

Perfluoroalkyl substances in groundwater: First survey in Wallonia and Brussels (Belgium)

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Abstract

Perfluoroalkyl substances (PFASs) include a wide range of synthetic compounds characterized by a high thermal and chemical stability, as well as by relatively unique water- and fat-repellent properties. As a result, they have been manufactured and used as surfactants in a wide range of industrial and domestic applications since the middle of the last century. However, PFASs are also toxic substances and concerns for human health increased over the past two decades as it was realized that their unique properties also render PFASs persistent in the environment and bioaccumulative in the trophic chain. PFASs are nowadays recognized to be ubiquitous substances in the environment.

In this study, a regional-scale survey of the presence of PFASs in groundwater has been conducted in Belgium. Five substances were measured: sodium perfluorooctanesulfonate (PFOS), perfluoro-n-octanoic acid (PFOA), perfluoro-n-hexanoic acid (PFHxA), perfluoro-n-heptanoic acid (PFHpA) and sodium perfluorohexanesulfonate (PFHxS). The survey covered both Wallonia and Brussels. In Wallonia, two sampling campaigns were conducted: one campaign exclusively focused on drinking water production wells, while the other campaign only included sites from the WFD monitoring network for groundwater. A total of 113 sites were monitored, including 79 wells used for drinking water production and 34 sites from the WFD network. In Brussels, 9 sites were sampled once or twice (yielding 14 samples in total). The samples were collected between May 2015 and November 2016.

In Wallonia, all PFASs are detected in 30% to 40% of the samples. The average concentration (i.e. computed based on all samples) remains under 1 ng/l for all 5 substances. Maximum concentration range between about 4 ng/l for PFHpA to about 40 ng/l for PFHxS. 90th percentile range between 1 ng/l and 2 ng/l. Those slight contaminations appear to be randomly located in our aquifers but they occur more often in industrial areas of the western, eastern and northern Wallonia. It seems they are old and diffuse in porous aquifers (chalk and sands) and linked to the intrusion of surface water in superficial aquifers (limestone and alluvia). In Brussels, although the number of samples is much more limited, the statistics are found to be very similar as in Wallonia.

Aims and scope

Why focus on perfluoroalkyl substances (PFASs)

- PFASs are synthetic substances manufactured to be **extremely resistant**.
- They are **bioaccumulable**.
- Numerous studies have found them to be **ubiquist** throughout the globe at very low concentrations.
- Certain PFASs are suspected to be **endocrine disruptors**.
- PFOS is a hazardous priority substance (Dir. 2013/39/EU).

Aims of the study

Conduct a first survey of the presence of 5 PFASs in groundwater in Wallonia and Brussels (Belgium)

Materials and methods

ULC/MS/MS method

- Autotrace Plus Solid phase extraction (Strata-X AW)
- UPLC Acquity H-class with Waters UPLC BEH-C18 column
- XEVO TQ-S Waters mass spectrometer

Compound	Internal standard	Parent ion (m/z)	Cone Voltage (V)	Daughter ion 1		Daughter ion 2	
				(m/z)	Ecoll. (V)	(m/z)	Ecoll. (V)
PFHxA	13C2 PFHxA	313	20	269	8	118.9	23
PFHxS	13C2 PFHxS	315	15	315	5	270	10
PFHpA	13C2 PFHpA	363	17	319	9	169	18
PFHxS	13C2 PFHxA	399	60	98.9	30	79.9	30
PFOA	13C4 PFOA	413	20	369	8	168.9	16
PFOS	13C4 PFOS	417	20	372	8	171.9	16
PFOS	13C4 PFOS	499	60	98.9	40	79.9	45
PFOS	13C4 PFOS	503	60	99	40	79.9	45

Sampling plan

122 sampling points for GW:

- 34 points from the Water Framework Directive (WFD) surveillance network in Wallonia
- 79 drinking water (DW) production points in Wallonia
- 32 out of 38 GW bodies covered in Wallonia with a sampling density adapted with respect to GW body vulnerability
- 9 sampling points in Brussels

137 samples taken and analyzed:

- Each sampling point is sampled once or twice
- 14 samples are taken in Brussels

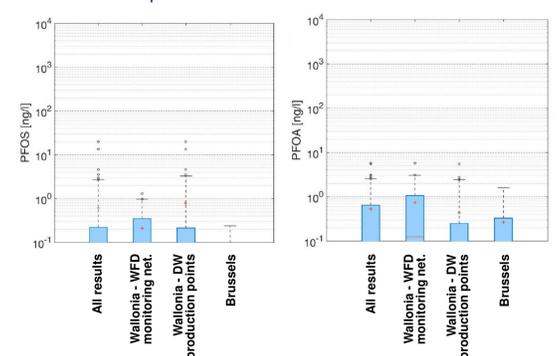
Selected results

General statistics – all PFASs

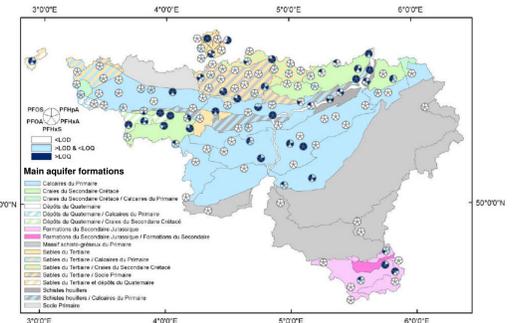
	LOQ [ng/l]	N [-]	F _{ND} [%]	F _Q [%]	C _{max} [ng/l]	C _{ave} [ng/l]	C _{med} [ng/l]	C ₉₀ [ng/l]
Wallonia								
PFHxA	0.5	122	61.5	23.8	11.53	0.72	0.00	1.97
PFHxS	0.5	122	64.8	13.1	41.02	0.84	0.00	0.81
PFHpA	0.5	122	66.0	14.9	3.93	0.22	0.00	0.75
PFOS	0.2	122	58.2	27.0	5.73	0.52	0.00	1.75
Brussels								
PFHxA	0.5	14	57.1	28.6	6.75	0.85	0.00	2.39
PFHxS	0.5	14	57.1	28.6	1.04	0.23	0.00	0.84
PFHpA	0.5	14	71.4	21.4	0.8	0.17	0.00	0.88
PFOA	0.5	14	71.4	14.3	1.59	0.19	0.00	0.67
PFOS	0.2	14	92.9	7.1	0.24	0.02	0.00	0.02

N - number of samples analyzed
F_{ND} - frequency of non detection (results under the detection limit)
F_Q - frequency of quantification (results above the limit of quantification)
C_{max} - maximum concentration measured
C_{ave} - average concentration
C_{med} - median concentration value
C₉₀ - 90th percentile value.

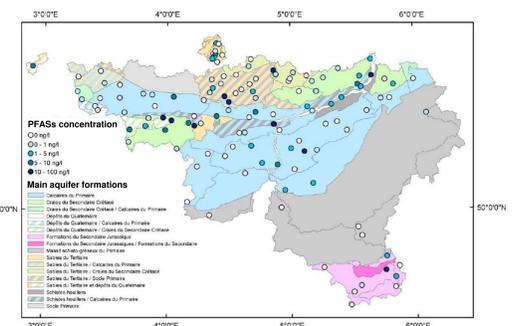
Selected box-plots – PFOS and PFOA



Spatial distribution – occurrence of PFASs



Spatial distribution – concentration (sum of PFASs)



Key conclusions

Take home messages

- PFASs are relatively ubiquitous in GW (found in 50-60% of the sites investigated).
- Concentration levels are generally lower than 0,01 µg/l. Locally, concentrations in PFASs can be higher but never exceed 0,1 µg/l.
- This survey only focuses only on 5 PFASs. Recent prioritization work shows that other PFASs could be present in GW and should be investigated.

Comparison with other types of water

