

Non-Extractable PFAS in Solid Matrices Using Draft 1633 Method, How to Improve Your Understanding?

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What to do with Single-Use, Spent Anionic Exchange Resin (AER)?

- Active Pump & Treat System:
 - Chemicals of concern: PFAS & VOCs
 - AER treated groundwater ~ 2-year period before PFAS breakthrough
 - Lead vessel containing ~17,800kg of spent AER for waste management

AFCEC BAA project

On-site full-scale destruction of PFAS and spent AER using Supercritical Water Oxidation (SCWO) technology



Lead vessel:
600 ft³
~17,800 kg AER



Spent Anionic Exchange Resin (AER)
Pump and Treat System Solid Waste

Why is Spent Media Characterization Important?

Managing PFAS laden solid waste

- Is it OK to landfill?
- For SCWO demonstration –
 - Need to quantify PFAS in spent AER to calculate PFAS destruction and removal efficiency (DRE)
 - PFAS mass balance



Spent AER Management Options



Spent AER Extraction Study – SCWO Mass Balance and DRE

- WSP was funded to develop and demonstrate destruction of PFAS-laden spent media using SCWO
- Mass balance study to be performed to support PFAS DRE

$$M_{Inputs} = M_{Outputs} + M_{\Delta}$$

$$M_{Inputs} = M_{Feedstock\ AER\ Slurry(s)} + M_{Feedstock\ AER\ Slurry(aq)}$$

- DRE is calculated as the relative percent difference of total mass inputs and outputs:

$$\%DRE_{PFAS} = \left(\frac{M_{Inputs,PFAS} - M_{Outputs,PFAS}}{M_{Inputs,PFAS}} \right) \times 100\%$$

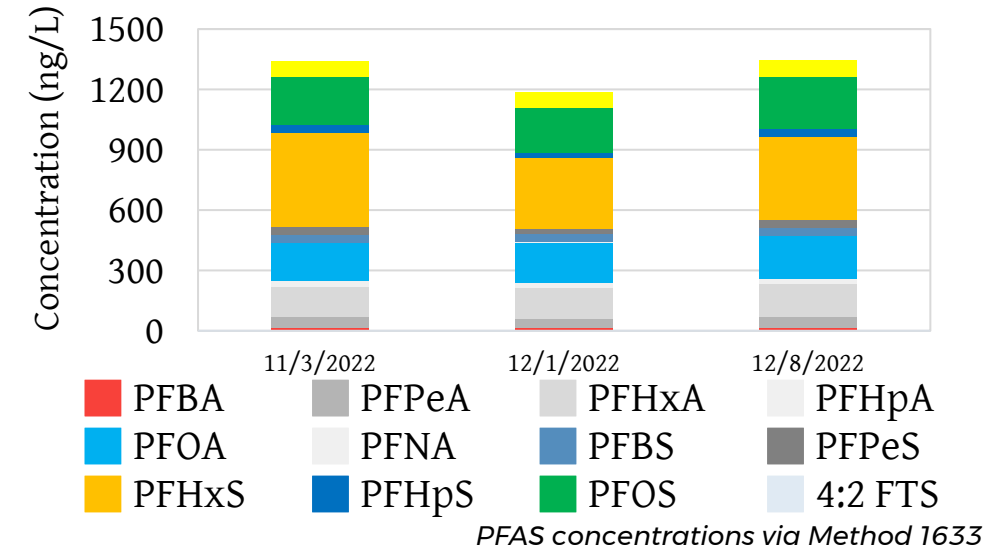
Initial PFAS Mass Estimate - System Operational Data

PFAS in the spent AER

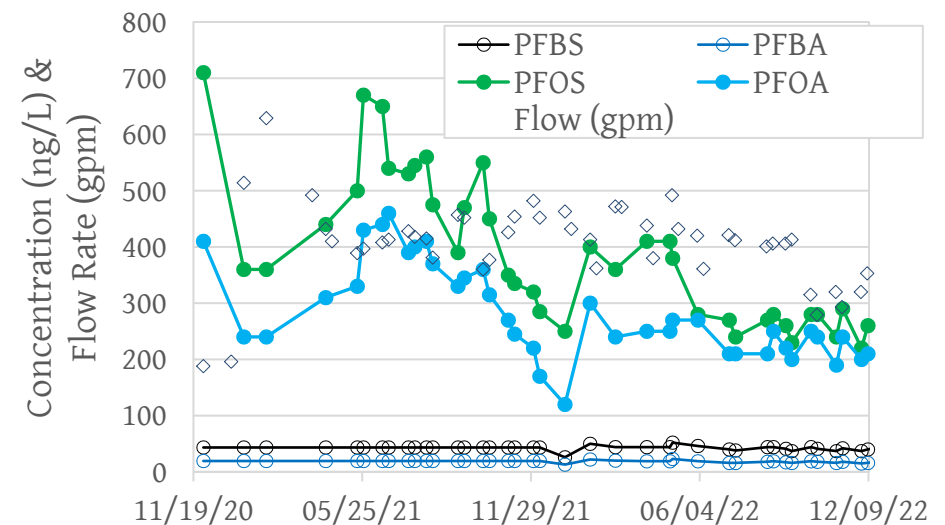
- PFAS present in influent:
PFHxS > PFOS > PFOA > PFHxA...
- Estimated PFAS loading in AER
based on system operational data:

~195 mg-PFAS/kg AER
(~127 mg-F/kg)

Detected PFAS in System Influent (Groundwater)



Influent Flow Rate & Tracked PFAS Concentrations



AER Extraction Study – Mass Balance and DRE



Spent AER

- Virgin AER
- Spent AER
- Cryomilled AER: **physical** mechanism to increase AER surface area

Wash

- Remove inorganic fluorine (IF)
- Use 5% sodium chloride (NaCl) wash, per manufacturer instructions

Extract

- Repeat 1633
- Test four **chemical** extraction solutions

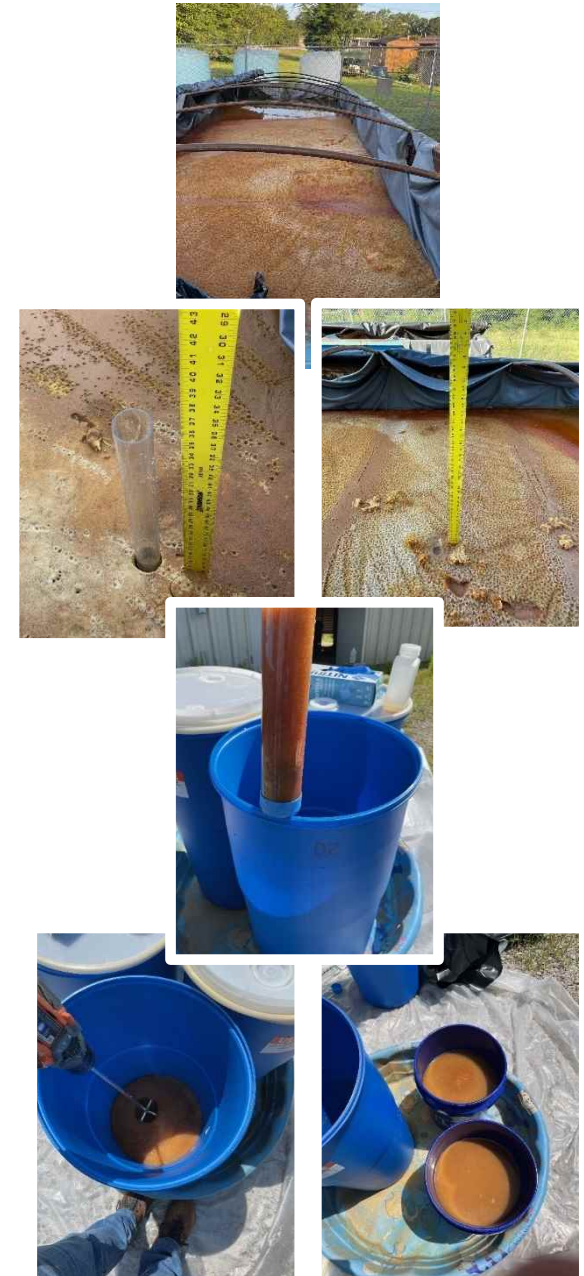
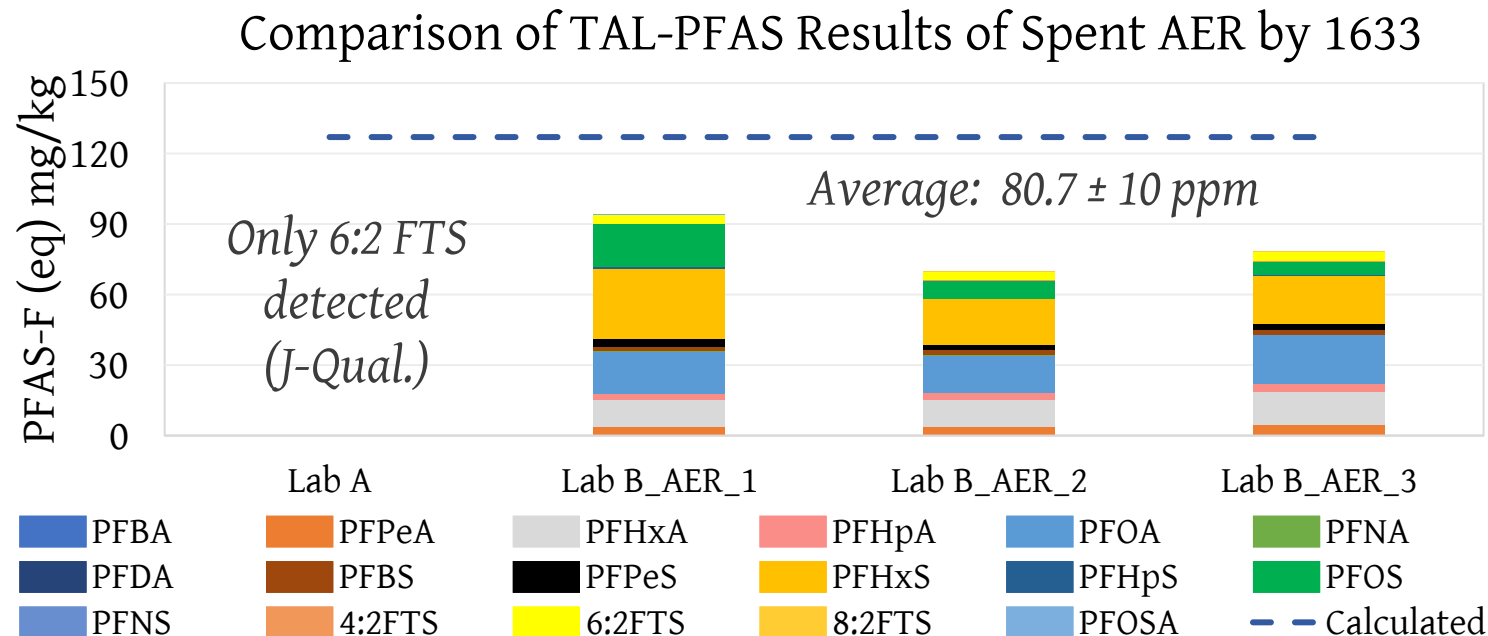
Analyze

- Solids: Unmilled, milled & post-extraction AER
- Liquids: Wash & extractants
- DRE: Target PFAS (Direct inject/1633)
- Mass Balance: total organic fluorine (TOF) via Direct Combustion Ion Chromatography (**dcIC**)

Laboratory Assessments of PFAS in AER (1633)

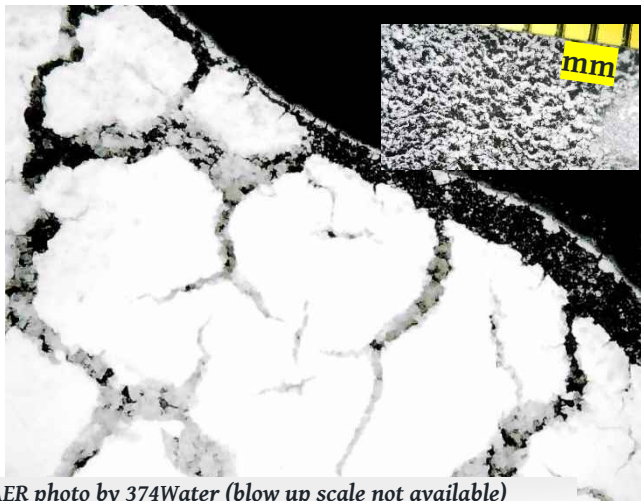
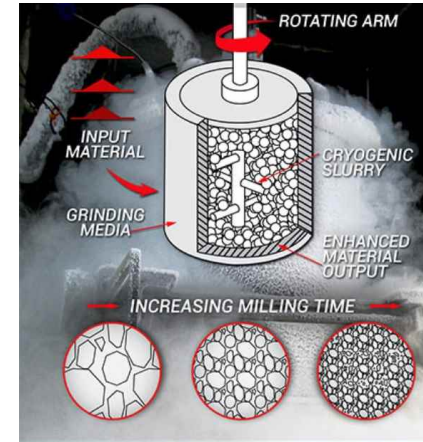
- WSP systematically collected composite samples of spent AER from rollofts to reassess PFAS load
- 1633 analysis performed by SGS (Orlando) detected higher levels of PFAS

Is there is better way to quantify PFAS in spent AER?

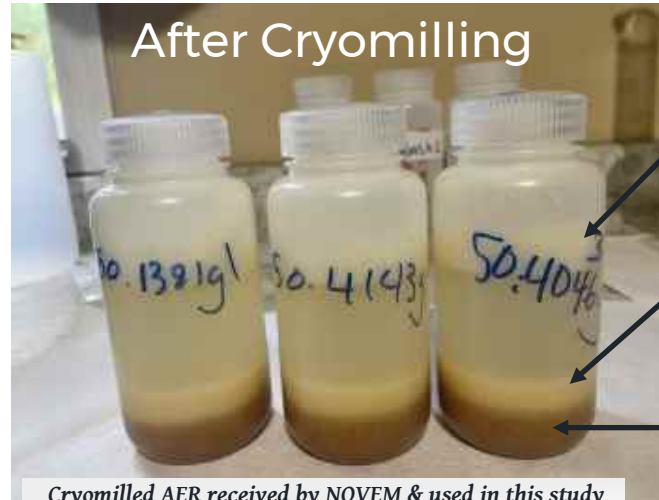


Cryomilling – Increase AER Surface Area to Enhance Desorption

- Cryomilling is laboratory-scale “ball milling” used commercially for product testing
- Uses liquid nitrogen cooling
 - Size constraints: 10x10 mm (~10 g)
 - Controls/optimization: milling cycles, frequency (Hz) or duration



Ground AER photo by 374Water (blow up scale not available)



Cryomilled AER received by NOVEM & used in this study

Wet foam
(collapsed)
Colloidal
powder
(~10% vol.)
Crushed AER
(~90% vol)

This study:

- Cryomilling performed per lab SOPs
- Two solid media produced

Chemical Extraction

Rinse

- 5% NaCl Wash (Remove IF; per manufacturer)

Extract

- Four extractants using organic solvents (methanol/acetone) and salts NaCl/ammonium chloride (NH_4Cl)¹:

A. 90% Methanol + 2% NaCl solution

B. 90% Methanol + 10% NH_4Cl solution

C. 90% Acetone + 2% NaCl solution

D. 90% Acetone + 10% NH_4Cl solution

- ✓ Mix 200 mL extraction solution with spent AIX (20 g)
- ✓ Shake for 30 min. (shaker table); centrifuge 10 min at 2800 rpms and repeat (x3; sequentially) to create composite solution

Analyze

- Extracts: Target PFAS (SGS - direct injection) and TOF (Novem - dCIC)
- Residual AER: Target PFAS (Method 1633 – SGS) and TOF (dCIC – Novem)

¹ Extraction solutions based on MacKenzie et. al. 2023, AXYS & WSP previous studies

TOF by Direct CIC (dCIC) – Mass Balance

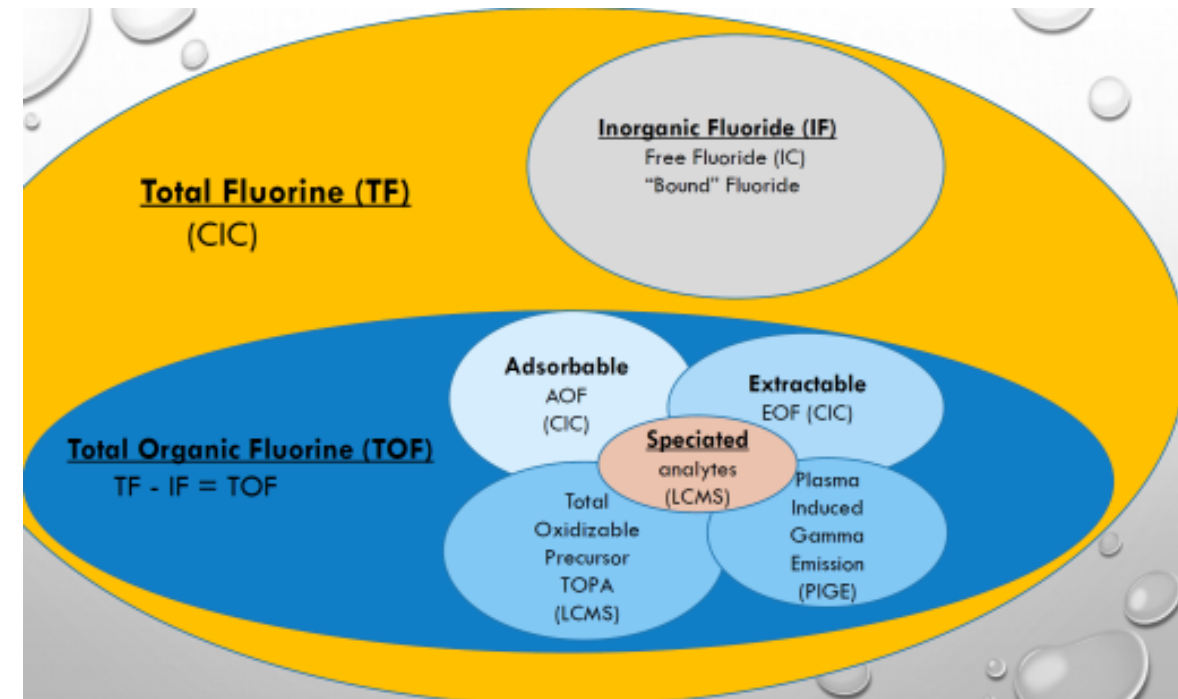
NOVEM's TOF Method

- No solvent extraction
- Not adsorbable organic fluorine (AOF) or extractable organofluorine (EOF)
- $\text{TOF} = \text{TF (total fluorine)} - \text{IF}$
- **Wash applied to remove IF *before* TF (TOF) analysis**
- Break C-F bonds and measure mineralized product (HF)
- Limit of detection:

1 milligram per kilogram (mg/kg)



Not an USEPA certified method

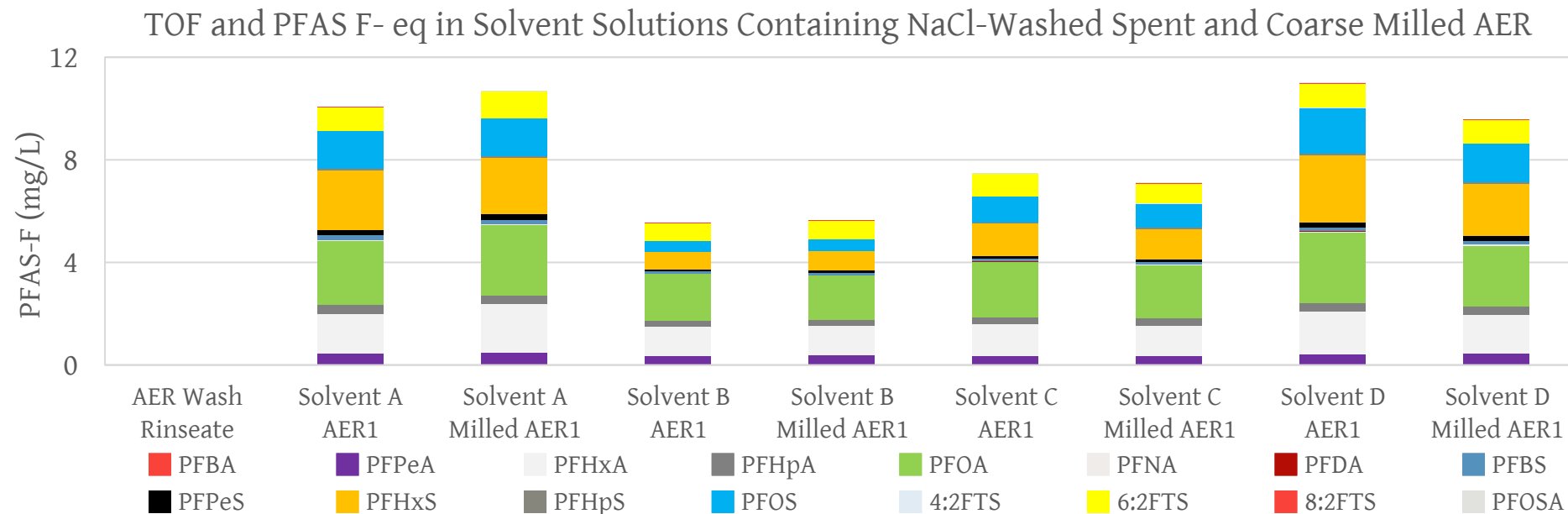


Extraction Solutions A-D - PFAS Removal

- A. 90% Methanol + 2% NaCl solution
- B. 90% Methanol + 10% NH₄Cl solution
- C. 90% Acetone + 2% NaCl solution
- D. 90% Acetone + 10% NH₄Cl solution

Extraction Solution Results

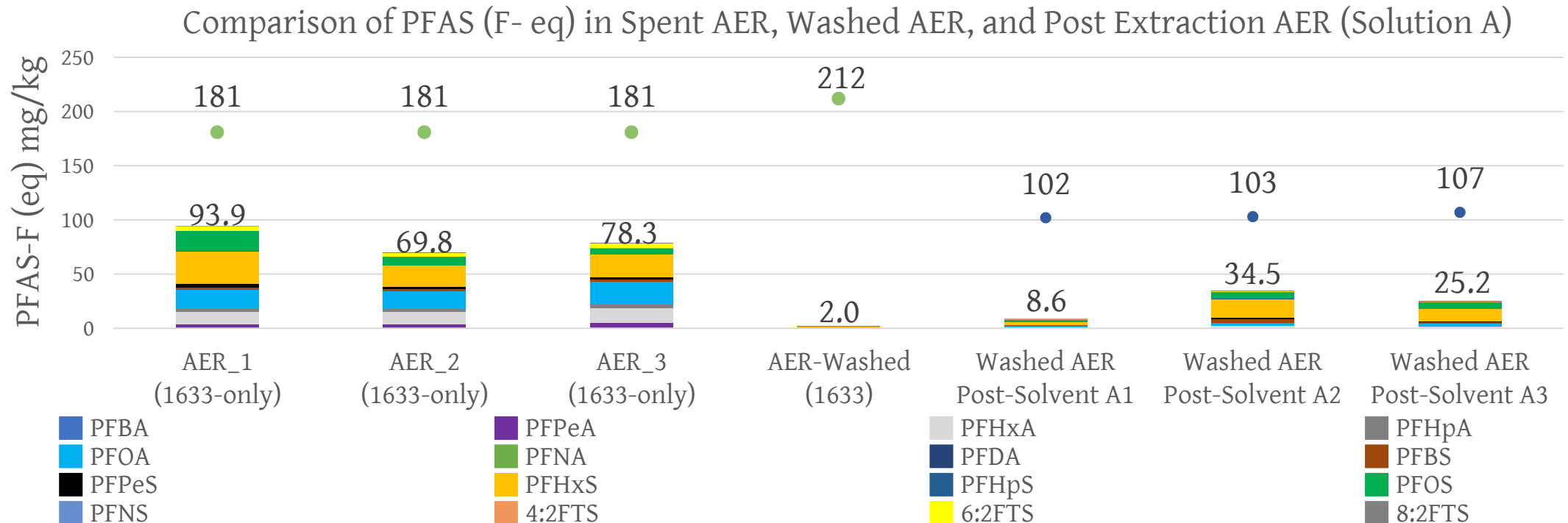
- PFOA, PFHxA, PFOS, PFHxS, PFPeA, 6:2FTS dominant in extraction solutions
- Similar results between coarse milled and unmilled AER samples
- PFAS are most extractable from spent AER using Solutions A and D



Solids: Comparing Spent, Washed & Post Extraction AER

PFAS in Spent AER – insights into 1633?

- 5% NaCl wash reduced measurable PFAS in the spent AER by 1633
- F-eq: TOF by dCIC > PFAS by 1633 (*No TOF detected in Virgin AER*)
- Some target PFAS remained in AER at completion of Solvent A extraction and could be further removed by 1633

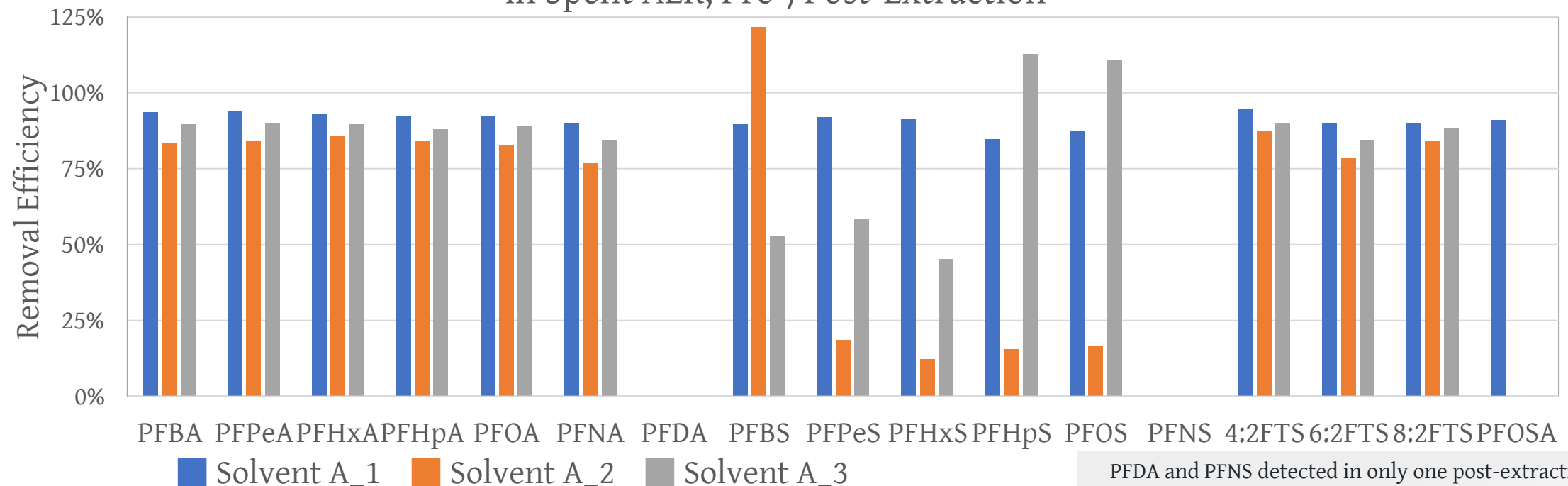


Further Assessment of Solution A Extraction Efficiency

What's missed: Comparison of PFAS in Spent AER (solids) Pre/Post Extraction

- Carboxylates (PFCAs) show consistent removal (typ. >80%)
- Sulfonates (PFSAs) show significant variation in replicates, including instances of improved desorption of PFBS, PFHpS and PFOS

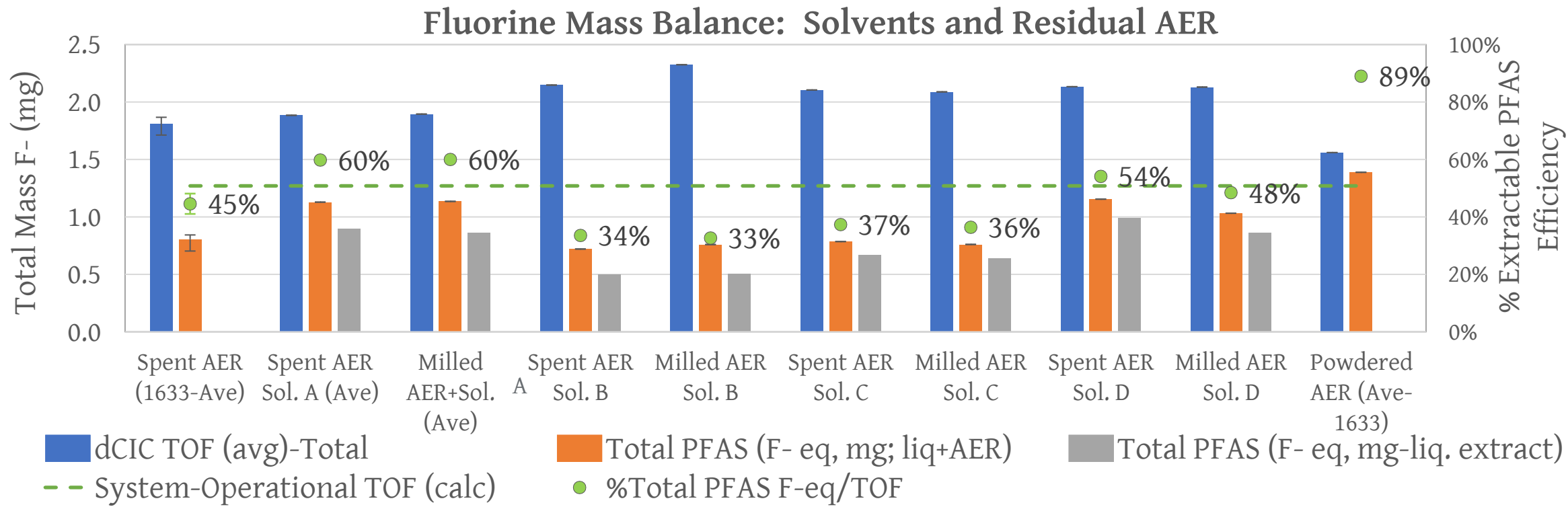
PFAS removal: Relative Percent Difference in Target PFAS
in Spent AER, Pre-/Post-Extraction



Mass Balance in Solids and Liquids to Improve DRE Calculations

Consider PFAS and TOF in both the solvent and residual solids (spent AER)

- TOF by dCIC supports hypothesis that system operational F- eq estimate is low
- Calculated F- eq of target PFAS < than TOF by dCIC
- Solvents A & D outperformed 1633 to *maximize* total target PFAS mass present
- Cryomilling (fine powder) analyzed by 1633 detected F- eq within 89% of TOF (dCIC)



WSP Summary and Next Steps

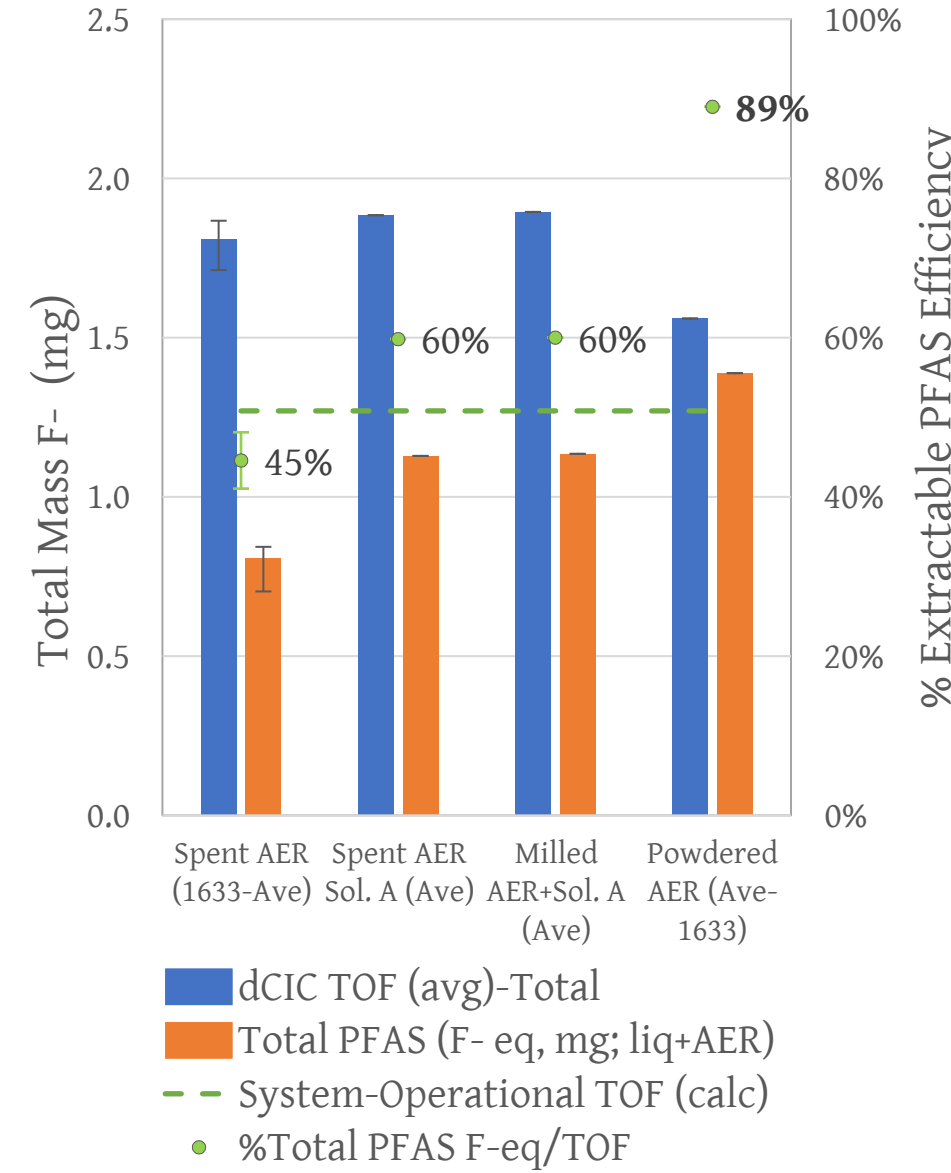
Key Findings

- Unmodified 1633 underestimated target PFAS and was affected by salt washing
- Solvent A quantified more PFAS than 1633
- Cryomilling to fine powder analyzed by 1633:
 - detected highest target PFAS
 - F-eq within 89% of TOF by dCIC
 - PFAS exceeds estimated influent loading
- dCIC provided critical QA/QC & assessment of extraction efficiency

Future Work

- Benchtop SCWO
 - DRE: Target PFAS via Cryomilling & 1633
 - Mass Balance: TOF/TF via dCIC
- Cryomilling: assess for potential PFAS destruction or transfer

Optimizing Target PFAS in Mass_{IN}



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Thank you