

Anthropogenic background values of PFAS in soil and groundwater

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04/06/2024 – 3rd International Congress on PFAS, Paris

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1. Introduction

PFAS

- Extensive plumes
- Groundwater might be diffusely enriched
- Difficult to delineate a contamination



2. Problem definition

- Belgian pollution standards are based on naturally occurring background values in non-polluted soil and groundwater. PFAS do not occur naturally in the environment → **diffuse anthropogenic presence**
- **Selection of 'non-suspect' locations** → combine data from multiple spatial data layers
- Avoiding interference from other contaminants that can influence the **low quantification limit/reporting limit**

What are the PFAS background values in soil and groundwater in Flanders?

Anthropogenic background values of PFAS in soil and groundwater

1



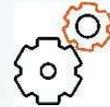
Introduction

2



Problem definition

3



Methodology

4



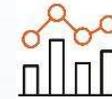
Sampling locations

5



Sampling & Analysis

6



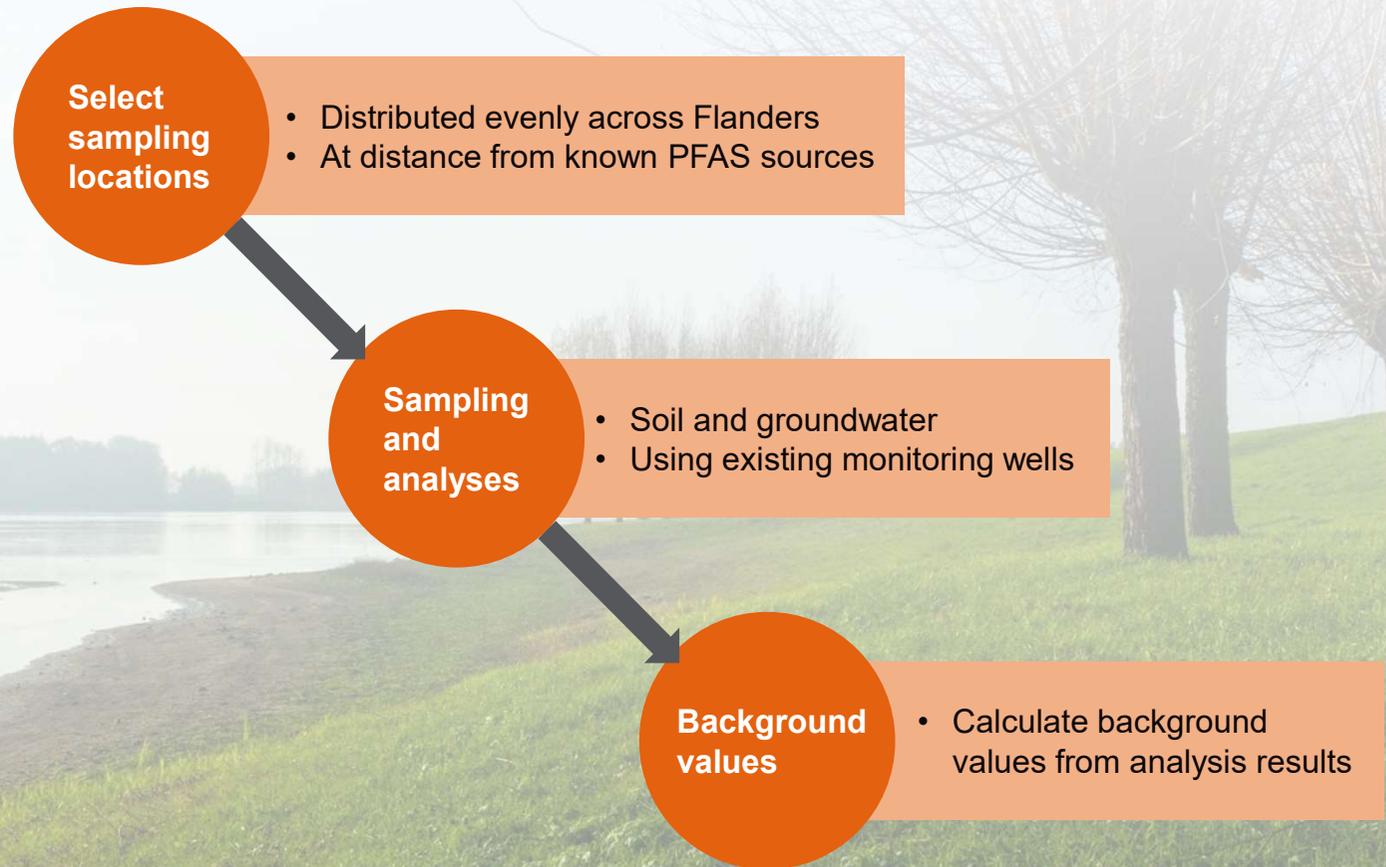
Results

7



Conclusions

3. Methodology



4. Sampling locations

Green zones

- Known PFAS contaminations
- Activities using PFAS (point sources)
- Inventory of fire fighting sites
- Inventory of known fires
- Sites discharging PFAS in waste water
- Known landfills
- Other sites with known soil contaminations
- Waste water treatment plants

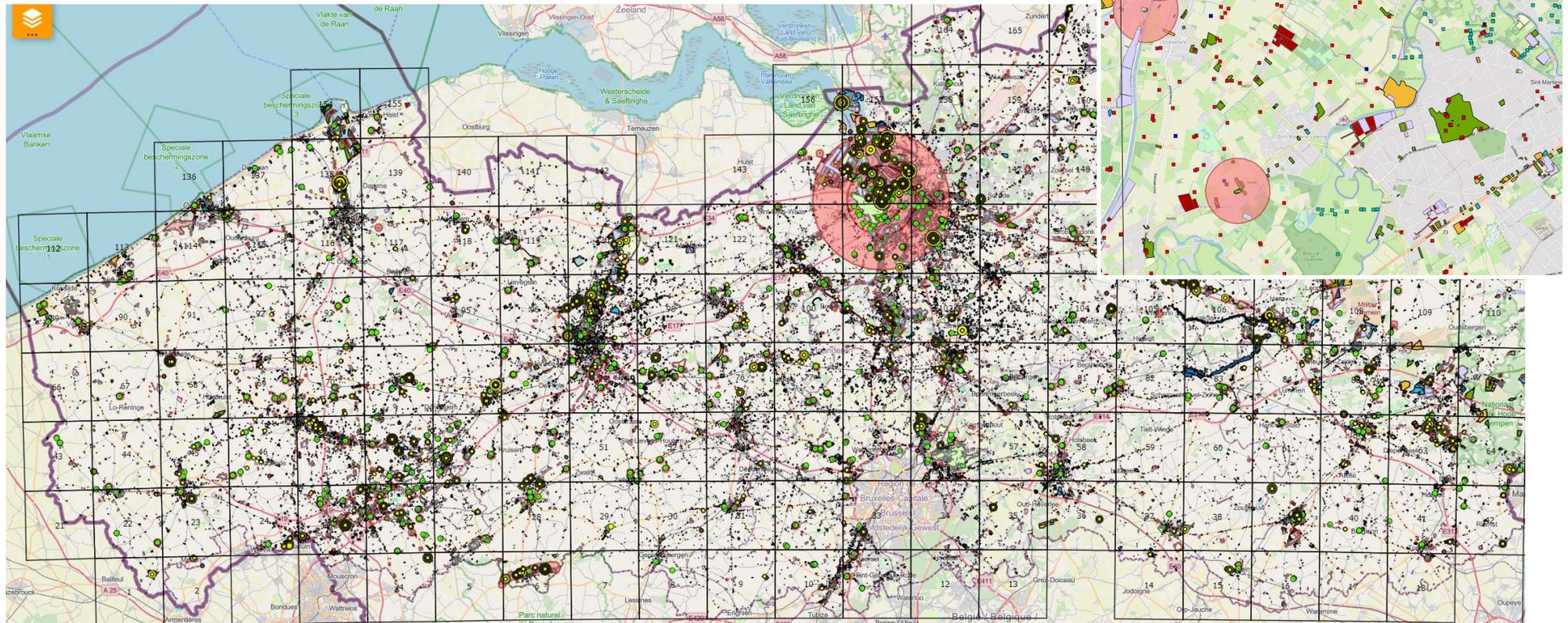
Evenly distributed

- Ca. 150 groundwater samples
- 75 soil samples
 - Complementary to existing DB of 50 samples
- Grid 10 x 10 km

Existing network of monitoring wells

- Network of wells in phreatic groundwater:
 - Ca. 3000 wells
 - Active wells
 - Recently used
 - Mostly in nature areas and agricultural areas

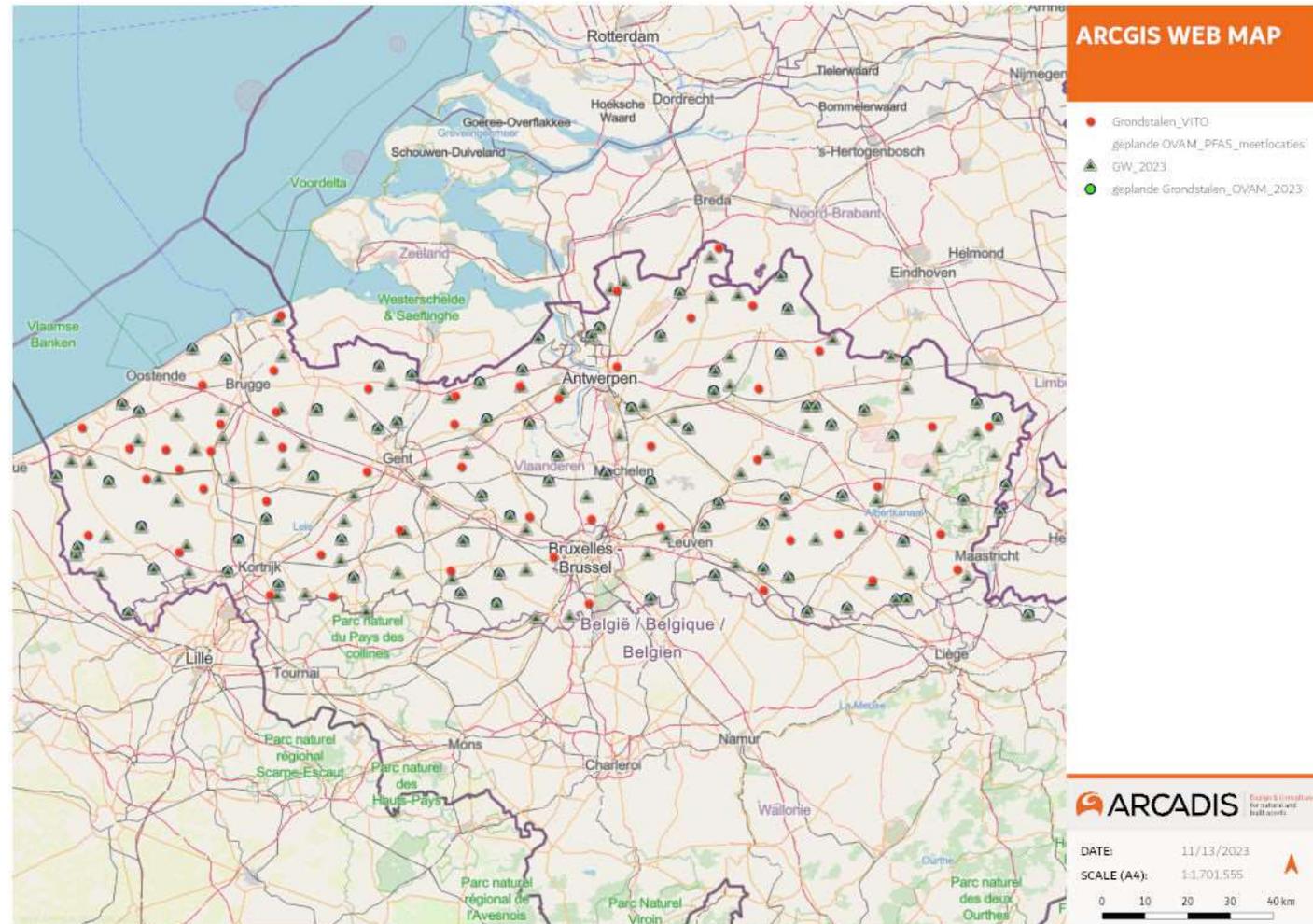
4. Sampling locations



- 149 of the 168 grid squares have a suitable sampling location

4. Sampling locations

- 149 of the 168 grid squares have a suitable sampling location
 - 127 in agricultural areas
 - 18 in natural reserves
 - 3 in recreational areas
 - 1 in residential area



5. Sampling and analyses

Groundwater

- Eurofins
- Sampling method
 - low flow, in accordance with procedure for soil investigation
 - high flow, diffuse dispersion commissioned by Flanders Environment Agency for their study

Soil

- Witteveen + Bos
- Sampling method
 - Complementary to existing study
 - top 20 cm-mv
 - for proper comparison
- Visual inspection of the area for signs of possible sources/contamination

Checklist prevention PFAS-contamination by field sampling

Quality control sampling

- By Witteveen + Bos
- By OVAM

In case the monitoring well was sampled for both groundwater and soil, the efforts were made to be present at the same time for monitoring.

5. Sampling and analyses

PFAS analyses were conducted by Eurofins Analytico

- Determined by LC-MS/MS analysis
 - Soil cf. CMA/3/D. (PFAS 40, 31 quantitatively, 9 indicatively)
 - Groundwater cf. WAC/IV/A/025 (PFAS 43, 34 quantitatively, 9 indicatively)
- Lab results were preliminarily checked
 - When values were above LOQ, samples were preserved for possible further analyses such as Total Oxidizable Precursors

6. Results - Groundwater

Dataset 1

- In 141 of the 147 samples, at least one PFAS component was measured above LOQ
- Most of the analysis results are below LOQ
- 11 compounds were never measured above LOQ
- The most prevalent compounds were PFBA, PFOA, PFBS and PFOS
- No normal, logarithmic or gamma distribution was recognized, and very high standard deviations were found

- How to calculate the total sum of PFAS compounds?
 - LOQ ↔ reporting limit (often 10 ng/L)
 - 141 ↔ 38 measurements

6. Results - Groundwater

Dataset 1

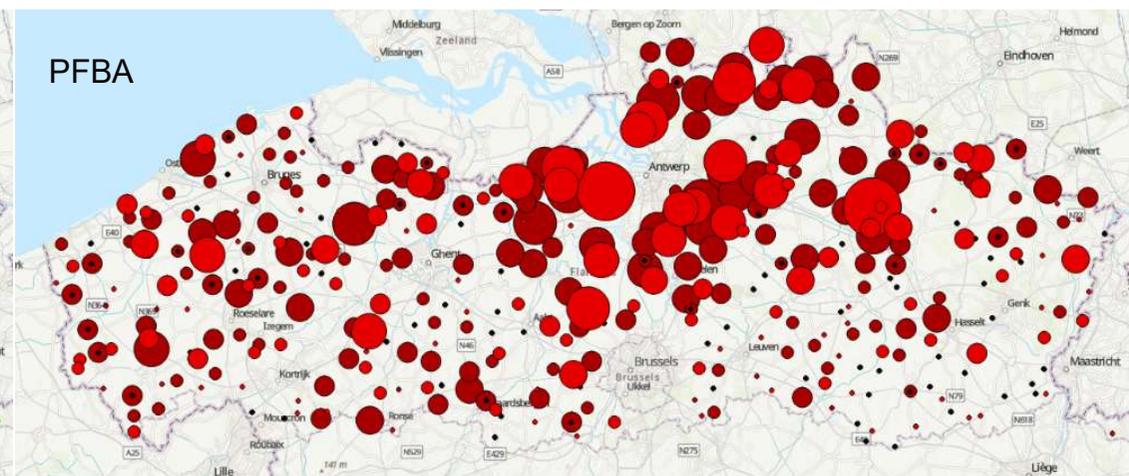
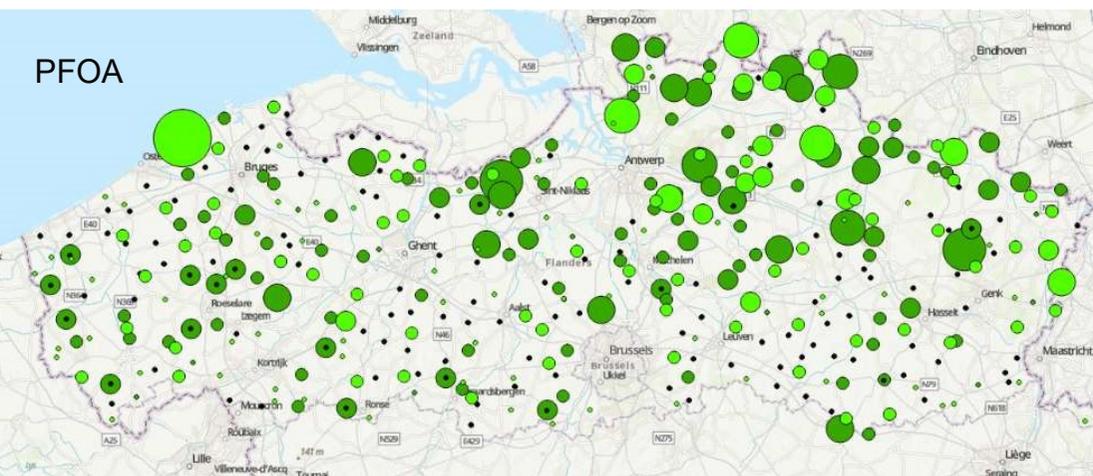
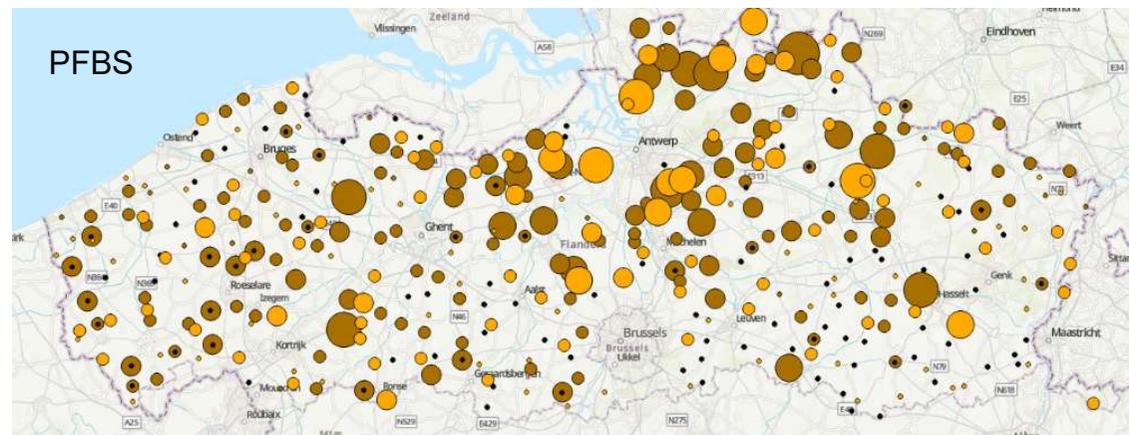
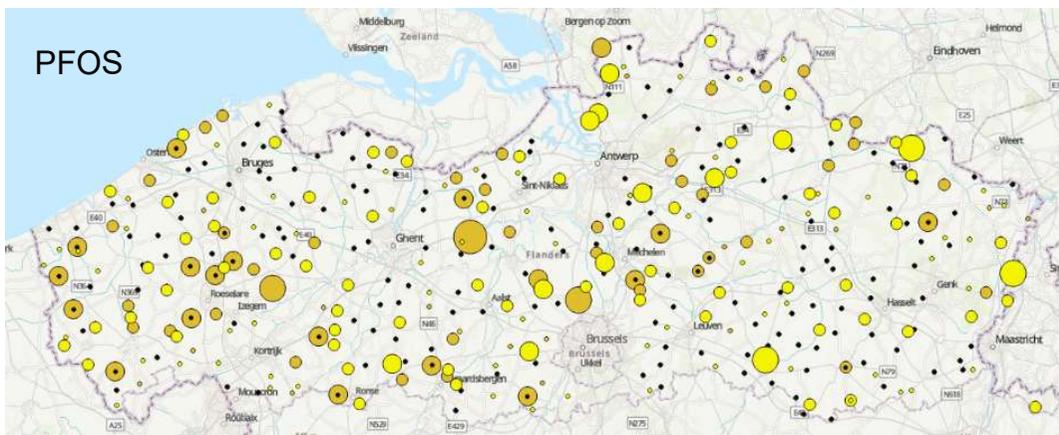
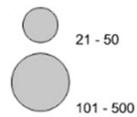
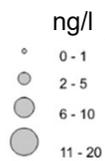
- 147 samples
- 4 compounds with 50 % detects > LOQ

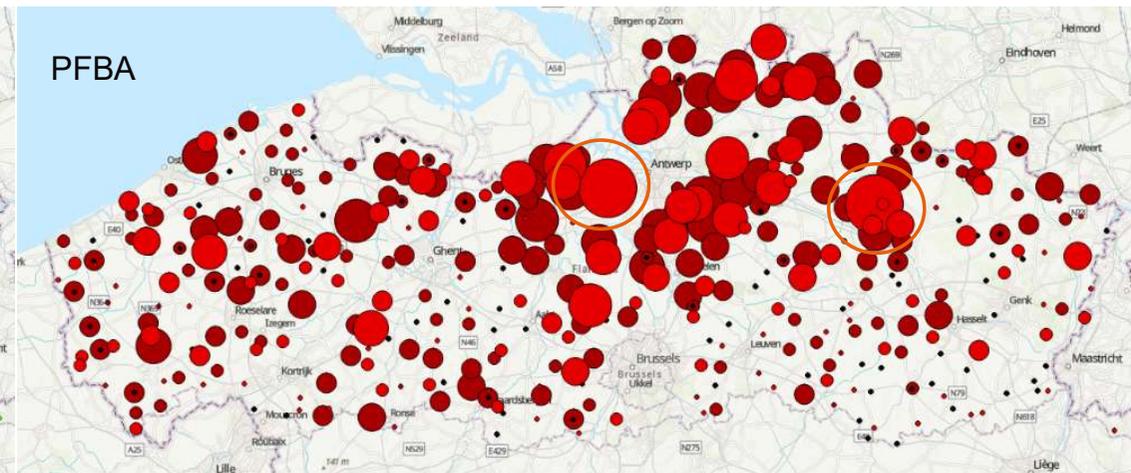
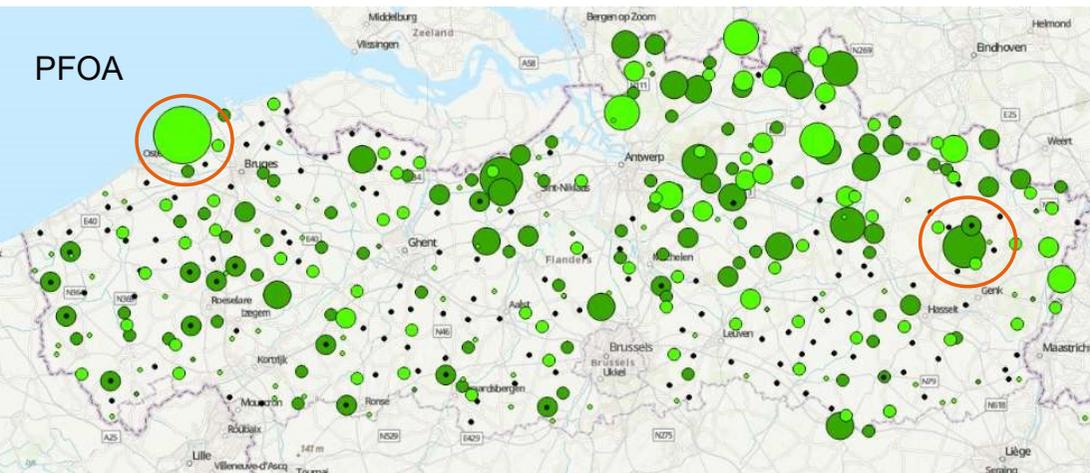
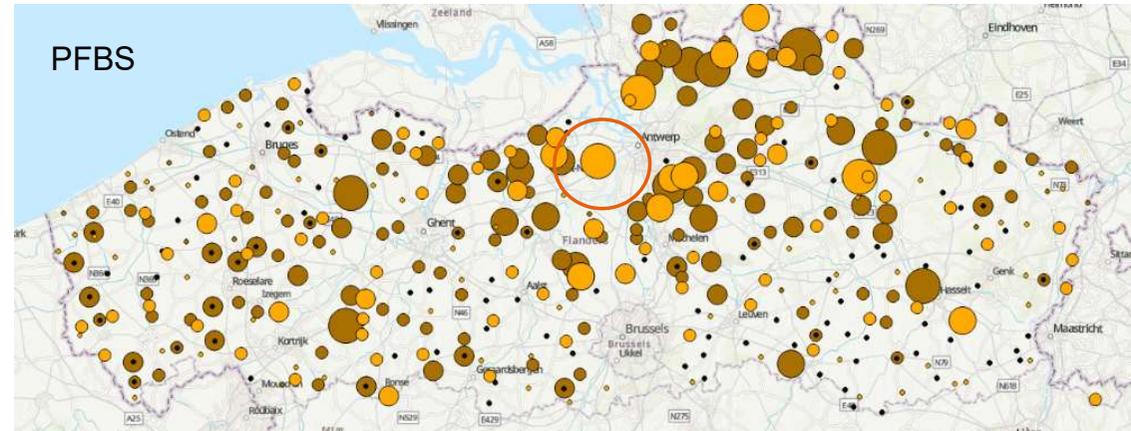
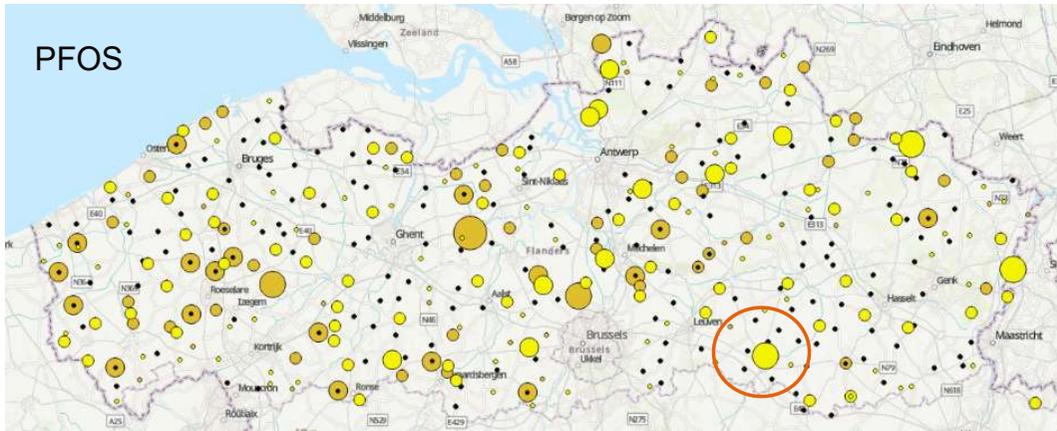
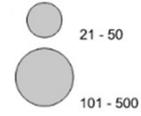
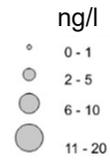
Analytes	LOQ	NumObs	#> LOQ	#<LOQ	Minimum	Maximum	Median	90%ile	95%ile
ng/l									
PFBA	1	147	92	55	1,07	201,0	2,3	23,5	42,6
PFBS	1	147	86	61	1,01	48,4	1,2	7,8	11,5
PFOAtot	1	147	82	65	1,02	112,9	1,2	6,5	9,6
PFOS _{tot}	1	147	77	70	1,03	18,4	1,0	4,7	7,1

Dataset 1+2

- Combined with 240 samples Flanders environmental agency (VMM)
- 3 compounds with ca. 50 % detects > LOQ

Analytes	LOQ	NumObs	#> LOQ	#<LOQ	Minimum	Maximum	Median	90%ile	95%ile
ng/l									
PFBA	1	370	220	150	1,0	201,0	3,0	21,1	34,5
PFBS	1	385	220	165	1,0	74,0	2,0	9,5	13,8
PFOAtot	1	387	191	196	1,0	112,9	< KL	8,1	13,2
PFOS _{tot}	1	387	132	255	1,0	26,0	< KL	5,0	8,0





6. Results

Dataset 1

- 73 samples
- Only PFOS (total) > 50% detects:

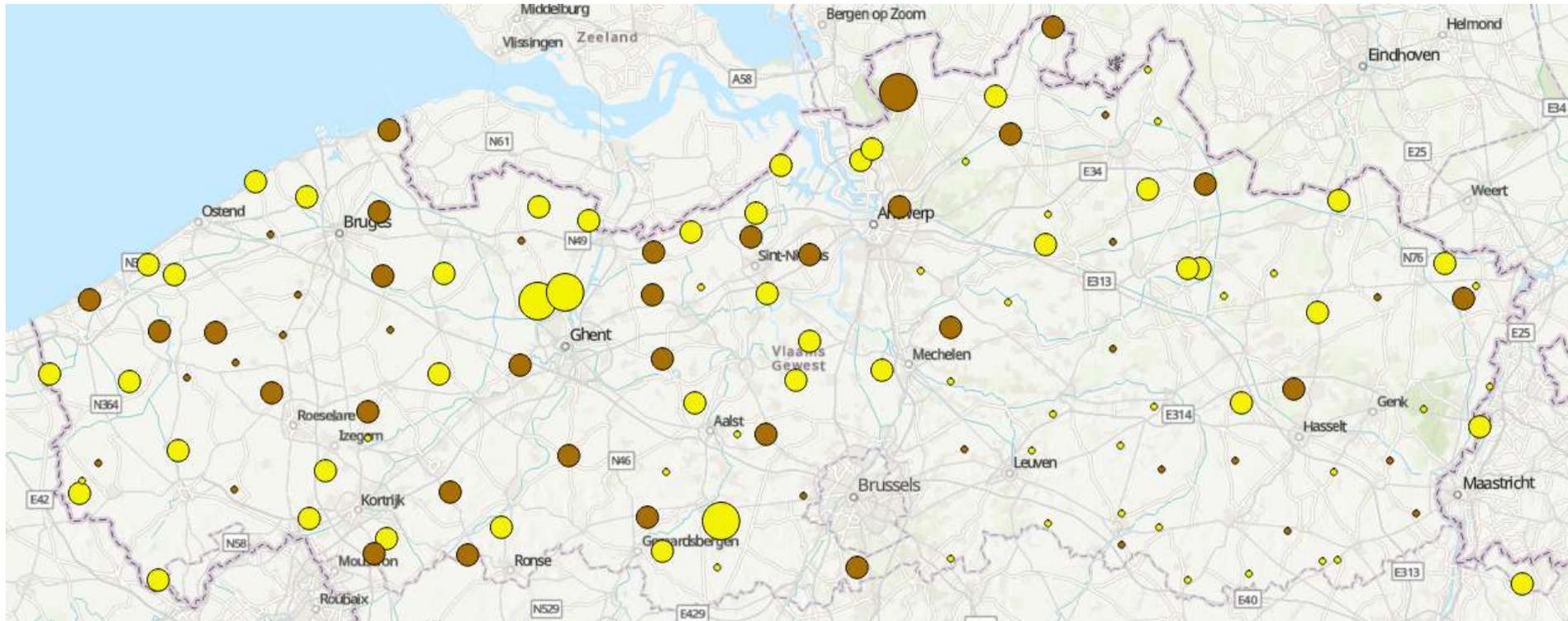
Analytes	LOQ	NumObs	# > LOQ	# < LOQ	Minimum	Maximum	Median	90%ile	95%ile
$\mu\text{g/kg ds}$									
PFOS total	0,5	73	42	31	0,5	2,6	0,6	1,4	1,8

- 90%ile in line with current background value of 1,5 $\mu\text{g/kg dm}$

Dataset 1+2

- Combined with 50 existing samples
- Only PFOS (total) > 50% detects:

Analytes	LOQ	NumObs	# > LOQ	# < LOQ	Minimum	Maximum	Median	90%ile	95%ile
$\mu\text{g/kg ds}$									
PFOS total	0,2/0,5	123	89	34	0,2	2,6	0,6	1,5	1,7



PFOS totaal - vaste deel van de aarde - dataset 2 ($\mu\text{g}/\text{kg ds}$) PFOS totaal - vaste deel van de aarde - dataset 1 ($\mu\text{g}/\text{kg ds}$)



6. Results

- Outlier analysis
- Proposed antropogenic background value: P90 after removal of outliers

analyte	Proposed antropogenic background value	
	Groundwater (ng/l)	Soil (µg/kg dm)
PFBA	21,0	/
PFBS	9,4	/
PFOAtot	8,0	1,0
PFOS_{tot}	(5,0)	1,5

7. Conclusions (1/2)

- **Sampling campaign to calculate background values for PFAS in soil and groundwater:**
 - 147 groundwater samples OVAM+ 240 samples Flemish Environmental Agency (VMM)
 - 73 new soil samples + 50 results from existing database
 - PFAS-unsuspected sampling locations

Groundwater

- In 341/387 locations at least 1 PFAS component was detected above LOQ (used in this study)
- Reported values are mostly below required reporting limit for soil investigation (10 ng/l)
- PFBA, PFBS and PFOA were found in ca. 50% of sampling locations
- A significant part of the current standard from the EU - DWD (100 ng/l for the sum of 20 PFAS) has already been filled by the anthropogenic background value of PFBA (21%)
- The antropogenic background value for PFBA exceeds the discharge standard in Flanders of 20 ng/l

7. Conclusions (2/2)

- **Soil**
 - High percentage of non-detects
 - Results for PFOS in soil similar to previous studies
 - No new anthropogenic background values were proposed.
- **Additional recommendations**
 - Samples were taken from rural and nature areas, additional research is required to determine the anthropogenic background in urban and industrial areas
 - The background values can be used in soil investigation- to motivate whether or not a measured concentration can be assigned with high probability to the investigated source

Anthropogenic background values of PFAS in soil and groundwater

- PFAS are diffusely spread, anthropogenic background values are present without nearby point source
- Background values for groundwater were determined for 3 compounds
- Background values for soil were validated for 1 compound
- This study helps the regulator evaluate soil investigation studies