Degradation of PFAS in historically contaminated soils: evidence of biotic processes

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Content of presentation

Context

Why study PFAS biodegradation in contaminated soils?

Materials and methods

Soil characterization, evidence of biodegradation and long-term incubation

Results : short-term evolution

Effect of bacterial inhibitor

Results : long-term evolution

Temporal changes in PFAS concentrations and evidence of precursor transformation

Mechanistic interpretation and perspectives

Working hypotheses and next analytical priorities

Context

Why study PFAS biodegradation in contaminated soils?

1- Major PFAS sources

PFAS manufacturing sites

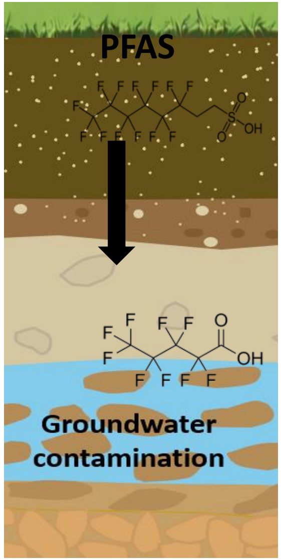
Use of AFFF

Landfill

Contaminated sludge

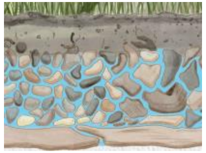
2- Environmental transfer

Transfer of PFAS from soil to groundwater



3- Why Soils matter

Long term reservoir of PFAS



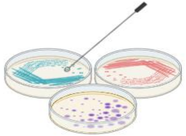
Potential source of groundwater contamination

Complex interactions with soil constituents and microorganisms

4- Scientific gap and objective

Most biodegradation studies : Isolated bacterial strains/ communities

No studies: Historically contaminated soil with indigenous microorganisms



Objective:

Understand PFAS biodegradation pathways in AFFF-contaminated soil:

- Parent compounds
- Degradation products
- Kinetics
- Half-lives

Materials and methods

Experimental strategy and soil used

1- **Short time experiment ± bacterial inhibitor (NaN_3)** to evaluate the possibility of PFAS biodegradation in historically contaminated soil

2- **Long term biodegradation experiment** to further investigate precursor transformation and degradation products

Soil used

Soil sampled from a historical fire training zone

Physico-Chemical Analysis of the Soil Used

Soil predominantly sandy (78 % sand, 15 % silt, 7 % clay)

Slightly alkaline pH (pH = 8.4)

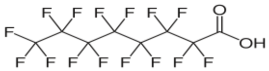
Relatively low Total organic carbon (TOC = 10 $g.kg^{-1}$)

PFAS concentration in the soil

Total PFAS concentration = 2,945 $\mu g.kg^{-1}$ dw

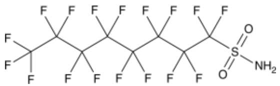
Concentrations (in $\mu g.kg^{-1}$ dw) of the different PFAS families

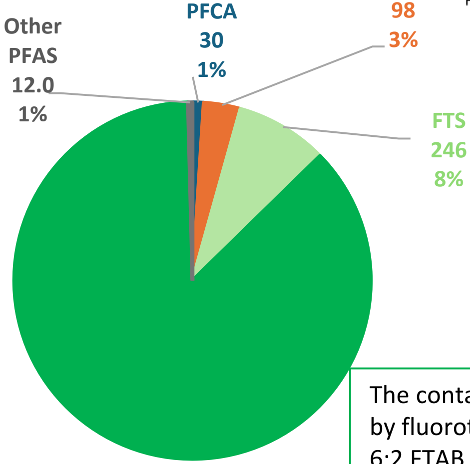
PFOA



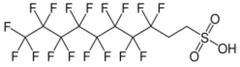
PFOS

PFOSA



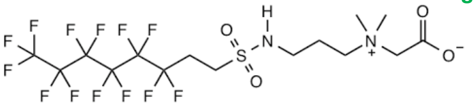


8:2 FTS



6:2 FTS

6:2 FTAB

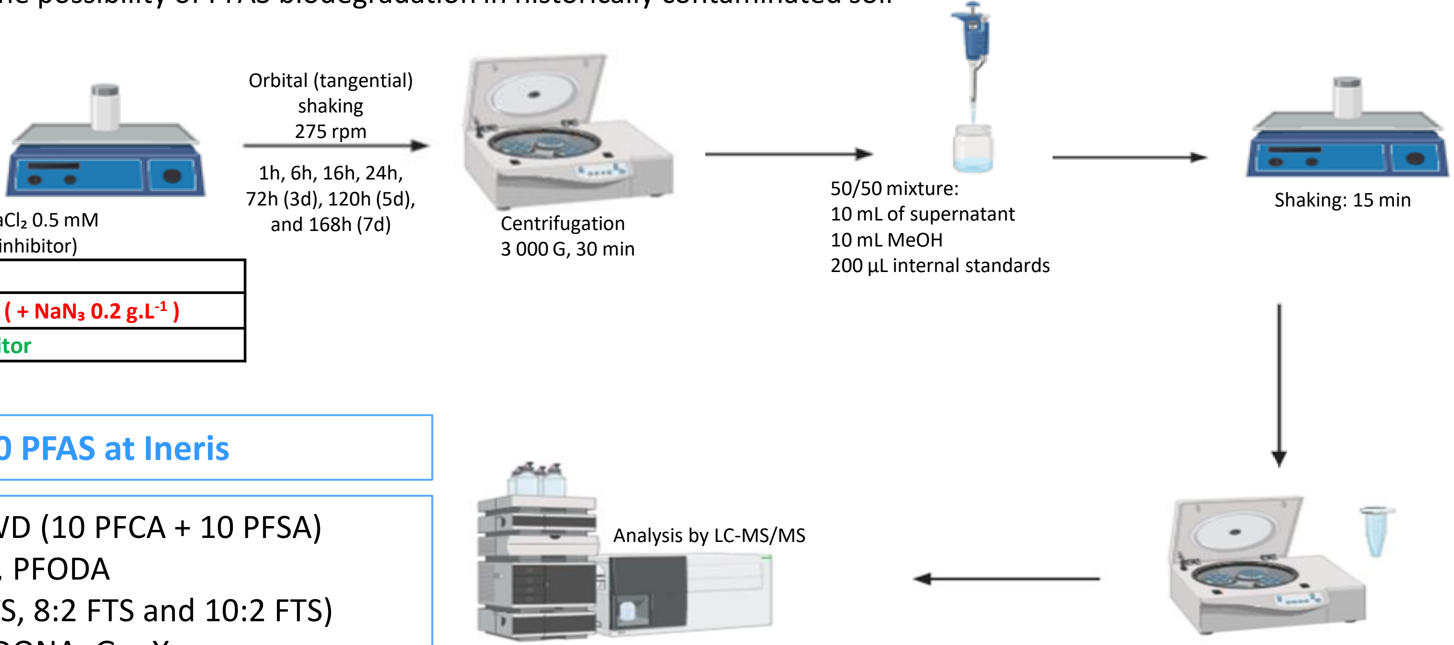


The contamination profile is dominated by fluorotelomer precursors, especially 6:2 FTAB and 6:2 FTS

Materials and methods

1- Short time experiment ± bacterial inhibitor (NaN_3)

Objective: evaluate the possibility of PFAS biodegradation in historically contaminated soil



Solution description
With bacterial inhibitor (+ NaN_3 0.2 g.L^{-1})
Without bacterial inhibitor

Quantification of 30 PFAS at Ineris

20 PFAS from the DWD (10 PFCA + 10 PFSA)
Other PFCA: PFTeDA, PFODA
4 FTS (4:2 FTS, 6:2 FTS, 8:2 FTS and 10:2 FTS)
PFOA substituent: ADONA, GenX
1 FASA: PFOSA
1 Cl-PFESA: 9Cl-PF3ONS

Results and discussion

2- Long-term biodegradation experiment

Experimental setup

80 g contaminated soil + 400 mL solution (same ratio “volume/mass” used in the first experiment)

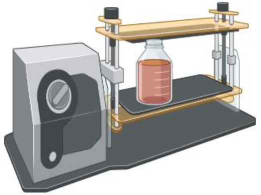
0.5 mM $CaCl_2$

Two tested conditions

With bacterial inhibitor (NaN_3 0.2 $g.L^{-1}$)

Without bacterial inhibitor

Equilibrium



Shaking (3 days)

Reach equilibrium
Separate release from degradation

Long-term monitoring

Static incubation for 1 year

Sampling over time: 3 mL collected for each sample

3d 7d 21d … 1 year

Objectives

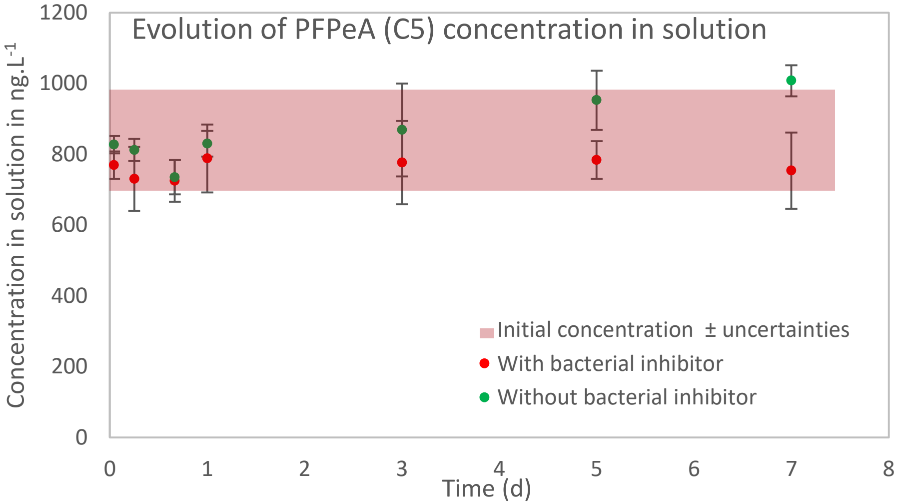
- ✓ Confirm whether biodegradation occurs
- ✓ Determine the transformation products formed
- ✓ Identify the parent compounds that degrade
- ✓ Determine biodegradation kinetics and half-lives

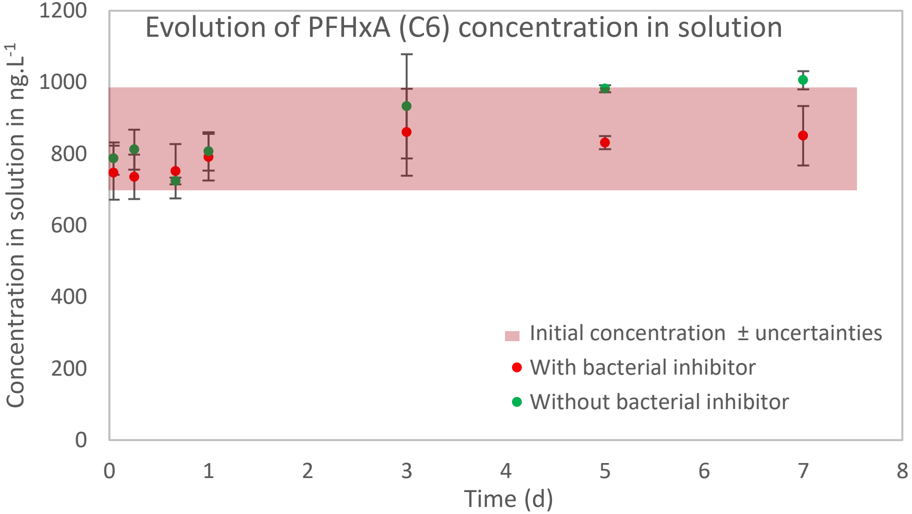
Results and discussion

Evaluation of PFAS biodegradation potential in historically contaminated soil

Effect of bacterial inhibitor NaN_3

Short chain PFCA (PFBA, PFPeA, PFHxA, PFHpA)





With bacterial inhibitor — Steady concentration over time

Equilibrium reached rapidly, within 1 hour

Without bacterial inhibitor

- Concentration increased over time
- Concentration significantly higher than with NaN_3 (5–7 days)

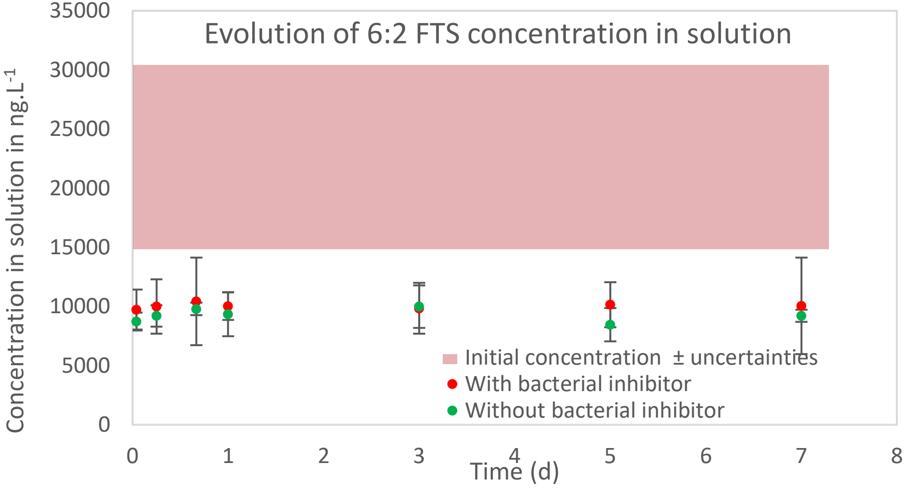
➔ **Possible biotransformation of precursors (e.g., FTS and / or FTAB)?**

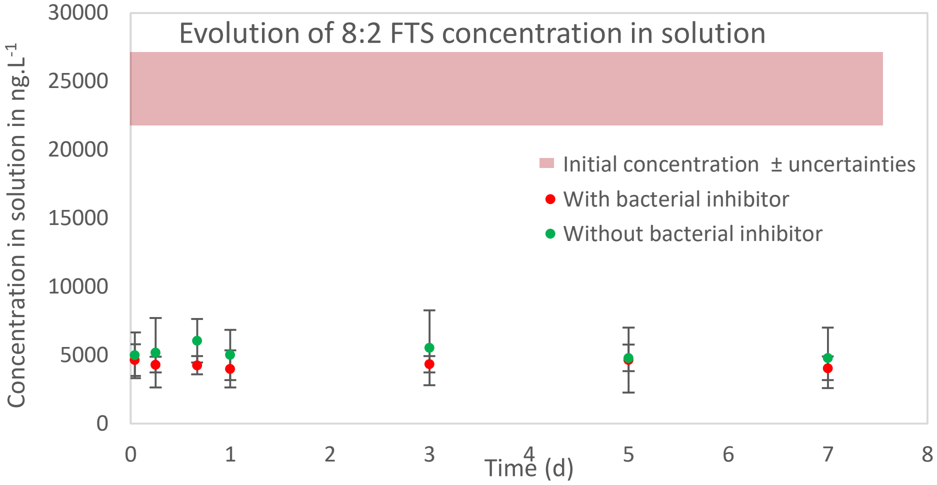
Results and discussion

Evaluation of PFAS biodegradation potential in historically contaminated soil

Effect of bacterial inhibitor NaN_3

FTS





With bacterial inhibitor Constant concentration over time

Equilibrium reached rapidly, within 1 hour

Without bacterial inhibitor

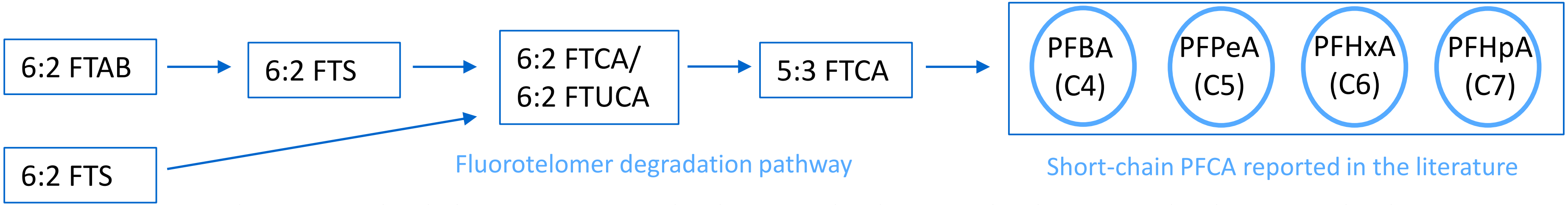
No decrease in FTS concentrations over time as expected
But high concentration in soil
6:2 FTS concentration may therefore be continuously formed while being simultaneously transformed

➔ Possible continuous formation of 6:2 FTS from 6:2 FTAB
➔ This may mask 6:2 FTS depletion and maintain apparent equilibrium in solution

Results and discussion

Literature evidence for precursor biodegradation into short-chain PFCA

Possible formation of C4–C7 from precursor degradation : 6:2 FTAB/ 6:2 FTS ?



Adapted from Wang et al. (2011), D'Agostino & Mabury et al. (2017), Zhang et al.(2016), Shaw et al. (2019), Mendez et al. (2022) and Yan et al. (2024)

Evidence for 6:2 FTS degradation

1- Wang et al. (2011) : activated sludge from WWTP, mixed microbial community, aerobic conditions and formation of PFPeA (C5) and PFHxA (C6)

2- Zhang et al.(2016) : river sediment with natural microbial communities, formation of PFPeA (C5) and PFHxA (C6)

3- Shaw et al. (2019): pure culture of Gordonia sp. NB4-1Y, rapid transformation of 6:2 FTS with PFBA (C4), PFPeA (C5) and PFHxA (C6) formation

4- Mendez et al. (2022): pure culture of Dietzia aurantiaca J3 with formation of PFPeA (C5) and PFHxA (C6)

5- Yan et al. (2024) : AFFF-contaminated soil microcosms , formation of PFBA (C4), PFPeA (C5), PFHxA (C6) ; PFHpA (C7)

Evidence for 6:2 FTAB degradation

1- Shaw et al. (2019): pure culture of Gordonia sp. NB4-1Y, 6:2 FTAB biotransformed to PFBA (C4), PFPeA (C5) and PFHxA (C6)

2- D'Agostino & Mabury (2017): aerobic WWTP sludge, slow 6:2 FTAB biodegradation with formation of PFPeA (C5) and PFHxA (C6)

In both studies, 6:2 FTS may be involved as an intermediate, but it was not clearly detected during 6:2 FTAB biotransformation.

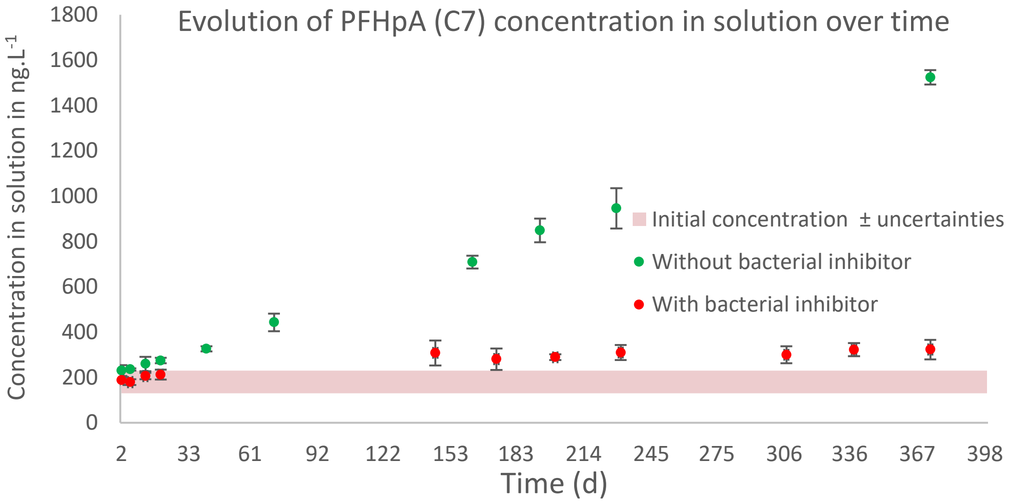
Interpretation for this study

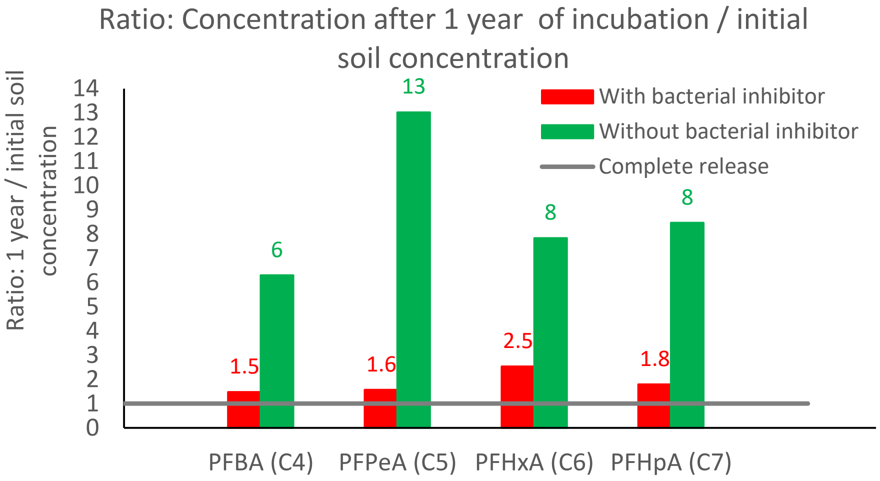
Fluorotelomer precursors can product C4–C7 PFCA

Results and discussion

Long-term result : increase of short-chain PFCA concentration in solution

Example shown for PFHpA (C7); same trend for PFBA (C4), PFPeA (C5) and PFHxA (C6)





With bacterial inhibitor : PFBA (C4), PFPeA (C5), PFHxA (C6) and PFHpA (C7) concentrations in solution increased up to~150 days and then stabilized

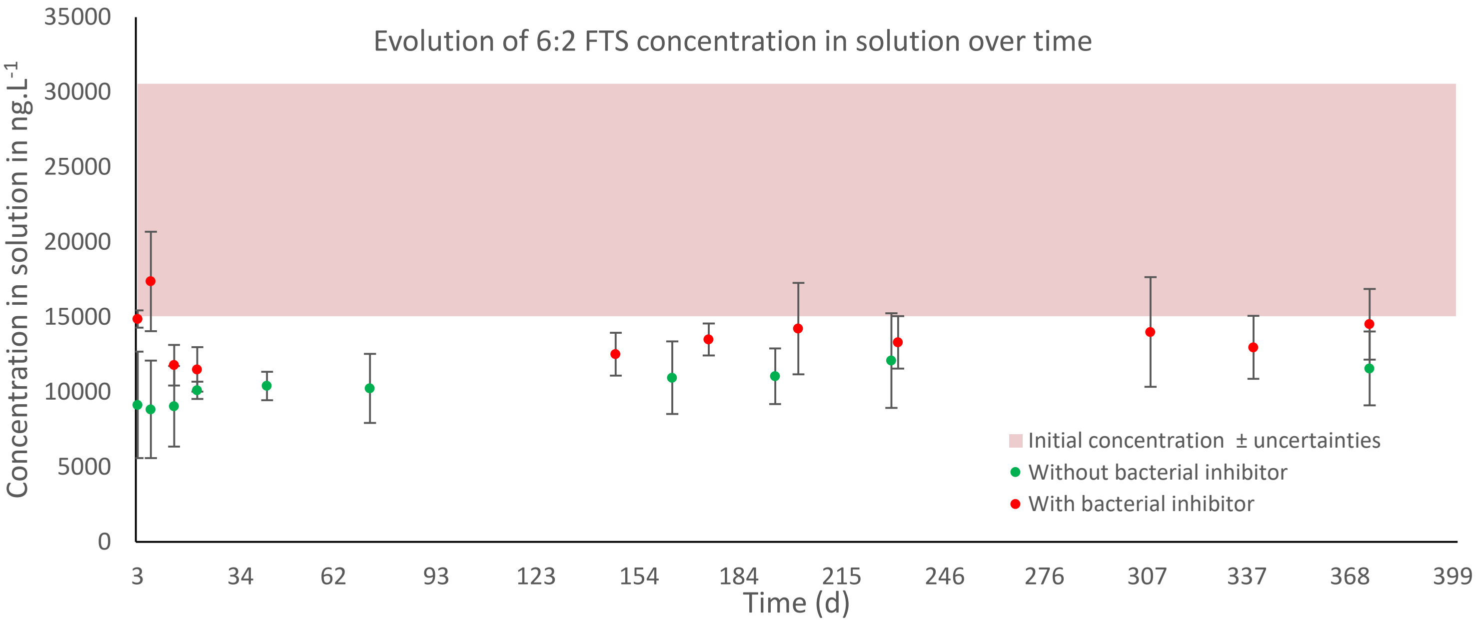
→ NaN_3 inhibition may decrease over long-term incubation
Microorganisms may not be fully inhibited

Without bacterial inhibitor : short-chain PFCA concentrations in solution increased much more strongly after 1 year, exceeding the initial concentration

→ Biotransformation of PFAS precursors

Results and discussion

FTS do not show the expected depletion despite PFCA formation



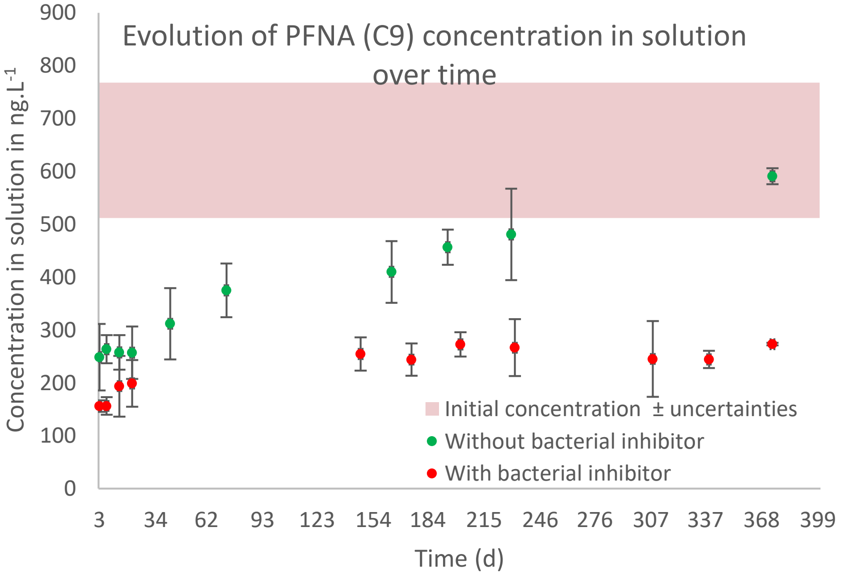
6: 2 FTS (same as 8:2 FTS) remains stable and close to its initial level in both conditions

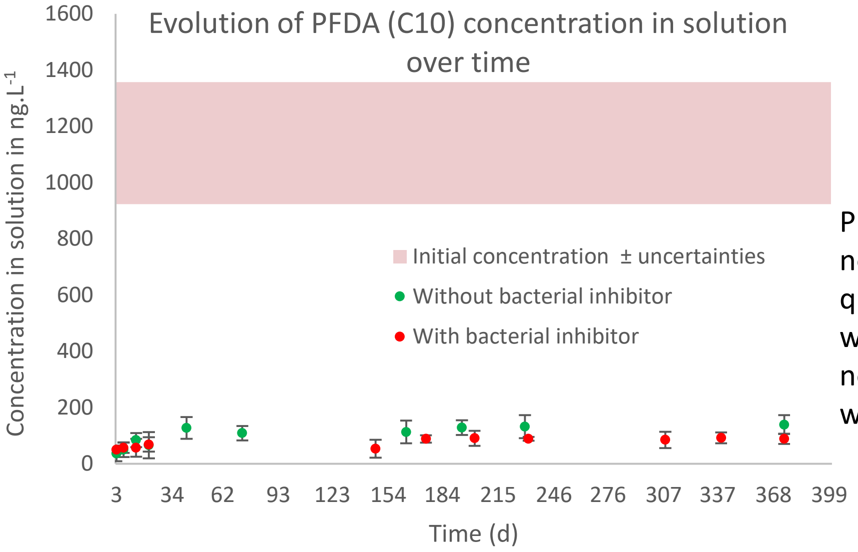
→

✓ A Stable 6:2 FTS concentration does not rule out biodegradation : 6:2 FTS may be continuously formed from 6:2 FTAB while being simultaneously biotransformed via 6:2 FTCA/6:2 FTUCA and 5:3 FTCA into short-chain PFCA

Results and discussion

Long-chain PFCA : additional release or biological contribution?





PFUnDA (C11) is near LOQ (limit of quantification) with inhibitor but not detected without inhibitor

PFNA (C9) and PFDA (C10) concentrations in solution increased more markedly in the absence of bacterial inhibitor

→ The increase in PFNA (C9) and PFDA (C10) without bacterial inhibitor may indicate a biological contribution, possibly through transformation of unidentified long-chain PFCA precursors; however, direct biodegradation of PFUnDA (C11) into PFDA (C10) and PFNA (C9) is not clearly demonstrated in soil systems

Conclusions and perspectives

Summary of the main results

Evidence of PFAS biodegradation (0 –7 d)

- With bacterial inhibitor (NaN_3) :
  - Rapid equilibrium, reached within ~ 1 h
  - Concentrations remained globally stable over time

- Without bacterial inhibitor (NaN_3) :
  - Higher concentrations of short-chain PFCA at 5 – 7 d

➔ Short term result : first indicator of biodegradation

Long-term incubation (1 year)

- PFBA (C4), PFPeA (C5), PFHxA (C6) and PFHpA (C7) concentrations in solution increased over time
- After ~ 150 d, concentrations tended to stabilize with inhibitor, but continued to rise much more strongly without inhibitor
- Short-chain PFCA (C4 –C7) increased while monitored FTS concentrations remained globally stable
- PFNA (C9) and PFDA (C10) concentrations increased more markedly in the absence of bacterial inhibitor

➔ Long-term result: concentration increases are consistent with biological contribution in addition to release

A stable 6:2 FTS concentration does not rule out biodegradation

Literature supports that precursor biotransformation can generate short-chain PFCA

Overall, the data support precursor transformation in contaminated soil, in addition to release

Conclusions and perspectives

Mechanistic interpretation : two hypotheses to test next

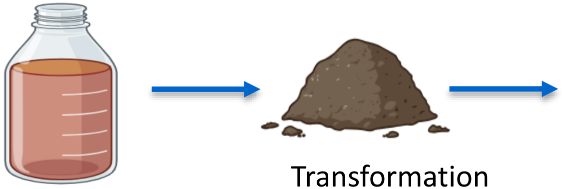
The results point to precursor transformation, but the parent compounds still need to be identified

How can FTS concentrations in solution remain stable while those of short-chain PFCA increased?

Short-chain PFCA (C4– C7):
Concentration in solution increased over time

6: 2 FTS :
Concentration in solution remained relatively stable

Hypothesis 1 : direct precursor transformation



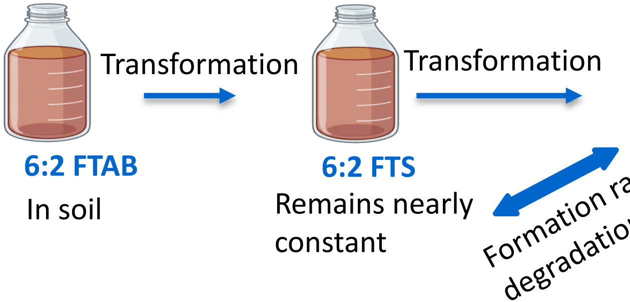
6:2 FTAB
Or other precursors in soil

Transformation in soil

Concentrations in solution of short chain PFCA(C4–C7) increase

➔ PFCA concentrations in solution increased without a visible decrease in monitored FTS

Hypothesis 2 : Pseudo-steady state of the 6:2 FTS



6:2 FTAB
In soil

Transformation

6:2 FTS
Remains nearly constant

Transformation

Short-chain PFCA (C4–C7) increase

Formation rate~ degradation rate

➔ Analysis in progress : analyze the precursor compound 6:2 FTAB to distinguish between the two metabolic pathways

➔ Next step: determinate the half-lives and degradation kinetics

Thank you for your attention

References

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