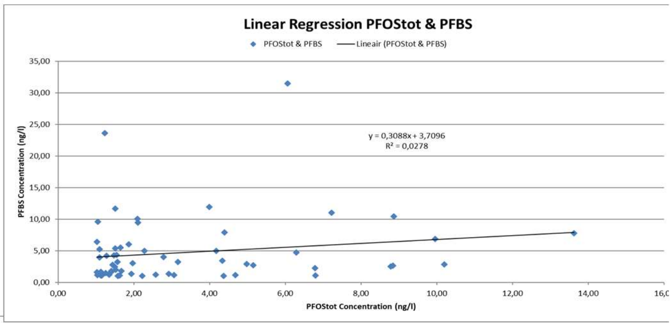
R-values	PFOA groundwater	PFOS groundwater	PFBA groundwater	PFBS groundwater	PFOS soil
PFOA groundwater	/	0.397	0.302	0.511	-0.335
PFOS groundwater	0.397	/	0.247	0.167	0.021
PFBA groundwater	0.302	0.247	/	0,605	-0.162
PFBS groundwater	0.511	0.167	0.605	/	-0.284
PFOS soil	-0.355	0.021	-0.162	-0.284	/

In a study by the RIVM in the Netherlands (RIVM, 2021), it was also investigated whether there is a correlation between the various PFAS components in soil and groundwater and among different PFAS components in groundwater. Similarly, no relationship was found between observations in the soil and groundwater. In groundwater, the detectability of mobile PFAS components showed a slight correlation. The association was strongest for PFHxA with PFHpA, and PFOA and PFOS linearly with their branched forms, although this was noted with caution, as a very large number of results were below the limits of quantification.









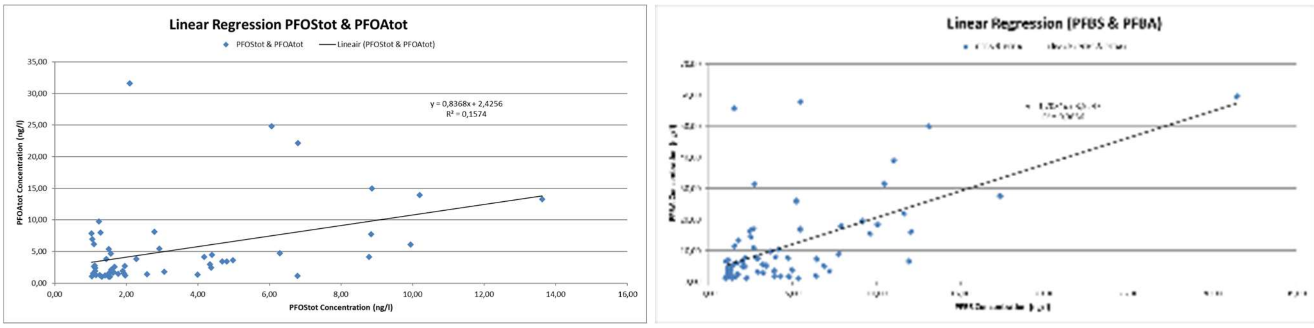


Figure 41: Correlograms groundwater

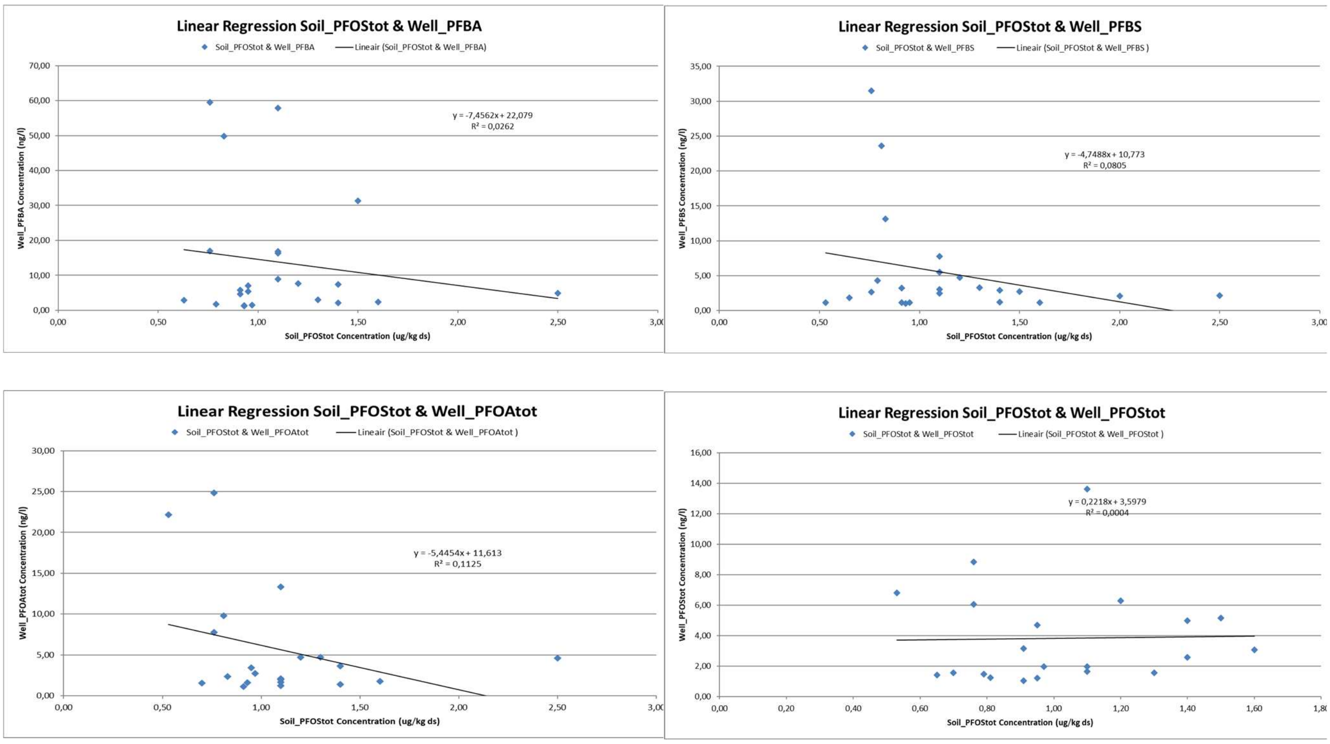


Figure 42: Correlograms soil and groundwater

9 EVALUATION TOP ANALYSES

TOP analyses were performed on 12 groundwater samples and 8 soil samples.

Figure 43 through Figure 46 show the results for the components where a difference was observed before and after oxidation.

From this, the following can be deduced:

- For the groundwater samples, the sum of PFAS after TOP analysis can be either higher or lower than before oxidation, while for the soil, the sum after oxidation is always lower.
- In groundwater, concentrations or proportion of short chain carboxylic acids (PFBA, PFPeA and PFHxA) generally increase after oxidation while longer chain carboxylic acids decrease (PFOA). This is not the case for the perfluorosulfonic acids, generally the sum of perfluorosulfonic acid in all samples is lower after oxidation.
- in the groundwater sample PB 651/63/2, the concentration for PFNA (C9) and PFDA (C10) increases after oxidation. Which may indicate that longer perfluorinated chains are still present in the sample that were subsequently degraded to PFNA and PFDA.
- Very little difference is observed in the samples from the soil before and after oxidation. The limit of quantification for several PFAS components is also higher after oxidation than before oxidation so small differences cannot be noticed. Only for PFDA, PFOA and PFOS are differences visible.

Overall, it can be concluded that taking into account the very low concentrations, the margins of error in the laboratory and the limits of quantification before and after oxidation, this type of analysis offers little added value in this measurement range and is better suitable for samples with higher concentrations of PFAS.

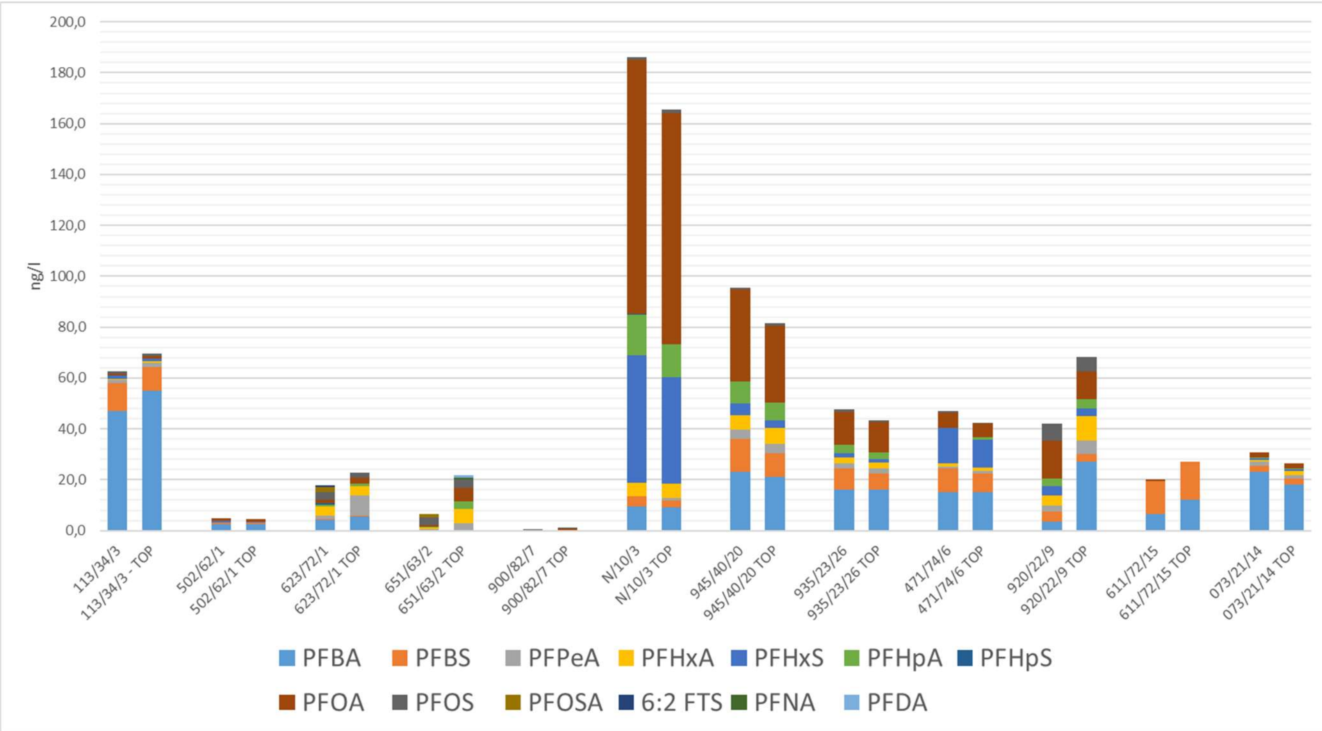


Figure 43: Analytical results PFAS per groundwater sample before and after oxidation

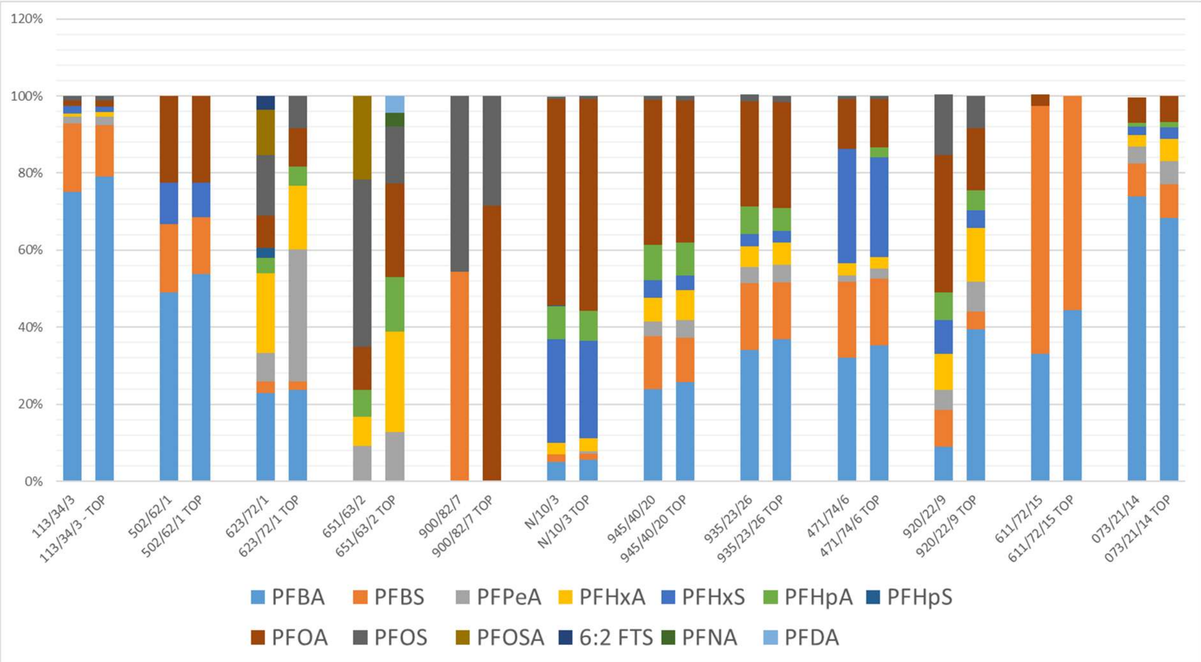


Figure 44: Percentage of PFAS component per groundwater sample before and after oxidation

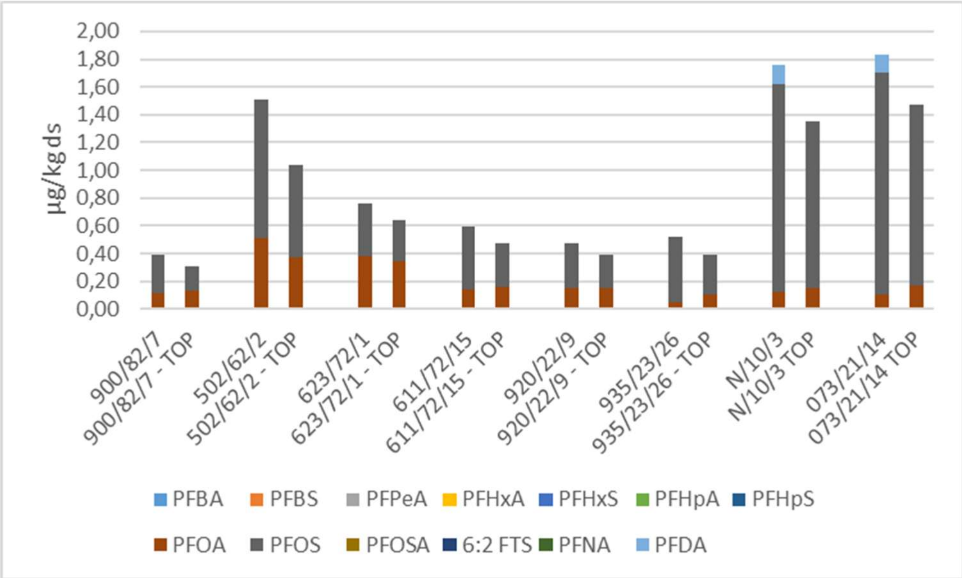


Figure 45: Analytical results PFAS per sample of the soil before and after oxidation

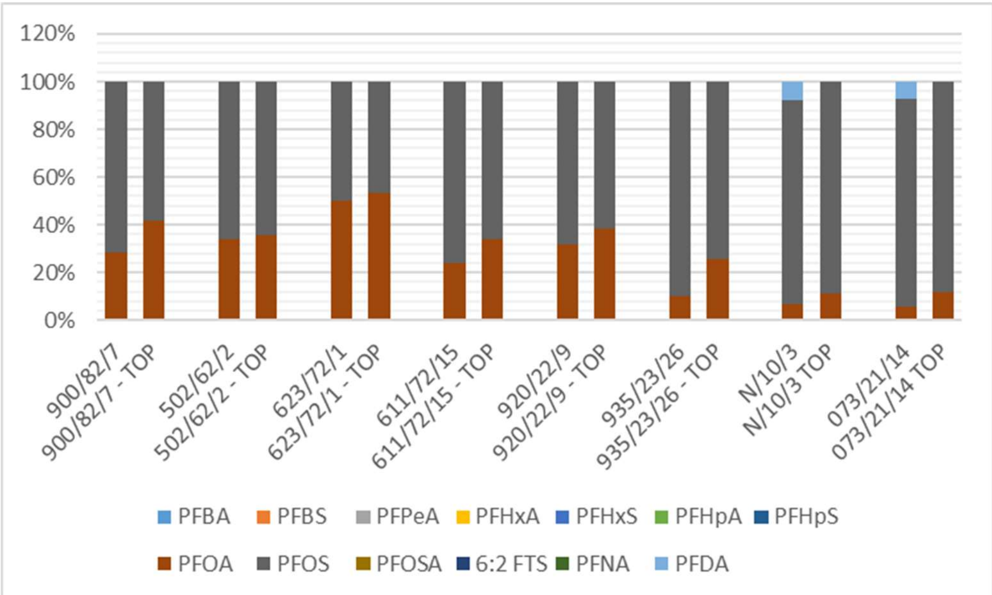


Figure 46: Percentage of PFAS per sample of the soil before and after oxidation

10 CONCLUSIONS AND RECOMMENDATIONS

PFAS are already widespread in groundwater in Flanders, even in unsuspected locations. In approximately 90% of the samples taken in unsuspected areas, at least 1 component was found above the limit of quantification.

'Anthropogenic background concentrations' as defined in the Soil Decree are "levels of contaminants found as background in unpolluted soils" where, according to the Soil Decree, groundwater is also part of soil. Because PFAS do not naturally occur in the environment, this refers to the diffuse anthropogenic presence of PFAS in the soil and in groundwater.

10.1 PROPOSED ANTHROPOGENIC BACKGROUND CONCENTRATIONS FOR GROUNDWATER

Based on the present study, anthropogenic background concentrations in groundwater are proposed as listed in Table GG. These are based on the 90-percentile of measured values. They are derived only for the components where 50% of the results exceed the limit of quantification. No anthropogenic background concentration is proposed for PFOS (34% of sites above the limit of quantification). The 90 percentile for PFOS is 5.0 ng/L.

Table GG: Suggested anthropogenic background concentrations groundwater

	ng/L
PFBA	21,0
PFBS	9,4
$PFOA_{total}$	8,0

For PFBS and $PFOA_{total}$, the proposed anthropogenic background concentrations are below the WAC reporting limits.

For PFBA, a relatively high value is obtained for the 90 percentile and proposal anthropogenic background concentration namely 21.0 ng/L.
This already fills a significant portion of the soil remediation standard for the sum of EU DWD20 PFAS (100 ng/L). The proposed anthropogenic background concentration PFBA is above the proposed discharge standard of 20 ng/L.

10.2 SUM PFAS

The calculated P90 for the sum PFAS is highly dependent on the reporting limits or quantitation limits, since components below these limits are not counted in the sum. The 90-percentiles remain below the current soil remediation value (500 ng/L for sum quantitative and PFAS total and 100 ng/L for sum PFAS EU DWD20, respectively) in both calculations.

	ng/L
Sum PFAS quantitative	30,5* 48,0**
Sum of PFAS (EU DWD20).	27,0* 47,0**
Sum of PFAS total	30,5* 48,4**

*taking into account WAC reporting limits (10 or 50 ng/L) - components below these limits are not counted in the sum (https://reflabos.vito.be/2023/WAC_IV_A_025.pdf)
** taking into account quantitation limits lower than the maximum reporting limits (1 ng/L for most components), components below these limits are not counted in the sum

When compared to the European Commission's proposed environmental quality standard for groundwater and surface water of 4.4 ng/L, where 24 components are summed via relative toxicity factor and where PFOA has factor 1, we find that the proposed anthropogenic background concentrations (P90) of PFOA and PFOS, already exceed this value of 4.4 ng/L individually. Although 3 of the 24 components in this sum were not analyzed in the present study, the proposed quality standard of 4.4 ng/L is already exceeded in 37% of sampled sites in unsuspected areas.

10.3 PROPOSED ANTHROPOGENIC BACKGROUND CONCENTRATIONS SOIL

Based on the present study, anthropogenic background concentrations in the soil are proposed. These are based on the 90-percentile of measured values. The anthropogenic background concentrations are only derived for the components where a sufficient number of results exceed the limit of quantification. This is only the case for PFOS.
The calculated percentiles in the present study confirm the already applicable anthropogenic background concentrations. Consequently, for the soil, it is proposed to retain the current anthropogenic background concentrations (1.0 µg/kg dm for PFOA and 1.5 µg/kg dm for PFOS).

For PFBA, large differences were observed between the dataset from the previous study (2021) and the dataset from the present study. Consequently, no anthropogenic background concentration is proposed yet based on the combined dataset. Additional research is recommended to explain these differences.

10.4 INFLUENCE OF LAND USE

The samples in the present study are taken from agricultural or natural areas and are not necessarily representative for urbanized or industrial areas. Given the use of PFAS in the daily environment, an increased diffuse presence of PFAS can also be expected in urbanized areas. The anthropogenic background concentration here is presumably higher than in agricultural or natural areas due to local enrichment from diffuse PFAS sources. These are regionally elevated concentrations that are no longer attributable to a specific source.

Further research in urban areas and in areas around industrial zones can provide more insights into the extent of anthropogenic elevated diffuse presence of PFAS in these areas.

It would also be interesting to investigate the no-regret delineated zones of 100 m and 200 m around sites where PFAS were used, to evaluate whether elevated diffuse concentrations of PFAS are present and which perimeter is significantly elevated compared to the anthropogenic background concentration derived in this study.

Additional research on the situation in other land use types (urbanized area, industrial area) can be done in several ways:

- Based on available PFAS data in completed soil investigations already included in the mistral database. The known analytical results can be collected and assigned to a particular land use type. The P90 per land use type can be calculated with minimal additional fieldwork effort:
  - The calculated value will be indicative and may be an overestimate of the background in these areas. This is because the data will primarily come from lands where there is PFAS suspected activity or known PFAS contamination. This overestimation can be partially nuanced by considering only the lowest concentration for each component measured at the site or using the average or median concentration at a given site.
  - This approach can confirm or refute in general terms whether the background values may be higher here than in rural and natural areas.
  - It should be taken into account that these results are likely to have been reported from the minimum reporting limits of the WAC (10 ng/l for quantitative PFAS), so background values lower than this reporting limit cannot be determined.
- Based on mistral data, a number of recently installed monitoring wells on public property, within urbanized and/or industrial areas scattered across Flanders could be selected and sampled for analyses for PFAS, supplementing the current dataset.

10.5 APPLICATION IN SOIL INVESTIGATION

In a soil investigation, it is mainly the guide values that are relevant in the context of delineation of a contamination. These guidance values are set by the Flemish Government and correspond to the content of pollutants or organisms on or in the soil, which allows the soil to fulfill all its functions without any restrictions having to be imposed.

The proposed anthropogenic background concentrations in the soil are used to derive the guidance values for the soil. These guidance values were derived and published for PFOS, PFOA and the sum of PFAS. Since the present study confirms the previously published anthropogenic background concentrations, the published guidance values for PFOS and PFOA in the soil can also be retained.

For groundwater, no guidance values have been determined yet . The results from the present study and more specifically the derived anthropogenic background concentrations (PFOA, PFBA and PFBS) can be used when interpreting results in a soil investigation:

- the anthropogenic background concentrations already occupy a significant portion of the value currently used todeliniate a contamination (100 ng/L for sum PFAS EU DWD 20). A soil expert can use the results of the present study in interpreting the delineation of contaminations. The anthropogenic background concentrations can be used as motivation to demonstrate where contamination can likely be attributed to the investigated source.
- The anthropogenic background concentrations from the present study can also be provisionally considered as an approximation of anthropogenic background concentrations in urban areas, this being a conservative approach, as higher anthropogenic background concentrations are expected in urban areas due to the presence of PFAS sources.

11 BIBLIOGRAPHY

Aro, R, et al. 2022. Extractable organofluorine analysis: A wa to screen for elevated per- and polyfluoalkyl substance contamination in humans? *Environment International.* 2022.

Environment Agency - UK. 2021. *Poly- and perfluoroalkyl substances (PFAS): sources, pathways and environmental data.* 2021.

—. water quality data archive. *https://environment.data.gov.uk/water-quality/view/landing.* [Online] 2023.

Eurofins. 2023. PFAS TOP-assay. *https://www.eurofins.de/food-analysis/food-news/food-testing-news/pfas-top-assay/.* [Online] 2023.

Federal Office for the Environment (FOEN, Switzerland). 2023. https://www.bafu.admin.ch/bafu/en/home/topics/water/info-specialists/state-of-waterbodies/state-of-groundwater/groundwater-quality/pfas-in-groundwater.html. [Online] 2023.

Frippiat, C., Bémelmans, S., Burlion, N., Carbonnelle, P., Chalon, C., Delvaux, A., Galloy, A., Marneffe,. 2018. *Recherche de perturbateurs endocriniens et d'autres substances d'intérêt récent dans les eaux en vue de la protection de la santé publique et de l'environnement. Programme de Recherche « BIODIEN » - Rapport final.* GISREAUX. 2018. p. 199.

Geological survey of Denmark and Greenland. 2023. https://data.geus.dk/geusmap/. *jupiter.* [Online] 2023.

Kurwadkar, S, et al. 2022. Per- and polyfluoroalkyl substances in water and wastewater: A critical review of their global occurrence and distribution. *Science of The Total Environment.* 2022.

L'Institut Scientifique de Service Public. 2019. Le Plan ENVIeS, qu'est-ce que c'est? *www.issep.be.* [Online] 7 3 2019. [Citaat van: 02 02 2023.] https://www.issep.be/events/event/le-plan-envies-quest-ce-que-cest/.

OVAM. 2021. *Afleiden van streefwaarden voor perfluorverbindingen en enkele andere "emerging contaminants" - Deel 2: afleiden sstreefwaarden voor perfluorverbindingen.* 2021.

—. 2015. *Afleiding en onderbouwing gemeenschappelijk normenkader voor gorndstoffen en uitgegraven bodem in Vlaanderen.* 2015.

—. 2016. *Basisinformatie voor risico-evaluaties: werkwijze voor het opstellen van bodemsaneringsnormen en toetsingswaarden, richtwaarden en streefwaarden.* 2016.

—. 2022. *Onderzoeksprotocol verkennend bodemonderzoek naar PFAS-verontreiniging door fluorhoudend blusschuim.* 2022.

—. 2022. *Toetsingswaarden voor PFOS en PFOA in bodem en voor PFAS in grondwater.* 2022.

PFAS in het Brussel Hoofdstelijk Gewest Update over de recente situatie . **Leefmilieu Brussel. 2023.** 2023.

RIVM. 2021. *Landsdekkend beeld van PFAS in Nederlands grondwater.* 2021.

Swedish University of Agricultural Sciences. 2016. *Screening of PFASs in groundwater and surface water.* 2016.

Vlaanderen.be/PFAS-vervuiling. https://www.vlaanderen.be/pfas-vervuiling/pfas-lozingsnormen-voor-bedrijven. [Online] [Citaat van: 18 12 2023.]

12 ANNEXES

ANNEX 1 SURVEY RESULTS

A brief international survey was conducted with the aim of collecting information on available data and research related to diffuse PFAS contamination in groundwater. The survey was distributed to several international contacts in Europe. Responses were received from 10 contacts Netherlands, France, United Kingdom, Denmark, Germany and Italy The responses given are summarized below.

1. **Is the presence of diffuse PFAS contamination in groundwater being investigated at the regional or national level, and/or will it be investigated in the (near) future?**

All ten respondents answered "yes" to this.

2. **What measures are being taken regarding diffuse PFAS contamination in groundwater.**
    - In the Netherlands, diffuse PFAS contamination is mainly focused on source reduction and PFAS phase-out. In addition, efforts are mainly directed at adjustments in the production of drinking water.
    - In France, monitoring measures are mainly taken where surface water is monitored for a limited number of PFAS components (4 to 6). Groundwater is monitored for about 20 PFAS components. Emission values for PFOS would also be proposed for ICPEs (Installations Classified for Environmental Protection) and later a threshold value will also be set for drinking water.
    - In the Veneto region, the Veneto Regional Agency for Environmental Prevention and Protection (ARPAV) measures PFAS in groundwater to determine hotspots, such as landfills. Based on these measurements, measures will then be taken such as including specific requirements in permit documents to reduce the adverse effects of PFAS.
    - In Germany, measures are being taken to avoid spread of PFAS to groundwater. It was not specified which measures. Also, known contaminated regions are being monitored.
    - In Denmark, measures are being taken such as setting limit values for various PFAS components in sewage sludge that may be used for fertilizing fields. Also, new projects must be subject to an environmental assessment whereby in case of PFAS contamination in groundwater this must be addressed.

3. **Are there PFAS data availability at the regional or national level.**
    - In the Netherlands, a study was conducted at the national level in 2021. Currently, provinces periodically monitor a network of monitoring wells and collect this in various databases. Some provinces have determined a background value for the soil.
    - In Germany, PFAS are analyzed in 15 federal states on an adhoc basis. Mainly these are focused on suspected sites. There is no systematic monitoring or national data collection.
    - In Denmark, there is a database that contains data from both contaminated and uncontaminated sites.
    - For Italy, reference is made only to available data from Regiono Veneto.

- In France, there is no systematic monitoring, however available results were collected in a number of European projects such as the final report of the Project "PREMIS: Priorisation of emerging Chemical compounds in soils" and ISSEP's BIODIEN report 2018.

4. **Are PFAS data available online**?

The following links to online publicly available data were shared:

- Italy: https://www.arpa.veneto.it/dati-ambientali/open-data/idrosfera/concentrazione-di-sostanze-perfluoroalchiliche-pfas-nelle-acque-prelevate-da-arpav
- Denmark: https://data.geus.dk/geusmap/?mapname=jupiter
- France: https://ades.eaufrance.fr/

5. **Have specific background values been determined for diffuse PFAS concentrations?**

In the Netherlands, studies have already been conducted to determine background values in of the soil. Values were approved for PFOS and PFOA. (https://www.rivm.nl/publicaties/achtergrondwaarden-perfluoralkylstoffen-pfas-in-nederlandse-landbodem). For groundwater, studies on concentrations of PFAS have also been conducted in the Netherlands, but no background value was determined from these (RIVM, 2021).

6. Is there a distinction by land use type when investigating diffuse PFAS concentrations in groundwater and which parameters are most common?

Both Italy and the Netherlands distinguished by type of land use.

The contacts surveyed indicate that PFOA and PFBA are the most common, followed by PFOS. After it, PFBS PFPeA and PFhxA are still the most frequently mentioned.

When asked whether these parameters in diffusely contaminated groundwater differ from identified parameters in PFAS risk sites, it is generally stated that too little data is yet available on this and that it depends on the activity of the risk site.

7. Insights on the spread of PFAS in relation to the source.

It is generally noted that

- short-chain PFAS are more likely to occur in groundwater and longer-chain PFAS are more likely to occur in the soil.
- short-chain PFAS are highly mobile and not necessarily identified close to the source.

Furthermore, it is also indicated that diffuse contamination seems more likely to come from airborne deposition.

It is generally indicated that knowledge about possible sources of PFAS is growing and therefore it is too early to conclude anything at this level.

8. Her was also asked about the use of "non-target" analytical methods (TOP, AOF and EOF) for determining diffuse PFAS concentrations in groundwater.

These methods of analysis are not often or on a larger scale, according to the contacts.

Additional Information

The following information was additionally relayed:

- Publications from Germany "Significance thresholds for the assessment of contaminated groundwater""
- https://www.lawa.de/documents/03_anlage_3_bericht_gfs_fuer_pfc_endfassung_22_11_2017_2_1552302208.pdf
- In 2023, BRGM is launching several actions on that topic supported by French ministries and research fundings
- A French ""National PFAS Action Plan"" has been announced on January 17, 2023
  https://www.ecologie.gouv.fr/plan-daction-ministeriel-sur-pfas
  2 actions concern monitoring:
  Line of action 1: Have standards on discharges and environments to guide public action;
  Line of action 3: Improve knowledge of discharges and the impregnation of environments, in particular aquatic environments, to reduce the exposure of populations."

ANNEX 2 CHECKLISTS

Available upon request.

ANNEX 3 LIMITS OF QUANTIFICATION FOR SOIL AND GROUNDWATER

PFAS - quantitative analysis	acronym	CAS nr	LOQ (ng / l)
Perfluoro-n-butanoic acid	PFBA	375-22-4	1
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	1
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	1
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	1
Perfluoro-n-octanoic acid linear	PFOA lineair	335-67-1	1
Perfluoro-n-octanoic acid branched	PFOA vertakt		1
Total perfluoro-n-octanoic acid	PFOA totaal		1
Perfluoro-n-nonanoic acid	PFNA	375-95-1	1
Perfluoro-n-decanoic acid	PFDA	335-76-2	1
Perfluoro-n-undecanoic acid	PFUnDA	2058-94-8	1
Perfluoro-n-dodecanoic acid	PFDoDA	307-55-1	1
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	1
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	1
Perfluoro-n-butanesulfonic acid	PFBS	375-73-5	1
Perfluoro-n-pentanesulfonic acid	PFPeS	2706-91-4	1
Perfluoro-n-hexanesulfonic acid linear	PFHxS lineair	355-46-4	1
Perfluoro-n-hexanesulfonic acid branched	PFHxS vertakt		1
Total perfluoro-n-hexanesulfonic acid	PFHxS totaal		1
Perfluoro-n-heptanesulfonic acid	PFHpS	375-92-8	1
Perfluoro-n-octanesulfonic acid linear	PFOS lineair	1763-23-1	1
Perfluoro-n-octanesulfonic acid branched	PFOS vertakt		1
Total perfluoro-n-octanesulfonic acid	PFOS totaal		1
Perfluoro-n-nonanesulfonic acid	PFNS	68259-12-1	1
Perfluoro-n-decanesulfonic acid	PFDS	335-77-3	1
Perfluoro-n-octanesulfonamide linear	PFOSA lineair	754-91-6	1
Perfluoro-n-octanesulfonamide branched	PFOSA vertakt		1
Total perfluoro-n-octanesulfonamide	PFOSA totaal		1
N-methylperfluoro-n-octanesulfonamide linear	MePFOSA lineair	31506-32-8	2
N-methylperfluoro-n-octanesulfonamide branched	MePFOSA lineair		4
Total N-methylperfluoro-n-octanesulfonamide	MePFOSA totaal		2
N-ethylperfluoro-n-octanesulfonamide linear	EtPFOSA lineair	4151-50-2	4
N-ethylperfluoro-n-octanesulfonamide branched	EtPFOSA vertakt		2
Total N-ethylperfluoro-n-octanesulfonamide	EtPFOSA totaal		4
N-methylperfluoro-n-octanesulfonamidoacetic acid	MePFOSAA	2355-31-9	1
N-ethylperfluoro-n-octanesulfonamidoacetic acid	EtPFOSAA	2991-50-6	1
4:2 fluorotelomer sulfonic acid	4:2 FTS	757124-72-4	1
6:2 fluorotelomer sulfonic acid	6:2 FTS	27619-97-2	1
8:2 fluorotelomer sulfonic acid	8:2 FTS	39108-34-4	1
8:2 fluorotelomer phosphate diester	8:2 diPAP	678-41-1	1
Perfluoro-2-propoxypropanoic acid	HFPO-DA	13252-13-6	1
4,8-dioxa-3H-perfluorononanoic acid	DONA	919005-14-4	1
Perfluoro-4-ethylcyclohexanesulfonic acid	PFECHS	646-83-3	1
Perfluoro-n-butanesulfonamide	PFBSA	30334-69-1	2
N-methylperfluoro-n-butanesulfonamide	MePFBSA	68298-12-4	10
N-methylperfluoro-n-butanesulfonylamidoacetic acid	MePFBSAA	159381-10-9	10
Perfluoro-n-hexanesulfonamide	PFHxSA	41997-13-1	10
Sum of quantitative PFAS			
Sum of EFSA PFAS			

PFAS WAC compounds	Afkorting	CAS nr	LOQ (ng / l)
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	1
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	2
Perfluoro-n-dodecanesulfonic acid	PFDoDS	79780-39-5	1
Perfluoro-n-undecanesulfonic acid	PFUnDS	749786-16-1	1
Perfluoro-n-tridecanesulfonic acid	PFTrDS	791563-89-8	1
6:2 fluorotelomer phosphate diester	6:2 diPAP	57677-95-9	10
6:2/8:2 fluorotelomer phosphate diester	6:2/8:2 diPAP	943913-15-3	10
10:2 fluorotelomer sulfonic acid	10:2 FTS	120226-60-0	4
Sum of indicative PFAS			

Sum EU DWD			
Som 20 EU DWD			

PFAS CMA quantitative analysis	acronym	CAS nr	LOQ (µg / kg dm)
Perfluoro-n-butanoic acid	PFBA	375-22-4	0.5
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	0.5
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	0.5
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	0.5
Perfluoro-n-octanoic acid linear	PFOA lineair	335-67-1	0.5
Total perfluoro-n-octanoic acid	PFOA totaal		0.5
Perfluoro-n-nonanoic acid	PFNA	375-95-1	0.5
Perfluoro-n-decanoic acid	PFDA	335-76-2	0.5
Perfluoro-n-undecanoic acid	PFUnDA	2058-94-8	0.5
Perfluoro-n-dodecanoic acid	PFDoDA	307-55-1	0.5
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	0.5
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	0.5
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	0.5
Perfluoro-n-butanesulfonic acid	PFBS	375-73-5	0.5
Perfluoro-n-pentanesulfonic acid	PFPeS	2706-91-4	0.5
Perfluoro-n-hexanesulfonic acid linear	PFHxS lineair	355-46-4	0.5
Total perfluoro-n-hexanesulfonic acid	PFHxS totaal		0.5
Perfluoro-n-heptanesulfonic acid	PFHpS	375-92-8	0.5
Perfluoro-n-octanesulfonic acid linear	PFOS lineair	1763-23-1	0.5
Total perfluoro-n-octanesulfonic acid	PFOS totaal		0.5
Perfluoro-n-nonanesulfonic acid	PFNS	68259-12-1	0.5
Perfluoro-n-decanesulfonic acid	PFDS	335-77-3	0.5
Perfluoro-n-octanesulfonamide linear	PFOSA lineair	754-91-6	0.5
Total perfluoro-n-octanesulfonamide	PFOSA totaal		0.5
N-methylperfluoro-n-octanesulfonamide linear	MePFOSA lineair	31506-32-8	0.5
Total N-methylperfluoro-n-octanesulfonamide	MePFOSA totaal		0.5
N-ethylperfluoro-n-octanesulfonamide linear	EtPFOSA lineair	4151-50-2	0.5
Total N-ethylperfluoro-n-octanesulfonamide	EtPFOSA totaal		0.5
N-methylperfluoro-n-octanesulfonamidoacetic acid	MePFOSAA	2355-31-9	0.5
N-ethylperfluoro-n-octanesulfonamidoacetic acid	EtPFOSAA	2991-50-6	0.5
4:2 fluorotelomer sulfonic acid	4:2 FTS	757124-72-4	0.5
6:2 fluorotelomer sulfonic acid	6:2 FTS	27619-97-2	0.5
8:2 fluorotelomer sulfonic acid	8:2 FTS	39108-34-4	0.5
8:2 fluorotelomer phosphate diester	8:2 diPAP	678-41-1	0.5
Perfluoro-2-propoxypropanoic acid	HFPO-DA	13252-13-6	0.5
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	0.5
Perfluoro-4-ethylcyclohexanesulfonic acid	PFECHS	646-83-3	0.5
Perfluoro-n-butanesulfonamide	PFBSA	30334-69-1	0.5
N-methylperfluoro-n-butanesulfonamide	MePFBSA	68298-12-4	0.5
Perfluoro-n-hexanesulfonamide	PFHxSA	41997-13-1	0.5
Sum of quantitative PFAS			
Sum of EFSA PFAS			

PFAS CMA indicative:	Afkorting	CAS nr	
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	1
Perfluoro-n-dodecanesulfonic acid	PFDoDS	79780-39-5	1
6:2 fluorotelomer phosphate diester	6:2 diPAP	57677-95-9	1
6:2/8:2 fluorotelomer phosphate diester	6:2/8:2 diPAP	943913-15-3	1
10:2 fluorotelomer sulfonic acid	10:2 FTS	120226-60-0	1
N-methylperfluoro-n-butanesulfonylamidoacetic acid	MePFBSAA	159381-10-9	1
Sum of indicative PFAS			

ANNEX 4 SAMPLING LOCATIONS

Available upon request.

ANNEX 5 MAPS

Available upon request.

ANNEX 5.1. MAPS DATASET 1 GROUNDWATER

Available upon request.

ANNEX 5.2. MAPS COMBINED DATASET GROUNDWATER

Available upon request.

ANNEX 5.3. MAPS DATASET 1 SOIL

Available upon request.

ANNEX 5.4. MAPS COMBINED DATASET SOIL

Available upon request.