Contribution of soil structure and colloidal particles to the dynamics of PFAS leaching from a firefighting contaminated site

rainfall simulation experiments on undisturbed soil columns

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Eric MICHEL, Chloé CAUREL, Pierre LABADIE, Hélène
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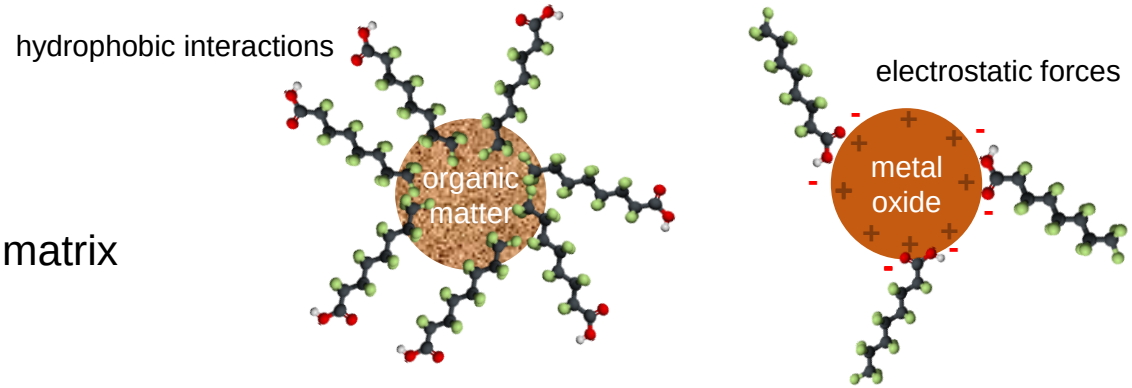
IPANEMA project funded by ADEME

PFAS conference
14.06.2023

State of the art : transport of PFAS



Interplay beween chemical interactions, flow conditions and soil matrix

- Often studied in **saturated and packed** and **model soils,** mostly **artifically contaminated**
  - ➢ major factors controlling PFAS transport: **organic matter / metal oxide content** and **chain-length of PFAS molecule**

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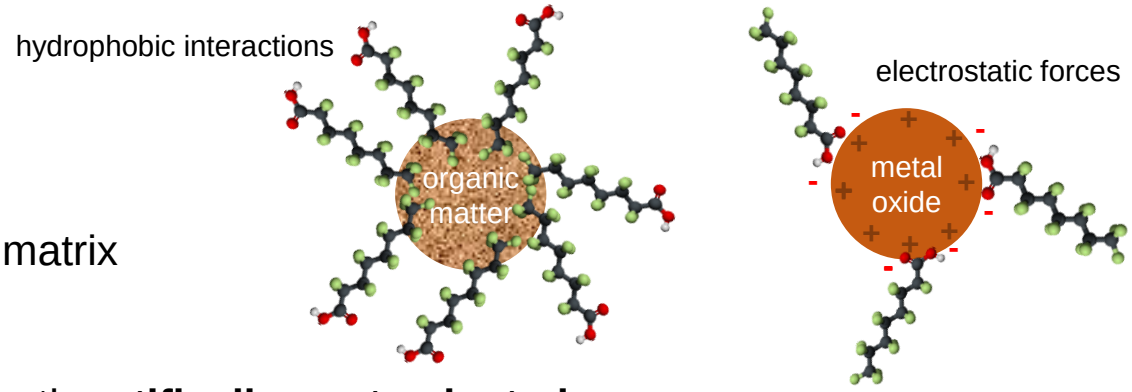

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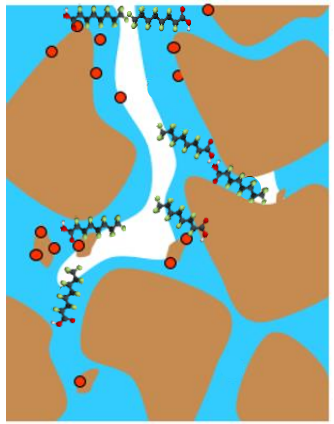
- Few studies in **unsaturated porous media**
  - ➢ moving AWI contributes to PFAS transport



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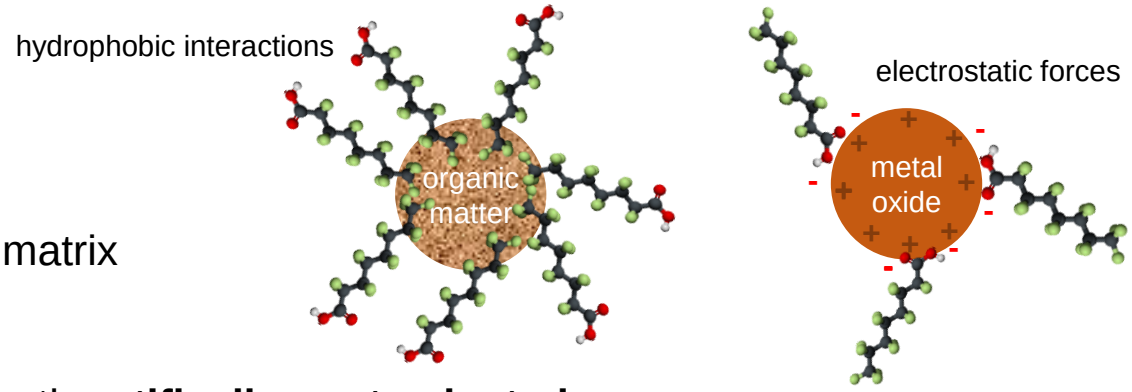

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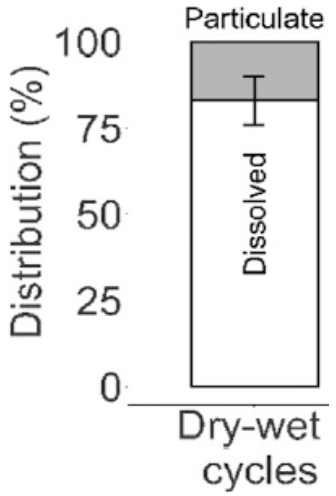

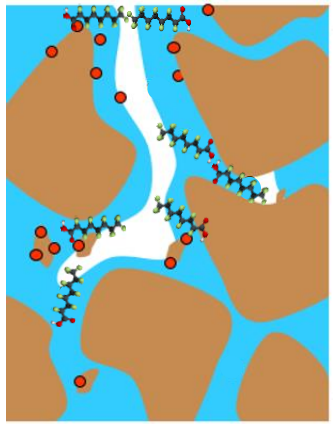

17 ± 7 % of leached PFOA was associated with soil colloids

Borthakur, A. et al (2021). *Journal of Hazardous Materials Letters*

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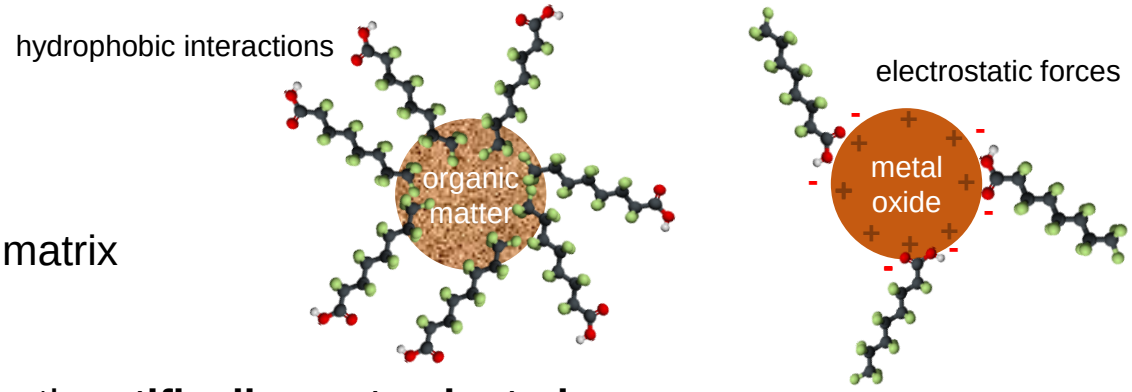

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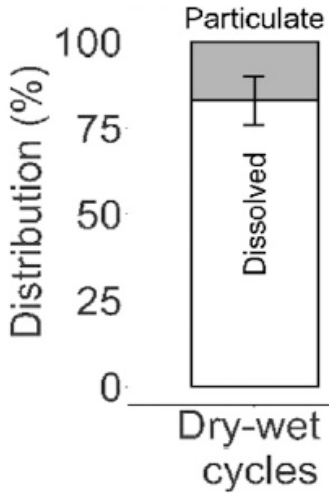
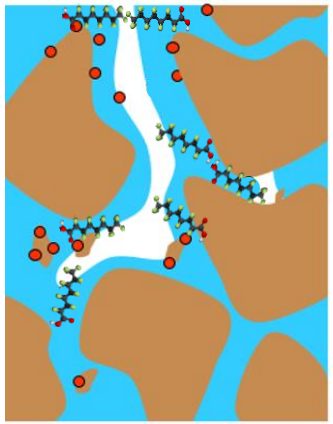
What happens in undisturbed soil ?
How are PFAS mixtures transported ?





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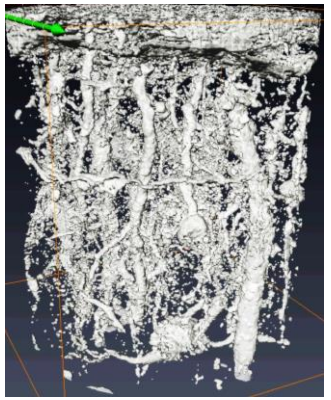
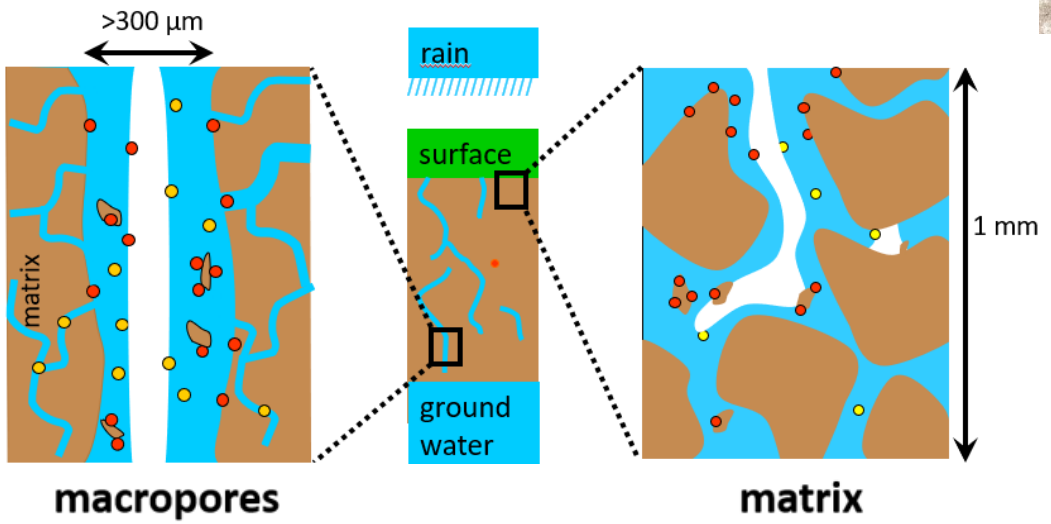
Current study : transport of PFAS

Interplay beween chemical interactions, flow conditions and soil matrix

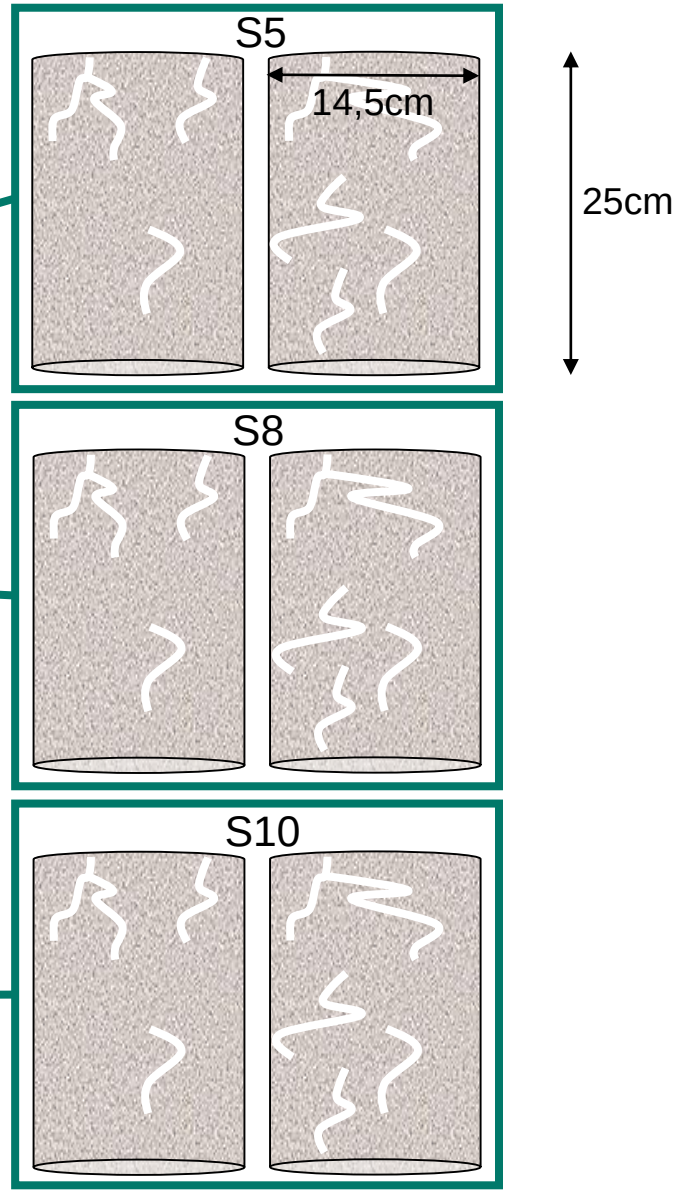
- Studies in **unsaturated porous media and natural soil** (heterogeneous soil matrix with macropores)
- PFAS analysis in the **liquid phase and adsorbed** to colloidal particles





Materials and methods : study area

fire fighting training site weekly used until 1996



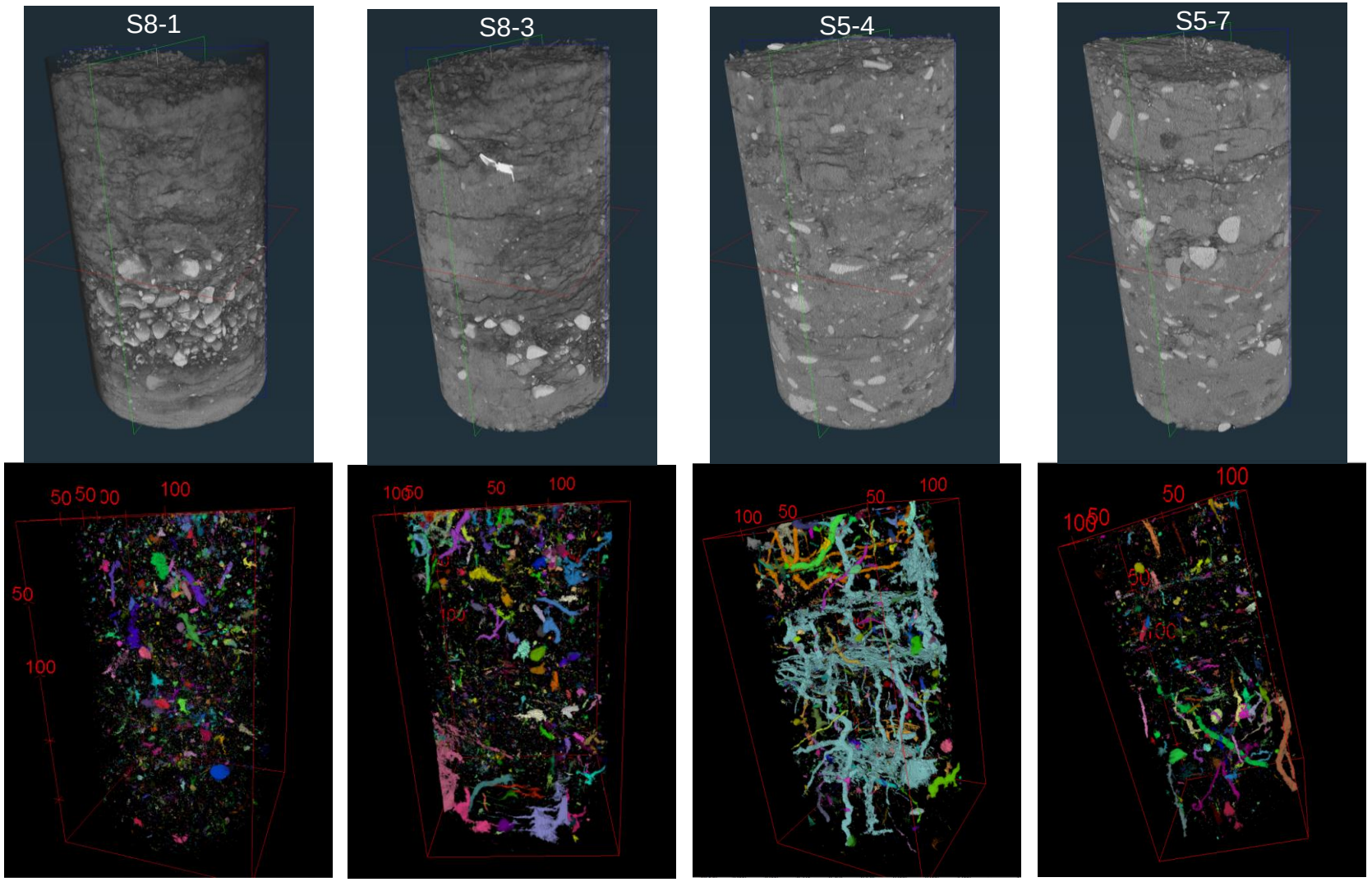
Materials and methods : undisturbed soil columns

X-Ray CT for the identification of macropore network

Area of high density = stones,
Area of low density = air → macro pores e.g. made by earth worms

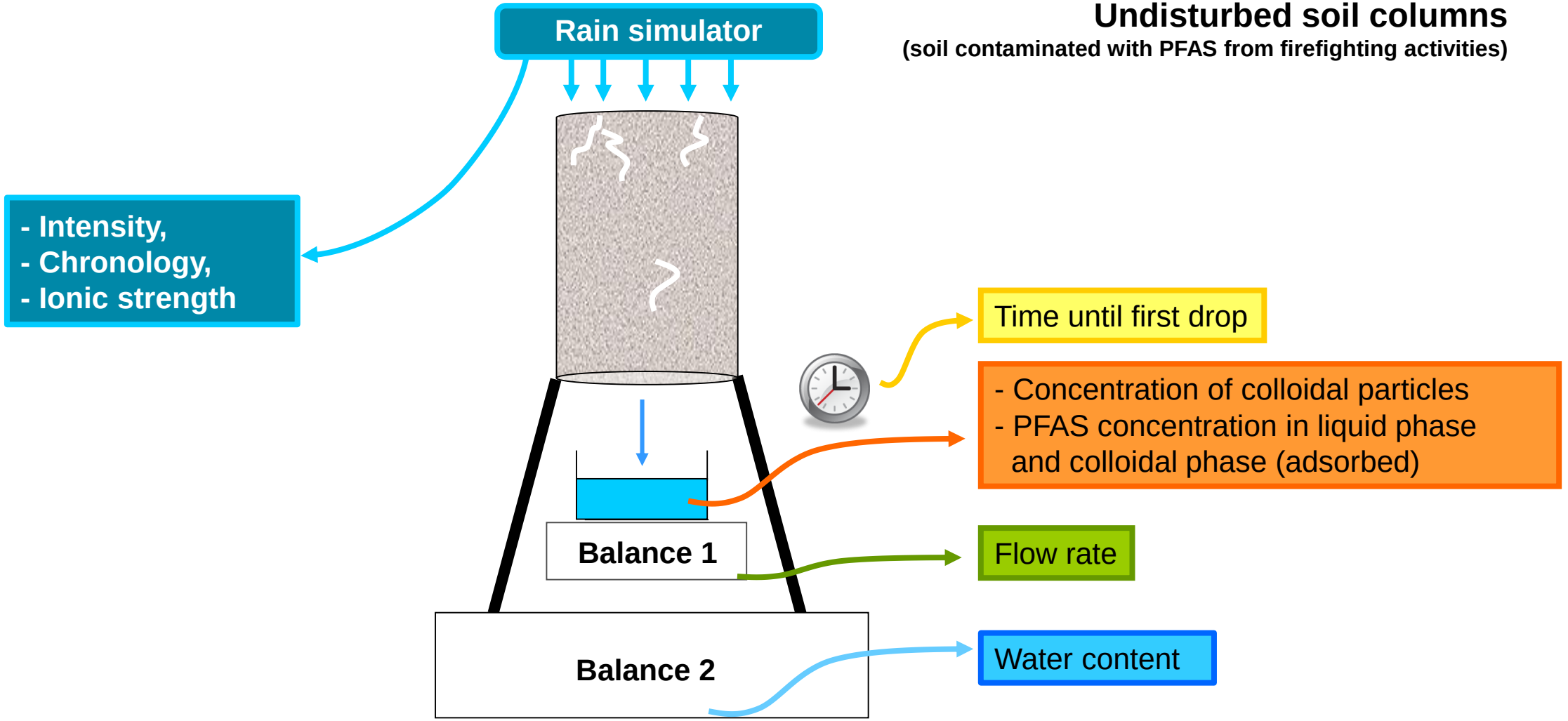
colored space = interconnected pore volume

Differences in macro/micro porosity of the soil (even between columns of the same position)



Materials and methods : pre-conditioning and leaching experiments

Undisturbed soil columns
(soil contaminated with PFAS from firefighting activities)



Materials and methods : pre-conditioning and leaching experiments

Undisturbed soil columns
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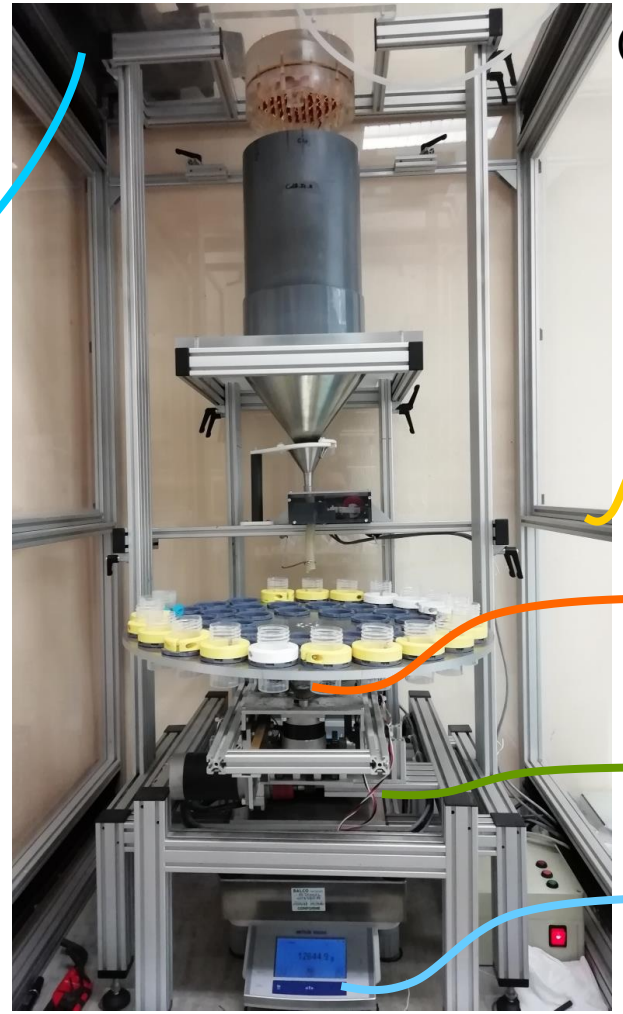
- Intensity,
- Chronology,
- Ionic strength



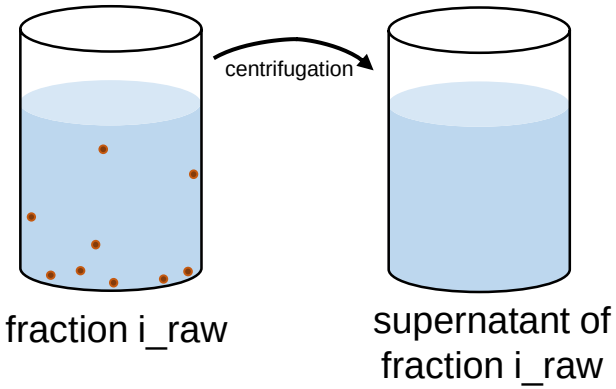
Time until first drop

- Concentration of colloidal particles
- PFAS concentration in liquid phase and colloidal phase (adsorbed)

Flow rate

Water content

Materials and methods : leaching experiments



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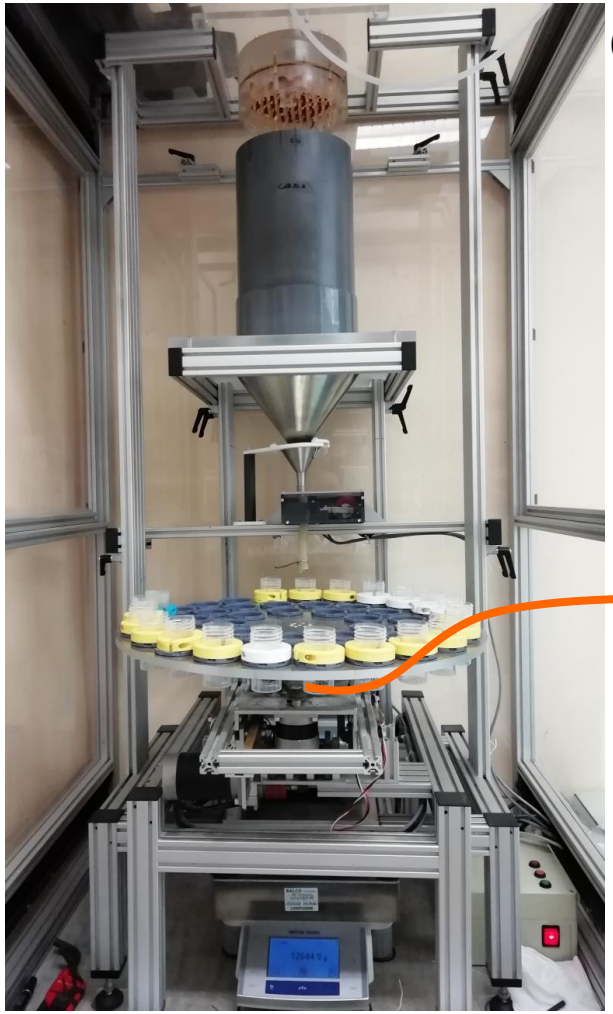

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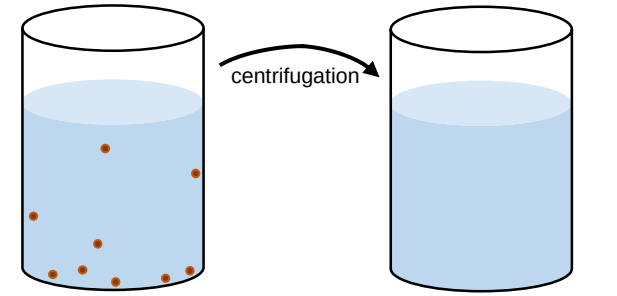

centrifugation at 20000g for 20 mins
expected cut-off at 20 nm

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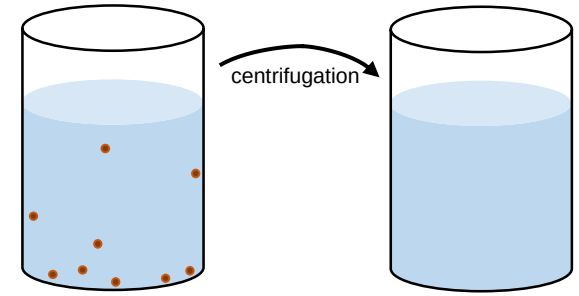

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Desorption of PFAS by adding 1:1 (vol) sample and Methanol
+
Measurement in LC/MS

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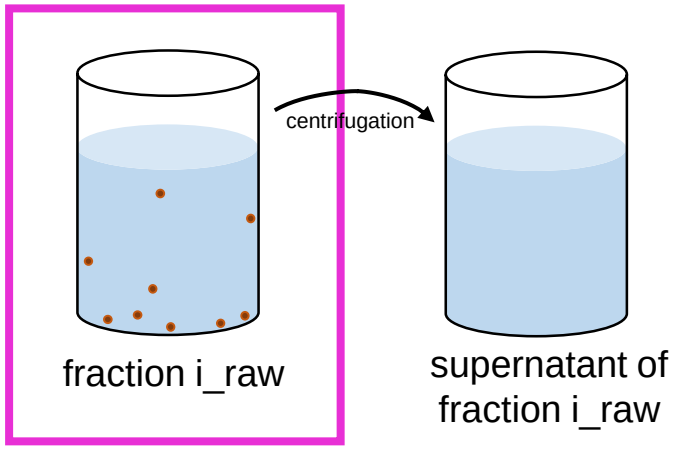

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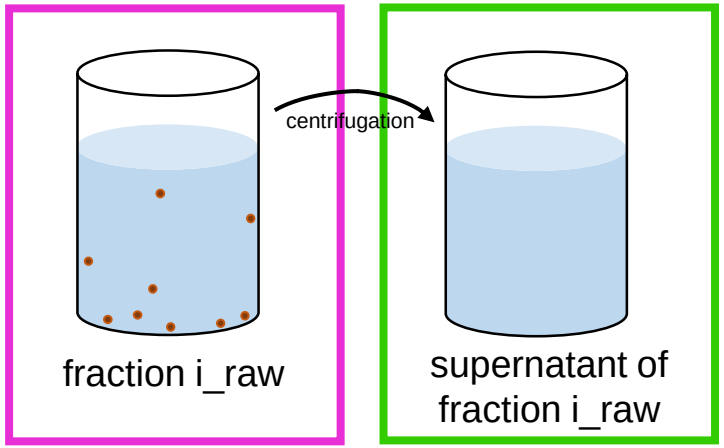

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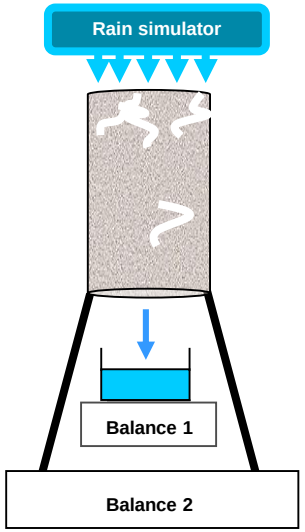
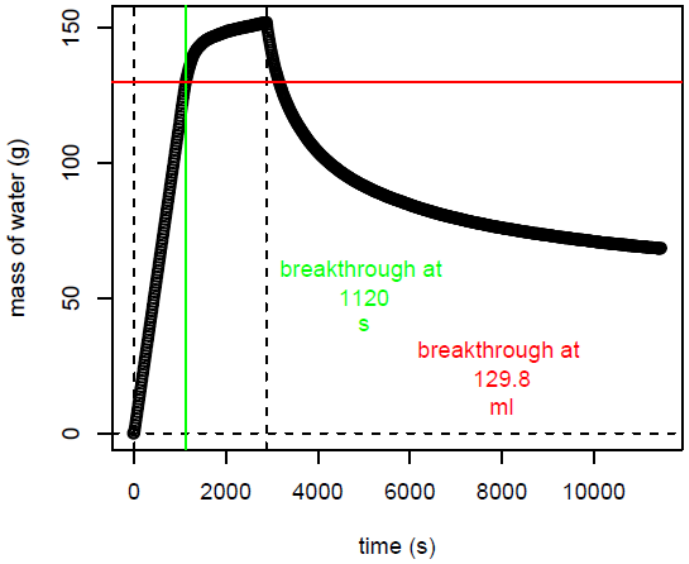
Preliminary results : hydrodynamics



Water content

column

S8-3



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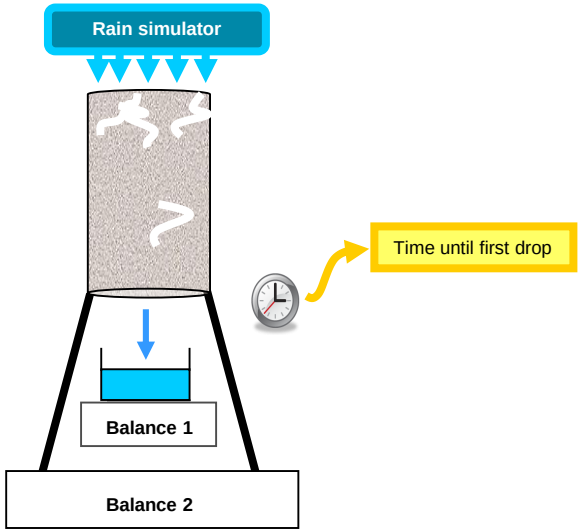

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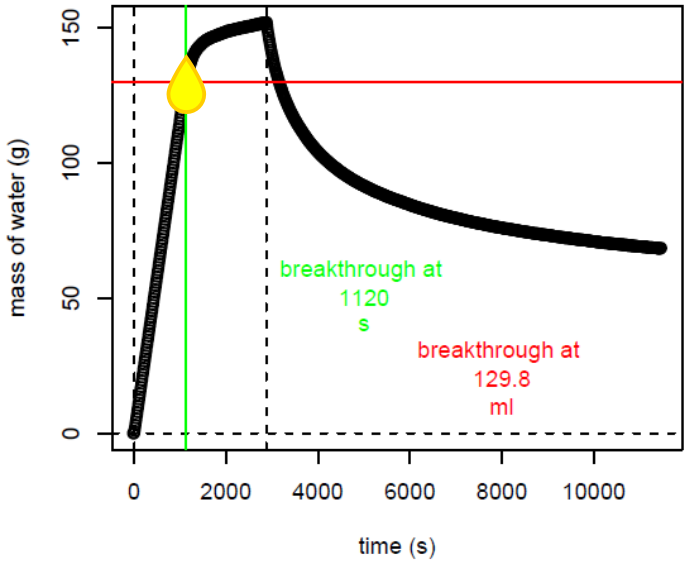

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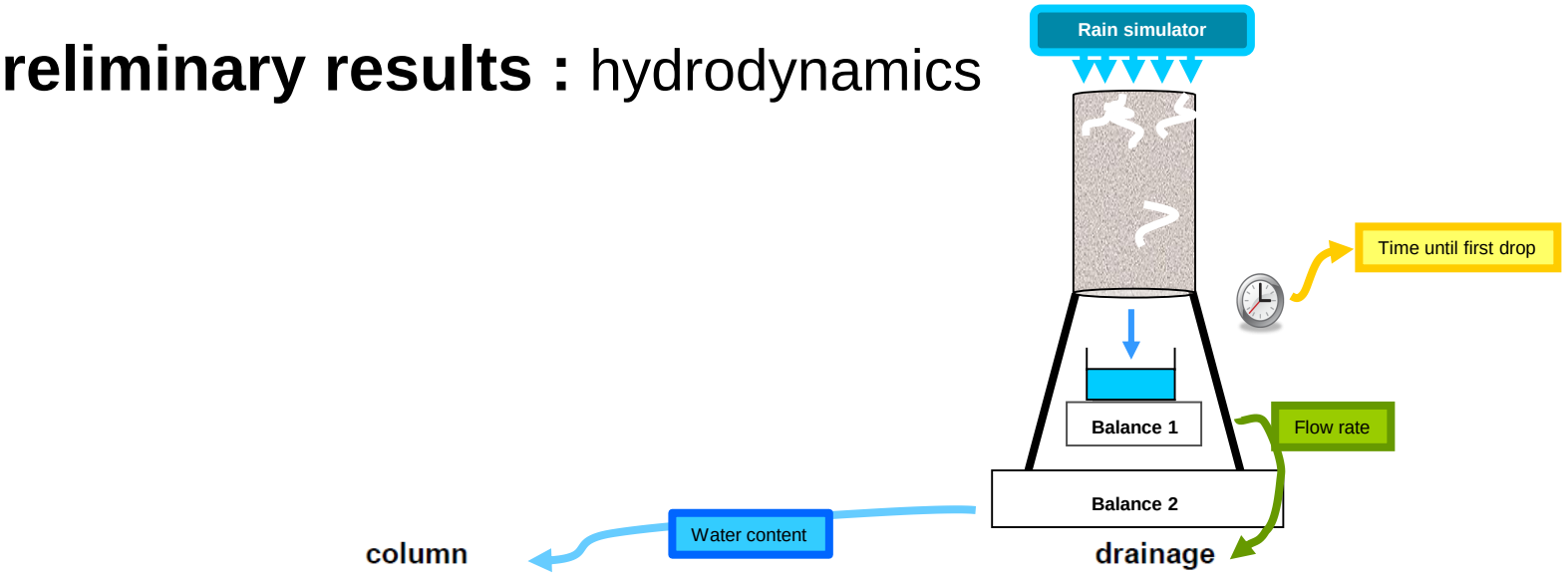

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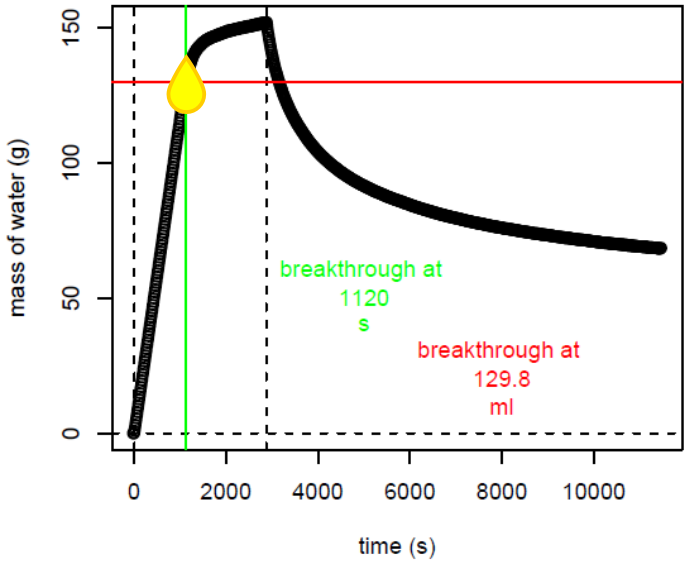

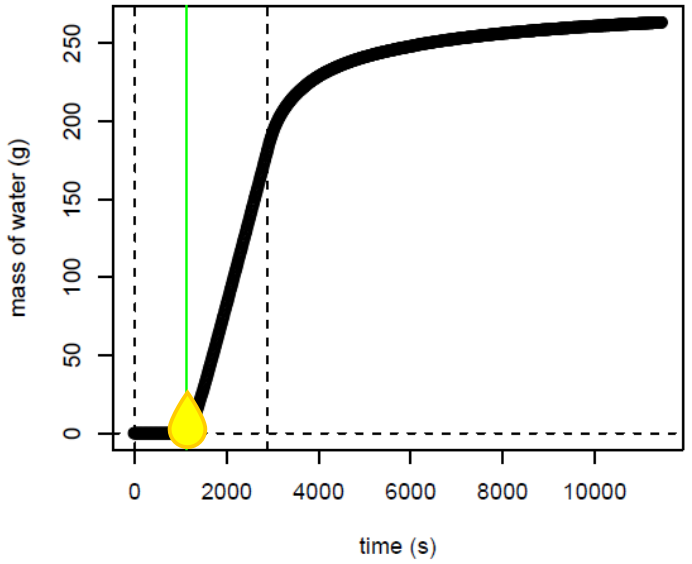

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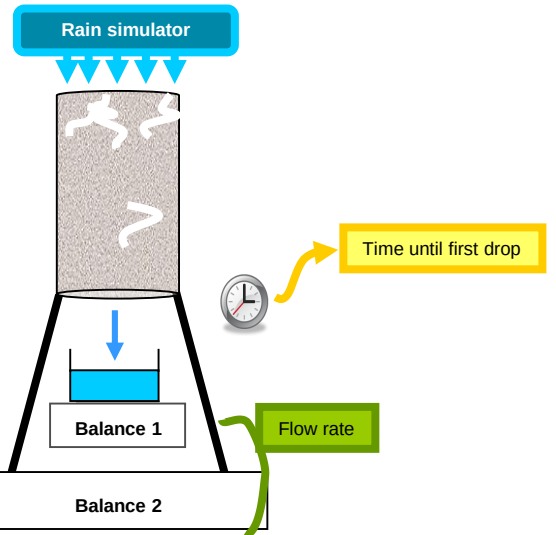
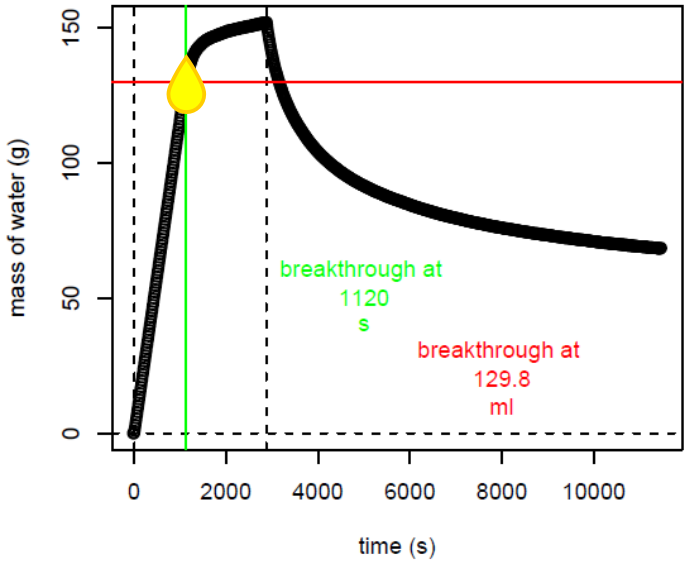
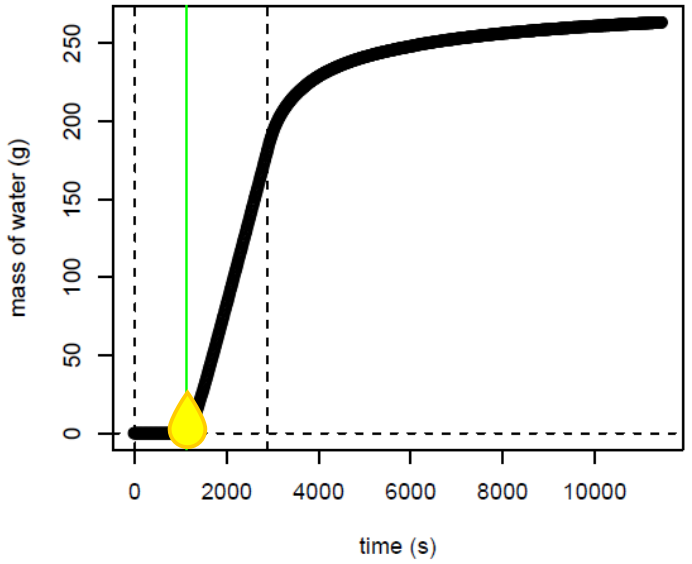


S8-3

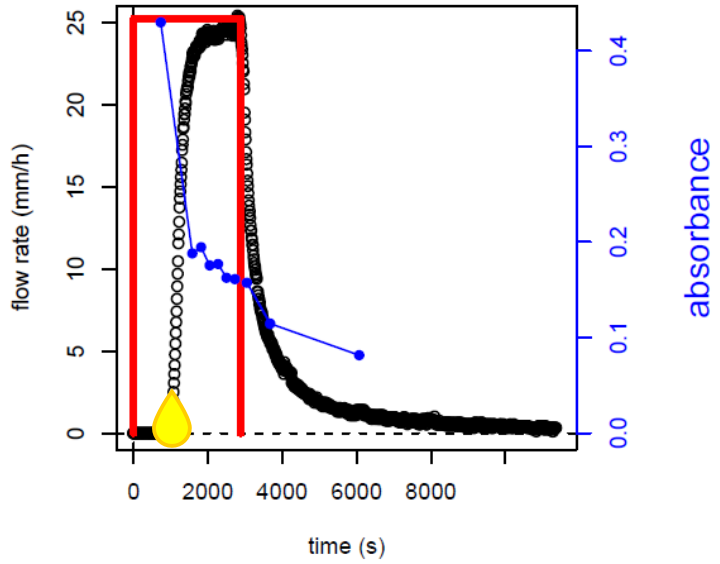
column



drainage

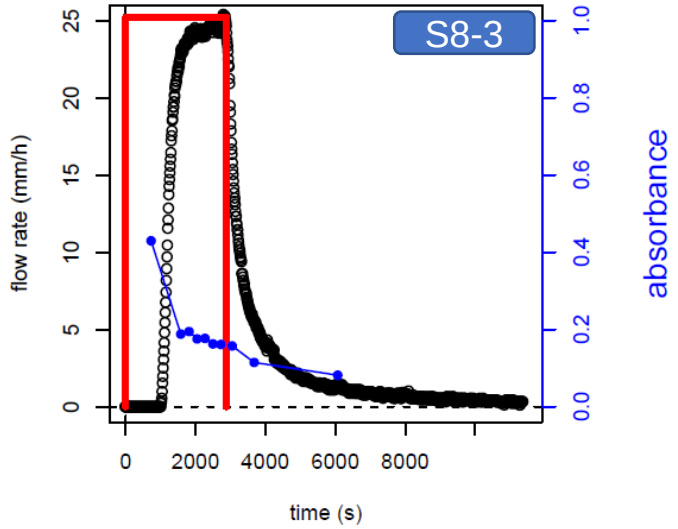


hydrograph+absorbance



Preliminary results : hydrodynamics and particle release

rain intensity 25mm/h, after rain interruption for 114h



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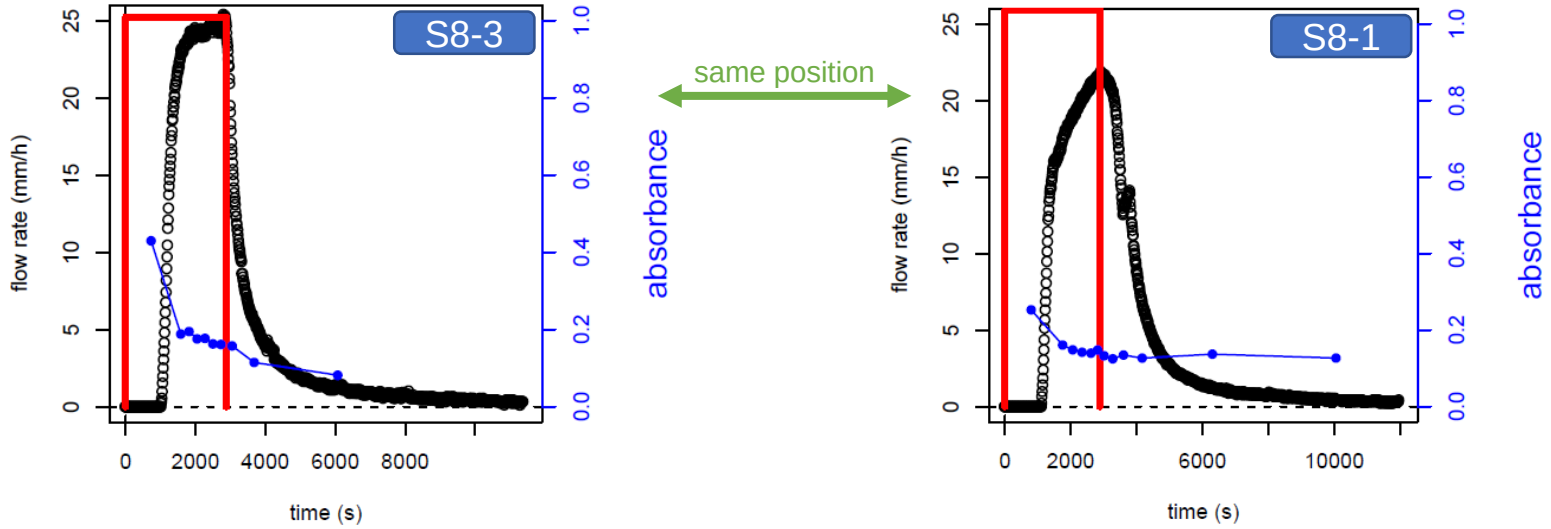

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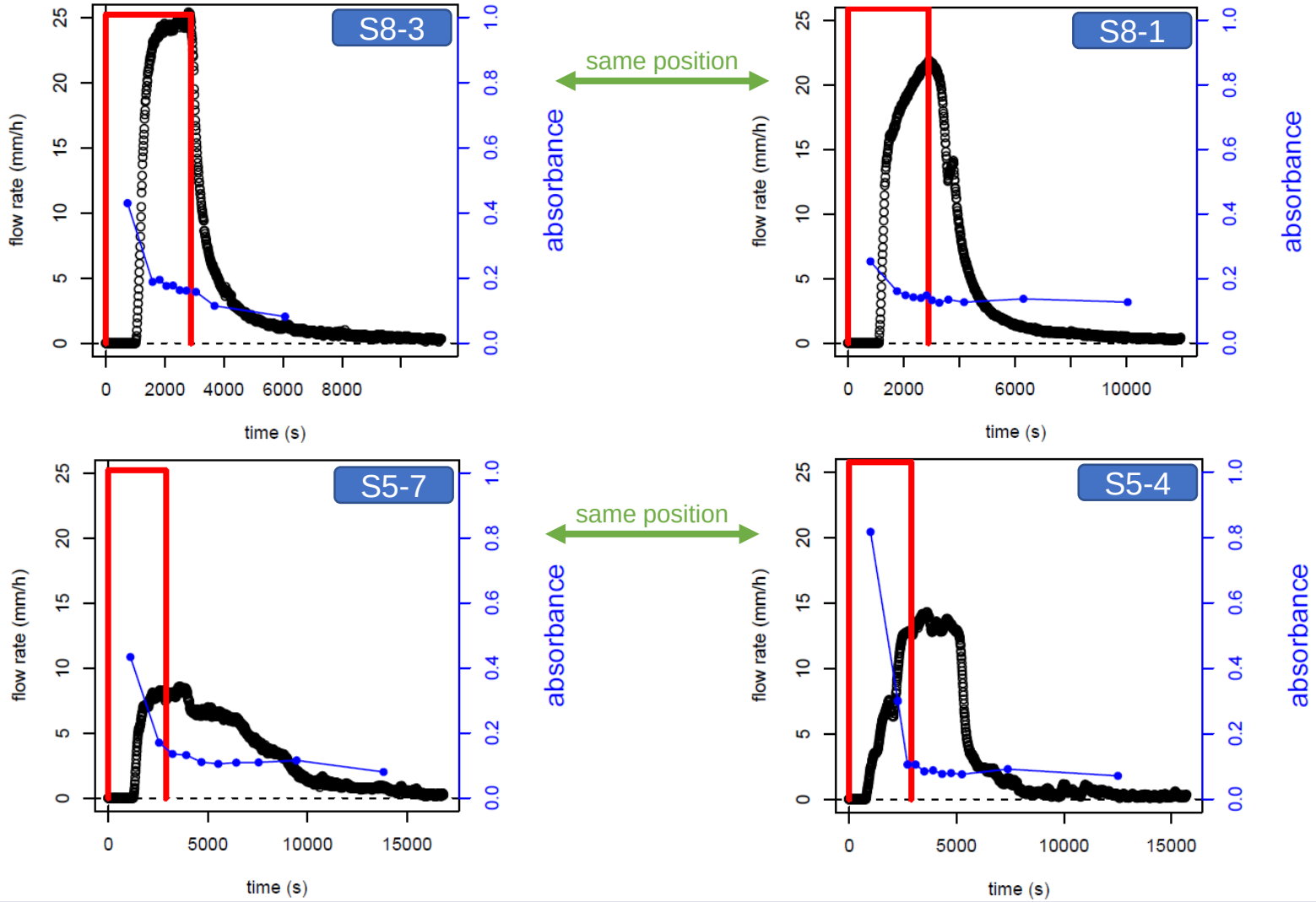

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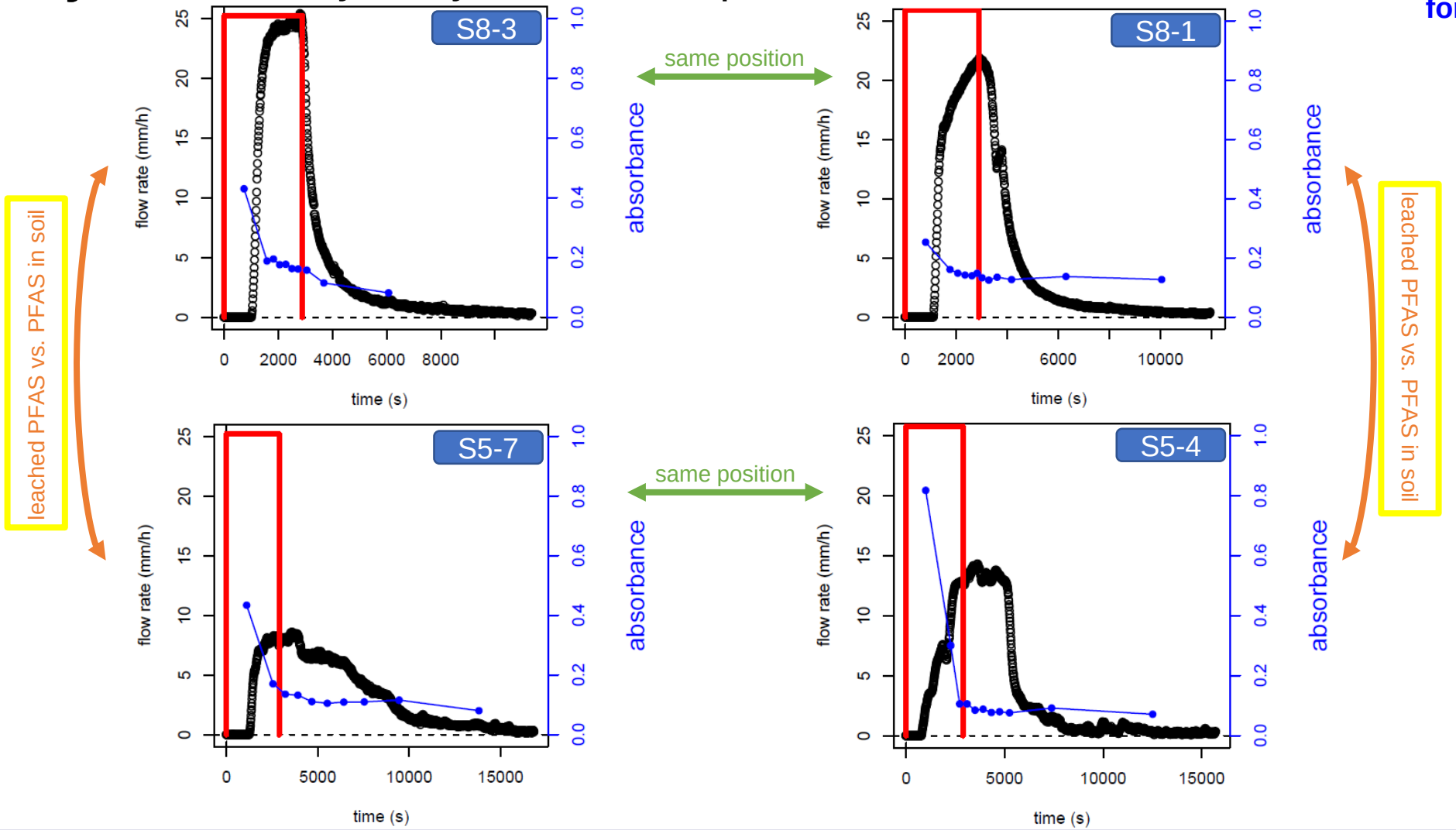
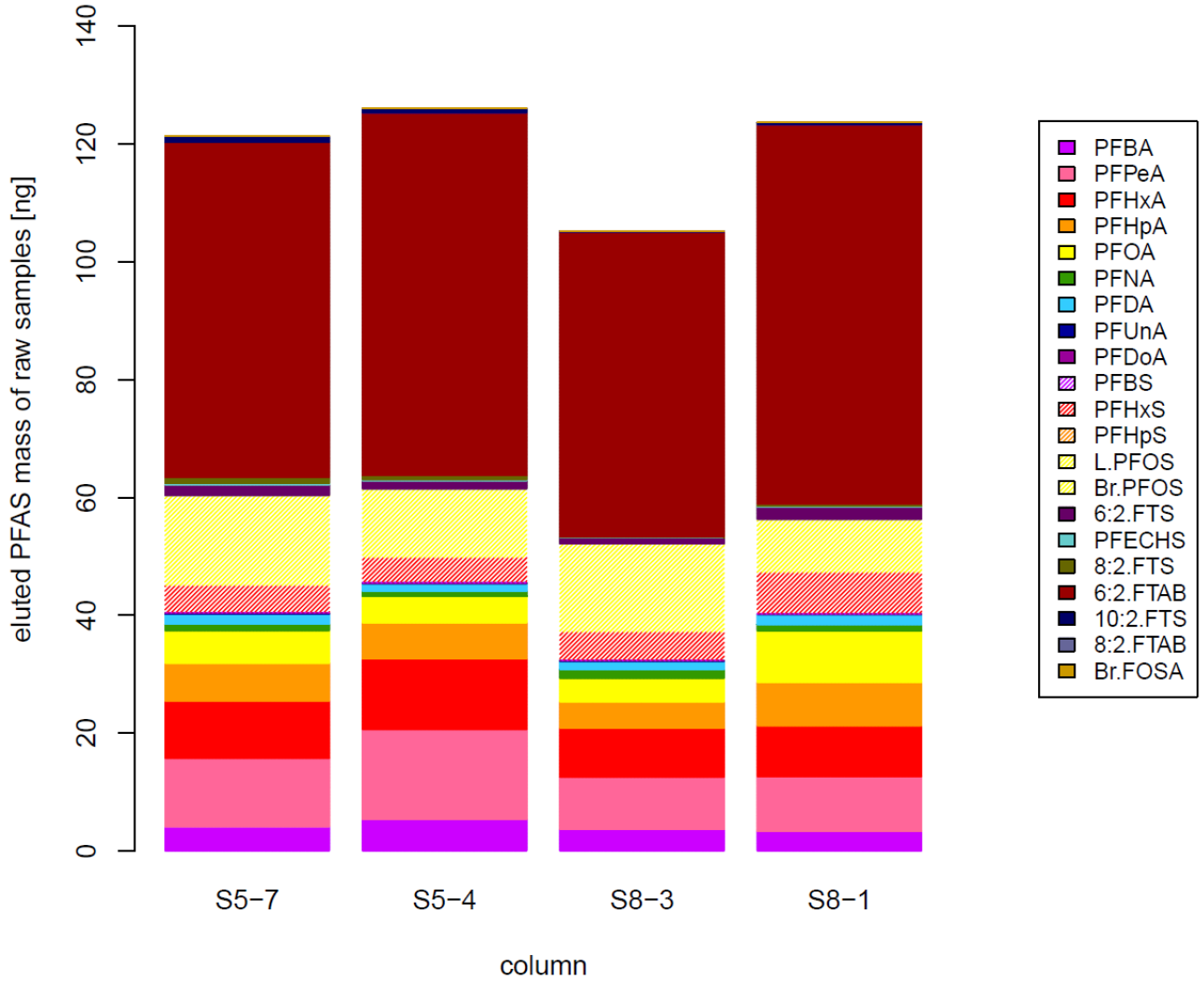


Preliminary results : repartition of PFAS molecules



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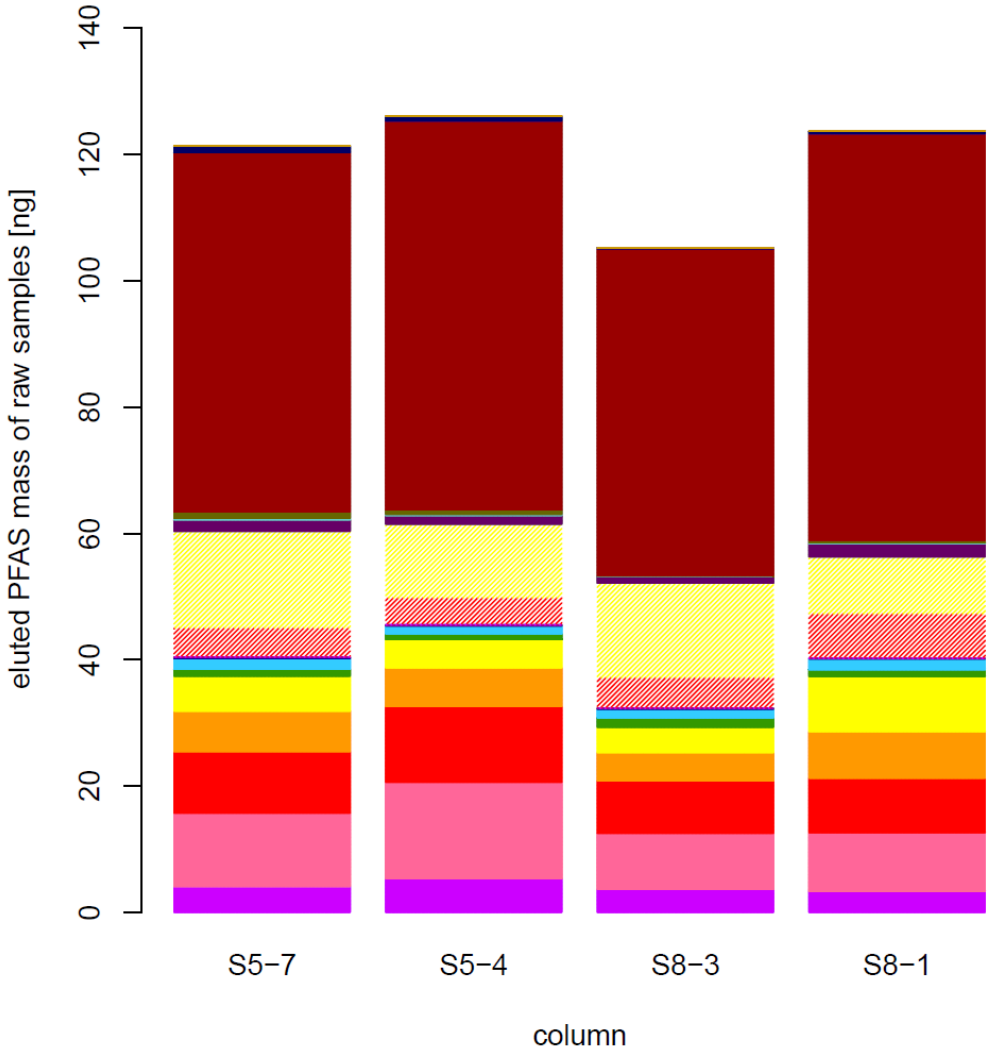

PFBA	C4	short chain	PFCA	$C_nF_{2n+1}\_COOH$
PFPeA	C5			
PFHxA	C6			
PFHpA	C7	long chain		
PFOA	C8			
PFNA	C9			
PFDA	C10			
PFUnA	C11			
PFDoA	C12			
PFBS	C4	short chain	PFSA	$C_nF_{2n+1}\_SO_3H$
PFHxS	C6			
PFHpS	C7	long chain		
L.PFOS	C8			
Br.PFOS	C8			
6:2.FTS				
PFECHS				
8:2.FTS				
6:2.FTAB				
10:2.FTS				
8:2.FTAB				
Br.FOSA				

PFAA, « terminal PFAS »

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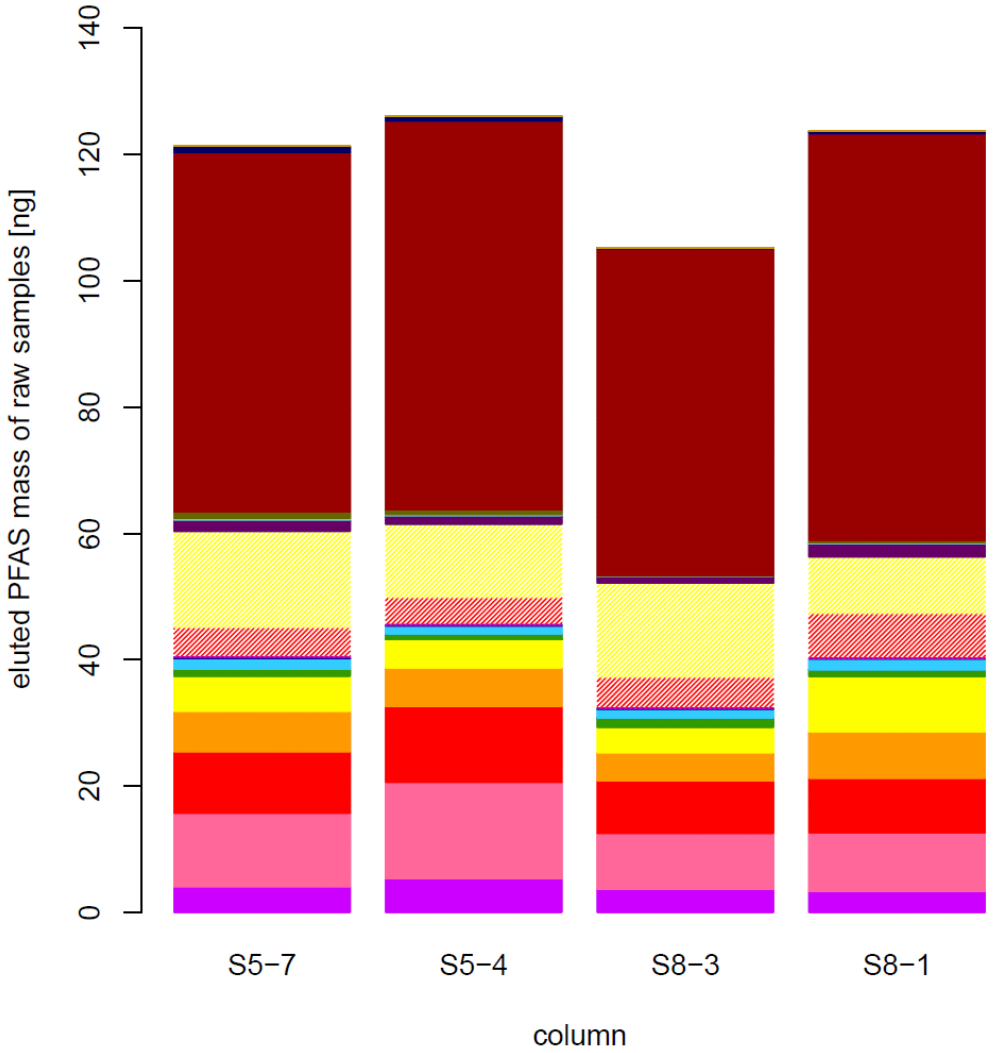

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6:2.FTS		others			Precursors, can transform into PFAA
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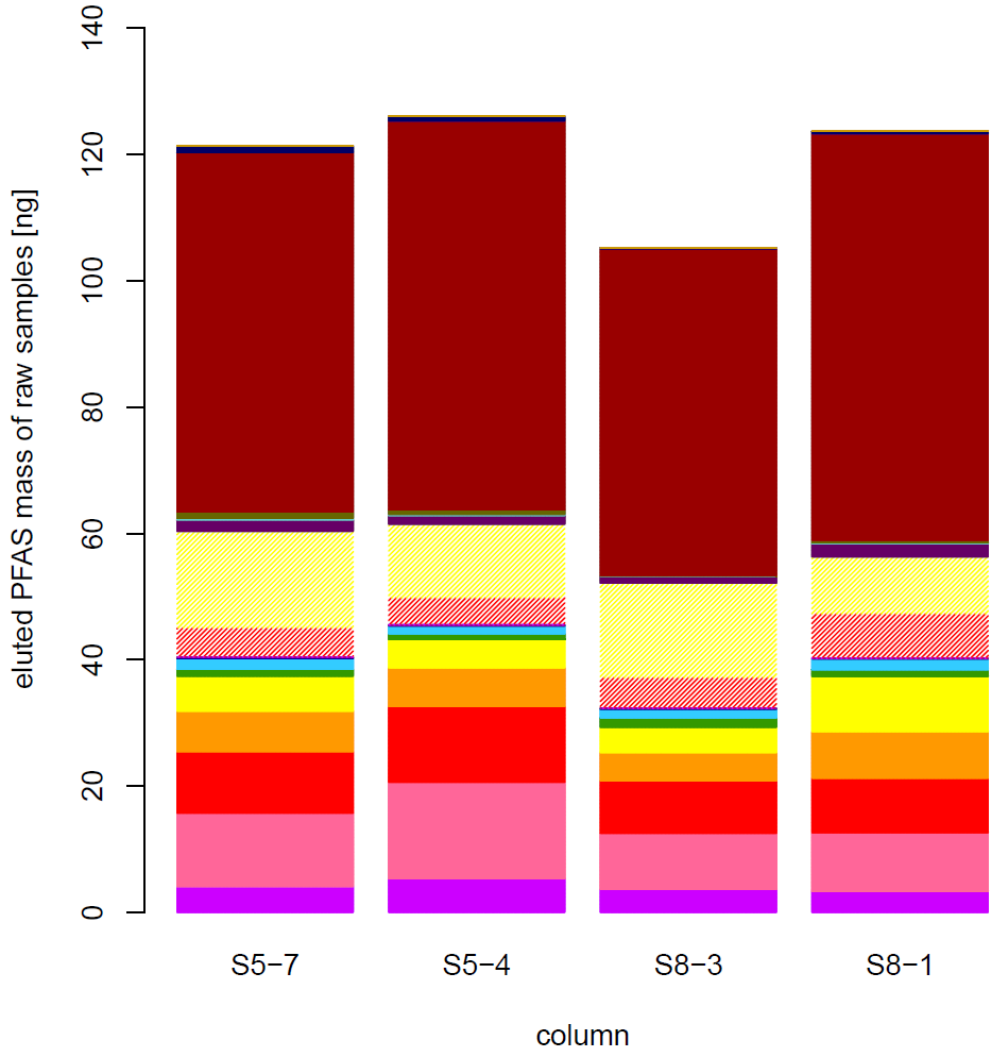
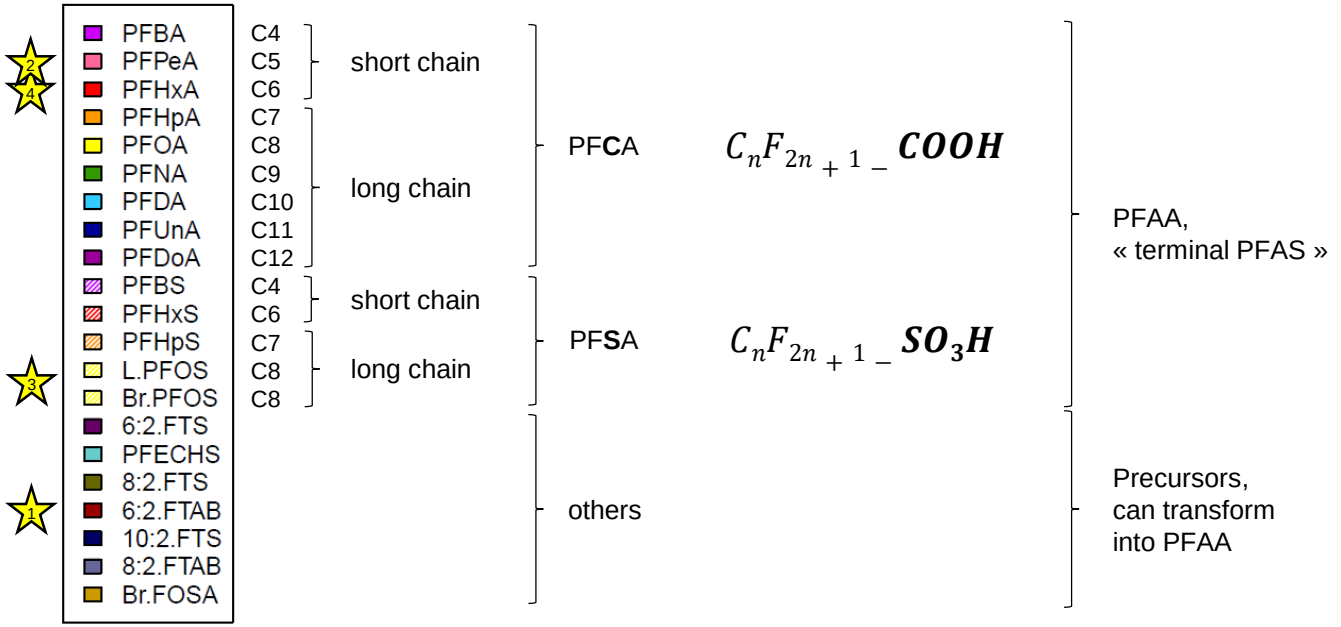
Preliminary results : repartition of PFAS molecules





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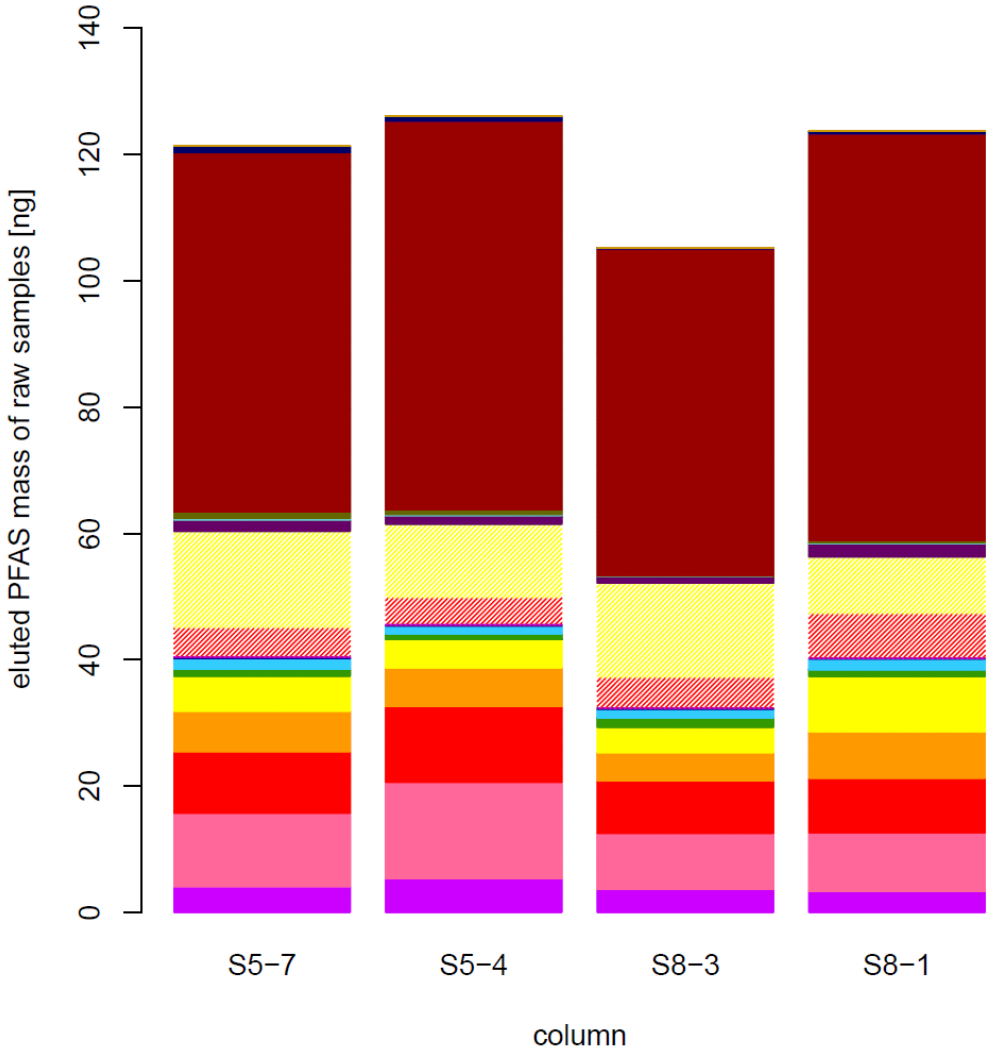

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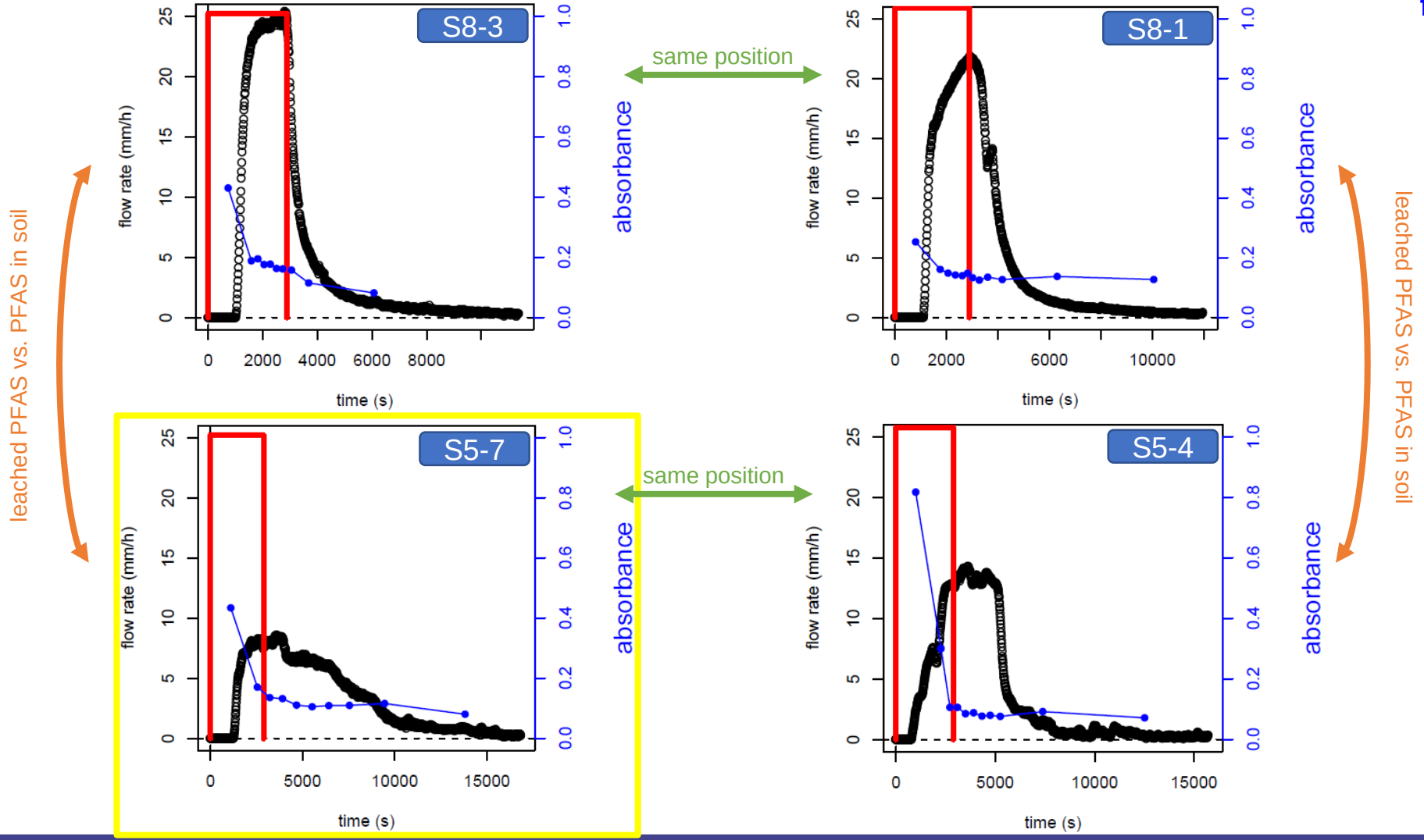
c(PFAS_soil_S5) * 0,5 ~ c(PFAS_soil_S8)
but
m(PFAS_leached_S5) ~ m(PFAS_leached_S8)

→ **Due to hydrodynamics during rainfalls ?**

Preliminary results : hydrodynamics and particle release

rain intensity 25mm/h, after rain interruption for 114h



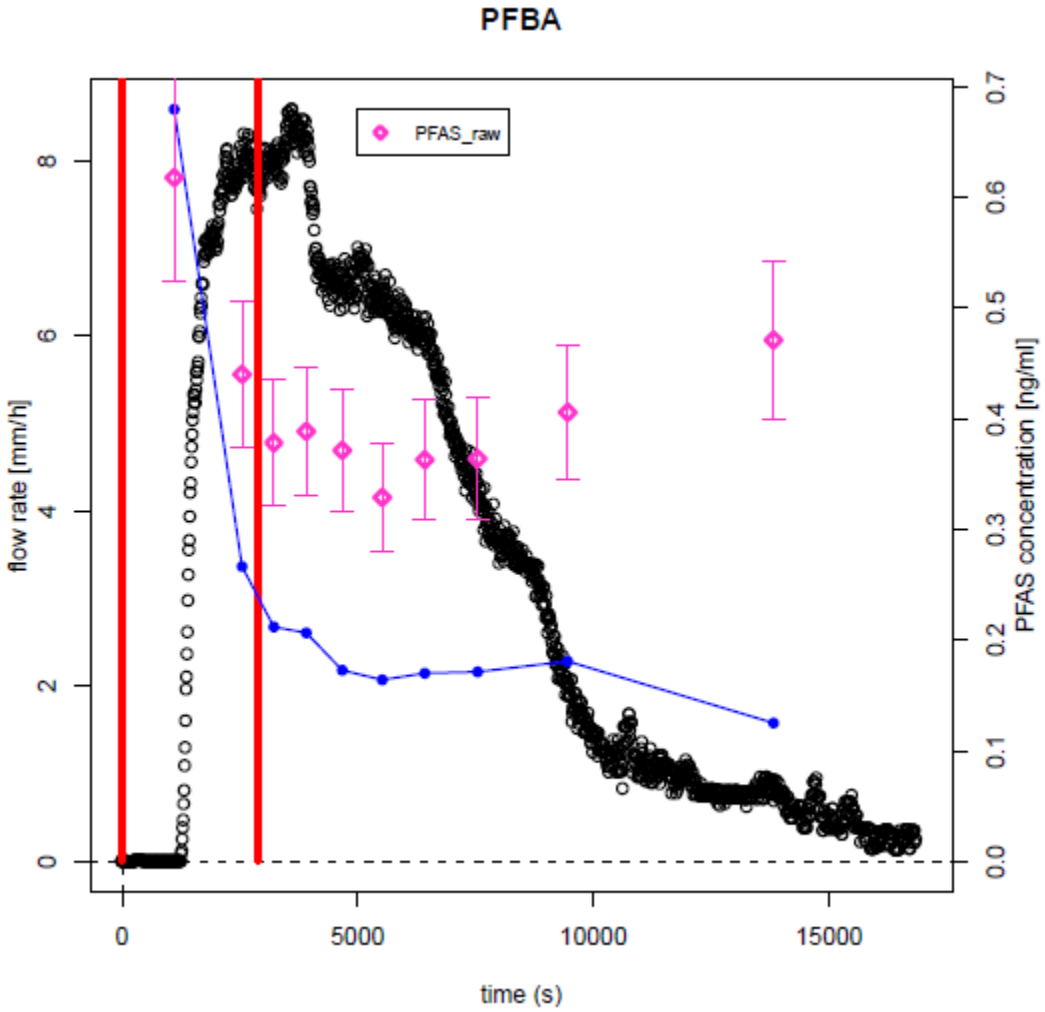
S5-7

Preliminary results : dynamics of PFCA leaching

C4
C5 — short chain
C6
C7
C8
C9 — long chain
C10
C11
C12
PFCA

maximal concentration
in the first flow

decreasing concentration
during « steady state »
infiltration



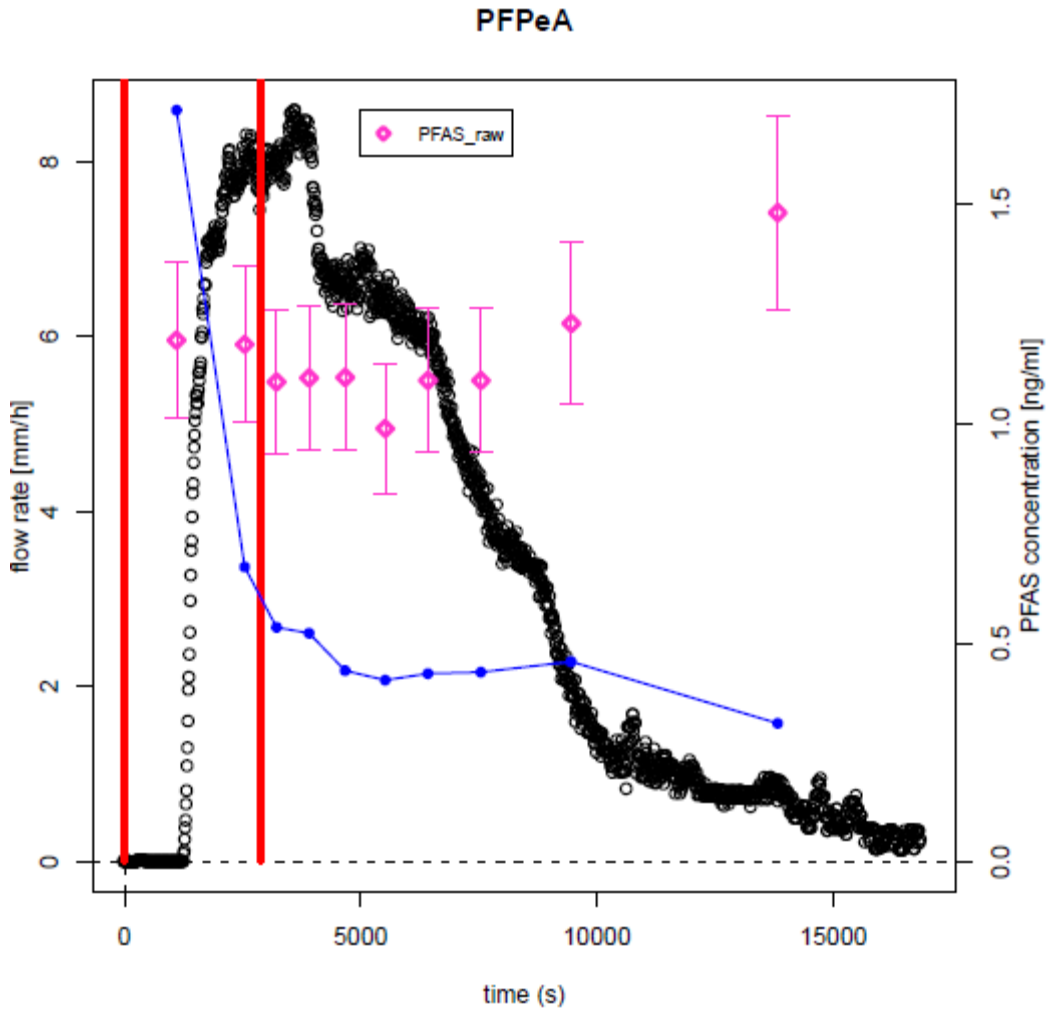
increasing concentration
during last flow

S5-7

Preliminary results : dynamics of PFCA leaching

C4
C5 — short chain
C6
C7
C8
C9 — long chain
C10
C11
C12
PFCA

maximal concentration in the first flow



decreasing concentration during « steady state » infiltration

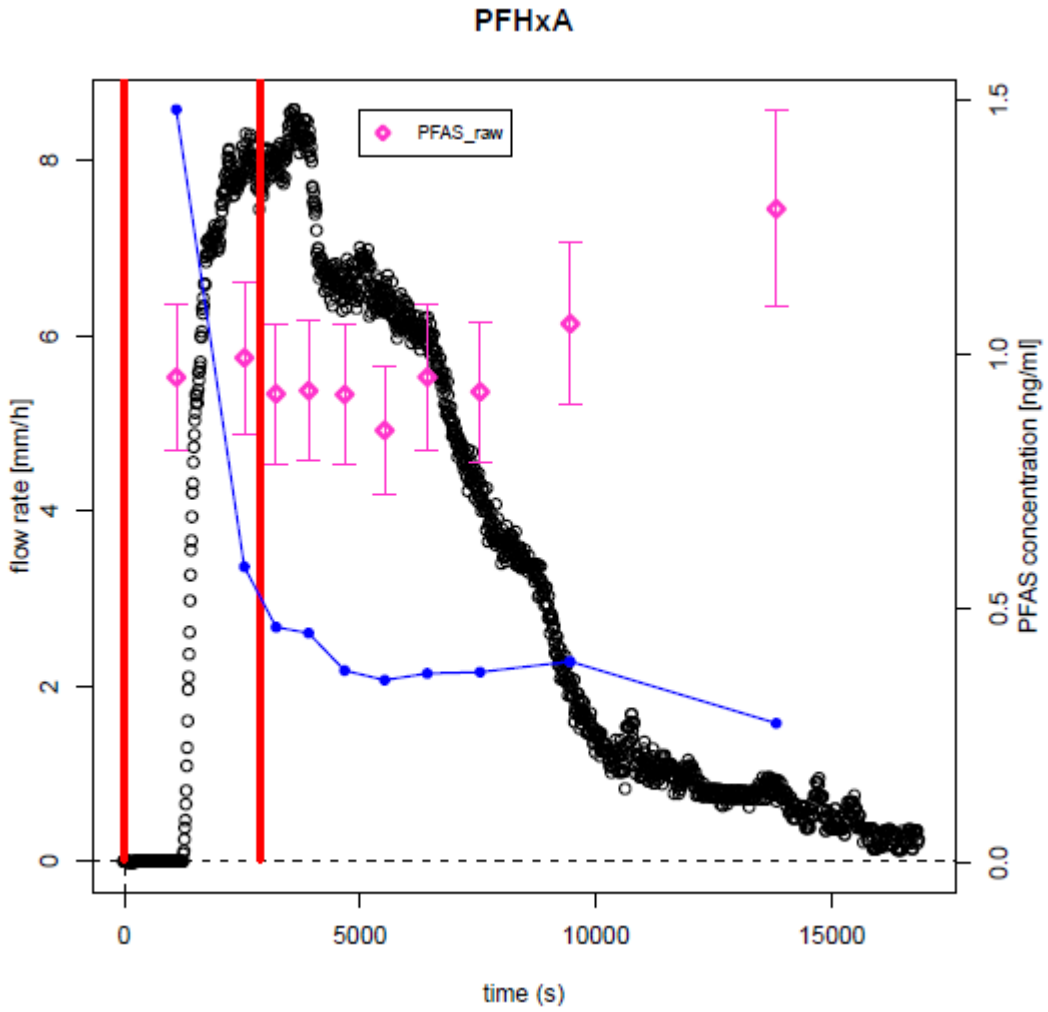
increasing concentration during last flow

Preliminary results : dynamics of PFCA leaching

C4
C5
C6 — short chain
C7
C8
C9
C10
C11
C12 — long chain

PFCA

maximal concentration in the first flow



decreasing concentration during « steady state » infiltration

increasing concentration during last flow

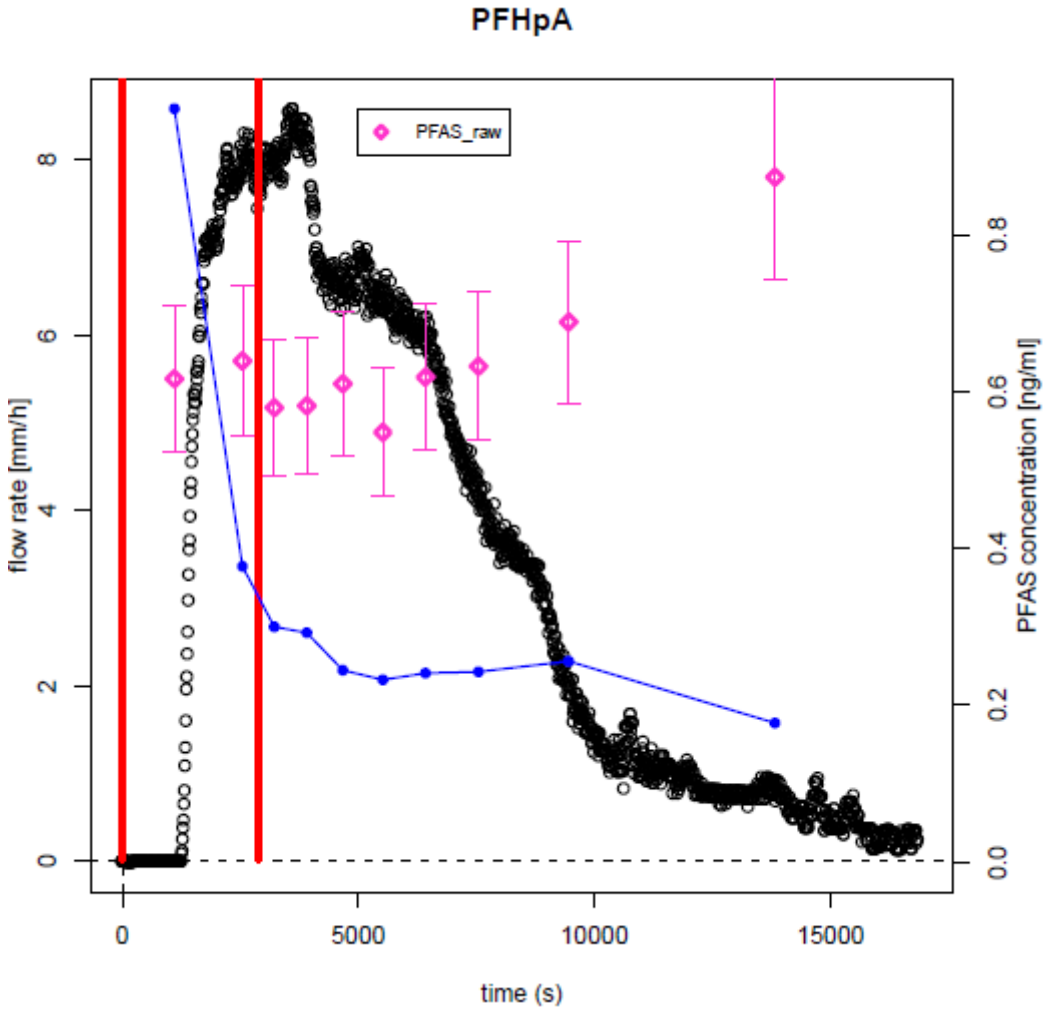
Preliminary results : dynamics of PFCA leaching

S5-7

C4
C5
C6 — short chain
C7
C8
C9
C10 — long chain
C11
C12

PFCA

maximal concentration in the first flow



decreasing concentration during « steady state » infiltration

increasing concentration during last flow

Preliminary results : dynamics of PFCA leaching

C4
C5
C6 — short chain
C7
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C10
C11
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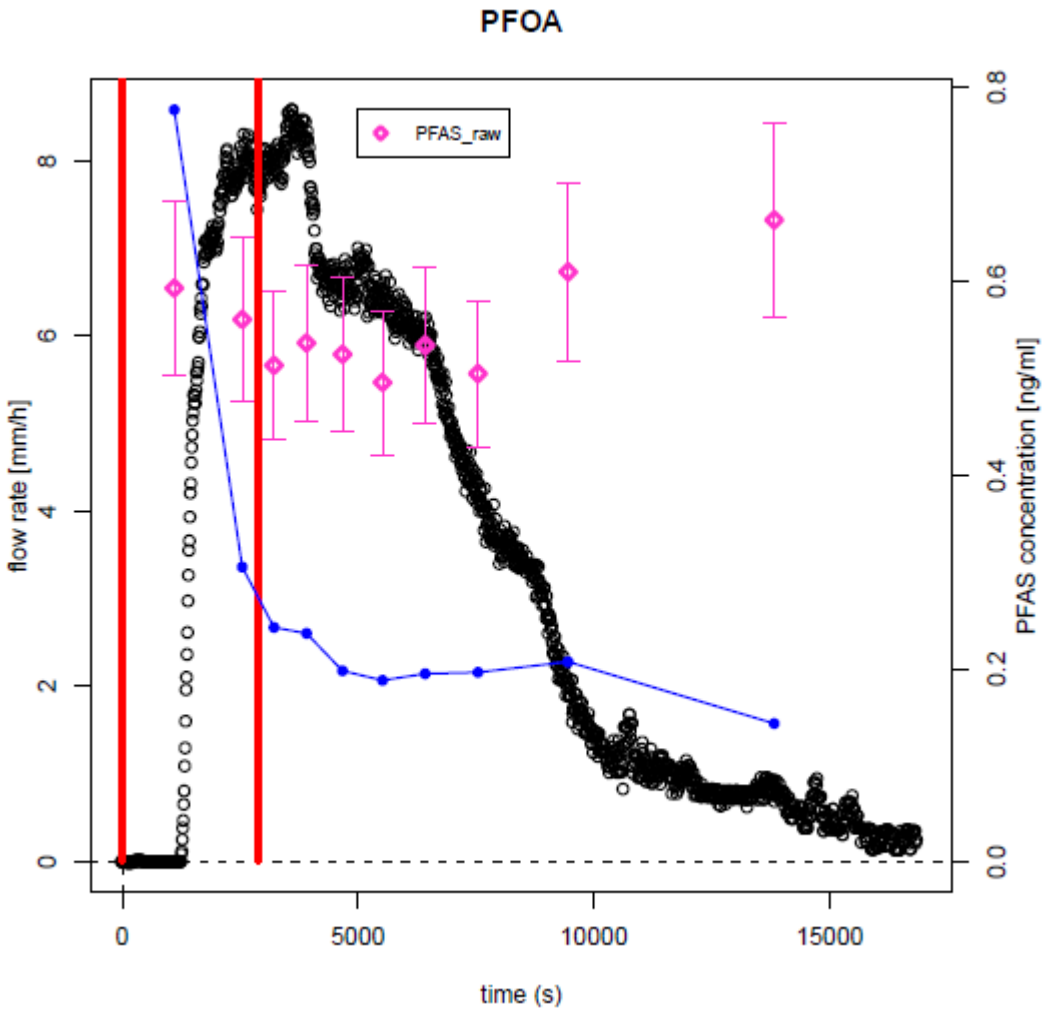
PFCA

maximal concentration in the first flow



decreasing concentration during « steady state » infiltration

increasing concentration during last flow

S5-7

Preliminary results : dynamics of PFCA leaching

C4
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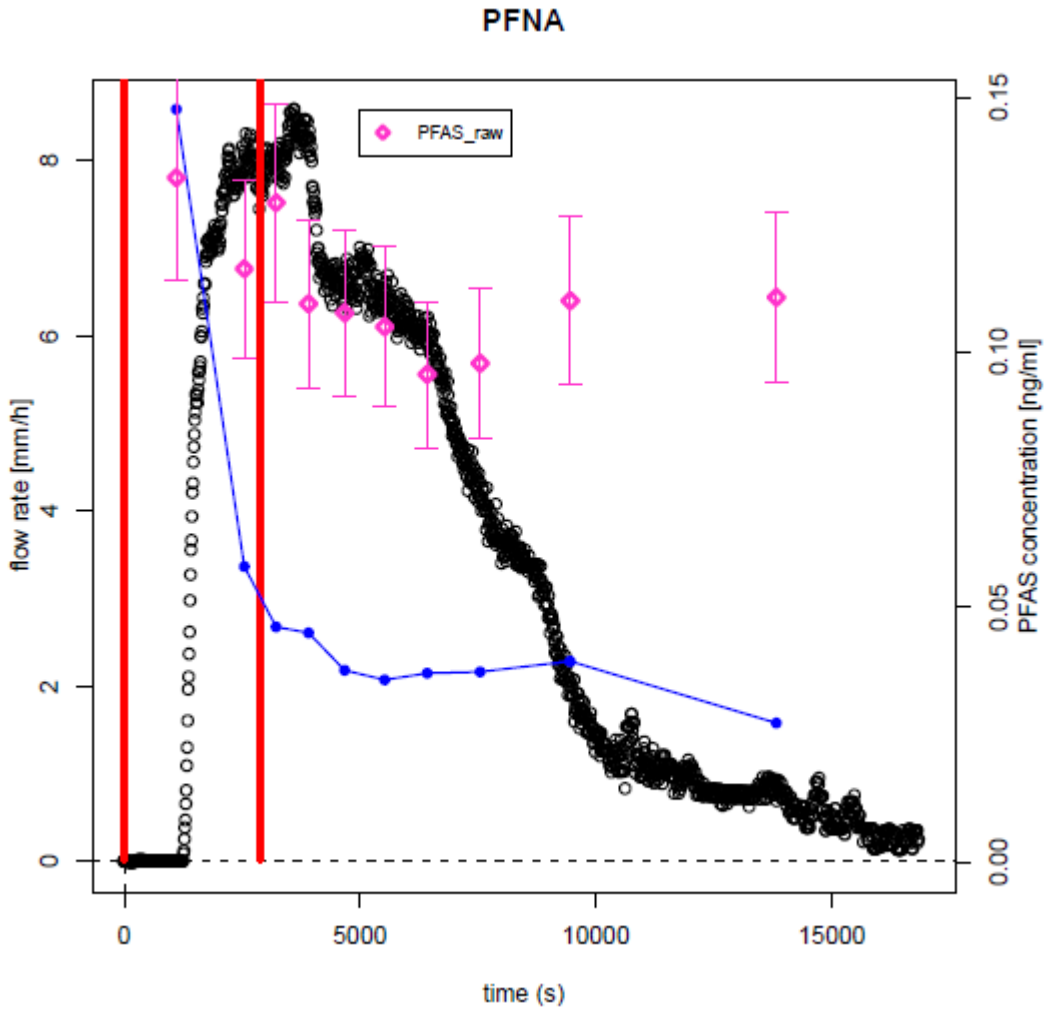
C9
C10
C11
C12 — long chain
PFCA

maximal concentration
in the first flow

decreasing concentration
during « steady state »
infiltration



increasing concentration
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maximal concentration
in the first flow

decreasing concentration
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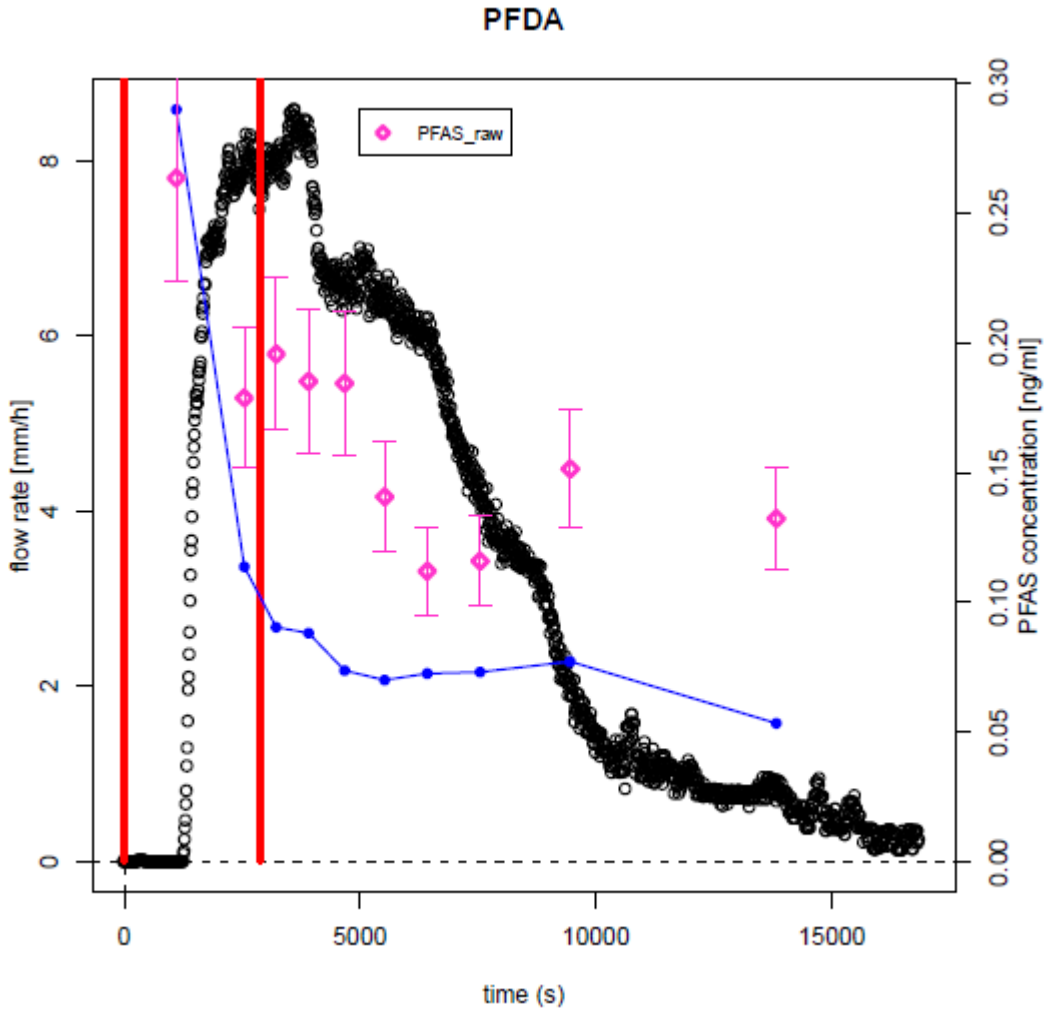
infiltration



decreasing concentration
during last flow

S5-7

Preliminary results : dynamics of PFCA leaching

C4
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C10
C11
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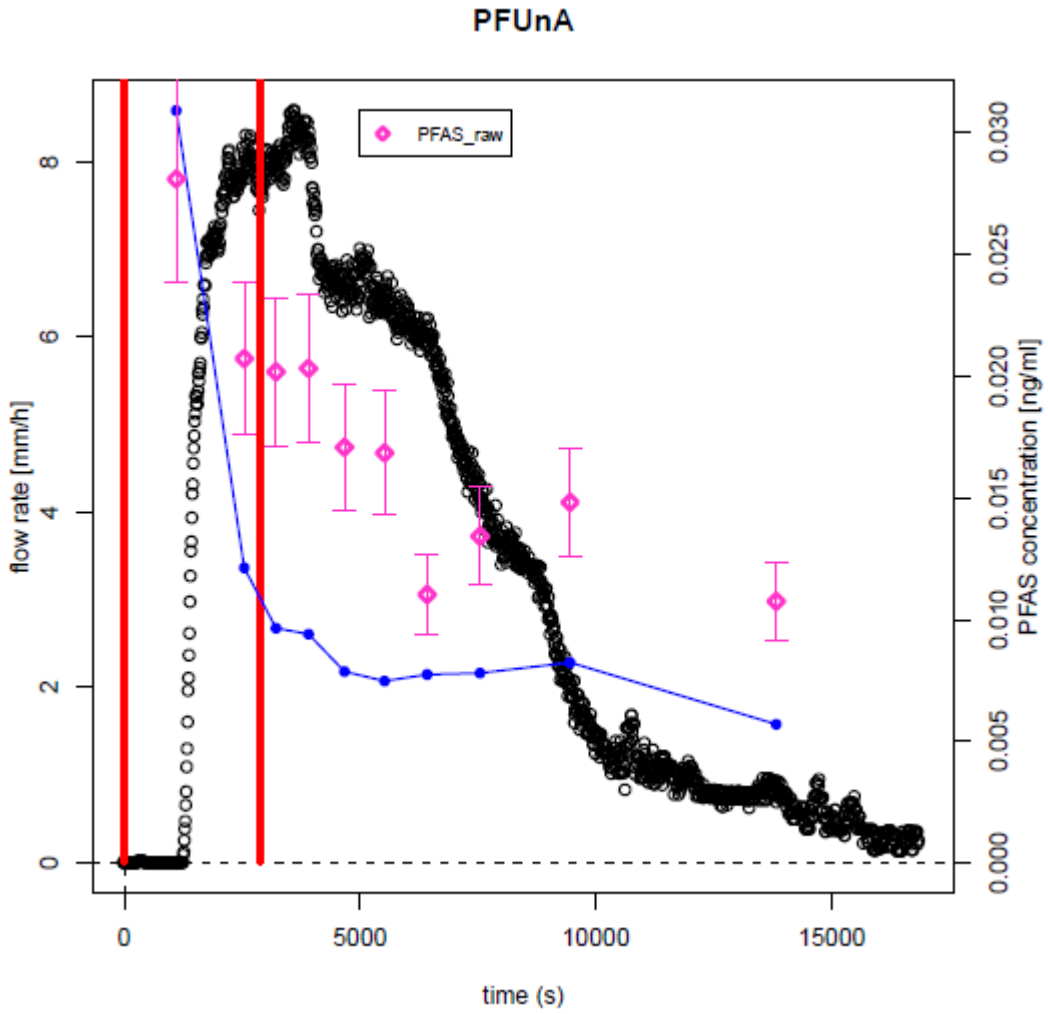
PFCA

maximal concentration
in the first flow

decreasing concentration
during « steady state »
infiltration



decreasing concentration
during last flow

Preliminary results : dynamics of PFCA leaching

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decreasing concentration
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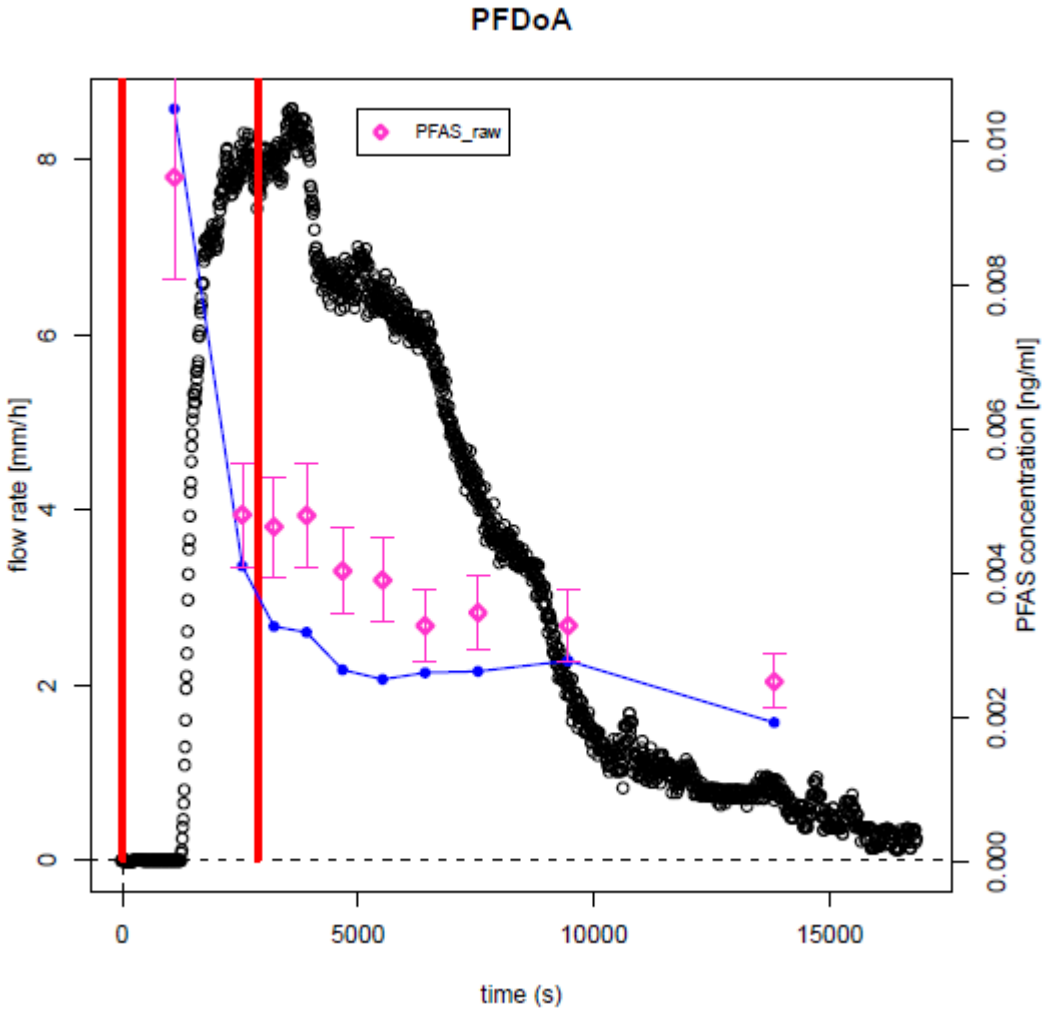
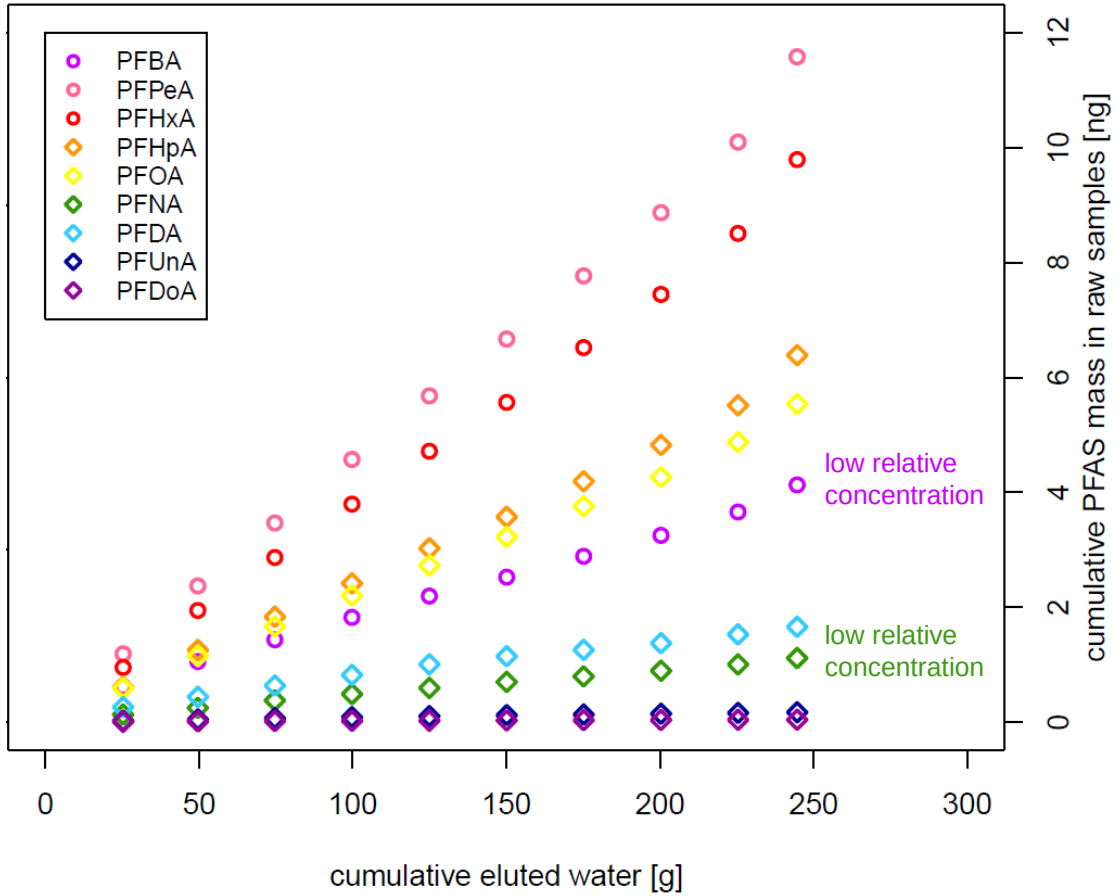
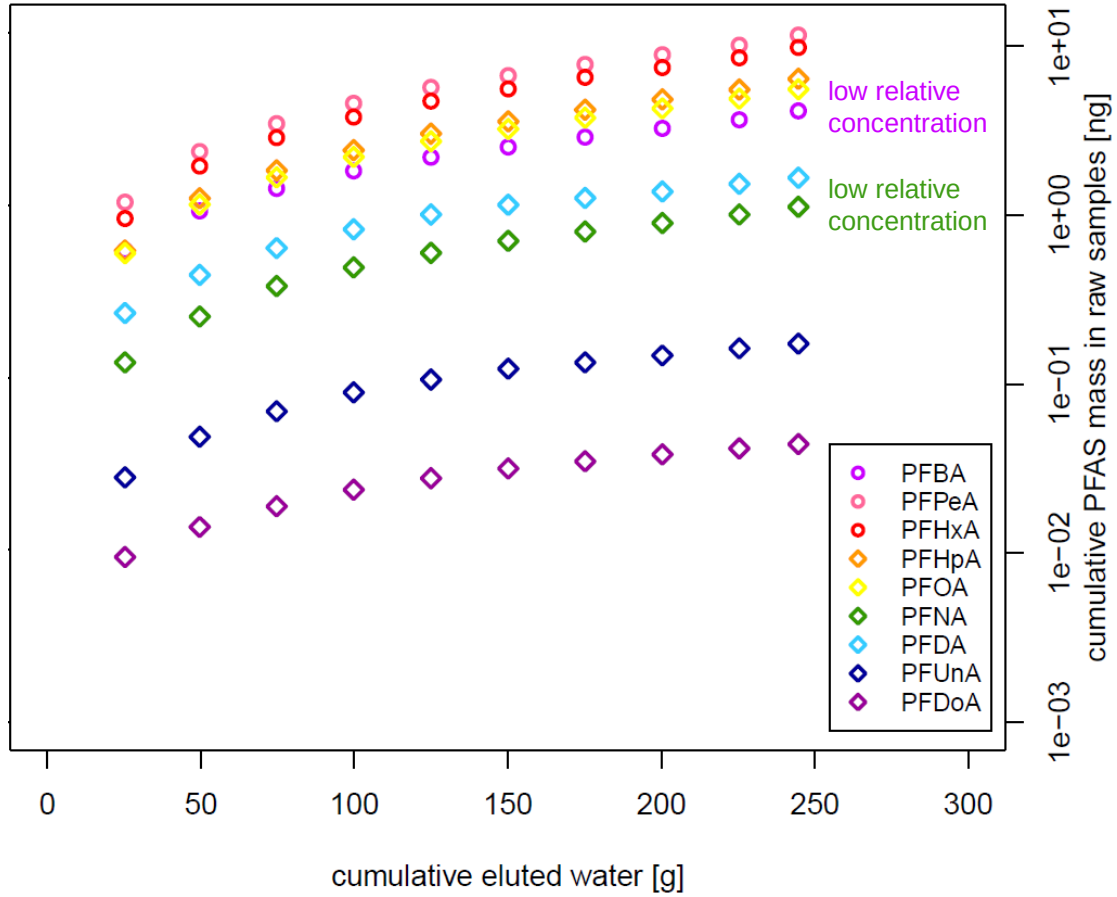
infiltration



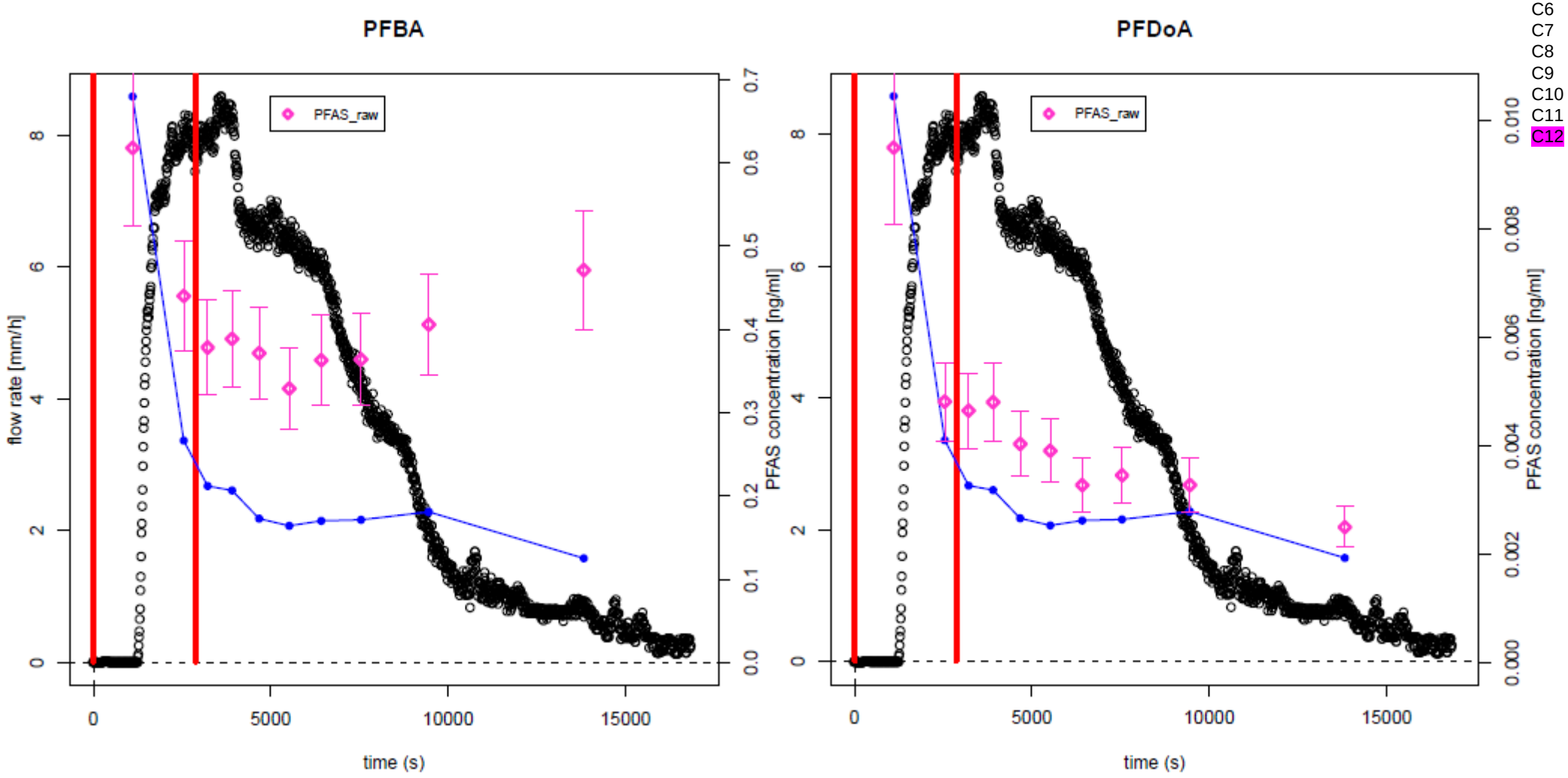
decreasing concentration
during last flow

Preliminary results : amount of leached PFCA



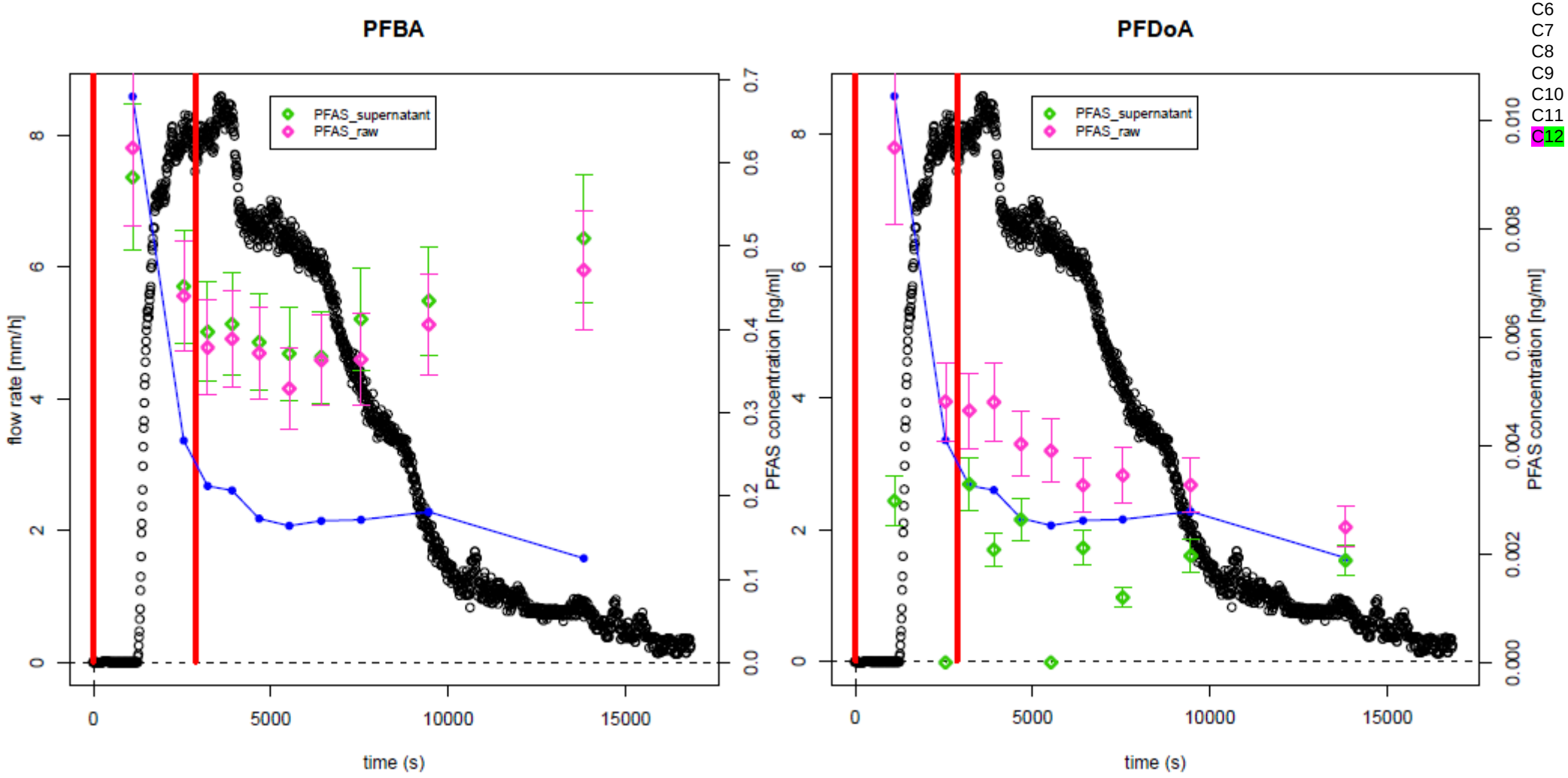


Preliminary results : dynamics of PFCA leaching



S5-7

Preliminary results : dynamics of PFCA leaching – raw vs. supernatant



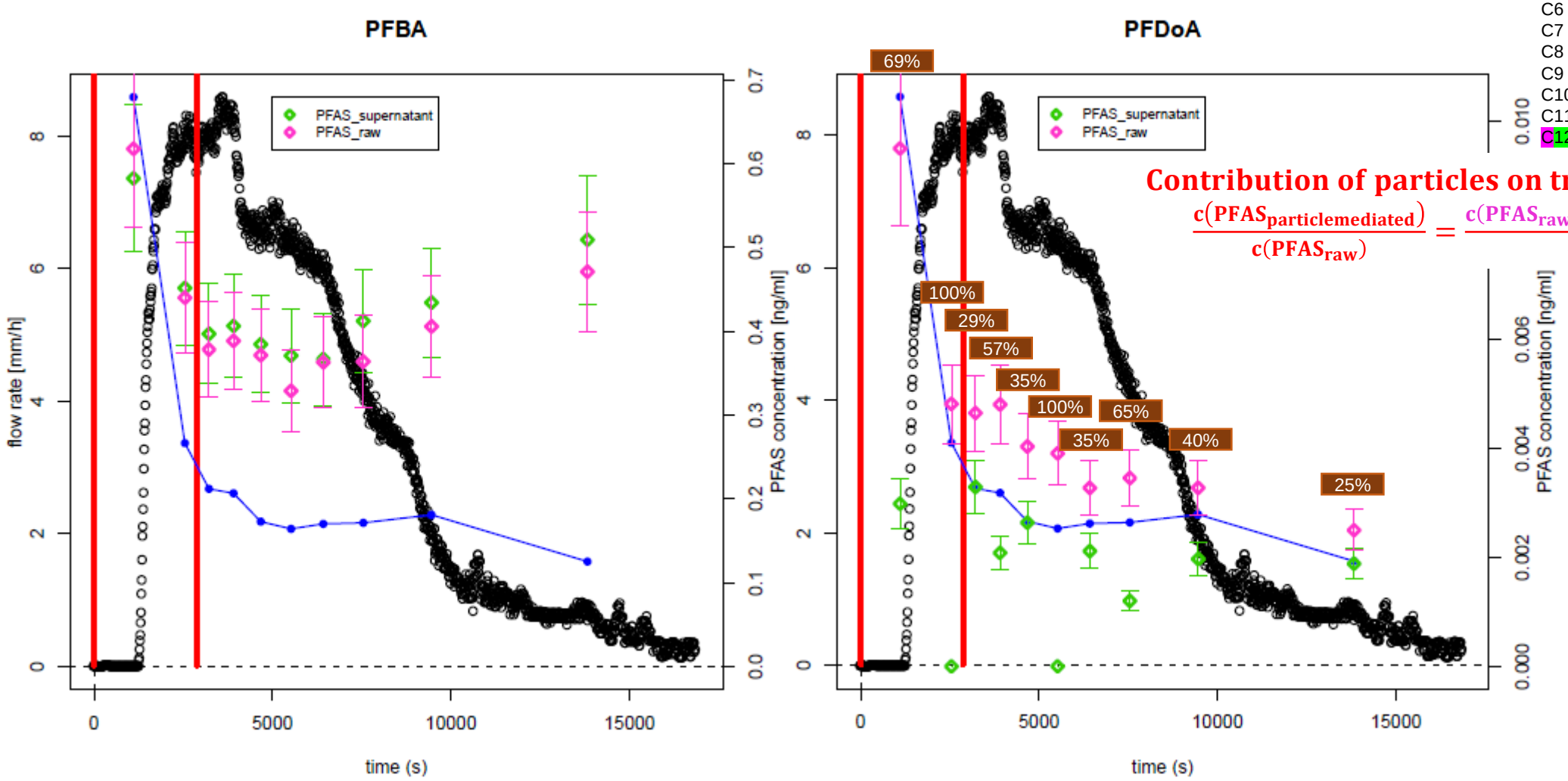
C4
C5
C6 — short chain
C7
C8
C9
C10
C11
C12 — long chain

PFCA

For **PFBA**:
no particle-mediated transport

For **PFDoA**:
particle-mediated transport

Preliminary results : dynamics of PFCA leaching – raw vs. supernatant



C4
C5
C6 — short chain
C7
C8
C9
C10
C11
C12 — long chain

PFCA

Contribution of particles on transport of PFAS =

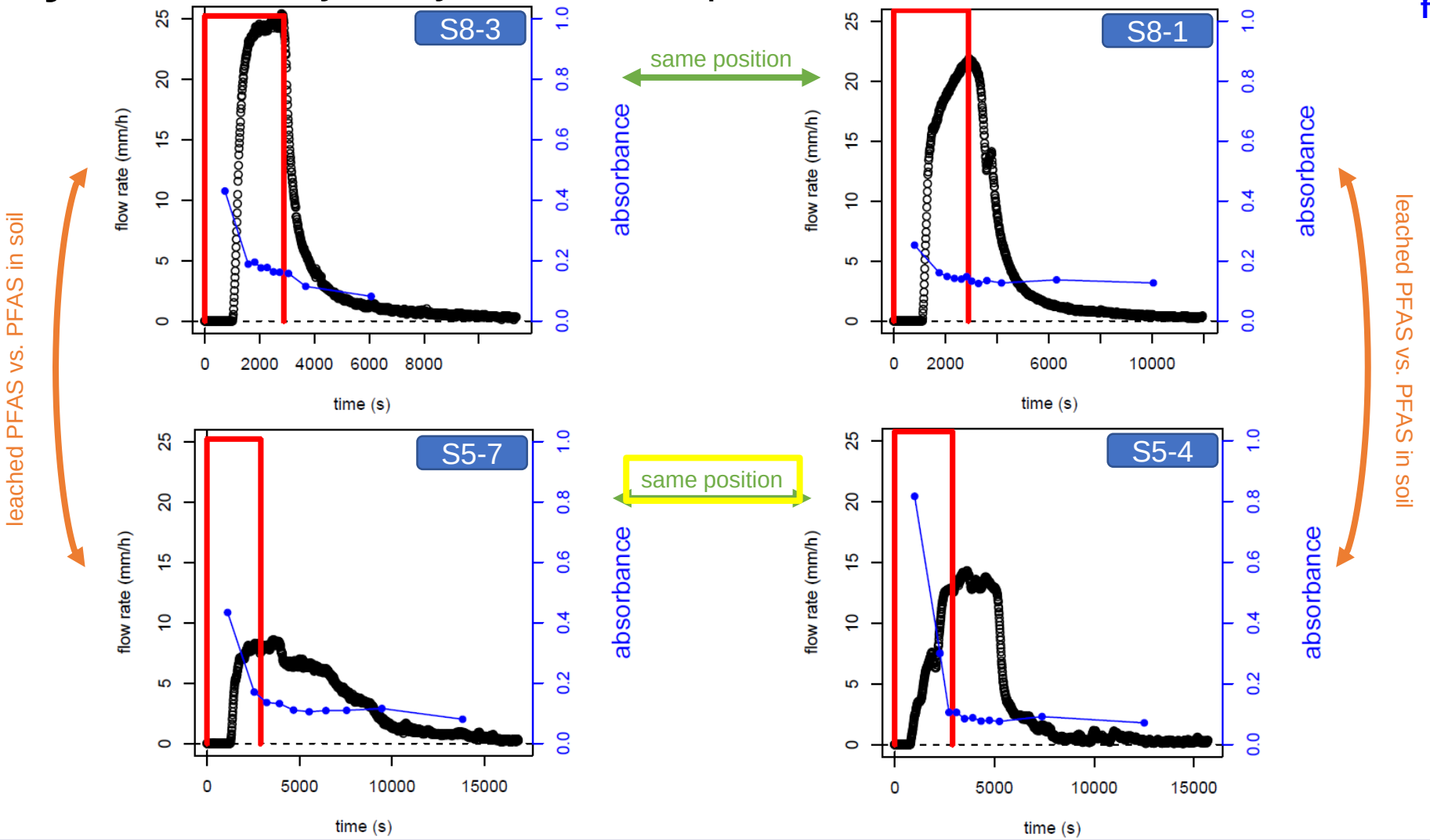
$$\frac{c(PFAS_{particlemediated})}{c(PFAS_{raw})} = \frac{c(PFAS_{raw}) - c(PFAS_{supernatant})}{c(PFAS_{raw})}$$

For **PFBA**:
no particle-mediated transport

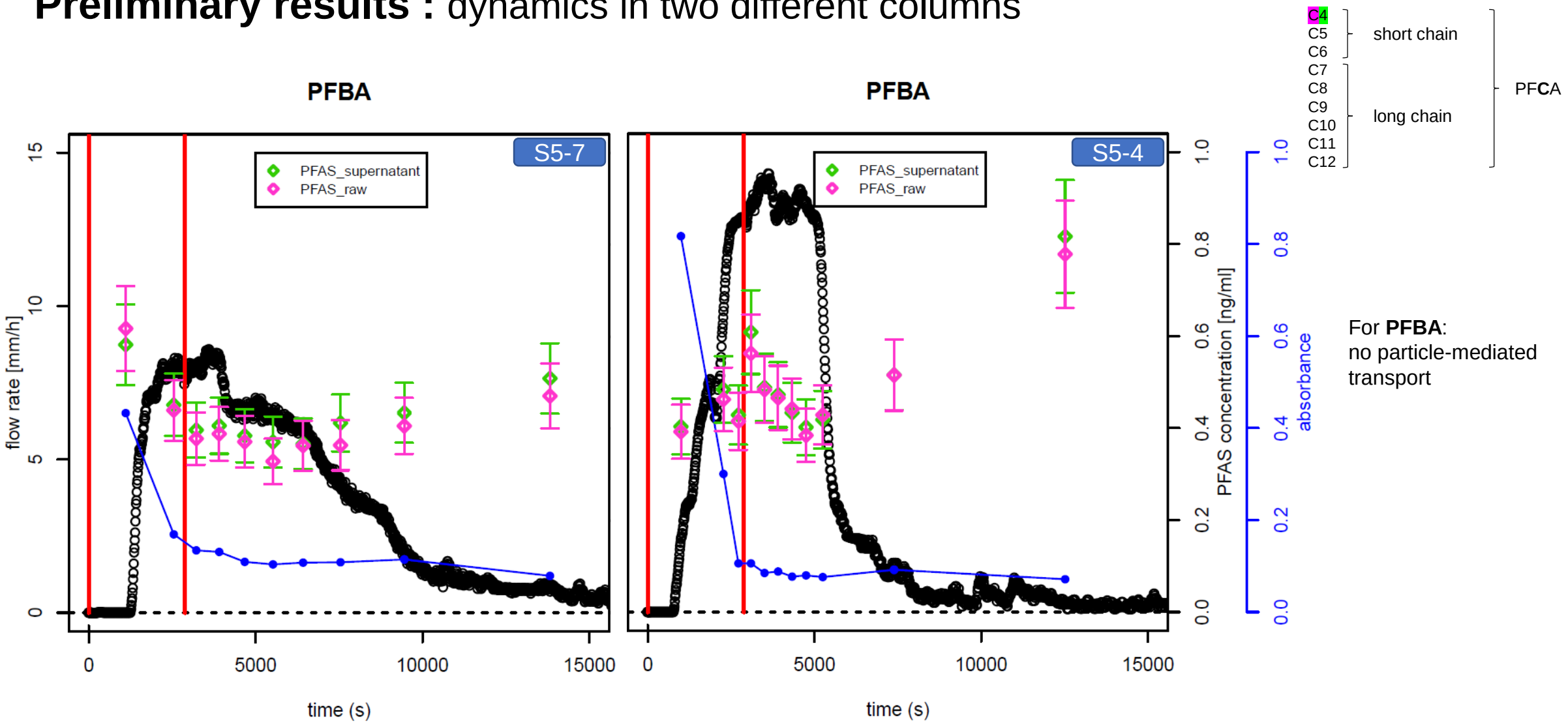
For **PFDoA**:
particle-mediated transport

Preliminary results : hydrodynamics and particle release

rain intensity 25mm/h, after rain interruption for 114h



Preliminary results : dynamics in two different columns



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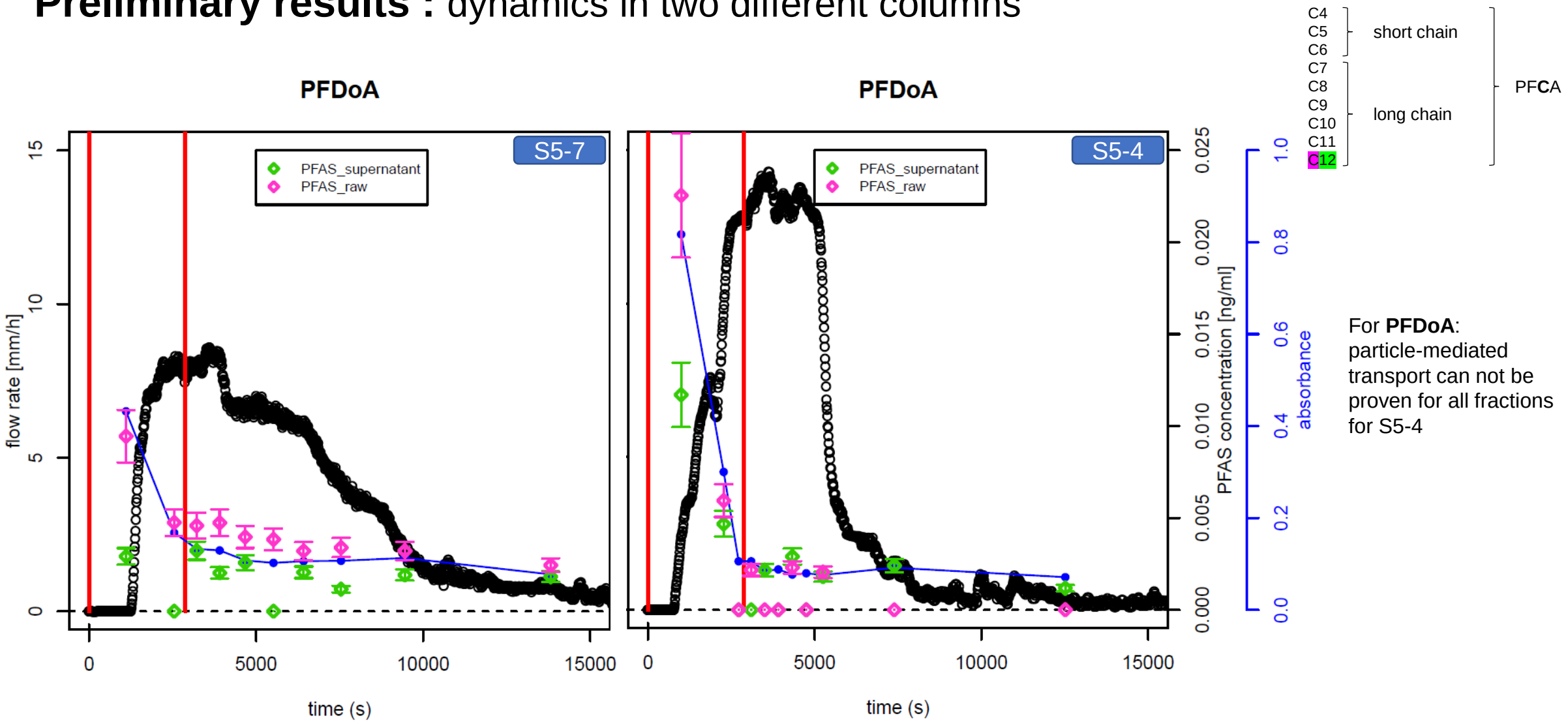
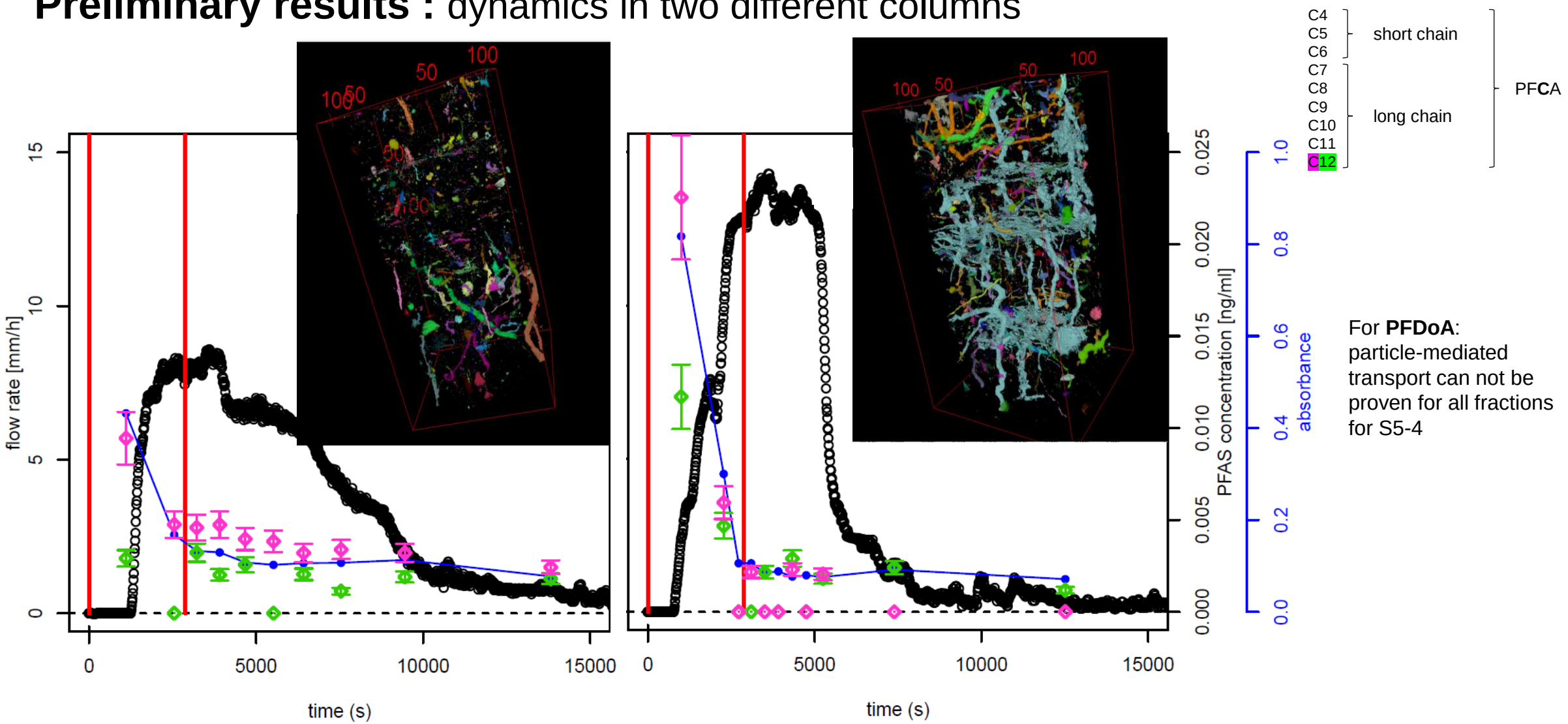
no particle-mediated transport

Preliminary results : dynamics in two different columns



For **PFDoA**: particle-mediated transport can not be proven for all fractions for S5-4

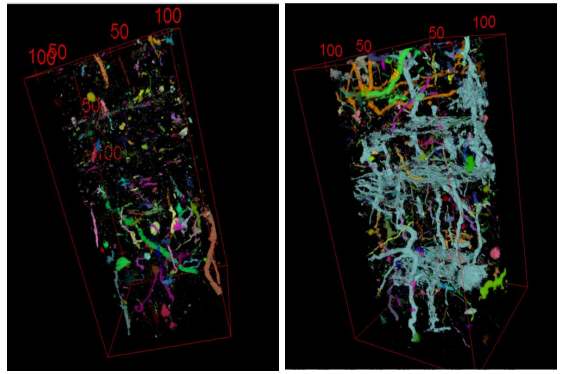
Preliminary results : dynamics in two different columns



For **PFDoA**: particle-mediated transport can not be proven for all fractions for S5-4

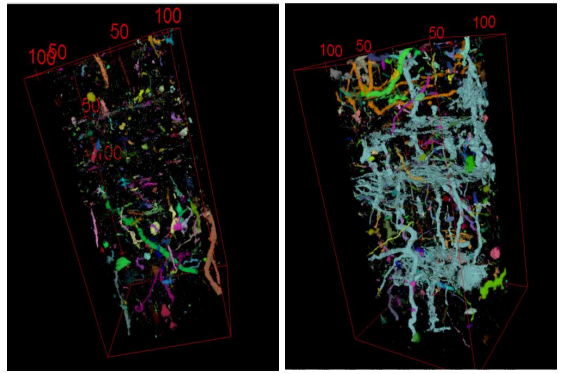
Conclusions

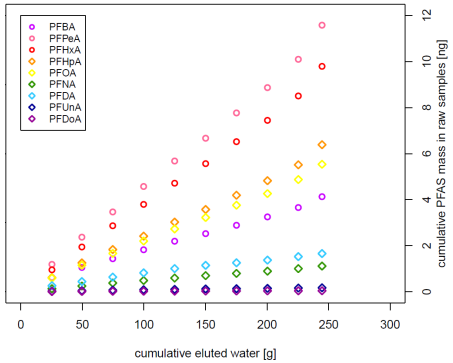
- PFAS leaching from natural soil depends not only on **initial soil contamination**, but also on **hydrodynamics**
  - ➢ **importance of soil pore « architecture » : macropore preferential flow (= bypass flow) vs. matrix flow**



Conclusions

- PFAS leaching from natural soil depends not only on **initial soil contamination**, but also on **hydrodynamics**
  - ➢ **importance of soil pore « architecture » : macropore preferential flow (= bypass flow) vs. matrix flow**
- Amount of leached PFCA **inversely proportional to perfluorinated chain length** (exept PFBA and PFNA)
  - ➢ **Even long-chain PFAS were leached : in some cases, soil colloidal particles act as a carrier-phase**





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  - ➢ **importance of soil pore « architecture » : macropore preferential flow (= bypass flow) vs. matrix flow**
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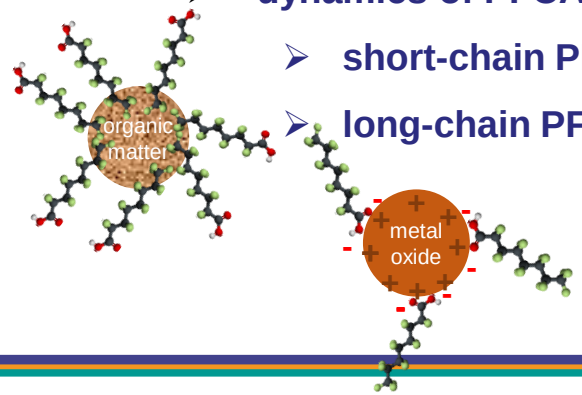
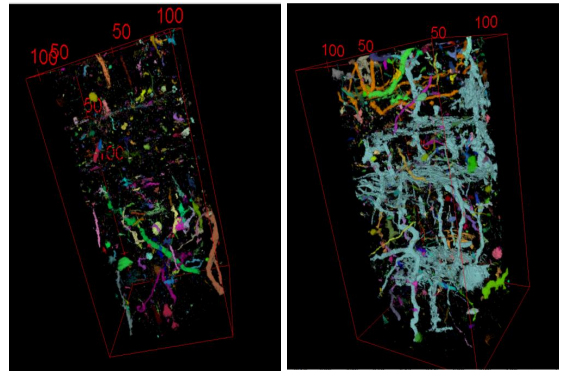
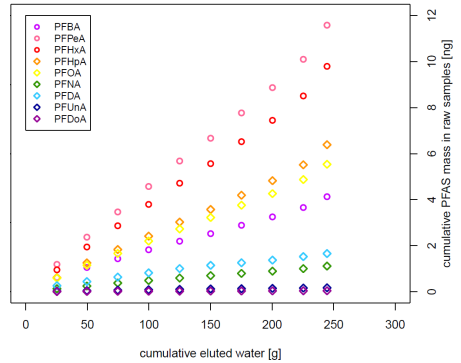
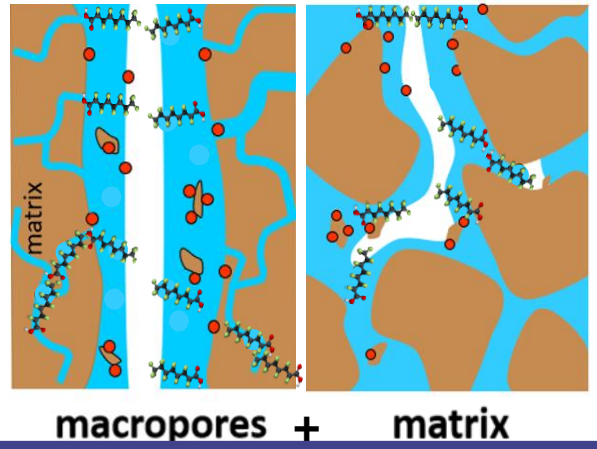
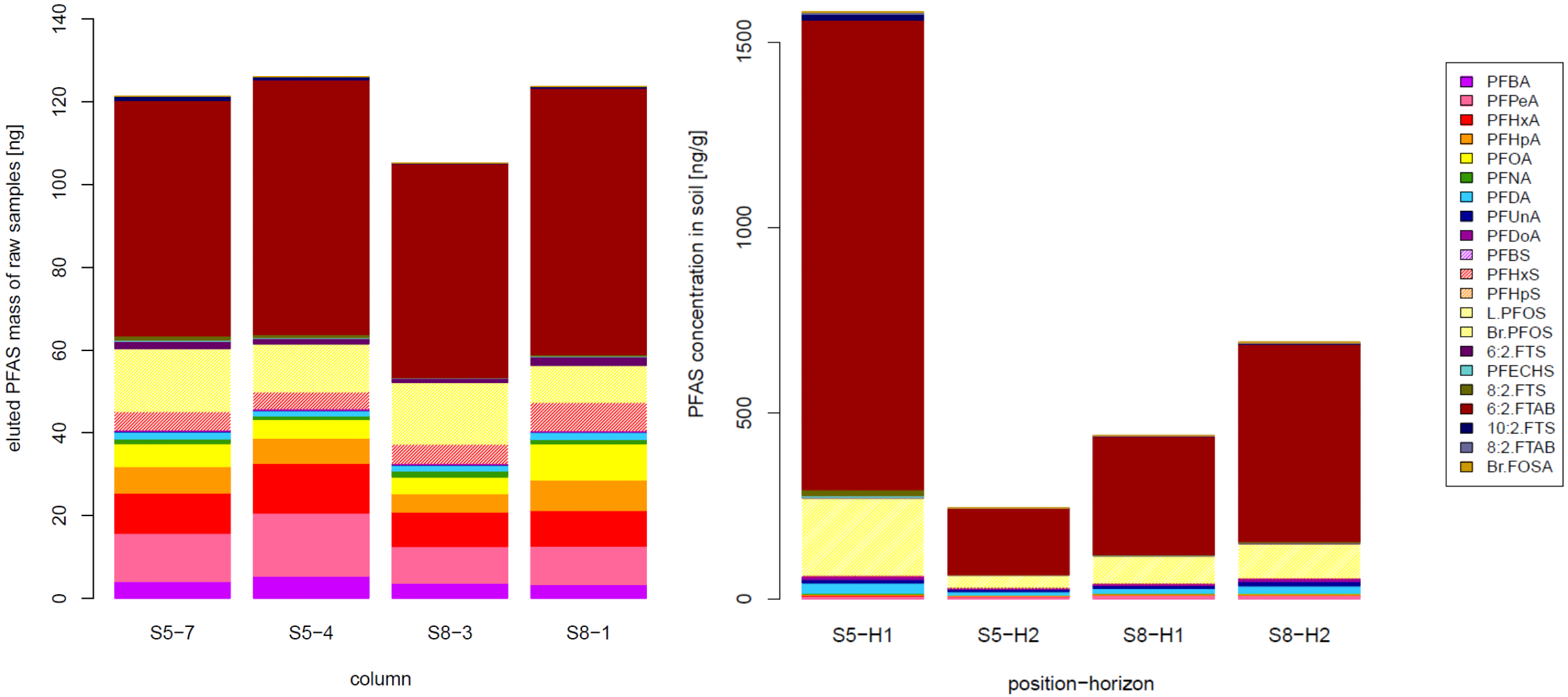
  - ➢ **Even long-chain PFAS were leached : in some cases, soil colloidal particles act as a carrier-phase**
- **Concentrations** of leached PFCA either high in **first flow**, and/or high during **last flow**
  - ➢ **dynamics of PFCA leaching influenced by molecule structure of PFCA :**
    - ➢ **short-chain PFCA tend to be leached with the moving AWI**
    - ➢ **long-chain PFCA seem to also be transported with soil colloidal particles**

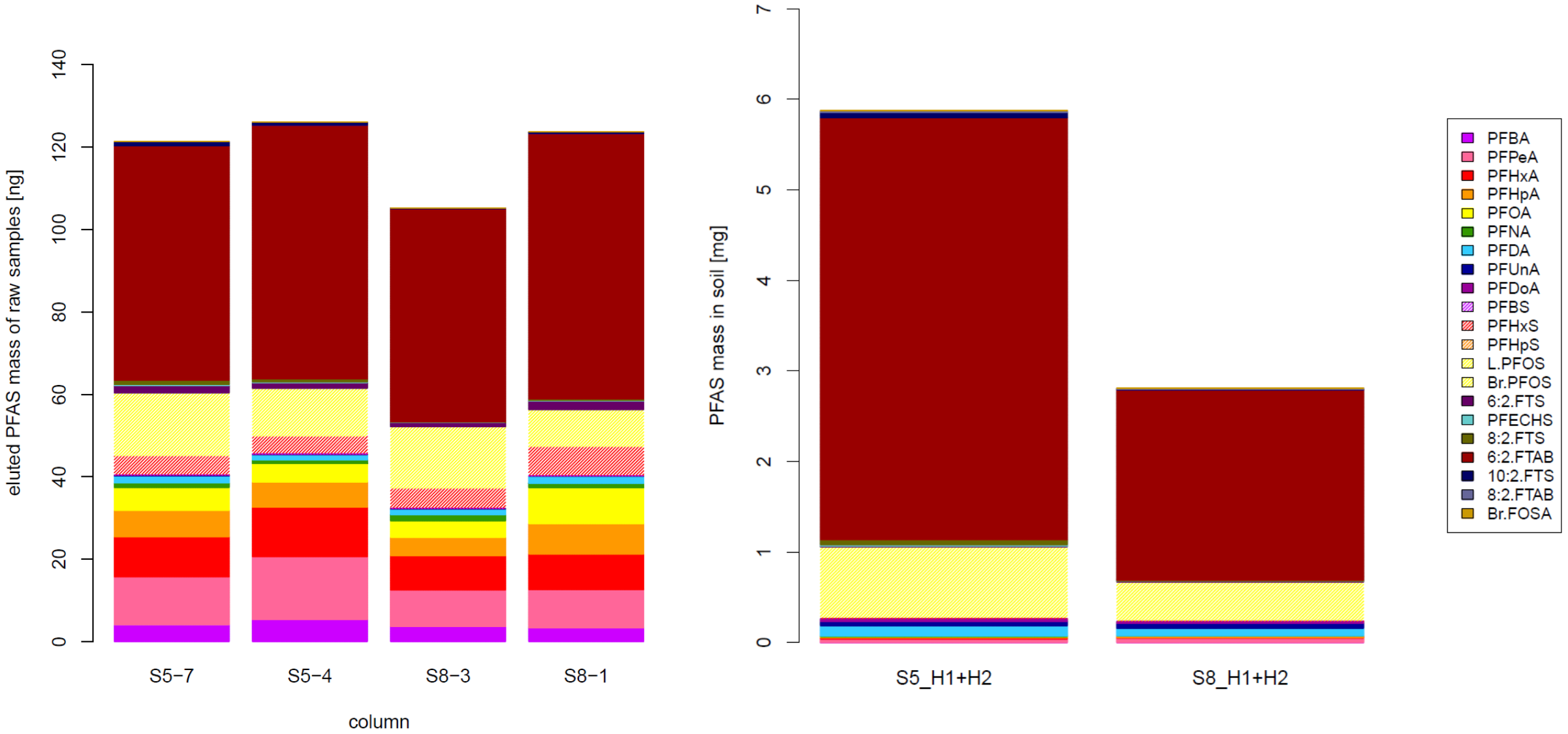









eluted PFAS mass of raw samples [ng]
0
20
40
60
80
100
120
140
S5−7
S5−4
S8−3
S8−1
column
PFAS concentration in soil [ng/g]
0
500
1000
1500
S5−H1
S5−H2
S8−H1
S8−H2
position−horizon
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnA
PFDoA
PFBS
PFHxS
PFHpS
L.PFOS
Br.PFOS
6:2.FTS
PFECHS
8:2.FTS
6:2.FTAB
10:2.FTS
8:2.FTAB
Br.FOSA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0
20
40
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100
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140
S5−7
S5−4
S8−3
S8−1
column
PFAS mass in soil [mg]
0
1
2
3
4
5
6
7
S5_H1+H2
S8_H1+H2
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnA
PFDoA
PFBS
PFHxS
PFHpS
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