EPA DRAFT METHOD 1633 FOR PFAS ANALYSIS:

EVALUATION OF SOLID PHASE EXTRACTION OPTIONS

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PROBLEM STATEMENT AND OBJECTIVES

Draft Method EPA 1633 is a 'performance-based' method and Section 1.5 provides guidance that *"modifications may be made without additional EPA review to improve performance … provided that all performance criteria in this method are met.* Requirements for establishing equivalency are in Section 9.1.2"

Section 6.7.1 specifies the use of the Waters Oasis WAX 150 mg cartridge (Cat # 186002493) *'or equivalent'* with the requirement that the sorbent must have a pKa above 8.

While such narrow specifications contribute to method consistency they also carry risks.

- The supply chain challenges being experienced by the industry are requiring a broadening of supplier options for lab supplies.
- The requirement of manual dispersive SPE (dSPE) during sample cleanup impedes full automation of the clean-up procedures and therefore presents a limitation to productivity at a time when demand for the testing is increasing.

OBJECTIVE

Evaluate alternative SPE cartridges for Equivalency according to the requirements of Section 9.1.2.

PFAS PARAMETERS EVALUATED

Target Analyte Name	Abbreviation
Perfluoroalkyl carboxylic acids	
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Perfluorotridecanoic acid	PFTrDA
Perfluorotetradecanoic acid	PFTeDA
Perfluoroalkyl sulfonic acids	
Acid Form	
Perfluorobutanesulfonic acid	PFBS
Perfluoropentansulfonic acid	PFPeS
Perfluorohexanesulfonic acid	PFHxS
Perfluoroheptanesulfonic acid	PFHpS
Perfluorooctanesulfonic acid	PFOS
Perfluorononanesulfonic acid	PFNS
Perfluorodecanesulfonic acid	PFDS
Perfluorododecanesulfonic acid	PFDoS

Target Analyte Name	Abbreviation
Fluorotelomer sulfonic acids	
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS
Perfluorooctane sulfonamides	
Perfluorooctanesulfonamide	PFOSA
N-methyl perfluorooctanesulfonamide	NMeFOSA
N-ethyl perfluorooctanesulfonamide	NEtFOSA
Perfluorooctane sulfonamidoacetic acids	
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA
Perfluorooctane sulfonamide ethanols	
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE
Per- and Polyfluoroether carboxylic acids	
Hexafluoropropylene oxide dimer acid	HFPO-DA
4,8-Dioxa-3H-perfluorononanoic acid	ADONA
Perfluoro-3-methoxypropanoic acid	PFMPA
Perfluoro-4-methoxybutanoic acid	PFMBA
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA
Additional Parameters	
Perfluorohexadecanoic acid	PFHxDA
Perfluorooctadecanoic acid	PFODA
10:2 Fluorotelomersulfonic acid	10:2FTS

Note: Three additional parameters included. All validations as per NELAP/DOD and EPA 1633 IDOC requirements (Section 9.1.2).

THE CARTRIDGES – ALL 6 ML

Waters Oasis WAX PFAS

150mg WAX
Part # 186002493

30 µm particles
80 Å pore size
pKas 3.70 and 8.95
(piperazine)

Phenomenex Strata-X-AW

150mg WAX
Part # 8B-S038-SCH

30 µm particles
80 Å pore size
pKa 6.09 and 9.27
(ethylenediamine)

pKas as per Janda et al., Env. Sci. Pollut. Res. (2019) 26:7326–7336

Phenomenex Strata WAX-GCB

200mg WAX / 50mg GCB
Part # CS0-9207
For water extraction

WAX
- 50 µm particles
- 80 Å pore size

GCB
- 120-400 mesh
- 85 m^2/g surface area

Phenomenex Strata GCB-WAX

50mg GCB / 200mg WAX
Part # CS0-9214
For soil/tissue extraction

GCB
- 120-400 mesh
- 85 m^2/g surface area

WAX
- 50 µm particles
- 80 Å pore size

VALIDATION PROCEDURE

Draft EPA 1633:

9.1.2 **…**the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternative extraction, concentration, and cleanup procedures, and changes in sample volumes, columns, and detectors.

9.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 9.2 Initial Demonstration of Capability

9.2.1 Initial precision and recovery (IPR). Extract, concentrate, and analyze four aliquots of the matrix type to be tested, spiked with the native standard solution, EIS solution, and NIS solution. At least one method blank, matching the matrix being analyzed, must be prepared with the IPR batch. All sample processing steps that are to be used for processing samples, including preparation and extraction, cleanup and concentration, must be included in this test.

9.2.2 Method detection limit (MDL). …establish MDLs for all the analytes using the MDL procedure at 40 CFR Part 136, Appendix B. An MDL determination must be performed for all compounds.

TNI Standard EL-V1M4-2016-Rev 2.0: 1.5.2.1.1 Initial determination of the MDL. c) the MDL determination shall include data from low level spikes and routine method blanks prepared and analyzed over multiple days.

MDL PROCEDURE AT 40 CFR PART 136, APPENDIX B

- Make an estimate of the detection limit
  - e.g. S/N=3; 3x standard deviation of replicate instrumental measurements
- Prepare and process seven samples in reagent blank matrix, spiked with a level of analyte between one and five times the estimated detection limit. [As per TNI: samples prepared and analysed over three days]
- Calculate the standard deviation (S) of the seven measurements.
- Calculate MDL: $MDL = t_{0.99}(S)$

  $t_{0.99}$ = 3.143 (n=7, df =6)

- TNI Standard:
  blank measurement must be < calculated MDL

Reference Matrices as per EPA 1633

7.2.1 Reagent water – purified water, Type I

7.2.2 Solids reference matrix – Ottawa or reagent-grade sand

MDL vs ML as per EPA 1633

9.2.2 The minimum level of quantification (ML) can be calculated by multiplying the MDL by 3.18 and rounding the result to the nearest 1, 2 or 5 x 10n, where n is zero or an integer.

Table 6 provides example matrix-specific method detection and quantification limits.

ACCEPTANCE CRITERIA - INITIAL PRECISION AND RECOVERY

Recovery:

DOD QSM 5.4 Table B-24:

Average % Recovery (%R)	
Natives:	40% - 150%
EIS:	20% - 150%

Precision:

DOD QSM 5.4 Table B-24 provides no guidance for Initial Demonstration of Precision (IDP) acceptance and BV in house control limits have not yet been established.

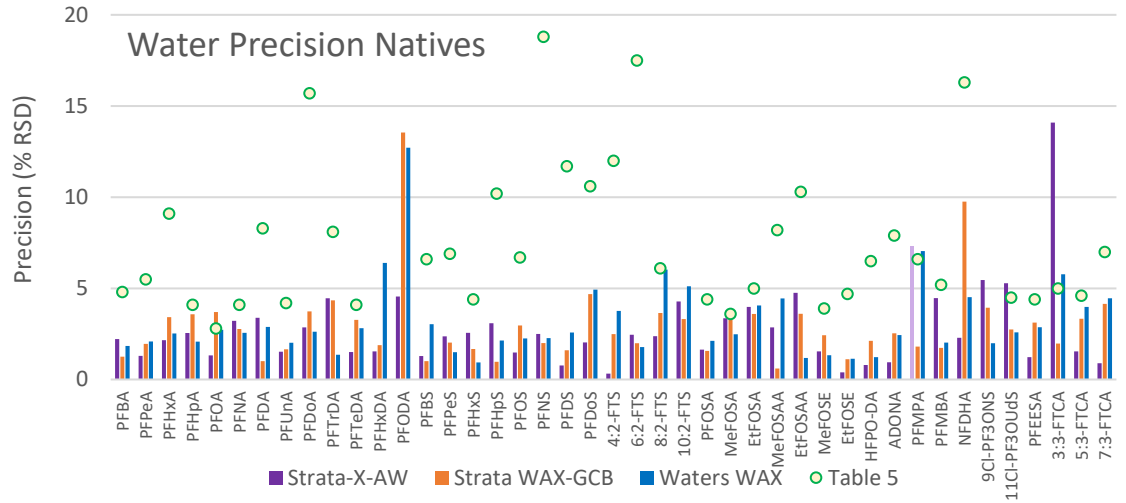
EPA 1633, Section 9.2.1.3. For each … compound, compare RSD and % recovery with the corresponding limits … in Table 5. If RSD and R for all compounds meet the acceptance criteria, system performance is acceptable. Table 5 footnote: Several sections of this method state that Table 5 criteria are required, this is standard language that will be applicable when the method is finalized.

EPA 537.1 Table 12 specifies IDP <20% RSD for four to seven replicate fortified blank samples near the midrange calibration concentration. This is consistent with the BV Corporate Quality Manual default criteria for IDP.

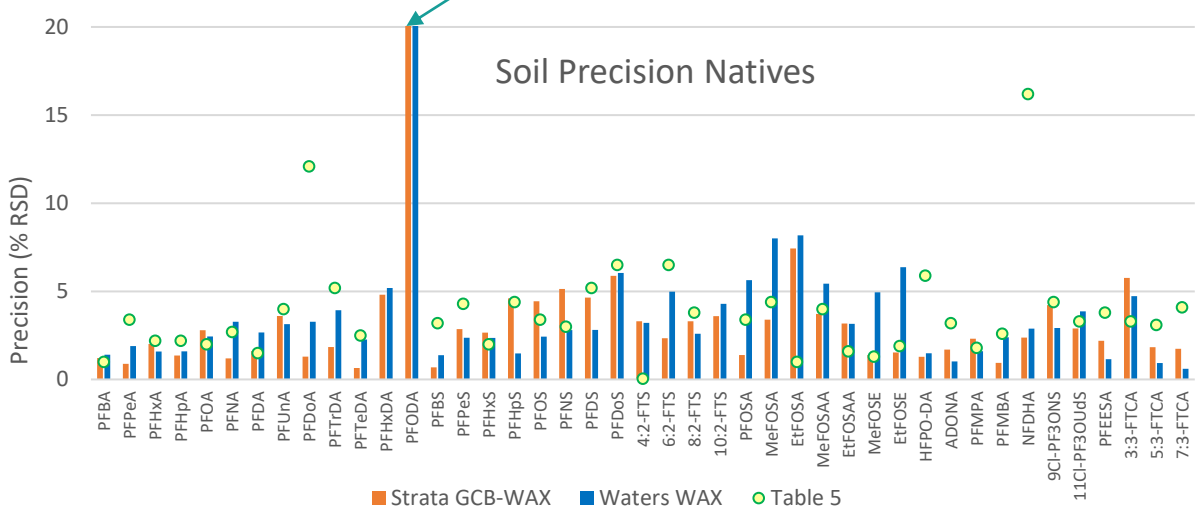
Average Precision (%RSD)	
Natives:	<20%
EIS:	<20%

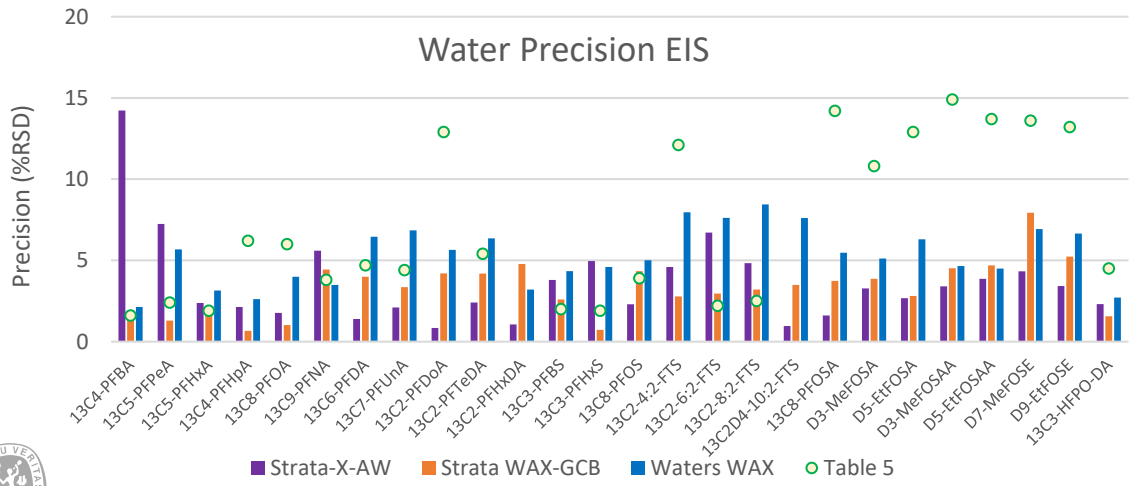
PRECISION RESULTS

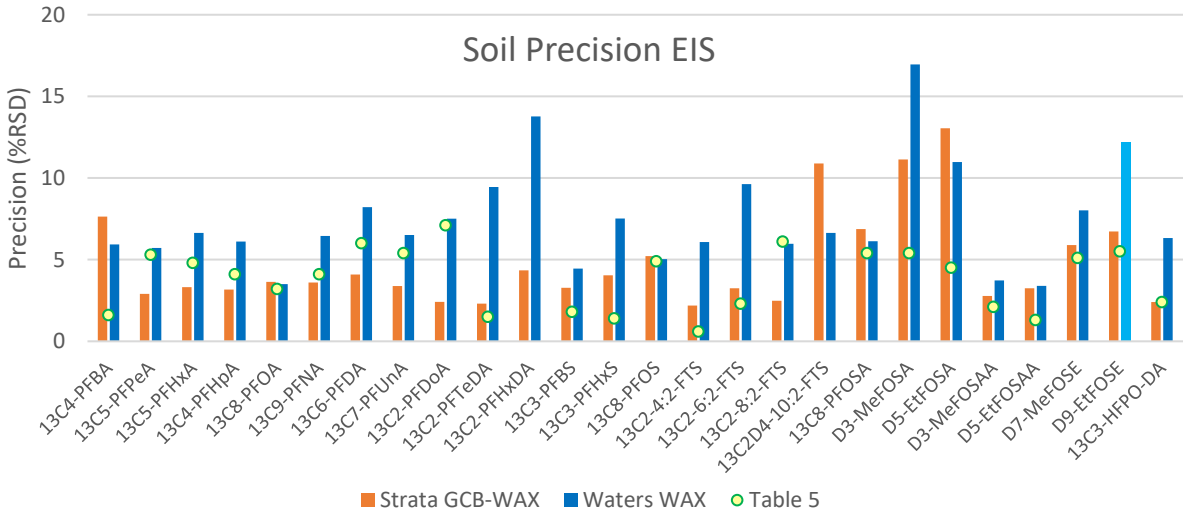
All EPA 1633 parameters in all cartridges <20% RSD



PFODA 21-23% RSD but not included in 1633







Precisions generally ≤6% (except Soil EIS)

RECOVERY DATA INTERPRETATION – WHEN IS A DIFFERENCE REAL VS NOT?

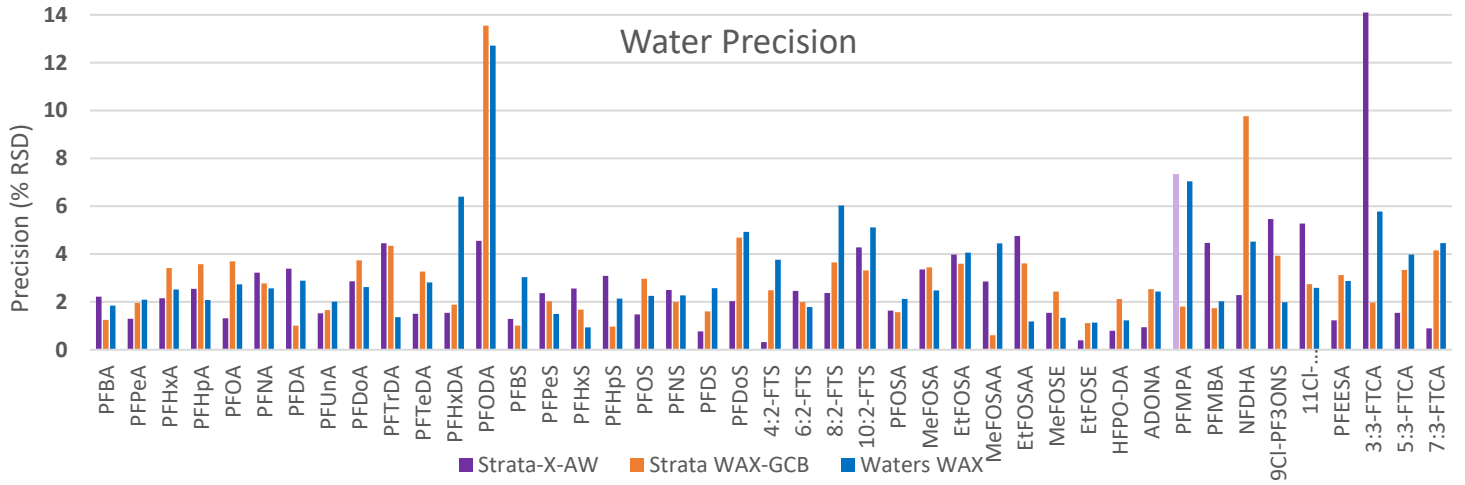
The 95% Confidence Interval (CI) may be used to determine how much of a difference between data points is significant.

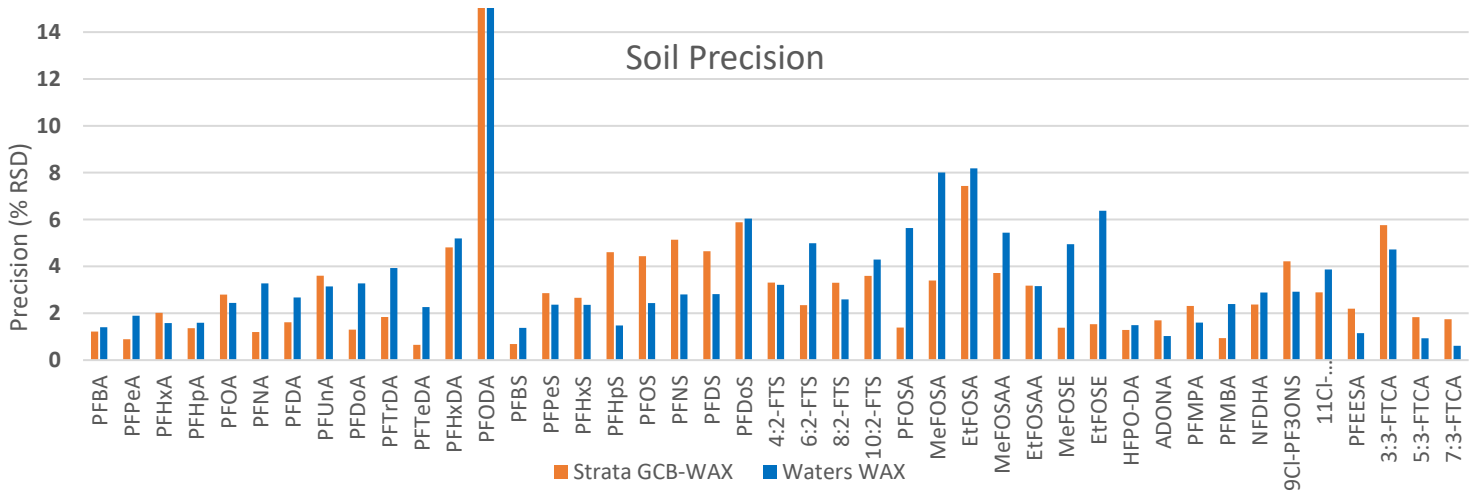
$$CI = \bar{x} \pm z\frac{s}{\sqrt{n}}$$

- $\bar{x}$ data mean
- s standard deviation
- n number of data points (4)
- z confidence level t-value
  $t_{0.95}$ = 3.182 (n=4, df =3)

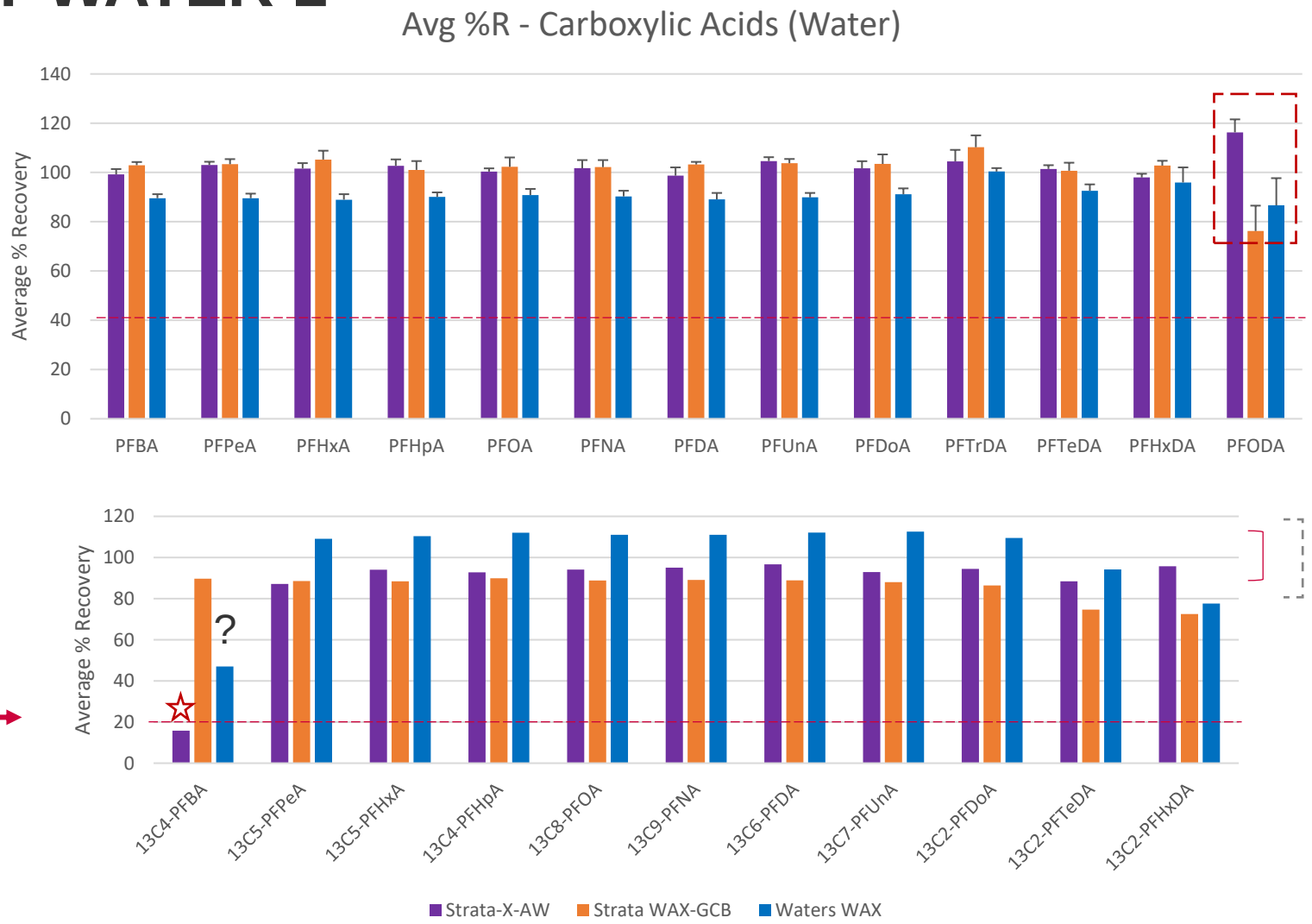
Calculate 95% Confidence Interval for Recovery:

For: $\bar{x}$ = 100% Recovery
s = 6% (10%)
n = 4
z = 3.182
CI ≈ ±10% (soil EIS ±15%)





RECOVERY WATER 1



DOD QSM 5.4 Table B-24 allows RPD ≤30% for sample duplicates.

30% RPD

95% Confidence Interval from precision data (all but PFODA)

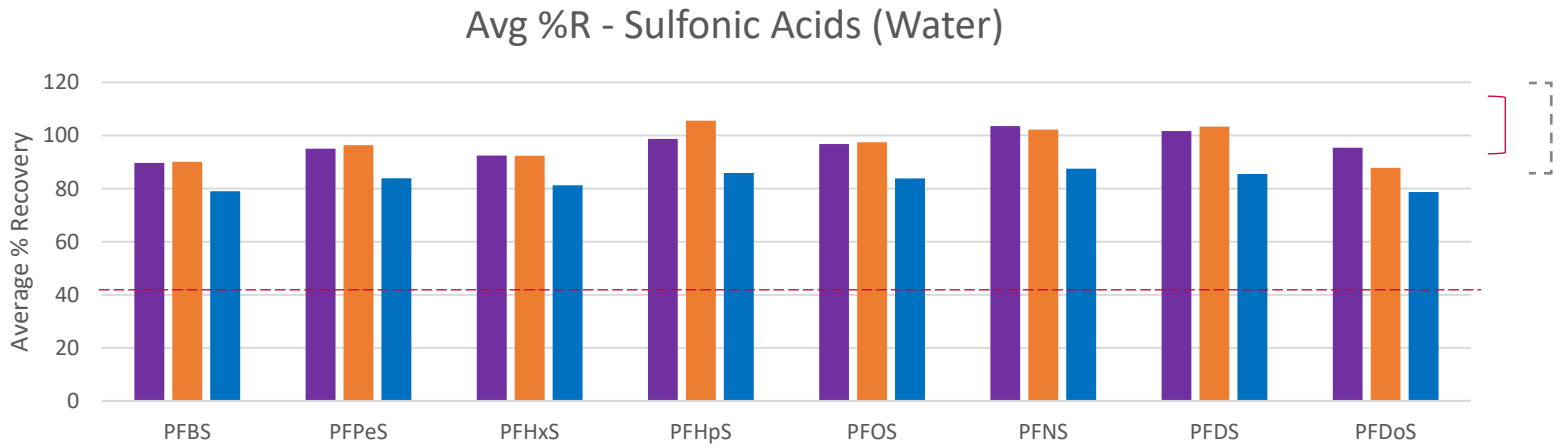
Lower %Recovery acceptance limits

All performance equivalent except 13C4-PFBA.

All cartridges pass except Strata-X-AW for 13C4-PFBA slightly low.

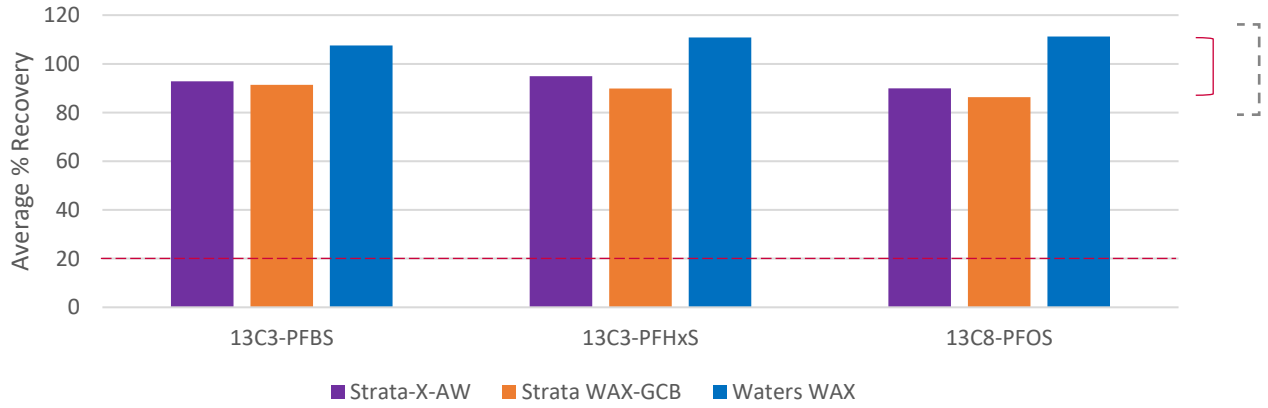
n=4, natives recoveries normalized to EIS

RECOVERY WATER 2



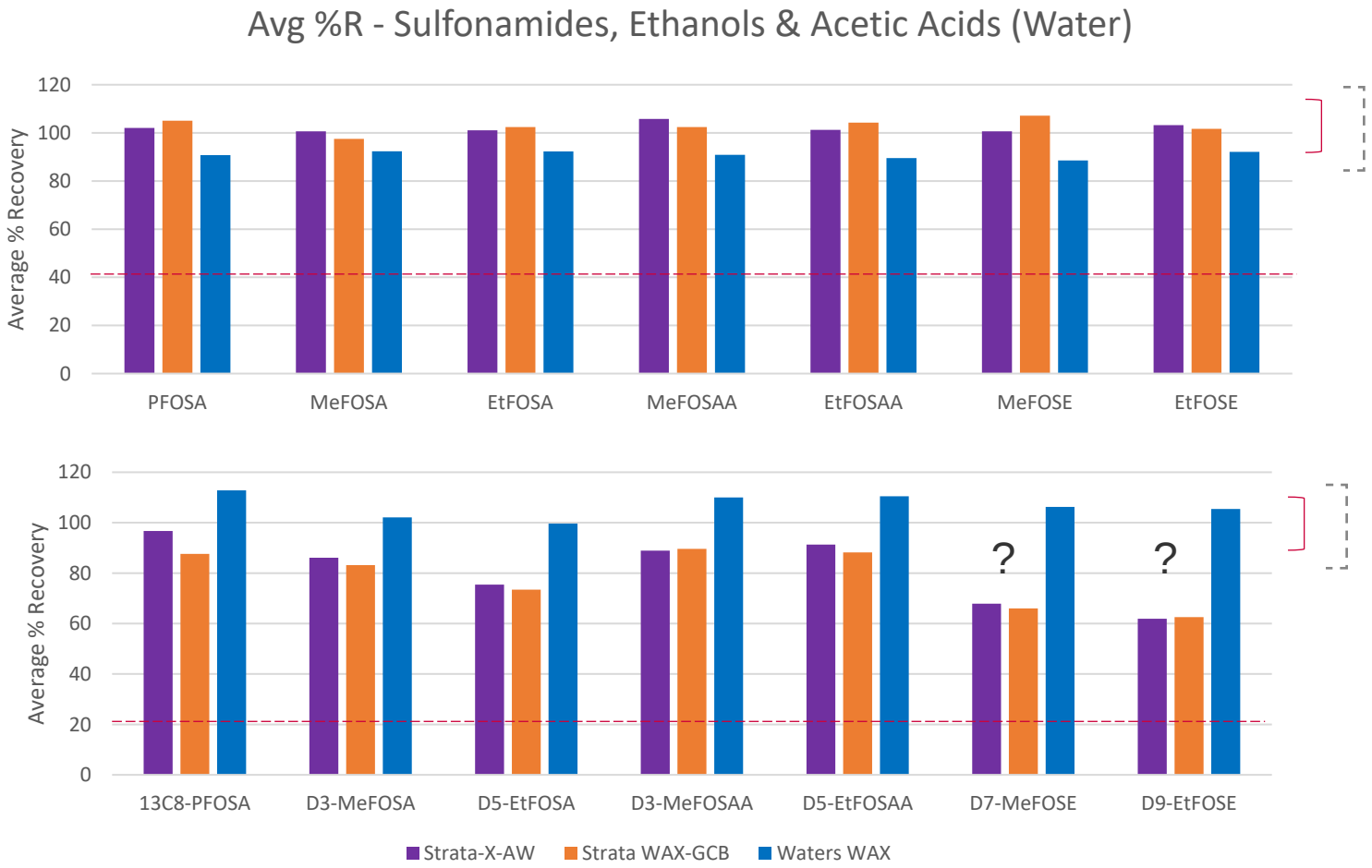
All performance equivalent.

All cartridges pass.



n=4, natives recoveries normalized to EIS

RECOVERY WATER 3

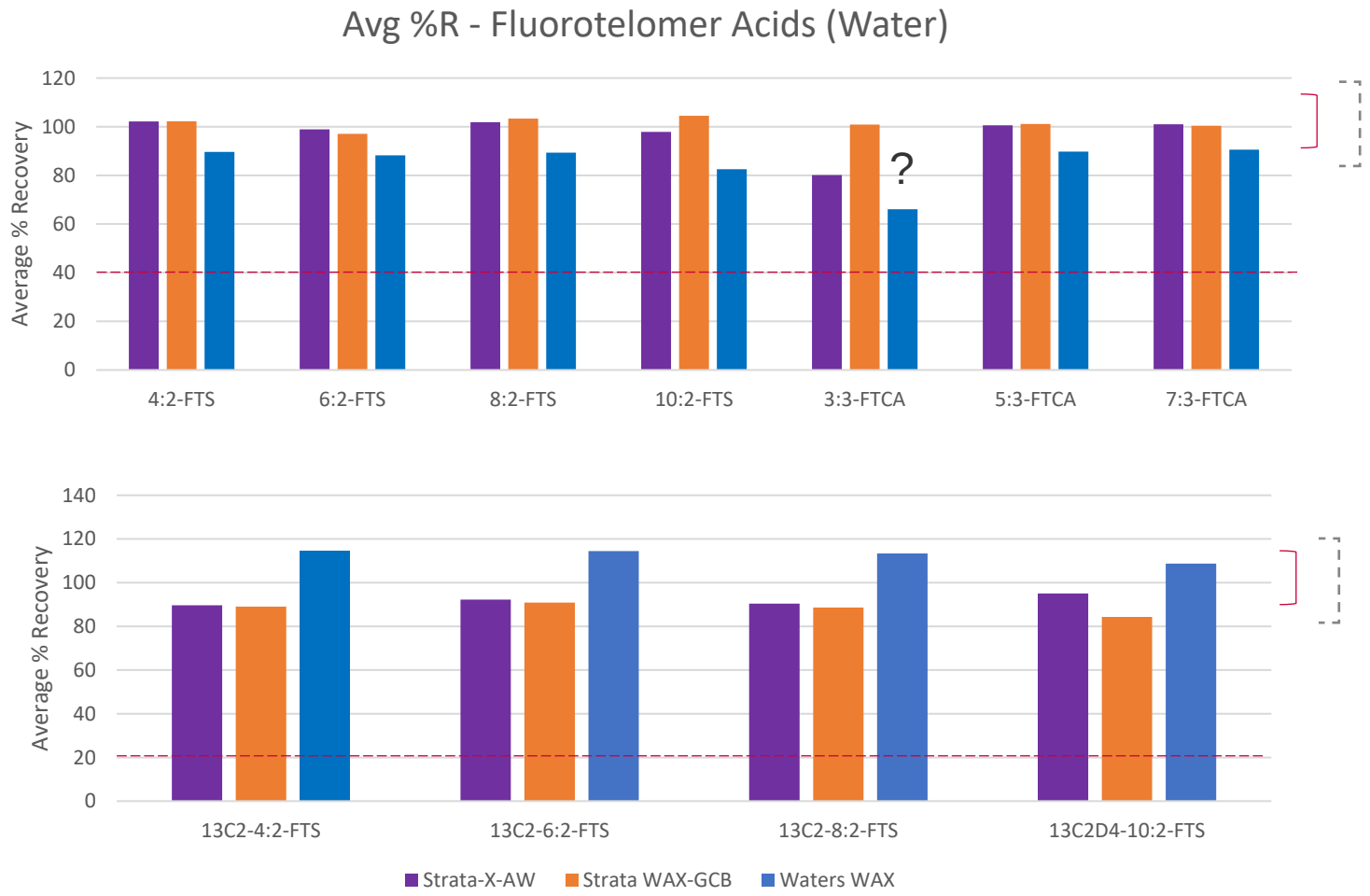


All performance equivalent except for MeFOSE/EtFOSE EIS, likely due to lab technique.

All cartridges pass.

n=4, natives recoveries normalized to EIS

RECOVERY WATER 4

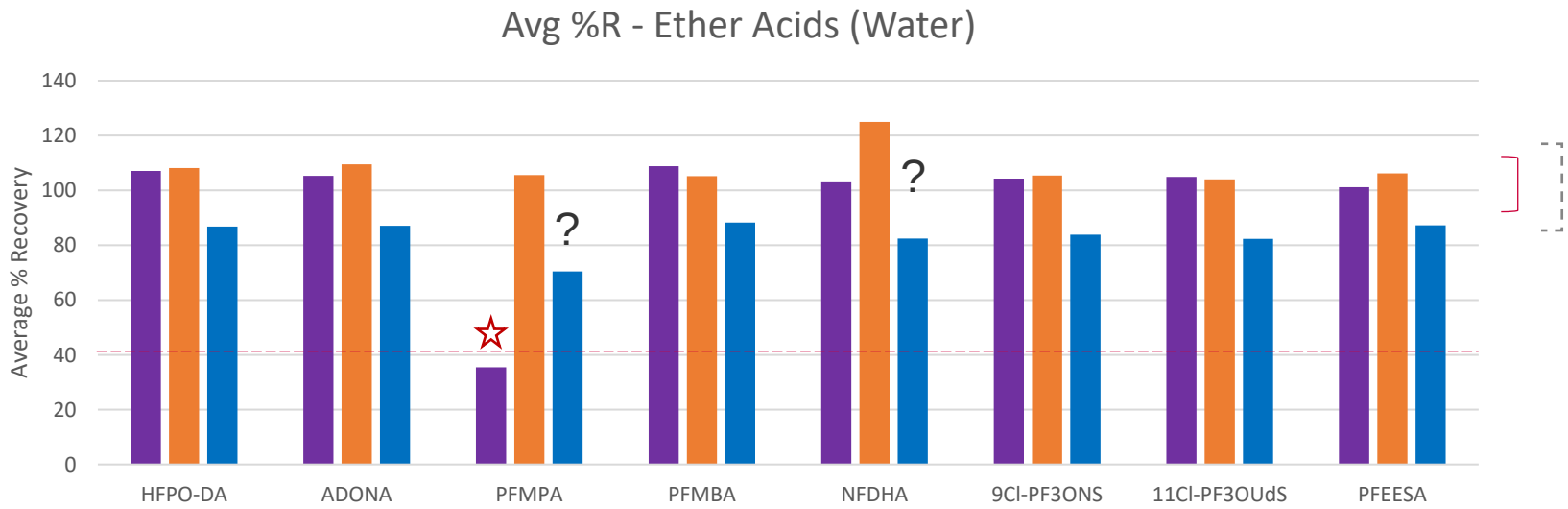


All performance (mostly) equivalent.

All cartridges pass.

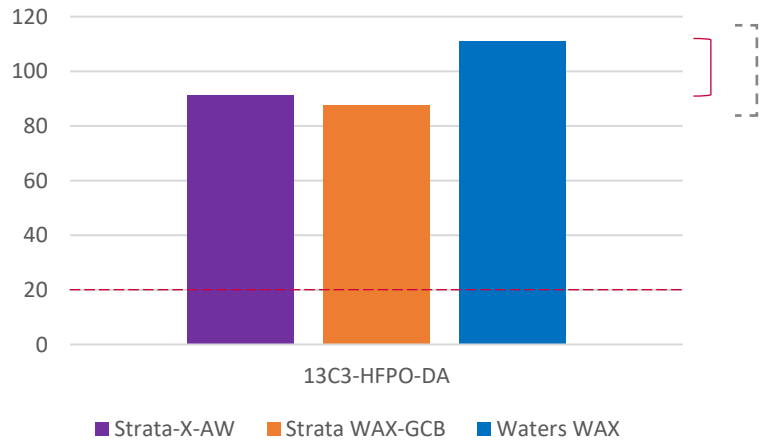
n=4, natives recoveries normalized to EIS

RECOVERY WATER 5



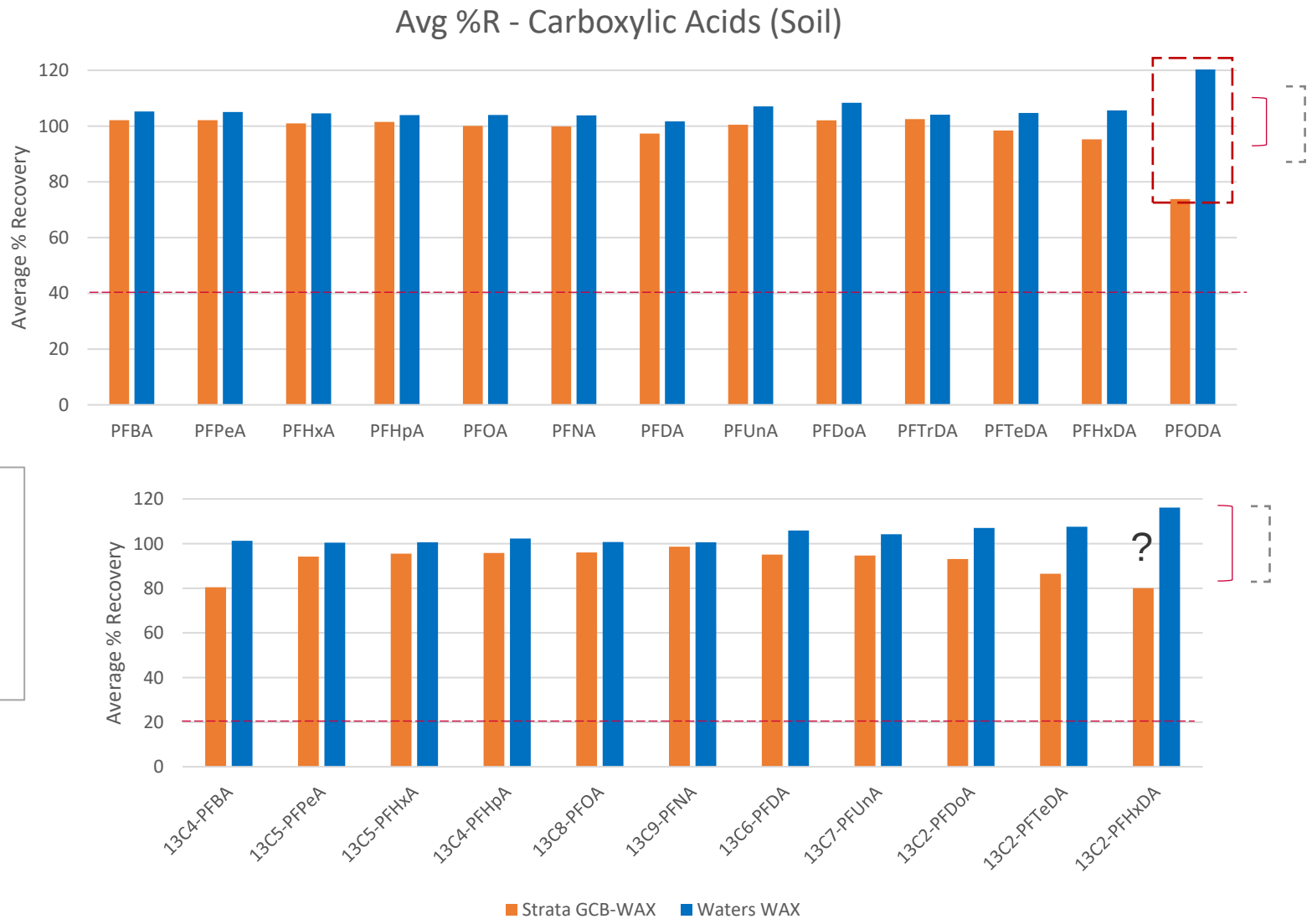
All performance equivalent except PFMPA & NFDHA.

All cartridges pass except Strata-X-AW for PFMPA slightly low.



n=4, natives recoveries normalized to EIS

RECOVERY SOIL 1

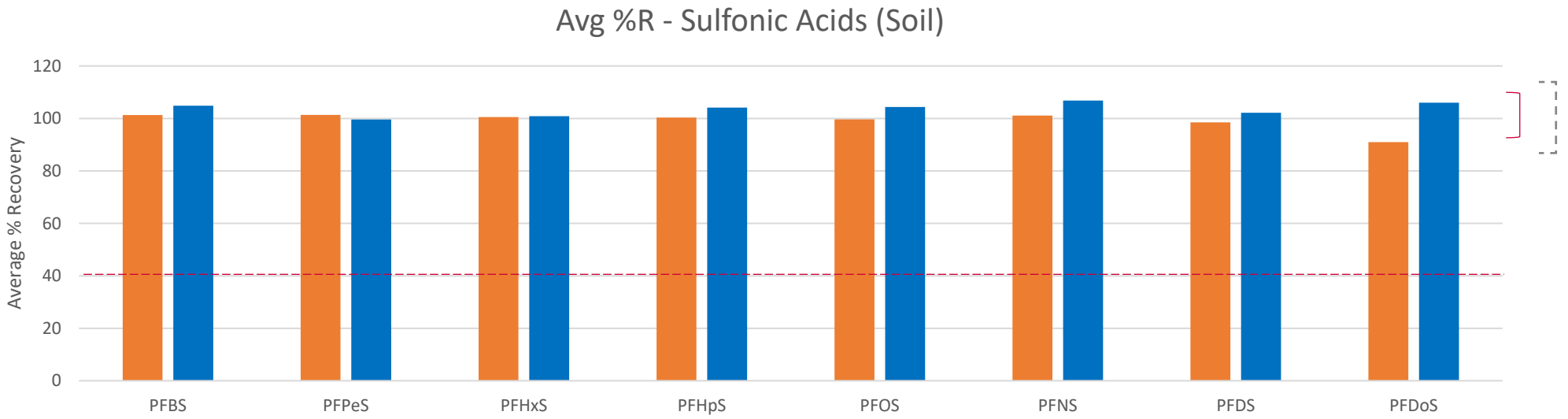


All performance equivalent except 13C2-PFHxDA (not a 1633 PFAS).

All cartridges pass.

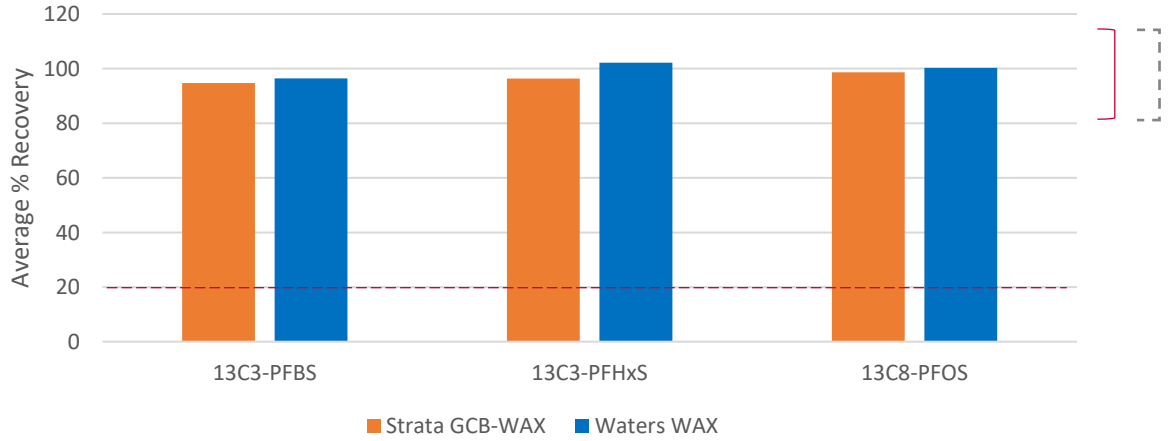
n=4, natives recoveries normalized to EIS

RECOVERY SOIL 2



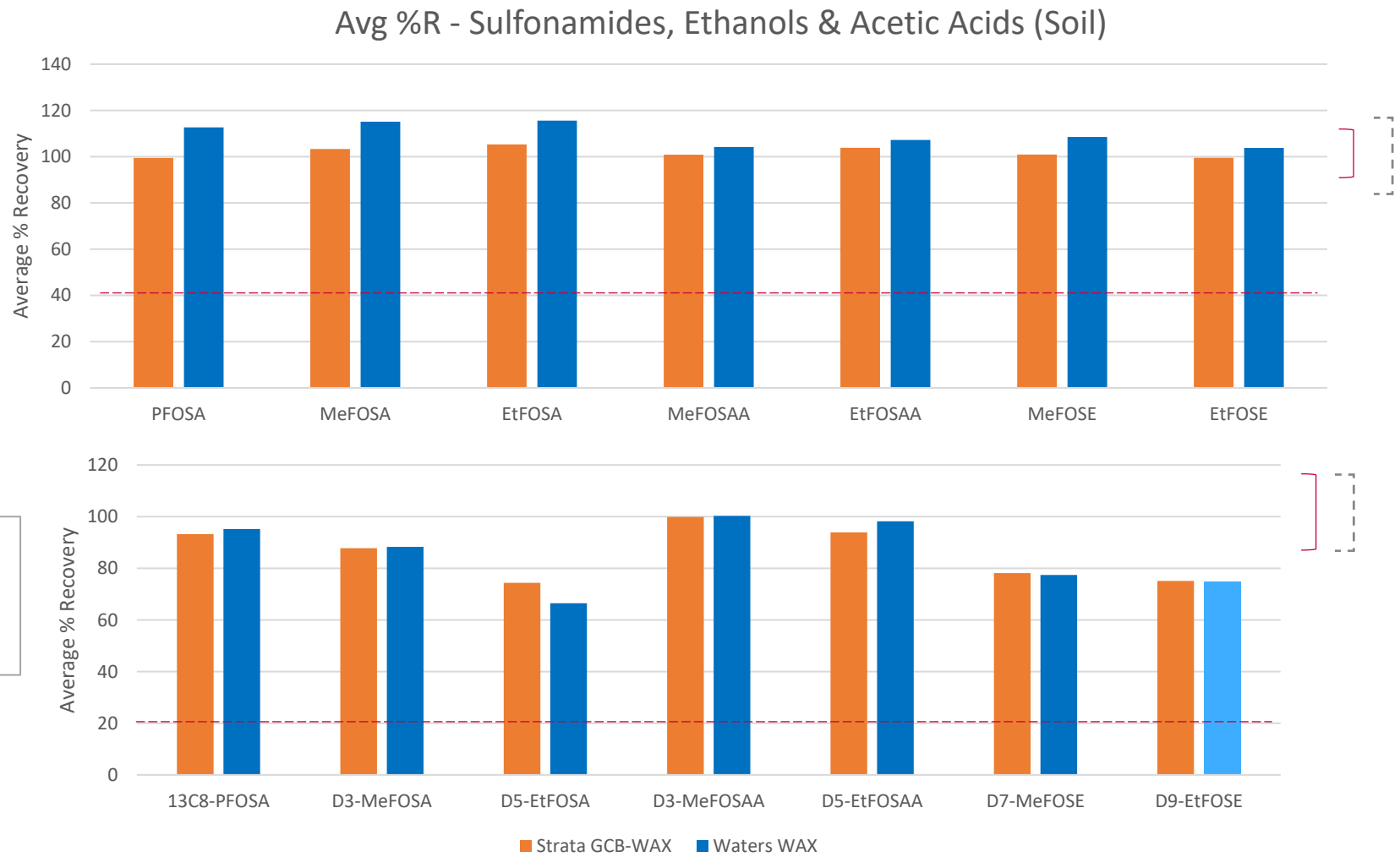
All performance equivalent.

All cartridges pass.



n=4, natives recoveries normalized to EIS

RECOVERY SOIL 3

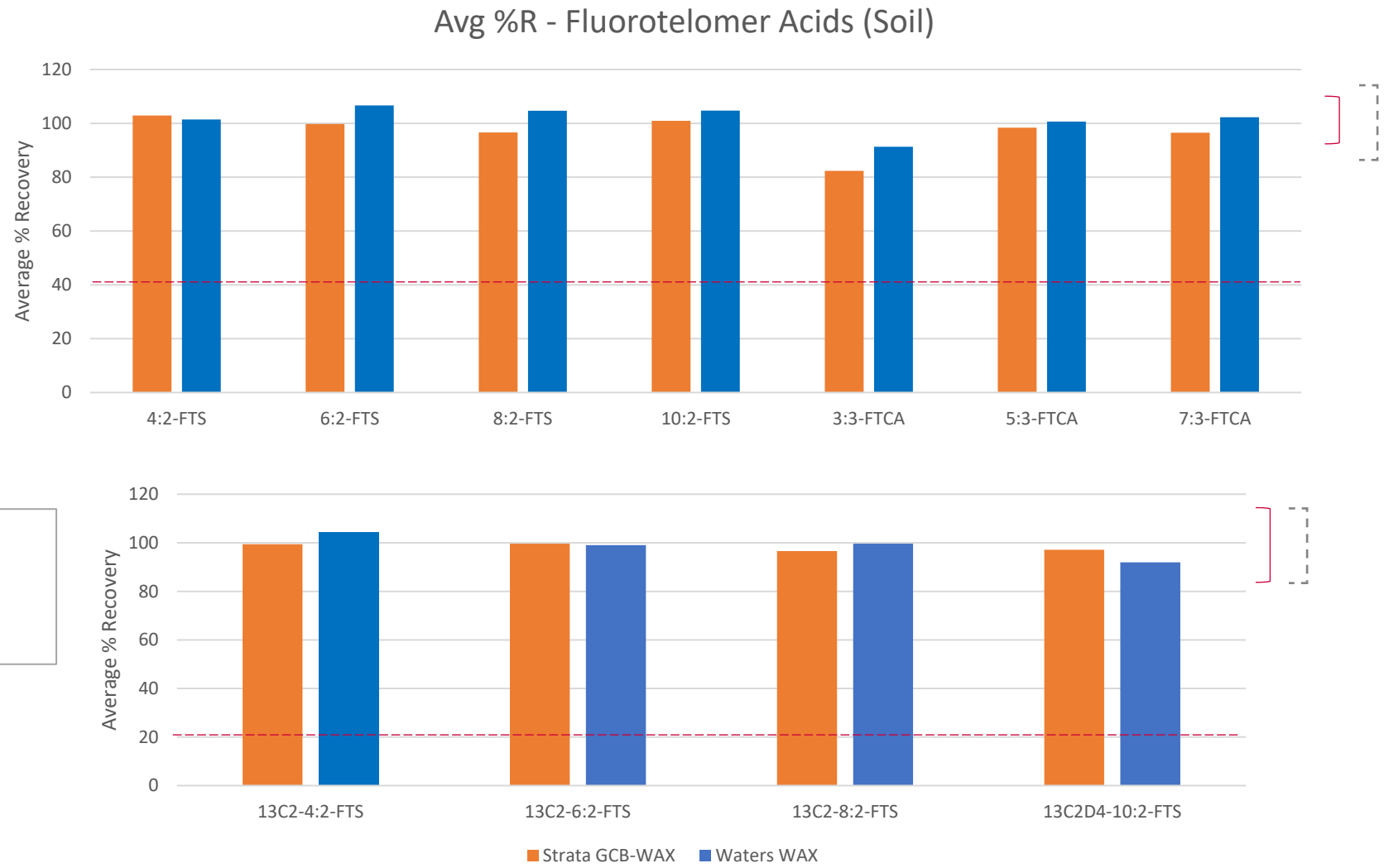


All performance equivalent.

All cartridges pass.

n=4, natives recoveries normalized to EIS
lighter shaded bar: one outlier removed

RECOVERY SOIL 4

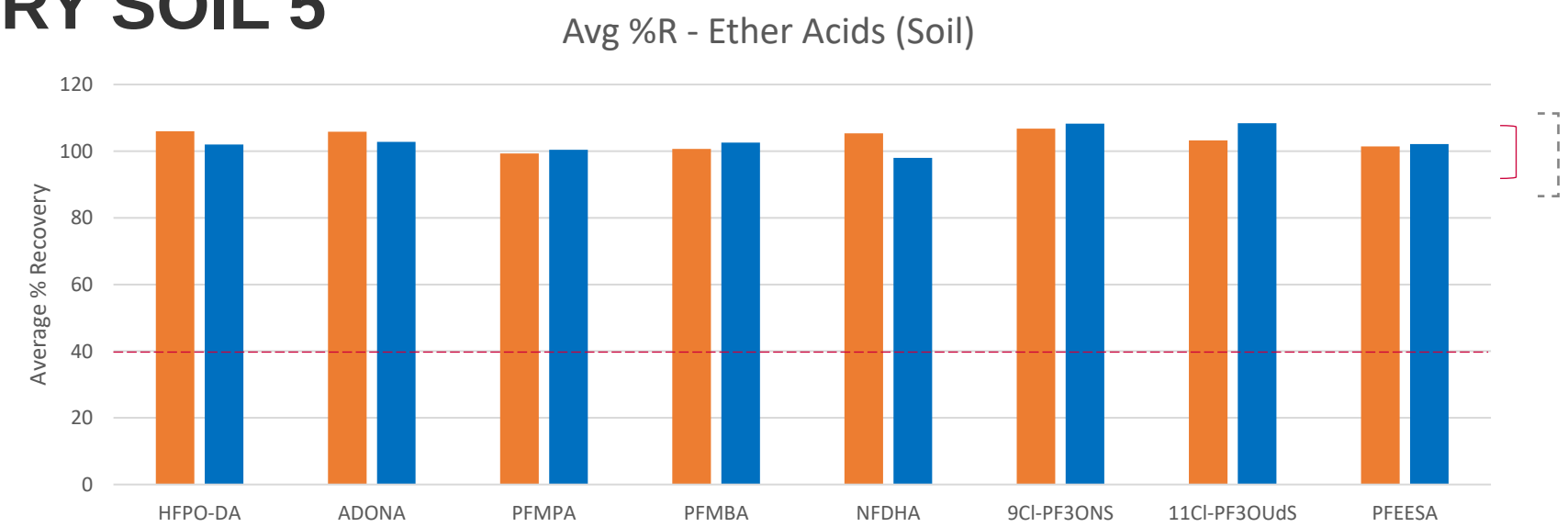


All performance equivalent.

All cartridges pass.

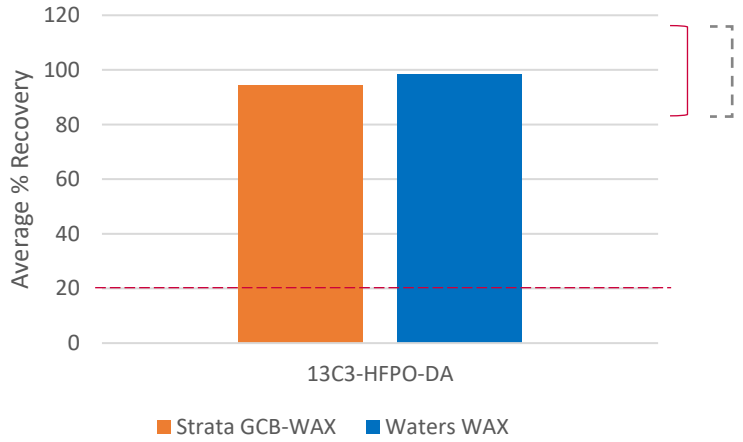
n=4, natives recoveries normalized to EIS

RECOVERY SOIL 5



All performance equivalent.

All cartridges pass.



n=4, natives recoveries normalized to EIS

AND NOW FOR SOMETHING COMPLETELY DIFFERENT!

Seriously? Blue extracts?

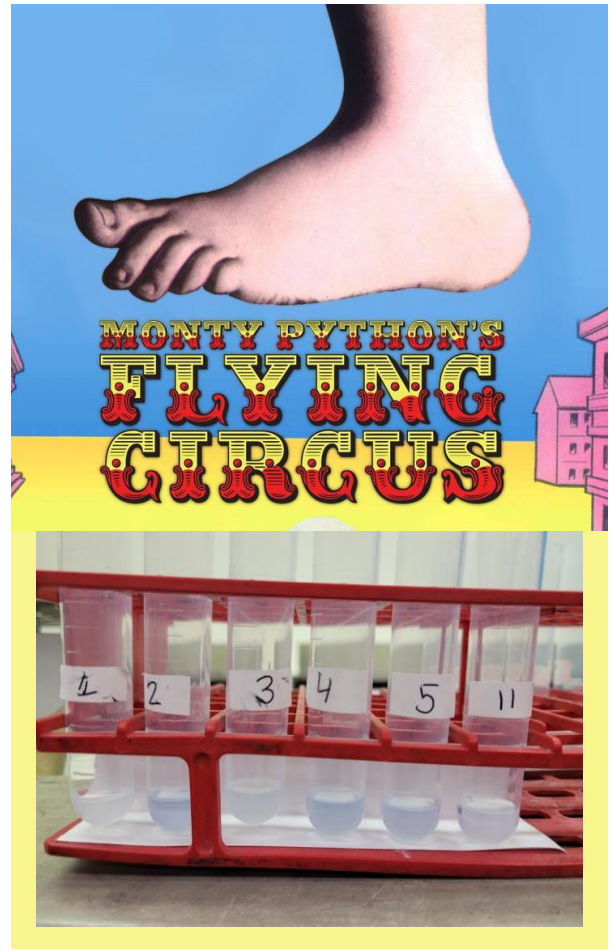
After about a month of method development our SPE extracts started turning blue!

Randomly at first, then more frequently, then constantly.
Made a mess of the MS source!

- Did we get blue sharpie ink in one of the reagents?? No
- Re-prepped all reagents and standards, no change.
- Tried different lots of various reagents, no change.

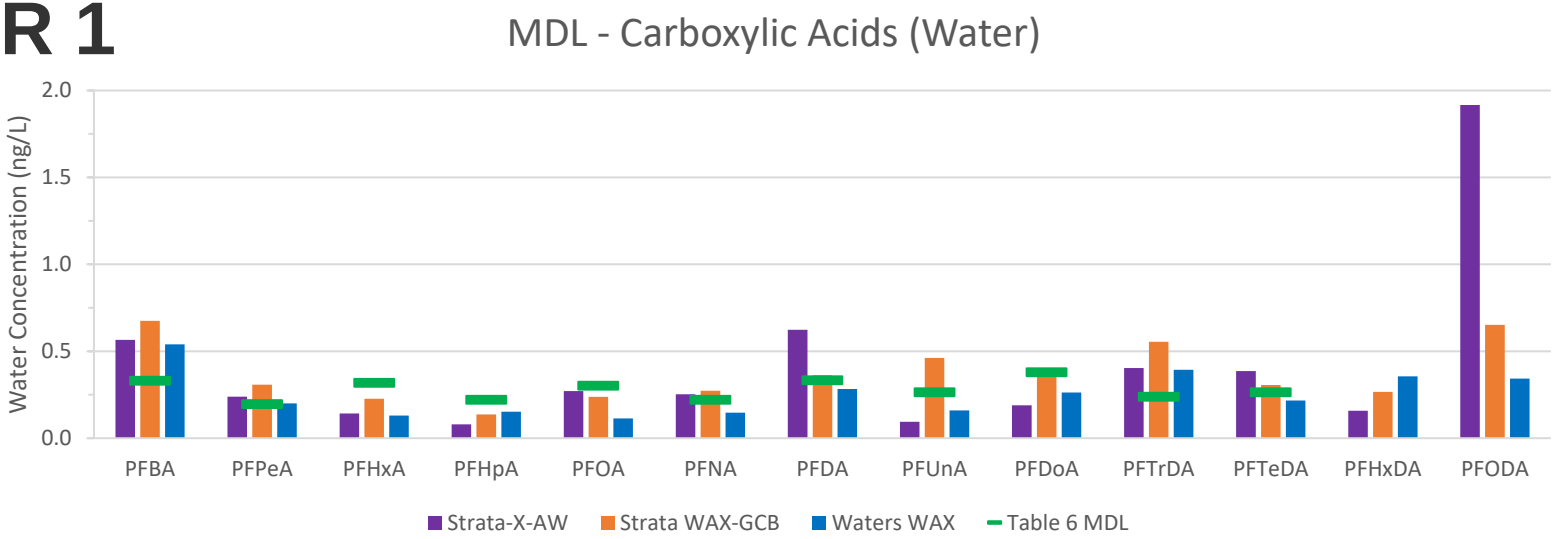
Finally – Discovered SPE eluent was corroding the insides of our stainless steel SPE extract delivery needles!

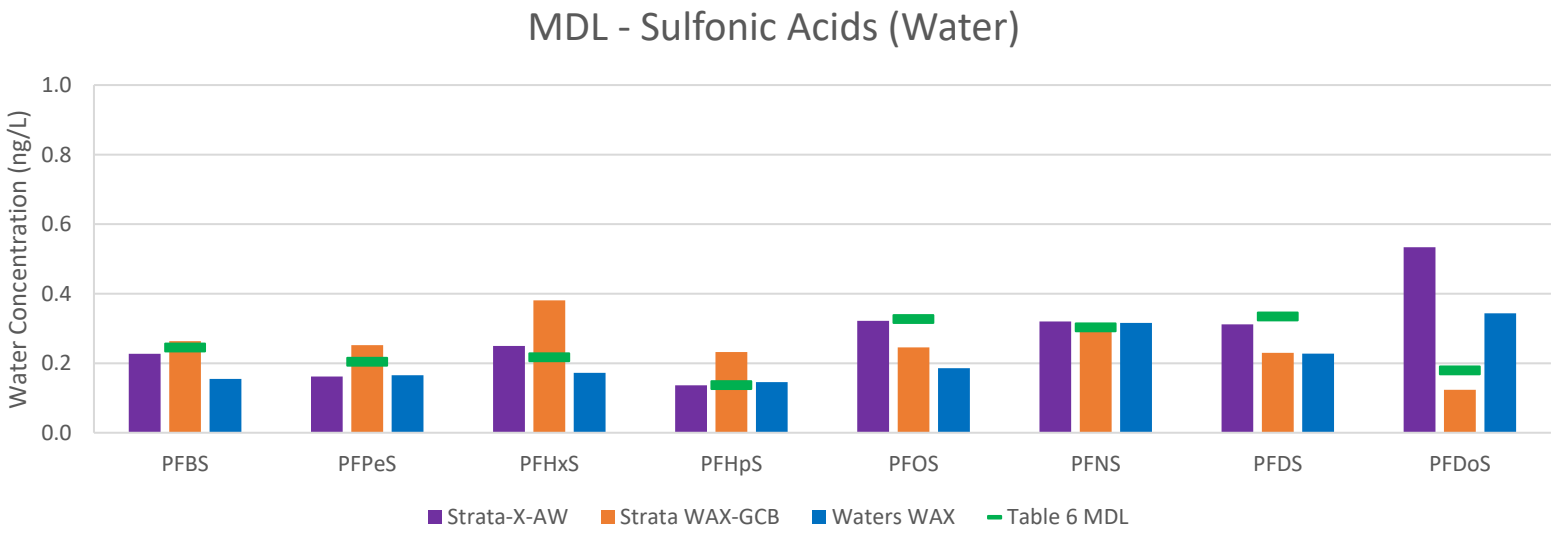
Solution – needles replaced with disposable pipet tips!



MDL WATER 1

Remember:
In the MDL charts, shorter bars are BETTER!

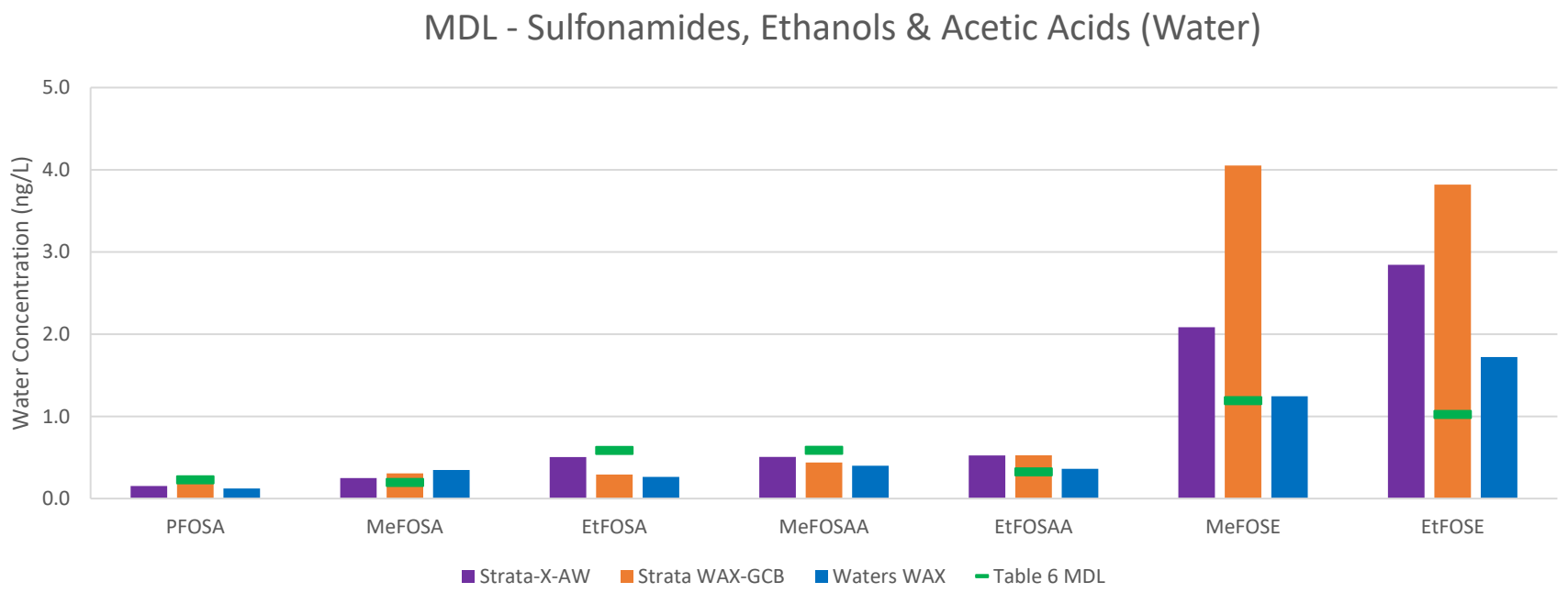




Cases of higher MDL are related to higher standard deviation among the seven replicates evaluated.

n=7, extracted and analysed over three days

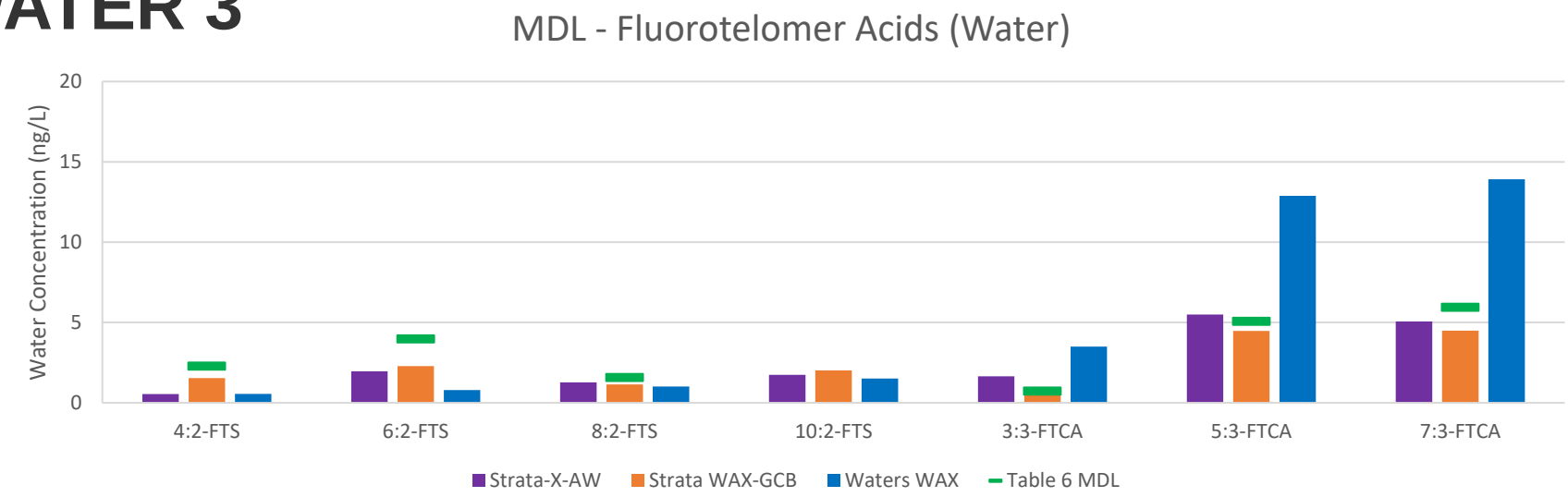
MDL WATER 2

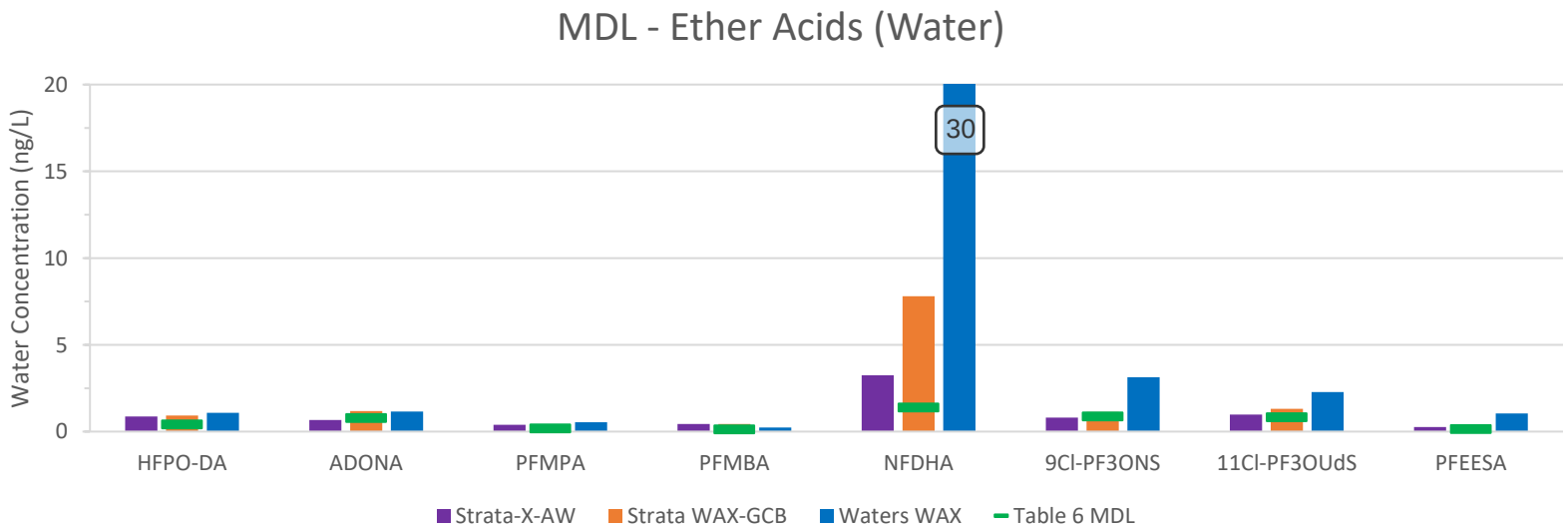


Higher standard deviation for FOSEs due to high volatility

n=7, extracted and analysed over three days

MDL WATER 3

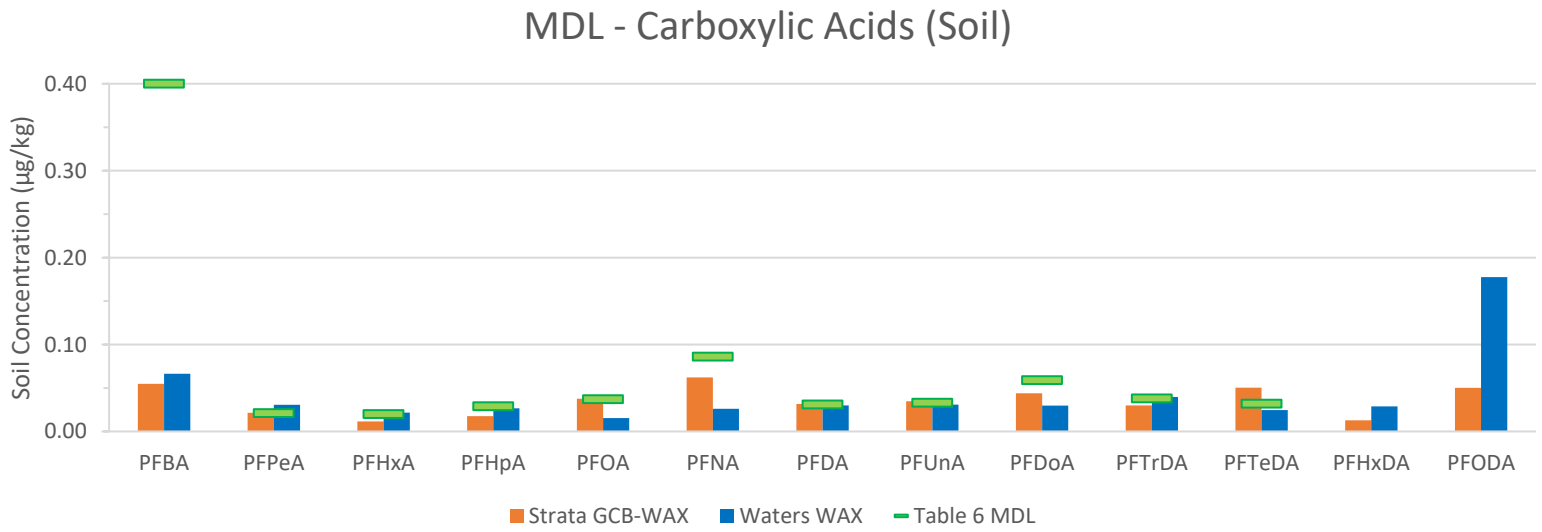


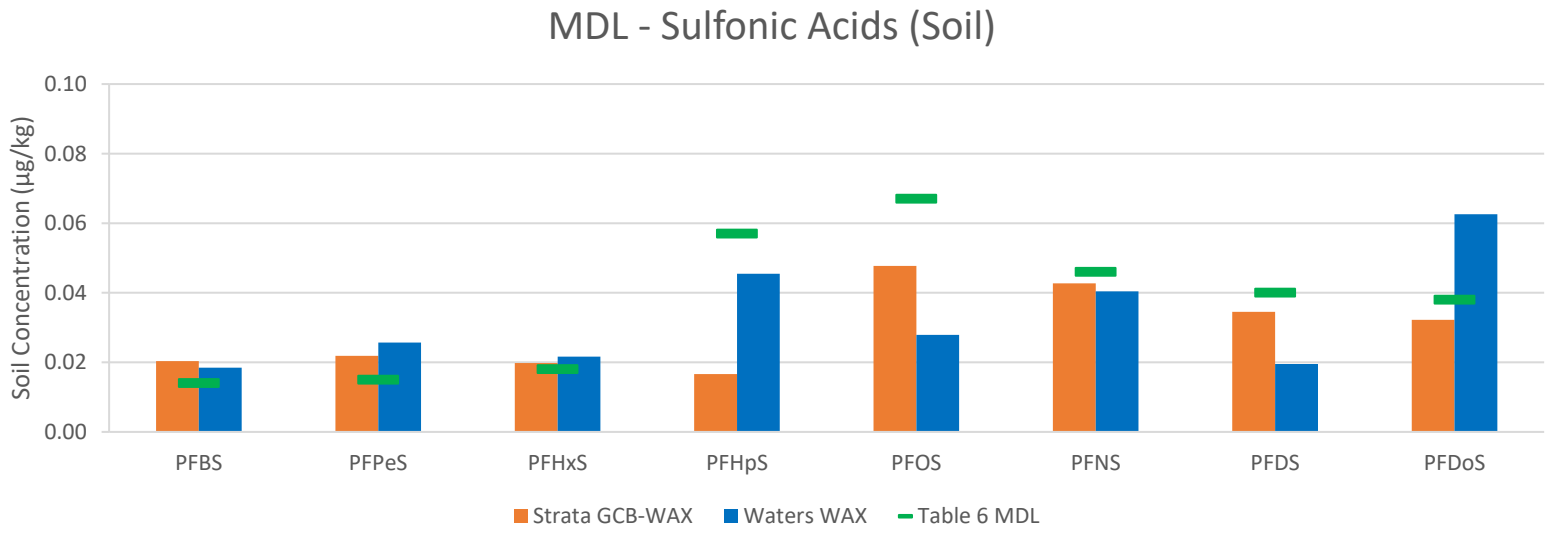


NFDHA is prone to degradation, particularly in the MS Source, resulting in higher standard deviation.

n=7, extracted and analysed over three days

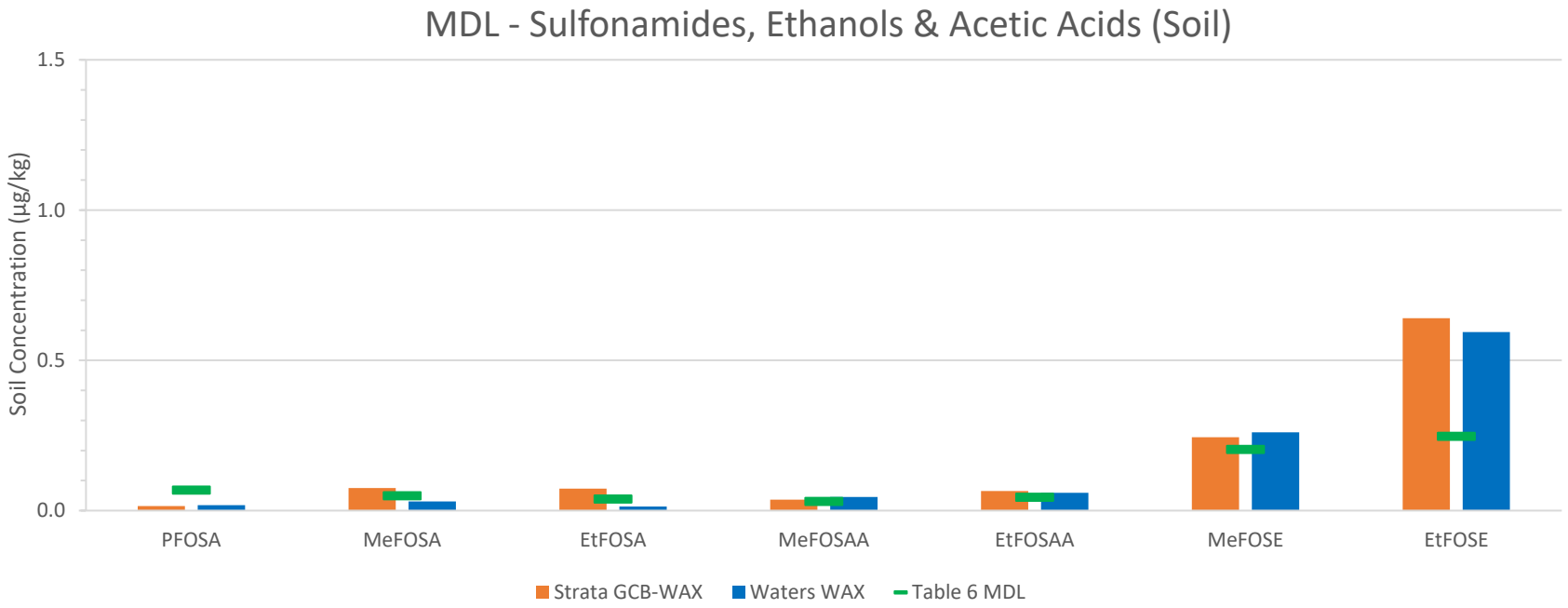
MDL SOIL 1





n=7, extracted and analysed over three days

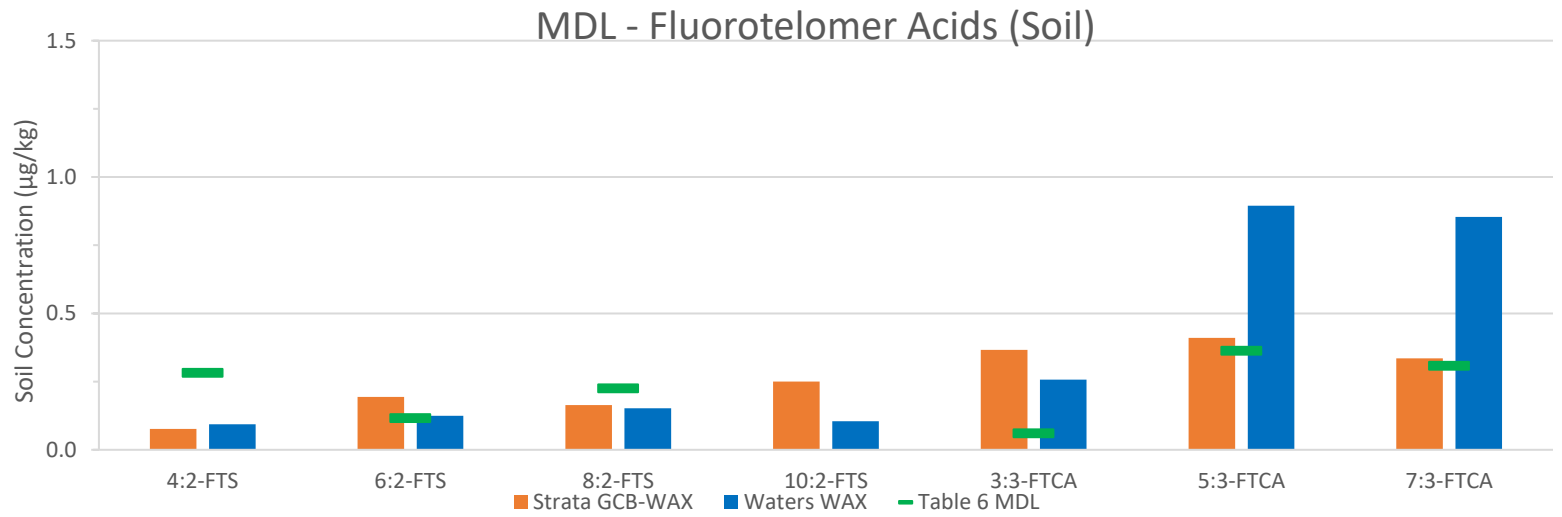
MDL SOIL 2

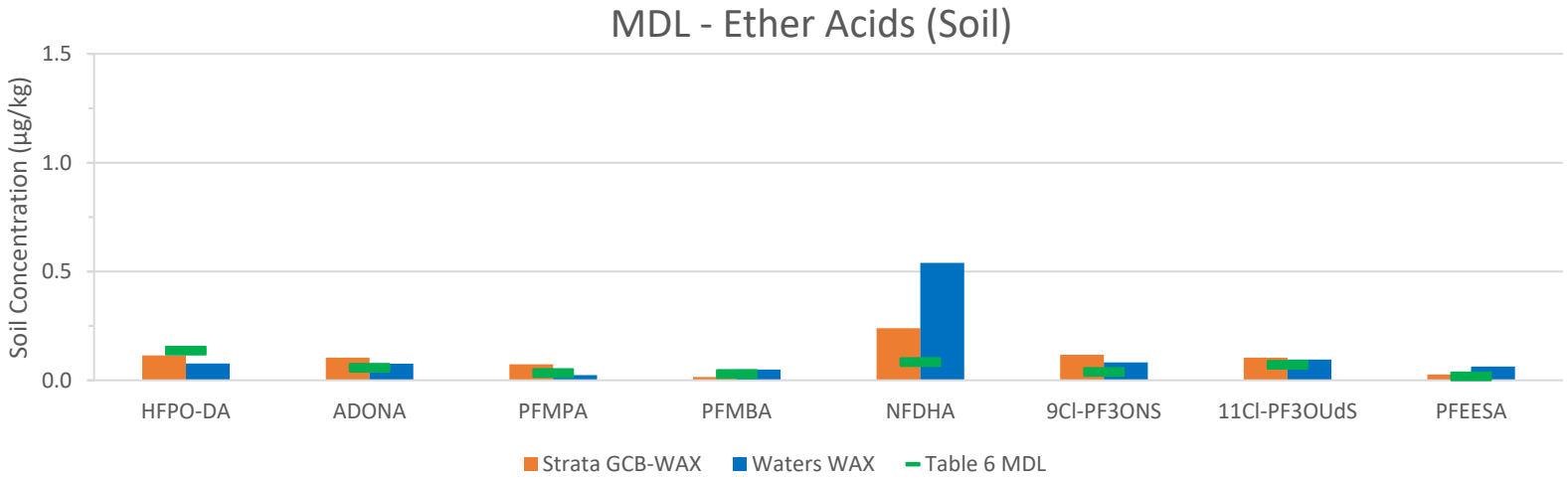


n=7, extracted and analysed over three days

MDL SOIL 3

In general, all MDL results show good consistency between the cartridges evaluated AND with the EPA 1633 Table 6 MDLs.





n=7, extracted and analysed over three days

CHALLENGE TEST – HIGH ORGANIC FINE GRAINED SOIL

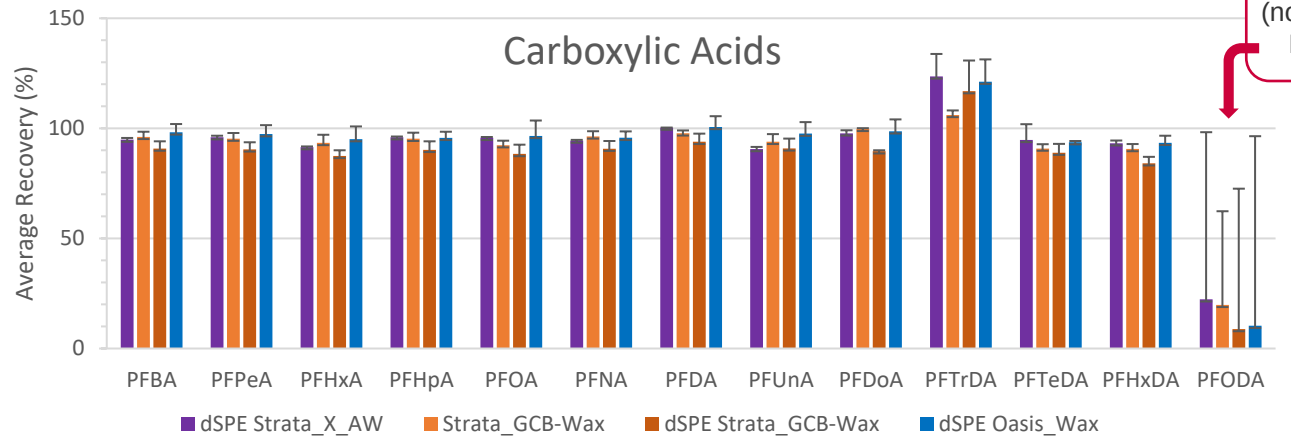
Matrix Spike + Matrix Spike Duplicate

Dark loam, clay & some roots
36% Moisture

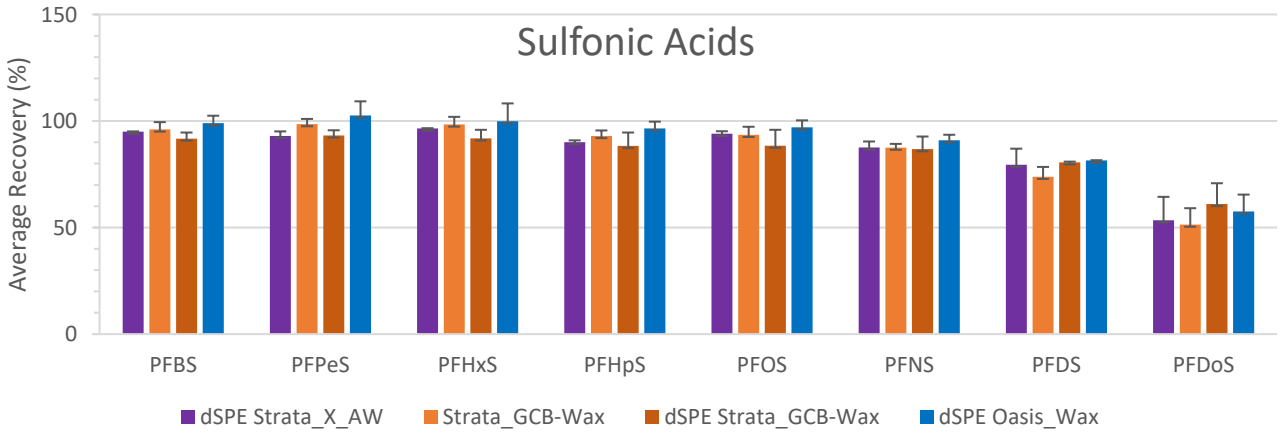
Acceptance Criteria:

Recovery 40% to 150%

RPD ≤30%



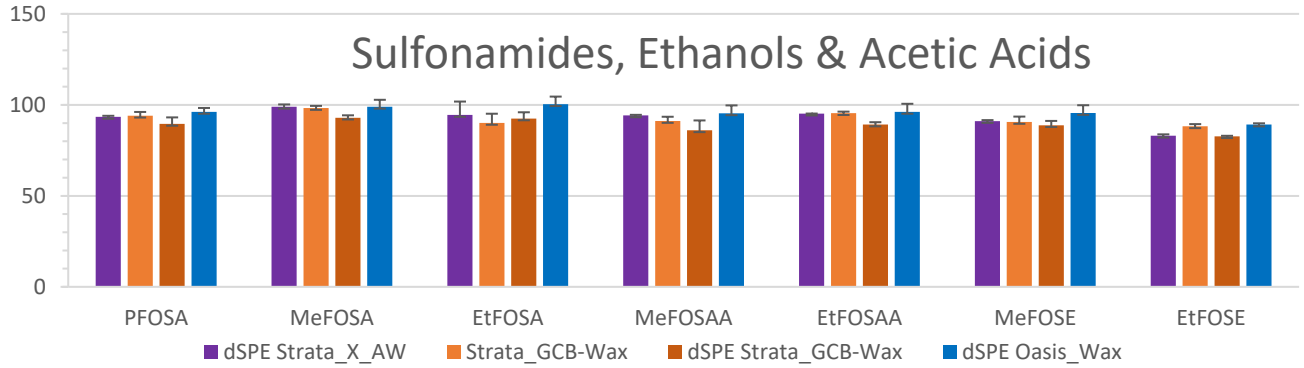
PFODA fails (not a 1633 PFAS)



n=2, one study, + error bars are ½ RPD

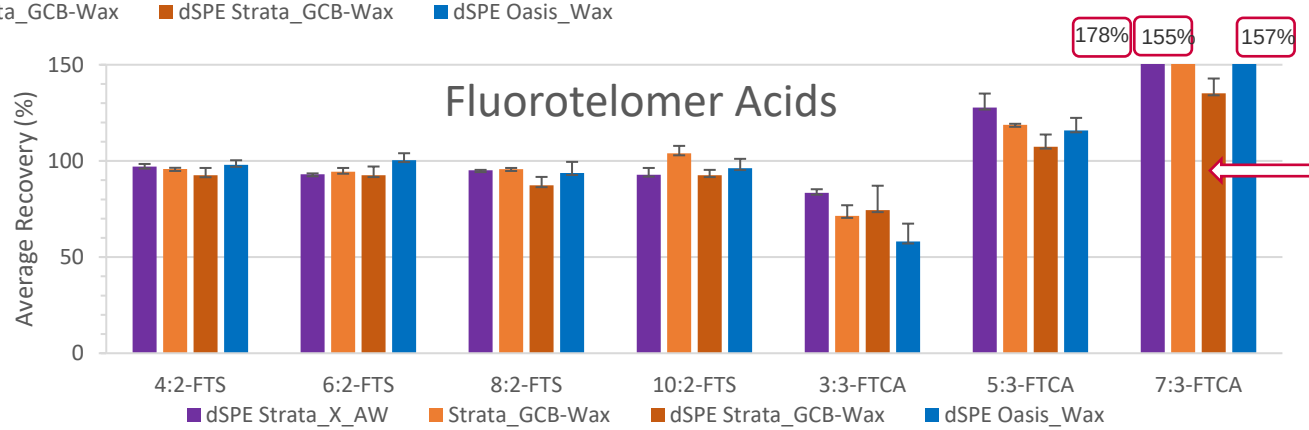
All Recoveries and RPD Pass (except PFODA)

CHALLENGE TEST – HIGH ORGANIC FINE GRAINED SOIL



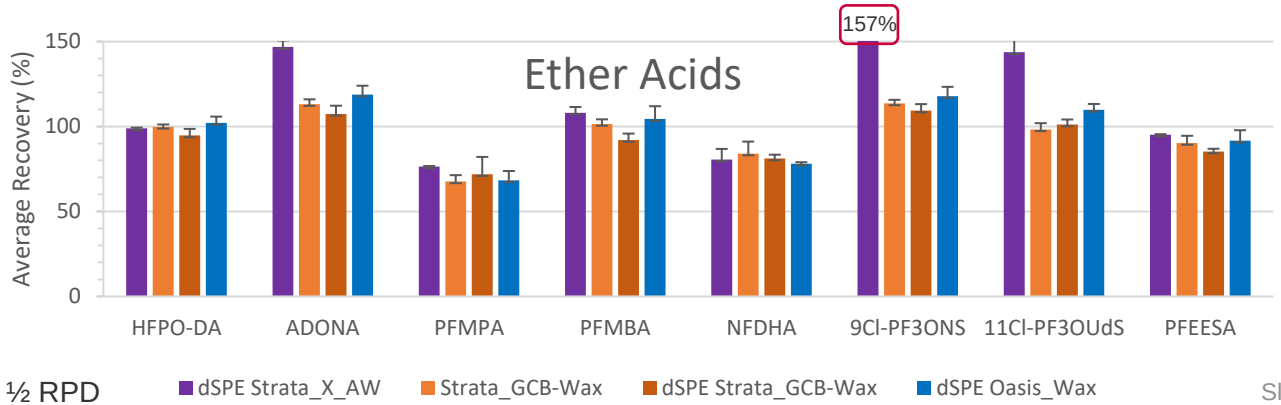
All RPD Pass

xxx% Four Recovery Failures (matrix interference)



Additional dSPE step reduces matrix interference so recovery passes!

Overall, EPA 1633 shows impressive performance for a very challenging soil sample



n=2, one study, + error bars are ½ RPD

CONCLUSIONS

- Dual layer cartridges plus elimination of dispersive SPE provides equivalent performance to the Waters Oasis WAX cartridge specified in Draft Method EPA 1633 for all 40 EPA 1633 parameters plus PFHxDA, PFODA and 10:2FTS for both soil and water, as per IDOC requirements (Section 9.1.2) and DOD QSM 5.4 Table B-24.
- For soil only PFODA failed the BV internal Initial Demonstration of Precision criterion for both cartridges tested. There is currently no criterion for IDP in EPA 1633 or QSM 5.4. Note: PFODA is not included in EPA 1633.
- Strata-X-AW cartridges passed all water extraction criteria for 41 of 43 compounds: 13C4-PFBA and PFMPA recoveries were marginally below acceptance thresholds. Further studies are underway to determine cause.
- MDLs for all Phenomenex cartridges tested are consistent with those of both the Waters cartridges and as cited in Draft EPA 1633.
- The elimination of dispersive SPE reduces labor per analytical batch (20 samples) by approximately 30 minutes for manual cartridge SPE clean-up. Elimination of the filtration step would provide a further 30 min labor reduction.
- Incorporation of the dual layer cartridges into the workflow enables automation of the full clean-up procedure, with the potential for a significant reduction in labor and improvements in data reproducibility.

COMMENTS AND QUESTIONS

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