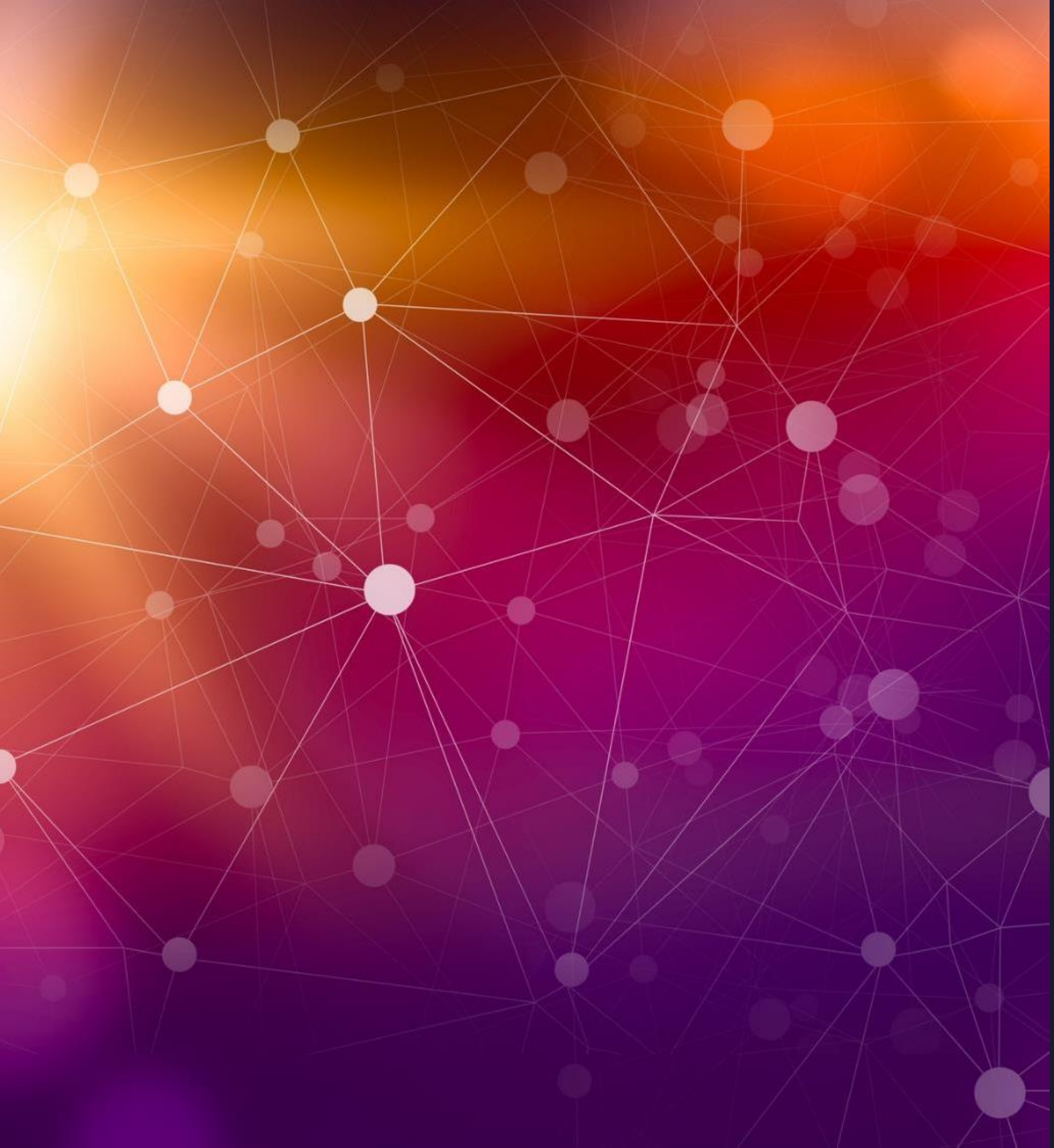

Using HRMS to Explore Chemical Space of PFAS Captured by SPE

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Outline

Importance of Chemical Space

Utility of Solid-Phase Extraction

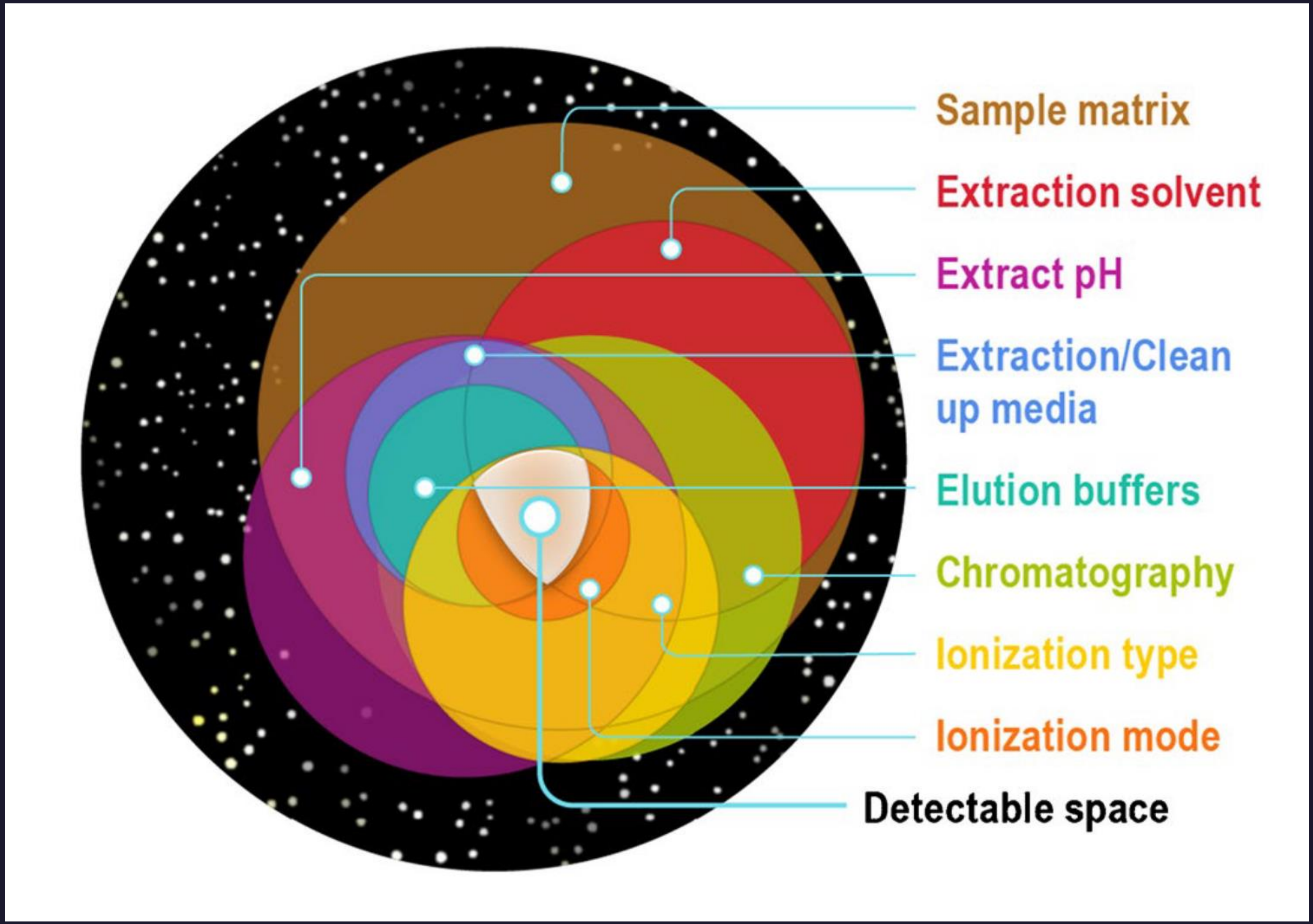
Case Study: Using High-Res Mass Spectrometry to Inform the bounds of PFAS capturability

Conclusion

All steps up to analysis limit the chemical space

Chemical Space

Analytical Chemistry - The domain of the ability to detect chemicals based on a procedure applied to a sample matrix



(Black et al., 2022)

Why Use Solid-Phase Extraction

HRMS analysis is done in full-scan (w/ ddMS2) – need more sensitivity

PFAS concentrations are often below ppb (ug/L) range

For drinking water (this work), concentrations are typically single digit ppt (ng/L)

Remove inorganic salts

Application Specific

Inherent Trade-offs using Solid-Phase Extraction in Non-Targeted Analysis

Experiment comparing EPA 533 and EPA 1633 and evaluate chemical space

Comparative Study Goals

- Determine if EPA 533 extract would suffice for future NTA analysis
- Use Statistical Tests (ANOVA) to determine method differences
- Retain PFAS extractability coverage (need to use WAX)
- Ability to retain new PFAS classes present in samples
- Refrain from complicated stacked cartridge procedures
- Expect/Accept limitations in chemical space
- To eventually support DW 2024-0002-DDW in California
  - Subset of samples analyzed for NTA and ultra-short chain PFAS
  - See https://waterboards.ca.gov/pfas/pfas_ddw_general_order/

General Method Comparisons

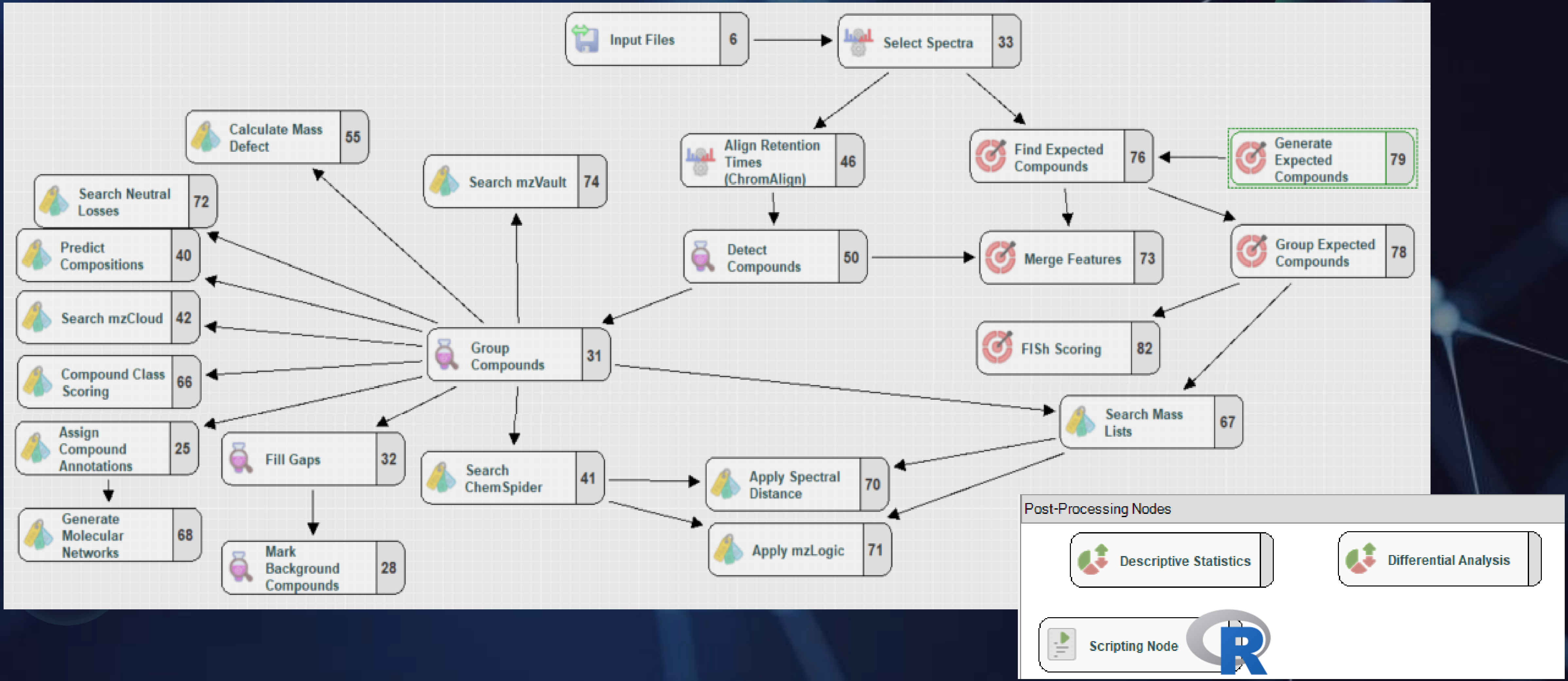
- EPA 533 extract goes to dryness during Evaporation process
- For EPA 533 used Phenomenex Strata-X-AW (500mg)
- For EPA 1633, used Phenomenex Strata-WAX/GCB (200mg/50mg)
- Both achieve mass accuracy +/- 10ppm, isotopes recovery 50-200%, excellent RT stability, perform replicates on all samples

General Data Acquisition Parameters

- Thermo Orbitrap Q-Exactive
- Full Scan
  - 100-1400 m/z Resolution 70,000 profile
- Data Dependent MS/MS Spectra TopN=5
  - Intensity Threshold at 200,000
  - Resolution 17,500 centroid
  - Stepped collision energy
- Acquire both positive/negative electrospray ionization
- Using Kinetex EVO C18 100x2.1mm
  - Organic and pH Gradient from 5 – 95% Methanol pH 4 to 8 over 20 minutes

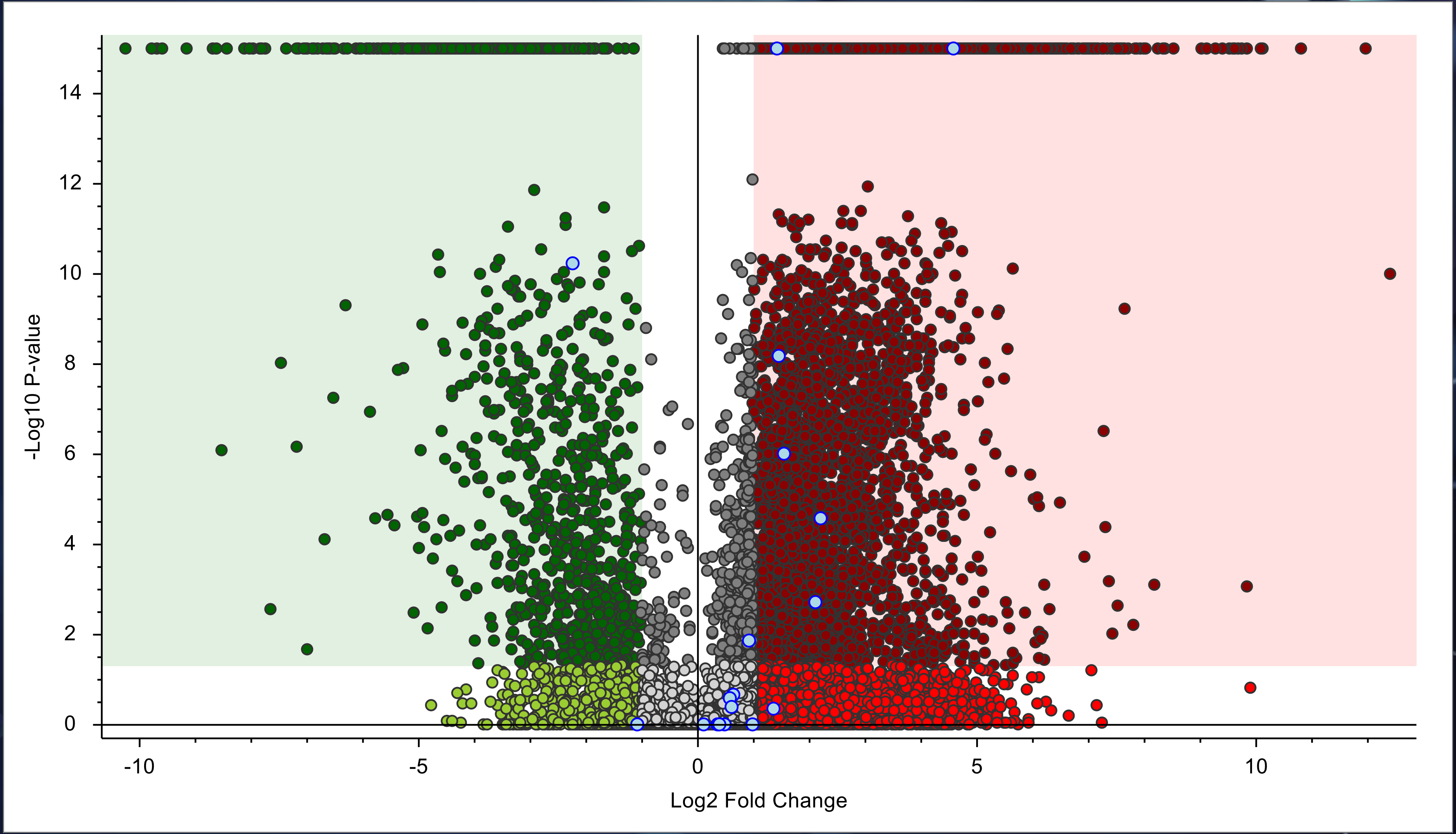
Complete NTA Workflow

Example – Thermo Compound Discoverer 3.3



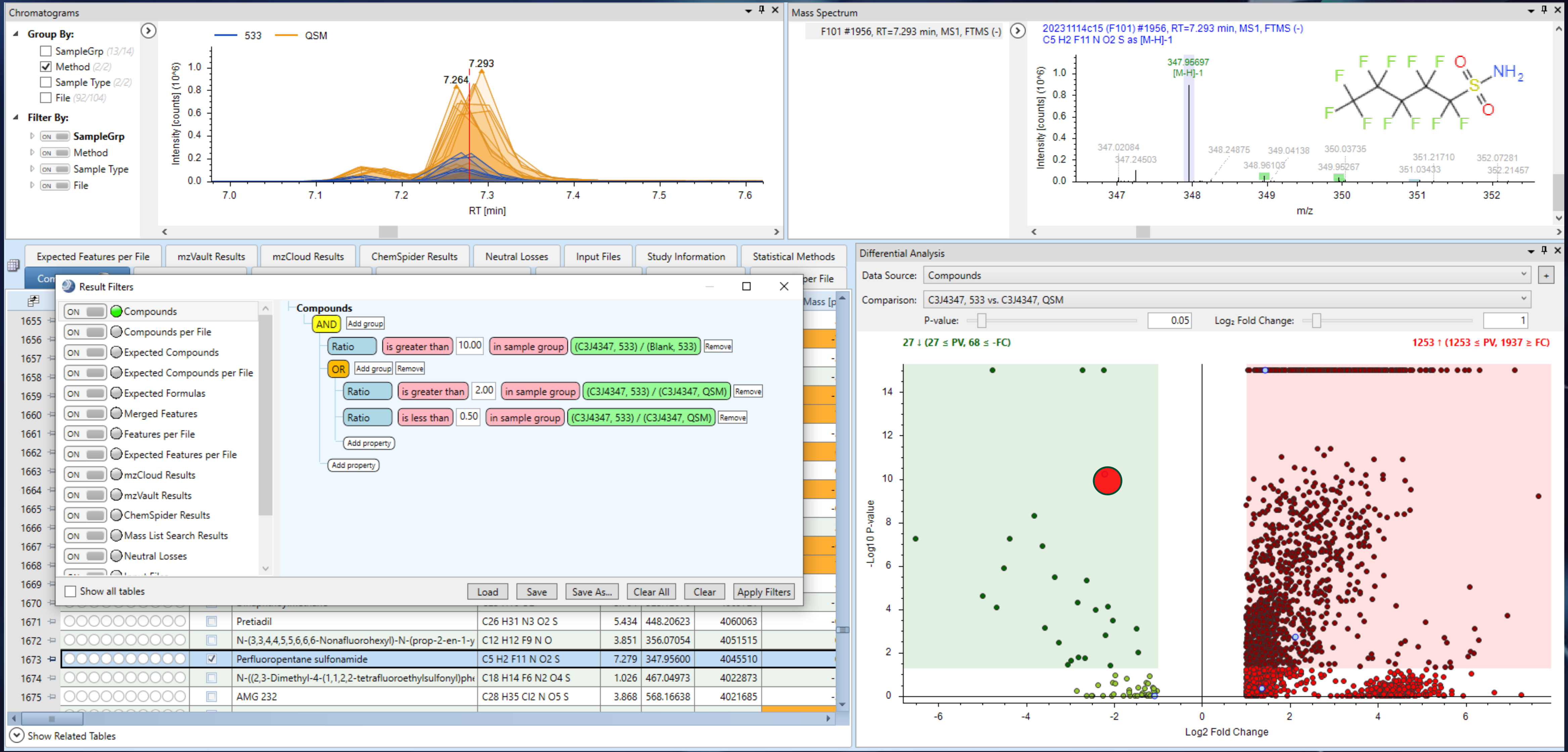
Differential Analysis - All Features

P-Value = 0.05, Log2 Fold > 1 or < -1 highlighted



Differential Analysis - Specific Features

Perfluoropentanesulfonamide - PFPeSA



Chemical Method Comparisons

- Features in 533 extracts NOT found in 1633 extract
  - Acesulfame (8/10 samples, %CV 0.5 to 20%, avg hit rate 2.0/3 replicates)
  - Bromacil (5/10 samples, %CV 5.3 to 77%, avg hit rate 1.8/3 replicates)
  - Imazapyr (6/10 samples, %CV 2.3 to 10%, avg hit rate 1.83/3 replicates)
  - Sulfamethoxazole (6/10 samples, %CV 2.3 to 10%, avg hit rate 1.83/3 replicates)

Concluded that the Post Loading Formic acid rinse removes these analytes from this SPE media. Also, 200mg vs. 500mg at play.

Chemical Method Comparisons

- Features in QSM extracts NOT found in 533 extract
  - Atrazine (8/10 samples, %CV 14 to 25%, avg hit rate 2.63/3 replicates)
  - Simazine (9/10 samples, %CV 13 to 31%, avg hit rate 2.67/3 replicates)
  - Diuron (5/10 samples, %CV 9 to 21%, avg hit rate 1.6/3 replicates)
  - Fluridone (2/10 samples, %CV 30%, avg hit rate 1.5/3 replicates)
  - PFPeSA (2/10 samples, %CV 14%, avg hit rate, 1.4/3 replicates)
  - PFHxSA (4/10 samples, %CV 10 to 39%, avg hit rate 1.75/3 replicates)
  - PFOSA (6/10 samples, %CV 9.5 to 23%, avg hit rate 1.5/3 replicates)

Concluded that the EPA 533 SPE media has different selectivity for Nitrogen pesticides. Also, evaporating down to dryness completely loses neutral PFAS.

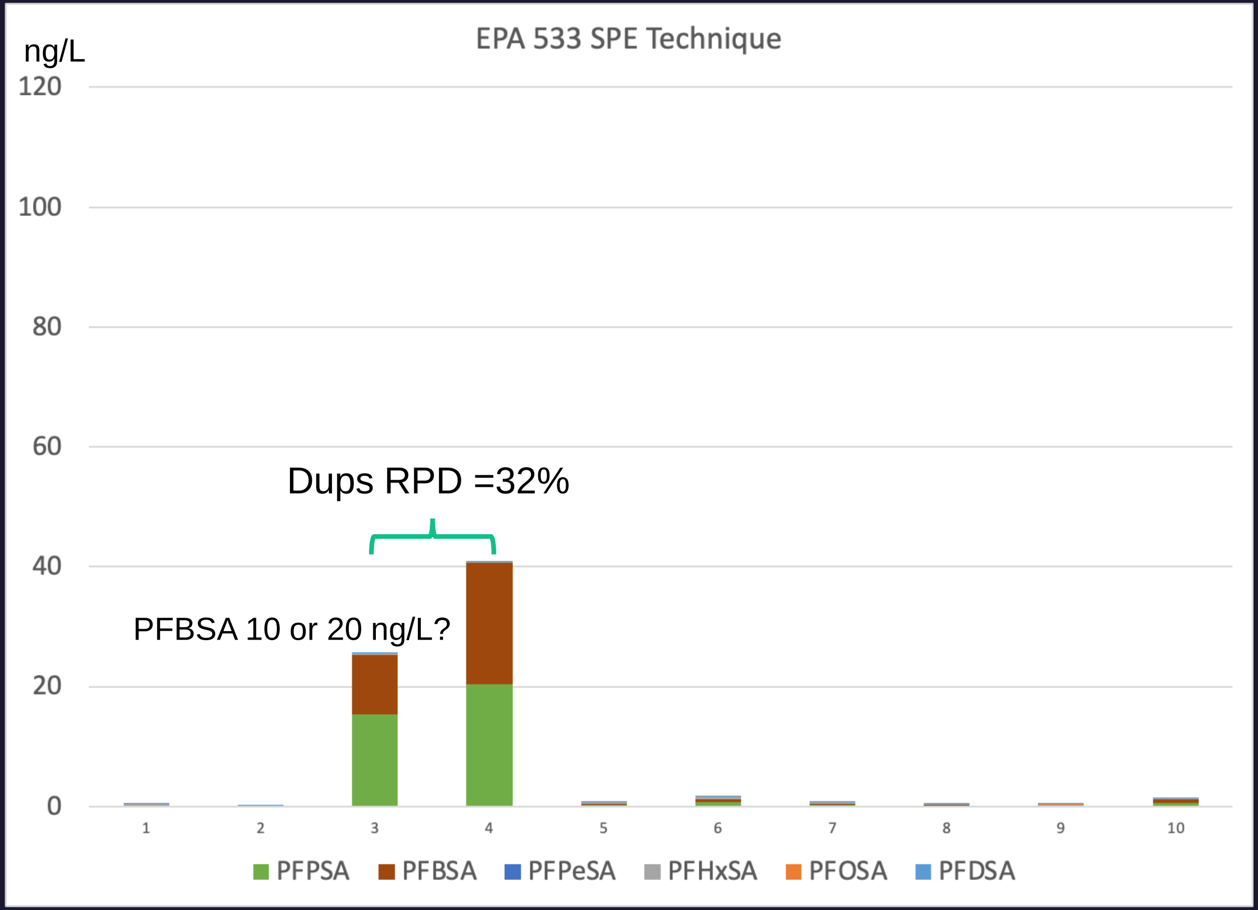
Chemical Method Comparisons

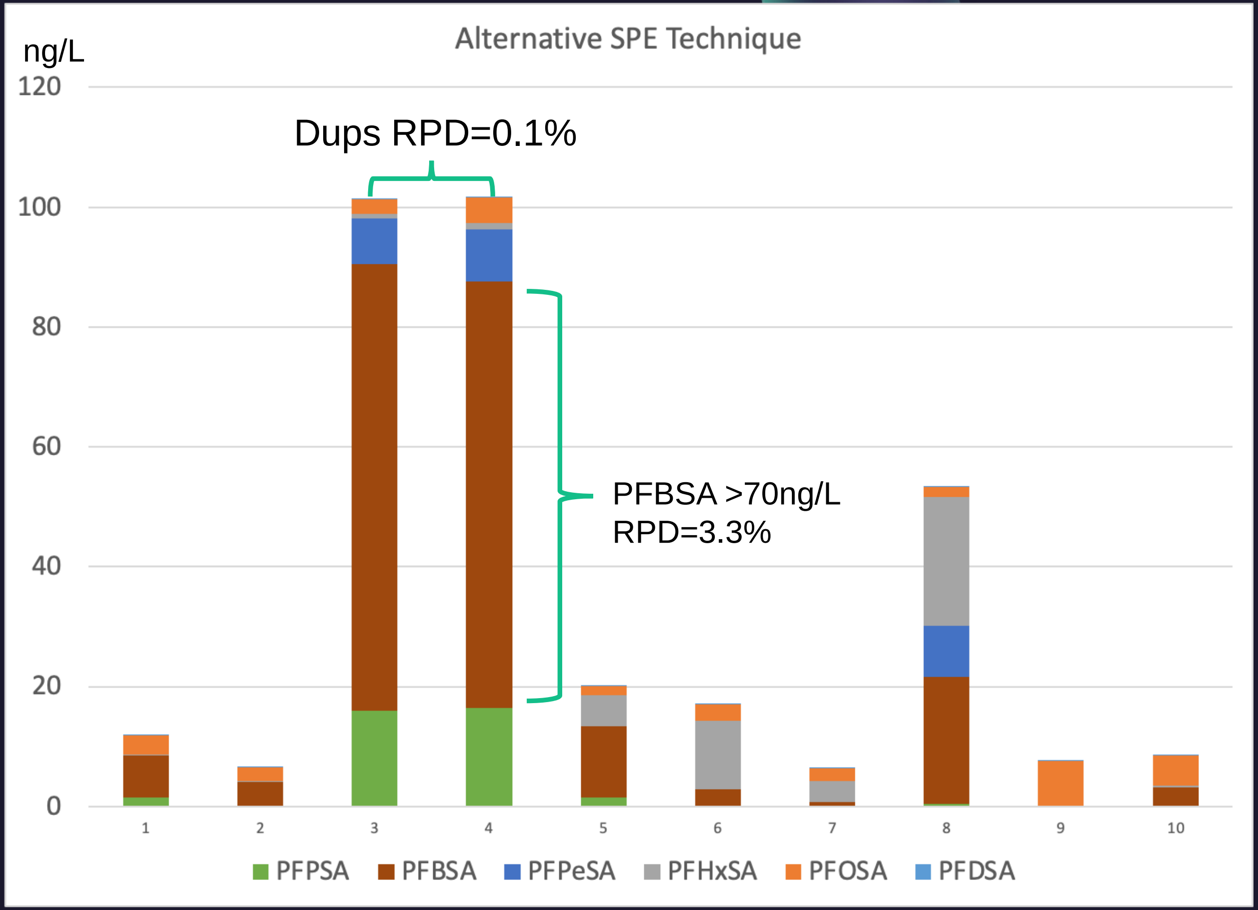
- Features Found in both extracts
  - Monuron, 1-methylbenzotriazole, N-Butylbenzenesulfonamide, C7H6Cl2O5S2,
  - PFPSA (3/10 samples in both extracts, %CV 12 to 14%, avg hit rate 2.0/3 replicates)
  - PFBSA (3 samples (533) 5 samples (QSM) in both extracts, %CV 2.0 to 27%, avg hit rate 2.0/3 replicates)

Concluded that ultra-short sulfonamides may be permanently charged (-) due to decreased distance of terminal CF3 (partial charge at play).

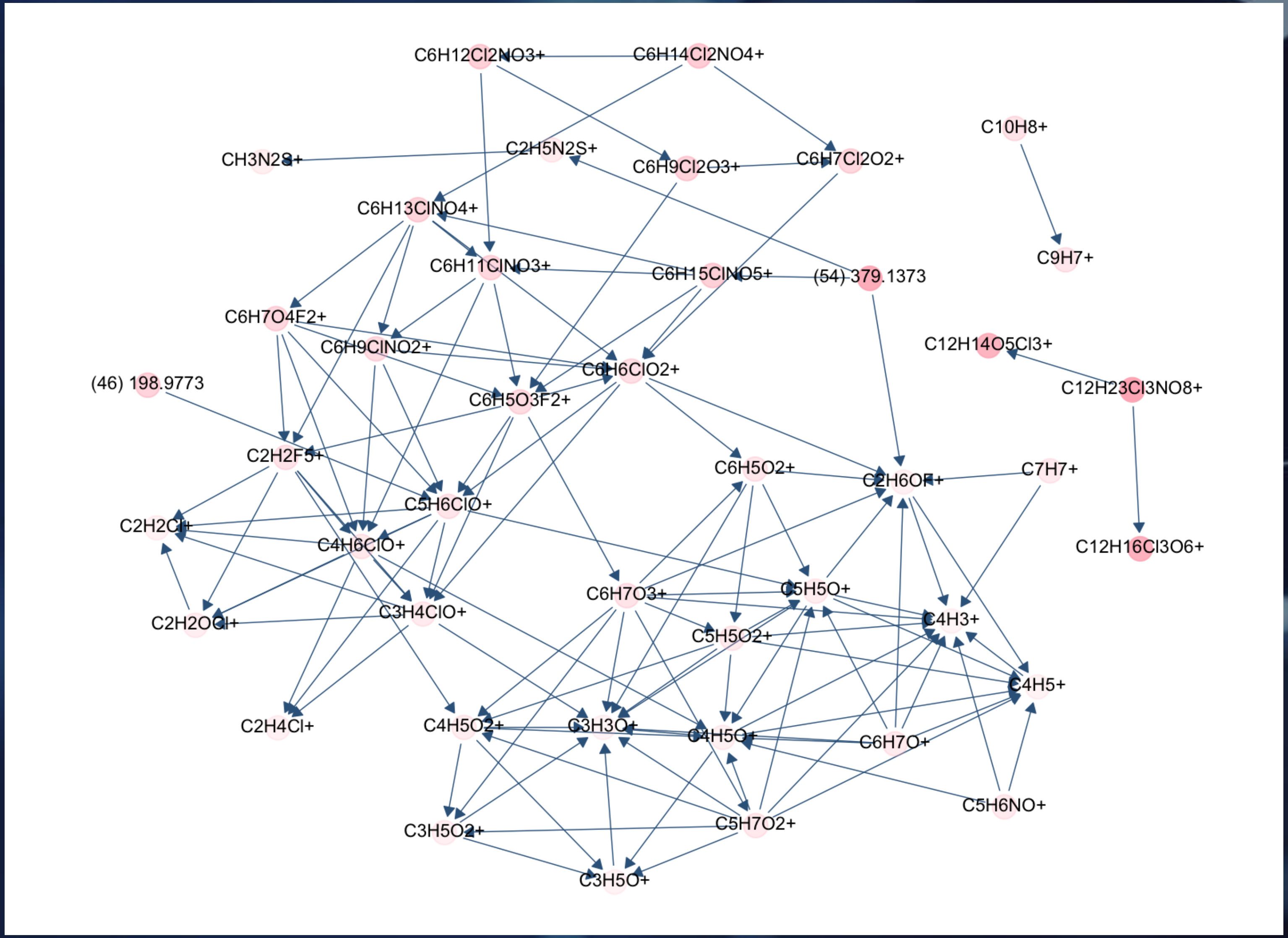
PF-Sulfonamides

Relevant class missed by complete dryness of extract
Detected PFOSA/PFBSA in 9 pre-treated groundwater samples





MS2 Deconvolution – Using Fragment Networking



Conclusions

- NTA Workflows can help assess Chemical Space for SPE Applications
- Could not use EPA 533 extracts for NTA Project
- Need to use EPA 1633-like procedure omitting post loading washes
- Implications for EPA 533-like prep used for Extractable Organic Fluorine (EOF) → *see Thursday Oral*
- Did notice that sulfate is extracted somewhat via WAX

Thank you

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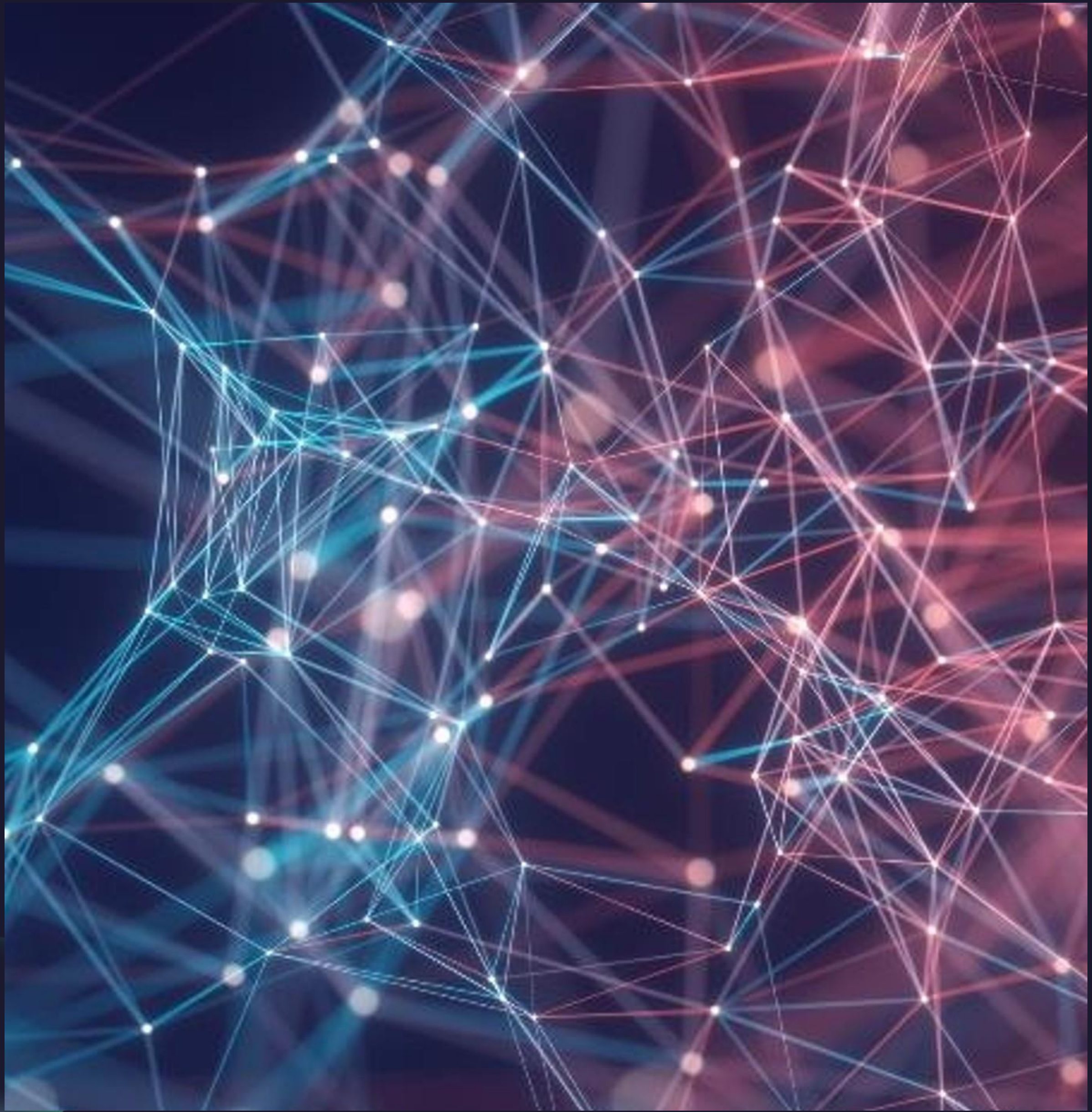

References

1. Black, G.; Lowe, C.; Anumol, T.; Bade, J.; Favela, K.; Feng, Y.-L.; Knolhoff, A.; Mceachran, A.; Nuñez, J.; Fisher, C.; Peter, K.; Quinete, N. S.; Sobus, J.; Sussman, E.; Watson, W.; Wickramasekara, S.; Williams, A.; Young, T. Exploring Chemical Space in Non-Targeted Analysis: A Proposed ChemSpace Tool. Anal Bioanal Chem 2022. https://doi.org/10.1007/s00216-022-04434-4.