PFAS and Water Resources: How to Determine the Best Treatment Solution?

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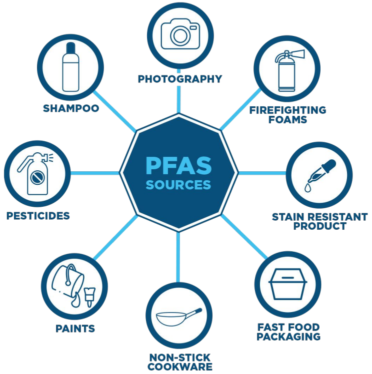
Descriptions contained herein apply exclusively to those examples and/or to the general situations specifically referenced, and in no event should be considered to apply to specific scenarios without prior review and validation.

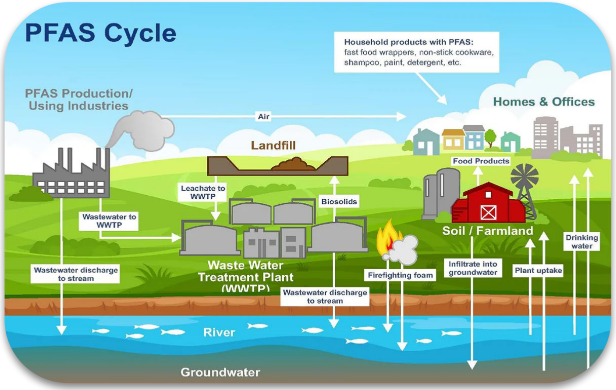
WHAT ARE PFAS?

Per- and **P**oly- **F**luoro**A**lkyl **S**ubstances (PFAS) are **man-made chemicals** (up to 15 000 PFAS known) that have been manufactured and used in a variety of industries around the world since the 1940s. They are known for their extreme **resistance**, due to the **C-F bonds** which is the strongest in organic chemistry.



https://smchd.org/pfas//

Because of their **toxicity** and **persistence**, regulations have been established worldwide. In **France,** the regulation for drinking water sets the **sum of 20 PFAS at 0.1 µg/L**



https://shop.knowyourh2o.com/blogs/news/pfas-and-forever-chemicals-a-new-man-made-cycle-the-pfas-cycle-that-must-be-broken

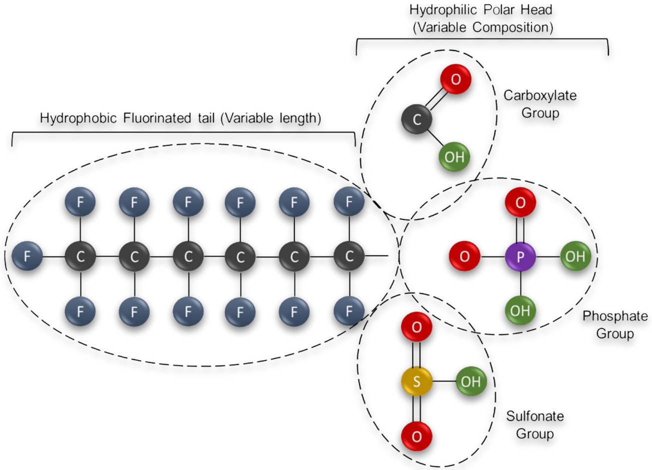
WHAT ARE PFAS?

PFAS typically contain a **hydrophobic fluorinated carbon chain** and a **hydrophilic functional group**. They are defined by having **at least one fully fluorinated carbon atom** (perfluorinated) or **having multiple** carbon atoms where fluorine has replaced hydrogen (polyfluorinated).

PFAS are also defined by the **carbon chain length**, and are divided into two main families: PerFluoroalkyl ether Carboxylic Acids (**PFCA**) and PerFluoroalkyl ether Sulfonic Acids (**PFSA**)

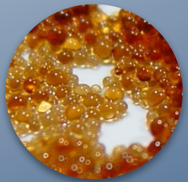
	Ultra-short-chain PFAS		Short-chain PFAS			Long-chain PFAS				
PFCA	C2	C3	C4	C5	C6	C7	C8	C9	C10	>C10
PFSA	C2	C3	C4	C5	C6	C7	C8	C9	C10	>C10

How to treat them in the contaminated water bodies?

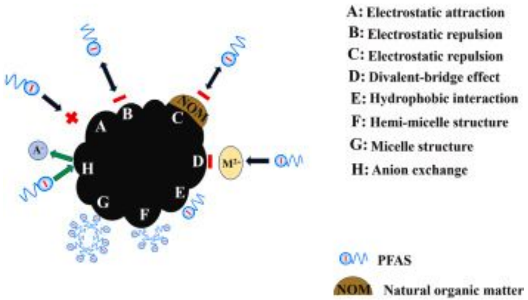


Panieri, E.; Baralic, K.; Djukic-Cosic, D.; Buha Djordjevic, A.; Saso, L. PFAS Molecules: A Major Concern for the Human Health and the Environment. Toxics **2022**, 10, 44. https://doi.org/10.3390/toxics10020044

WHAT ARE THE EFFECTIVE TREATMENT PROCESSES?



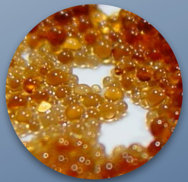
Adsorption is one of the most efficient and easy-to-deploy technology to tackle PFAS challenges in water bodies. It involves the binding of PFAS molecules to the surface of a material such as .. ↴



Xiaobo Lei et al., A review of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities, Environmental Pollution, Volume 321, 2023

- **Activated Carbon** (AC) adsorption, especially GAC - *Effectively removes many PFAS compounds*
- **Ion Exchange Resins** (IER) - *Particularly effective for short-chain PFAS that GAC for instance may not capture very well*
- **Reverse Osmosis/Nanofiltration** - *High removal efficiency (>95%) for most PFAS compounds*

WHAT ARE THE EFFECTIVE TREATMENT PROCESSES?



How to predict the PFAS adsorption treatment efficiency at full scale without having to go through time-consuming and costly continuous pilot tests?

Diabolo® and **RSSCT** are two accelerated lab-scale methodologies allowing to generate the sufficient data to scale-up the performances to an industrial unit.

What accelerated lab-scale methodology is the most accurate?

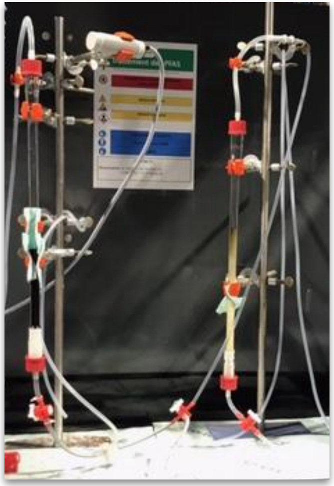
RAPID SMALL-SCALE COLUMN TEST (RSSCT)

RSSCTs are widely used to **simulate full-scale adsorber performance**, establishing **breakthrough profiles of fixed-bed units**. It can simulate months of full-scale adsorber operation in several days given that the **media is crushed**.

Full-scale Column *(Large Column)*	**RSSCT** *(Small Column)*
$d_{P,\ GAC} = 0{,}128$ cm	$d_{P,\ crushed\ GAC} = 0{,}0232$ cm

$$(1)\ \frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{d_{p,LC}}{d_{p,SC}}\right)^{x-2}$$

$EBCT_{LC} = 10$ minutes	**$EBCT_{SC} = 0{,}327$ minutes**



VEOLIA FEEDBACK FROM THE FIELD

Veolia North America operates around **40 PFAS treatment plants** in the **regulated water sector**, for which RSSCT tests were systematically carried out prior to design and construction.

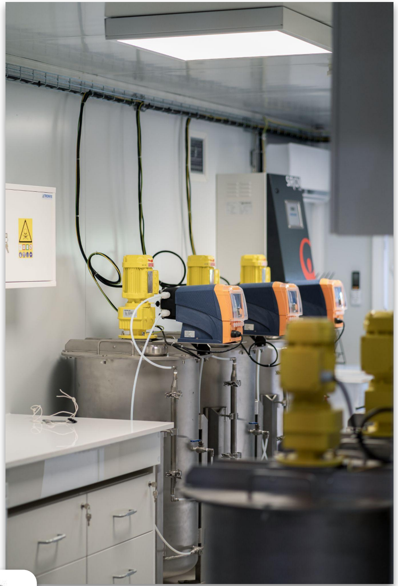
Plants	PFAS	Breakthrough (C/C_0, %)	BV Full-scale (m^3/m^3)	BV RSSCT (m^3/m^3)	RSSCT prediction error (%)
Plant #1	PFHpA	75	29 372	33 333	**13.5**
	PFHxA	20	18 029	20 000	**10.9**
	PFOA	25	25 558	33 333	**30.4**
	PFPeA	20	12 828	13 333	**3.9**
Plant #2	PFOA	15	9 712	19 424	**100**
		25	23 956	50 000	**109**
	PFPeA	25	9 712	20 000	**106**
		100	23 956	60 000	**150**

DIABOLO ® METHODOLOGY

The **Diabolo®** experimental approach consists of selecting the **best adsorbents** in terms of technical and economical performances to treat PFAS in liquid matrices.

The **data generated** at bench-scale on a **short-term period** (few weeks), comparatively to continuous pilot-scale column tests.

The data are used to feed **physical models** to **predict the performances at full scale** with the determination of the **lifetime** (or dosage) of the adsorbents and the **optimum contact time** (*e.g.* EBCT) to be applied.



$$q_e = Q_m * \frac{b*C_0}{1+b*C_0}$$

$$-\varepsilon \cdot D_a \cdot \frac{d^2C}{d^2z} + \nu \cdot \frac{dC}{dz} + \varepsilon \cdot \frac{dC}{dt} + \rho_{app} \cdot k \cdot (q_e - \bar{q}) = 0$$

$$q_e = K_F * C_0^{1/n}$$

$$\frac{\partial \bar{q}}{\partial t} = k(q_e - \bar{q})$$

DIABOLO® METHODOLOGY

It is divided into **3 phases**, all performed in **batch** allowing the generation, on a short-term period, of reliable data to **predict the performances at full scale**.

Phase 1 - Rapid **Screening** of several adsorbents to **compare** their PFAS adsorption performances

Phase 2 - Adsorption **Isotherms** to determine maximum adsorption capacities (**thermo** aspects)

Phase 3 - **Mini-Column** batch test to determine the optimum contact time (**diffusion kinetic** aspects)

DIABOLO® vs. RSSCT vs. FULL-SCALE

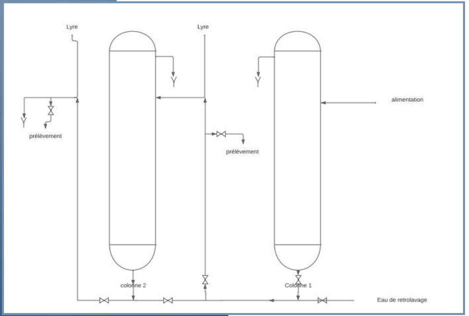
The comparative study Diabolo® *vs.* RSSCT *vs.* full-scale continuous test has been performed on a **drinking water LPRO concentrate**.

DOC (ppm)	Conductivity (mS/cm)	pH	Alkalinity (°F)	Hardness (°F)	Calcium (mg/L)	Sulphates (mg/L)
8.50	2.89	7.90	125	185	664	400

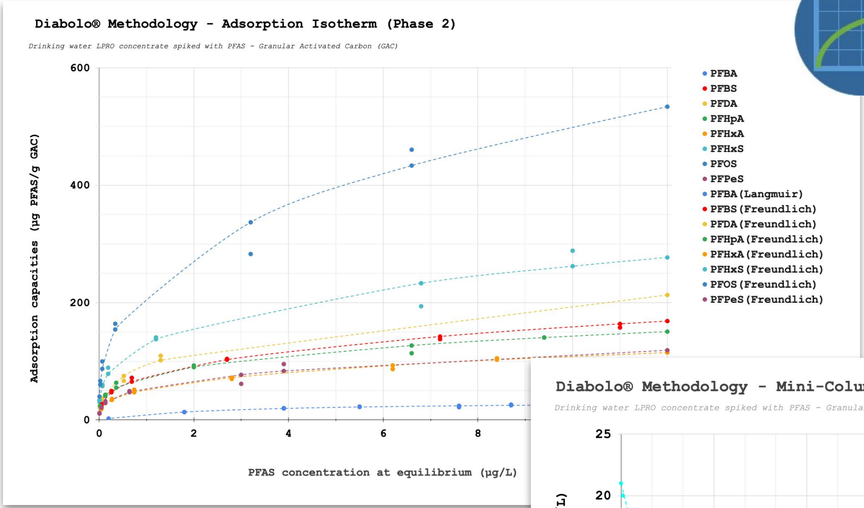
PFBA (µg/L)	PFHxA (µg/L)	PFHpA (µg/L)	PFOA (µg/L)	PFDA (µg/L)	PFDoA (µg/L)
3.6	8.3	9.1	16.7	11.7	2.1

PFBS (µg/L)	PFPeS (µg/L)	PFHxS (µg/L)	PFOS (µg/L)	PFDS (µg/L)
16.8	12.6	23	19.4	3.2

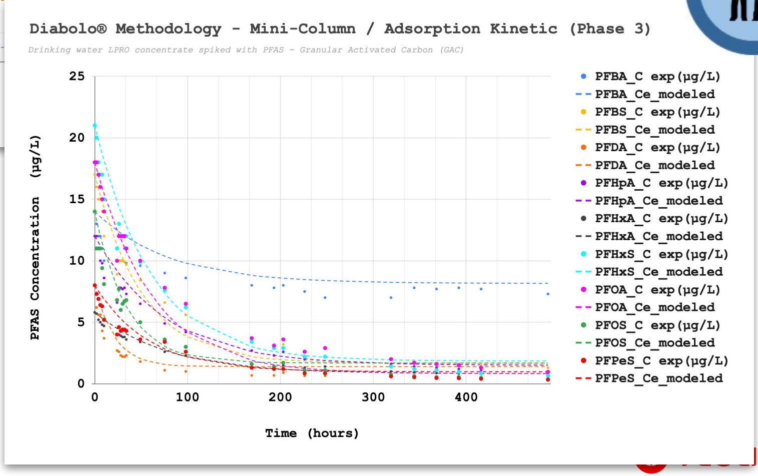
Full-scale Pilot Unit



DIABOLO® vs. RSSCT vs. FULL-SCALE

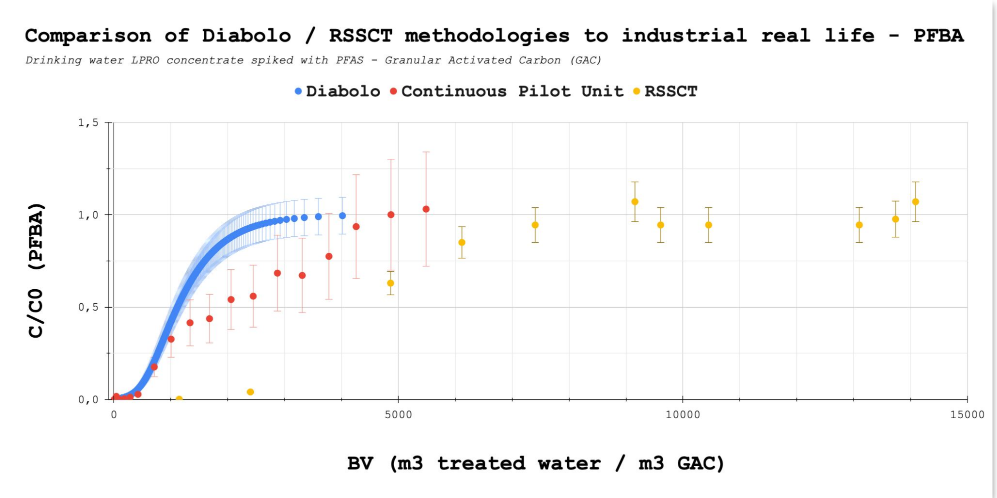


Phase 2 - **Adsorption Isotherm** (Diabolo®)



Phase 3 - **Adsorption Kinetic** (Diabolo®)

DIABOLO® vs. RSSCT vs. FULL-SCALE



	Diabolo®	RSSCT	Continuous Pilot Unit
BV at 100% breakthrough	4 017	7 403	4 869
%prediction error	**17.5**	**52.1**	-

Contact

TAKE HOME MESSAGES

➔ **Diabolo**® precision

- **More than 80% of accuracy** to predict full-scale **breakthrough** / performances, and to recommend the best **contact times** to be applied in the design of process units
- *Nota Bene: When it comes to simulate treatment train like a lead-lag configuration, better to go on a full-scale -like continuous test (e.g. pilot-scale tests) to get better accuracy in the lag performances prediction.*

➔ **RSSCT** reliability

- 90% of the time not accurate to predict full-scale performances, **less than 80% reaching even 50% of accuracy** for several case studies (REX from more than 40 PFAS treatment plants in DW for which RSSCTs have been carried out beforehand)
- **Grinding the materials** introduces **biases** into the estimation of adsorption capacity that cannot be corrected when scaling it up
- **Need a full-scale unit and data to adjust the scaling factor**
- Good to make **adsorbent comparisons**