Decontamination of PFAS contaminated fire suppression system pipes –

Treatment verification with time-of-flight elastic recoil detection analysis (ToF-ERD)

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Thank You!!

Lutz Ahrens

Matthew Sharpe

Geraint Williams

Ian Ross

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Questions Tor Today

- How can we remove PFAS from surfaces of fire suppression systems?
- Which parameters affect the removal of PFAS from surfaces?
- How effective are treatments that we apply on contaminated surfaces?
- How can we measure / quantify PFAS concentration on surfaces?

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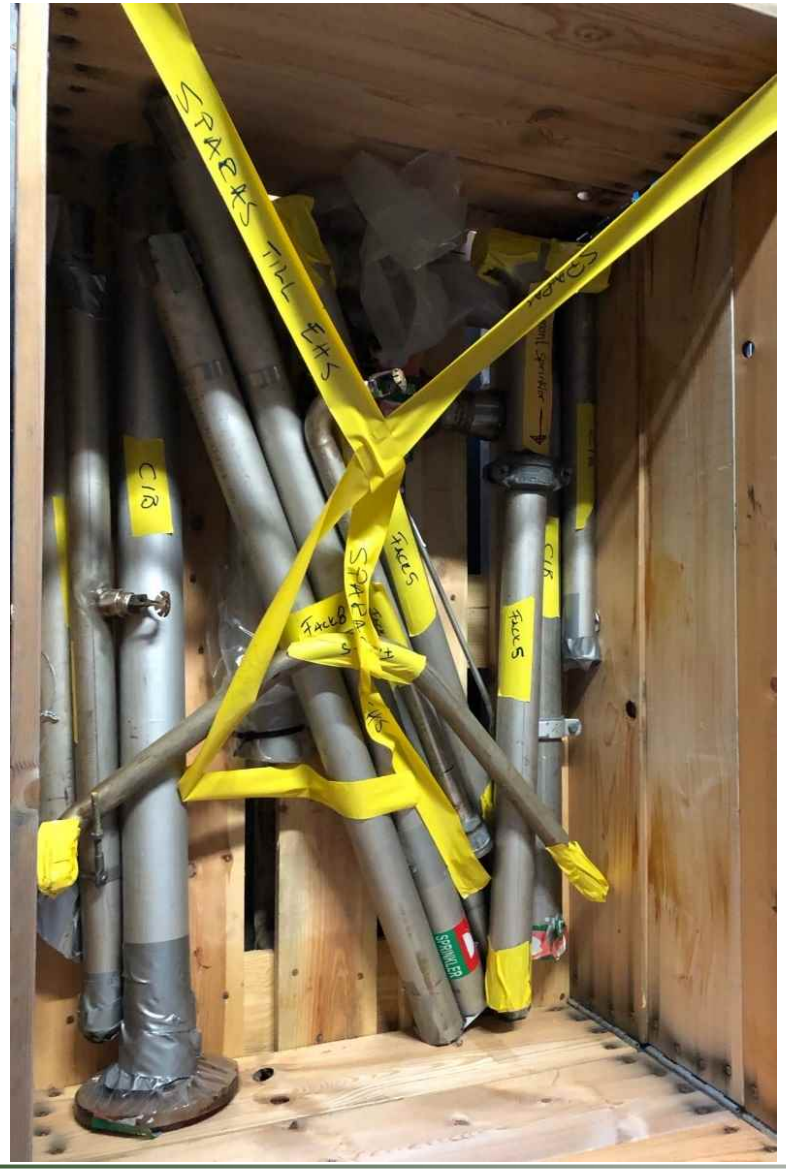
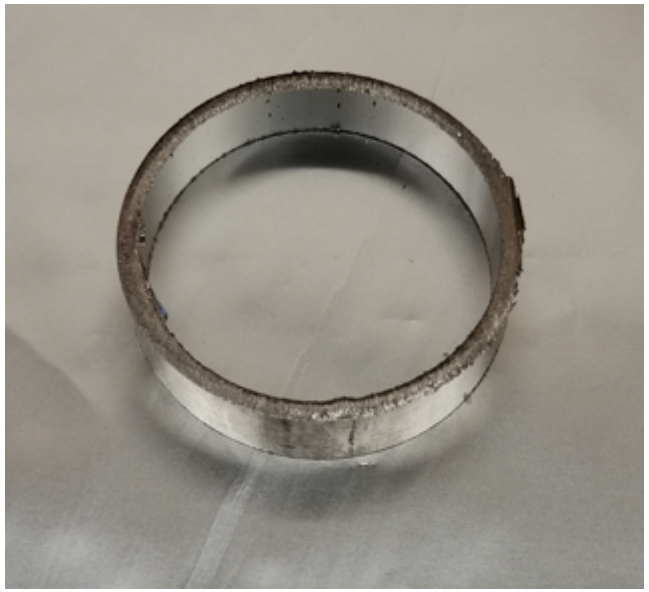
Material - History



- Decommissioned pipes of a stationary sprinkler system
- Stainless steel
- 2-3 decades of operation
- 4 different AFFF concentrates were used (ECF and Fluorotelomer foams)
- Phase out of PFOS based AFFF in 2011

Material – Pre-investigation



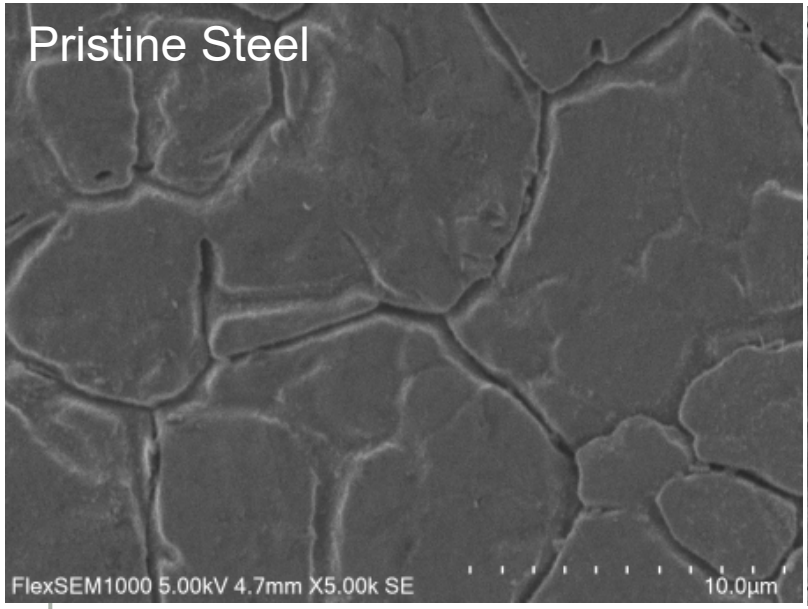
Objective – Use Most Impacted Pipe Sections

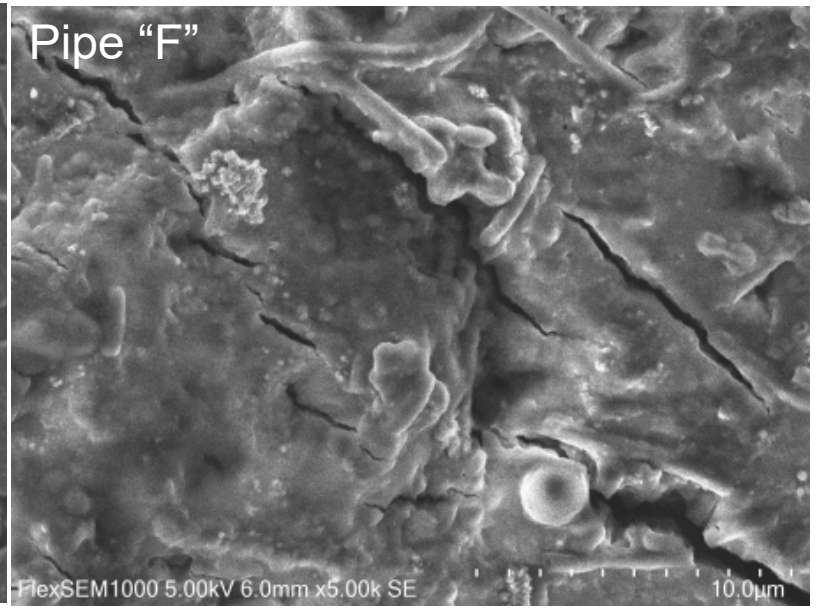
1. **Sonication in methanol (MeOH)**
   - 1 cm wide pipe sections
   - 30 min sonication
   - Analysis of MeOH via UPLC-MS/MS

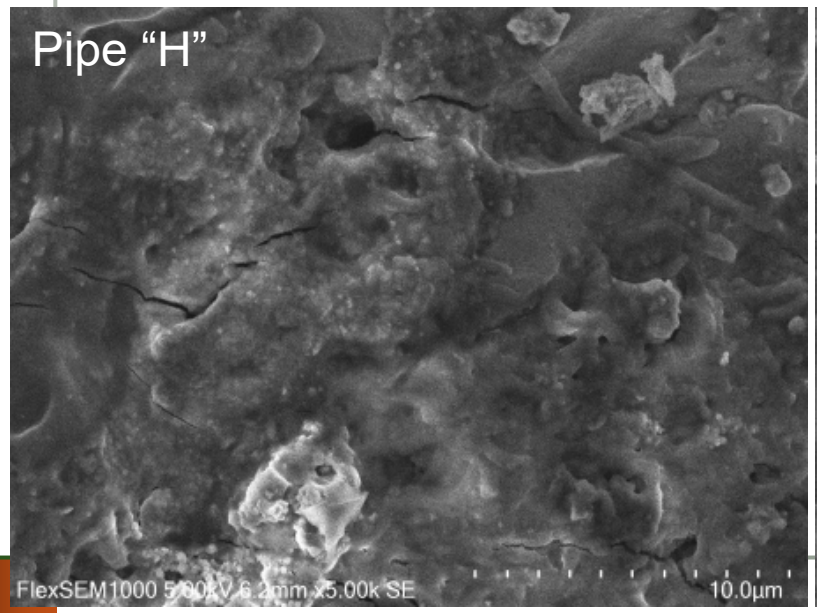
   → Pipe sections for further experiments: **F, H, I**

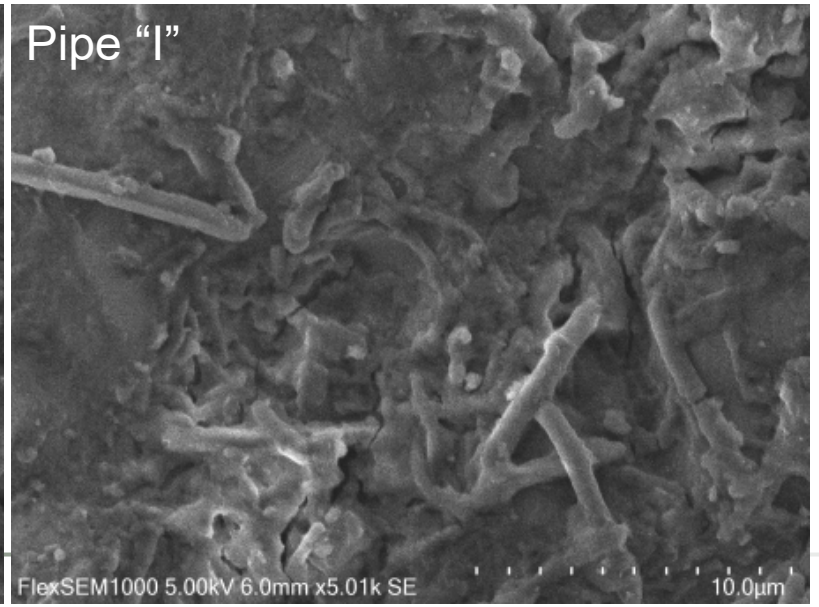
2. **Scanning Electron Microscopy (Energy-Dispersive Spectroscopy) SEM-(EDS)**
   - “Visualize” PFAS supramolecular assemblies on pipe surfaces
   - Compare surface structure to pristine stainless steel

Material – Scanning Electron Microscopy (SEM)









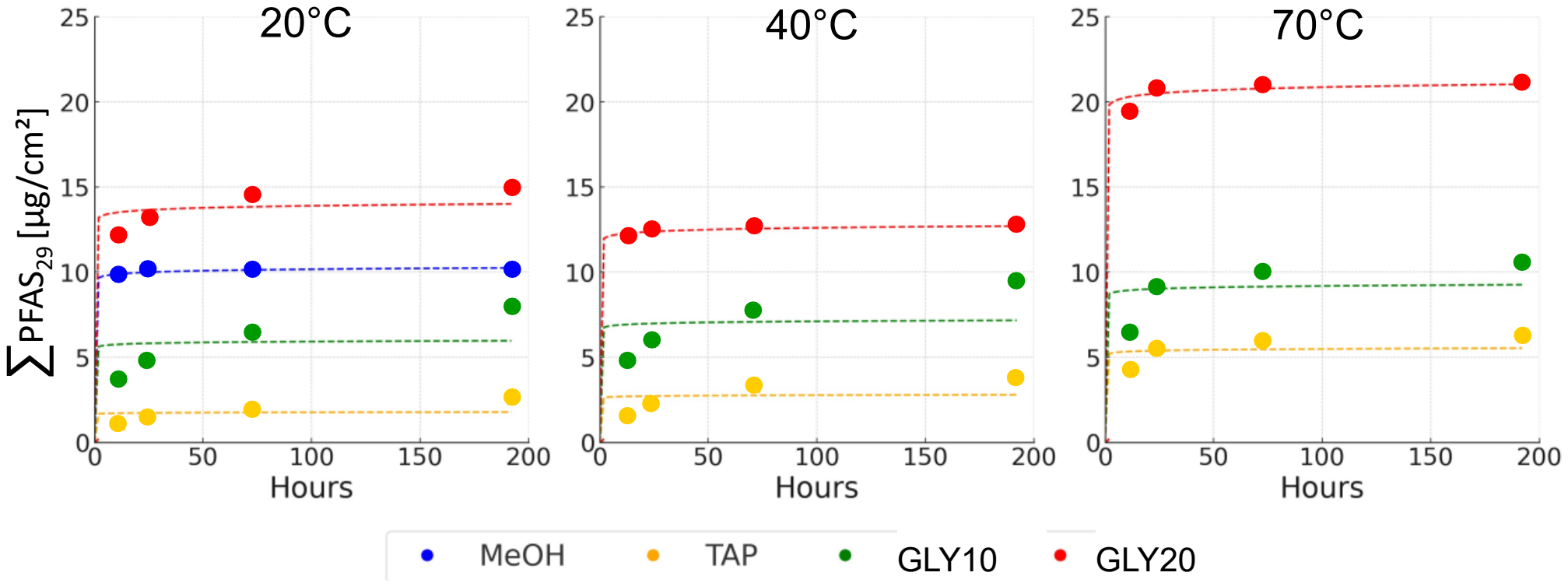
- Successful Visualization
- “AFFF-layer” covering the steel surface
- Multilayer structure → qualitative
- Layer thickness is unknown

Project Design – Soaking Experiment

	MeOH	TAP	GLY10	GLY20
20°C (RT)	✓	✓	✓	✓
40°C		✓	✓	✓
70°C		✓	✓	✓

- MeOH = Methanol
- TAP = Tap water
- GLY10 = Glycol (10%)
- GLY20 = (Glycol 20%)
- Time intervals: 12h, 24h, 72h and 8 days → **4 time points**
- **Unit µg/cm²**

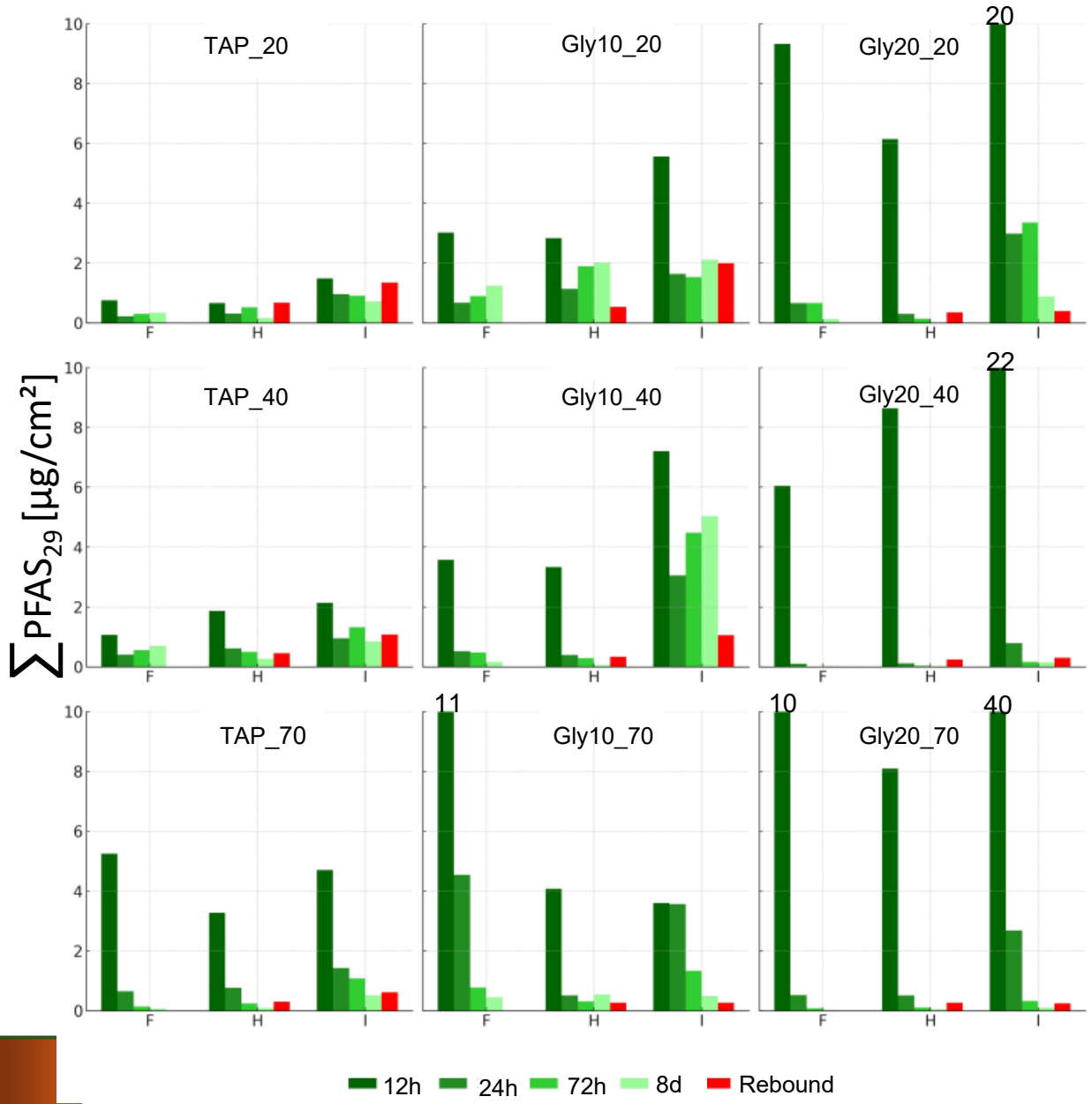
Results – Soaking Experiment



Trends:

- Cleaning solution: GLY20 > (MeOH) > GLY10 > TAP
- Temperature: 70°C > 40°C > 20°C
- Highest rate of removal within initial incubation interval (12 hours)
- Highest removed PFAS concentration (average) for Gly20 at 70°C (**≈21 µg/cm²**)

Results – Soaking Experiment



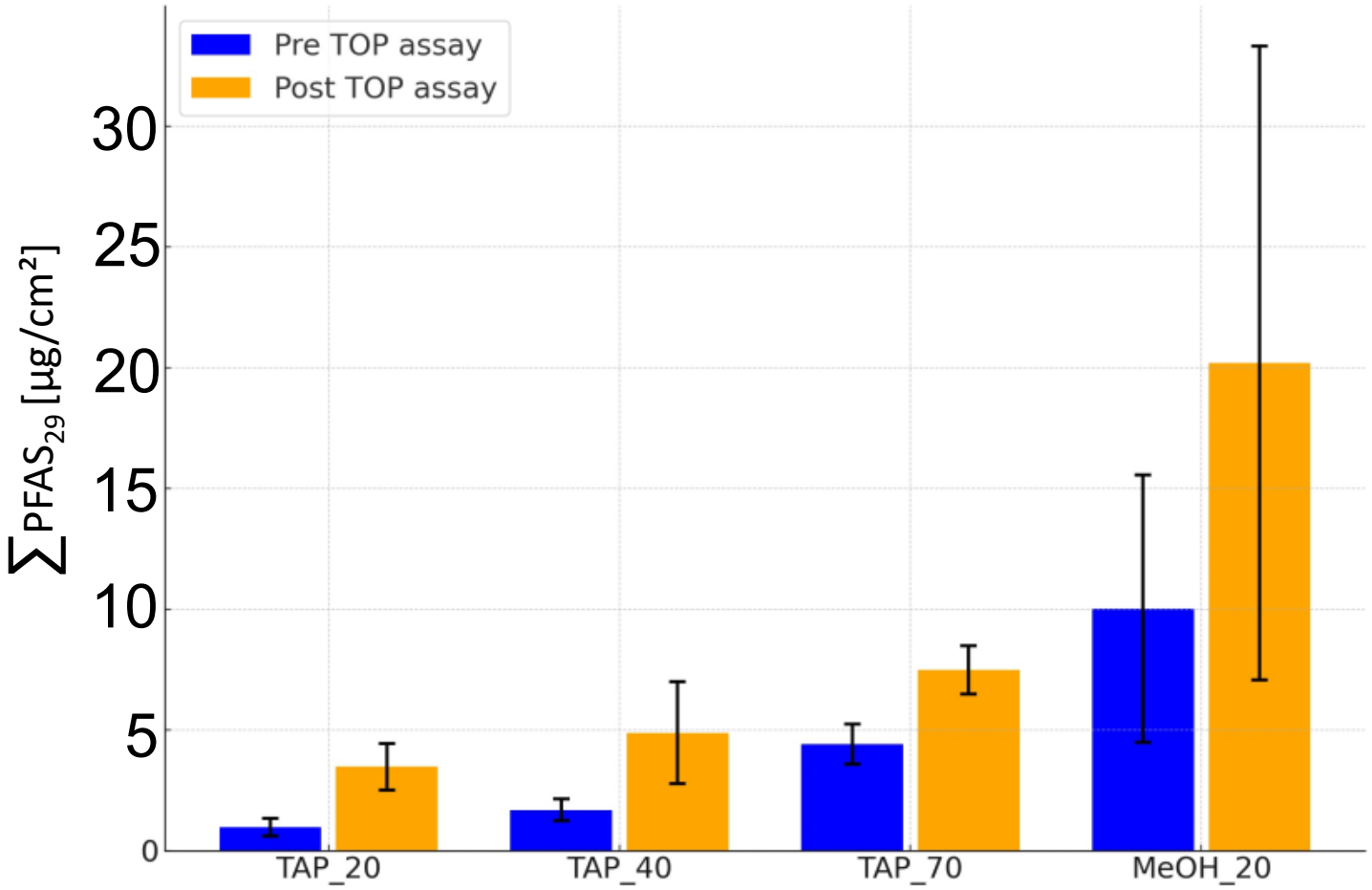
Explanation:

- Non accumulated, non averaged PFAS concentration removed into solution from pipe surfaces
- After 8 days, pipe sections were left to dry for to 2 months and then soaked in TAP for 1 week to measure „**Rebound**“.

Trends:

- Rebound higher for less efficient treatments
- Highest removal of PFAS with >40 µg/cm² (pipe I, Gly20, 70°C, within 12 hours)

Results – TOP assay



- Increase in PFAS concentration following TOP assay
- Presence of glycols (10-20%) inhibited oxidation of PFAS during TOP assay
- Not analyzed for ultra-short chain PFAS

Conclusions – Soaking Experiment

Soaking Experiment:

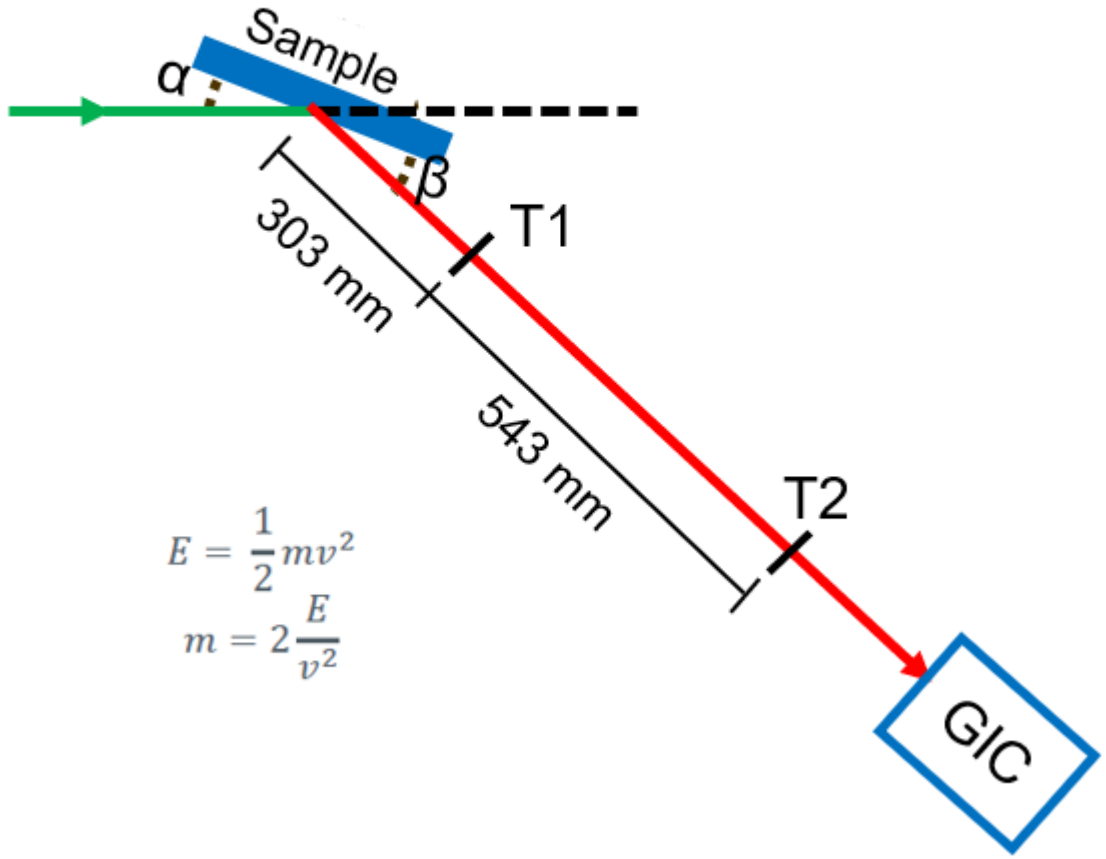
- Heated glycol solution at 70°C removes PFAS from surfaces most efficiently
- Hot glycols 2 - 8 fold more effective at PFAS removal than hot water
- Hot glycols 10 - 20 fold more effective than cold water
- Reduction in removal rate with repeated incubation intervals is **not evidence of successfull decontamination**
- PFAS rebound into TAP, especially for treatments with lower removal efficiency

→**How much PFAS mass is present on surfaces (before or after treatment)?**

→**Determination of treatment efficiency impossible without surface assessment of PFAS!**

Surface analysis – ToF-ERD

Time-of-Flight Elastic Recoil Detection Analysis



$$E = \frac{1}{2}mv^2$$

$$m = 2\frac{E}{v^2}$$

- Primary beam of iodine ions enter the sample and cause atoms on the surface to be forward recoiled
- Recoiled atoms pass two timing foils → velocity **v**
- Then, gas ionization chamber (GIC) → Energy **E**

→ **determination of elemental mass**

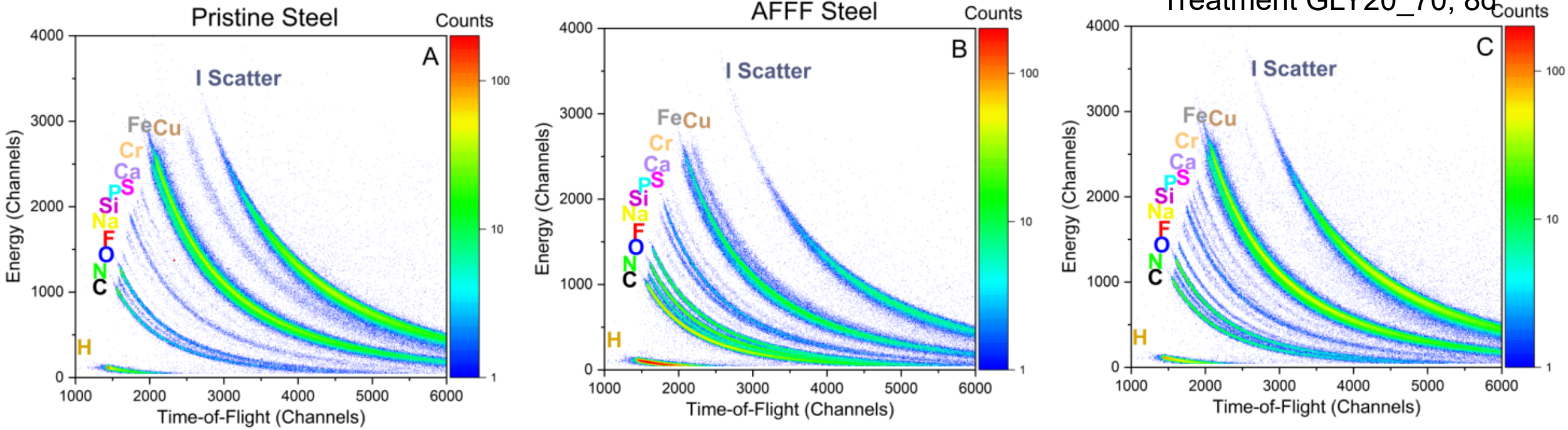
→ **Accuracy 0.1 at(omic)%**

Information:

- Elemental composition of the pipe surface

  → Fluorine **F**, Iron **Fe**
- Assumption F = PFAS
- Depth information

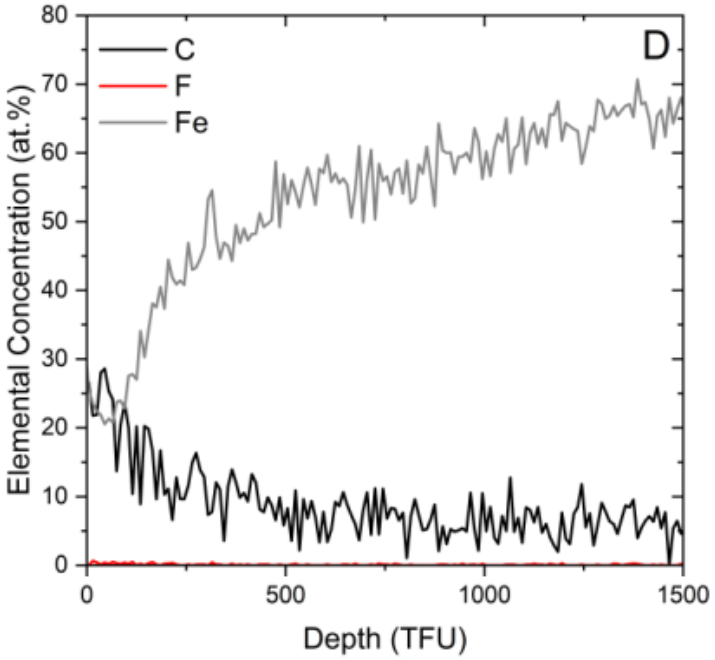
Surface analysis – Elemental composition



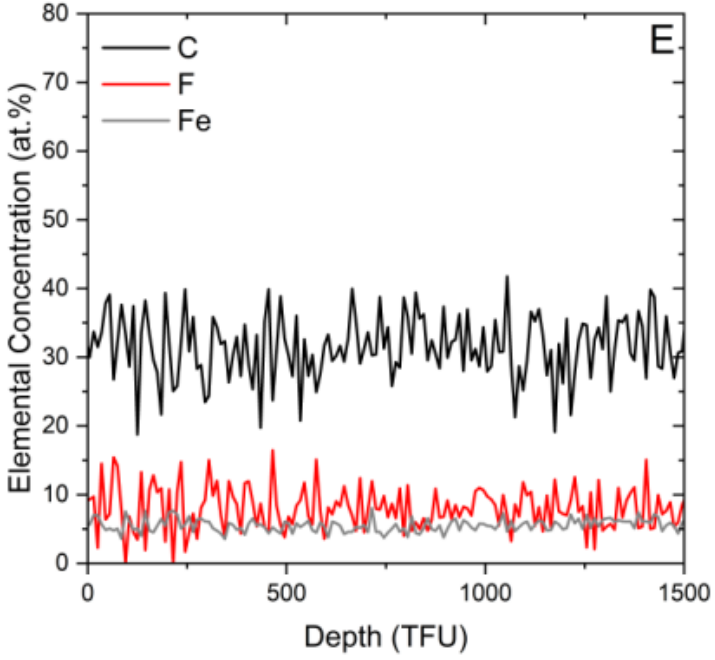
	Pristine Steel	AFFF Steel	Gly20, 70°C, 8d
Fluorine [at.%]	0.1	8.0	1.1
Iron [at.%]	52.4	5.5	35.4

Surface analysis – Depth Analysis

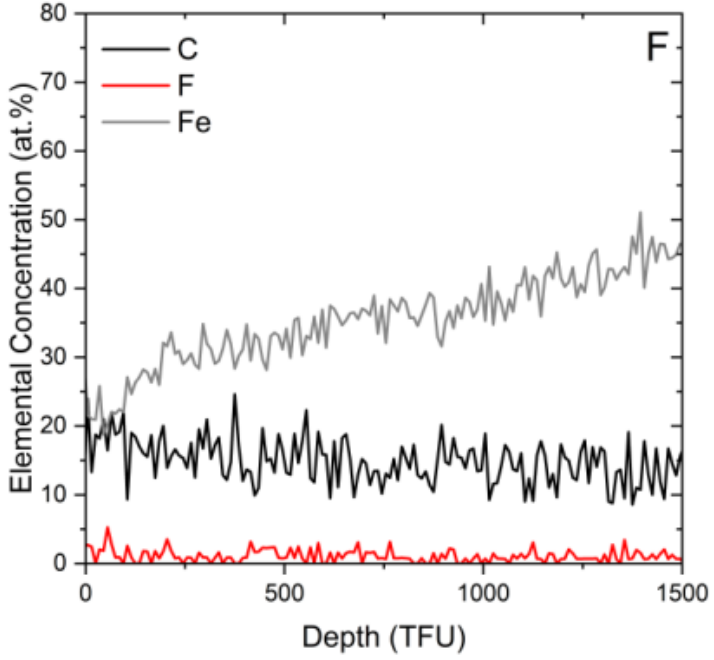
Pristine Steel



AFFF Steel



Treatment GLY20_70, 8d



Conclusion – Surface Analysis

ToF-ERD:

- ToF-ERD great technique to analyze surface composition
- Confirmed presence of Fluorine after treatment → potential for **rebound**
- Reduction of „AFFF-Layer“ confirmed by increasing Iron concentration at shallow depth

Limitations

- Not a table-top instrument
- Staff (group) of highly skilled physicists and engineers to operate
- <5 machines in the world
- Expensive

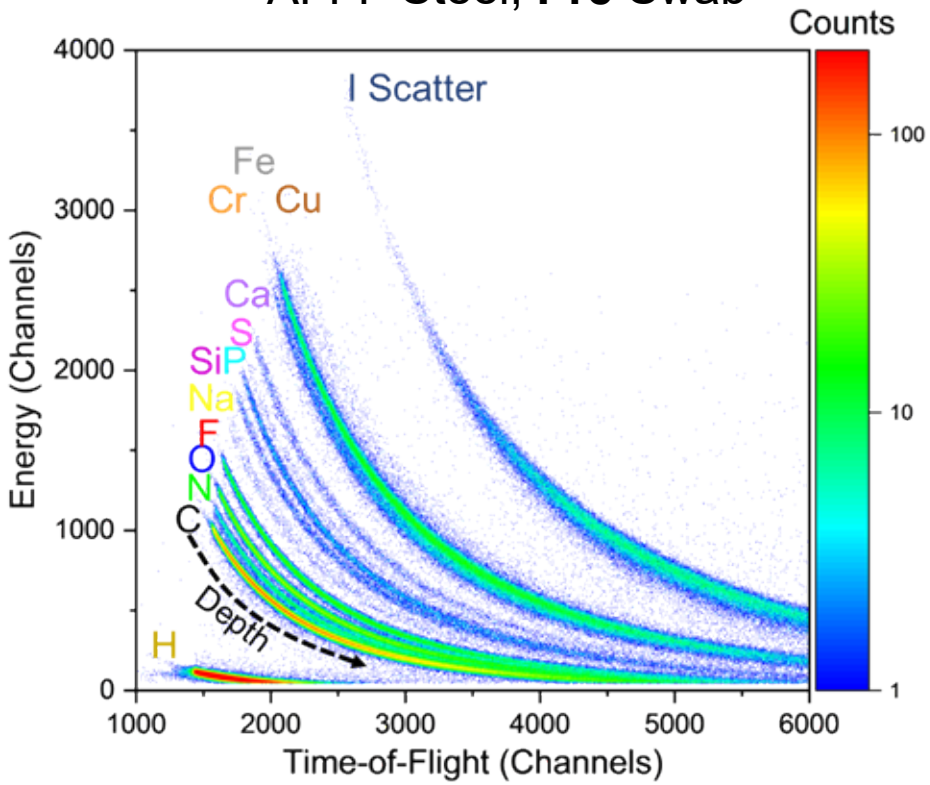
Overcoming Limitations – Swab sampling method

Swab sampling method:

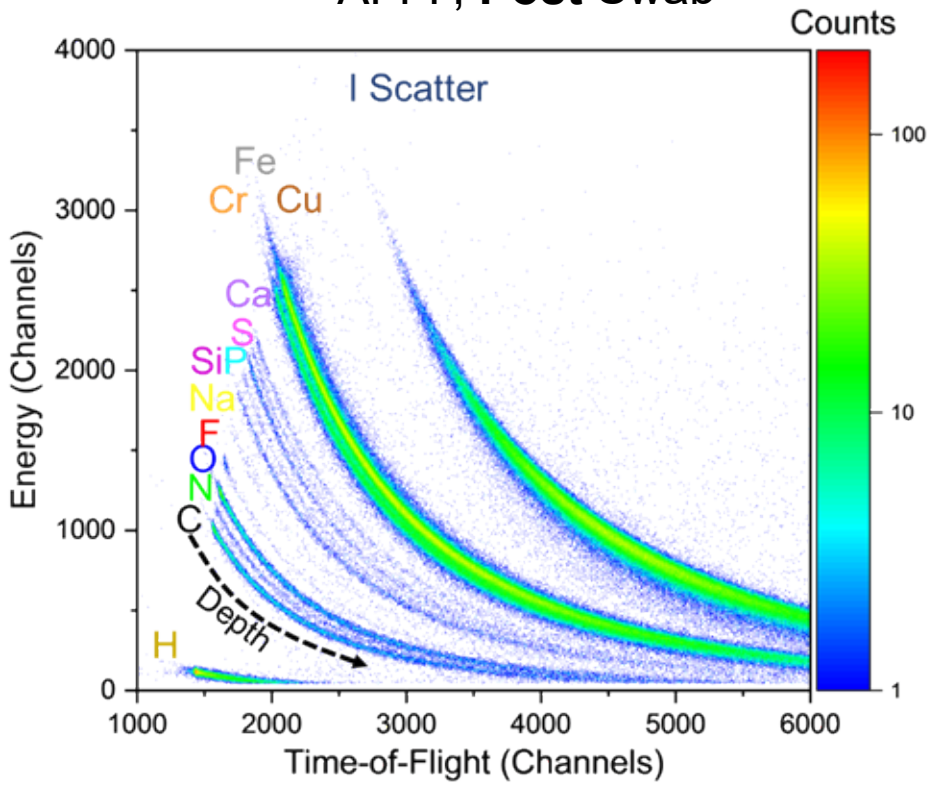
- Cotton gauze swab (medical supply)
- Sequential swabbing of pipe surface with
  in **basic MeOH** (0.4% KOH) and
  in **acidic MeOH** (0.1 M HCL)
  time of application: 5 min each
- Analysis of pipe section **before** and **after** swabbing with **ToF-ERD**
- Standardised methology followed i.e. **swab time** and **pressure** required

Results – Swab sampling method

AFFF Steel, **Pre** Swab



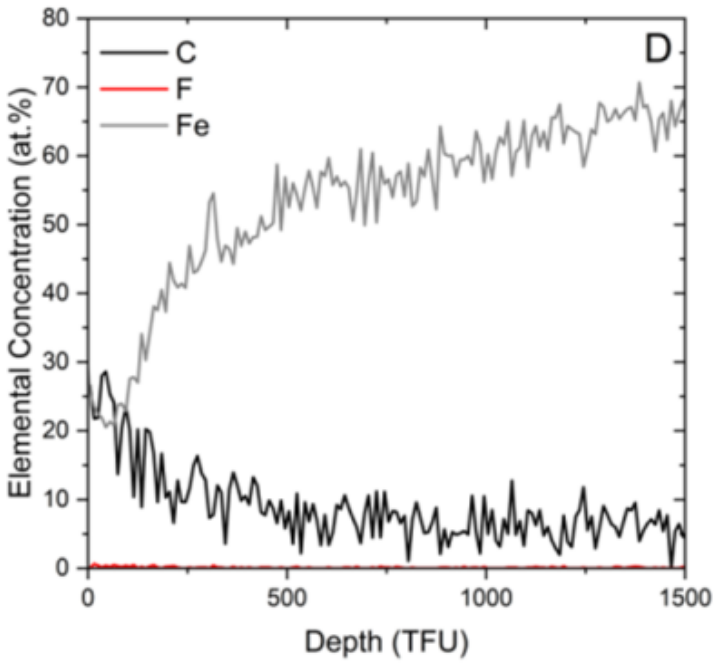
AFFF, **Post** Swab



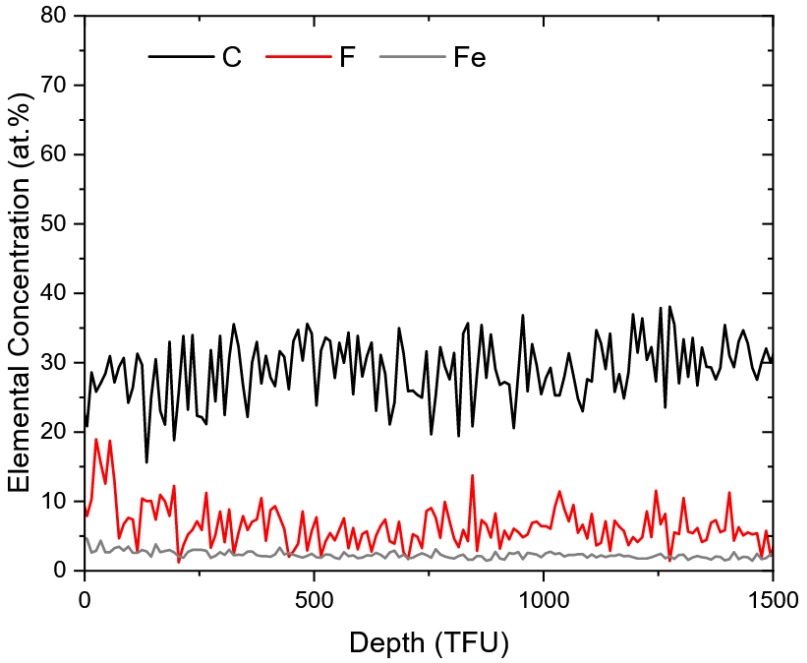
	Untreated Pipe	Swabbed Pipe
Fluorine [at.%]	6.3	0.3
Iron [at.%]	2.2	44.3

Results – Swab sampling method

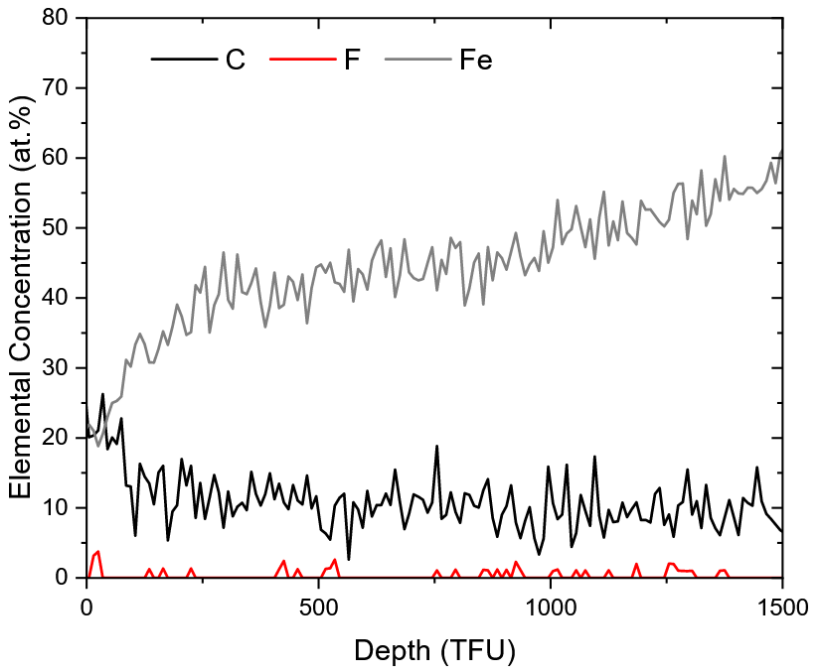
Pristine Steel



AFFF Steel, **Pre** Swab



AFFF, **Post** Swab



Conclusion – Swab Sampling

- Swab sampling methodology is usally removing >90% of PFAS from surfaces
- Low level of fluorine (baseline: 0.2-0.3 at.%) remains on surfaces after swabbing

Important for performing the swab sampling:

- Consistency!!
- standardization progressing
- applicable in practice and good method to determine total PFAS mass on surfaces
- possibility to determine efficiencies of removal techniques

The road ahead – Next steps in research

Soaking experiment:

+ heated glycols remove most PFAS mass

- considerable PFAS mass left

Swab sampling:

+ Application of physical force removes PFAS (almost) completely

- not applicable as a treatment technique

- Use heated glycol solution with attrition
  - Pressure washing
  - Ultrasonication
- Different materials

Thank You for your attention!!

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podcast PFASology on Spotify and Castbox!

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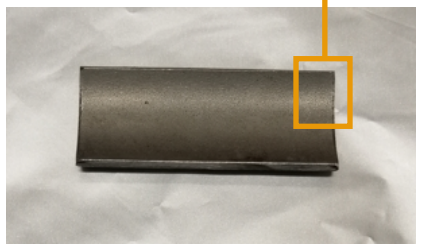
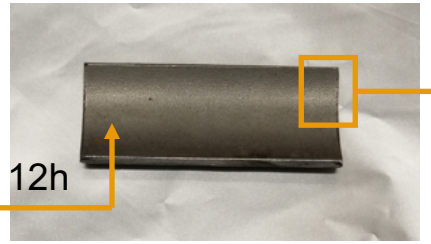
Surface analysis – Sample Preparation

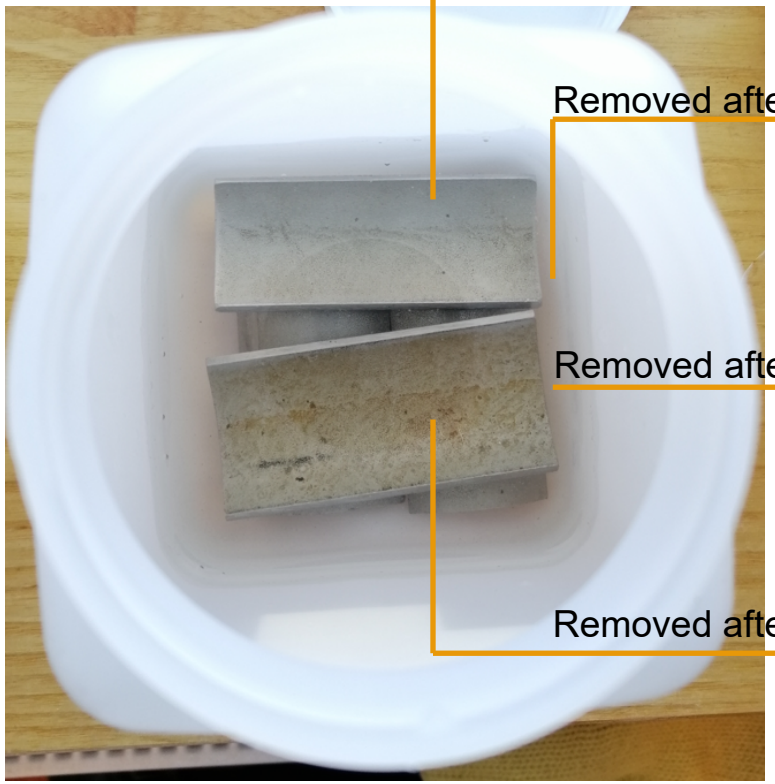
1 cm x 1 cm

No treatment

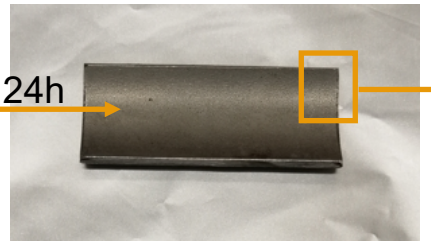


Removed after 12h

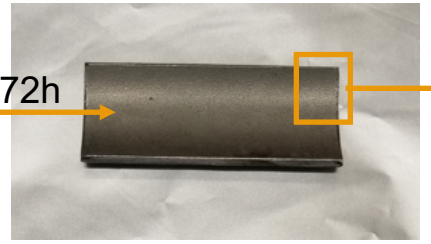




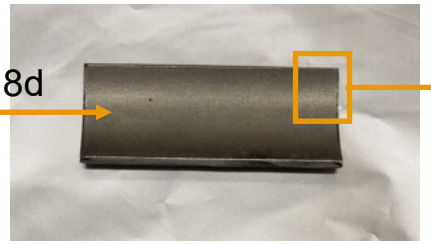
Removed after 24h

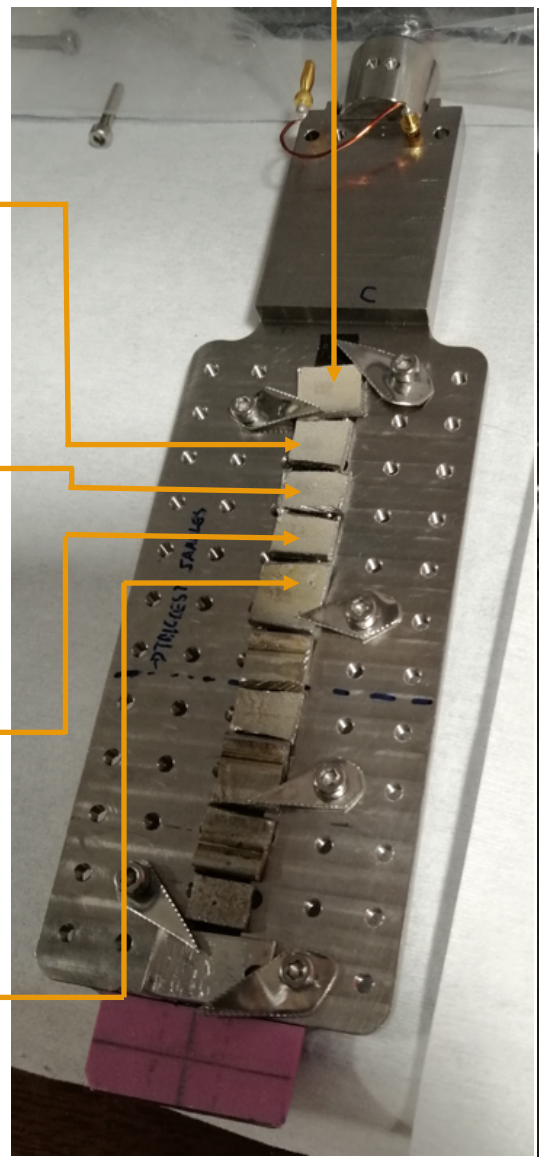


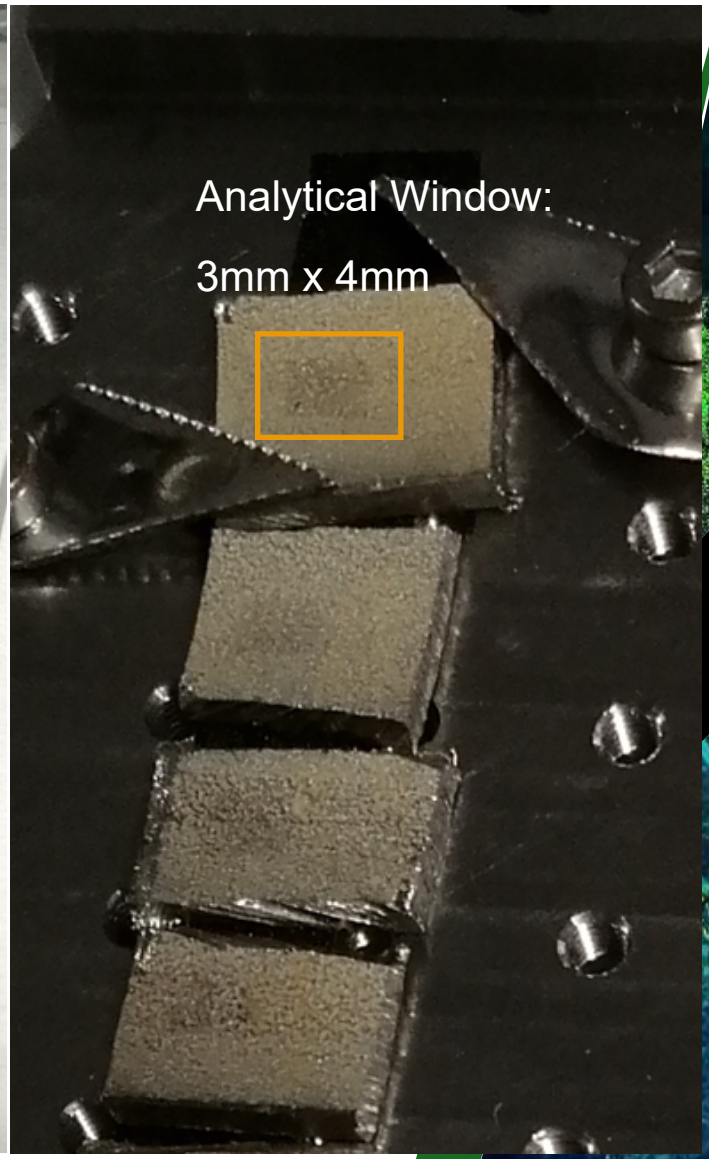
Removed after 72h



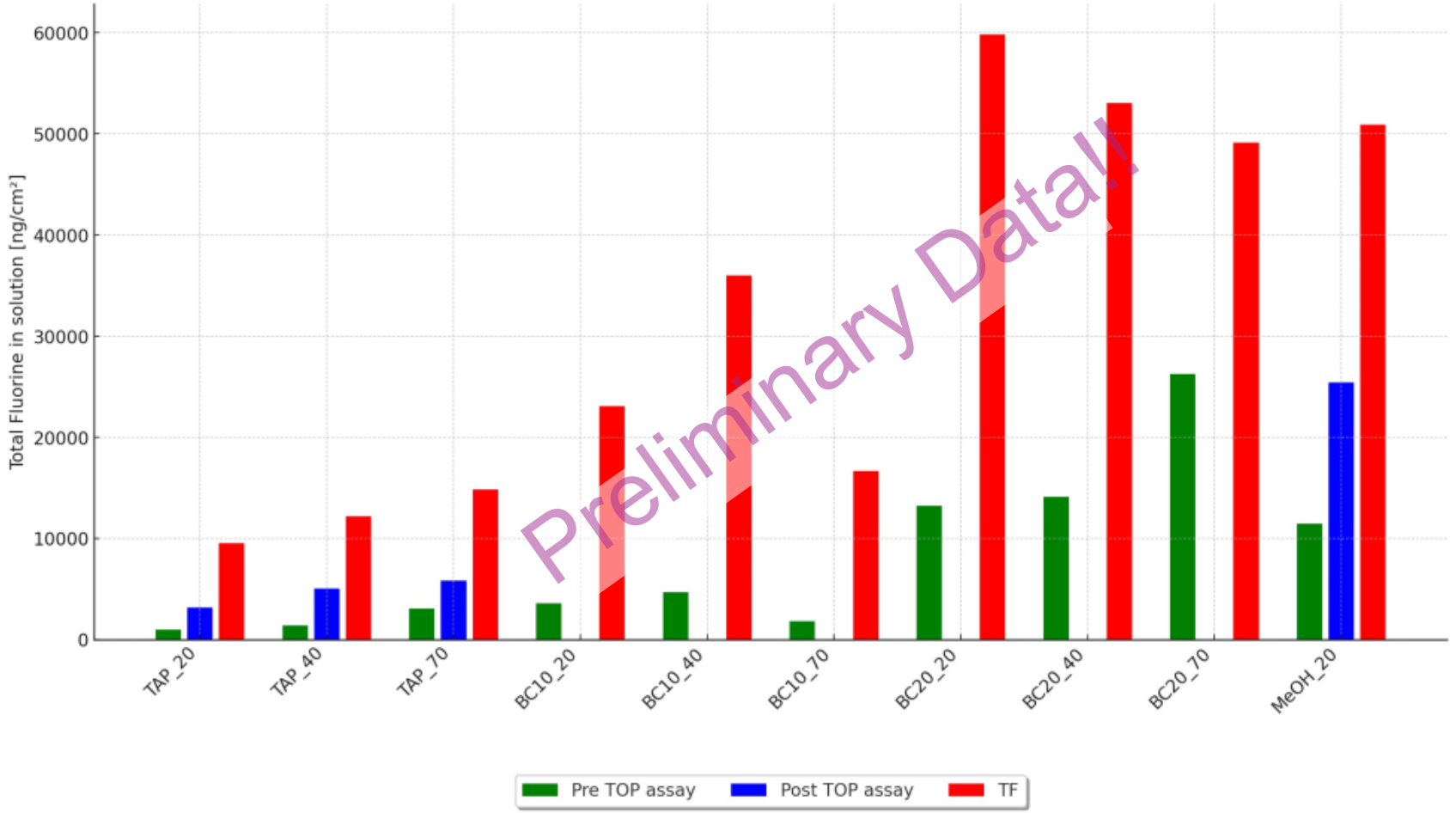
Removed after 8d







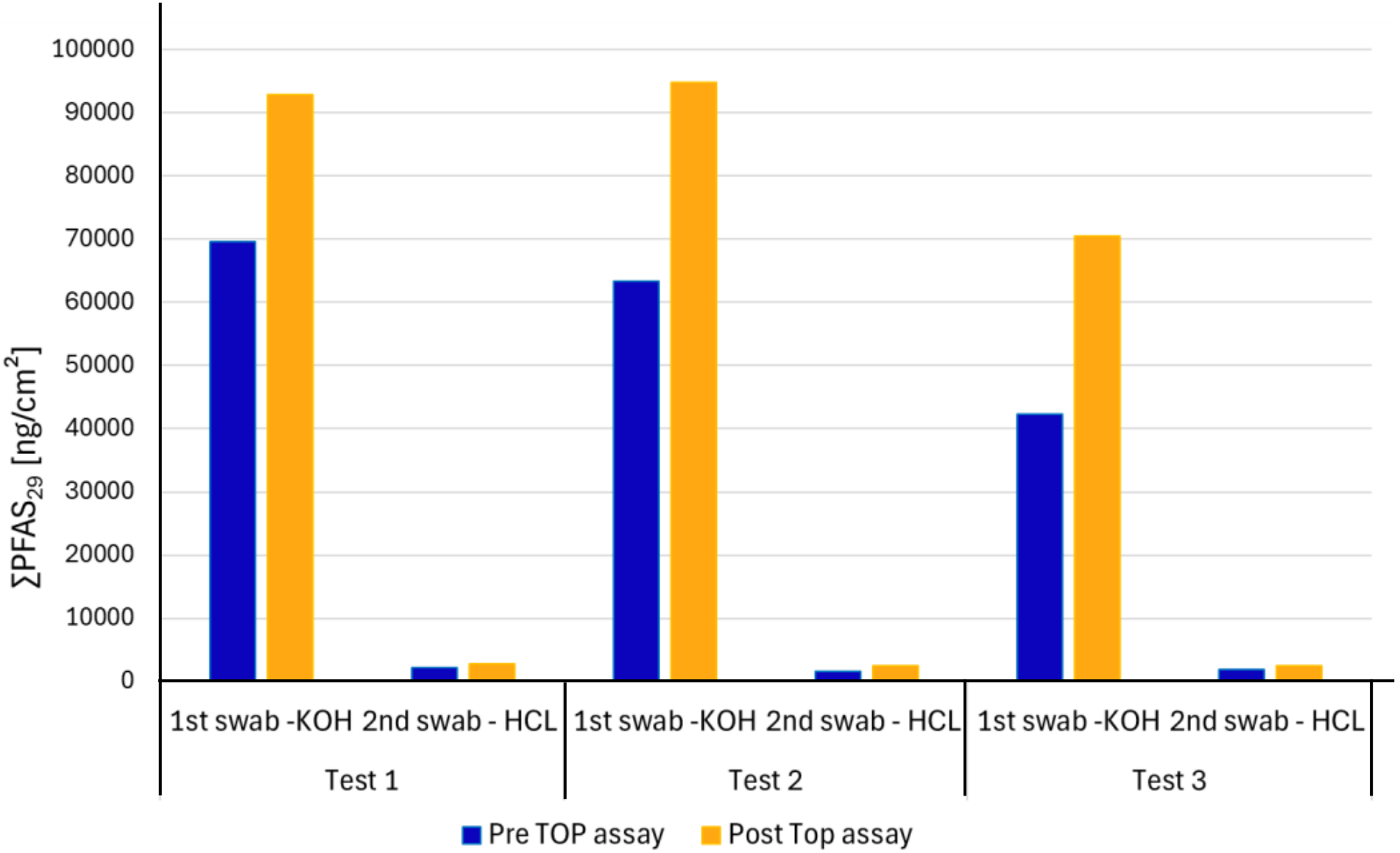
Results – Comparison Target – TOP assay - TF



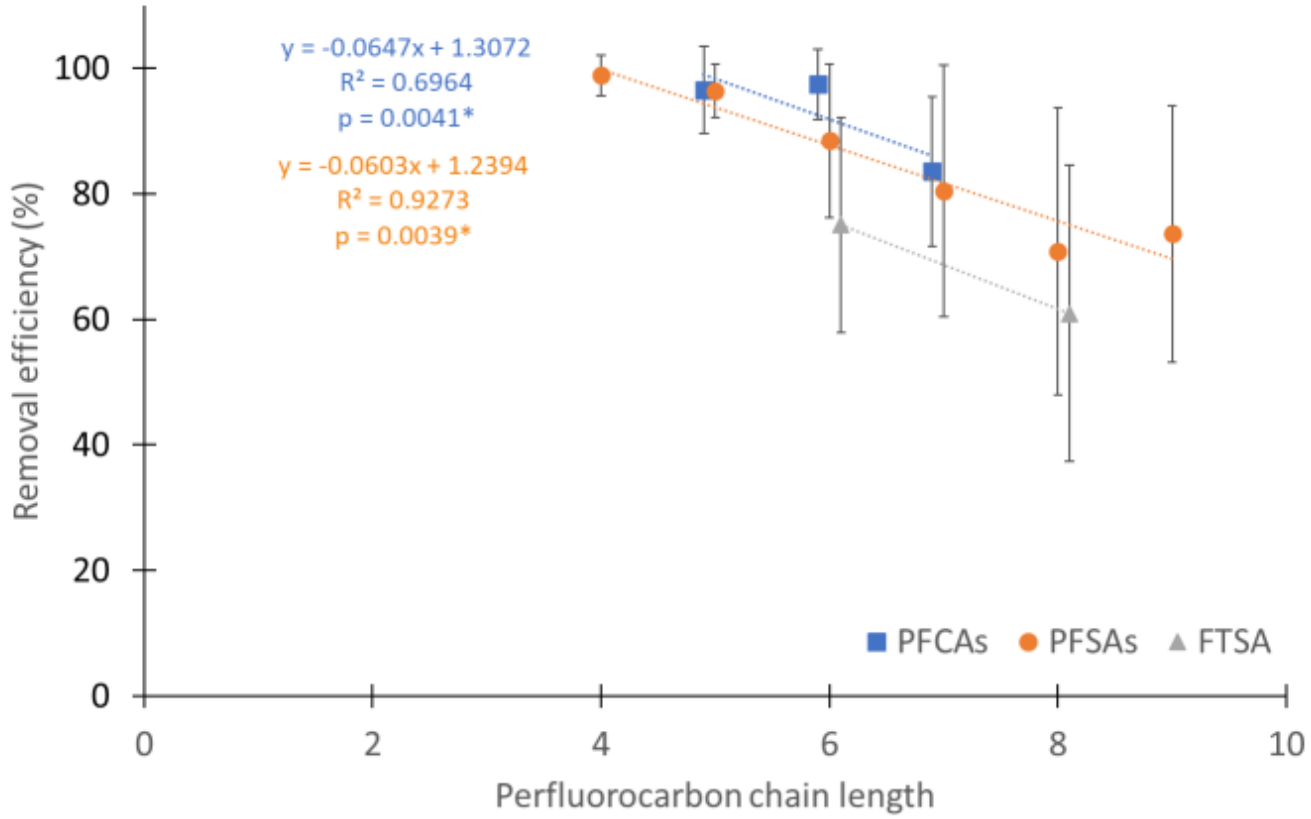
Trends:

- Target < TOP assay (factor 2-4) < TF (factor 2-11)
- Target: Long chain PFSAs 68% - 97%; short PFCAs 0-2% overall contribution
- TOP assay: Long chain PFSAs 17% - 53%; short PFCAs 32-67% overall contribution
- First timerval 12h

Results – Extraction of swabs

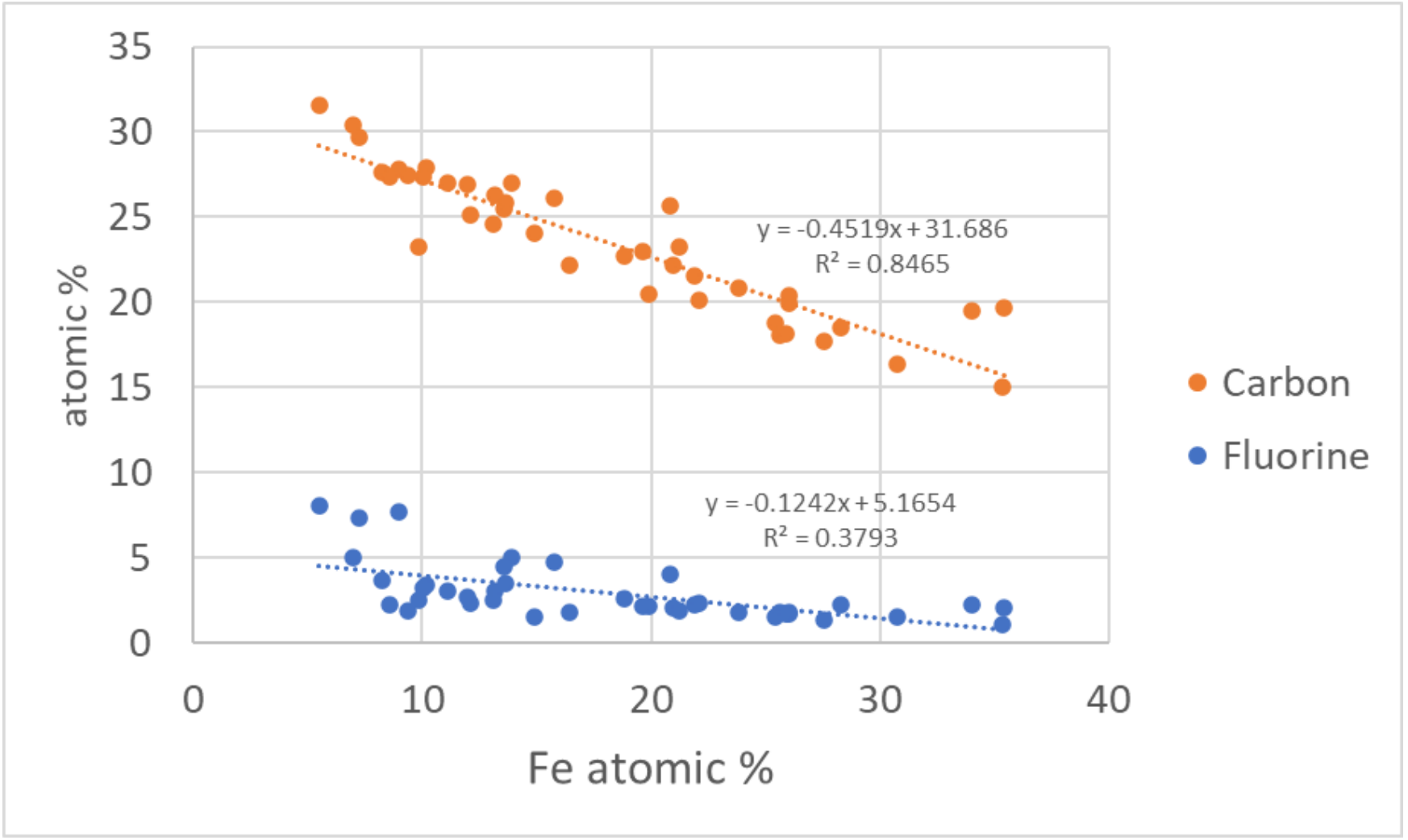


Results – Chain length dependency

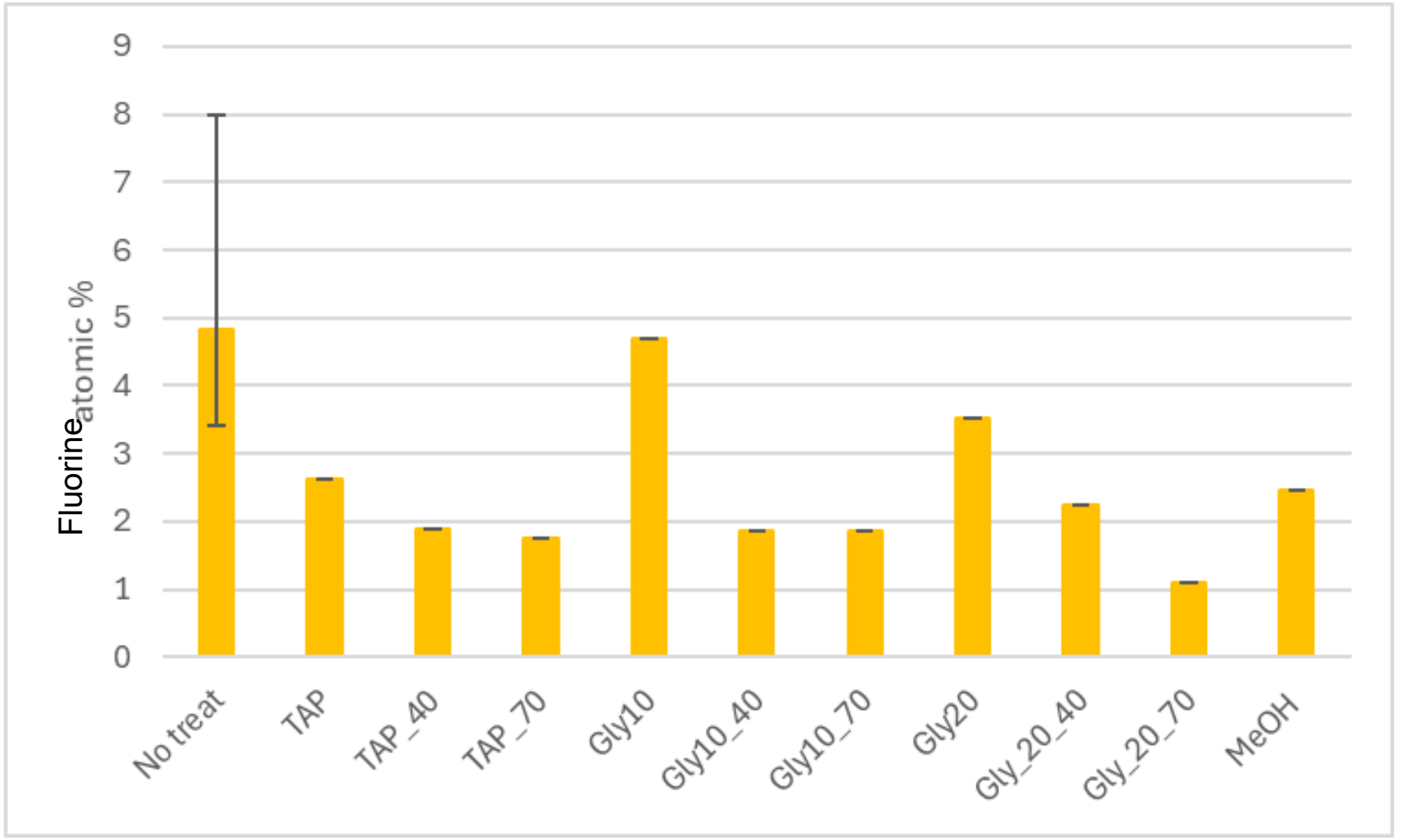


→ C8 impacted pipes more difficult to decontaminate vs C6

Surface analysis



Surface-Bound Fluorine after Treatment



Results

- Swab sampling methodology is usally removing >90% of PFAS from surfaces
- Low level of fluorine (baseline: 0.2-0.3 at.%) remains on surfaces after swabbing
- Pristine steel contained 0.97 at% F
- Limit of Detection is 0.1% at%F