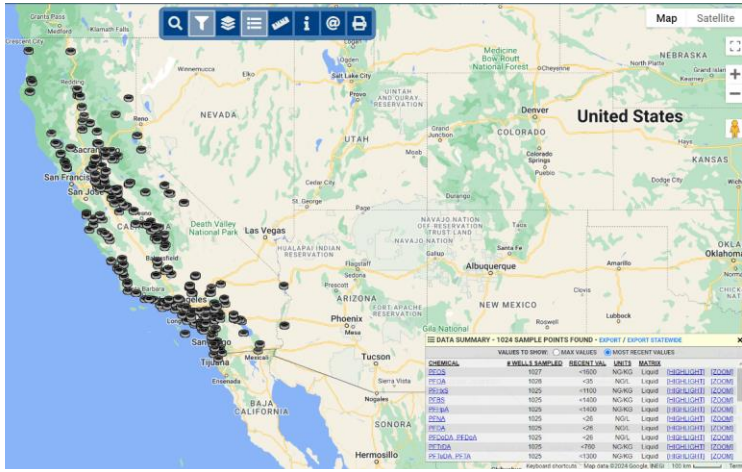
Applications of Machine Learning Approaches to Predict PFAS Profiles and Fate in Wastewater

Christopher I. Olivares
chris.olivares@uci.edu

Department of Civil and Environmental Engineering
University of California, Irvine

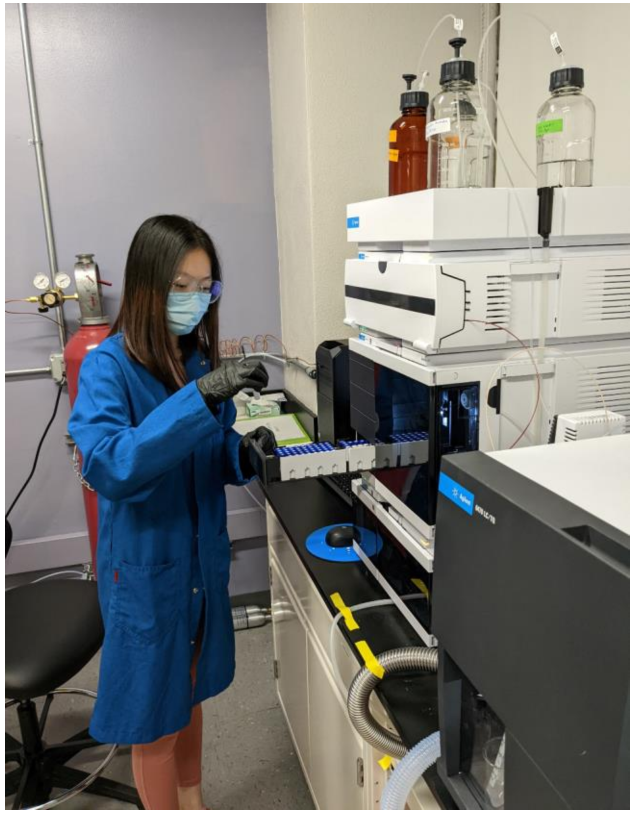
PFAS concerns

- Sampling and measurement of PFAS in WWTP
- Observed increase in quantifiable PFAS in effluents
- Biosolids – heterogenous matrix



Data Availability

Low PFAS cross-contamination LC-MS/MS



Field Sampling

Skilled data interpretation

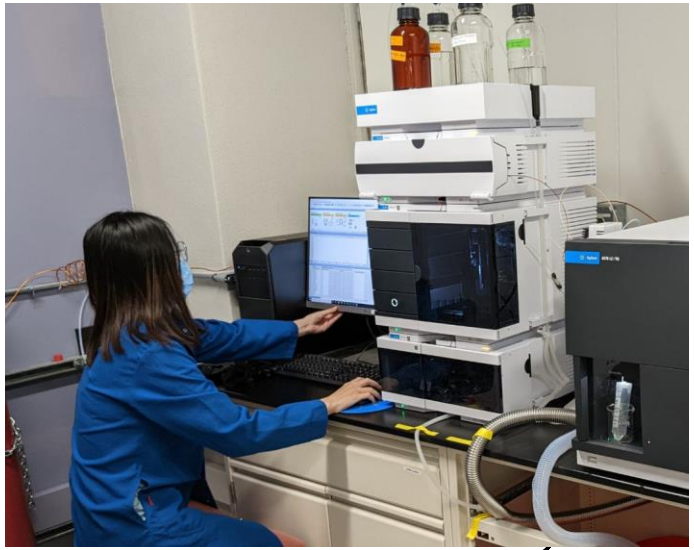
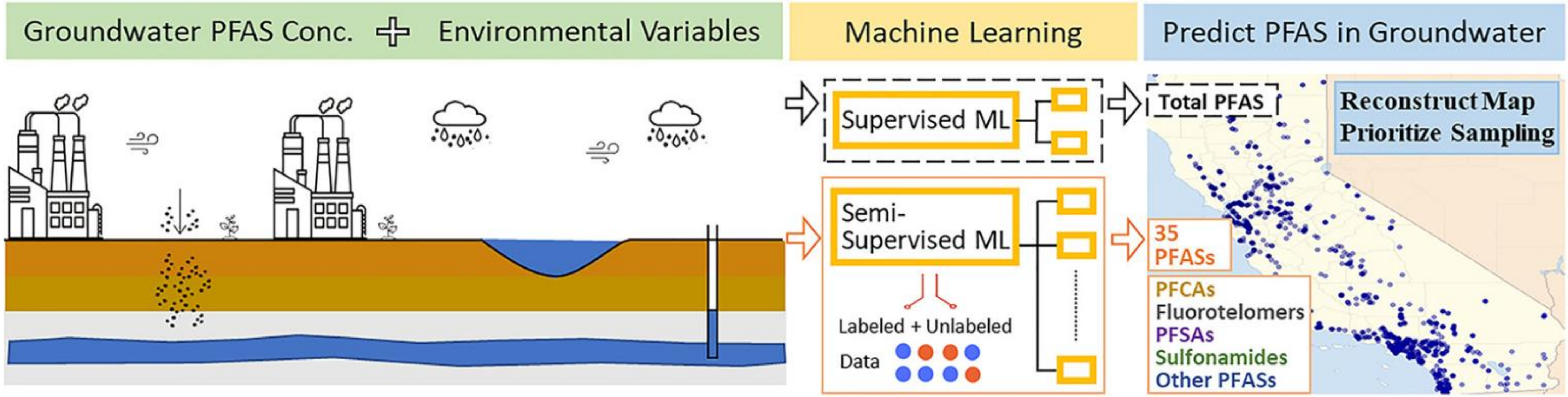
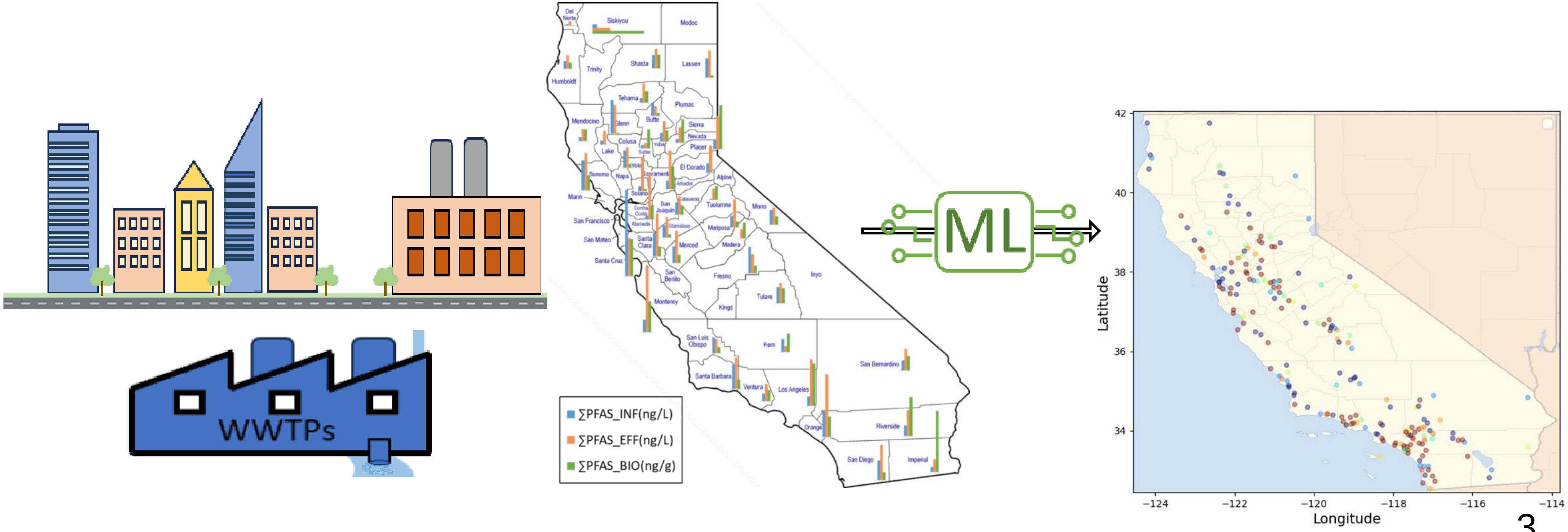


Figure adapted from AgriLife Today (TAMU)

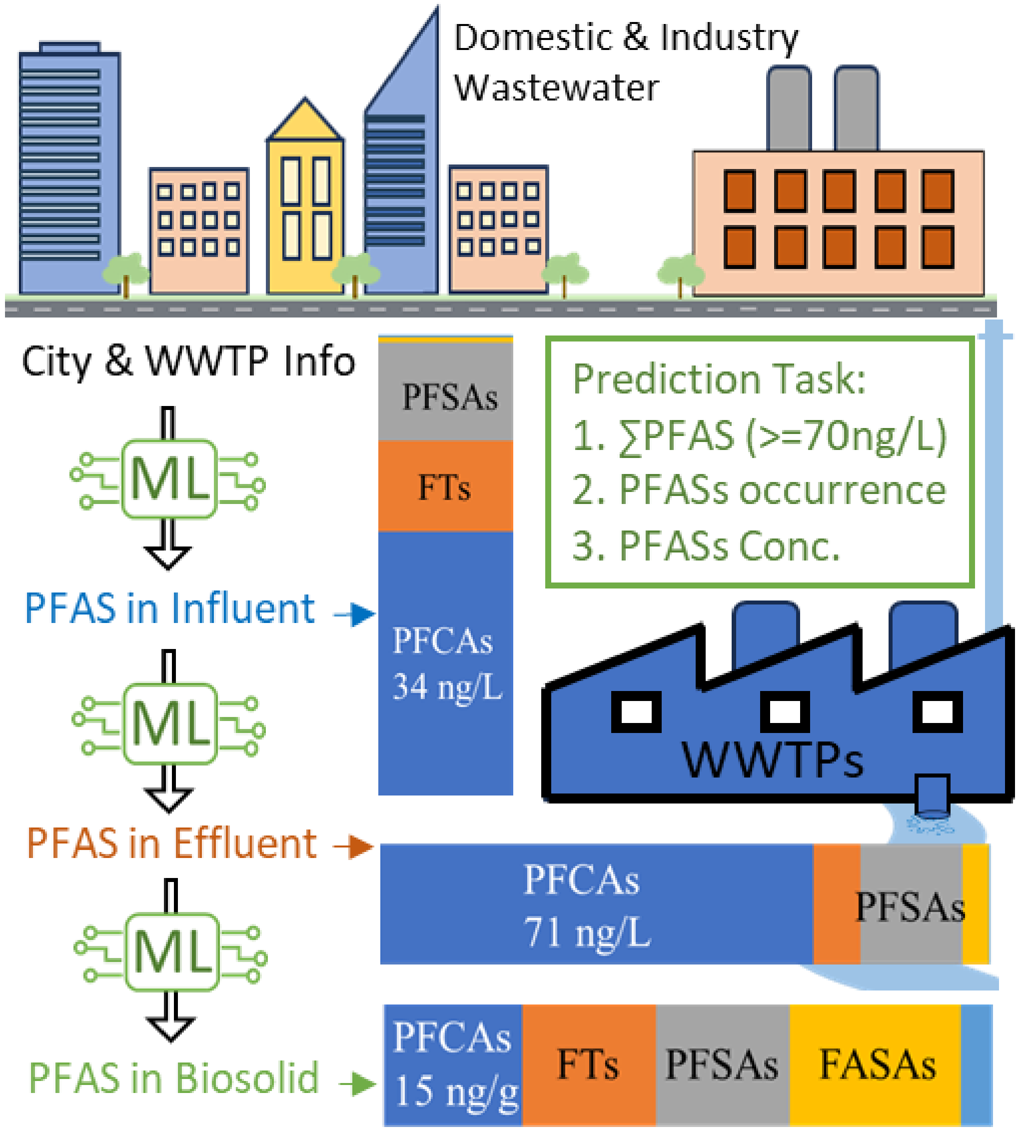


Groundwater PFAS Conc.
Environmental Variables
Machine Learning
Predict PFAS in Groundwater
Supervised ML
Semi-Supervised ML
Labeled + Unlabeled
Data
Total PFAS
Reconstruct Map
Prioritize Sampling
35 PFASs
PFCAs
Fluorotelomers
PFSAs
Sulfonamides
Other PFASs



WWTPs
∑PFAS_INF(ng/L)
∑PFAS_EFF(ng/L)
∑PFAS_BIO(ng/g)
ML
Latitude
Longitude
42
40
38
36
34
−124
−122
−120
−118
−116
−114

Machine Learning Approaches to predict PFAS profiles in WWTPs



Objective

- ➢ Statewide WWTP database (PFAS, wastewater characteristics, treatment)
- ➢ Machine learning models to predict PFAS in effluent and biosolids
- ➢ Identify features that influence PFAS composition in effluents, biosolids

Data sources

California Water Boards

- Geotracker - PFAS
- Geotracker - Questionnaire
- Water Quality – WWTP Effluent Self-Monitoring Report Data
- Wastewater User Charge Data - Sewage
- COVID-19 Wastewater Surveillance data

US Census Bureau, other agencies

- Demographics by City, Town, County
- County Gross Domestic Product
- etc

PFAS data validation

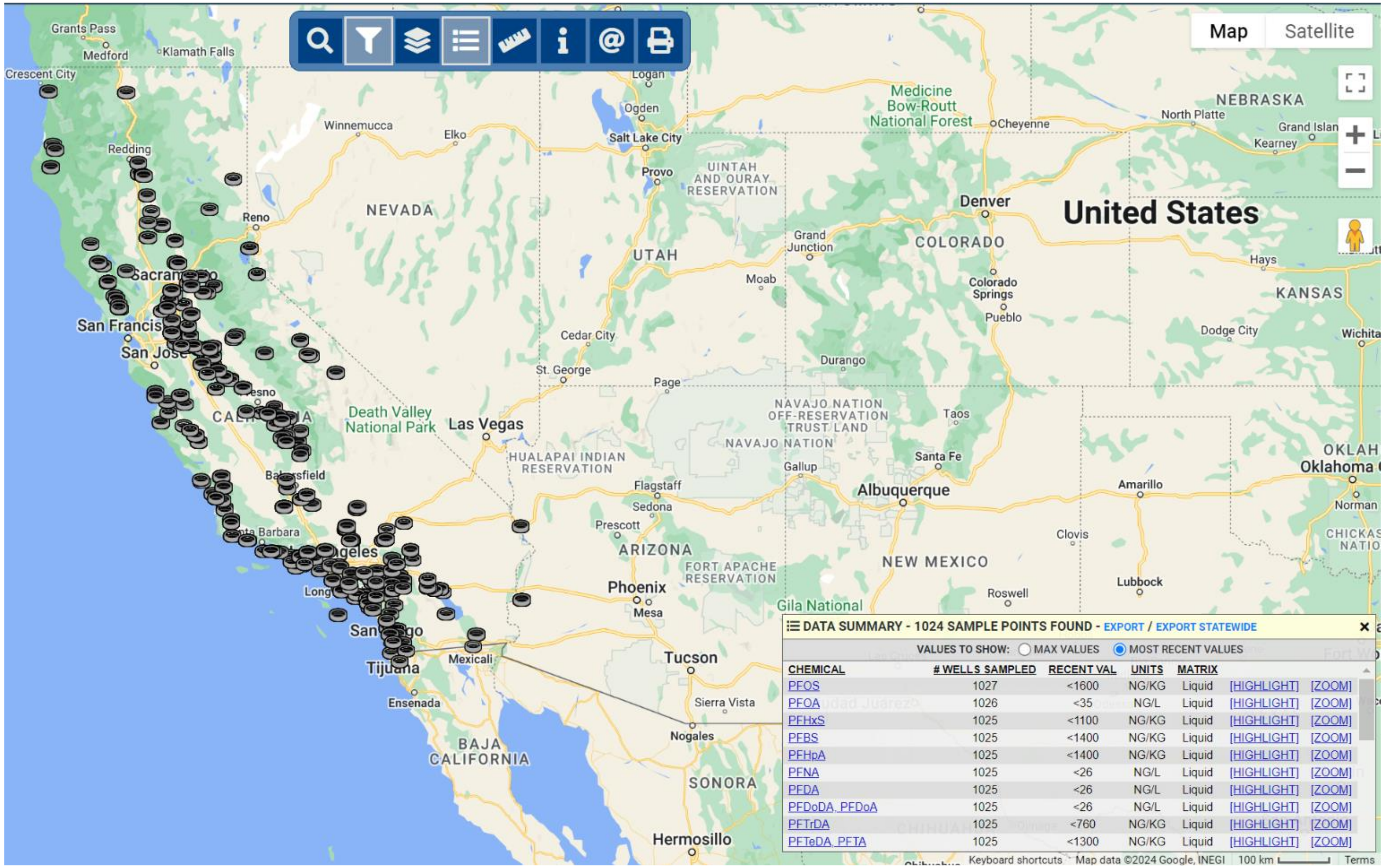
We scrutinized data in scenarios:

- PFASs were detected in both influent and effluent but not in biosolids
- No PFASs were detected in any of the liquid, solid matrices
- PFASs were detected in biosolids but not in influent or effluent
- Outliers in PFASs concentration in any of these phases.

PFAS Sampling locations & WWTP locations

The compiled dataset includes:

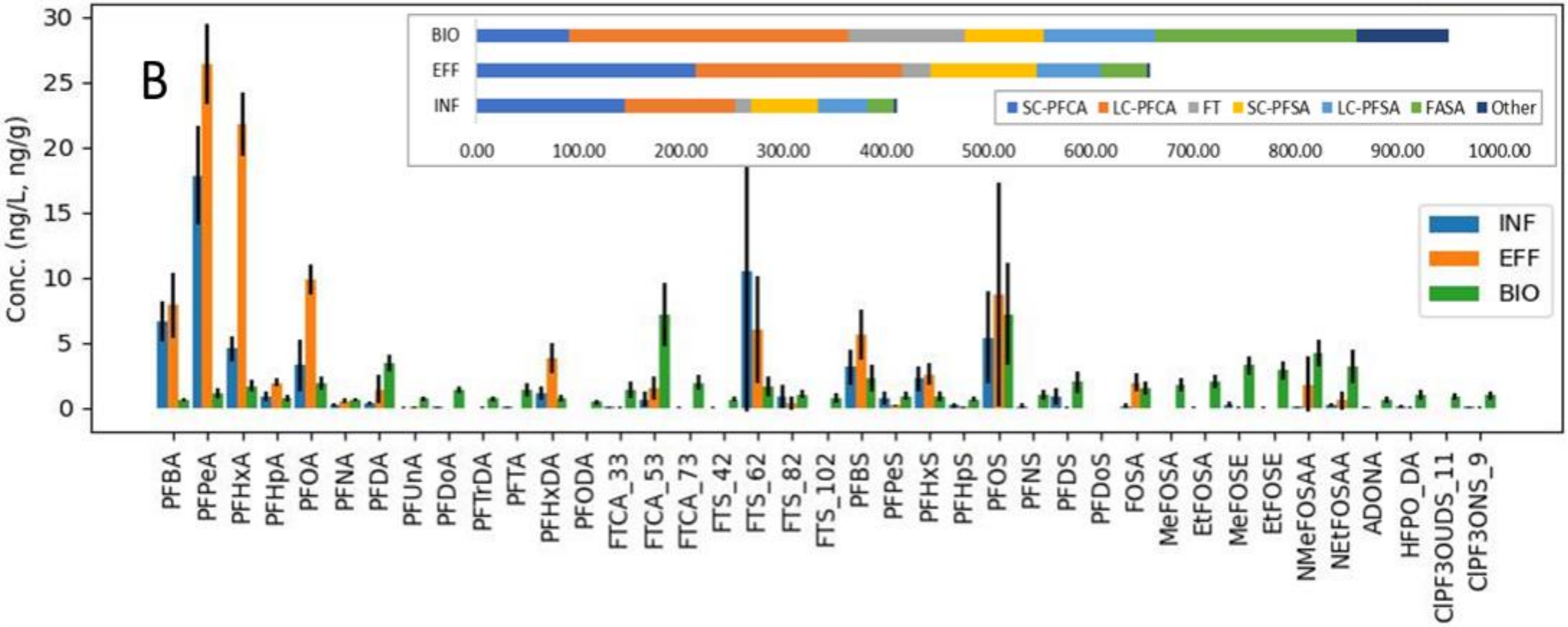
- 213 WWTPs from California
- 2020 - 2023
- 39 PFASs concentrations in influent, effluent, and biosolids
- Features:
    - Wastewater source
    - WWTP information (e.g., location, sample date, WWTP size, treatment process, water quality indicators)
    - Socioeconomic factors
- 380 columns, 931 rows



Geotracker map showing sampled WWTPs

Results – Statistical Summary

PFAS occurrence and profile in California WWTPs.



Effluent > influent concentrations for perfluorinated alkyl acids, some fluorotelomers and sulfonamides

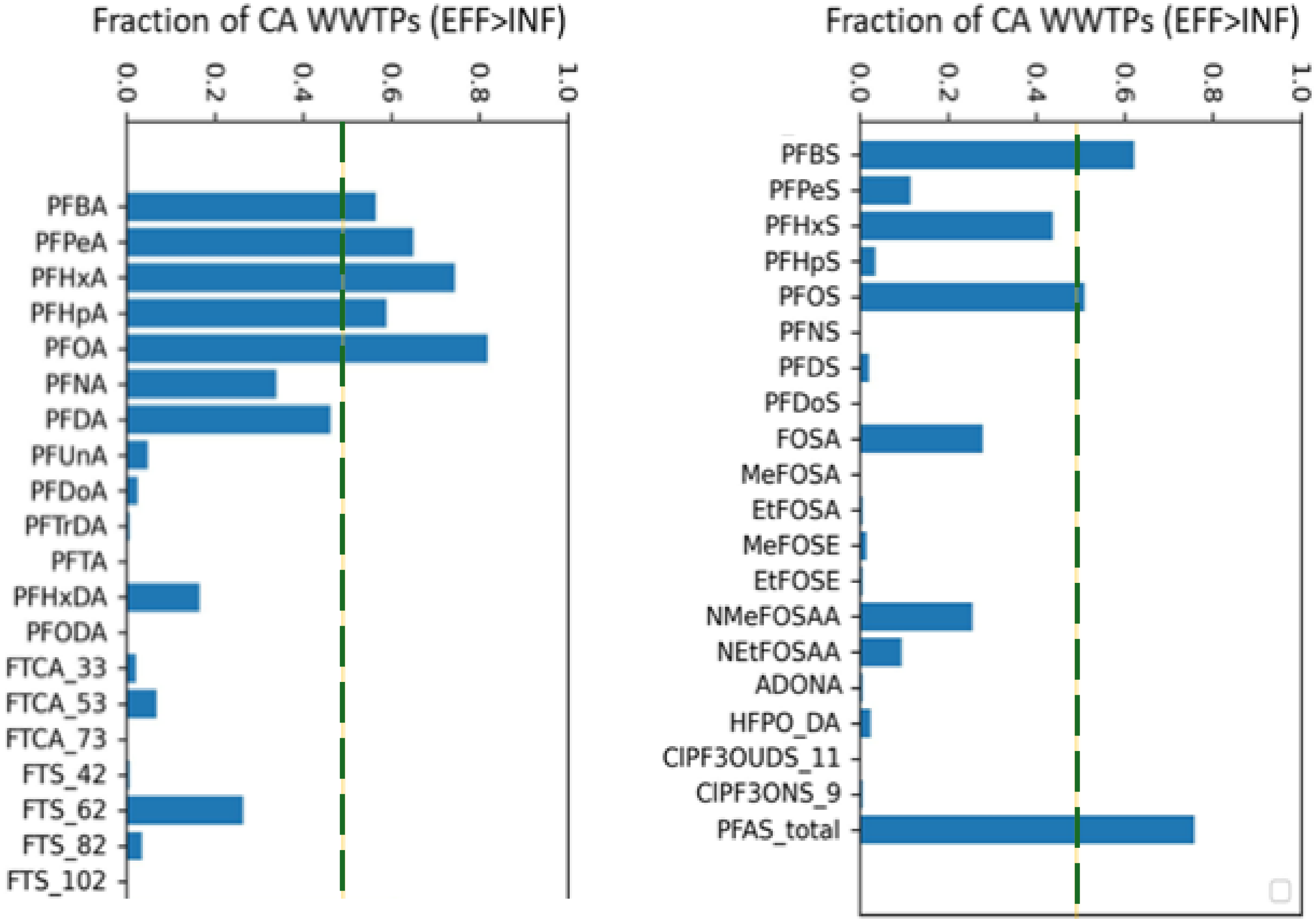
Precursors

(a)biotic transformation

Other precursors/Intermediates

(a)biotic transformation

PFCAs, PFSAs
Other stable intermediates



Effluent > influent concentrations for perfluorinated alkyl acids, some fluorotelomers and sulfonamides

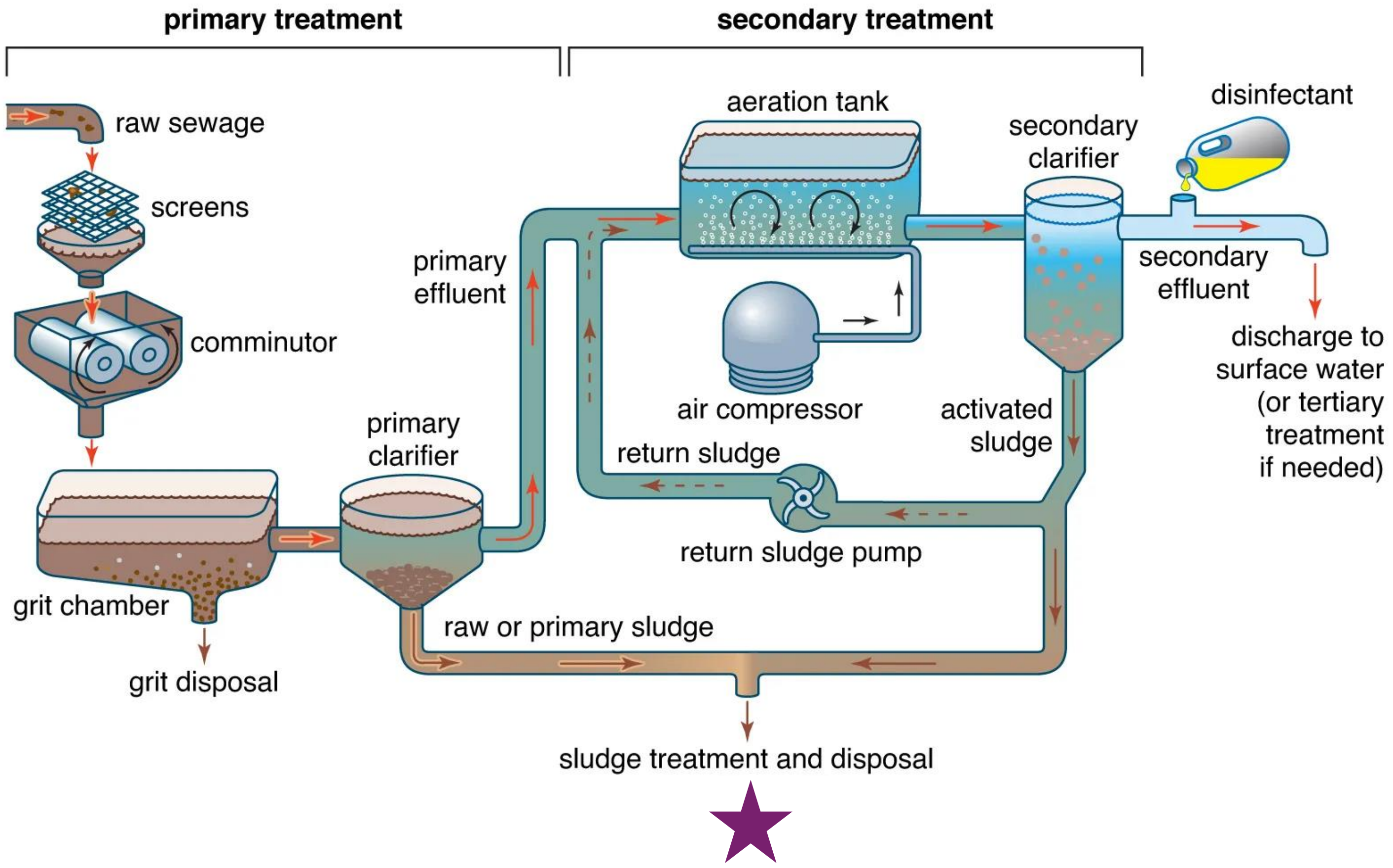
Precursors

★ *(a)biotic transformation*

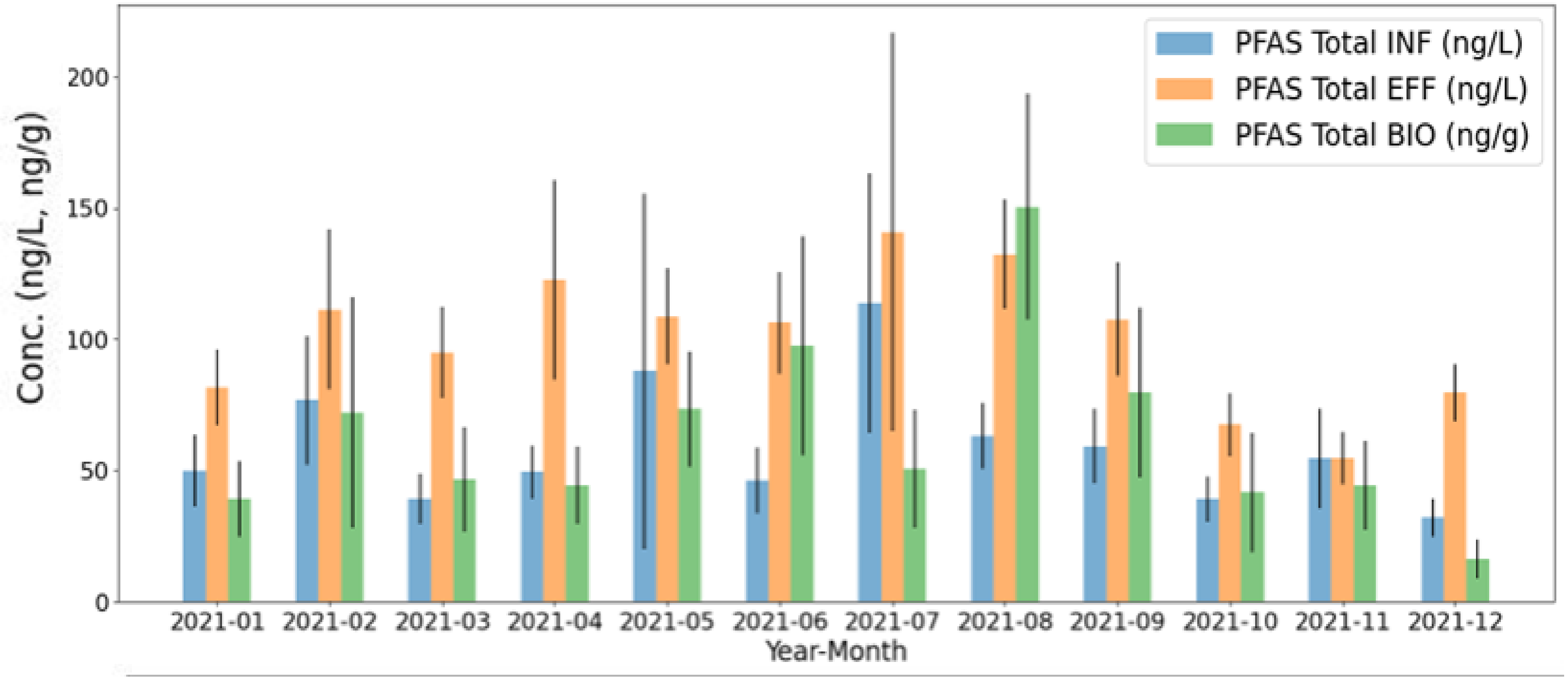
Other precursors/Intermediates

★ *(a)biotic transformation*

PFCAs, PFSAs
Other stable intermediates



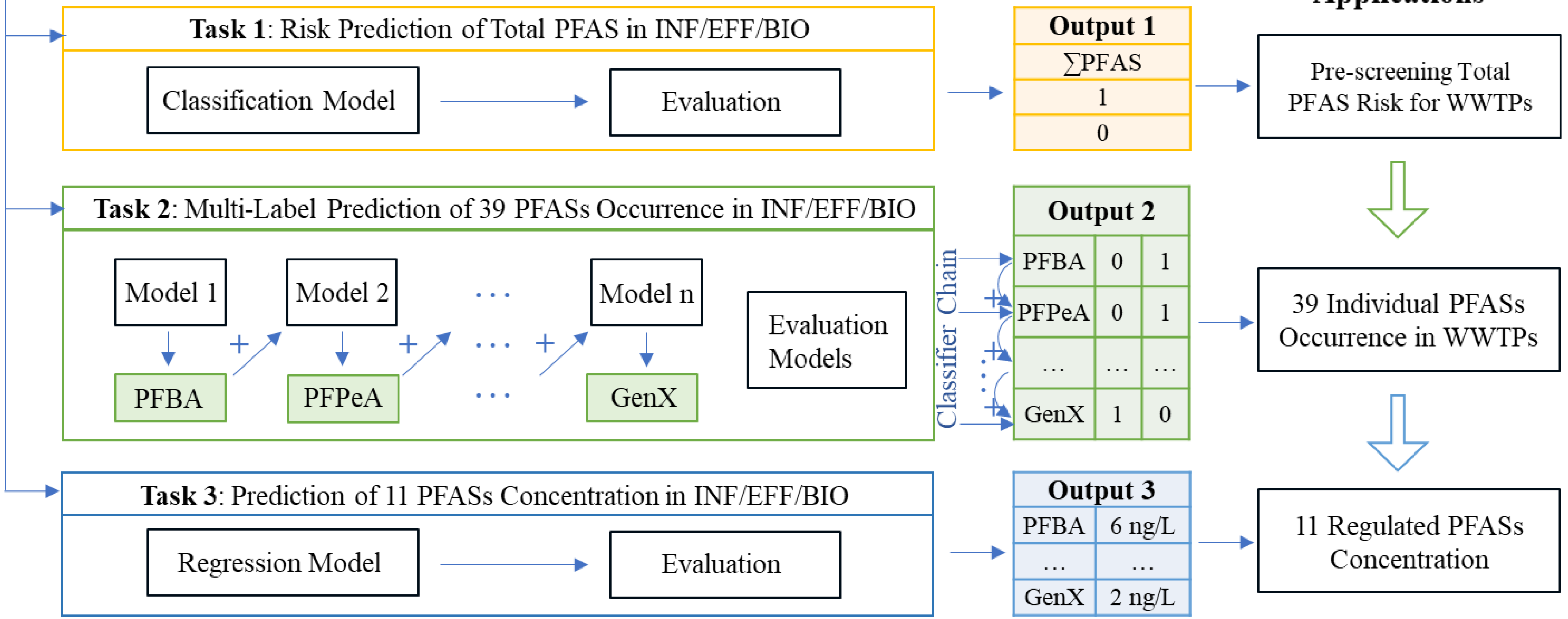
Slight seasonal pattern (year 2021)

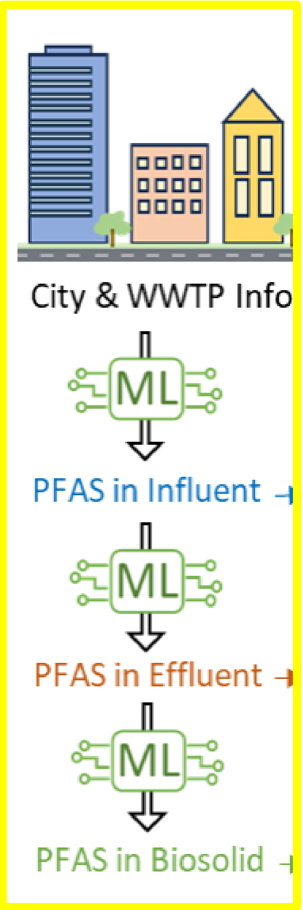


Machine Learning Approaches

ML

Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

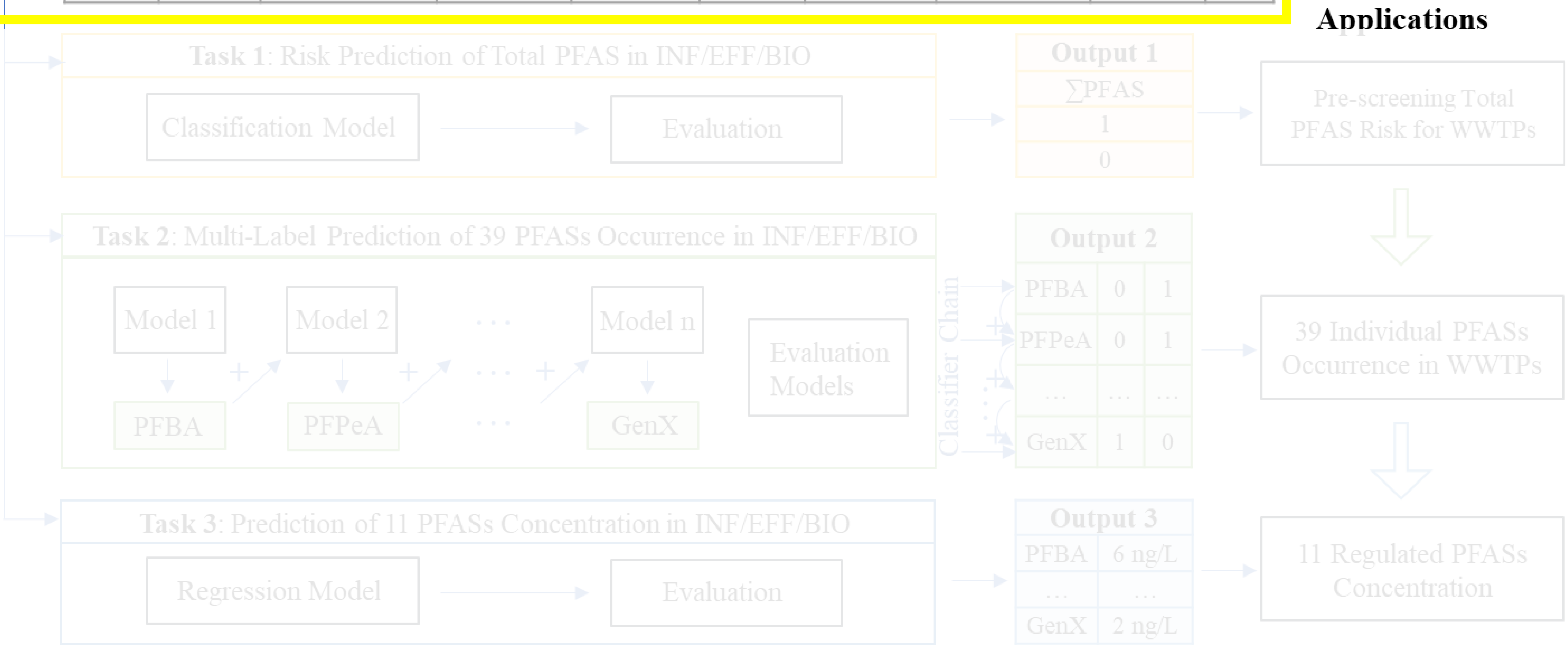


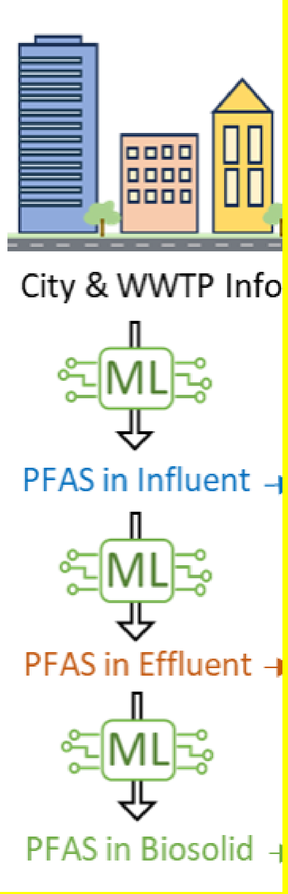


Machine Learning Approaches

ML

Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

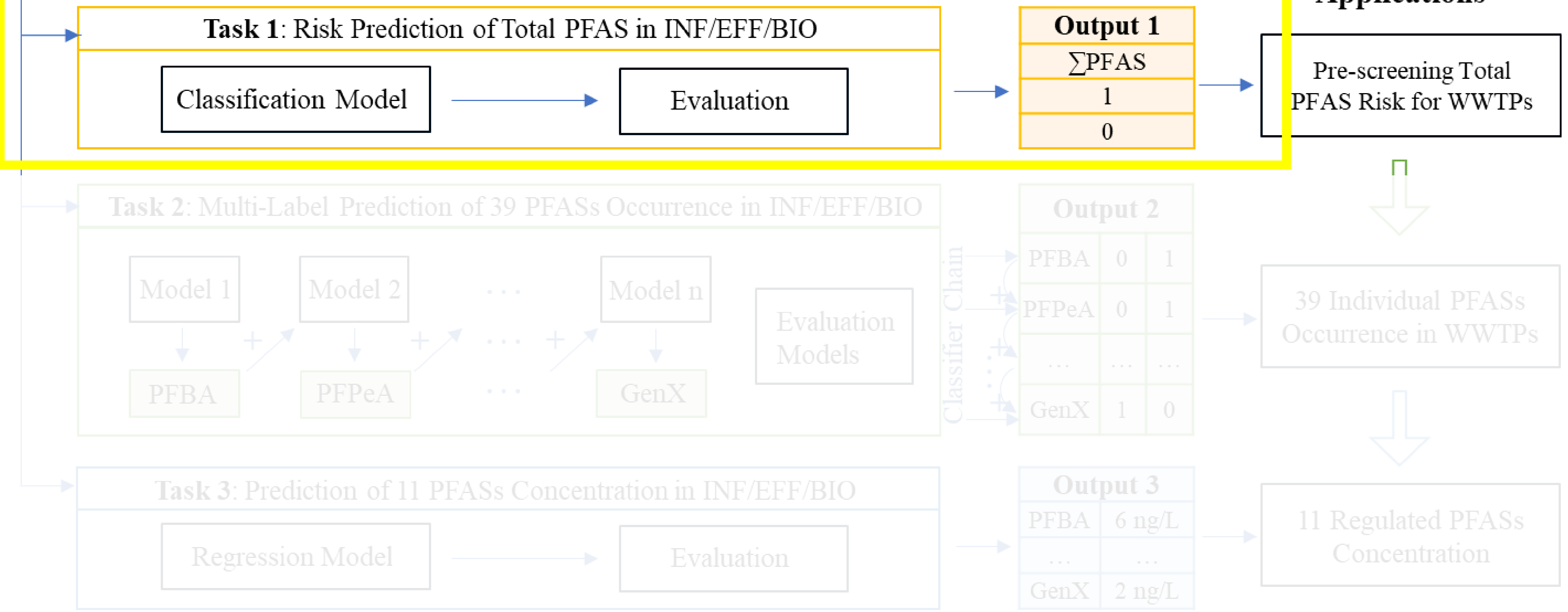


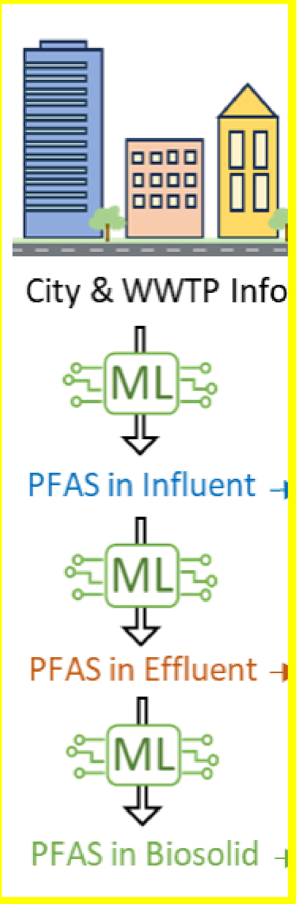


Machine Learning to predict Sum PFAS (classification)

ML

Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

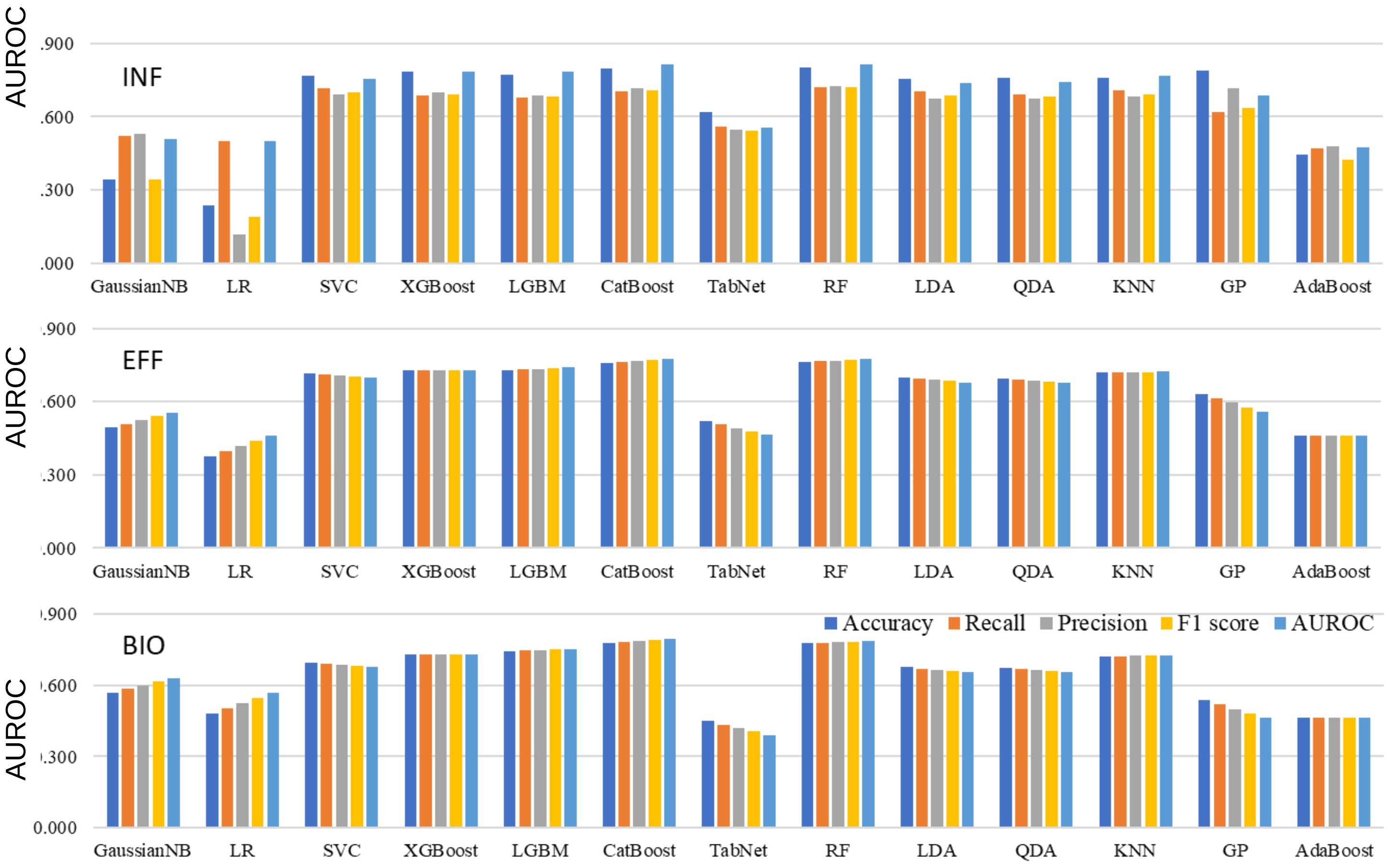




Result - Prediction of ∑PFAS: influent, effluent (70 ng/L threshold), biosolids (any detected concentration)

Matrix	Algorithm	Accuracy
Influent	Random Forest	80.1%
Effluent	Random Forest	76.4%
Biosolids	CatBoost	77.9%

Performance evaluation of ∑PFAS in INF, EFF, BIO

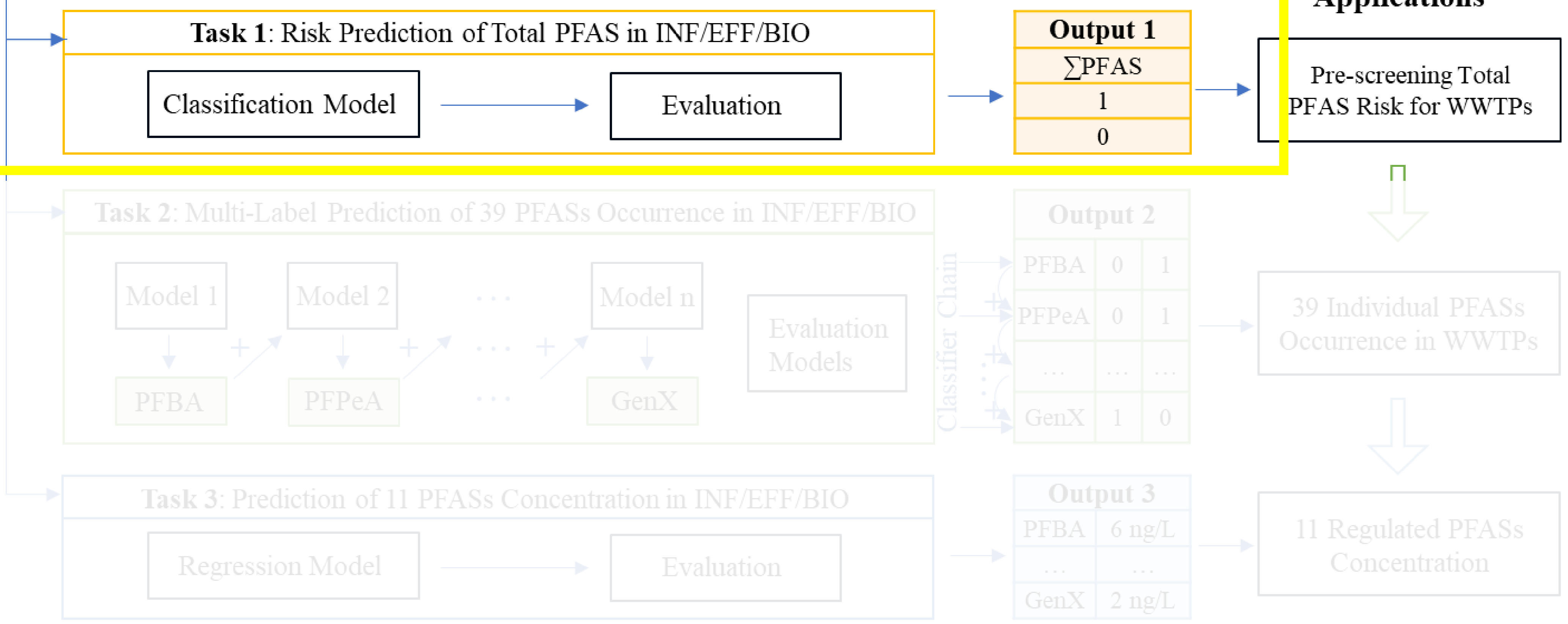


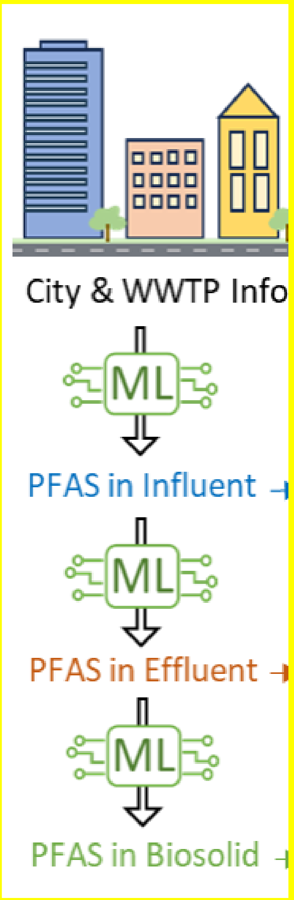
GaussianNB: Gaussian Naive Bayes; LR: Logistic Regression; SVC: Support Vector Classifier; XGBoost: Extreme Gradient Boosting; LGBM: Light Gradient Boosting Machine; CatBoost: Categorical Boosting; TabNet: Tabular Network; RF: Random Forest; LDA: Linear Discriminant Analysis; QDA: Quadratic Discriminant Analysis; KNN: K-Nearest Neighbors; GP: Gaussian Process; AdaBoost: Adaptive Boosting.

Machine Learning to predict Sum PFAS

ML

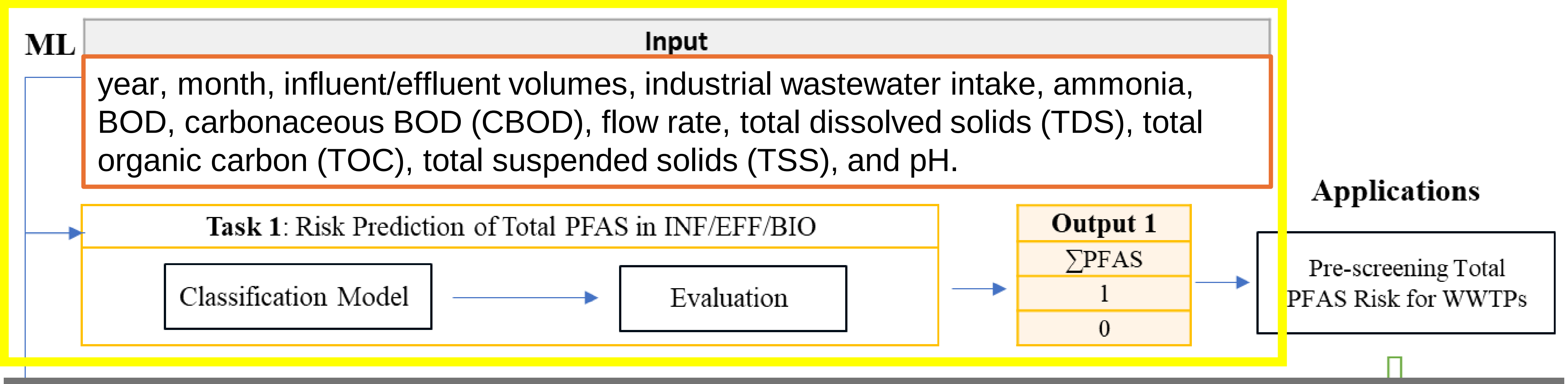
Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

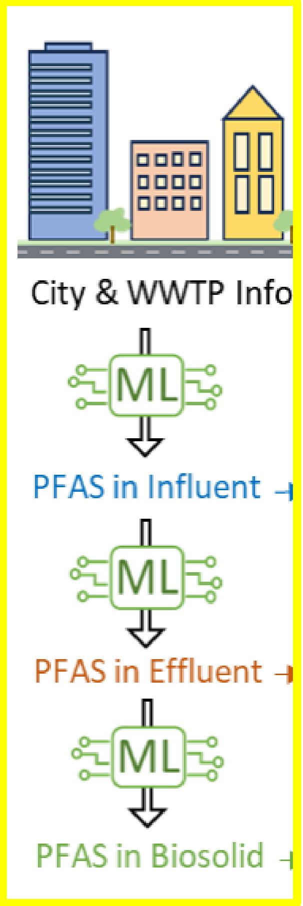




Machine Learning to predict sum PFAS (70 ng/L)

But this time only with commonly measured wastewater features





Influent 80%→ 74% accuracy (CatBoost)

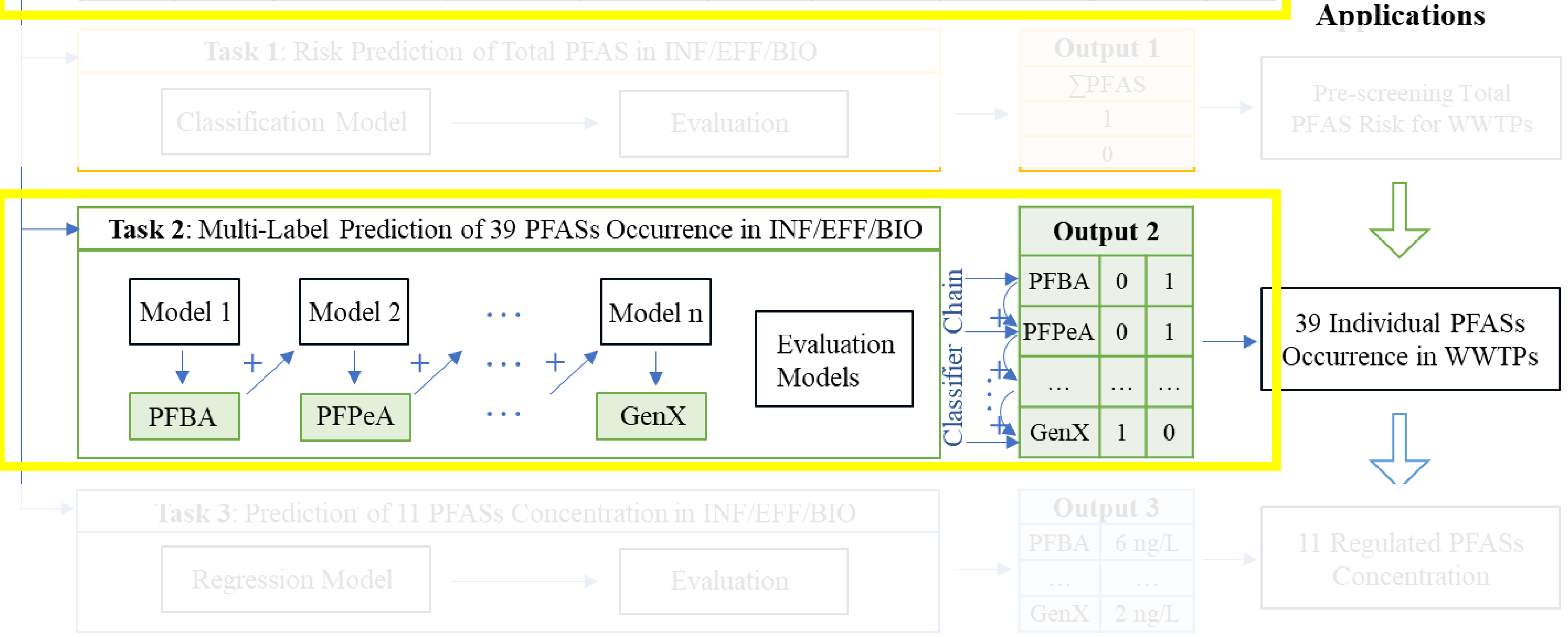
Effluent 76% →73% accuracy (CatBoost)

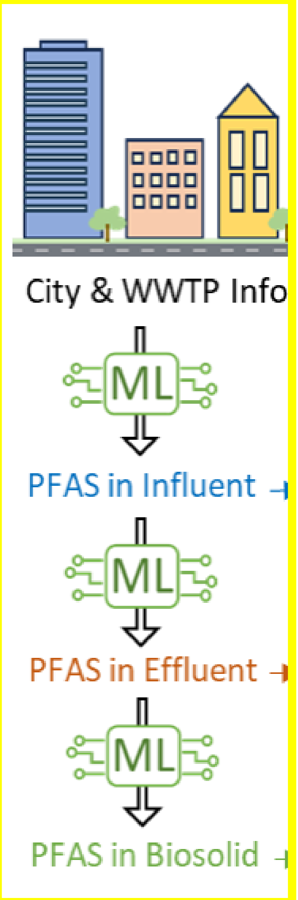
Biosolids 78% → 78% accuracy (CatBoost)

Machine learning to predict 39 PFASs (classification)

ML

Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

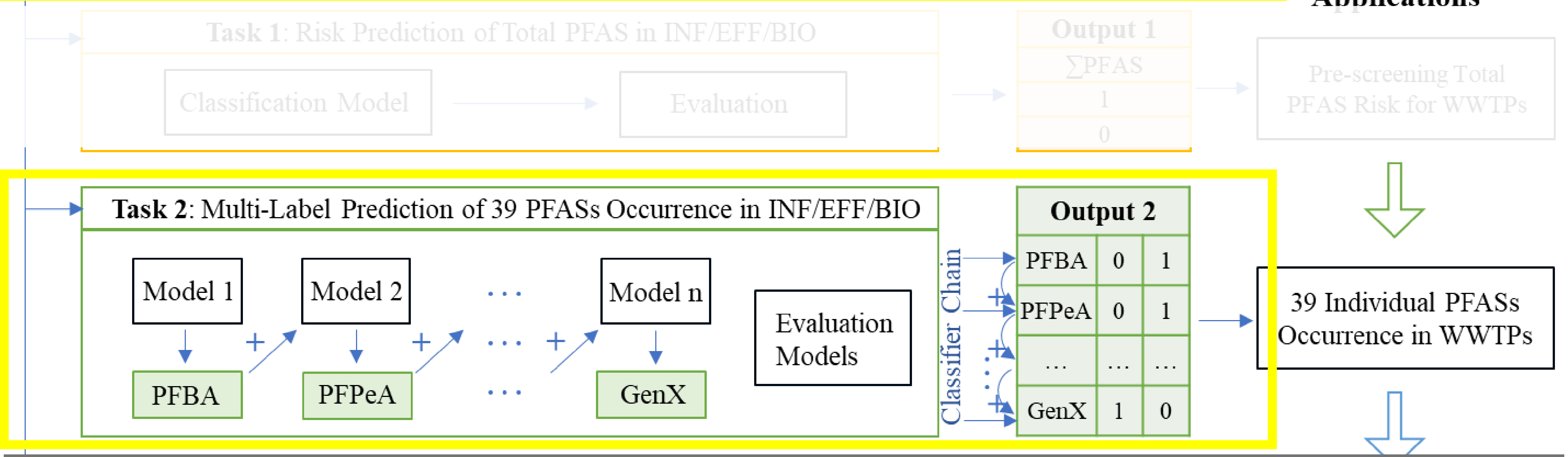


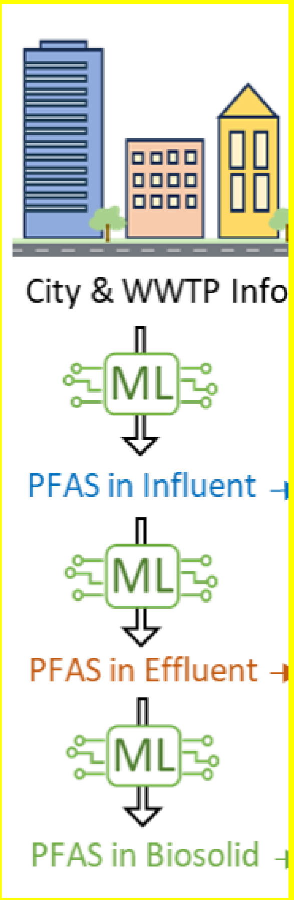


Machine learning to predict 39 PFASs (classification, 2 ng/L as threshold)

ML

Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...





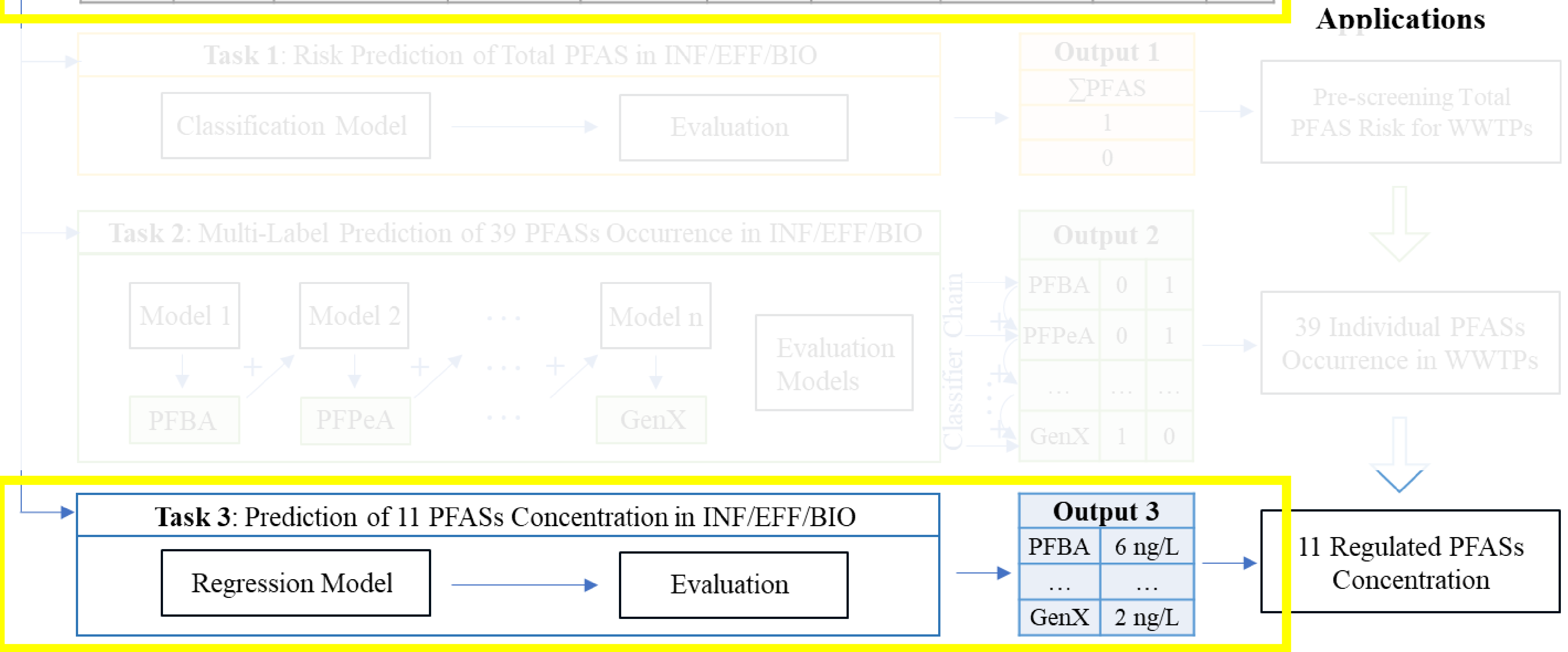
Influent (68-98%) accuracy
Effluent (80-98%) accuracy
Biosolids (80-98%) accuracy

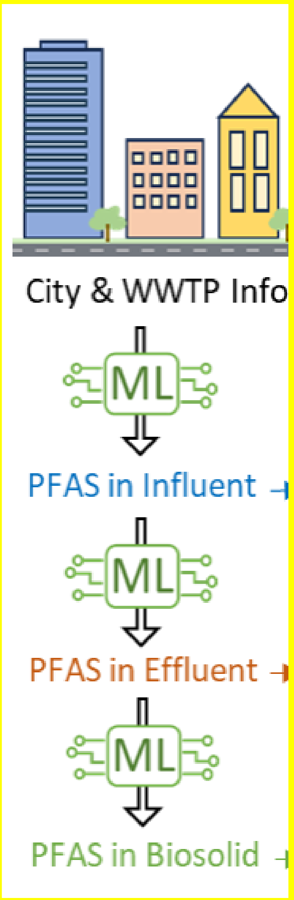
Dependent on PFAS detection frequency

Machine learning to predict concentrations of 11 PFASs (regression)

ML

Input									
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

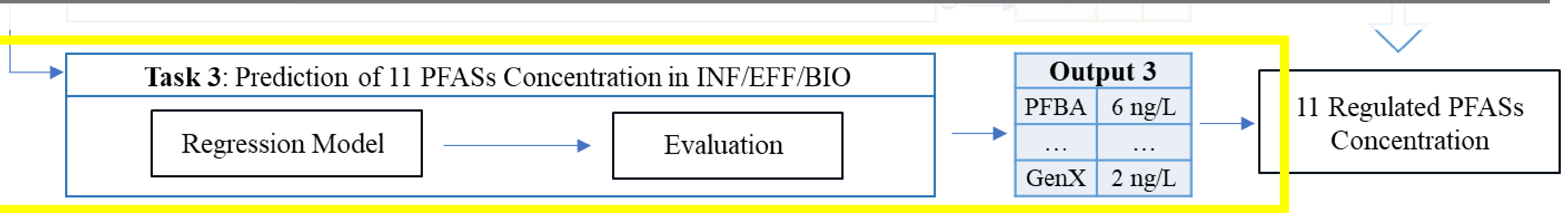


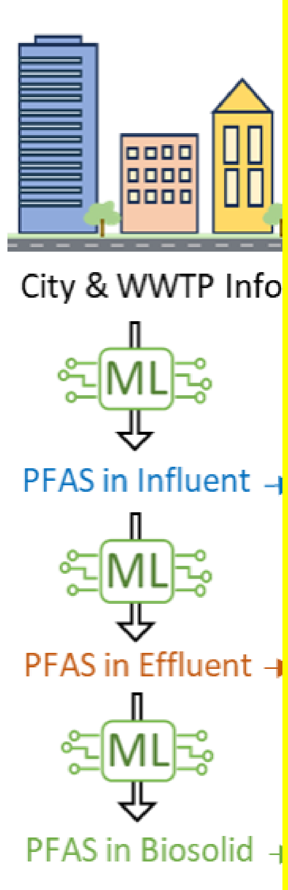


Machine learning to predict concentrations of 11 PFASs (regression)

ML	Input								
Month	Flow	Industrial_W%	Landfills_W	BOD	TSS	Ammonia	Treatment	City_POP	...
1	3.6	20	1	26.40	168	15.5	Level 2	62007	...
12	15.3	5	0	41.80	133	77.4	Level 3	57047	...

XGBoost
Influent: PFHpA, PFBA performed best 0.97 R^2
Effluent: PFHpA, PFBA, PFOS performed best 0.99 R^2
Biosolids: PFHpA, PFOA, PFNA, GenX performed best 0.98 R^2

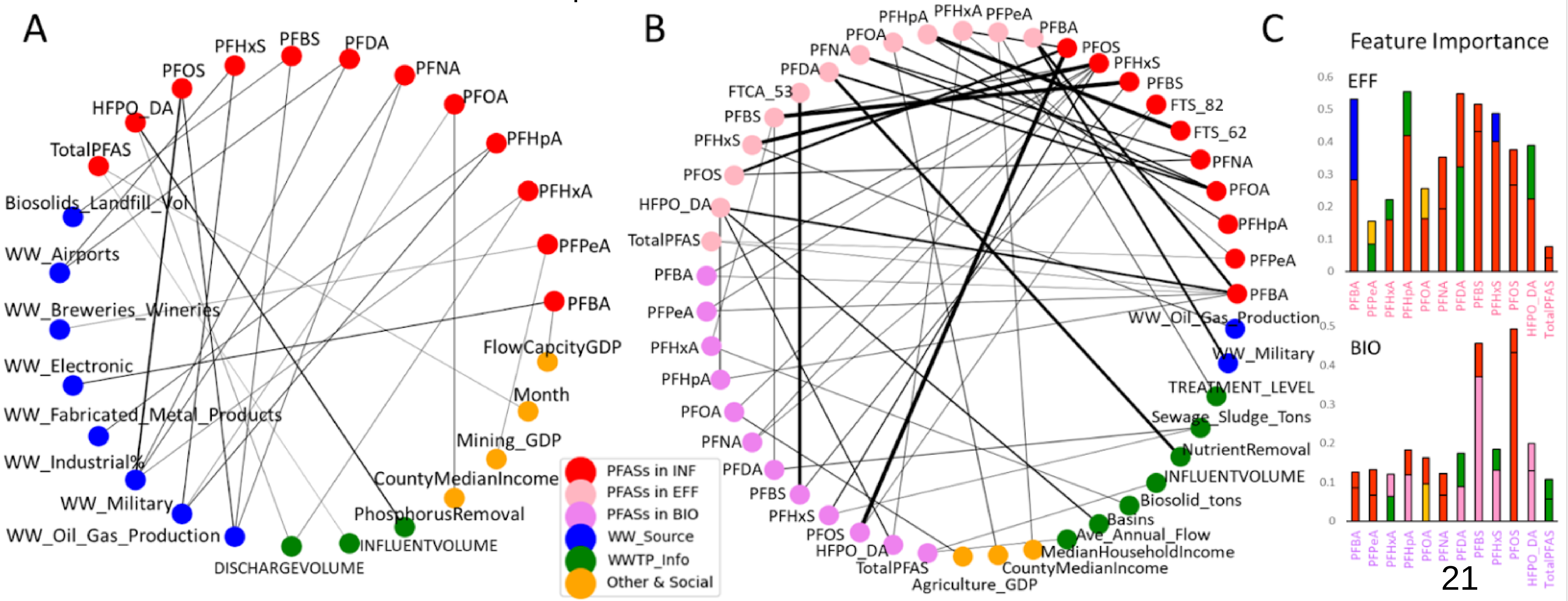




Environmental Variables Influencing PFAS Prediction

- All matrices, **size** and **operational capacity** of WWTPs significant predictors.
- **Wastewater source** impact on the PFAS profile in the influent, as well as the prediction. (e.g., PFBA, electronic waste)
- PFASs in influent → impact effluent PFAS
- PFASs in influent & effluent → impact biosolid PFAS

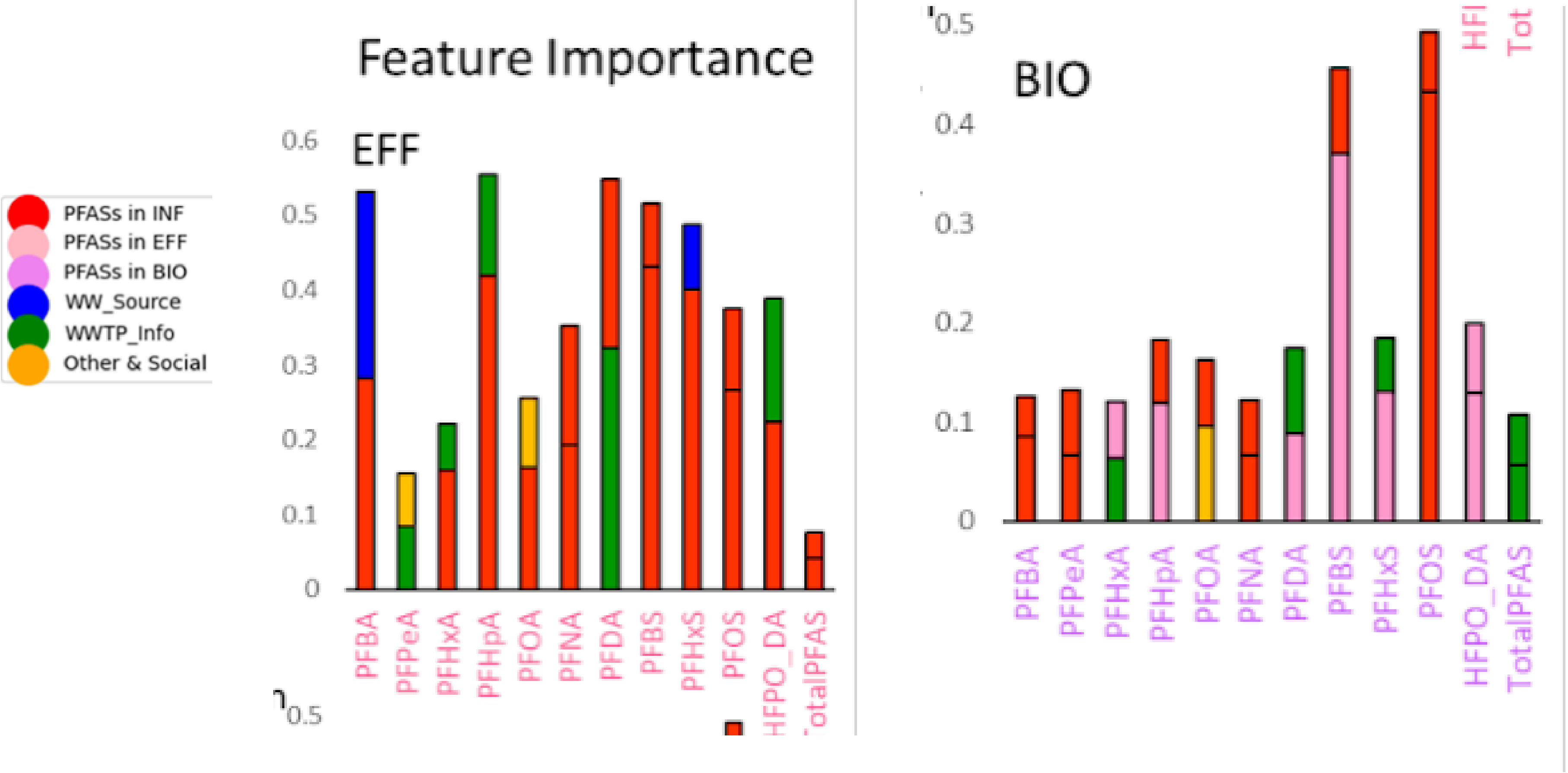
Relative contributions of the top 2 variables for the total and individual PFASs in INF, EFF, and BIO.



Result - Environmental Variables Influencing PFAS Prediction

- Socioeconomic factors (county population and GDP)
- Nutrient removal → PFDA in the effluent.
- Influent PFBA levels → effluent GenX concentrations and GenX in biosolids

Relative contributions of the top 2 variables for the total and individual PFASs in INF, EFF, and BIO.



We’re developing a public website tool

Prediction Tool for PFAS in California WWTPs

Machine Learning for Monitoring Per- and Polyfluoroalkyl Substance (PFAS) in California's Wastewater Treatment Plants: An Assessment of Occurrence and Fate

Jialin Dong[1], Seungjun Kim[2], Sean D. Young[2,3], Chengxi Li[1], Zhichao Jin[4], Dylan Lee [5], and Christopher I. Olivares[1]

[1] Department of Civil and Environmental Engineering, University of California, Irvine, CA
[2] Department of Informatics, University of California, Irvine, CA
[3] Department of Emergency Medicine, University of California, Irvine, CA
[4] Department of Physics and Astronomy, University of California, Irvine, CA
[5] Department of Computer Science, University of California, Irvine, CA

Correspondance: chris.olivares@uci.edu

Paper Link   GitHub Link   Lab Website Link   Data Link

Home
Prediction PFAS for WWTP Influent
Prediction PFAS for WWTP Effluent
Prediction PFAS for WWTP Biosolid

Risk Prediction of Total PFAS in Influent

This ML model classifies PFAS levels in WWTP influent as high risk (1) if they exceed 70 nanograms per liter (ng/L), and low risk (0) if they fall below this threshold. The model utilizes commonly monitored standard operational parameters of WWTPs as inputs, including: year, month, influent/effluent volumes, industrial wastewater intake, total organic carbon (TOC), ammonia, biochemical oxygen demand (BOD), carbonaceous biochemical oxygen demand (CBOD), flow rate, pH, total dissolved solids (TDS), and total suspended solids (TSS).

When using the model, please ensure that all inputs are in the correct format. Input values should strictly be numerical floats; avoid using letters or non-numeric characters. The default values visible upon loading the website are set to median values derived from the dataset used during model training. These defaults serve as starting points for predictions and can be adjusted based on your specific input data.

Select a Year

2024 − +

Select a Month

January

Flow in Influent (The flow rate of the influent to the facility (MGD))

3.1334

Influent Volume (acre-feet/month)

387

Discharge Volume in Influent (acre-feet/month)

169.25

Biochemical Oxygen Demand in Influent (BOD was measured in 5 days at 20 deg. C (ng/L))

255668102.2

Carbonaceous Biochemical Oxygen Demand in Influent (CBOD was measured in 5 days at 20 deg. C (ng/L))

645000000

Total Dissolved Solids in Influent (TDS (ng/L))

507170067

Total Organic Carbon in Influent (TOC (ng/L))

16043614

Total Suspended Solids in Influent (TSS (ng/L))

240900372.8

pH of Influent

7.0

Make Prediction

The PFAS risk is greater than 70 nanograms per liter (70 ng/L).

WWTP_PFAS_prediction_website

Summary and Key Points

- Database of PFAS WWTP concentrations, other effluent quality parameters, socioeconomic factors
- PFAS profiles vary depending on matrix (transformation, sorption)
- Classification models (threshold) had highest accuracy for sum of PFAS predictions
- Concentration prediction worked for frequently detected PFAS
- Key predictive factors: WWTP size, wastewater source, county population, and GDP.

- Data and (data validation) is key

Acknowledgements

Olivares Lab

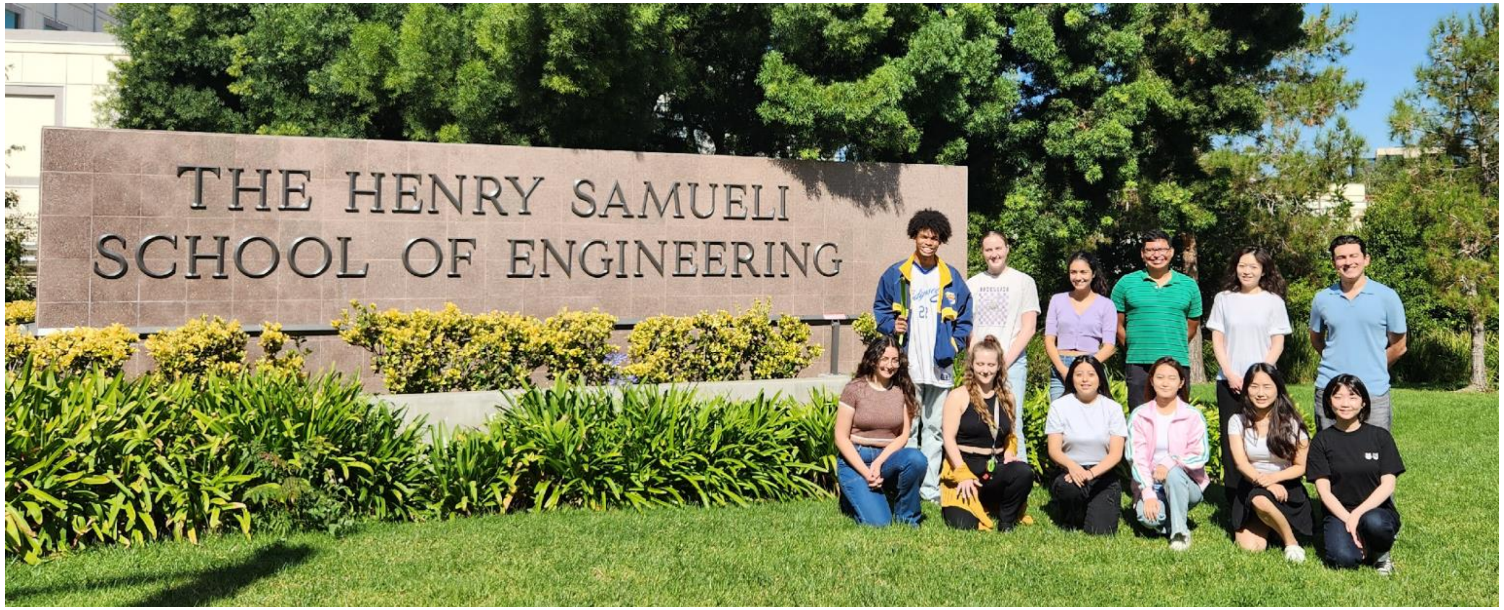
Graduate Students
Jialin Dong
Zixin Hu
Meng-Chia Li
Theodore Jagodits
Seungjun Kim
Sachin Thyaharajan

Undergraduate Students
Takumi Takasugi
Steven Li
Xiaojun Tang
Nicolas Villota
Zhichao Jin
Dylan Lee
Manulya Gunasekera

Jialin Dong

Funding

Startup funds for C. Olivares



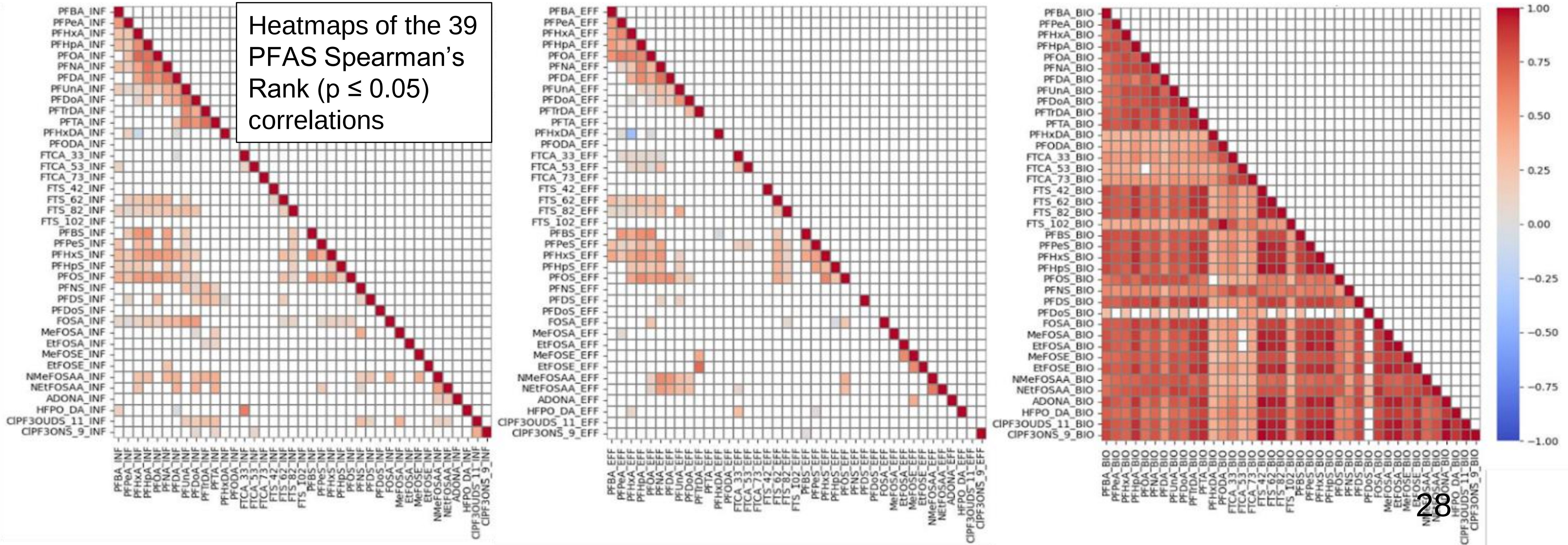
Applications of Machine Learning Approaches to Predict PFAS Profiles and Fate in Wastewater

Christopher I. Olivares
chris.olivares@uci.edu

Department of Civil and Environmental Engineering
University of California, Irvine

Result - California WWTPs PFAS Analysis

- **Positive correlations** observed among various PFASs □ sources or similar properties.
- Strong correlations (>0.6) among short-chain PFCAs, longer-chain C8–C10 PFCAs, and PFSAs with similar chain lengths;
- Effluent patterns mirror those in influent, with clearer correlations between C4–C9 PFCAs and C4–C8 PFSAs (biotransformation pathways, e.g., FTSs to PFCAs)
- Biosolids show strong correlations, C9-C13 PFCAs (correlation coefficients >0.75) (a tendency for these compounds to accumulate in the solid phase) longer chain lengths and greater affinity for solids.



Heatmaps of the 39 PFAS Spearman's Rank (p ≤ 0.05) correlations

Result - Prediction of total PFAS risk in INF, EFF, and BIO

- Developed a machine learning model with limited input features that consistently predicts total, with minor performance drops
- **CatBoost**, fine-tuned with SMOTE oversampling, outperformed other models in predicting PFAS concentrations

 Optimized CatBoost model to serve as a reliable tool for WWTP monitoring, even with fewer variables, suggesting broad applicability for PFAS risk prediction

Performance evaluation of total PFAS classification ML in INF, EFF, BIO

		GaussianNB	LR	SVC	XGBoost	LGBM	CatBoost	TabNet	RF	LDA	QDA	KNN	GP	AdaBoost
Total PFAS in INF	accuracy	0.274	0.237	0.656	0.699	0.737	**0.742**	0.763	0.710	0.522	0.280	0.650	0.753	0.237
	recall	0.493	0.500	0.555	0.591	0.631	0.627	0.500	0.606	0.475	0.520	0.583	0.681	0.500
	precision	0.484	0.118	0.549	0.588	0.634	0.636	0.382	0.603	0.481	0.572	0.568	0.666	0.118
	f1 score	0.256	0.191	0.550	0.590	0.632	**0.631**	0.433	0.604	0.459	0.255	0.569	0.673	0.191
	AUROC	0.483	0.500	0.508	0.651	0.638	**0.663**	0.500	0.661	0.515	0.570	0.648	0.741	0.493
Total PFAS in EFF	accuracy	0.500	0.500	0.624	0.699	0.710	**0.737**	0.495	0.688	0.554	0.511	0.640	0.634	0.489
	recall	0.500	0.500	0.624	0.699	0.710	0.737	0.495	0.688	0.554	0.511	0.640	0.634	0.489
	precision	0.500	0.240	0.630	0.701	0.716	0.745	0.249	0.694	0.445	0.515	0.643	0.641	0.373
	f1 score	0.425	0.333	0.619	0.698	0.708	**0.734**	0.331	0.686	0.445	0.474	0.638	0.630	0.338
	AUROC	0.482	0.500	0.633	0.805	0.787	**0.833**	0.495	0.771	0.564	0.536	0.688	0.657	0.485
Total PFAS in BIO	accuracy	0.543	0.468	0.629	0.780	0.769	**0.780**	0.516	0.731	0.586	0.581	0.699	0.640	0.349
	recall	0.513	0.500	0.619	0.779	0.769	0.779	0.486	0.732	0.575	0.556	0.698	0.627	0.342
	precision	0.603	0.234	0.632	0.779	0.768	0.779	0.362	0.731	0.585	0.639	0.698	0.653	0.334
	f1 score	0.391	0.319	0.615	0.779	0.768	**0.779**	0.350	0.731	0.567	0.491	0.698	0.617	0.335
	AUROC	0.555	0.500	0.659	0.830	0.833	**0.836**	0.486	0.803	0.640	0.586	0.740	0.714	0.357

PFAS leachability from contaminated pavement materials

Prashant Srivastava

Australia's National Science Agency

CSIRO

CSIRO-Defence PFAS Research Program

Objectives

To understand:

- the presence of PFAS in relevant concrete and asphalt infrastructure and spatial and vertical distribution
- the potential water leachability of PFAS from concrete and asphalt materials

Identify and assess management strategies and/or mitigation approaches for PFAS leaching in concrete and asphalt materials for recycling, repurposing and/or reuse (on-site/off-site)

CSIRO

How do PFAS get into concrete and asphalt?

https://www.pdsigns.ie/contentFiles/productImages/Large/FS
K2.jpg

https://content.presspage.com/uploads/1912/1920_firescienceprogram-pastliveburnexercise-dmcwestcampus.jpg?10000

https://gray-wilx-prod.cdn.arcpublishing.com/resizer/yOGIGwD3nxnkJDSMfkDzHjuXnTg=/1200x675/smart/cloudfront-us-east-1.images.arcpublishing.com/gray/O5CSQV4ALZJJXPDSUCZPI4GHOE.jpg

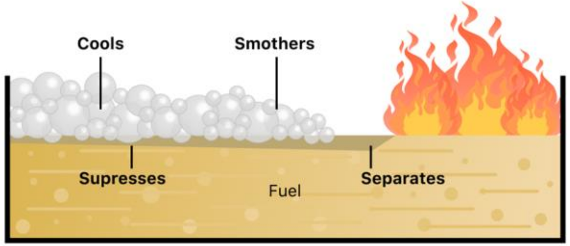
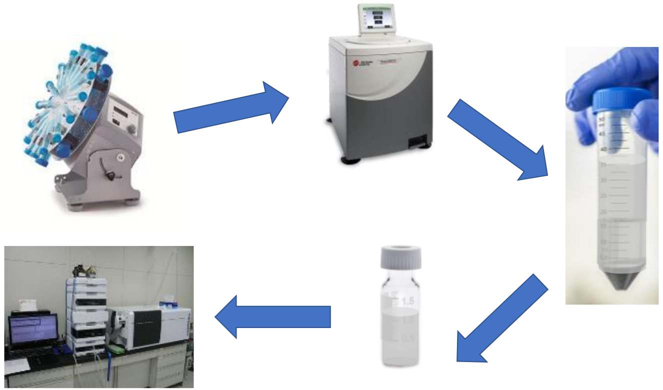


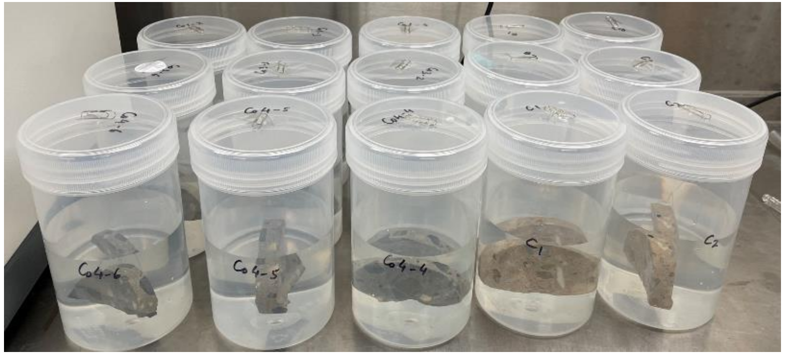
Image source: https://www.consumernotice.org/environmental/afff/

CSIRO

Leaching Approaches

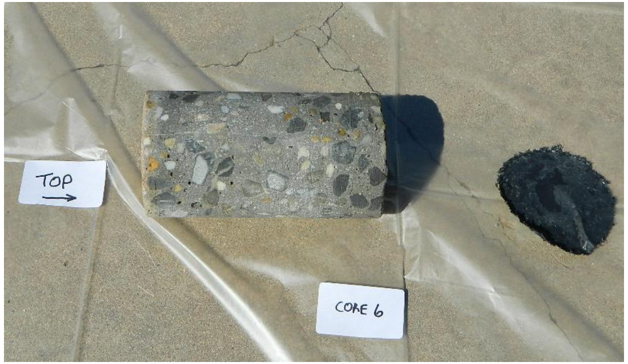
- Australian Standard Leaching Protocol (ASLP)
  - Leaching period
  - Particle size
  - Temperature
- Leaching Environmental Assessment Framework (LEAF) 1313
  - pH
- Leaching Environmental Assessment Framework (LEAF) 1315
  - Intact monolith
  - Normally over 9 weeks

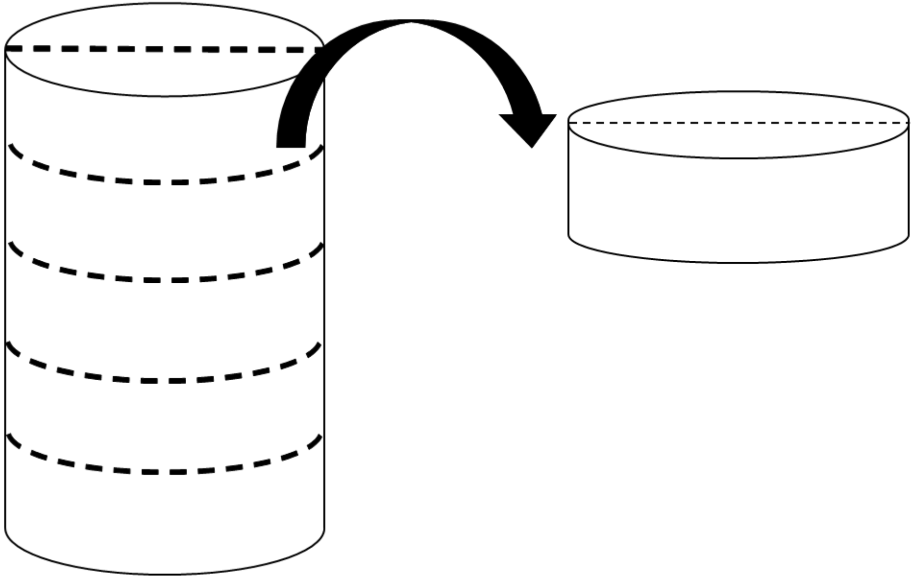




CSIRO

Sampling of PFAS-contaminated pavements





CSIRO

Concrete core characterisation

Core No.	Replicate	PFHxA	PFOA	PFHxS	PFOS	PFHxS + PFOS
		(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
Core 3	R1	**19**	313	408	553	962
Core 3	R2	26	273	390	673	1063
Core 3	R3	39	42	155	511	666
Core 1	R1	37	**28**	**140**	**458**	599
Core 1	R2	39	32	155	475	629
Core 1	R3	57	412	533	824	1357
Core 4	R1	34	**939**	**1013**	1067	2081
Core 4	R2	50	834	919	**1137**	2056
Core 4	R3	**76**	309	611	778	1390

Low **Intermediate** **High**

CSIRO

Asphalt core characterisation

Core No.	Replicate	PFHxA	PFOA	PFHxS	PFOS	PFHxS + PFOS
		(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
Core 2	R1	13	7	41	492	533
Core 2	R2	7	6	23	219	242
Core 4	R1	12	8	43	469	512
Core 4	R2	12	9	40	471	511
Core 6	R1	5	2	6	54	60
Core 6	R2	7	3	8	58	66

Low **Intermediate** **High**

CSIRO

PFAS leaching from intact concrete and asphalt

CSIRO

PFAS leaching from intact concrete and asphalt

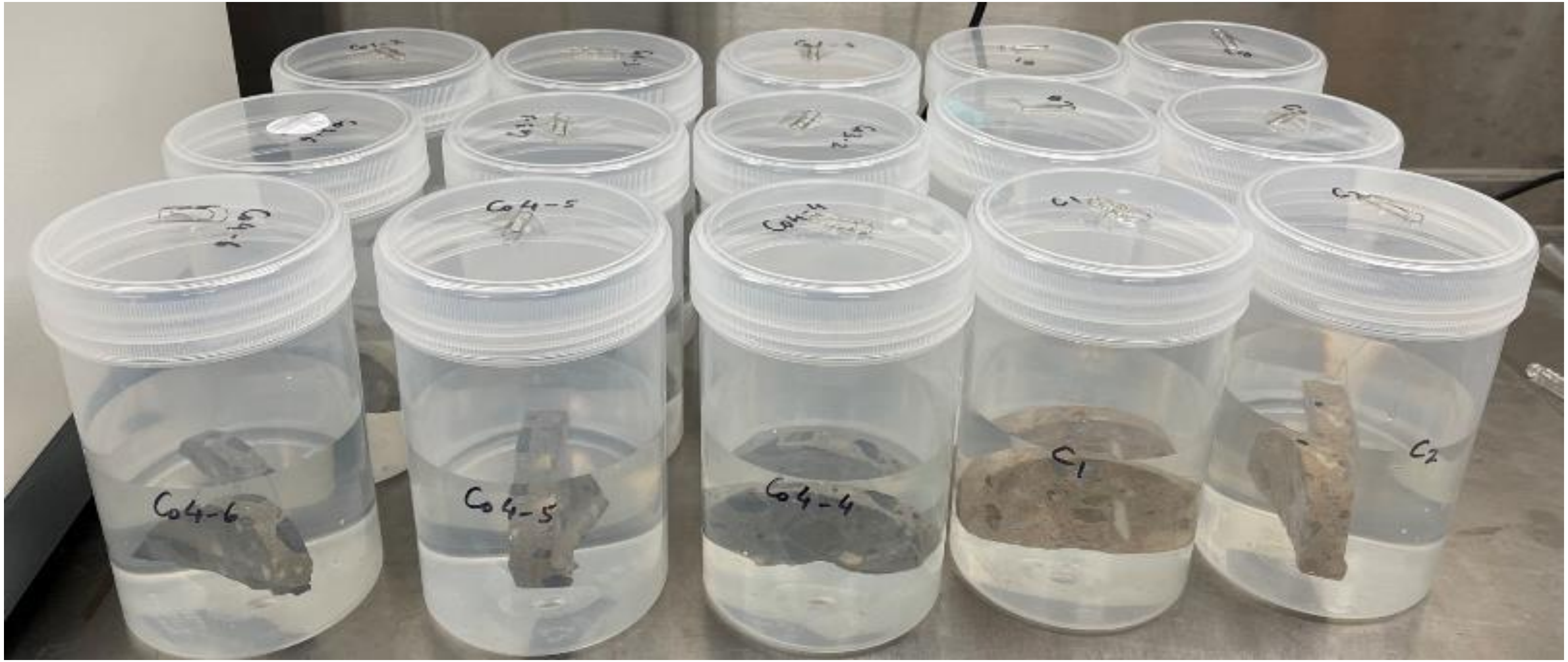
Leaching Environmental Assessment Protocol (LEAF) 1315

- Originally developed for inorganic contaminants (e.g. metals) and matrices such as soils, fly ash etc.
- Optimisation and validation required for PFAS and concrete/asphalt
- Current SERDP project (ER23-37611)
  - Texas Tech University – Jenn Guelfo
  - Vanderbilt University – David Kosson
  - University of Wisconsin – Craig Benson
  - CSIRO – Prashant Srivastava

CSIRO

PFAS leaching from intact concrete and asphalt

Leaching Environmental Assessment Framework (LEAF) 1315



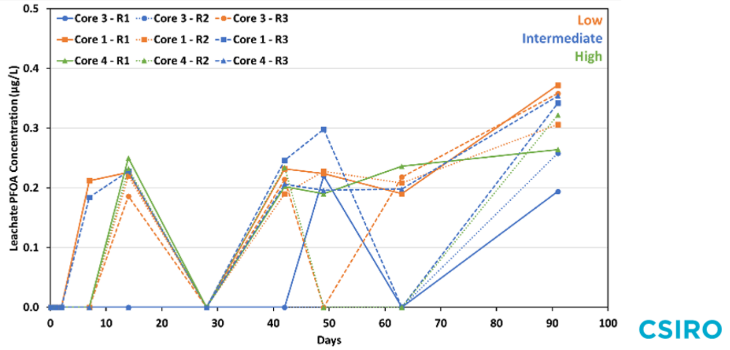
PFAS leaching from intact concrete and asphalt

Leaching Environmental Assessment Framework (LEAF) 1315

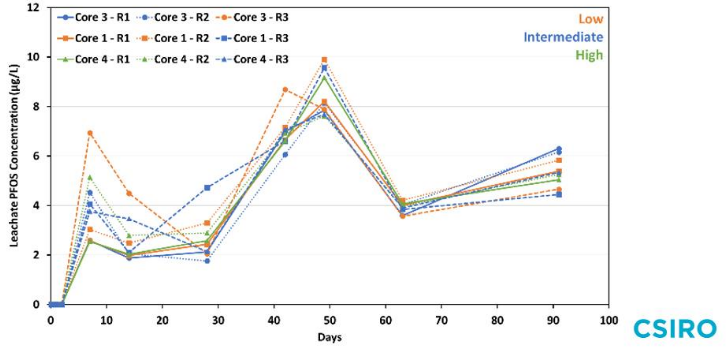
Interval	Interval Duration (h)	Interval Duration (d)	Cumulative leaching time (d)
T01	2.0 ± 0.25	–	0.08
T02	23.0 ± 0.5	–	1
T03	23.0 ± 0.5	–	2
T04	–	5.0 ± 0.1	7
T05	–	7.0 ± 0.1	14
T06	–	14.0 ± 0.1	28
T07	–	14.0 ± 0.1	42
T08	–	7.0 ± 0.1	49
T09	–	14.0 ± 0.1	63
T09	-	28 ± 0.1	91

Leachate PFAS concentration (intact concrete)

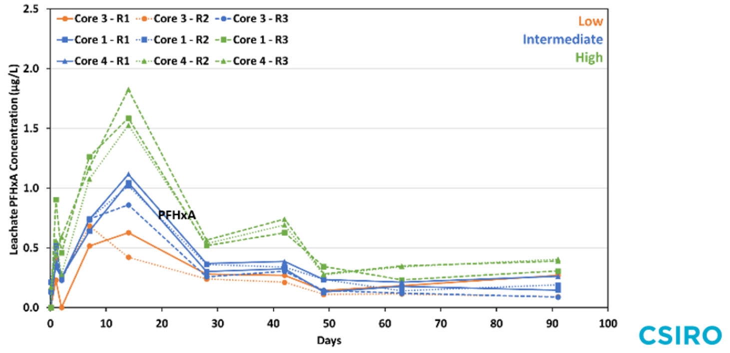
Leachate PFOA concentration (intact concrete)



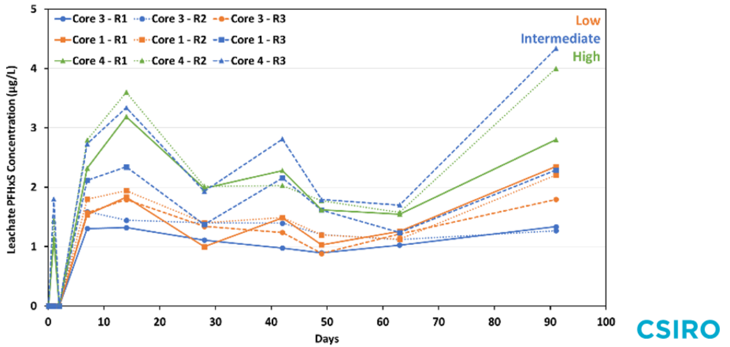
Leachate PFOS concentration (intact concrete)



Leachate PFHxA concentration (intact concrete)



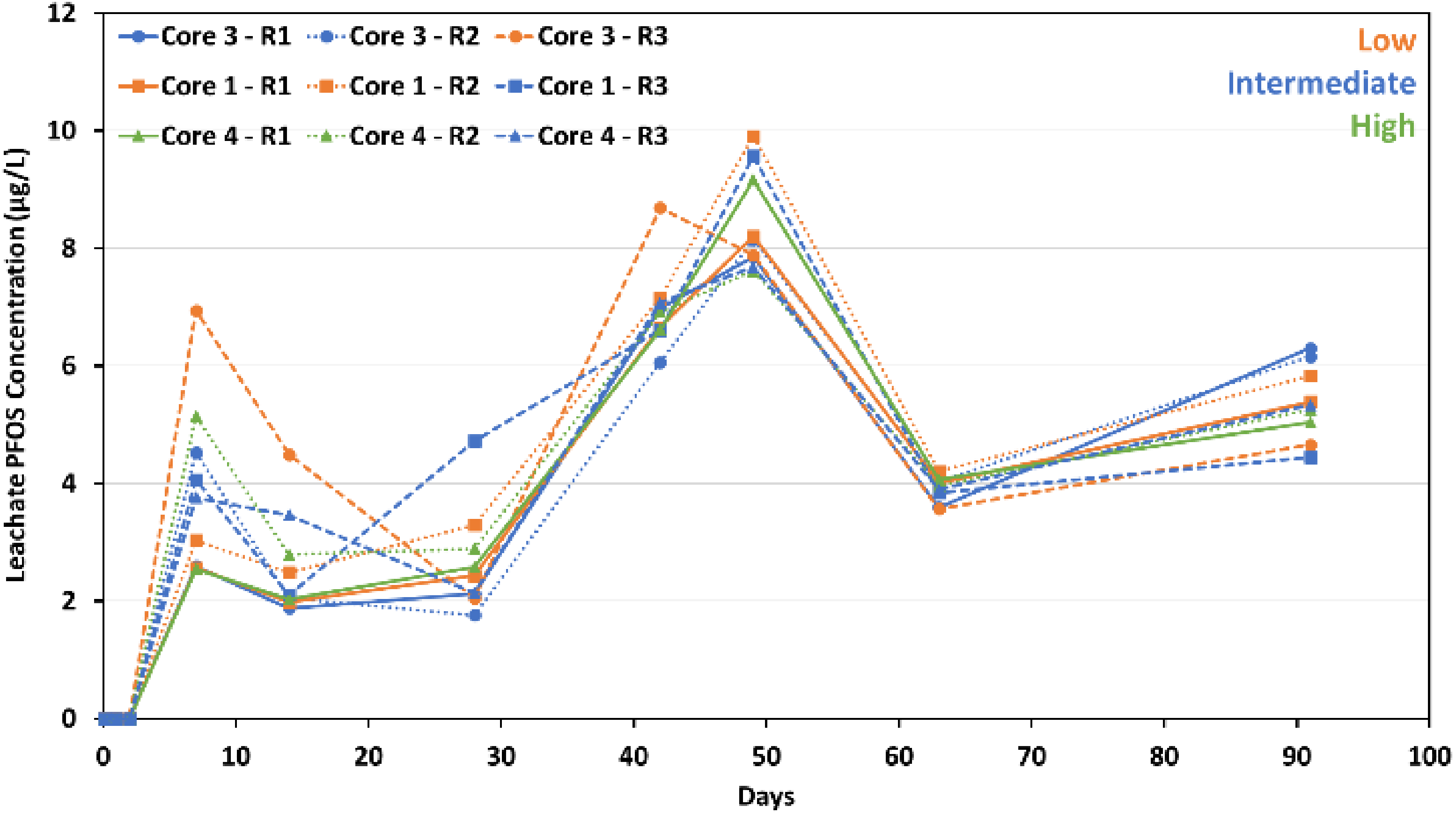
Leachate PFHxS concentration (intact concrete)



Similar pattern irrespective of initial PFAS concentration in the concrete (low, intermediate and high).

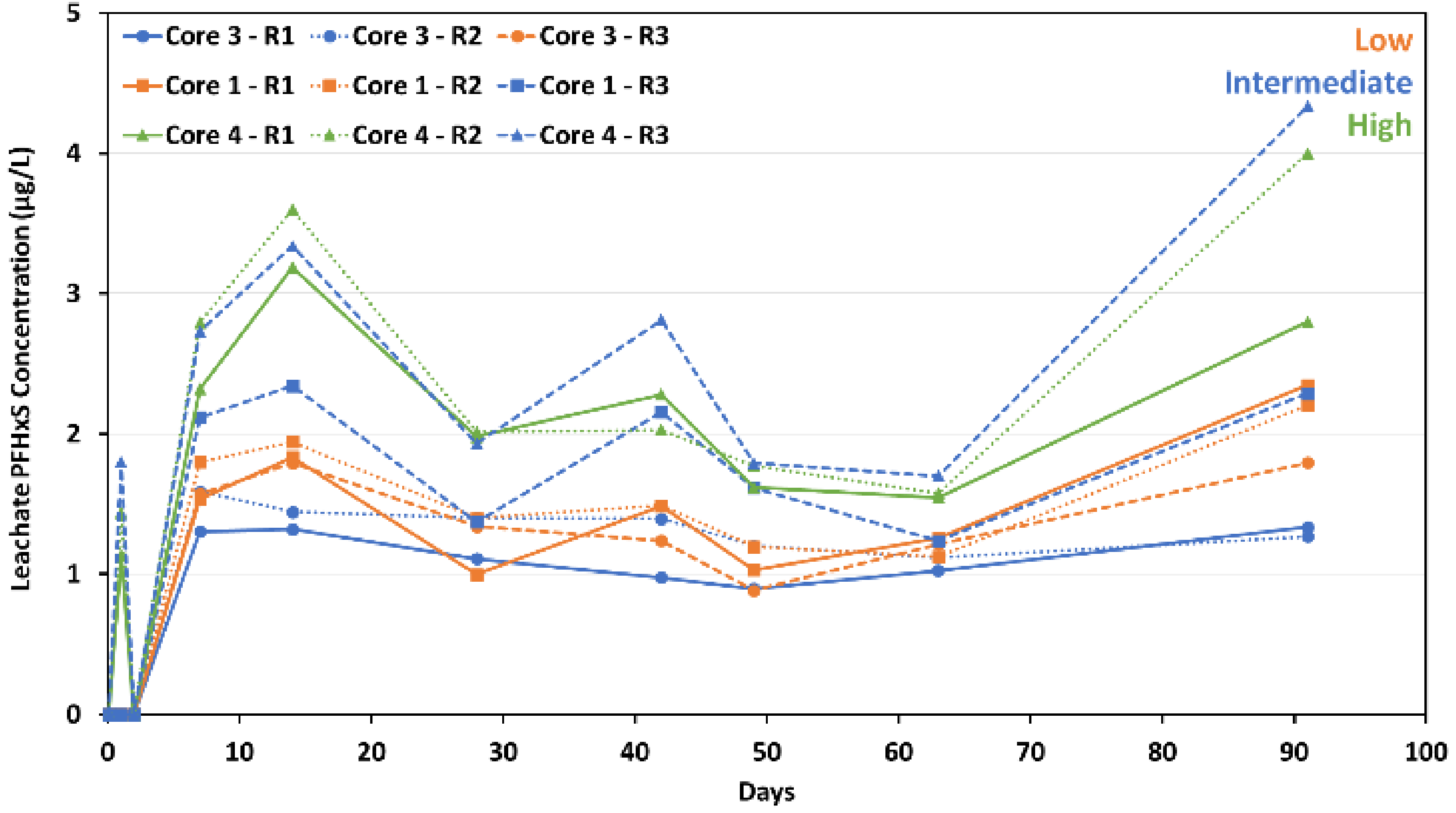
CSIRO

Leachate PFOS concentration (intact concrete)



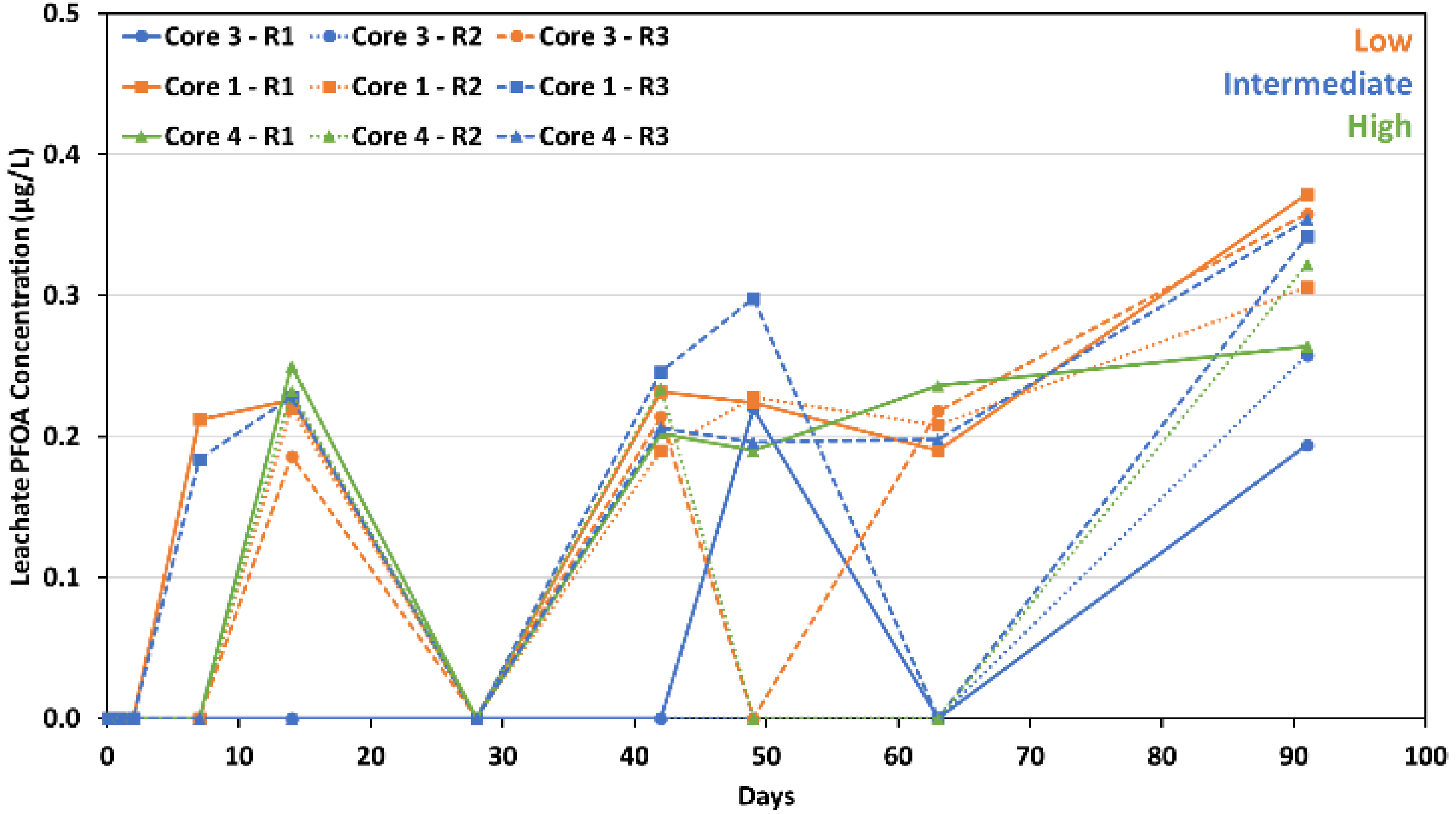
CSIRO

Leachate PFHxS concentration (intact concrete)



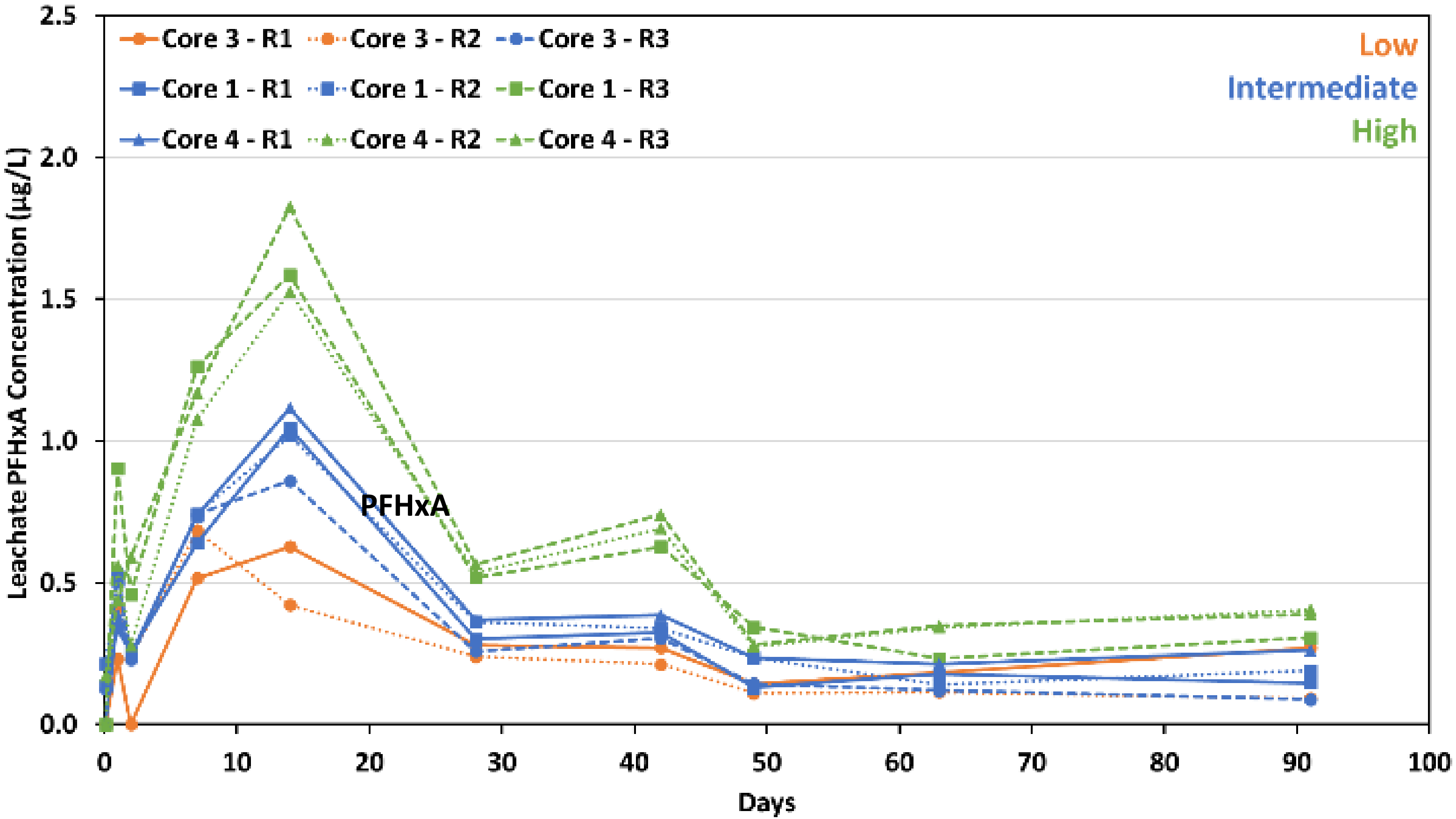
CSIRO

Leachate PFOA concentration (intact concrete)



CSIRO

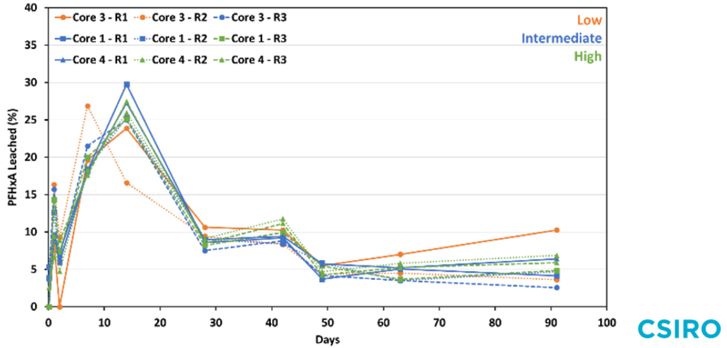
Leachate PFHxA concentration (intact concrete)



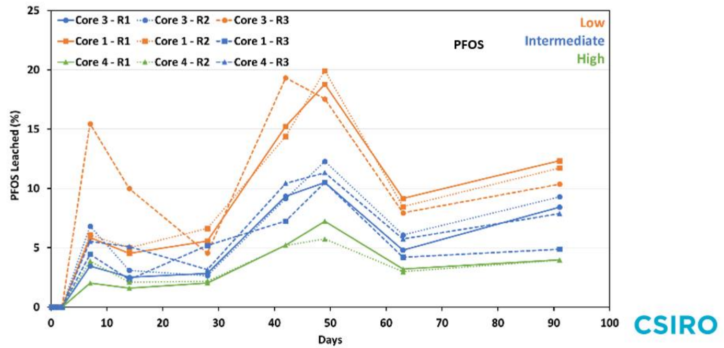
CSIRO

Proportion of PFAS leached from intact concrete

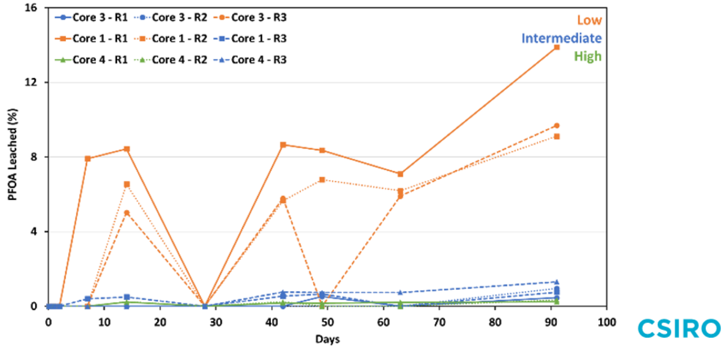
Proportion of PFHxA leached from intact concrete



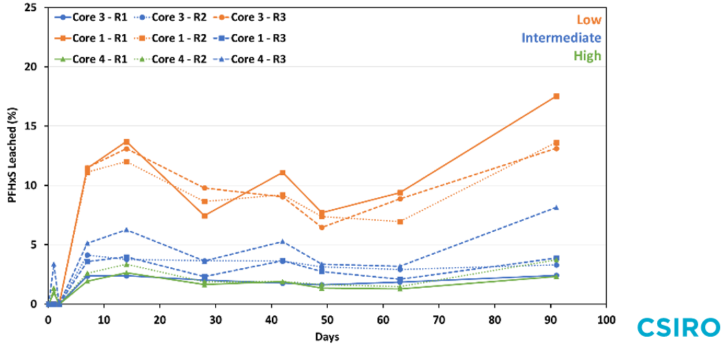
Proportion of PFOS leached from intact concrete



Proportion of PFOA leached from intact concrete



Proportion of PFHxS leached from intact concrete



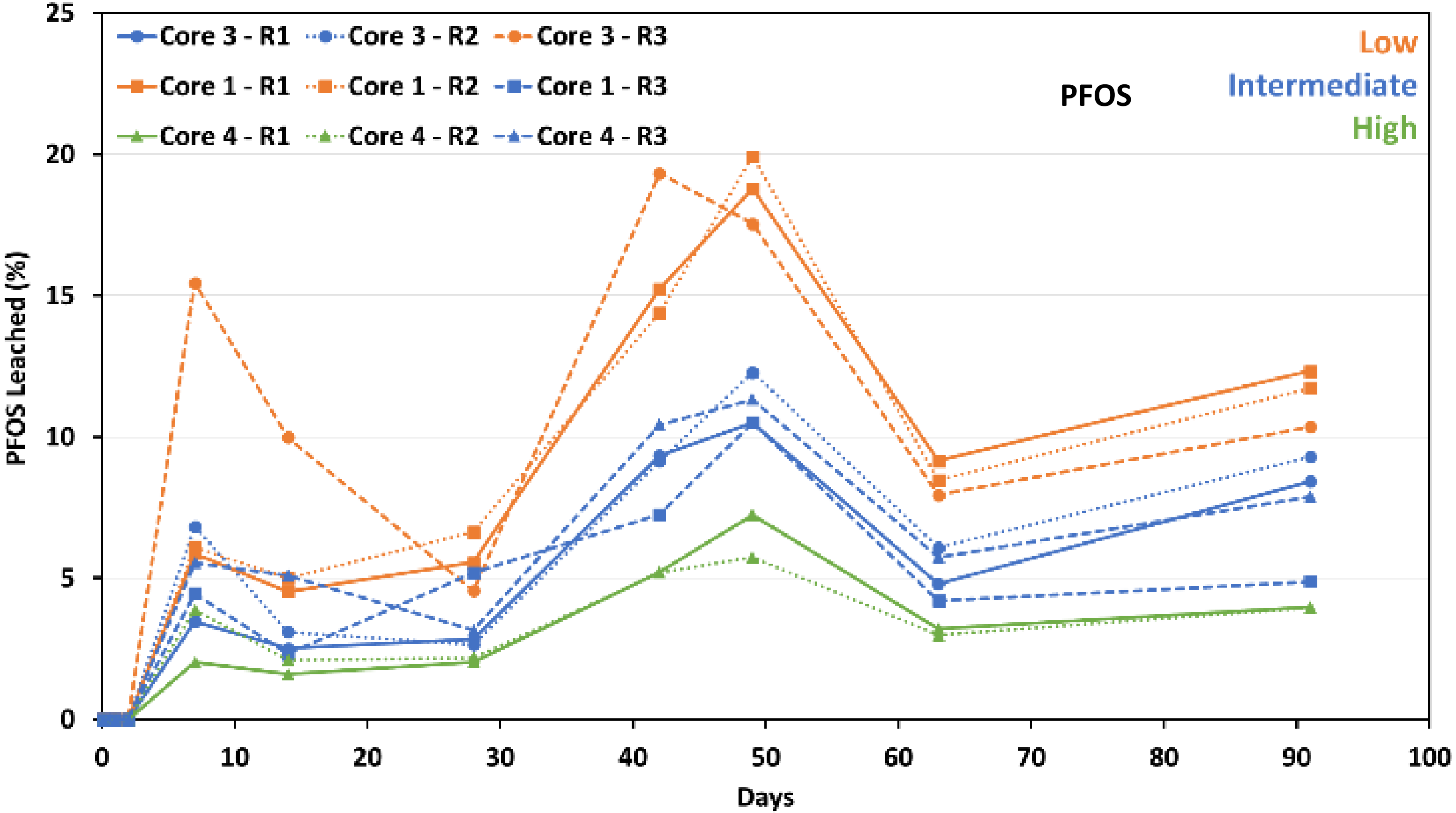
Long-chain PFAS

Concentration ↑

Leaching ↓

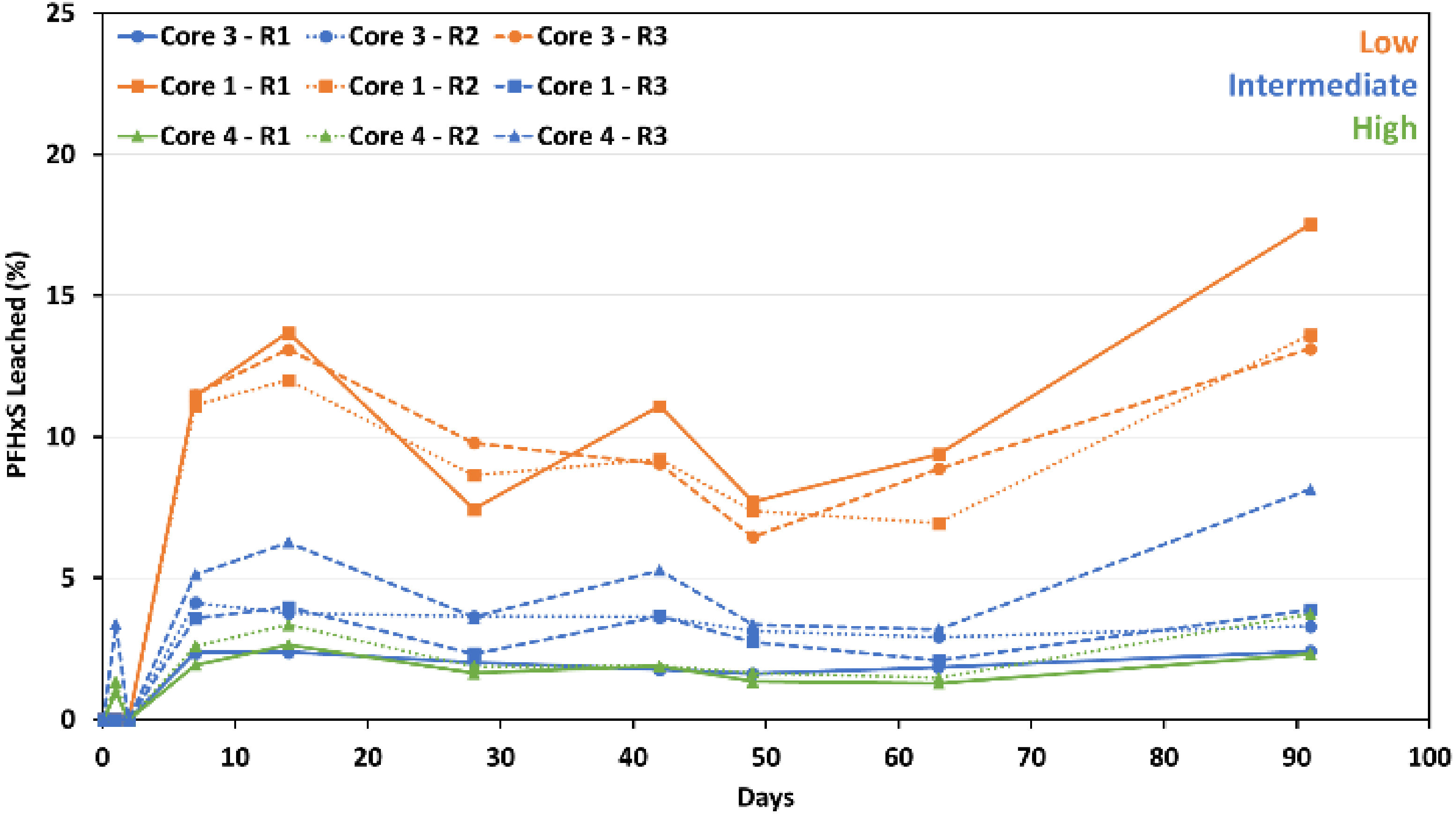
CSIRO

Proportion of PFOS leached from intact concrete



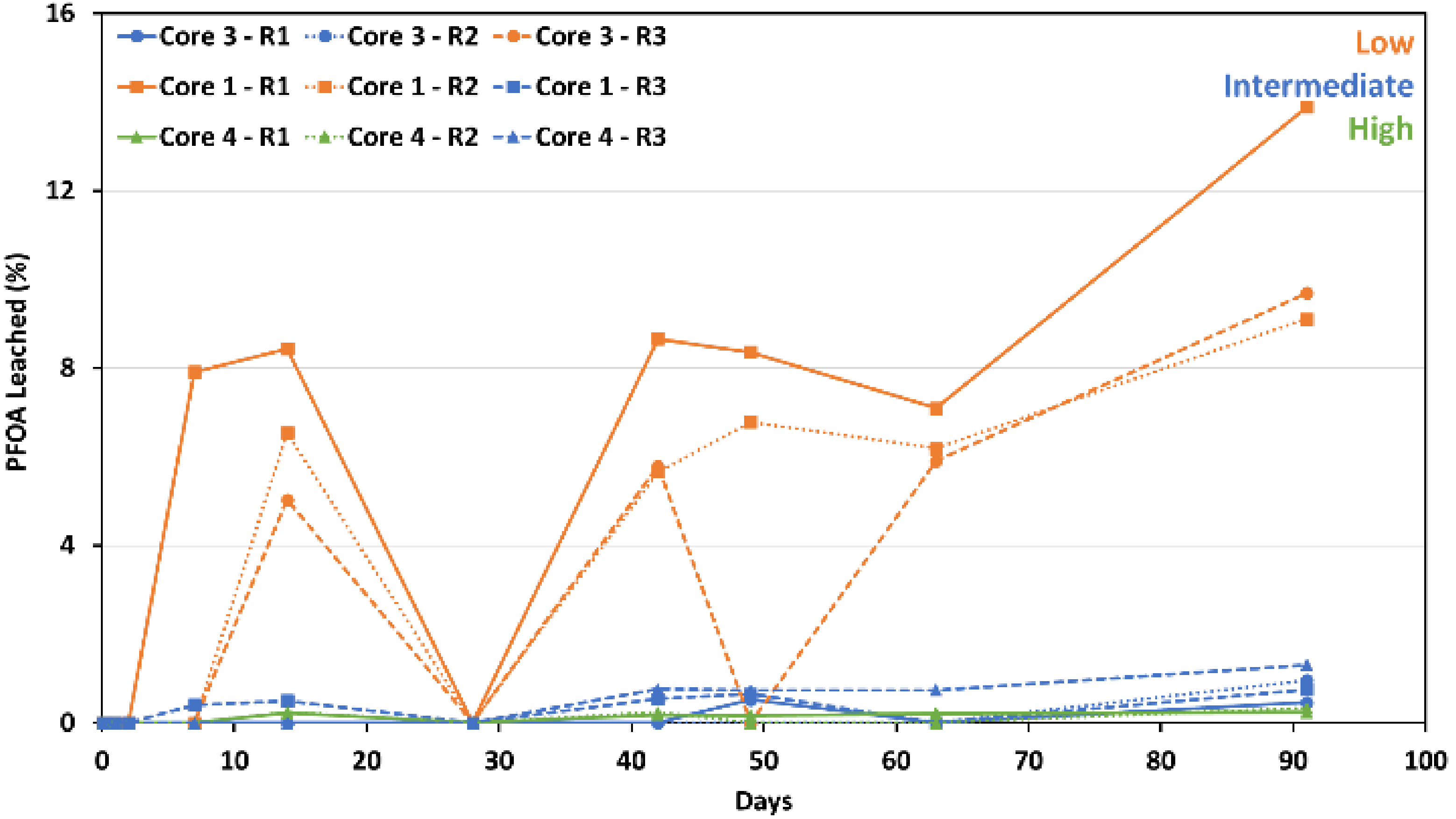
CSIRO

Proportion of PFHxS leached from intact concrete



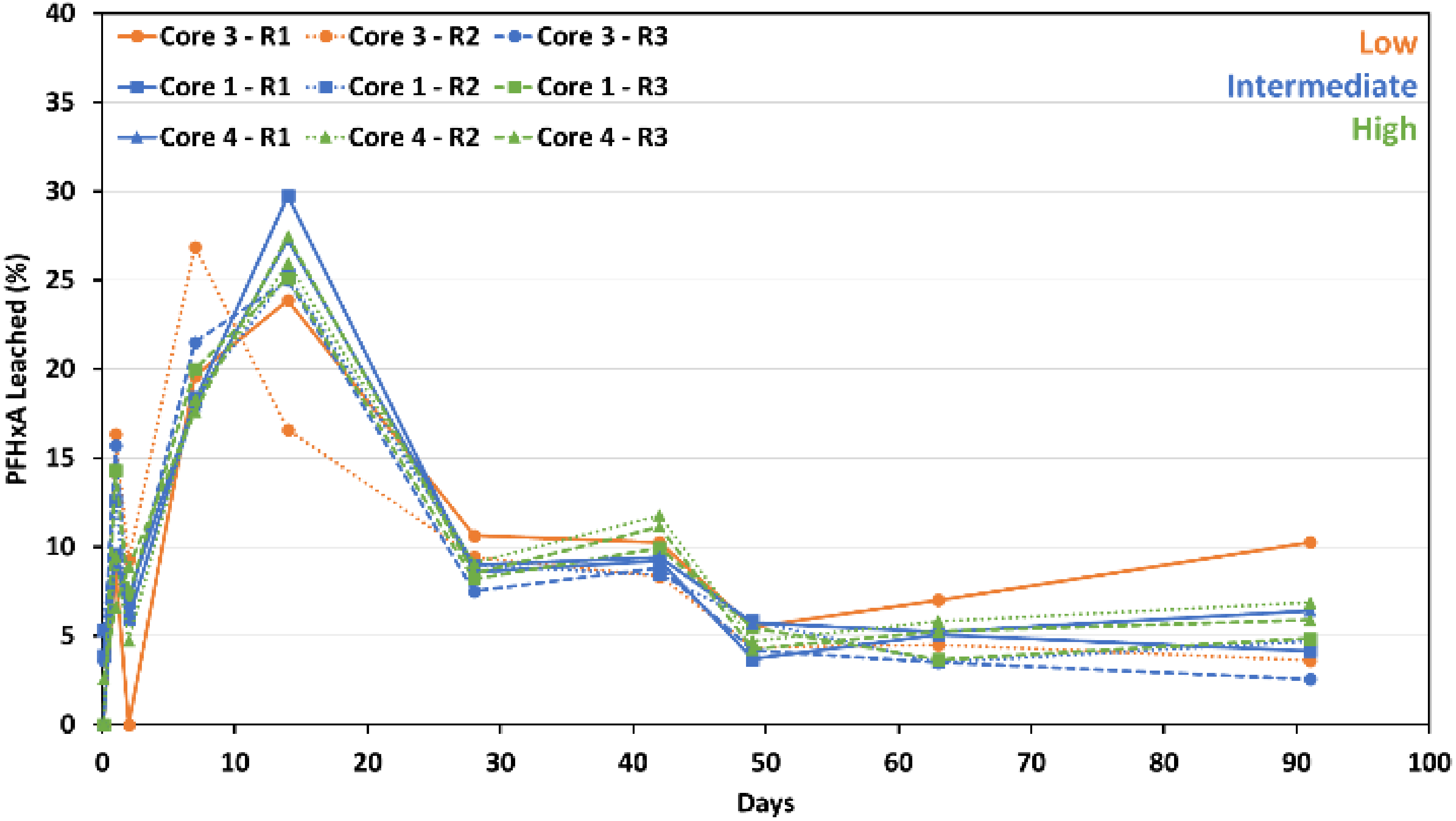
CSIRO

Proportion of PFOA leached from intact concrete



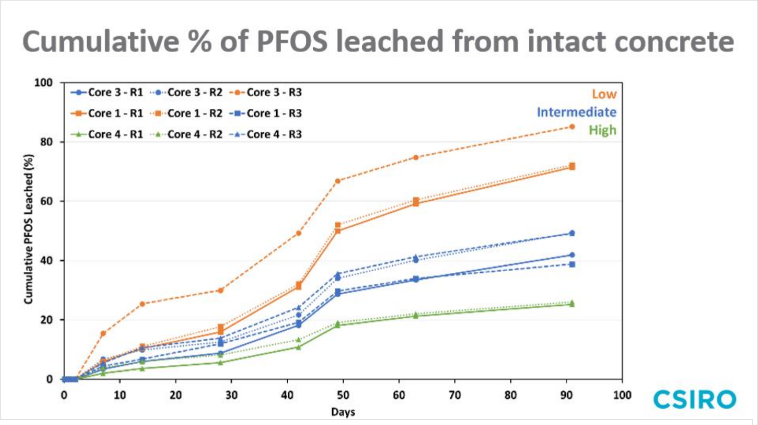
CSIRO

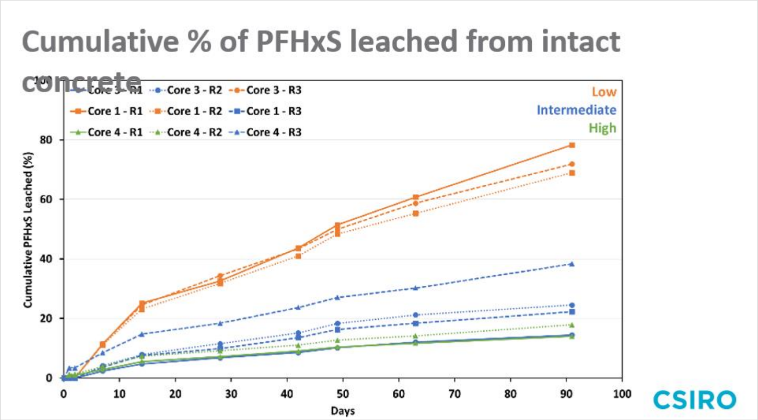
Proportion of PFHxA leached from intact concrete

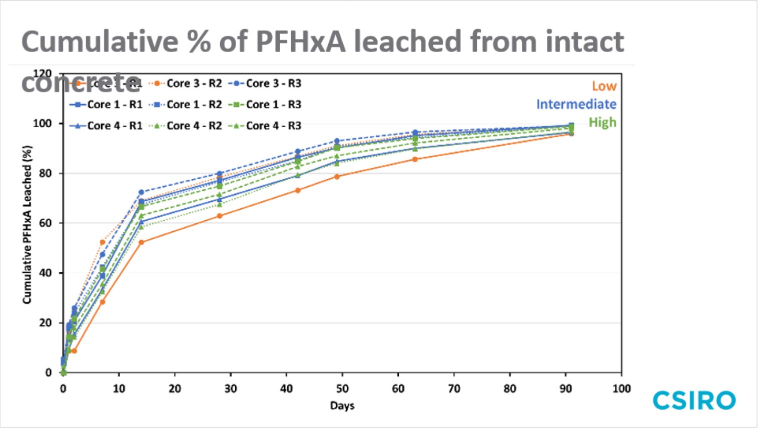


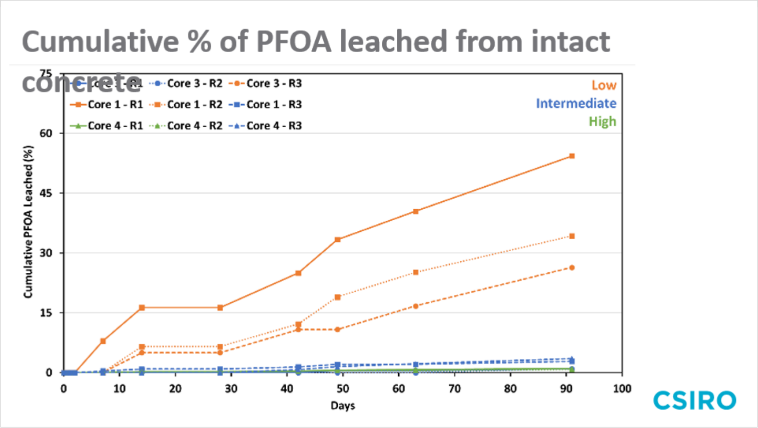
CSIRO

Cumulative % of PFAS leached from intact concrete









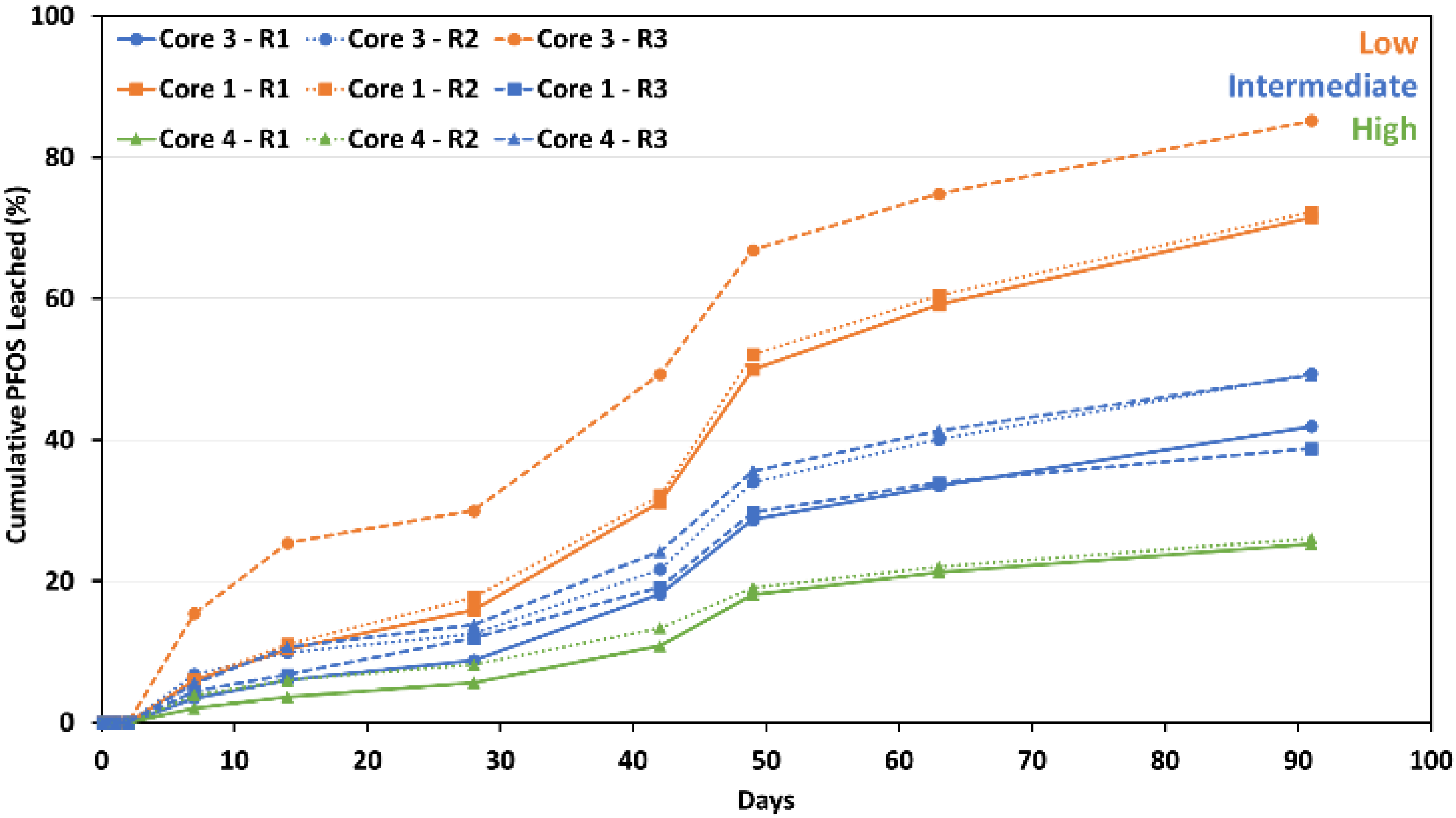
Long-chain PFAS

Concentration ↑

Leaching ↓

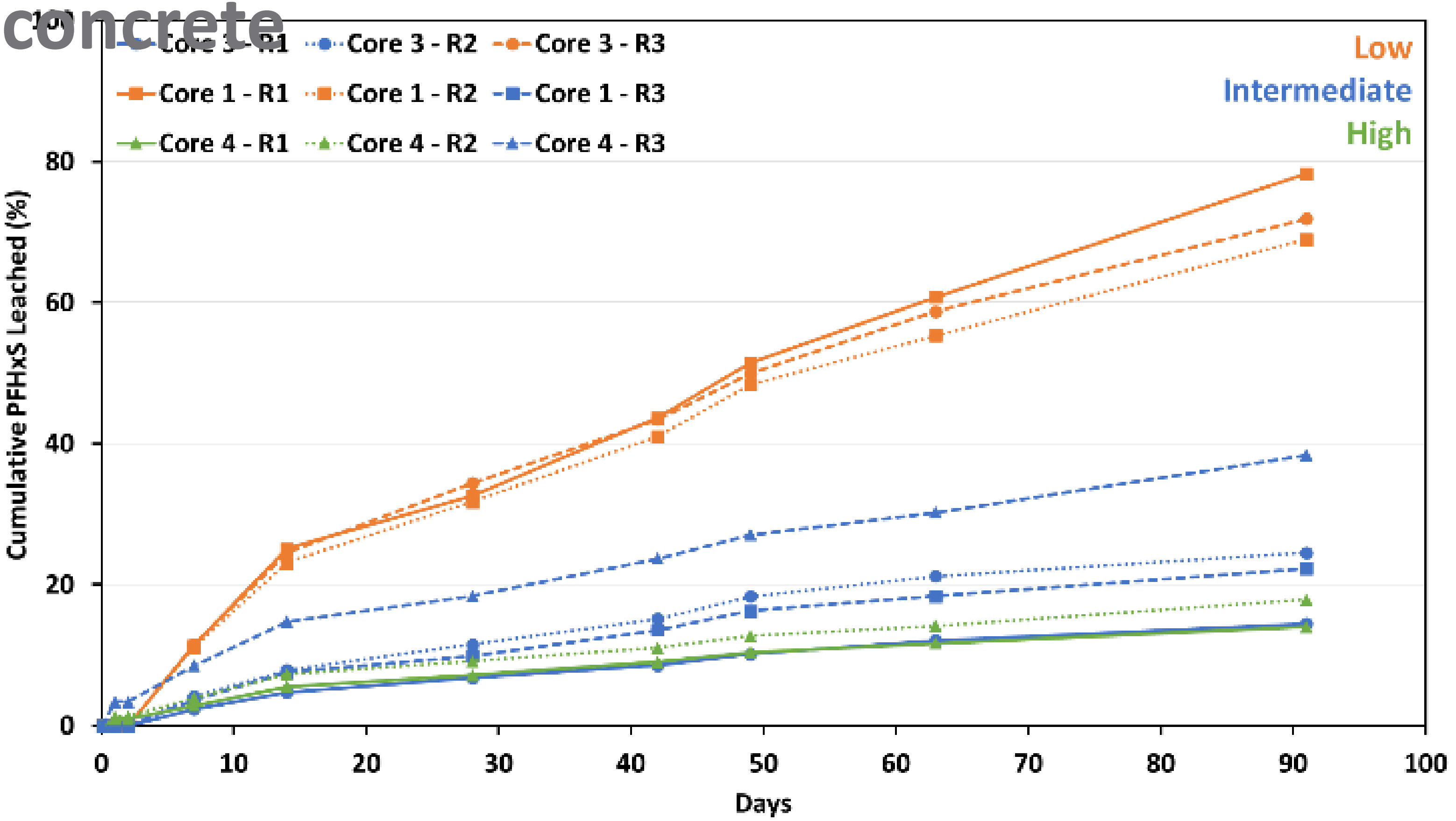
CSIRO

Cumulative % of PFOS leached from intact concrete



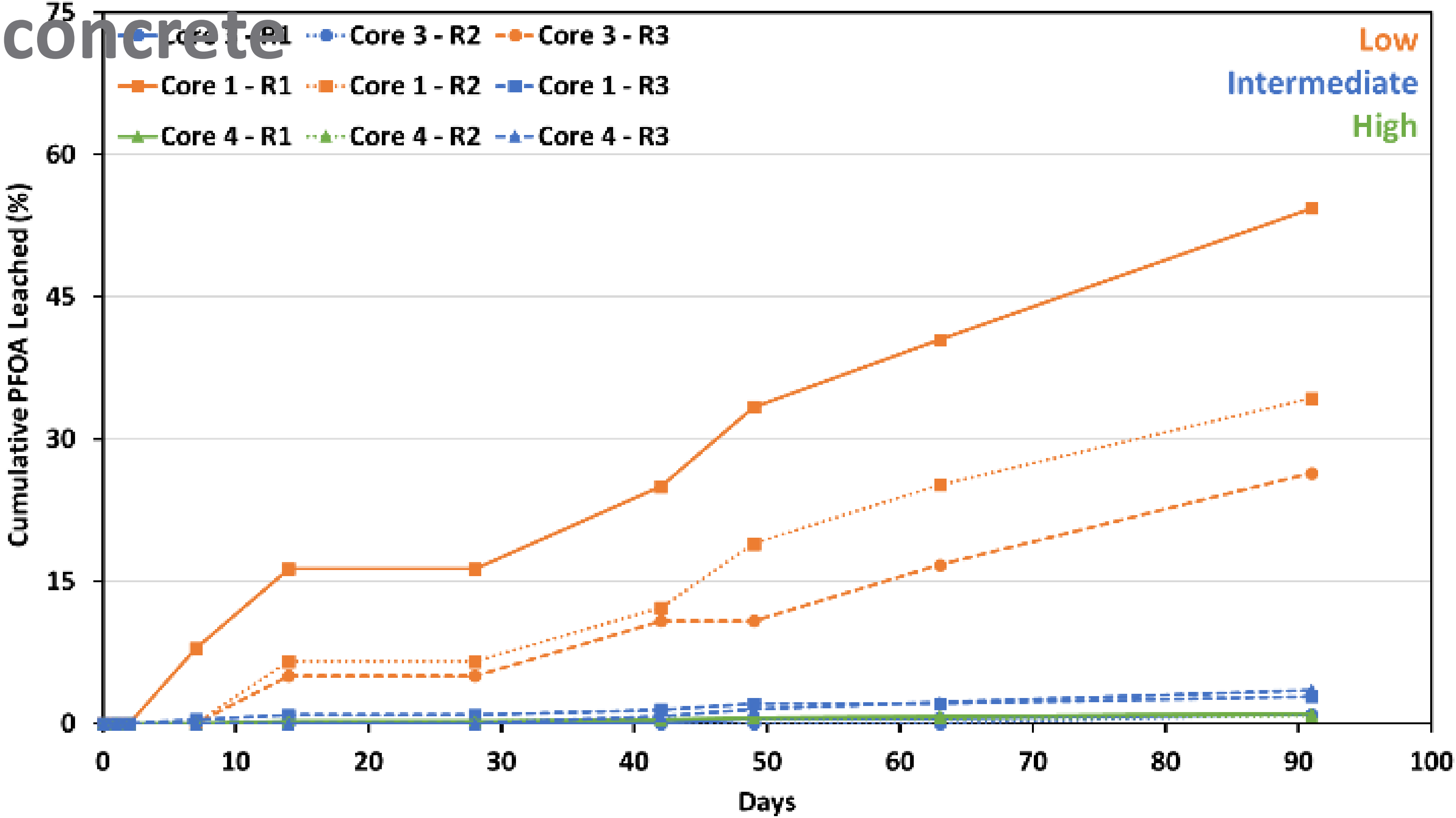
CSIRO

Cumulative % of PFHxS leached from intact concrete



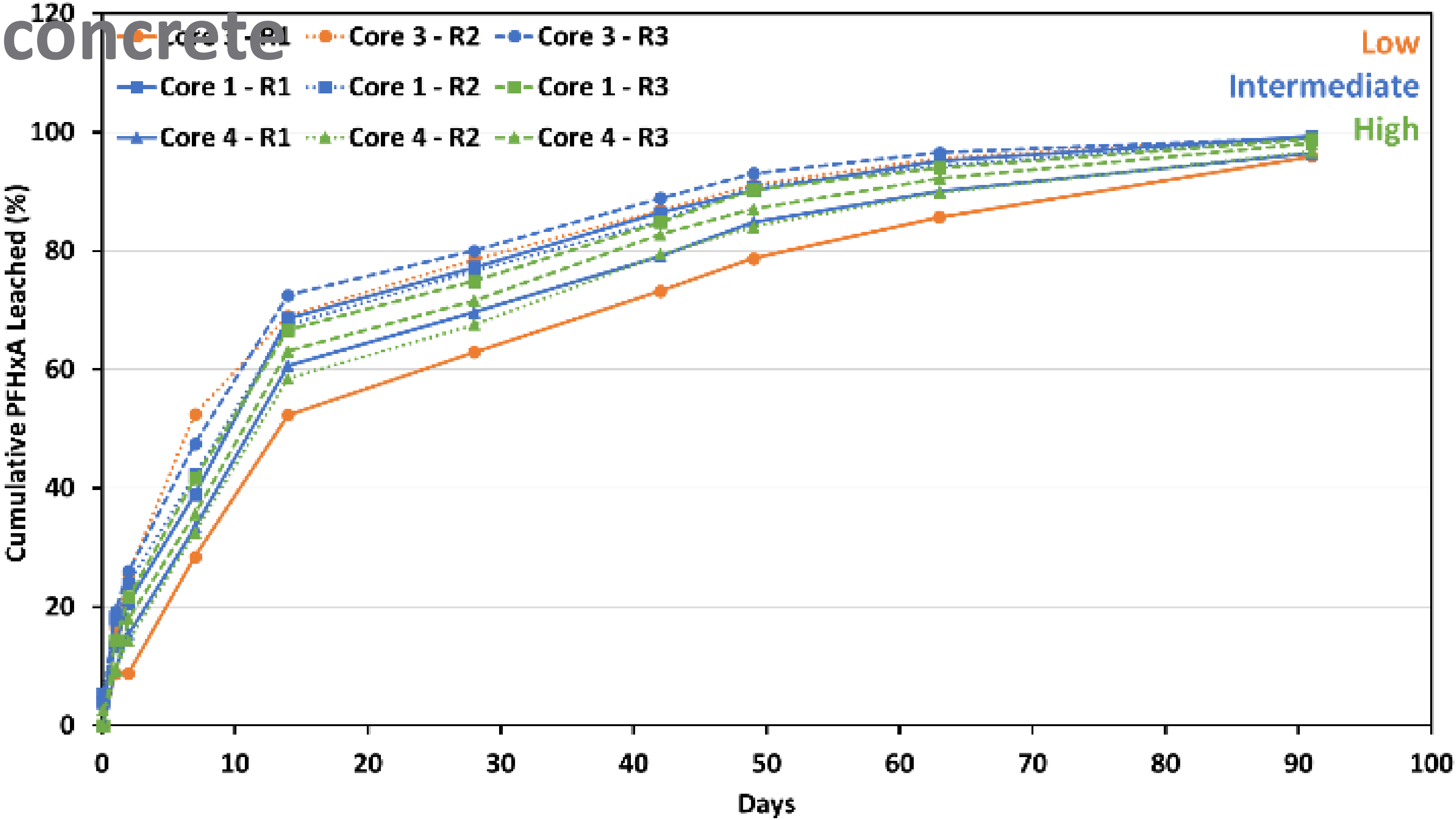
CSIRO

Cumulative % of PFOA leached from intact concrete



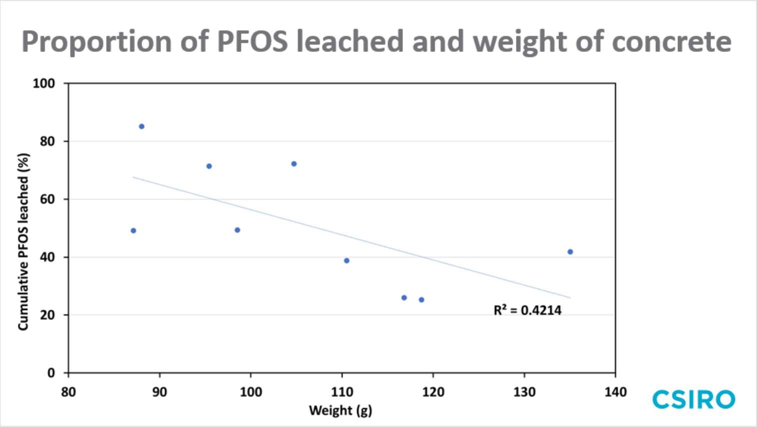
CSIRO

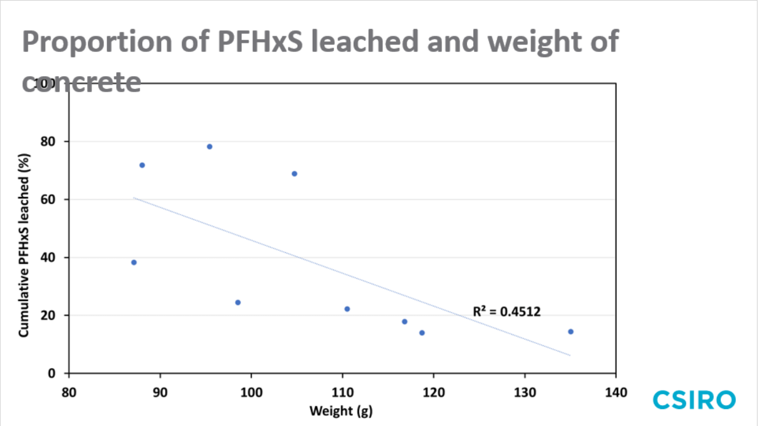
Cumulative % of PFHxA leached from intact concrete

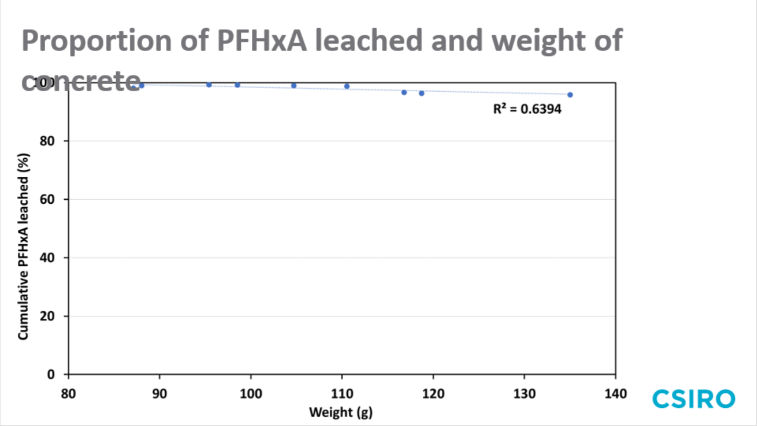


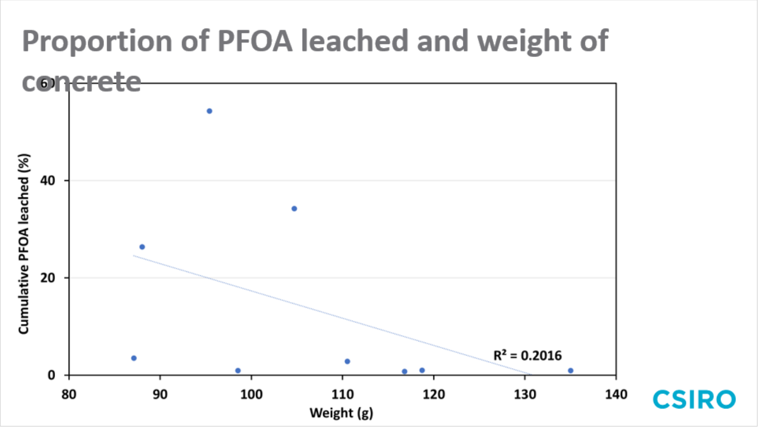
CSIRO

Proportion of PFAS leached and weight of concrete









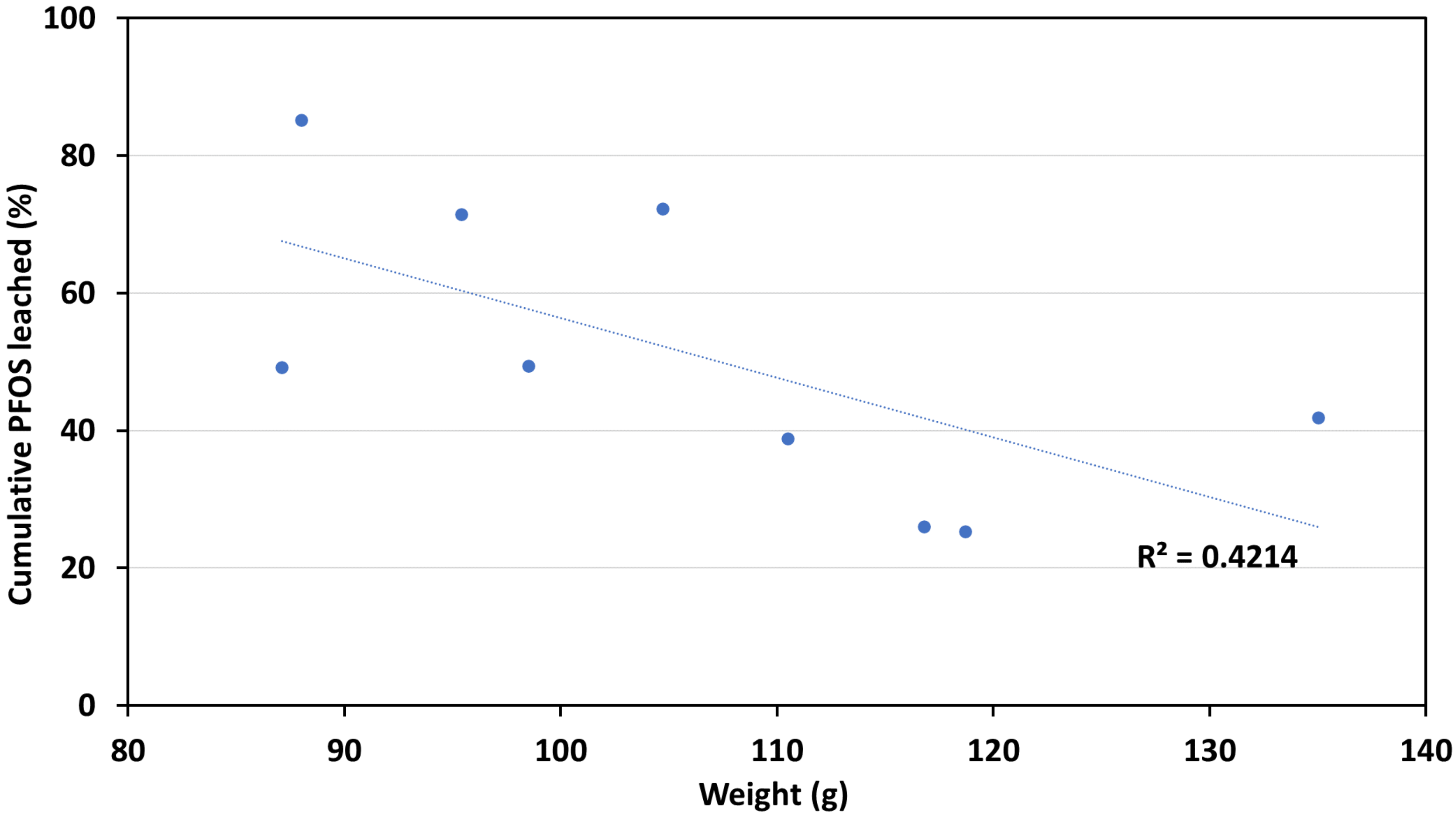
Short-chain PFAS

Proportion leached

∝

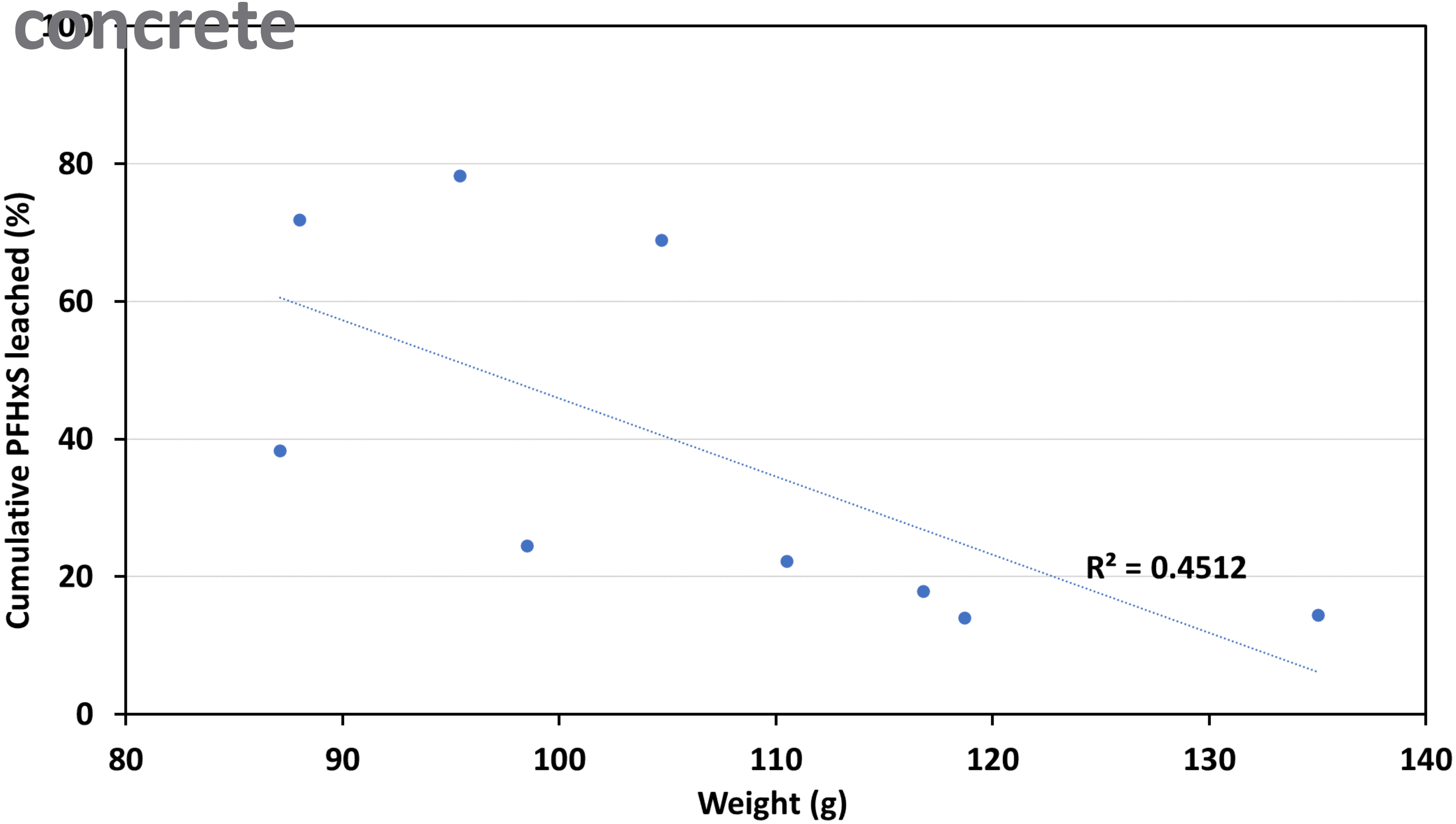
Weight of concrete

Proportion of PFOS leached and weight of concrete



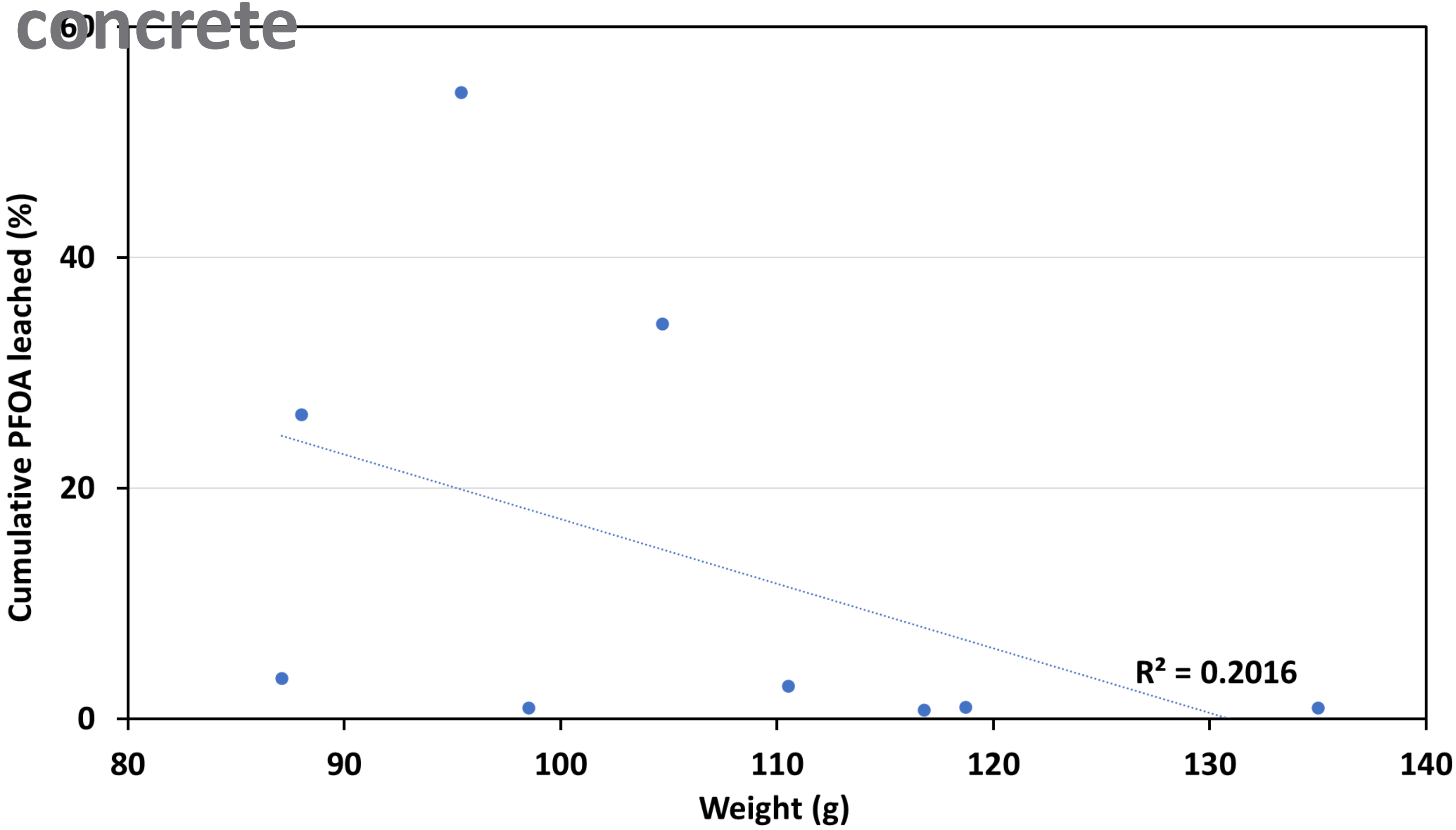
CSIRO

Proportion of PFHxS leached and weight of concrete



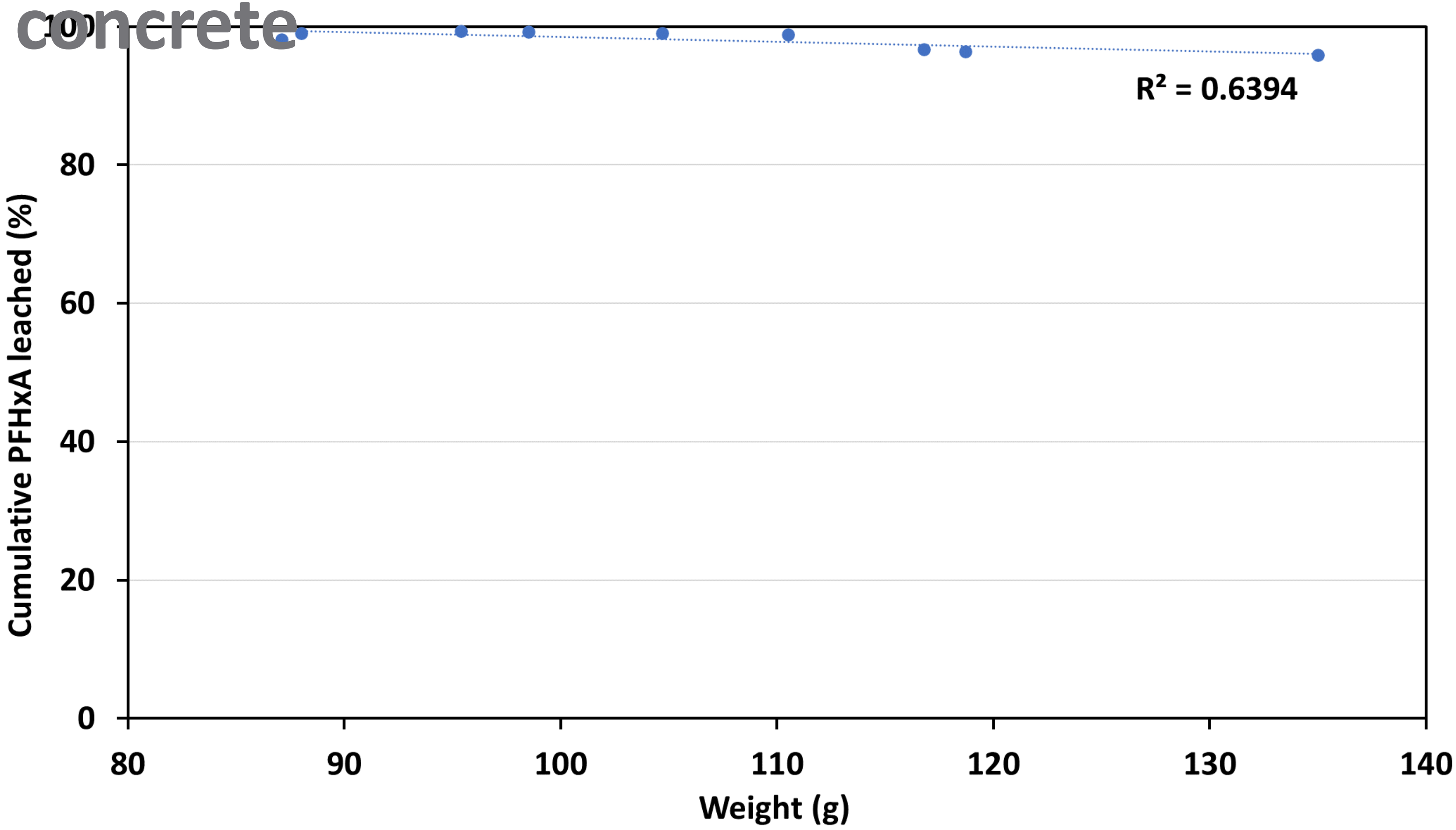
CSIRO

Proportion of PFOA leached and weight of concrete



CSIRO

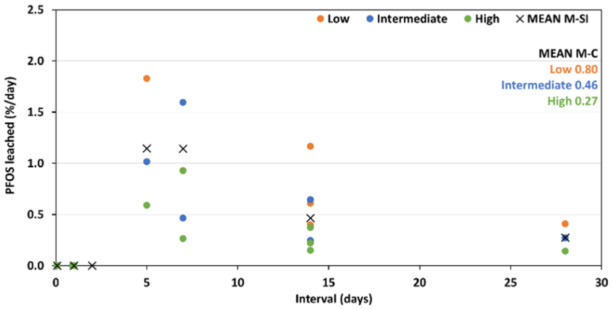
Proportion of PFHxA leached and weight of concrete



CSIRO

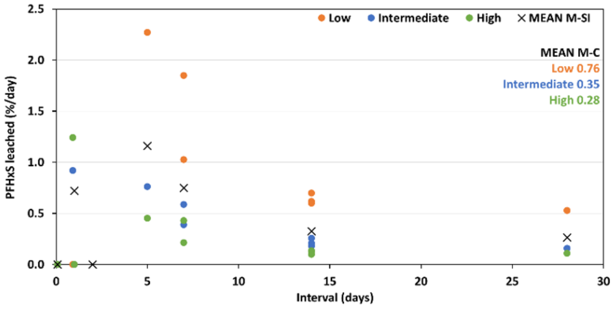
Rate of PFAS leaching from intact concrete

Rate of PFOS leaching from intact concrete



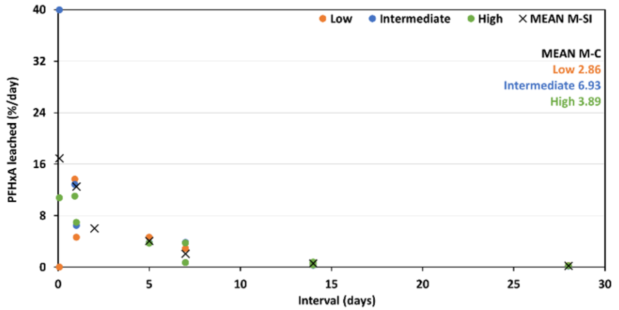
CSIRO

Rate of PFHxS leaching from intact concrete



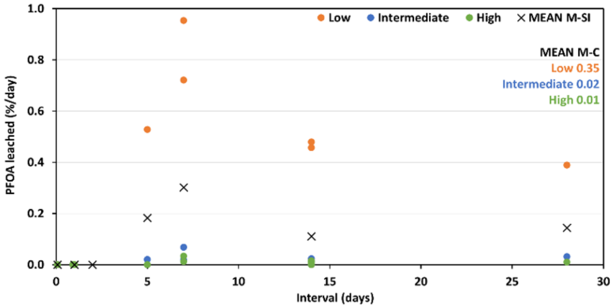
CSIRO

Rate of PFHxA leaching from intact concrete



CSIRO

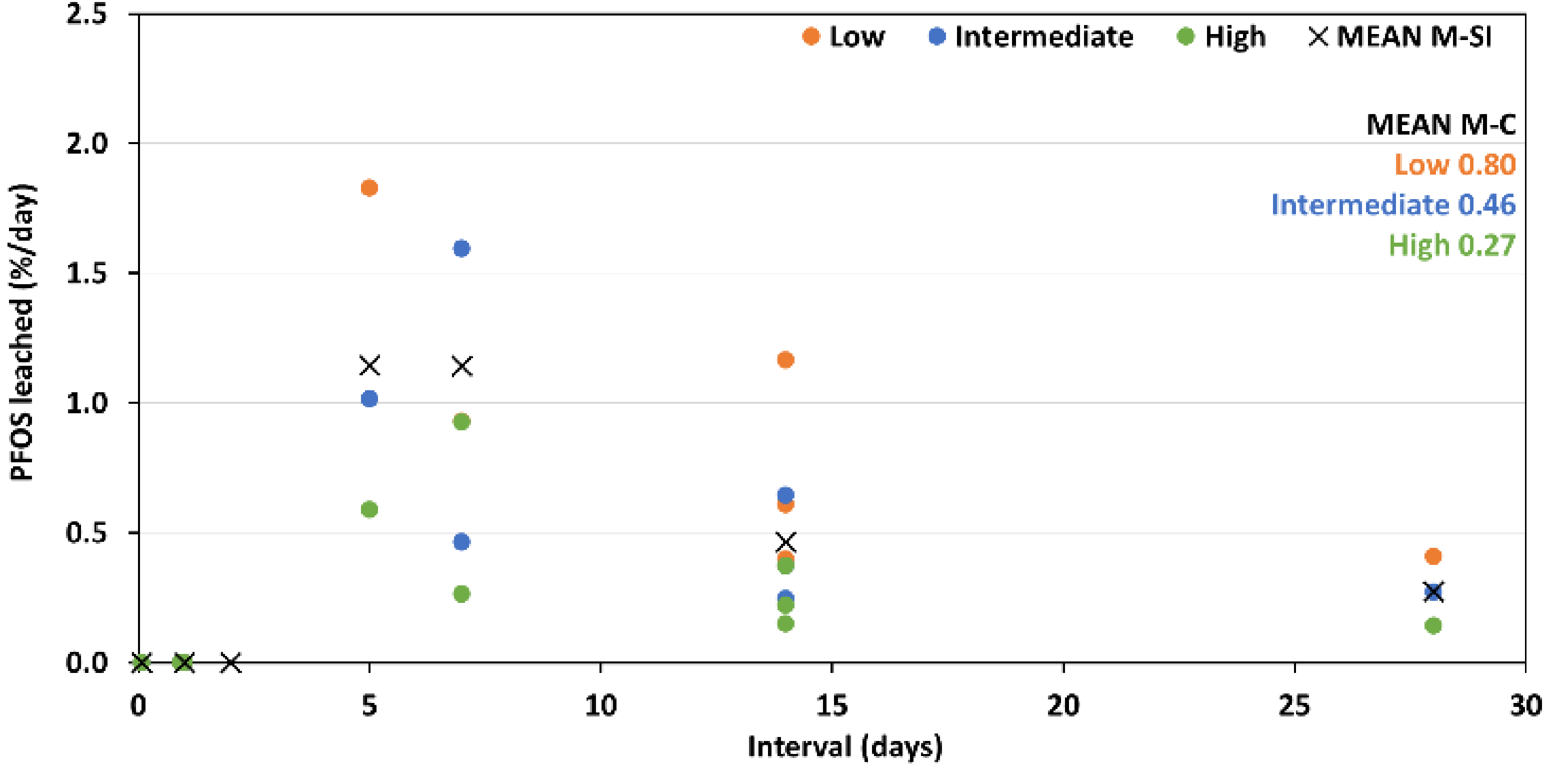
Rate of PFOA leaching from intact concrete



CSIRO

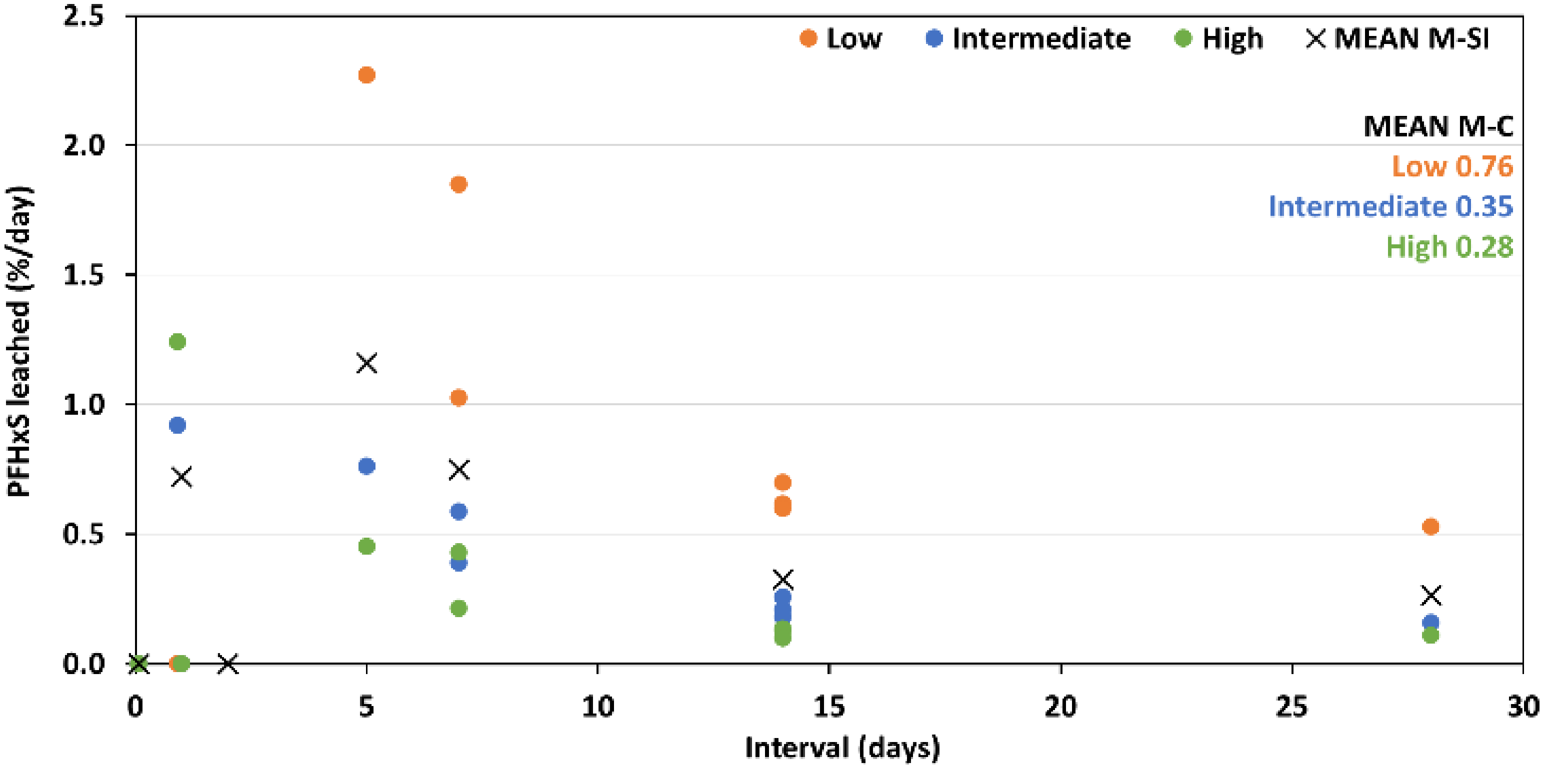
CSIRO

Rate of PFOS leaching from intact concrete



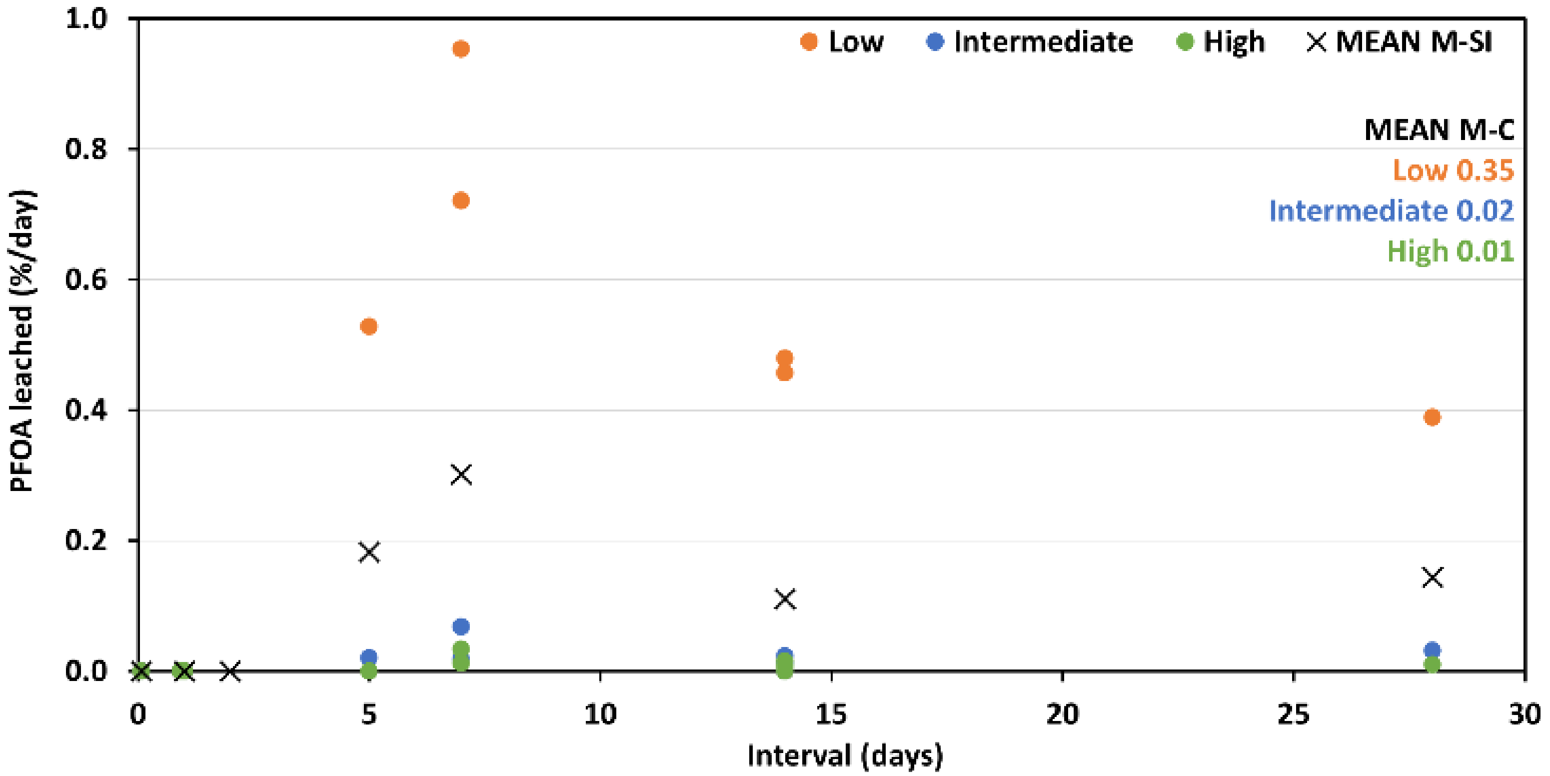
CSIRO

Rate of PFHxS leaching from intact concrete

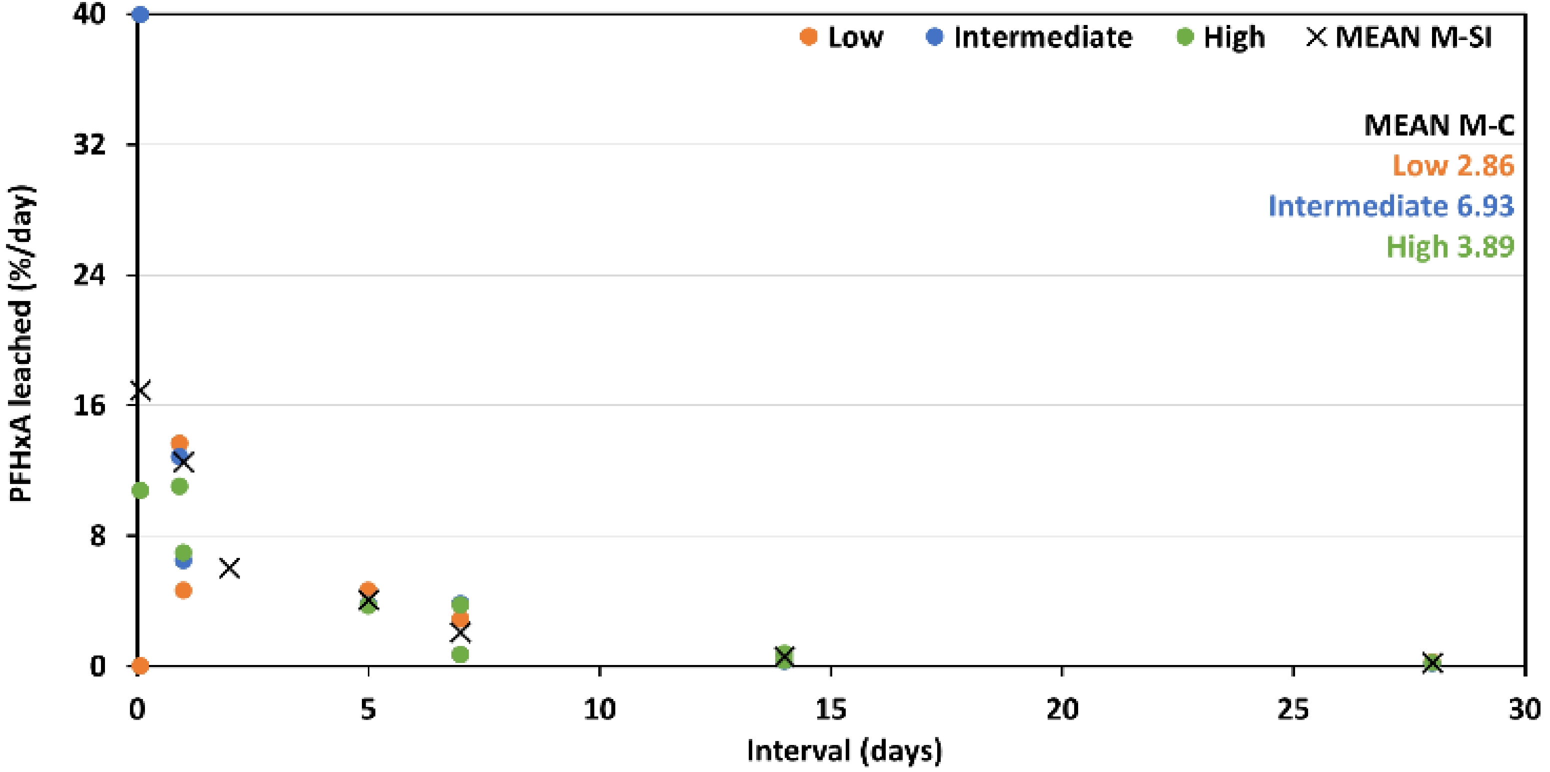


CSIRO

Rate of PFOA leaching from intact concrete



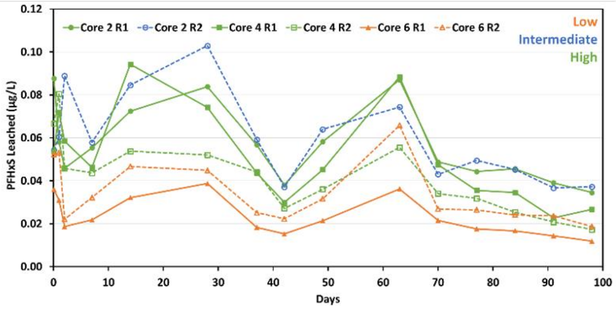
Rate of PFHxA leaching from intact concrete



CSIRO

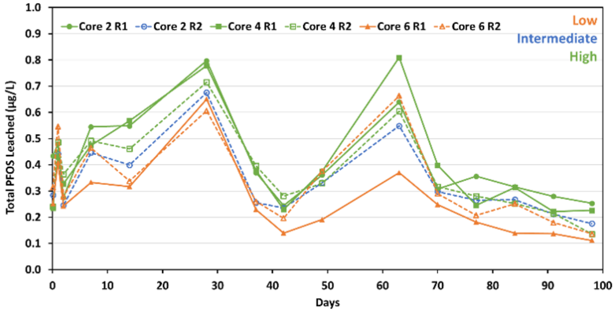
Leachate PFAS concentration (intact asphalt)

Leachate PFHxS concentration (intact asphalt)



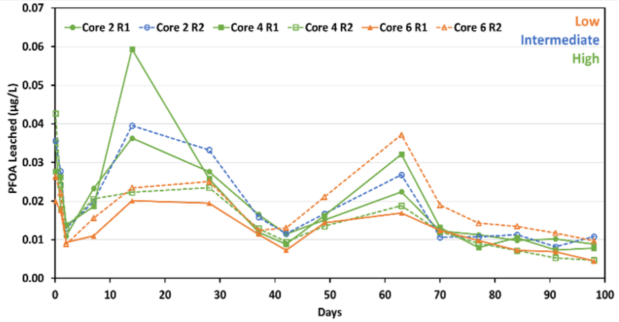
CSIRO

Leachate PFOS concentration (intact asphalt)



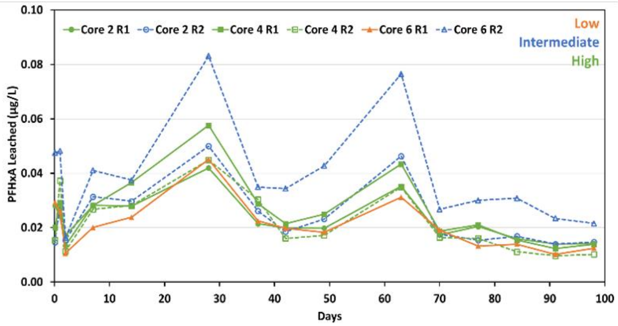
CSIRO

Leachate PFOA concentration (intact asphalt)



CSIRO

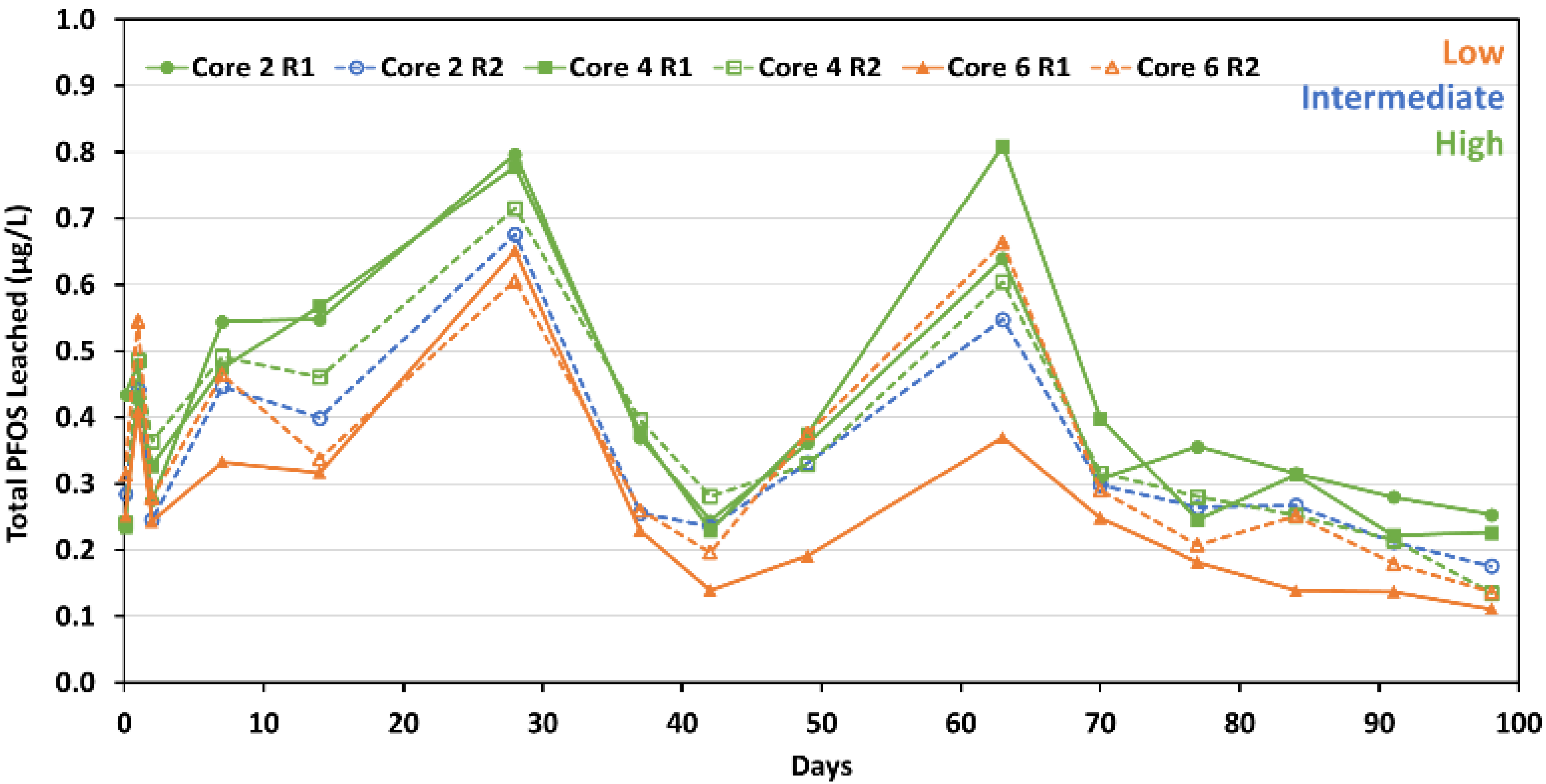
Leachate PFHxA concentration (intact asphalt)



CSIRO

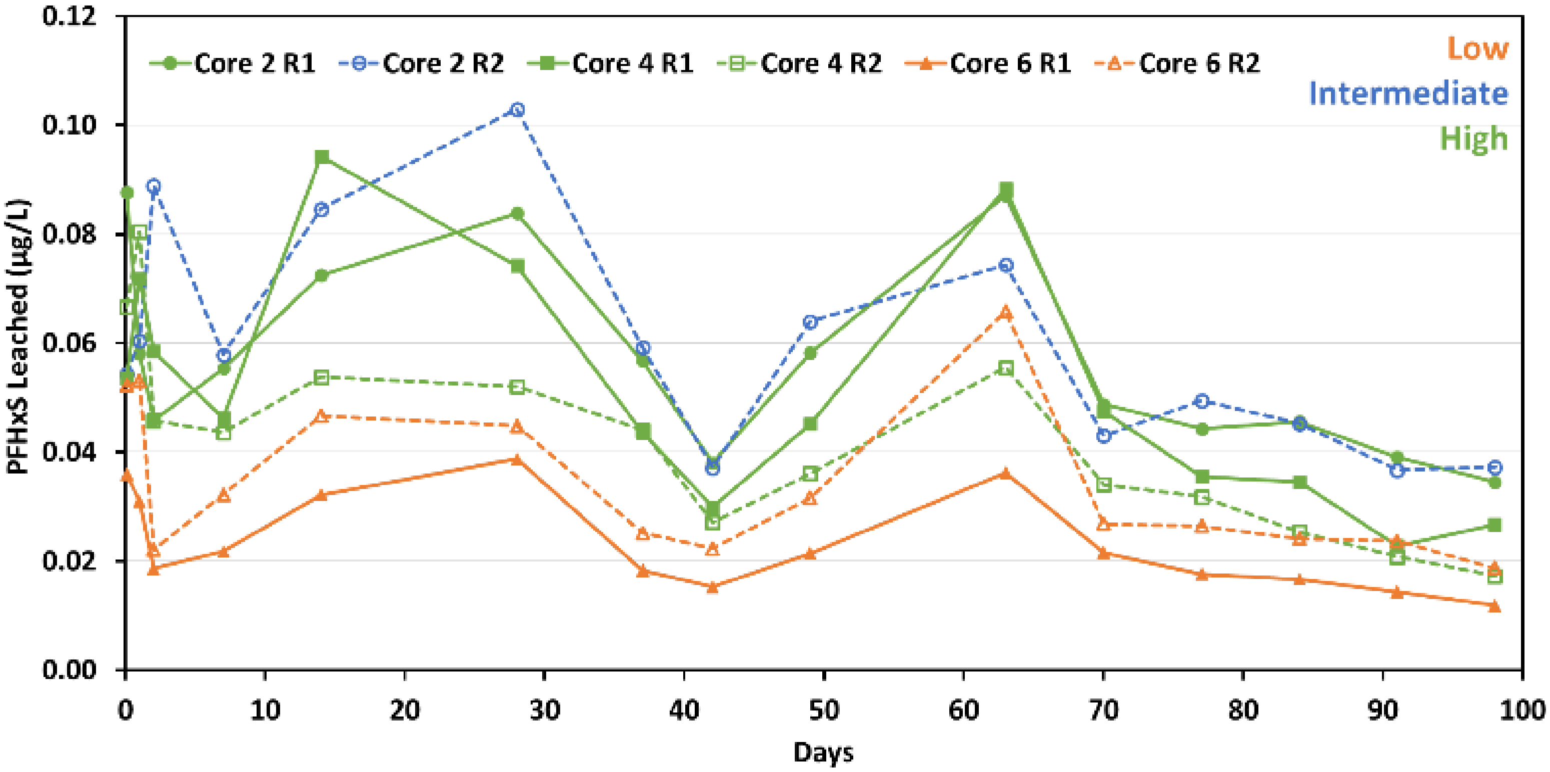
CSIRO

Leachate PFOS concentration (intact asphalt)



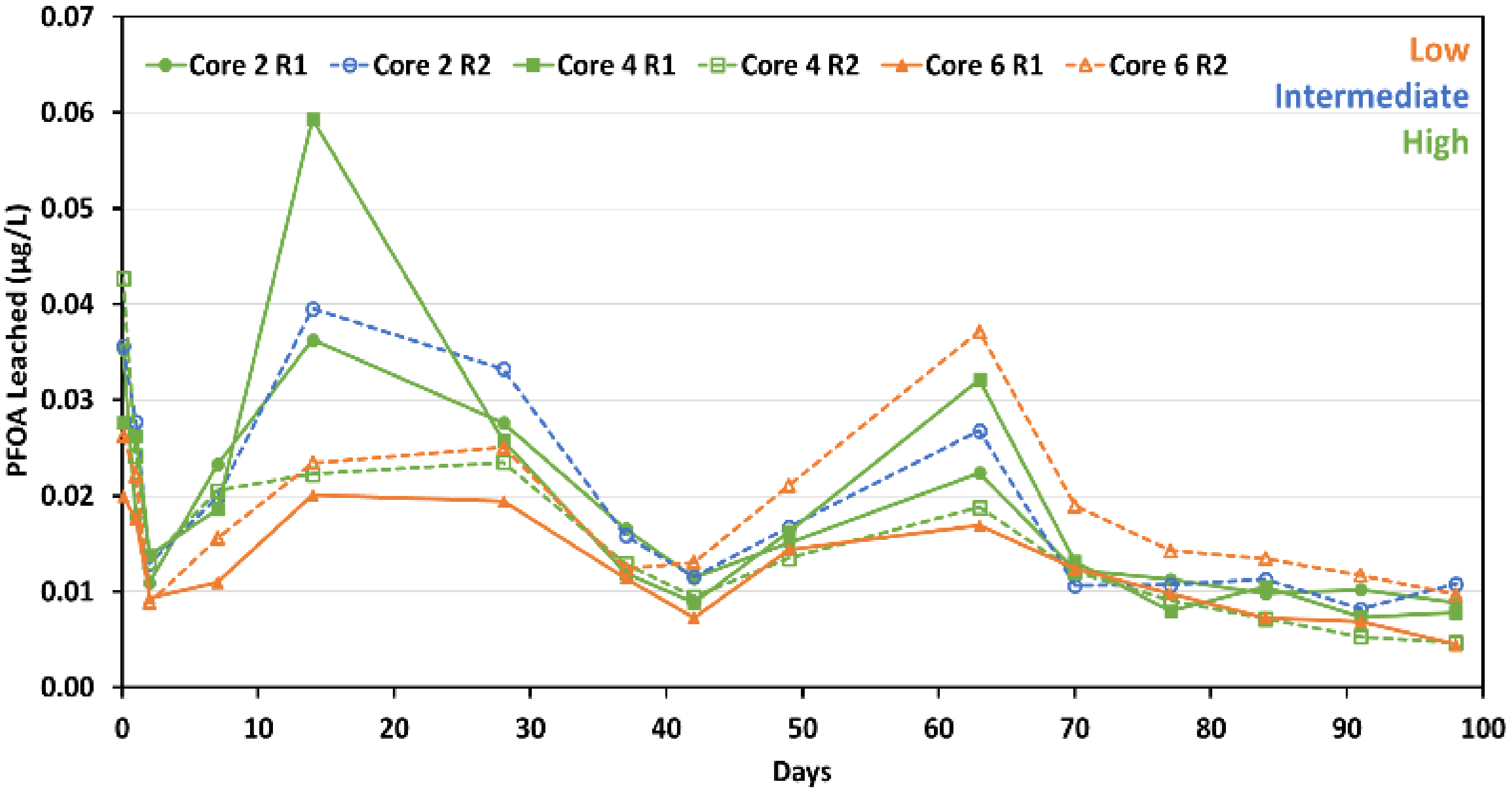
CSIRO

Leachate PFHxS concentration (intact asphalt)



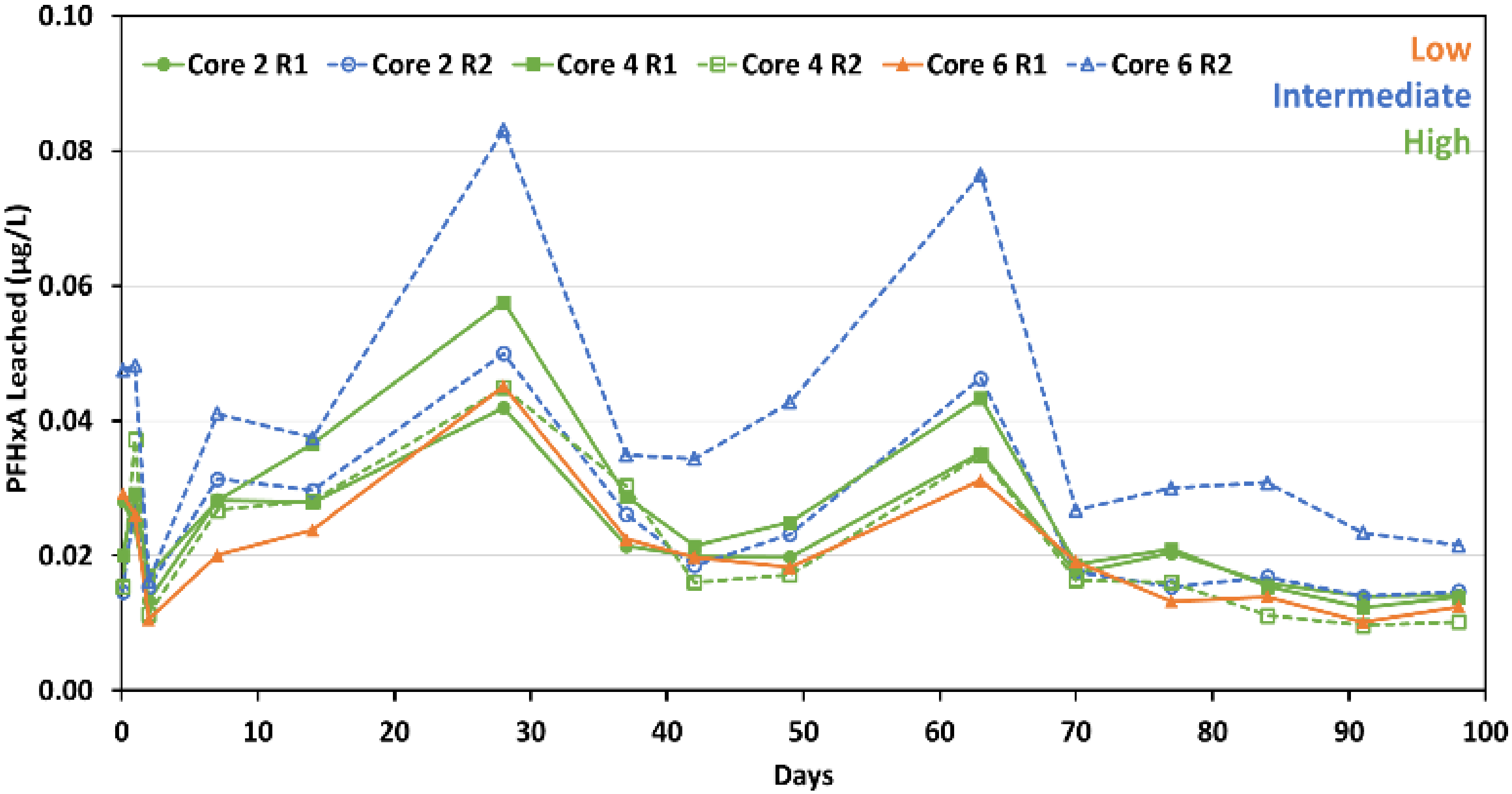
CSIRO

Leachate PFOA concentration (intact asphalt)



CSIRO

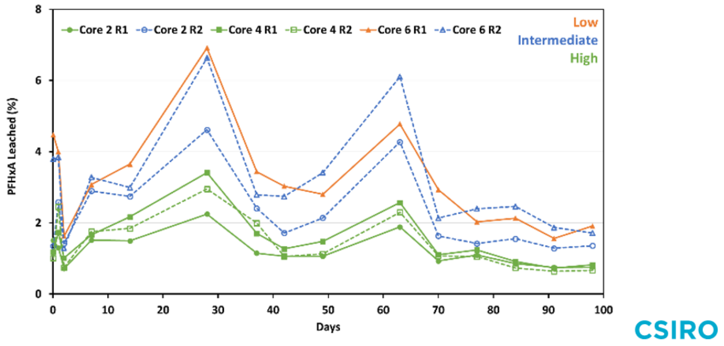
Leachate PFHxA concentration (intact asphalt)



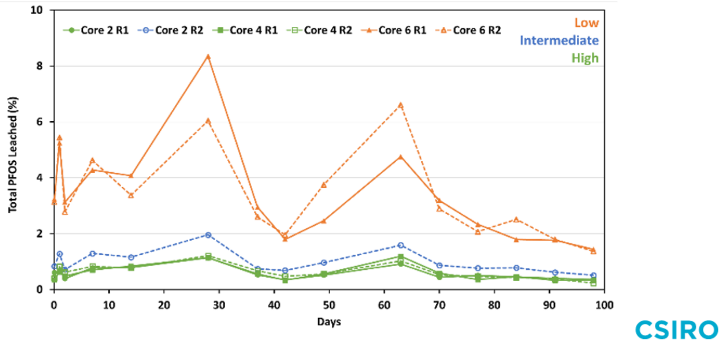
CSIRO

Proportion of PFAS leached from intact asphalt

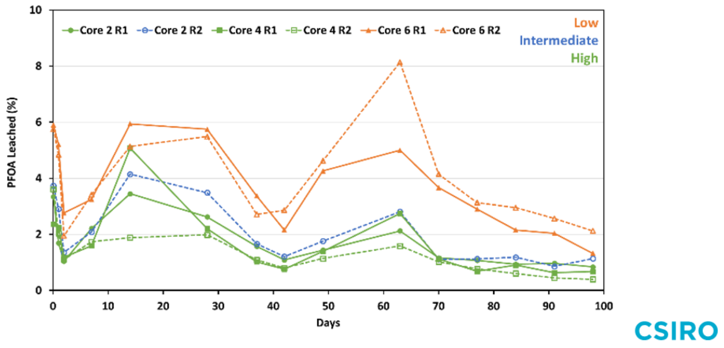
Proportion of PFHxA leached from intact asphalt



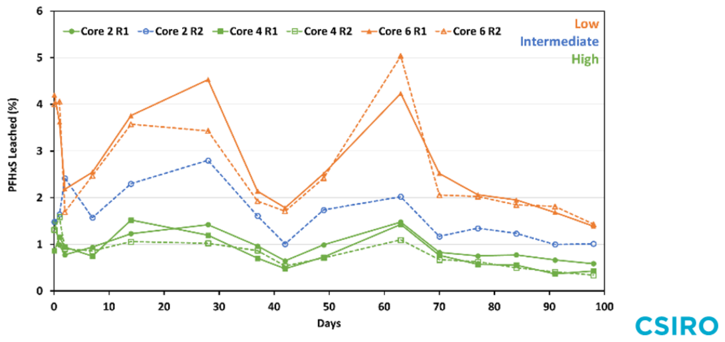
Proportion of PFOS leached from intact asphalt



Proportion of PFOA leached from intact asphalt



Proportion of PFHxS leached from intact asphalt



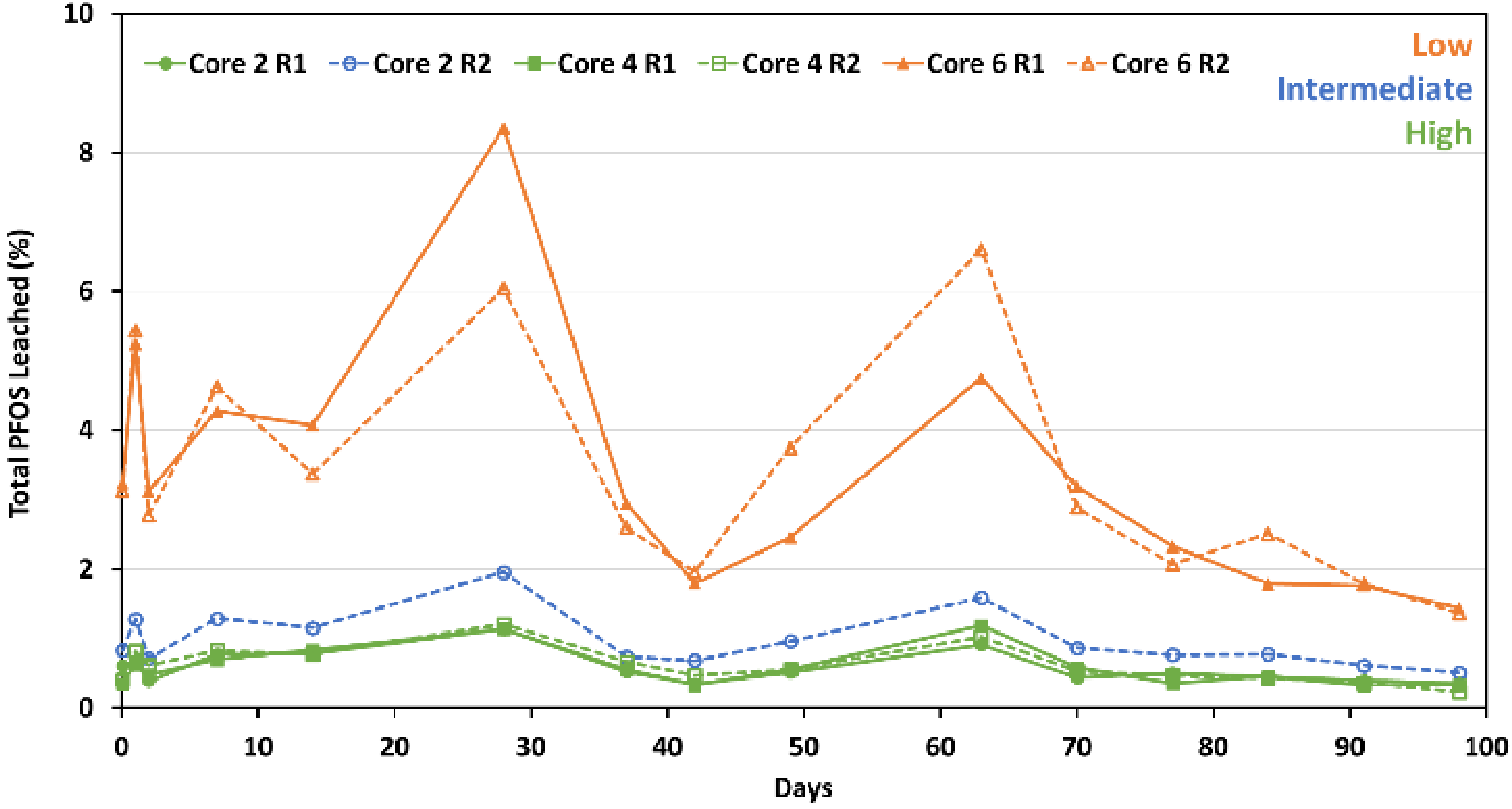
Long-chain PFAS

Concentration ↑

Leaching ↓

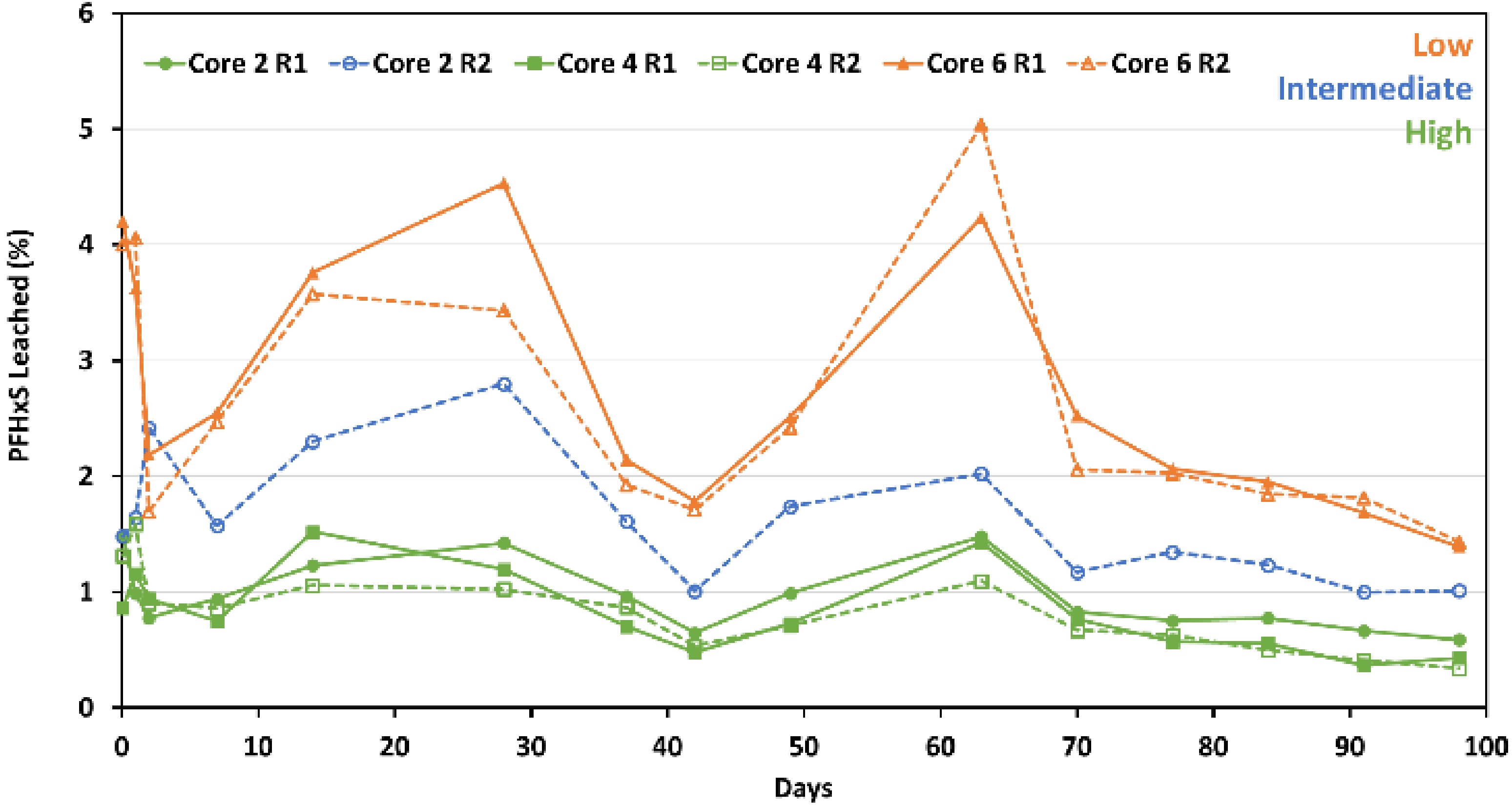
CSIRO

Proportion of PFOS leached from intact asphalt



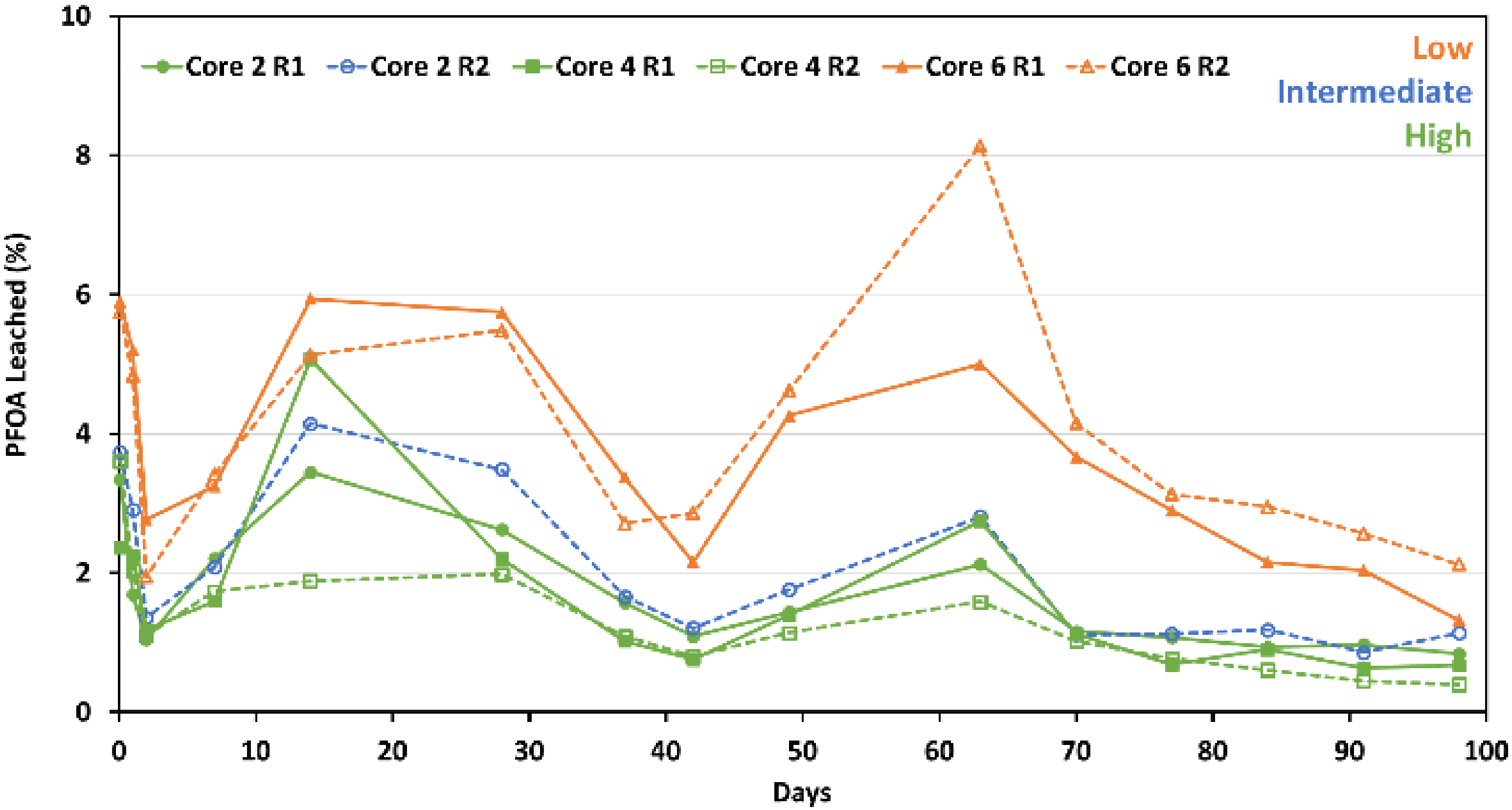
CSIRO

Proportion of PFHxS leached from intact asphalt



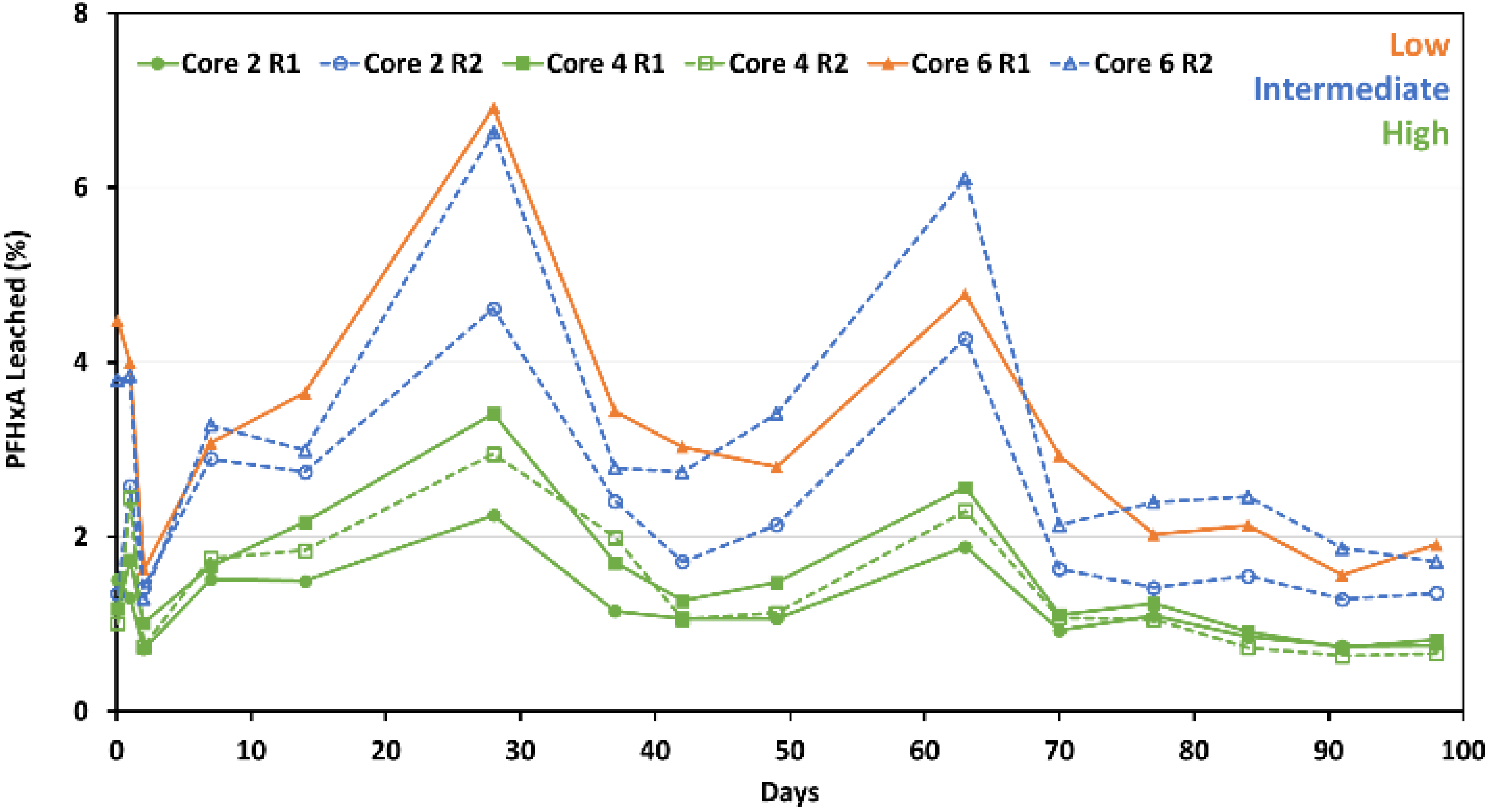
CSIRO

Proportion of PFOA leached from intact asphalt



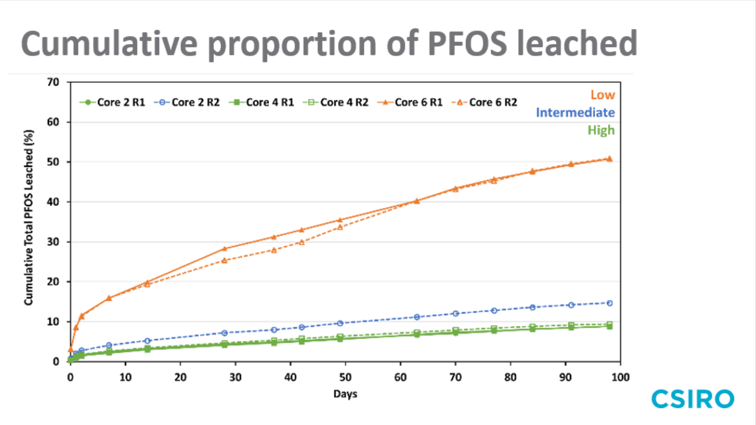
CSIRO

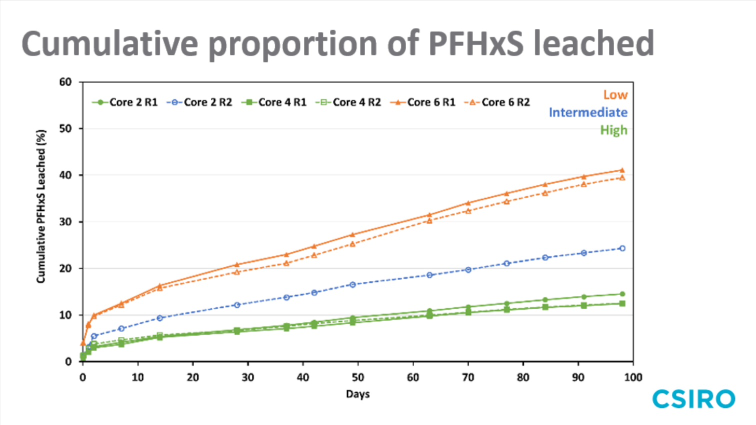
Proportion of PFHxA leached from intact asphalt

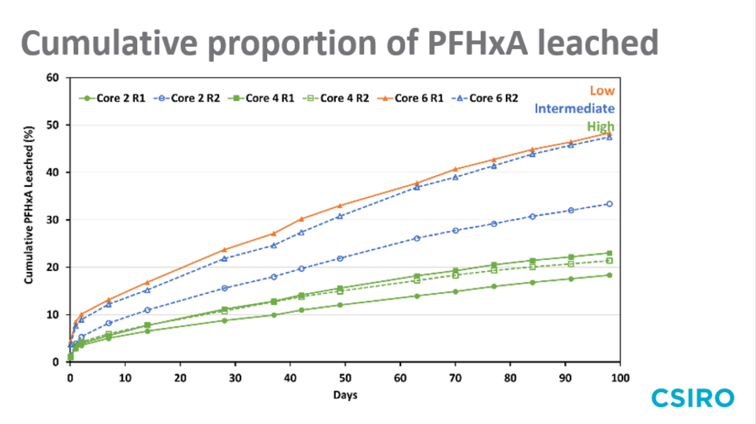


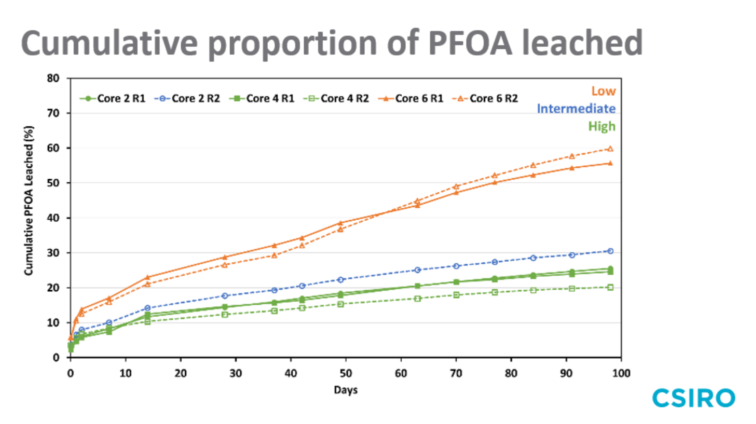
CSIRO

Cumulative % of PFAS leached from intact asphalt









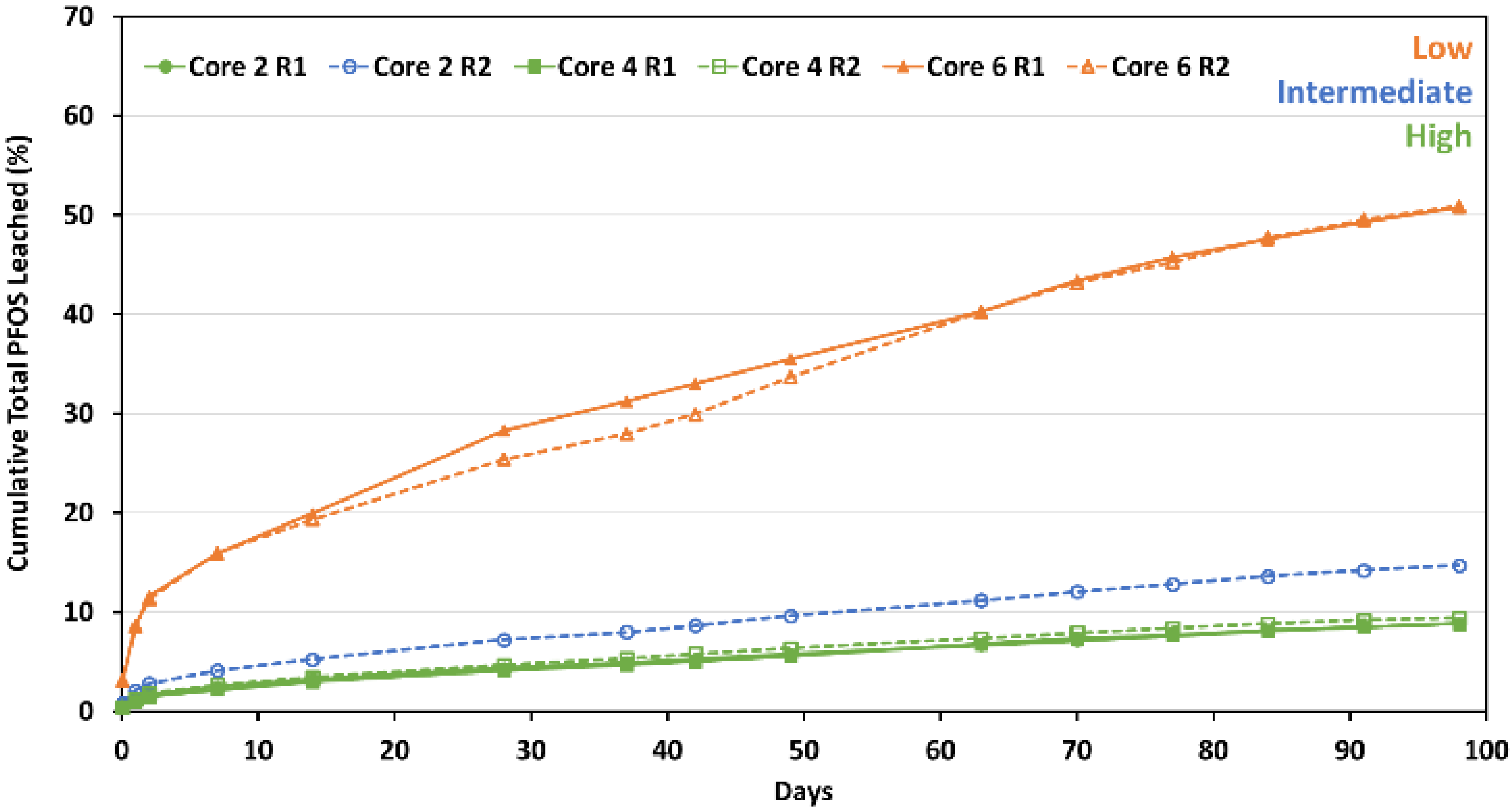
Long-chain PFAS

Concentration ↑

Leaching ↓

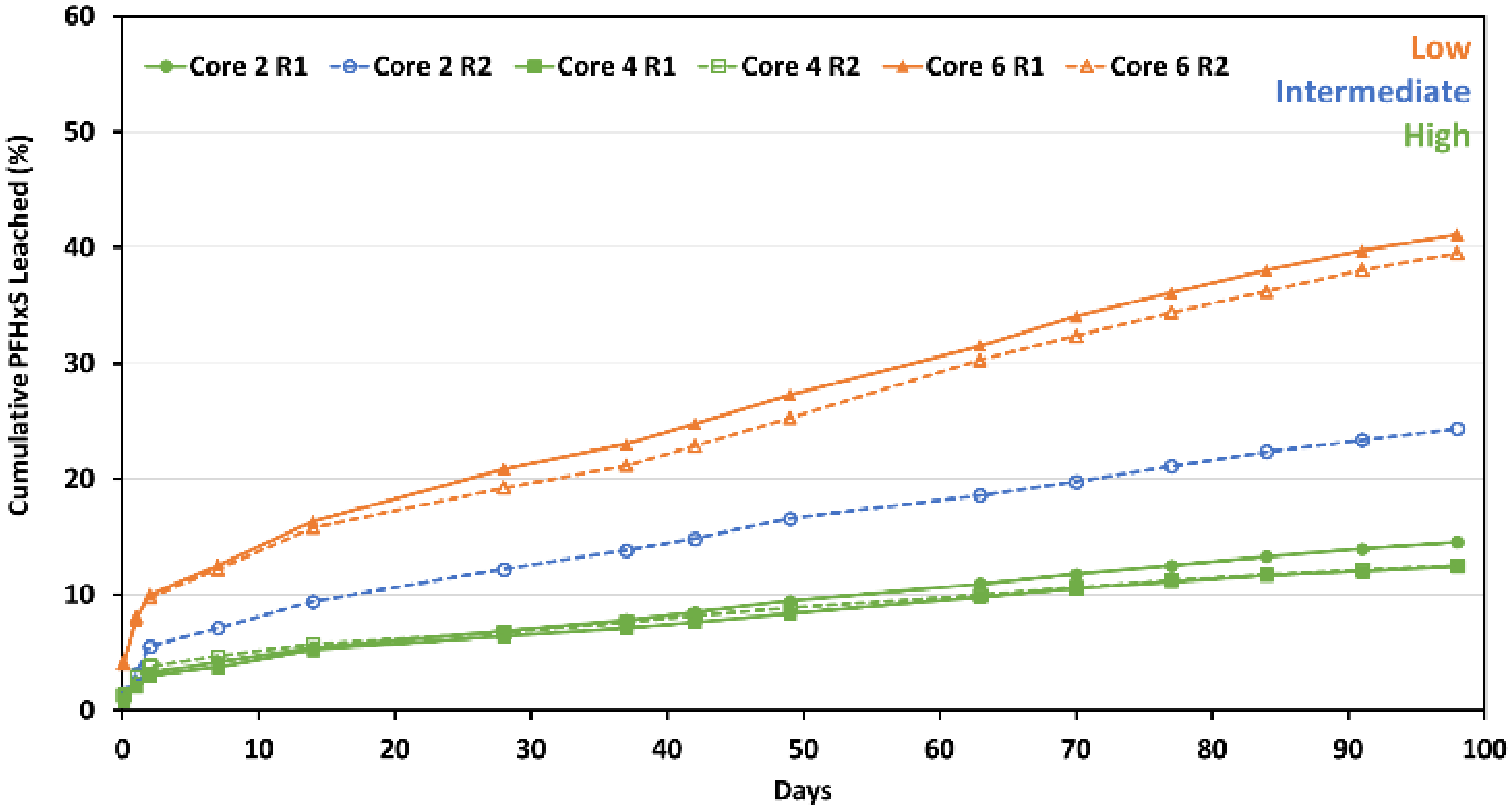
CSIRO

Cumulative proportion of PFOS leached



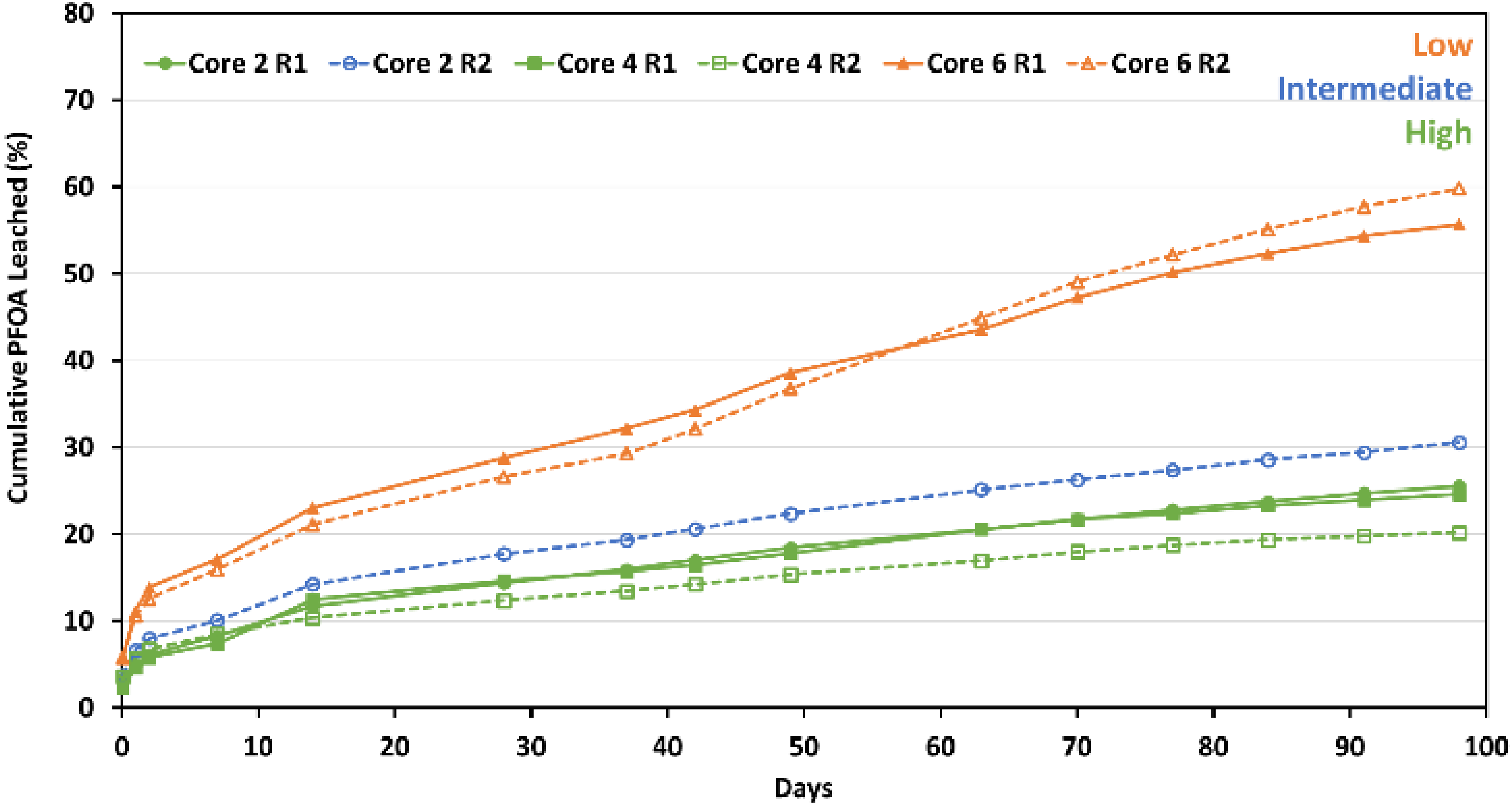
CSIRO

Cumulative proportion of PFHxS leached



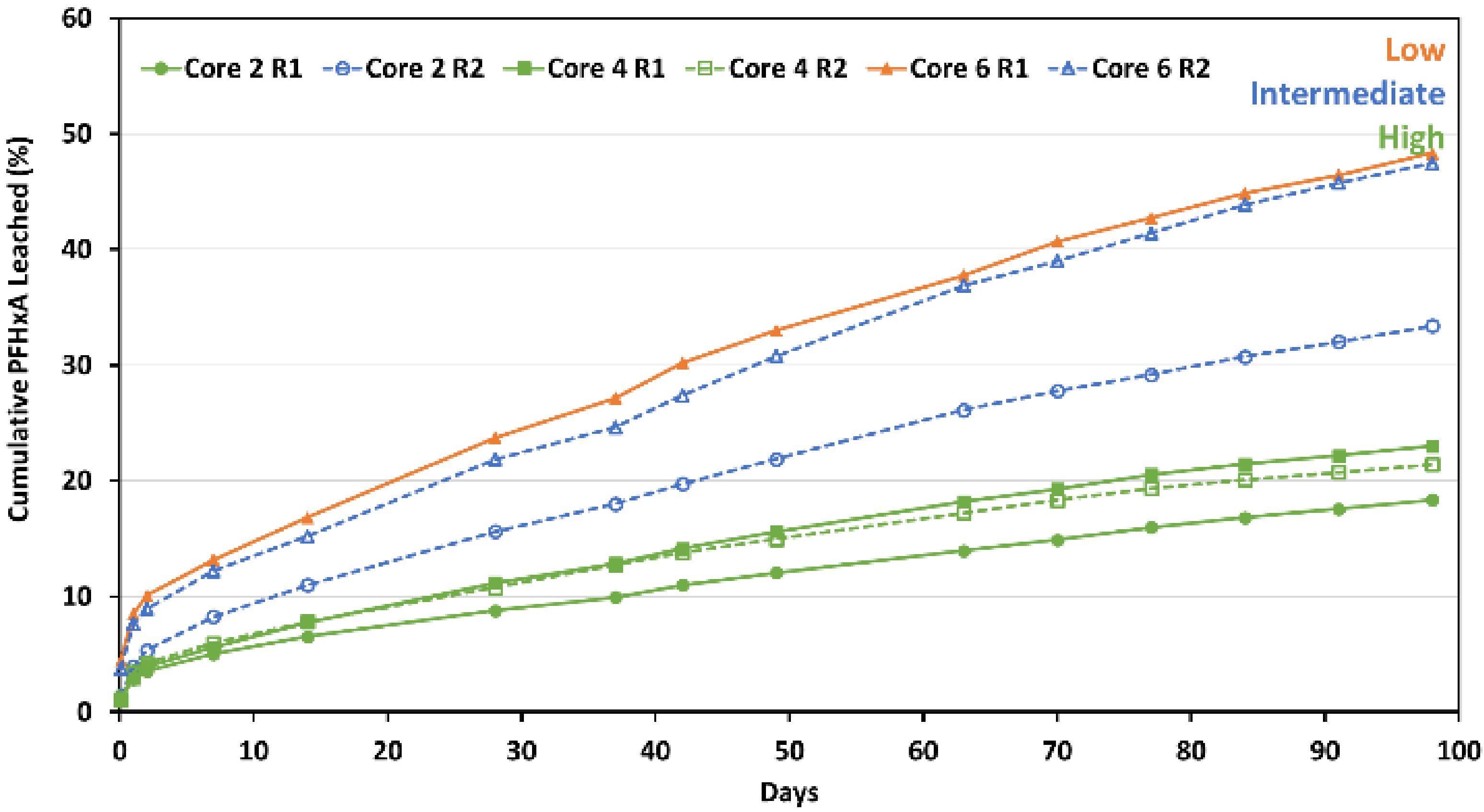
CSIRO

Cumulative proportion of PFOA leached



CSIRO

Cumulative proportion of PFHxA leached



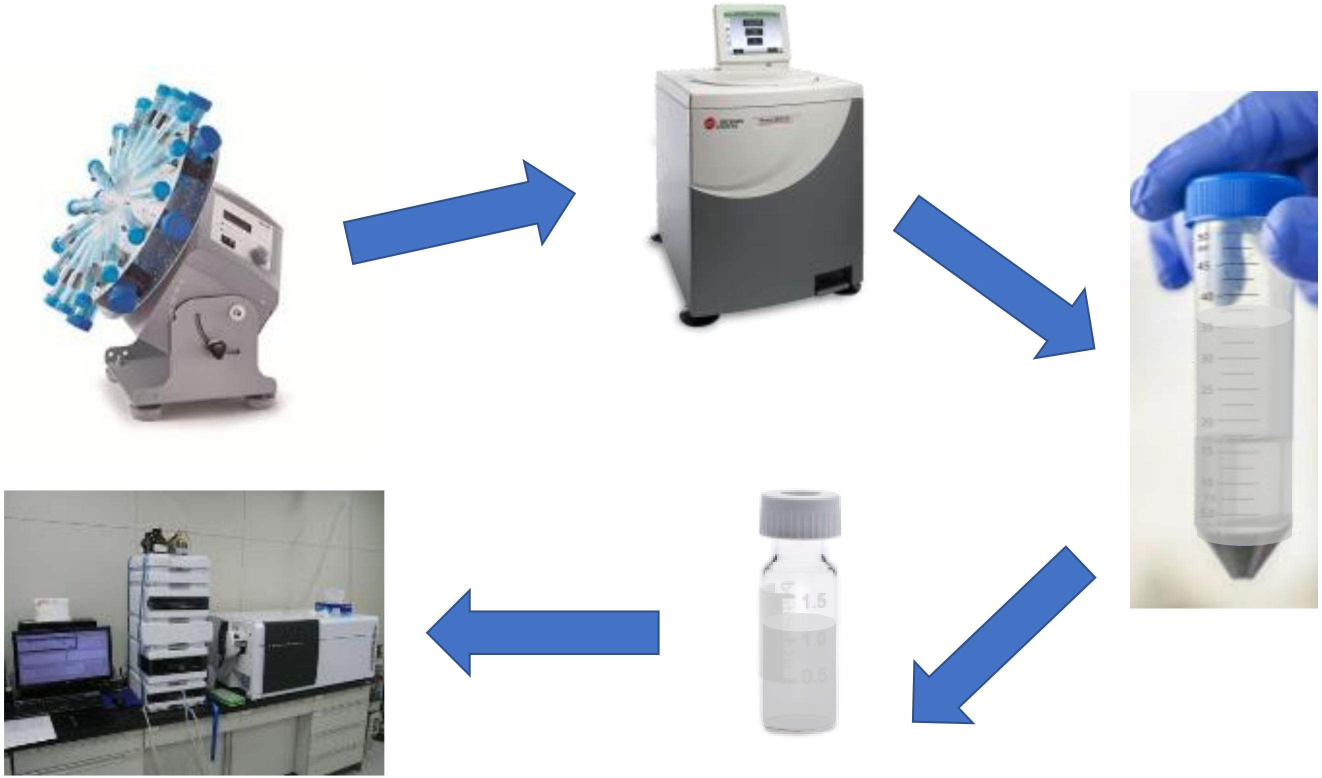
CSIRO

PFAS leaching from powdered concrete and asphalt

CSIRO

PFAS leaching from powdered concrete and asphalt

ASLP
LEAF 1313



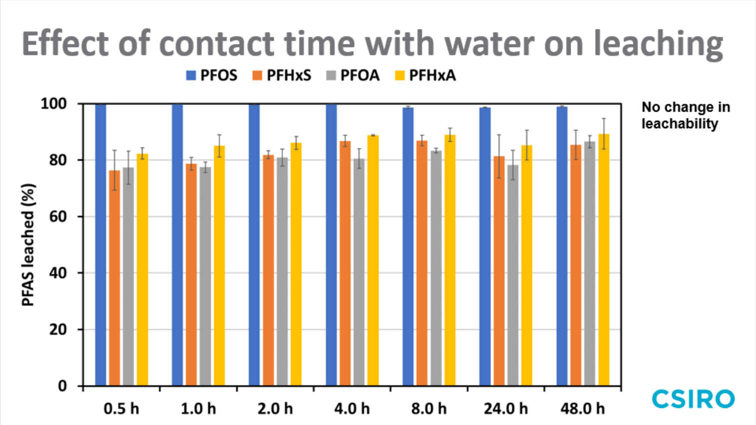
CSIRO

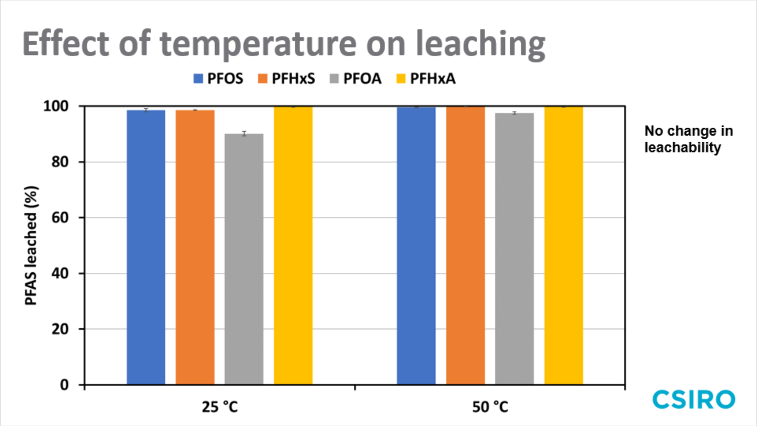
Experimental conditions for ASLP leaching

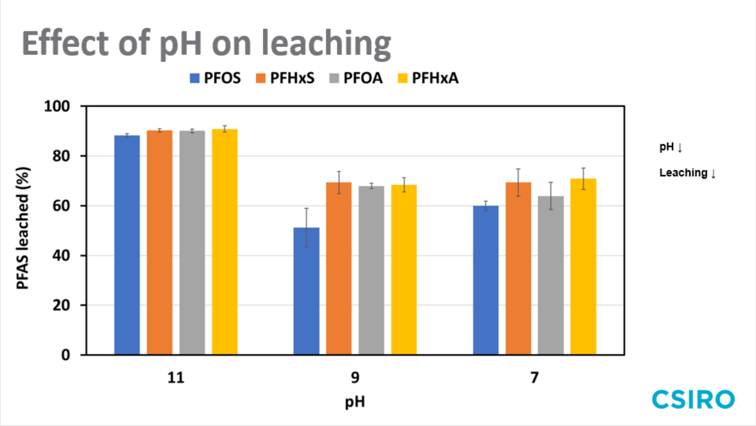
Variable	Shaking time (h)	Temperature	Particle size	Liquid/Solid (L/S) ratio
Contact time	0.5, 1, 2, 4, 8, 24, 48	25 °C	< 2 mm	20
Particle size	24	25 °C	< 2 mm, 2-20 mm, > 20 mm	20
Temperature	24	25 °C / 50 °C	< 2 mm	20

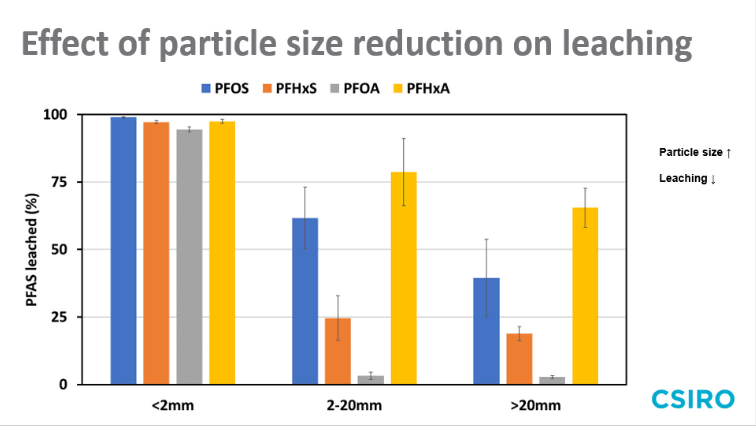
CSIRO

PFAS leaching from powdered concrete

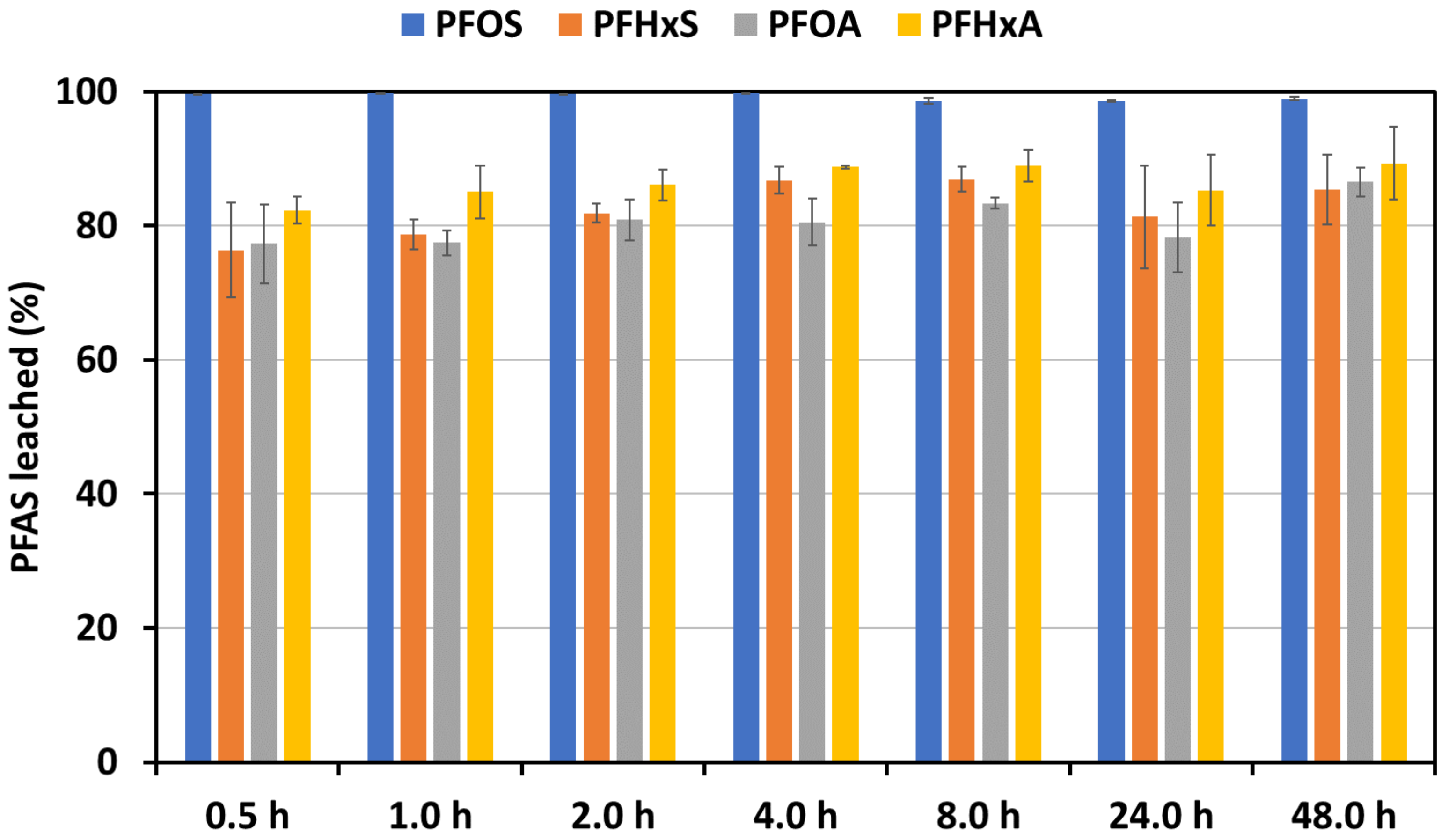








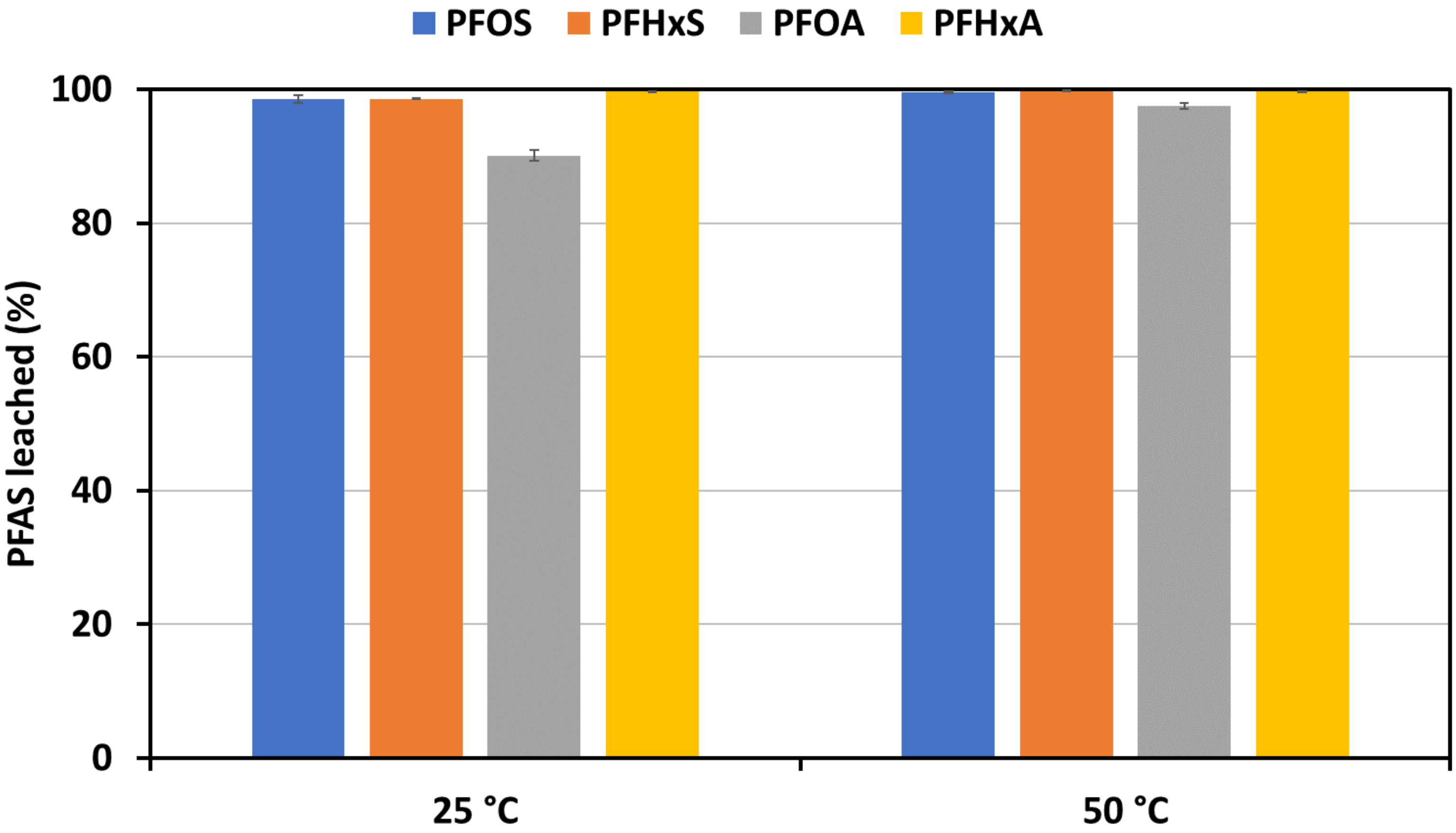
Effect of contact time with water on leaching



No change in leachability

CSIRO

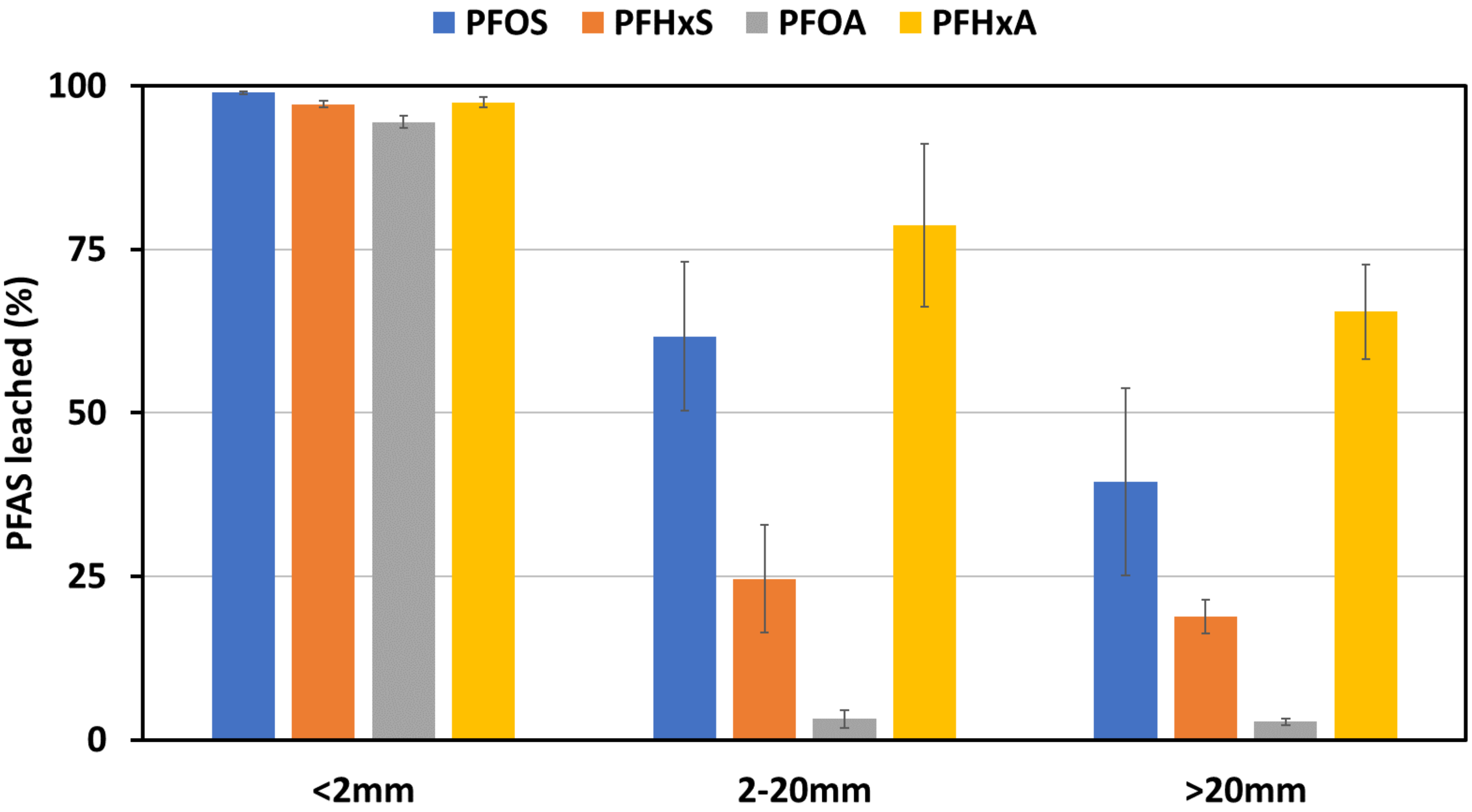
Effect of temperature on leaching



No change in leachability

CSIRO

Effect of particle size reduction on leaching

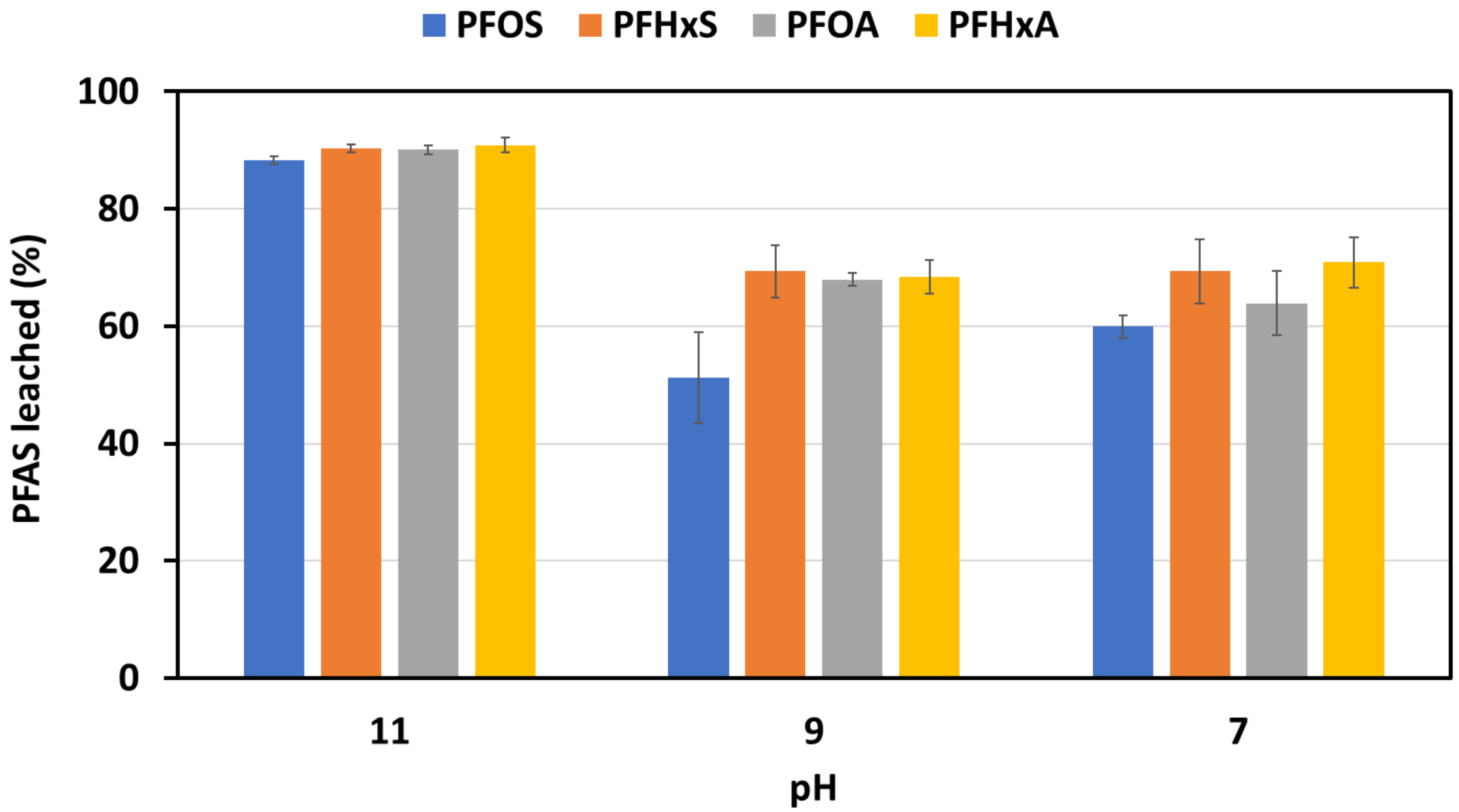


Particle size ↑

Leaching ↓

CSIRO

Effect of pH on leaching



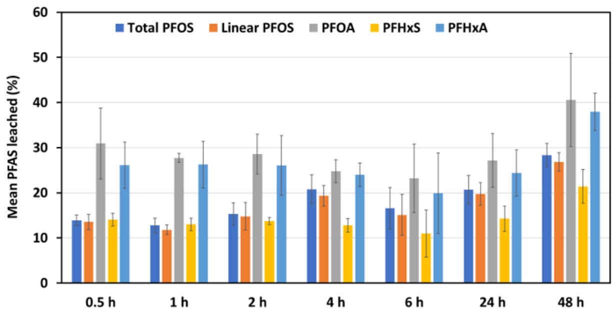
pH ↓

Leaching ↓

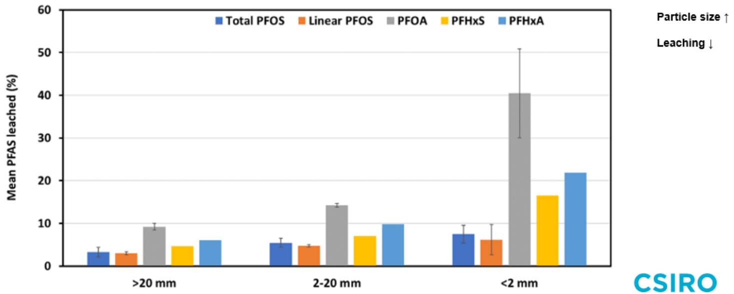
CSIRO

PFAS leaching from powdered asphalt

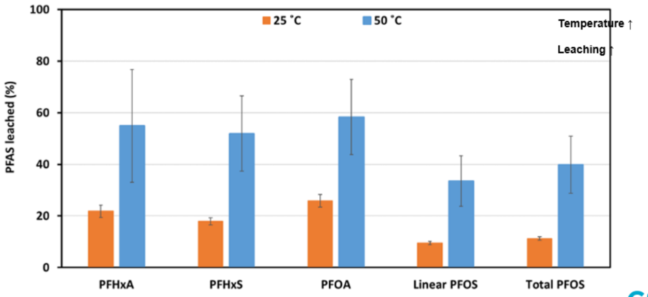
Effect of contact time with water on leaching



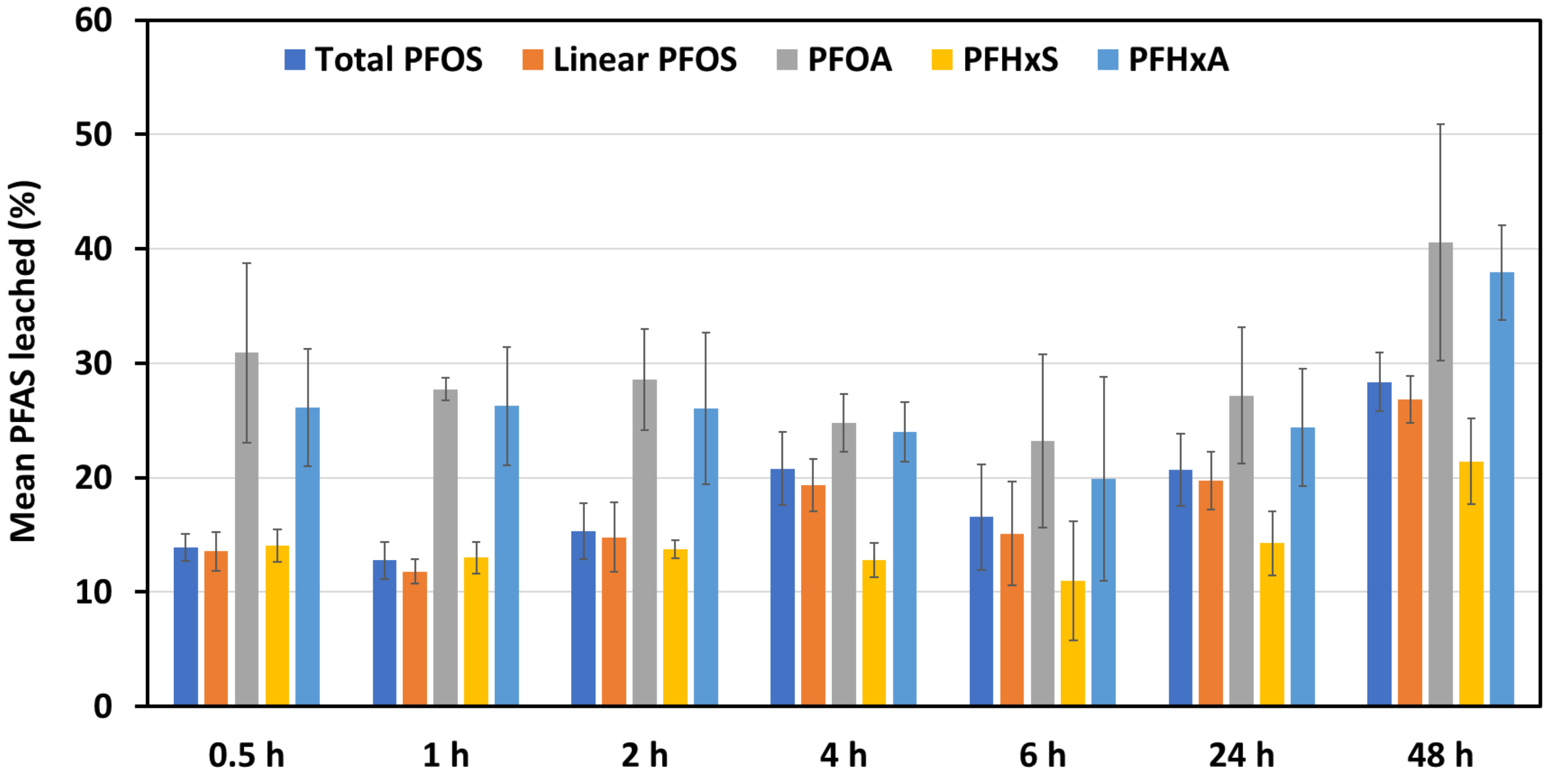
Effect of particle size reduction on leaching



Effect of temperature on leaching

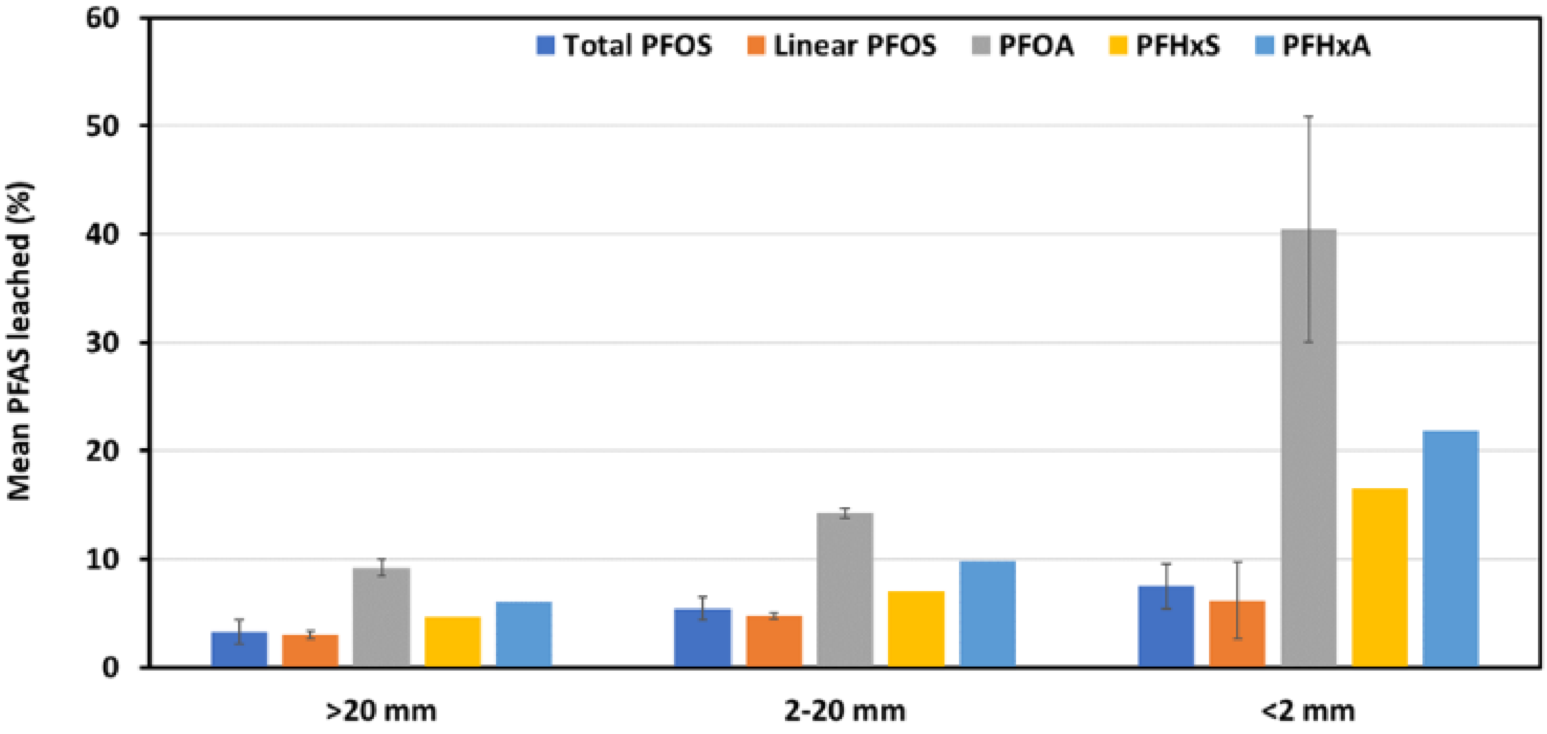


Effect of contact time with water on leaching



CSIRO

Effect of particle size reduction on leaching

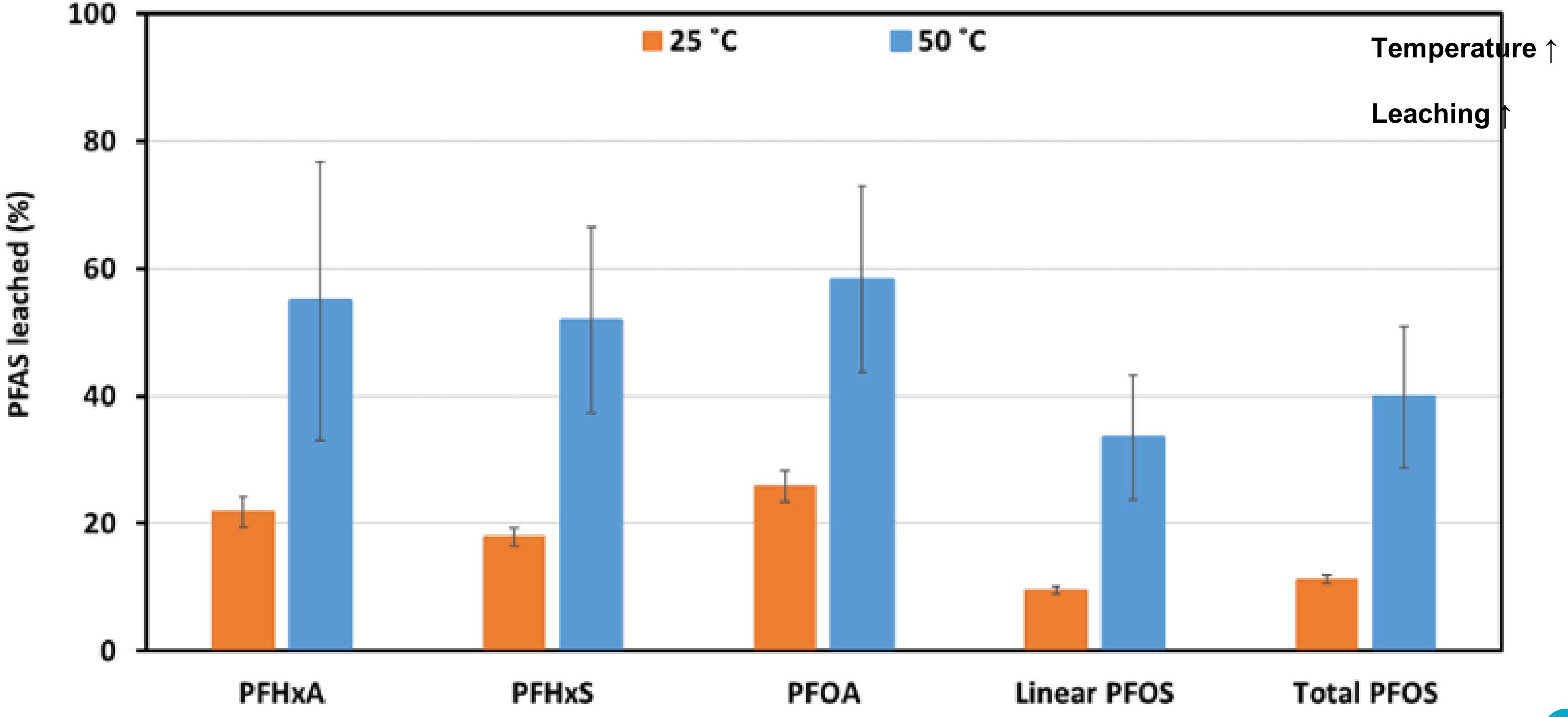


Particle size ↑

Leaching ↓

CSIRO

Effect of temperature on leaching



CSIRO

Key takeaways

General findings

- Significant variability in PFAS concentration in concrete/asphalt;
- PFAS readily leachable from contaminated concrete/asphalt;
- Concrete more leachable than asphalt;
- PFAS chemistry dominant factor in determining their leaching from concrete/ asphalt.

CSIRO

PFAS leaching from Intact concrete/asphalt

- PFAS leaching time-dependent; and
- Low-concentration monoliths leached a relatively greater proportion of PFAS.

CSIRO

PFAS leaching from powdered concrete/asphalt

- PFAS leaching time-independent;
- Particle size reduction increased PFAS leaching;
- Increased temperature increased PFAS leaching from asphalt; and
- Lowering the pH of concrete reduced PFAS leaching.

CSIRO

CSIRO

General findings

- Significant variability in PFAS concentration in concrete/asphalt;
- PFAS readily leachable from contaminated concrete/asphalt;
- Concrete more leachable than asphalt;
- PFAS chemistry dominant factor in determining their leaching from concrete/ asphalt.

CSIRO

PFAS leaching from Intact concrete/asphalt

- PFAS leaching time-dependent; and
- Low-concentration monoliths leached a relatively greater proportion of PFAS.

CSIRO

PFAS leaching from powdered concrete/asphalt

- PFAS leaching time-independent;
- Particle size reduction increased PFAS leaching;
- Increased temperature increased PFAS leaching from asphalt; and
- Lowering the pH of concrete reduced PFAS leaching.

Acknowledgements

- Funding support: Department of Defence
- Operational and logistical support: Dr Karl Bowles, Mr Garbis Avakian, Ms Nelma Akhund, Mr Stephen Corish, Mr Darren Skuse and Mr Mark Bauer.
- CSIRO researchers: Dr Grant Douglas, Dr Rai Kookana, Dr Greg Davis, Dr Mike Williams, Dr Jason Kirby
- CSIRO Laboratory support: Dr Trinh Nguyen, Ms Thanh Huong Nguyen, Ms Manvi Gandhi, Ms Claire Wright, Ms Catherine Fiebiger, Ms Caroline Johnston.

CSIRO

Thank you

Prashant.Srivastava@csiro.au

CSIRO

Australia's National Science Agency

REMTEC

& EMERGING CONTAMINANTS

SUMMIT

OCTOBER 15-17, 2024

Practical Considerations of Linear and Branched PFAS Isomers for Evaluating PFAS Fate, Transport and Attenuation

Track 7 PFAS Fate and Transport Considerations

Dora Chiang, Ph.D., P.E.

Jacobs

Distributions of PFAS Isomers in the Environment

Significance of PFAS Isomers on Site Investigation

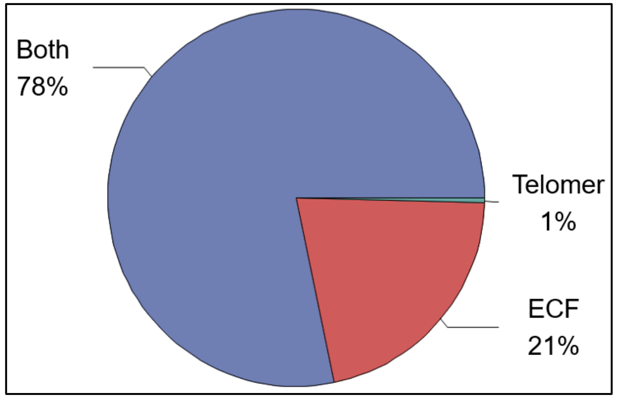
PFAS Isomer Distribution Impacted by Remediation

Case Study

Summary

Introduction

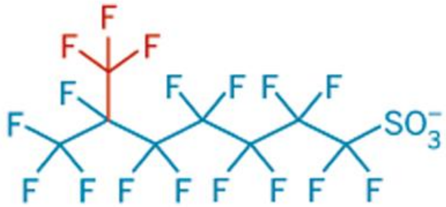
- ECF processes produced linear and branched perfluorinated isomers from the 1950s through 2002
- Research conducted on 3M Co. ECF process (Benski et al, 2010; Buck el.al, 2011; Londhe et. al, 2022):
  - PFOA 78% linear and 22% branched isomers
  - PFOS 70% linear and 30% branched isomers
- Following the 2002 phase-out, linear PFOA (L-PFOA) and other L-PFCAs have predominantly been produced by the fluorotelomerization process
- Different branched isomers exhibit varying chemical and physical properties, consequently leading to distinct toxicological, persistence and bioaccumulation potentials (Fang et al. 2016; Houde et al. 2008).
- Most sites have been impacted by both ECF and FT formulations, the significances of linear and branched isomers on conceptual site model are rarely investigated.



Distribution of formulations identified at AFCEC's AFFF-impacted sites (Anderson, 2019)

PFOS Linear Isomer

Linear Isomer



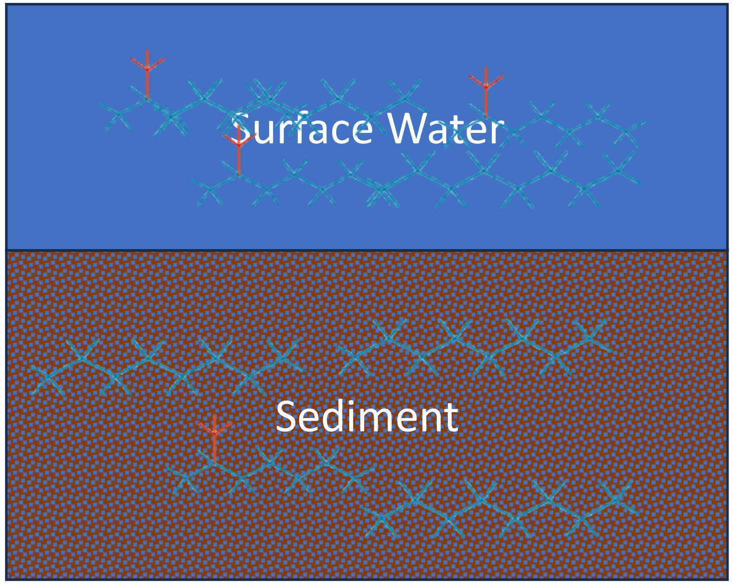
PFOS Branched Isomer (P6MHpS)

Branched Isomer

Environmental Factors Contributing to the Variations of Linear vs Branched Isomer Ratios

Once PFAS isomers were released into the environment, both natural and anthropogenic processes can modify the ratio between linear and branched isomers.

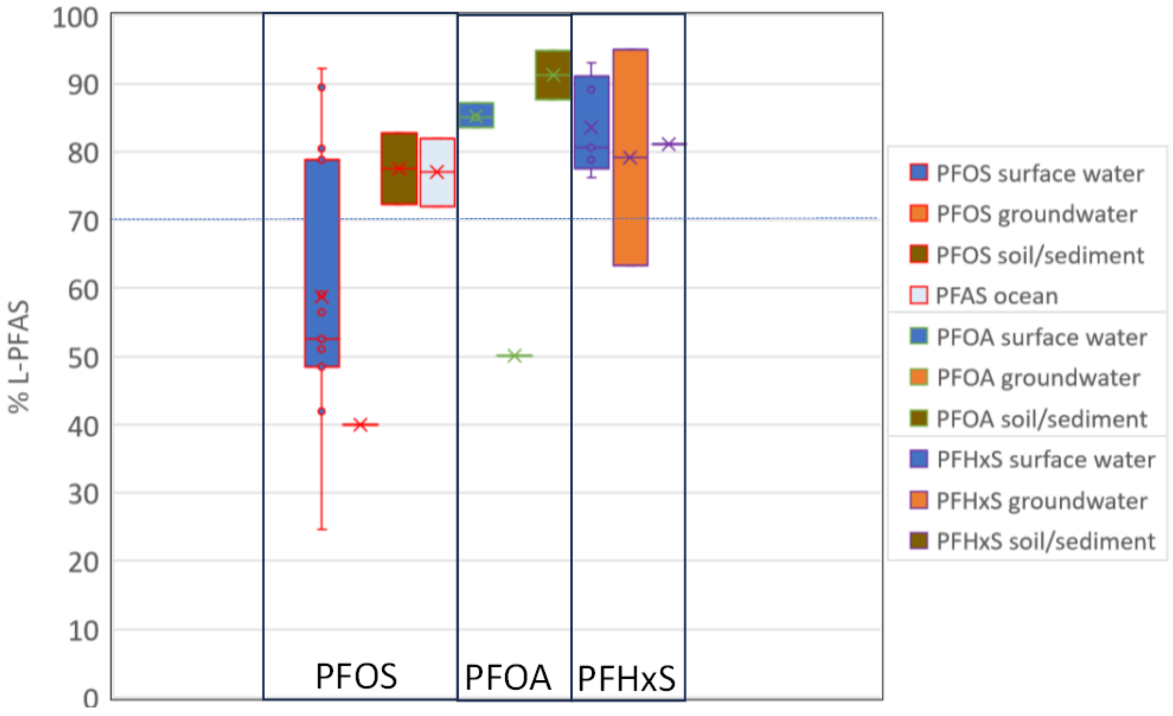
- Interactions with **hydrogeological and geochemical processes** *in situ. For example,* L-PFAS sorption on aquifer materials(e.g., sediment) would lead to higher Br-PFAS ratios (enriched Br-PFAS) in water matrices
- Isomer-specific **precursor transformation**. As terminal products (e.g. PFOS) are likely generated through more than one pathways or precursors, the final isomer ratio is determined by several upstream reactions
- Interactions with **remediation activities** at the site (preference of removing/degrading linear or branched PFAS)
- However, the isomer research is also limited by the availability of branched isomer standards



Br-PFOS/L-PFOS=0.63

Br-PFOS/L-PFOS>1

PFAS Isomers Distribution in the Environment



(Original data: Schultz et al. 2020)

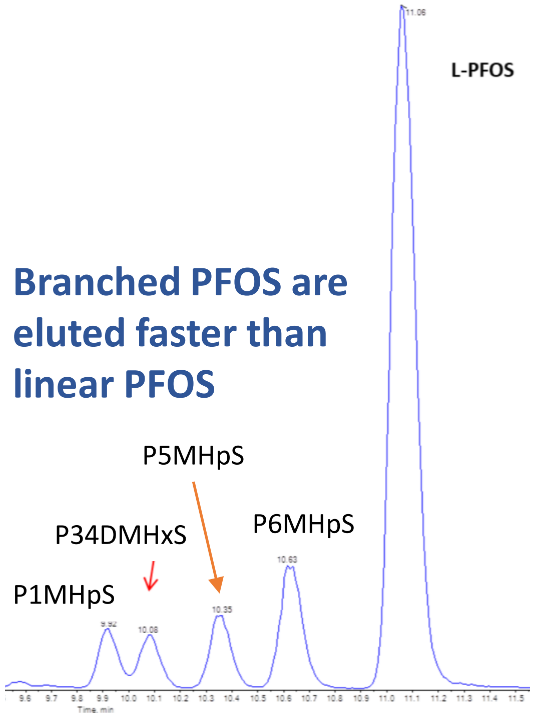
- L-PFOS, L-PFOA and L-PFHxS were found enriched in sediment and soil due to higher hydrophobic sorption thank branched PFAS
- L-PFOS% in surface water exhibit wide variability with averages lower than 70%, indicating the potential enrichment of branched PFOS (Br-PFOS) in surface water because of the L-PFOS sorption onto soil/sediment
- Br-PFOS “precursors” are more susceptible to transformation into Br-PFOS, in soil microcosm (Liu et al 2019)
  - Preferential transformation of branched precursors can therefore lead to an enrichment of Branched terminal PFAA products.
- Overall, the distribution of PFAS data reveal ***significant variations*** in the concentrations of branched and linear PFAS in the environment

Significance of Remediation to L/Br-PFAS Ratios

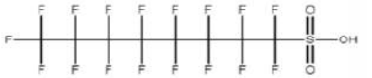
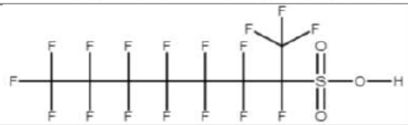
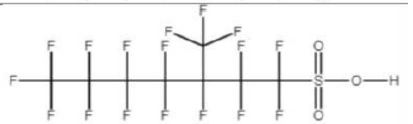
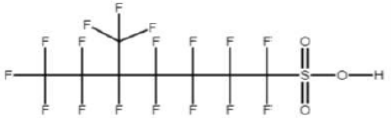
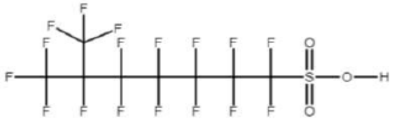
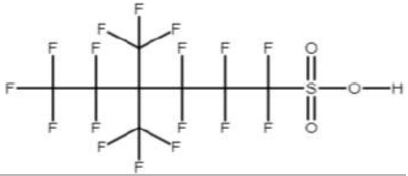
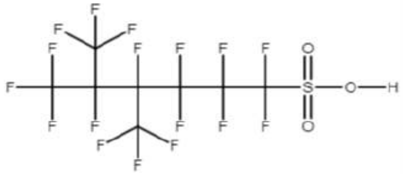
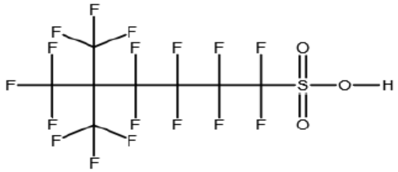
Treatment	Mechanism	Enriched isomers in effuent	Significance	Reference
GAC	Sorption	Branched	Preferential removal of linear isomer, rapid breakthrough of branched isomers	Belkouteb et al 2020; Eschauzier et al., 2012; McCleaf et al., 2017 ; Rodowa et al, 2020
Anion exchange resin	Electrostatic interactions	None	Br- and L- have similar electrostatic interactions	McCleaf el. Al., 2017; Park et. al., 2020
Reductive defluorination	Reductive defluorination	Linear	Greater Br- isomer degradation than L-isomers	Ochoa-Herrera et al. 2008
Electron beam	Electron affinity	Linear	Greater Br- isomer degradation than L-isomers	Trojanowicz et al. 2020
UV-Sulfite	Degradation	Linear	Tertiary -CF3 in Br-isomer is more susceptible to degradation	Yamamoto et al. 2007; Gu et al. 2016; Liu et al. 2020
Electrochemical oxidation	PFAS sorption followed by direct electron transfer and mineralization by hydroxyl radicals	Branched	Br-PFAS enriched in treated water because sorbed L-PFAS are more susceptible to electrochemical oxidation	Chaplin 2014; Radjenovic and Sedlak 2015; Uwayezu et al. 2021; Wang et al. 2020

Branched Isomer Analysis

- PFAS isomers are difficult to be separated and identified individually by established analytical methods
- USEPA methods currently mandate the users to integrate branched and linear peaks together and report total concentrations rather than isomer-specific concentrations.
- The final revision of USEPA Method 1633 still necessitates PFAS to be reported as a single result



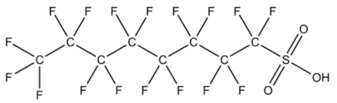
(Research data source: Jenny Zenobio, Jacobs)

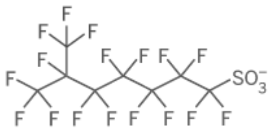
Target isomer	Acronym	Chemical structure
Perfluorooctanesulfonate	L-PFOS	
Perfluoro-1-methylheptane sulfonate	P1MHpS	
Perfluoro-3-methylheptane sulfonate	P3MHpS	
Perfluoro-5-methylheptane sulfonate	P5MHpS	
Perfluoro-6-methylheptane sulfonate	P6MHpS	
Perfluoro-4,4-dimethylhexane sulfonate	P44DMHxS	
Perfluoro-4,5-dimethylhexane sulfonate	P45DMHxS	
Perfluoro-5,5-dimethylhexane sulfonate	P55DMHxS	

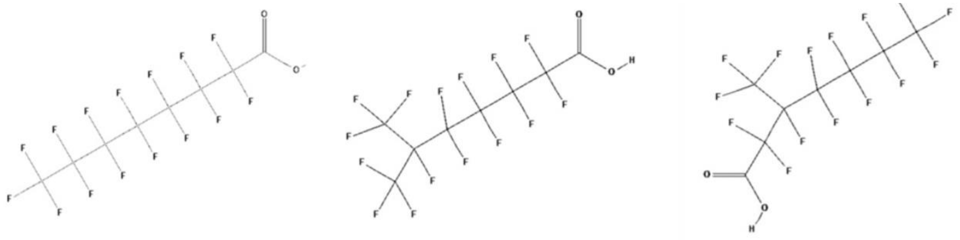
PFOS isomers, acronyms and chemical structures (Lennikov 2021)

General Understanding of Linear vs Branched Isomers in Groundwater at a Site

- **Linear isomers**
  - PFAS in ECF-based AFFF are expected to have Br/L ratios close to 30/70,
  - Fluorotelomers and their transformation products (PFCAs) would be theoretically all linear (Br/L 0/100)
  - When a site used both ECF and FT-based AFFF, Br/L PFCA ratios can be much less than 30/70 due to linear precursor transformation into linear PFCAs
- **Branched isomers**
  - Branched isomers exhibit lower partition coefficients between soil and water (Kd) or soil organic matter and water (Koc), branched isomers are less retarded than linear isomers
  - Br/L can be greater than 30/70 downgradient from the source when more L- isomers are retarded in the source area

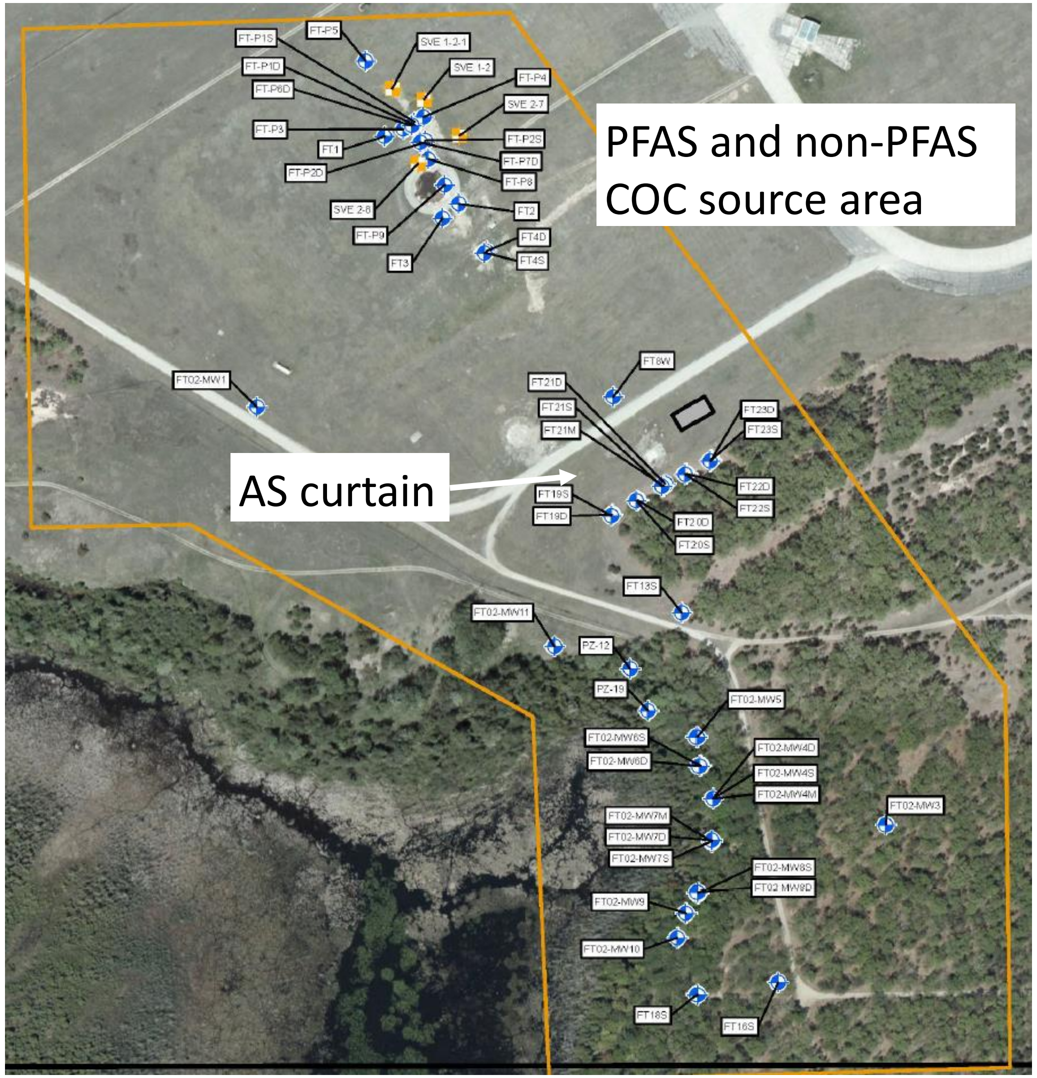






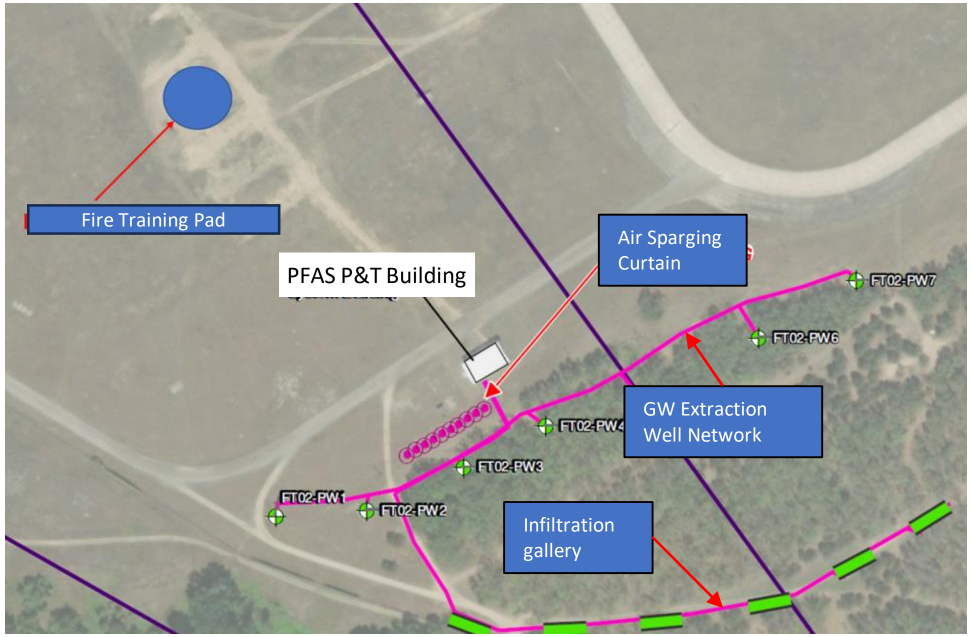
Case Study

Site Background



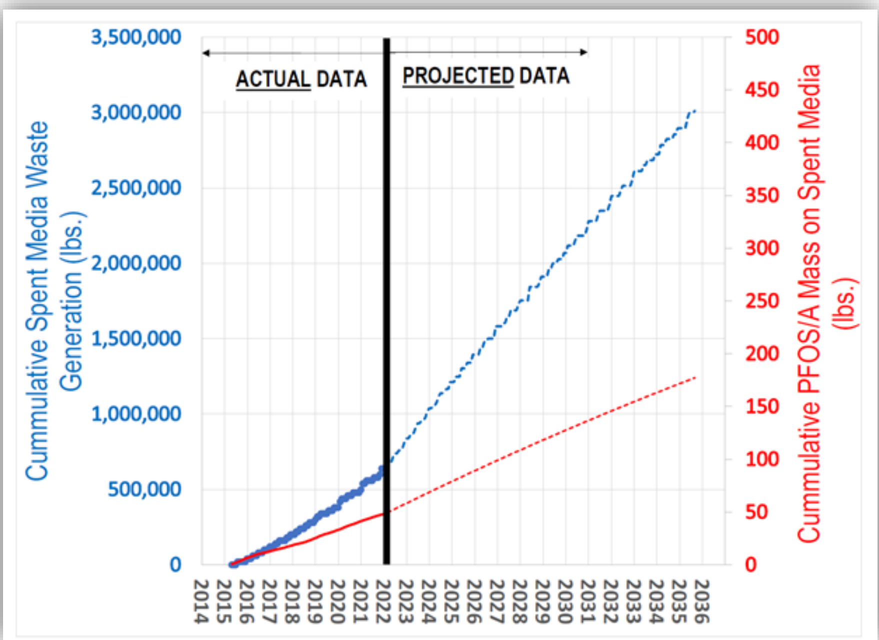
- Non-PFAS remedial actions completed at the Site
  - SVE for contaminated soils
  - Air sparging to treat smear-zone soils
  - MNA for VOC in groundwater
  - In-situ anaerobic biodegradation pilot study for nitrate reduction proximal to the source
  - AS curtain installation downgradient of the source area to address dissolved-phase
- The PFAS groundwater treatment system was installed and has been operated for ~10 years

GAC Treatment for PFAS Removal



Groundwater Extraction and Treatment

Full-scale GAC treatment of extracted groundwater



Estimated quantities of PFAS and spent media requiring waste management after 20 years of system operation
(Data source: WSP)

Detected PFAS in Groundwater at the Site

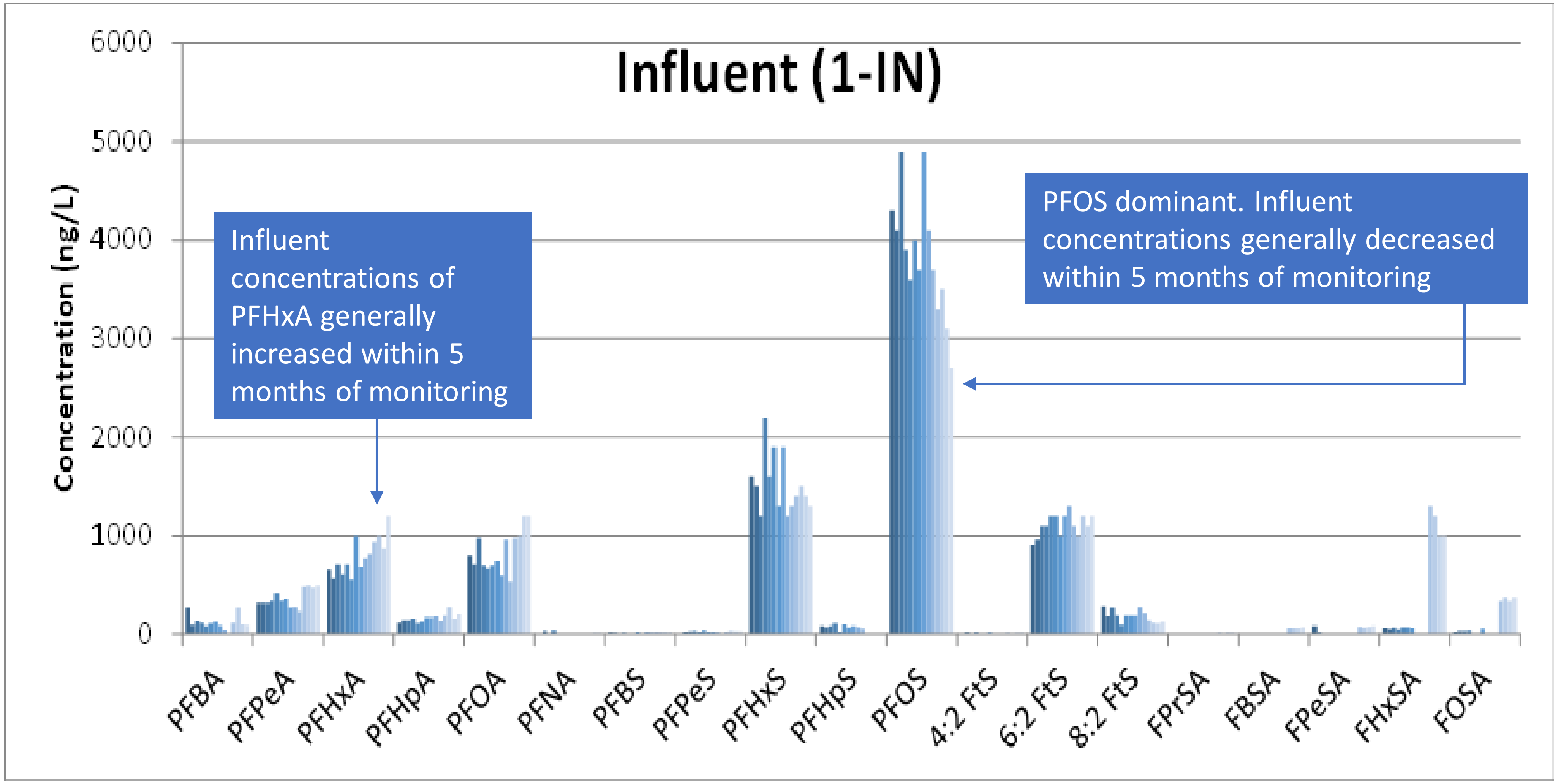
Groups	Chain length	ECF-Linear	ECF-Branched	FT Linear	Relevance to CSM
PFCAs	C6-C14	☑	☑	☑	
PFSAs	C4, C6 and C8	☑	☑		
Fluorotelomer sulfonates	4:2, 6:2, 8:2			☑	Intermediates of FT-based AFFF ingredient transformation
N-SP-FASA	C4-C6	☑	☑		
FASA	C3-C6	☑	☑		
PFASi	C4-C6, C8	☑	☑		Possible indicator of anaerobic conditions
n:2 FASO2PA-MePS	C6, C8			☑	Possible oxidized degradation product of FT-based AFFF active ingredient
N-CMAmP-*n*:2 FASA	C4-C6			☑	Possible active ingredient in FT-based AFFF
N-AP-*n*:2 FASA	C4-C6			☑	Possible active ingredient in FT-based AFFF

Focused Pilot Study to Investigate PFAS Removal Using GAC

- Monitor for sorption of PFAS precursors
- Investigate linear and branched PFAS in a GAC treatment system
- Weekly sampling for 5 months

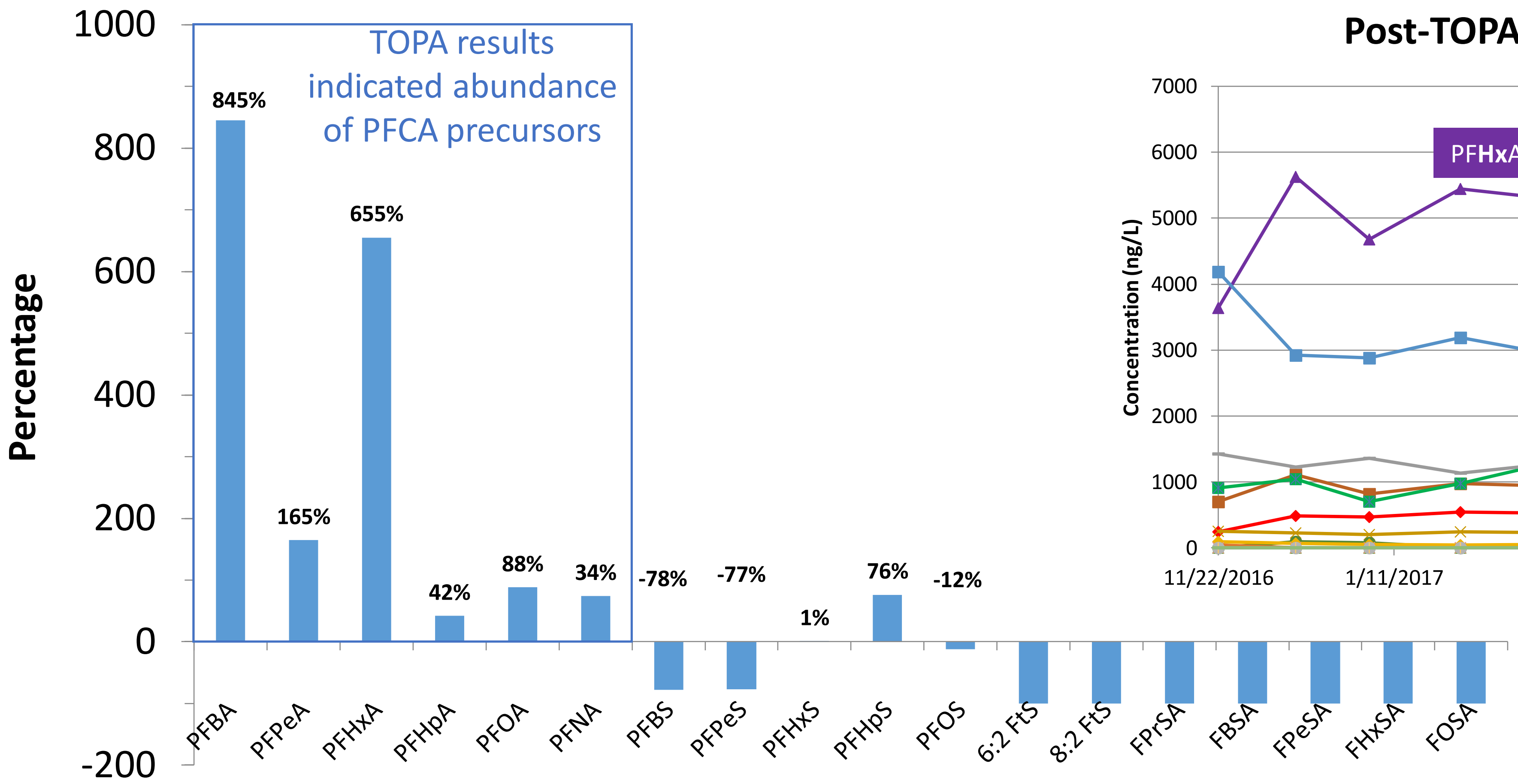
Analytical Parameter	Frequency	Laboratory	Method
PFOS and PFOA (screening purpose)	Weekly	Dr. Huang/UGA	UPLC/MS/MS
Volatile Organic Compounds	Monthly	Commercial Labs	USEPA 8260B
Total Organic Carbon	Monthly	Commercial Labs	TOC 5000A
Fluoride	Monthly	Dr. Huang/UGA	IC-MS
Optimized WAFB Site Specific PFAS List	Weekly	Dr. Field/OSU	Orthogonal HPLC MS/MS Quadrupole Time-of-Flight Mass Spectrometry
Total Oxidizable Precursor Assay (TOPA)	Weekly	Dr. Field/OSU	PFAS analyses, same as above
Particle-Induced Gamma-ray Emission (PIGE)	Weekly	Dr. Graham Peaslee/U of Notre Dame	PIGE

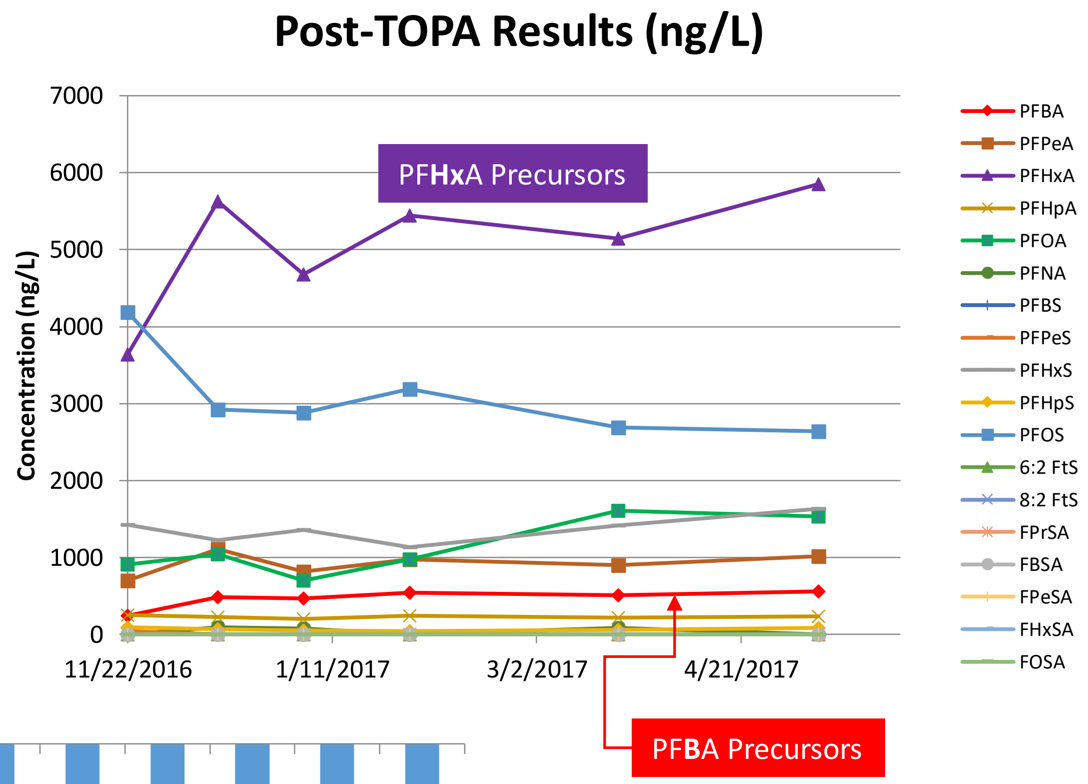
PFAS in the Influent of Pilot-Scale GAC System



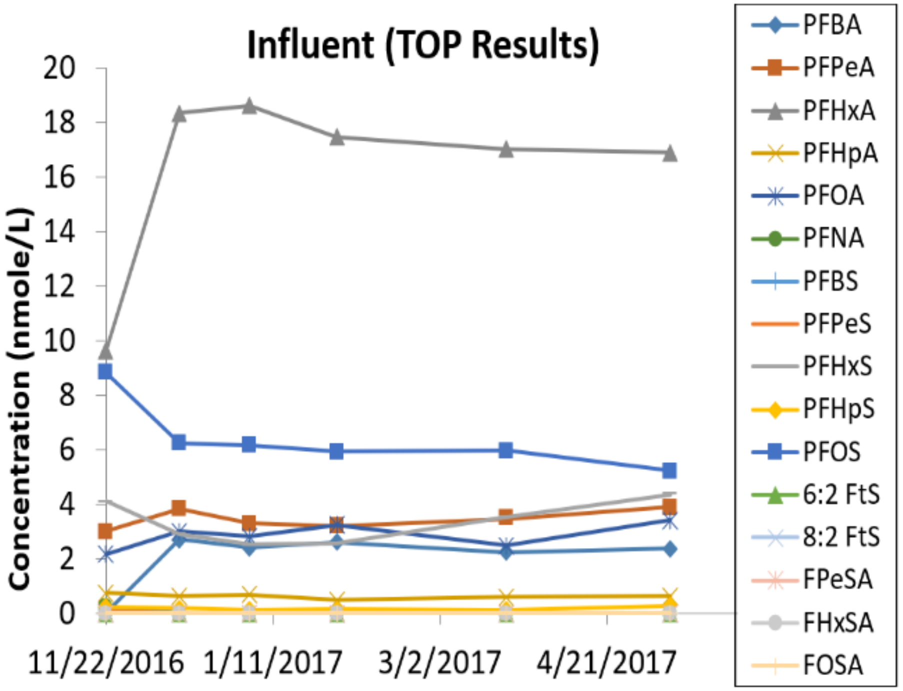
Many PFAS detected in groundwater were not detected in the influent

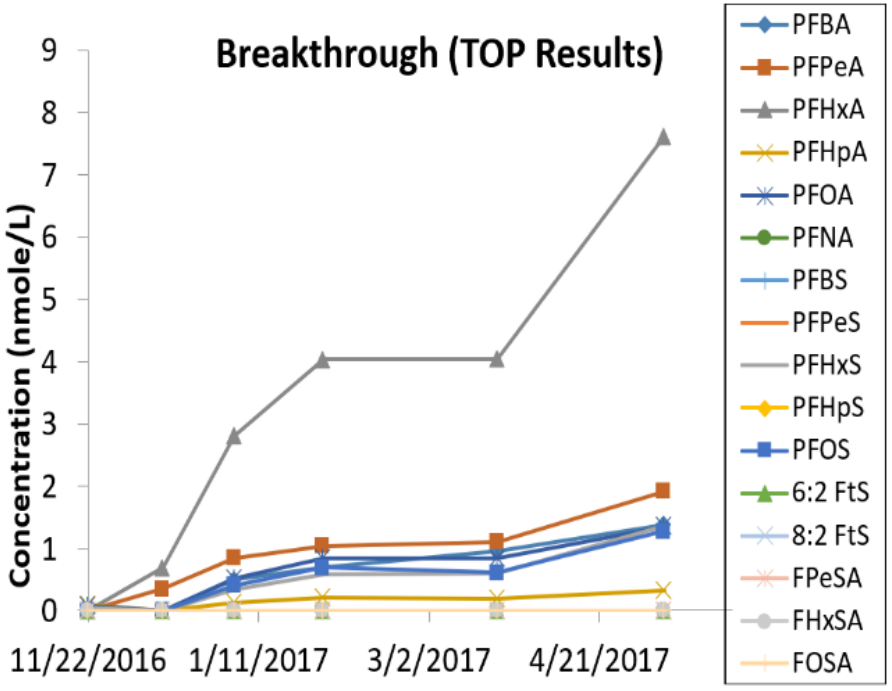
PFAS Precursors in the Influent of Pilot-Scale GAC System (TOP Assay Results)





Breakthrough of PFAS Precursors in the Effluent of Pilot-Scale GAC System (TOP Assay Results)





Linear vs Branched Isomers in in the Influent of Pilot-Scale GAC System

PFAS	Average Influent Concentration (ng/L) Branched	Linear	Branched/Linear (30/70=0.43)
PFBA	<LOQ	100 ± 22	<0.43
PFPeA	19 ± 2.5	350 ± 47	0.054
PFHxA	<LOQ	740 ± 70	<0.43
PFHpA	15 ± 2.0	150 ± 20	0.1
PFOA	81 ± 7.2	820 ± 73	0.1
PFNA	<LOD	18 ± 5.7	<0.43
PFBS	<LOD	17 ± 3.0	<0.43
PFPeS	<LOD	30 ± 9.0	<0.43
PFHxS	190 ± 29	1400 ± 210	0.14
PFHpS	29 ± 5.5	62 ± 11.9	0.47
PFOS	1200 ± 110	1900 ± 170	0.63
4:2 FtS	NA	13 ± 3.0	No branched isomers
6:2 FtS	NA	1000 ± 76	
8:2 FtS	NA	170 ± 35	
FPeSA	<LOQ	125 ± 5.8	<0.43
FHxSA	700 ± 48	2100 ± 140	0.33
FOSA	100 ± 9.4	200 ± 19	0.5
N-TAmP FHxSA	51 ± 21	97 ± 40	0.52

<0.43: Linear isomers are dominant and enriched

L- PFCAs were enriched (Br/L<0.43) in the influent possibly due to FT-precursor transformation at the site

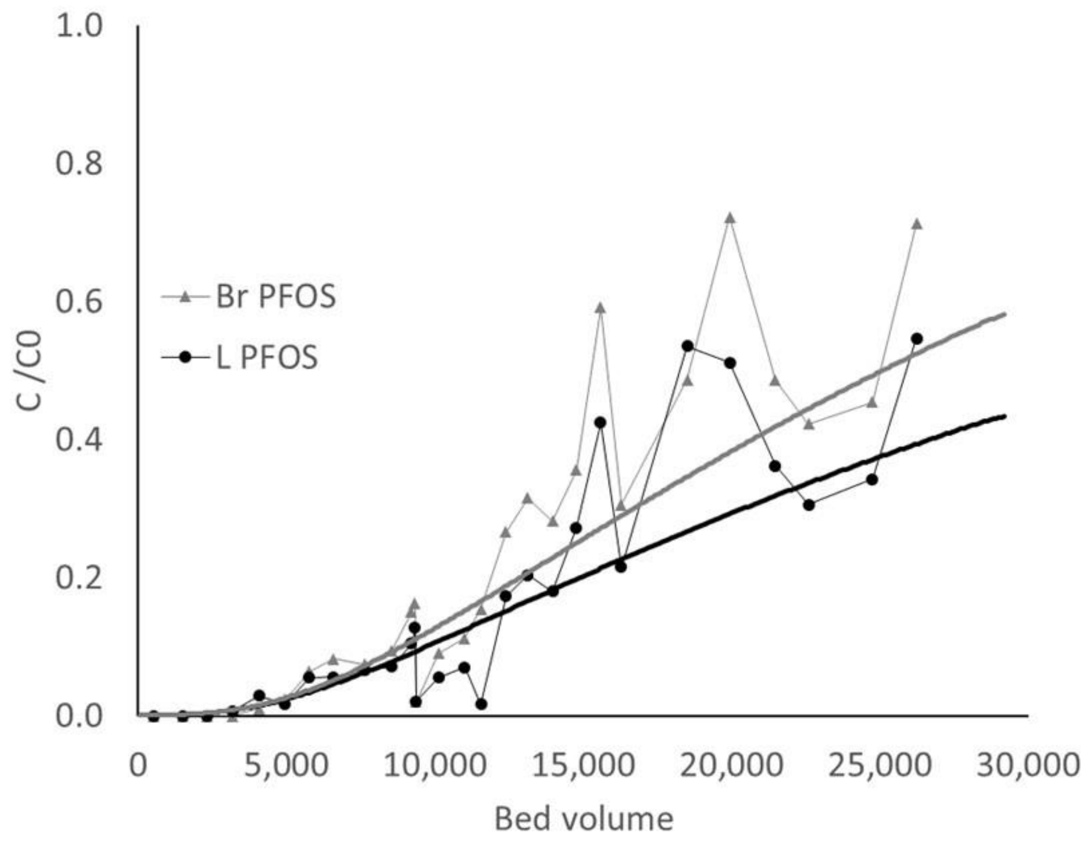
Low detections, no branched isomers detected

Br-PFSAs and Br-FASAs were enriched (Br/L>0.43) possibly due to L-PFSAs retained in the aquifer materials

Linear only, indicators of FT based foams

Transformation products of ECF foams

Breakthroughs of Linear and Branched PFOS in the Effluent of Pilot-Scale GAC System

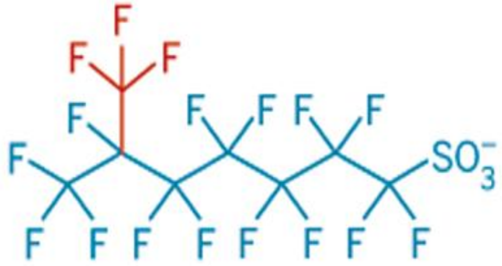


- Average Br-PFOS/L-PFOS = 0.63 in the influent
- The breakthrough curve shows Br/L>1 indicating greater retention of L-PFOS in GAC vessels

Takeaways

- Data collected from influent monitoring
  - Characterization of influent provides preliminary assessment of PFAS fate and transport
  - Mixed uses of FT and ECF AFFF could be verified using multiple lines of data collection (target and isomer analyses)
  - L- PFCAs were enriched (Br/L<0.43) in the influent suggesting abundant uses and releases of fluorotelomers (L isomers only) that have been converted into linear PFCAs over time
  - L-PFCA precursor transformation may be impacted by the site remediation actions (SVE and air sparging)
  - GW data showed branched PFSA and FASA isomer enrichment (Br/L>0.43) in the influent
    - Linear PFSA and FASA adsorbed in the aquifer materials

PFOS Linear Isomer



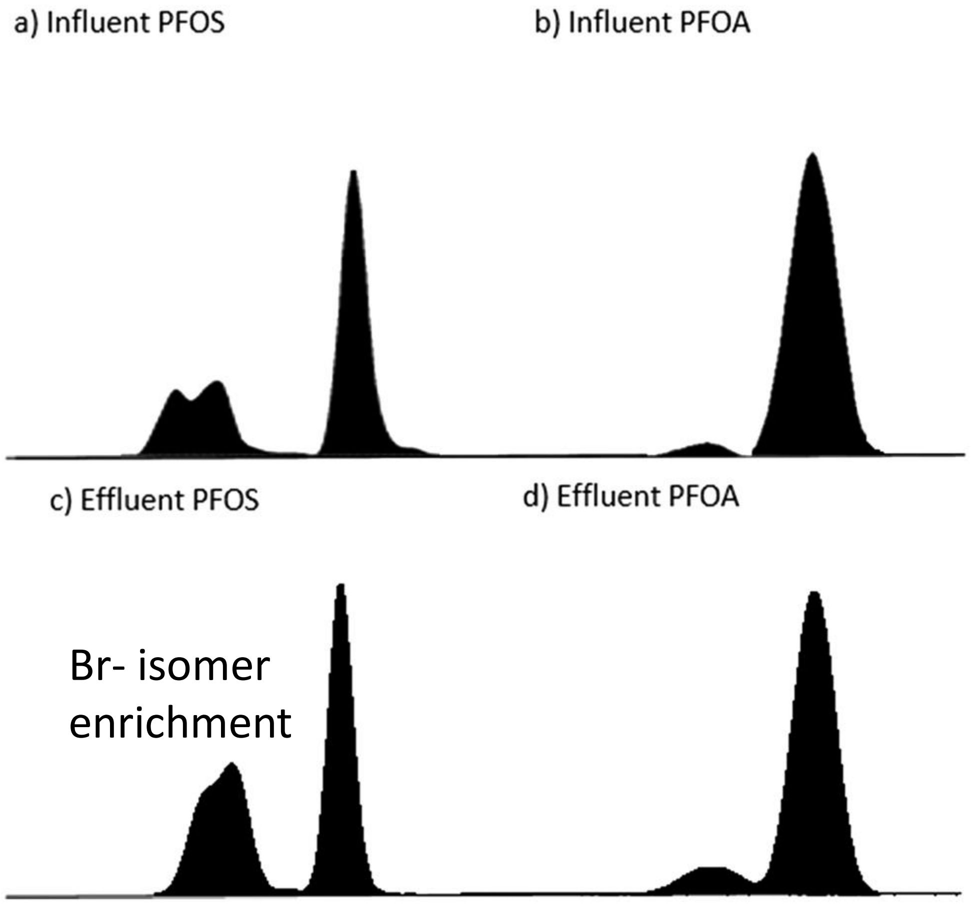
PFOS Branched Isomer (P6MHpS)

Takeaways

- Precursors do migrate and travel in this case study. The branched and linear isomers do have impact to the understanding of PFAS CSM and treatment effectiveness

- Branched PFSAs would also be more leachable in the aquifer than linear isomers. This is evident by the enriched Br isomers in PFSAs and FASAs in the influent

- Branched isomers with lower Kd and Koc than linear isomers
  - Break through GAC faster than L isomers
  - Br isomer enrichment in the effluent



Br and L isomers for a) PFOS and b) PFOA in influent and c) PFOS and d) PFOA in lead vessel effluent at 11 000 bed volumes.

Summary

Standardized analytical approaches are needed to differentiate and quantify the PFAS isomers for site investigation and treatment

PFAS isomer characterization will allow the system design and operation to cope with Br-PFAS that are more difficult to be removed by GAC

When the stringing federal and state regulatory limits are near zero, enrichment of branched isomers in the influent can increase OM&M costs

More research is needed to assess degradation rates, reaction mechanisms, and competitive sorption of specific isomers not only in the environmentally realistic mixtures, but also in the phase of bioaccumulations and evaluating PFAS treatment options.

Higher resolution of PFAS investigation and establishment of monitoring program to monitor for the changes of PFAS composition overtime will help establish a better CSM and ultimately optimize the selection of PFAS treatment technologies for site cleanup.

Acknowledgement

University of Georgia
Dr. Jack Huang and his research team

Oregon State University
Dr. Jennifer Field and Dr. Alix E. Rodowa

Thank You

Dora Chiang, Ph.D.
Jacobs
Atlanta, GA
Dora.Chiang@jacobs.com
(404)4051214