Non target and suspect screening PFAS

Werkgroep 28/11/2023

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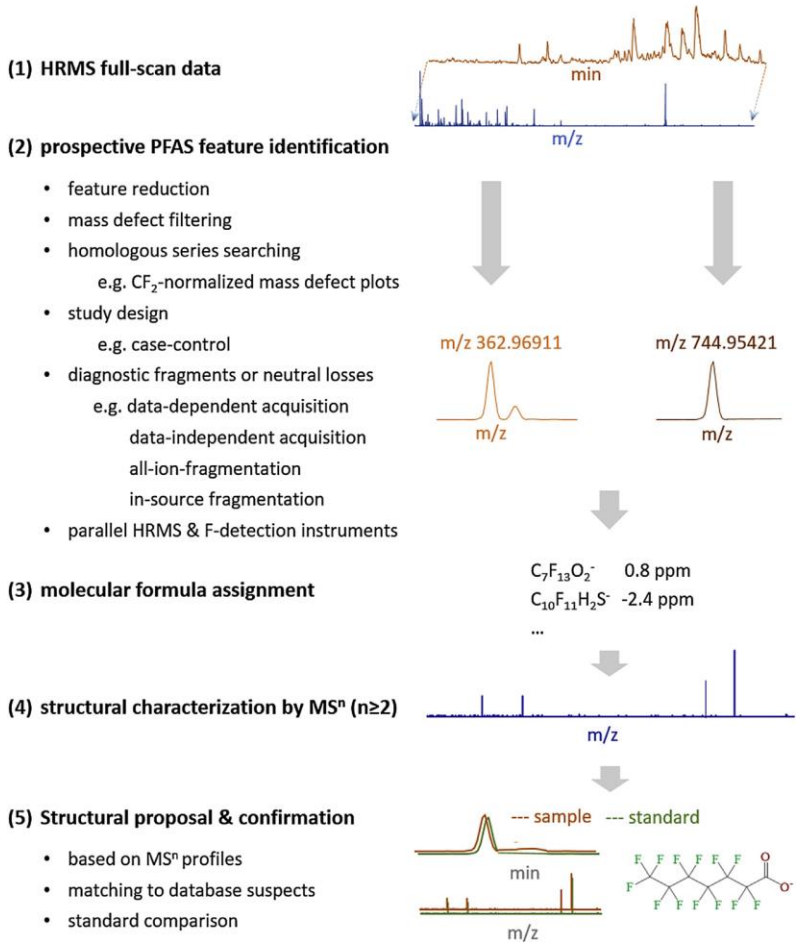
NTS and SS PFAS

Non target screening PFAS

- Extraction and analysis according to WAC/IV/A/025
- Record full scan (pos and neg)
- Record fragmentation data (ddMS2)
- Data processing
  - Deconvolution
  - Retention time alignment (triple injections)
  - Prioritization of data
    - Mass defect and md/C – m/C plot
  - Molecular formula assignment
  - Structure proposal
    - Search in databases (fragmentation and structures)
  - Quantification or sem-quantification

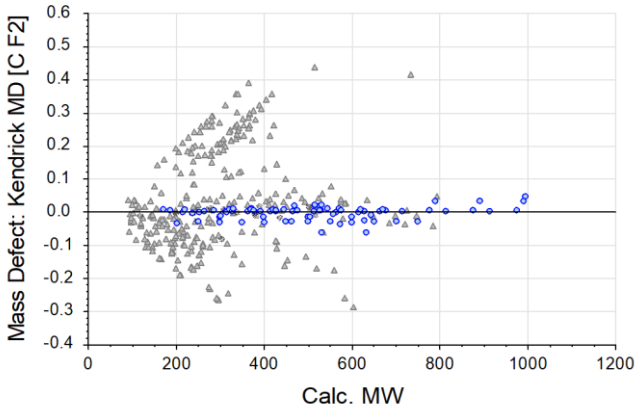


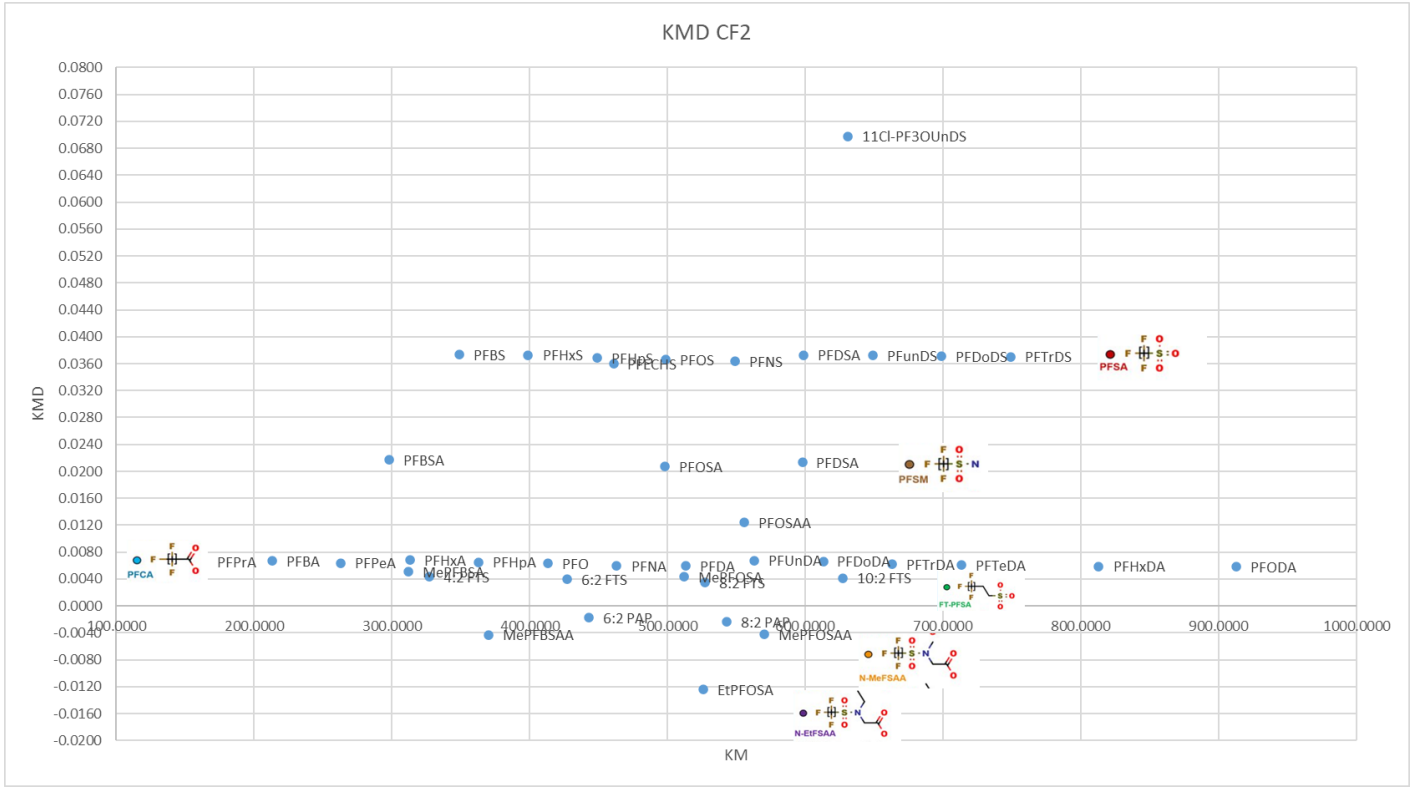
Liu *et al*, *Trends in Anal. Chem.* **2019**

NTS and SS PFAS

Non target screening PFAS

- Prioritization via
  - Kendrick mass defect (CF2)





NTS and SS PFAS

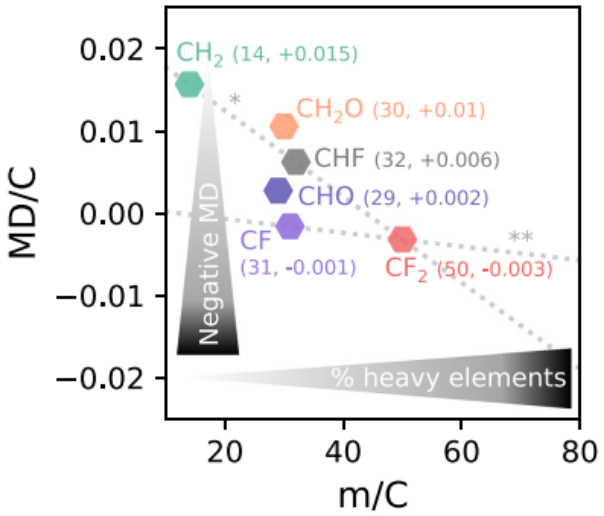
Non target screening PFAS

- Prioritization via
  - Md/C – mC approach
    - Kaufman et al. 2022 DOI: 10.1093/jaoacint/qsac071
    - Zweigle et al. 2023; DOI: 10.1007/s00216-023-04601-1

C = 100 * abundance of the first isotopic peak / abundance of the corresponding monoisotopic peak / 1.1145

Mass over carbon "*m*/C" was calculated by dividing the measured mass of the monoisotopic peak over the estimated number carbon atoms "C."

Mass defect over carbon "md/C" was calculated by dividing the measured mass defect "md" of the monoisotopic ion over the estimated number of carbon atoms "C."



$$MD/C_{CH_xF_{2-x}} \approx -5.24 \times 10^{-4} \cdot m/C + 0.023 \quad (1)$$

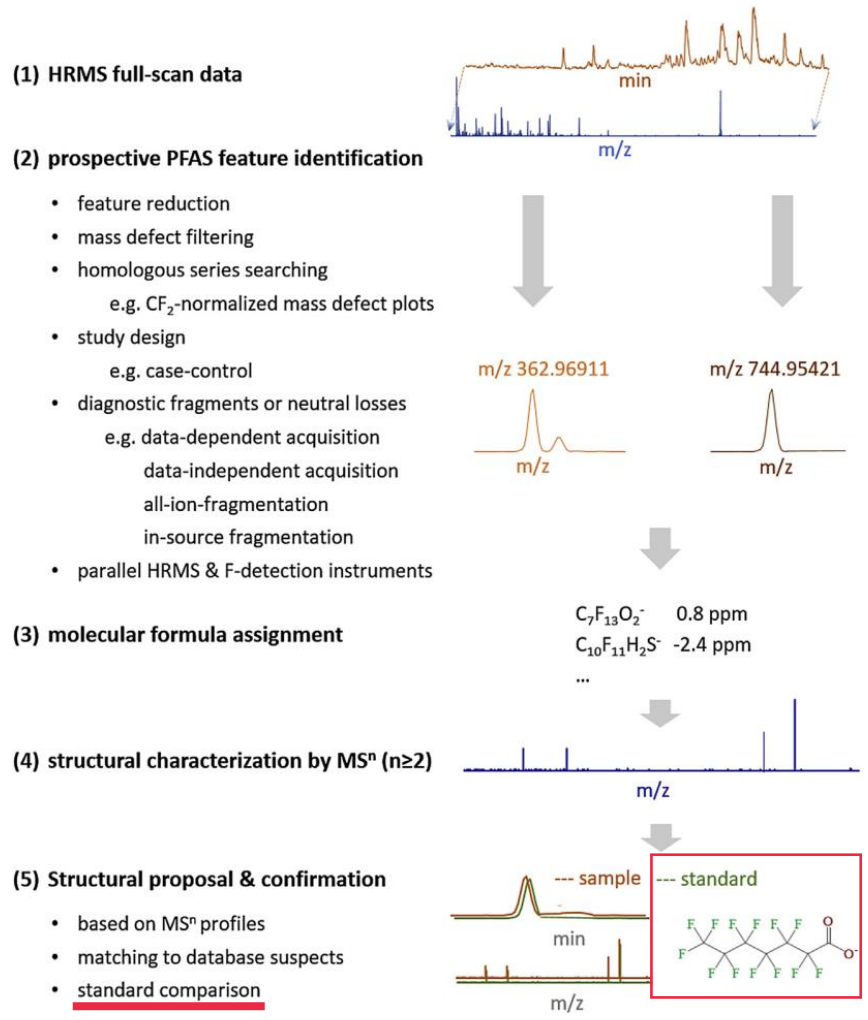
$$MD/C_{CF_x} \approx -8.406 \times 10^{-5} \cdot m/C + 0.001 \quad (2)$$

NTS and SS PFAS

Suspect screening

- After identification of unknown PFAS
  - How much is present in the sample?
- Not always reference standards commercially available
- How to quantify?

LC-HRMS Workflow for nontarget discovery of PFAS



Not always available!

Liu *et al*, *Trends in Anal. Chem.* **2019**

Current NIST PFAS list (v1.5)

> 4500 PFAS

EPA master list

>10000 PFAS

LC-ESI(-)-HRMS

50 target PFAS standards commercially available

30 PFAS labeled standards (int. std. or surrogate)

LC-ESI(+)-HRMS

5 target PFAS standards commercially available

0 PFAS labeled standards

How to estimate suspect PFAS concentration without each individual standards being commercially available?

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How to estimate suspect PFAS concentration?

Guidelines to choose the best target-surrogate pair:

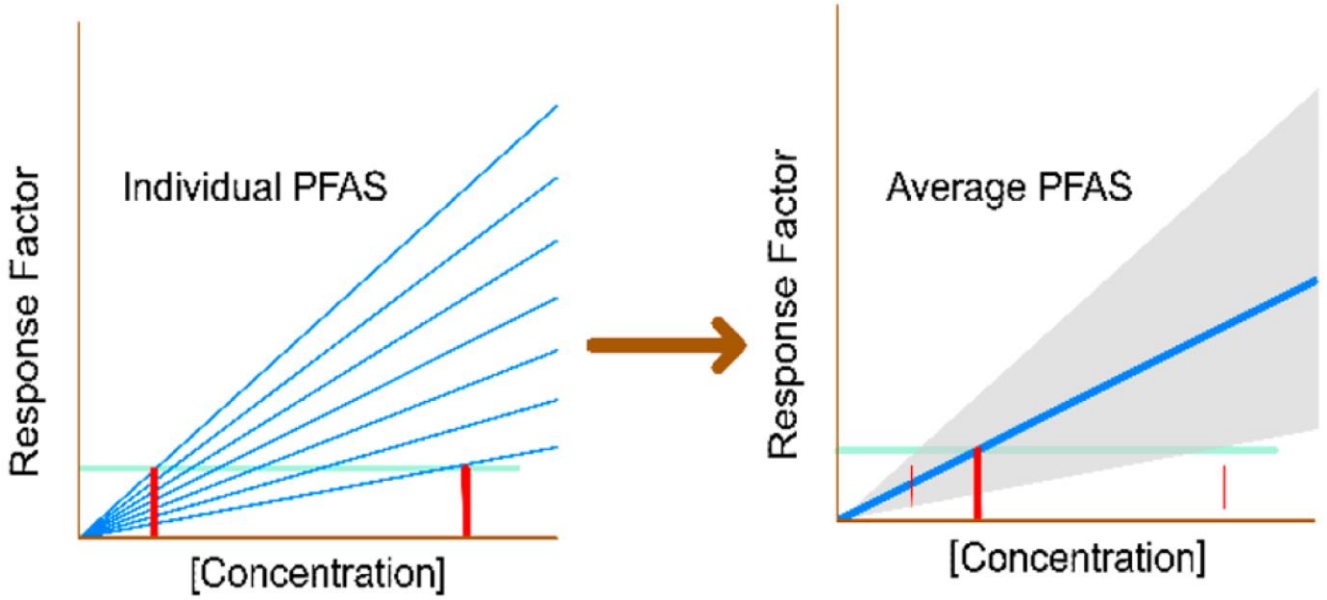
Same number of F | Same head group | **Same class**

Same chain length | Similar retention time

} 1:1 matching strategies **Currently used but no universal selection**

Molar response factors vary within a given PFAS class!

Alternative approach: Use **average** target PFAS response factor



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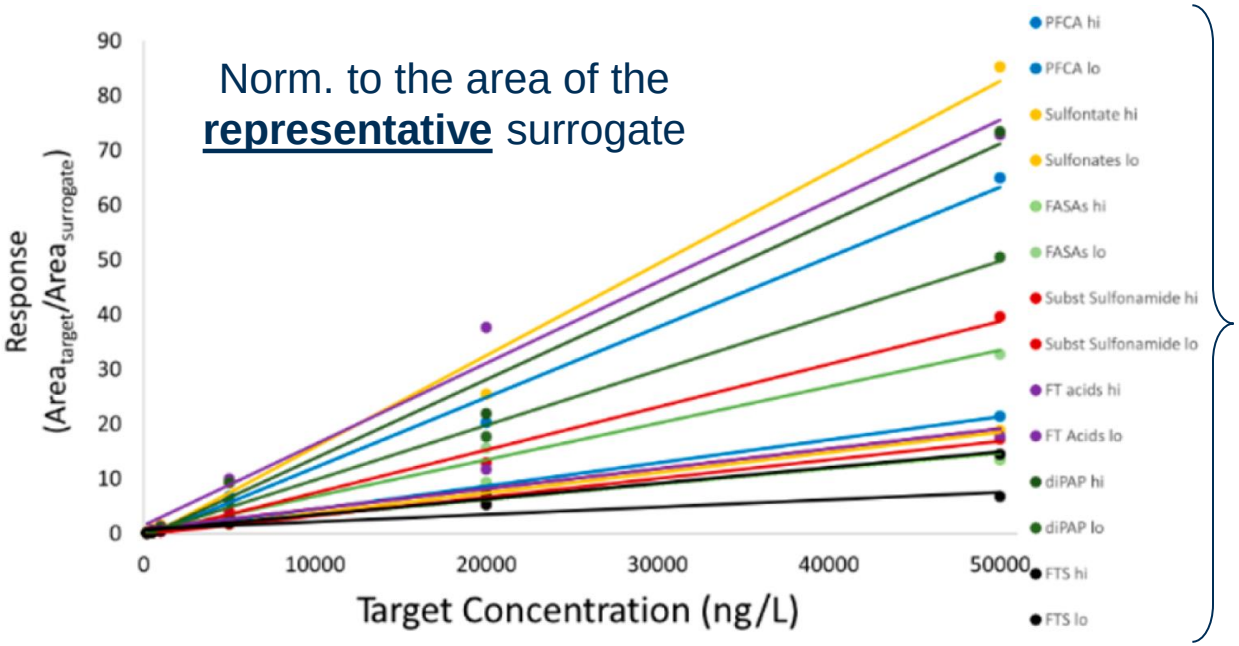
The concept of "average calibration curve"

- → 50 anionic target PFAS
- → 30 labeled anionic (non)matched surrogate standards
- → 5 zwitterionic/cationic target PFAS
- → Prometon-d3, metolachlor-d6 as nonmatched surrogate standards

Response of PFAS by classes

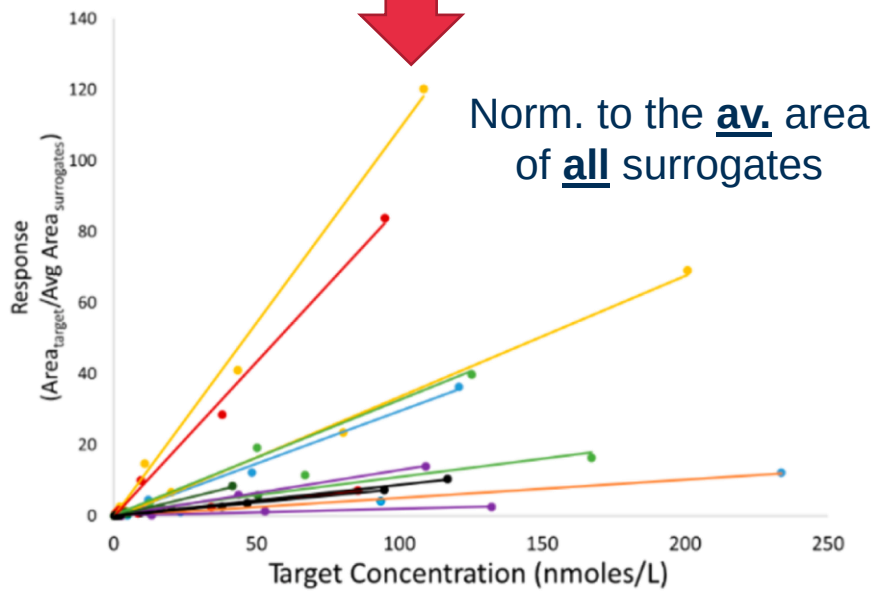
High and lowest response within each PFAS class



7 classes

All other homologues within each class give calibration curves that fell within the maximum and minimum of the class

- → Nanomolar response for all classes
- → Response vary by head group and F tail length
- → Overlapping response ranges
  - → PFAS classes can be also treated together



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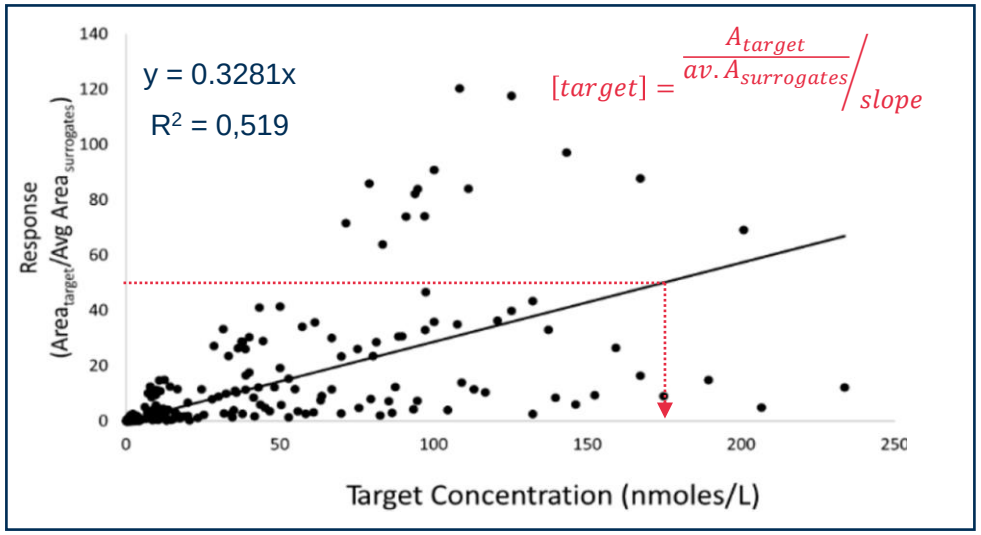
The concept of "average calibration curve" – Performance

Average calibration curve

1/ x weighted linear regression (forced to 0)



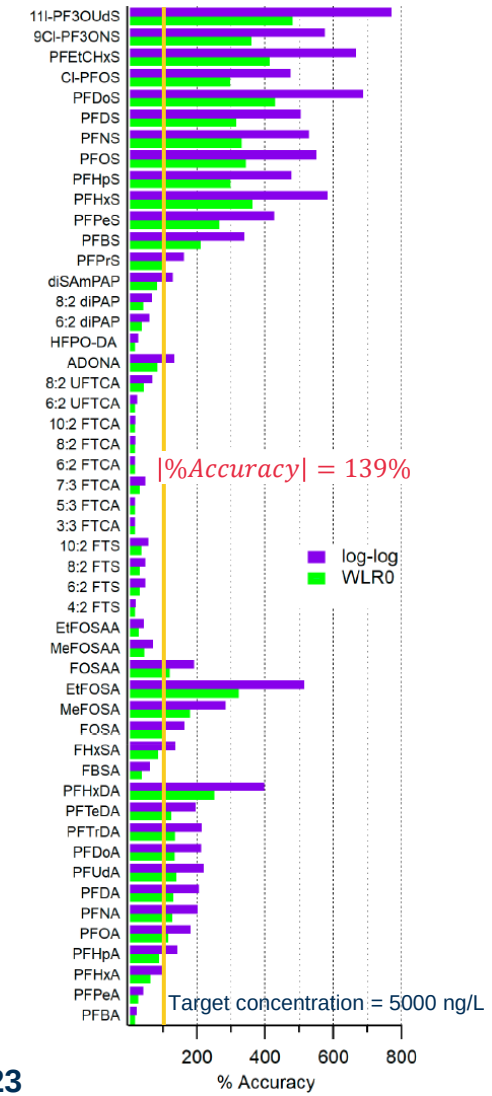
overestimated

underestimated

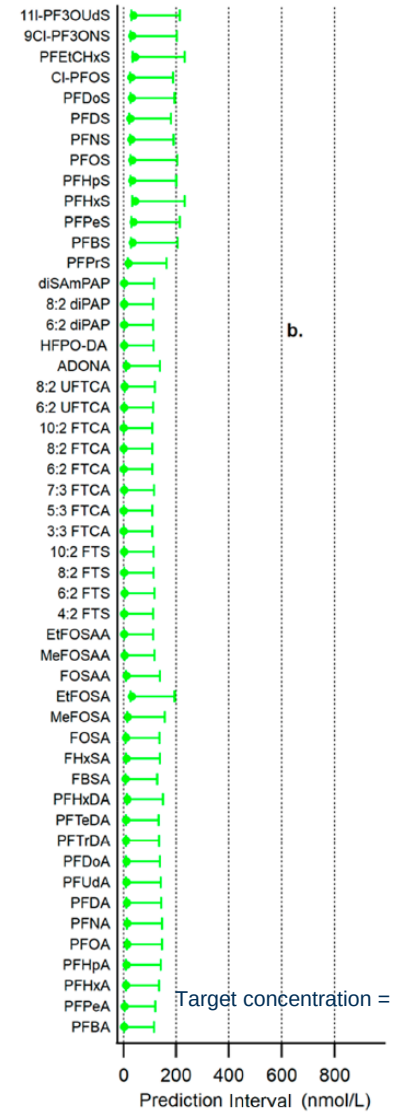
Advantage:

- → No preliminary knowledge of the suspect response or structure are required to estimate the concentration.
- → Continuous expansion of the average calibration curve to include new standards.
- → Average curve can be constructed for each PFAS class.
- → Fast, reproducible over time.
- → More uniform reporting of suspect concentrations.

$$\%Accuracy = \frac{[target]_{fit}}{[target]_{expected}} * 100$$



Upper and lower bounds from 95% prediction intervals



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Practical aspects

- Next steps:
    - Apply the approach to WAC compounds and samples
- New WAC method will be available in 2024 for suspect screening
    - that include semi-quantification via the average calibration curve
- Ring trial needed for NTS and/or SS?