Reducing and Replacing DCM in Semi-Volatile Organic Compound Extraction through Optimized SPE Workflow

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Background - Drinking Water Contaminants

- **A public health concern** - contamination of drinking water by Semi-Volatile Organic Compounds (SVOCs)
- Common substances include **pesticides, PCBs, PAHs and phthalates**
- Liquid-liquid extraction (**LLE**) is a traditional method for SVOCs, still used by many
- **EPA Methods 525.2 and 525.3** addresses long list of SVOCs in drinking water using Solid Phase Extraction (**SPE**)

Background - Dichloromethane Health Effects

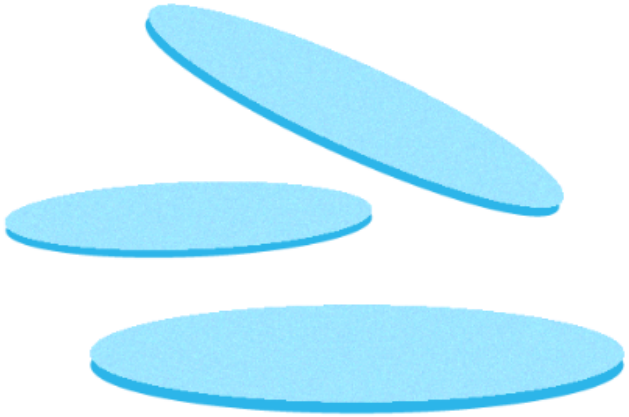
- DCM is widely used as a solvent in many SVOCs applications
- Exposure poses significant health risks:
  - Increased cancer risk
  - Neurotoxicity
  - Organ Damage
  - Skin/Eye/Respiratory irritation
- **LLE** of SVOCs uses **copious amounts of DCM**
- **SPE** methods offer **significant DCM reduction**
- **Manual SPE** extraction **can increase human exposure** to DCM

Background - EPA Regulations on DCM Exposure

- July 8, 2024 – EPA issued final rule on the regulation of DCM
- May 5, 2025 – Mandatory employee DCM exposure monitoring
- How can environmental labs adapt?
  - Reduce DCM use by switching from LLE to SPE
  - Reduce personnel exposure by adopting automation
  - Reduce or eliminate DCM entirely

Extraction Approach

- Procedure based on EPA Method 525.3
- Using PromoChrom SPE-03, SPE Mini-disks and Inline Drying Columns



DISKS

Pros:
- High flow
- Clog resistance

Cons:
- Limited options
- System compatibility
- High solvent use

MINI-DISKS
- **High flow**
- **System compatibility**
- **Low solvent use**
- **Clog resistance**

CARTRIDGES

Pros:
- Widely available
- Compact
- Low solvent use

Cons:
- Low flow
- Easily clogged

Procedure Summary

Sample Preparation

~30 mins

Extraction with Mini-disk and Inline Drying

128-148 mins

Concentration and Micro-vialing

~60 mins

Matrix matched calibration is used to quantify the result

Solvent Preparation and Assignment

Solvent 1 = Methanol (MeOH)

Solvent 2 = Water

Solvent 3 = Ethyl Acetate (EtOAc)

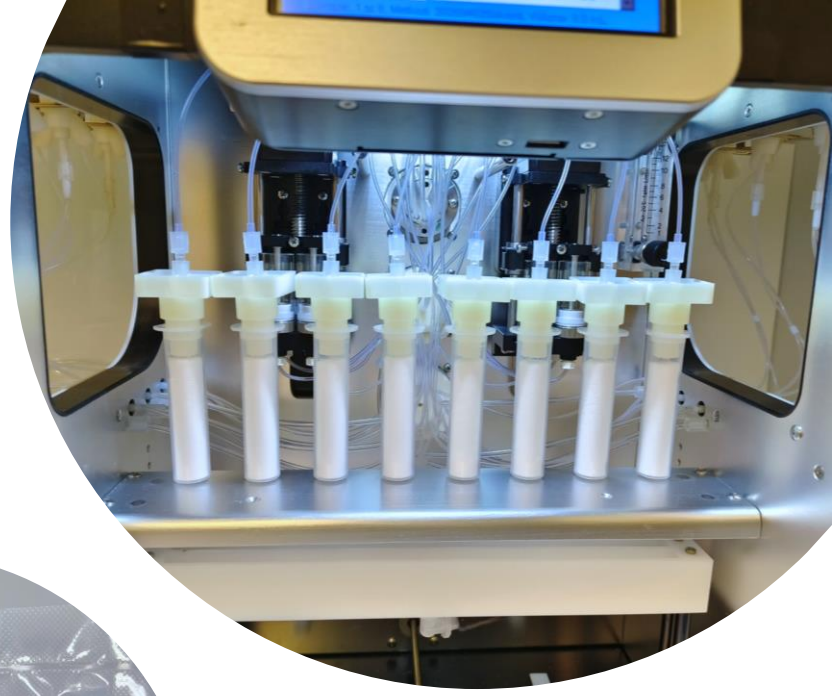
Solvent 4 = DCM

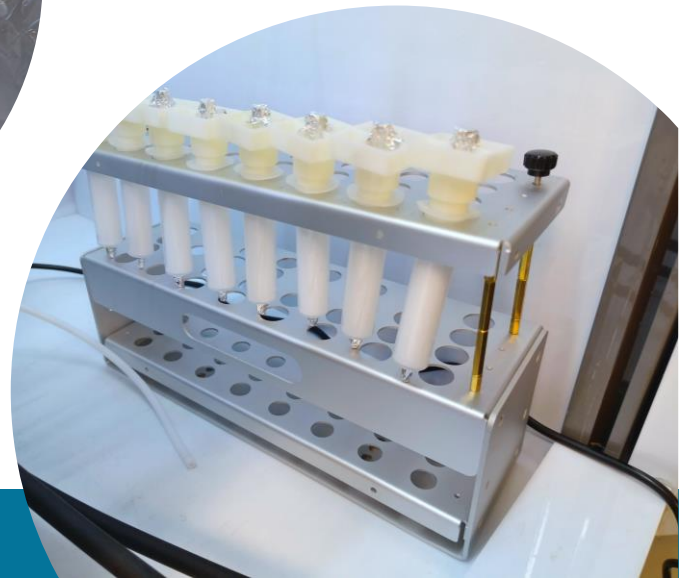
Solvent 5 = 1:1 DCM : EtOAc

Solvent 6 = pH2 Water

Preparing Sodium Sulfate (Na_2SO_4) drying column

- Enable extracts to be **dried in-line**. Minimize solvent usage and variability
- Na_2SO_4 column can be preconditioned on the same system using built-in “Na2SO4 wash” method
- The method preconditions Na_2SO_4 with 10mL of DCM and 10 mL of EtOAc, to be set aside for use within the same day





Pre-extraction

Prepare and spike 1 L of drinking water as per EPA 525.3

- Add preservatives: 0.1g Ascorbic acid; 0.35 g EDTA; 9.4 g Potassium Citrate; resulting pH ~3.8
- Spiking native and surrogate in 2 mL MeOH, add to bottle with 2 x methanol rinse, and mix well

Extraction

- Load samples onto SPE system and cover each bottle with aluminum foil
- Connect Mini-disks (MD-525-30)
- Run EPA 525 SPE method

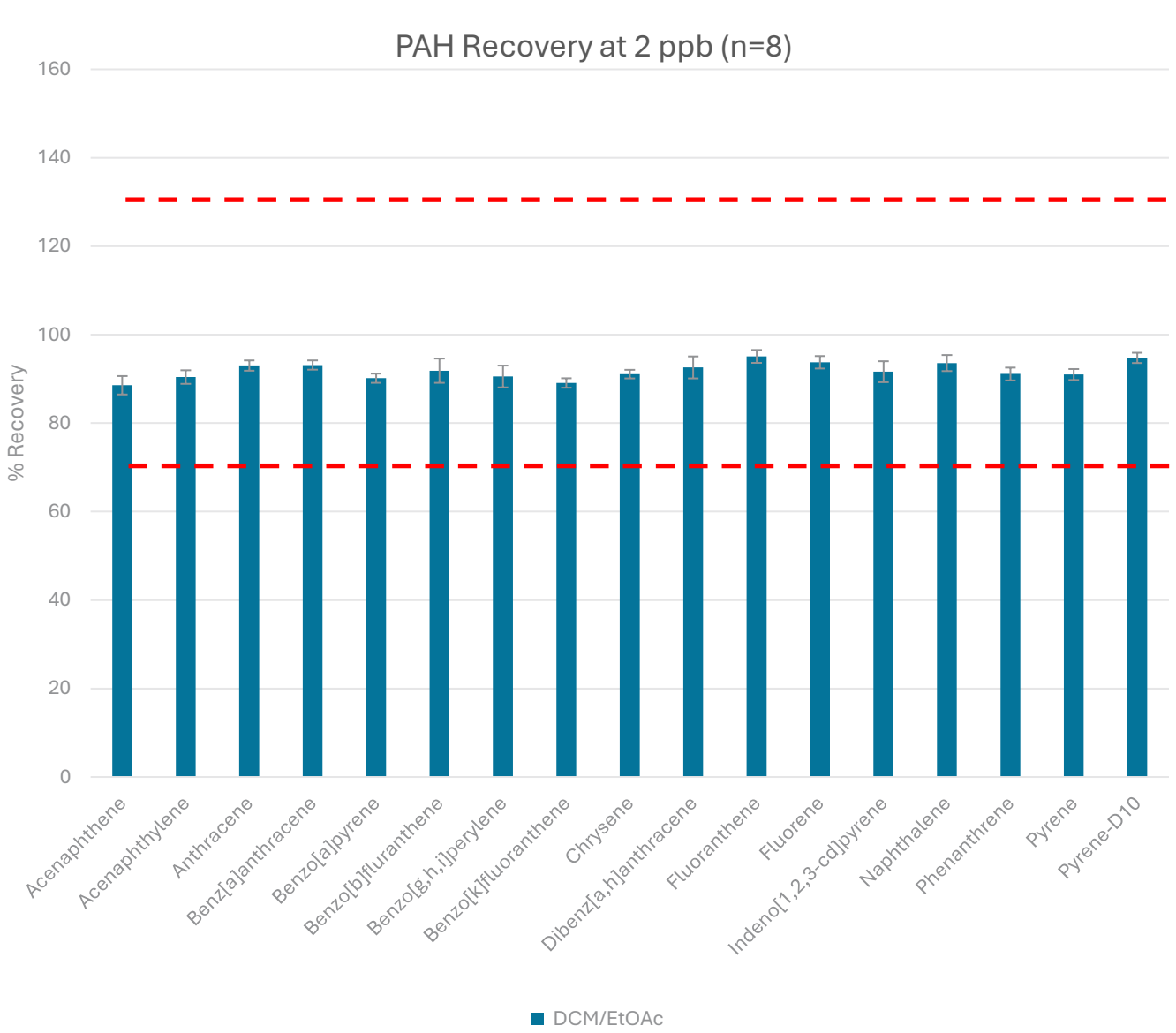
Elution and Connecting Na_2SO_4 Column

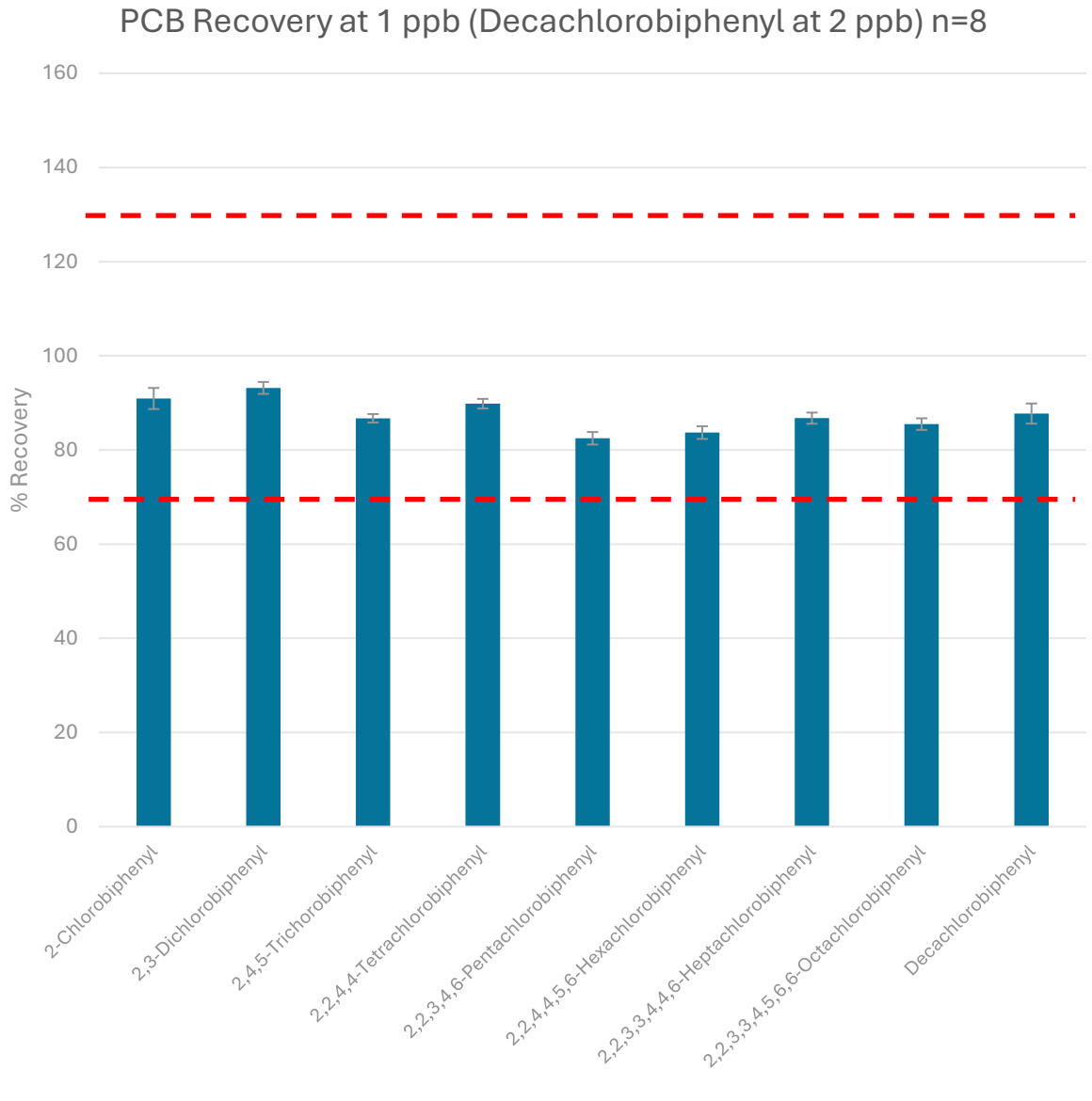
- Conditioning, sample loading and Mini-disk drying are performed without drying column
- Connect drying column inline with Mini-disk just prior to the elution steps
- Continue and collect with K-D tube

Concentration and Micro-vial Preparation

- Concentrate the final extract to below 1 mL
- Transfer to 1 mL volumetric flask
- Spike IS and top up to 1 mL
- Transfer to GCMS vial

Results – PCB and PAH Recoveries





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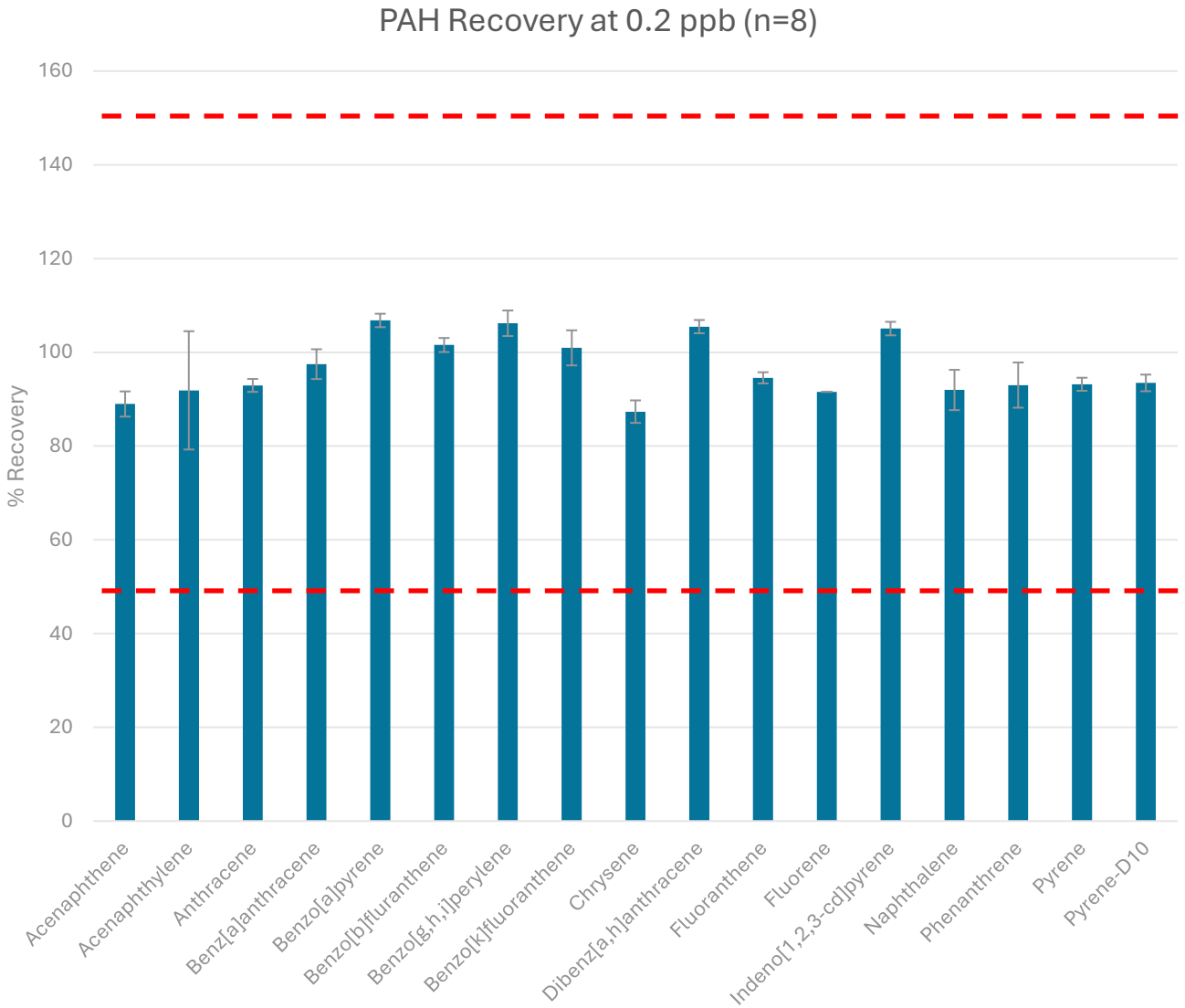
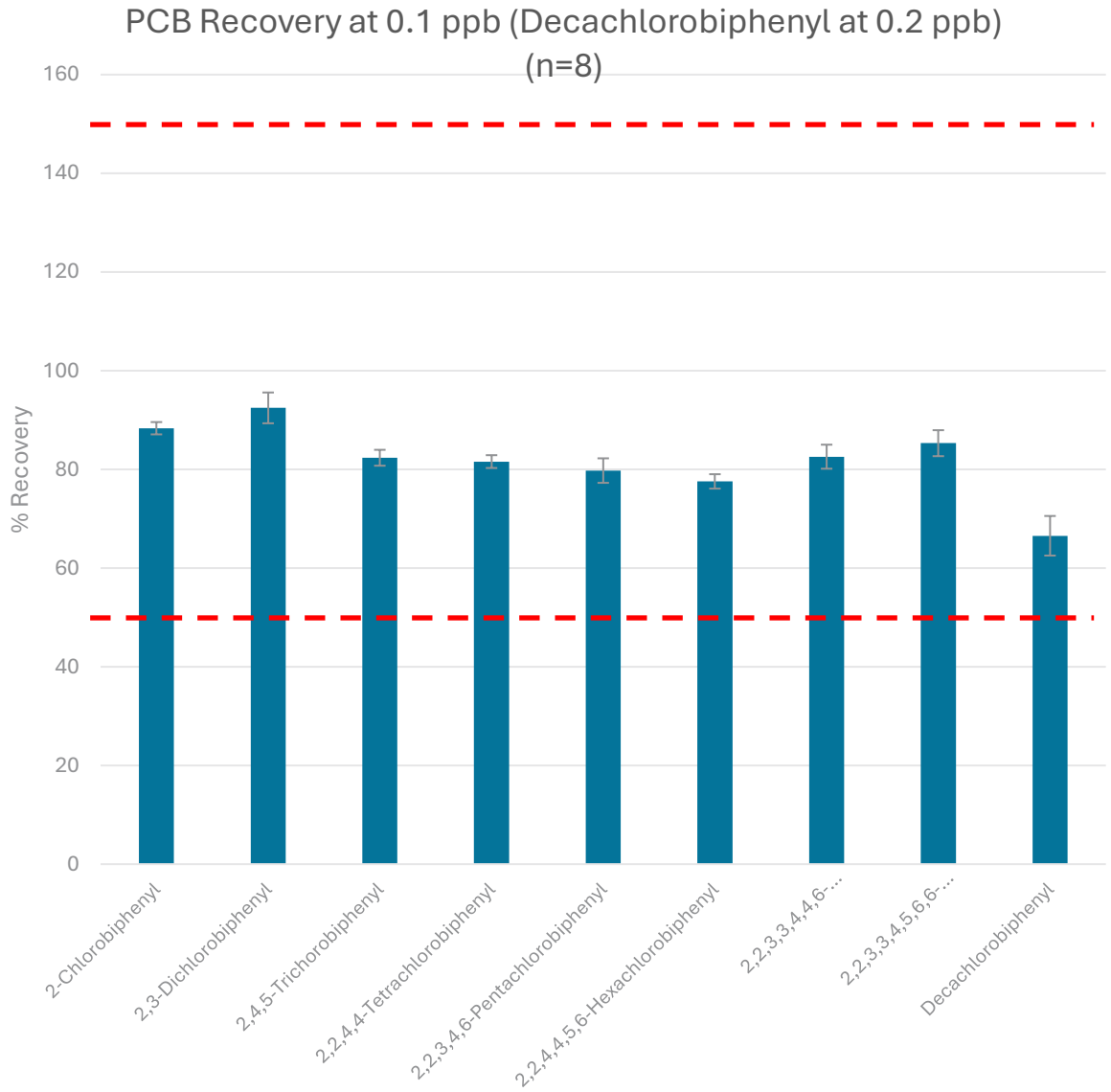
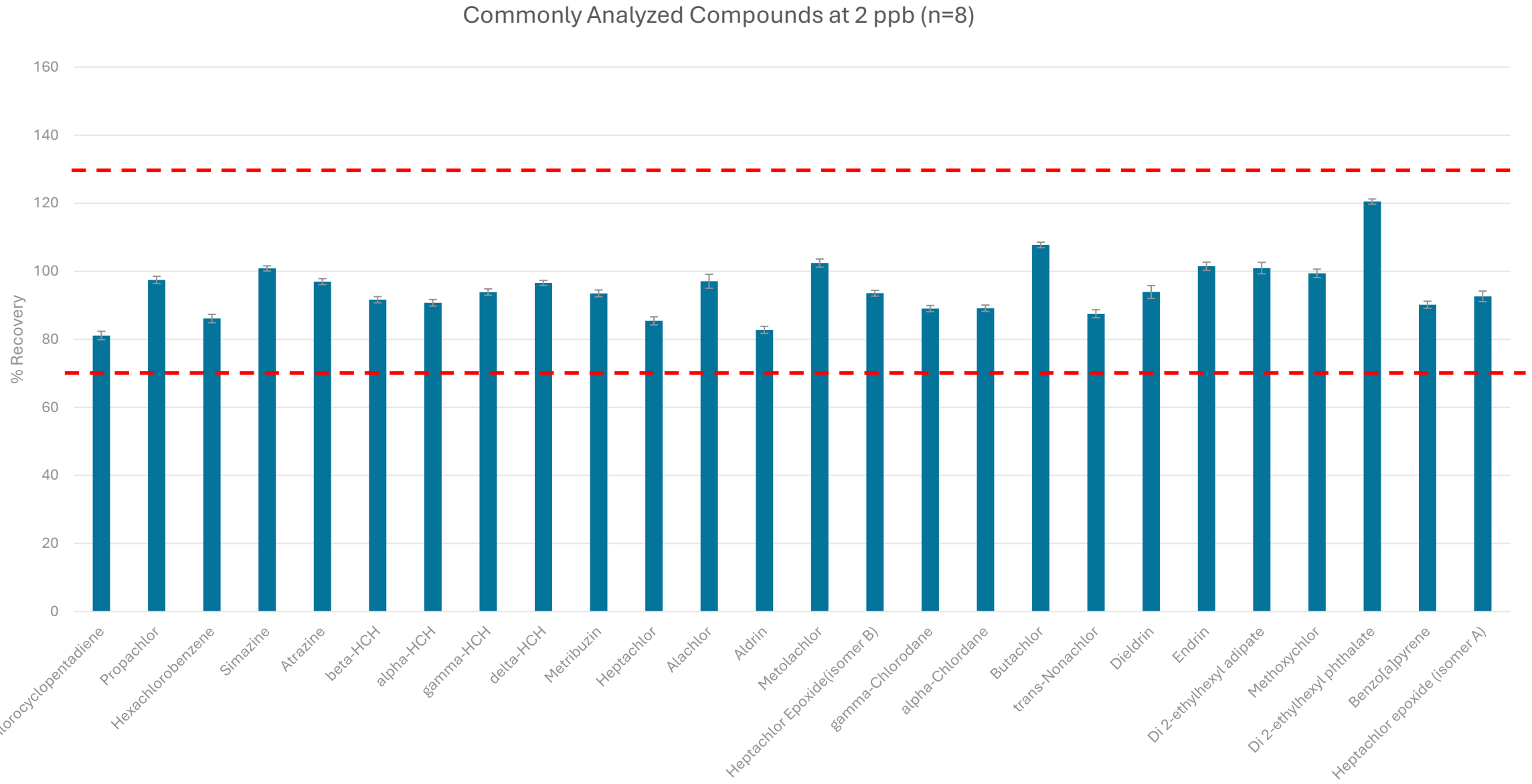




Results – Commonly Analyzed Compounds



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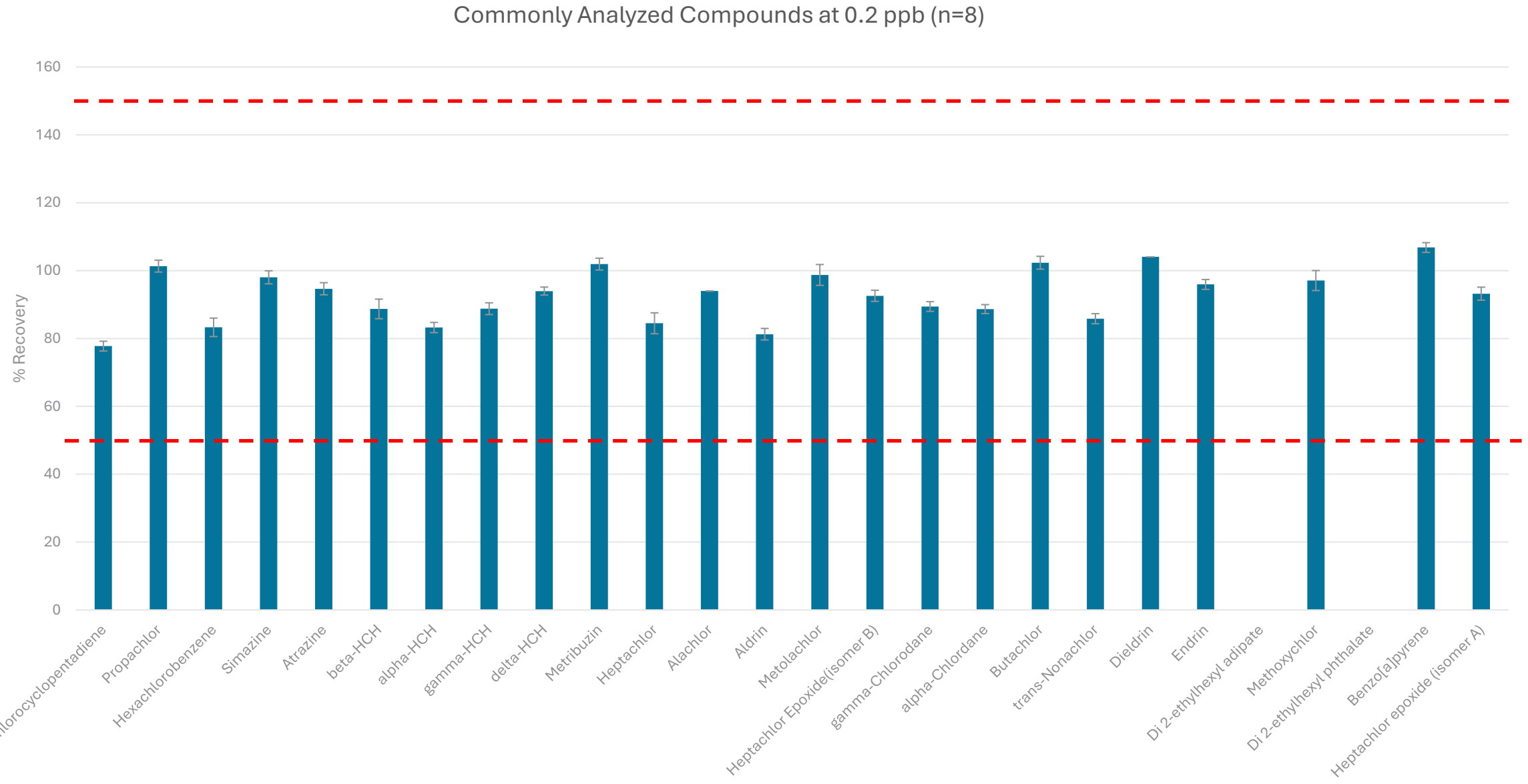
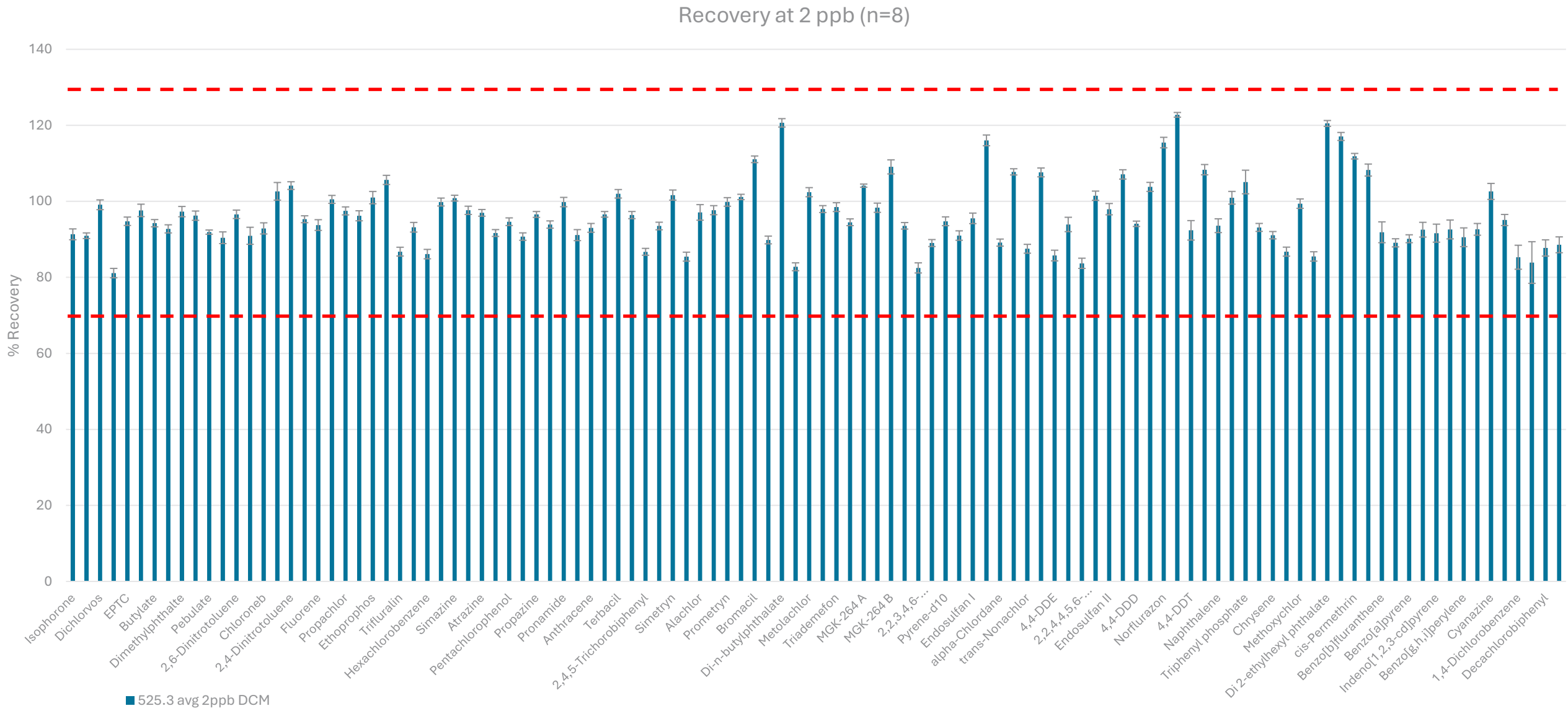


Results – All Compounds at 2 ppb



Discussion on DCM/EtOAc Extraction

- All tested analytes spiked at 2 ppb (1 ppb for PCBs) recover within 70-130%
- At 0.2 ppb (0.1 ppb for PCBs), most of the analytes also recover within 70-130% while the allowable recovery range at these low levels are 50-150% per EPA Method 525.3
- Total extraction time on the SPE-03 is 148 min for 8 x 1 L samples. Using the inline drying column, the full process including downstream steps can be completed within 3-4 hours
- Total solvent usage is 35 mL EtOAc and **25 mL DCM** per sample (including drying column conditioning and extraction).

Using Alternative Solvents

Can DCM be Eliminated?

Initiative to Eliminate DCM

Extraction with Hex/EtOAc

Solvent 1 = MeOH

Solvent 2 = Water

Solvent 3 = EtOAc

Solvent 4 = Hexane

Solvent 5 = 1:1 Hex:EtOAc

Solvent 6 = pH2 Water

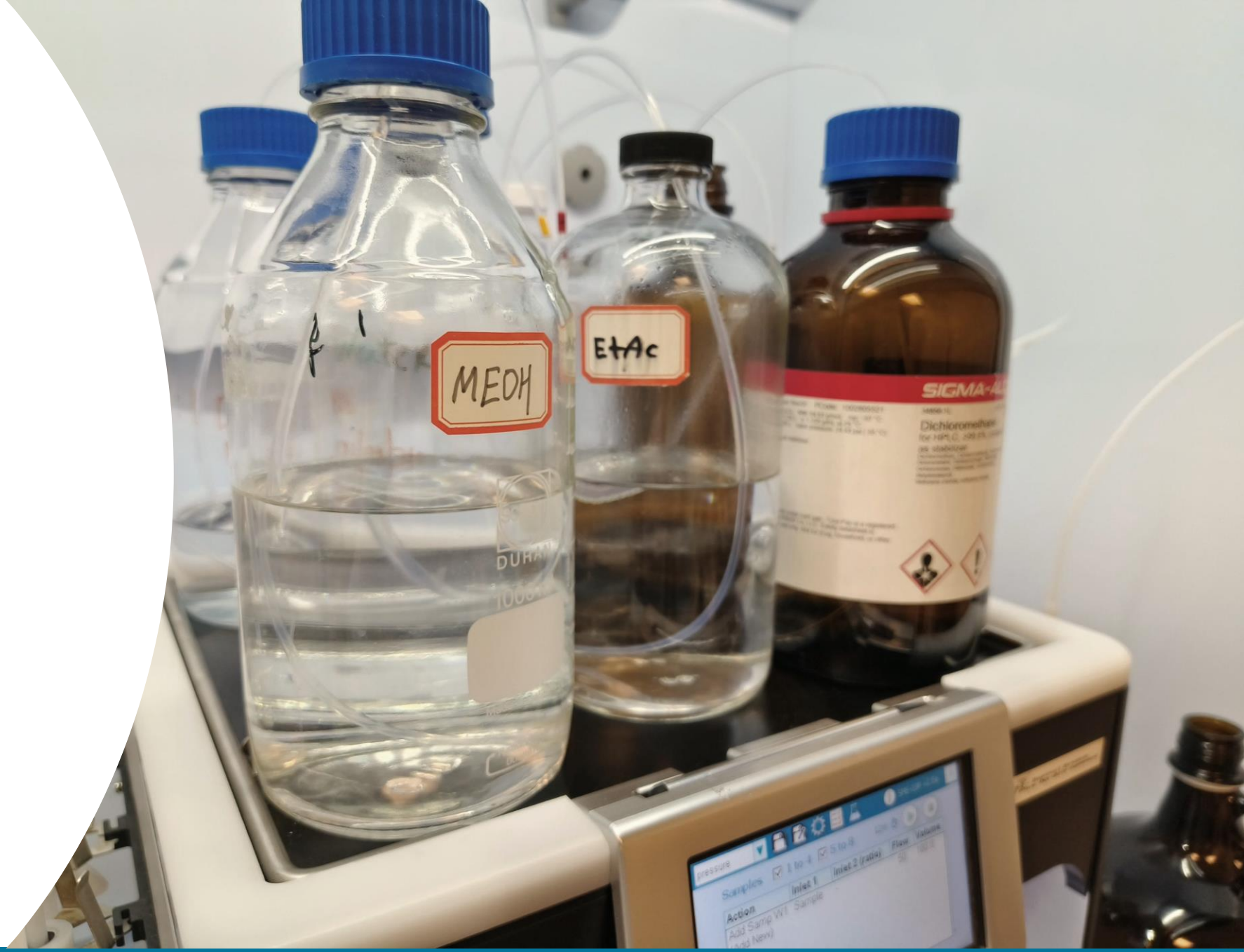
Extraction with Pure EtOAc

Solvent 1 = MeOH

Solvent 2 = Water

Solvent 3 = EtOAc

Solvent 6 = pH2 Water



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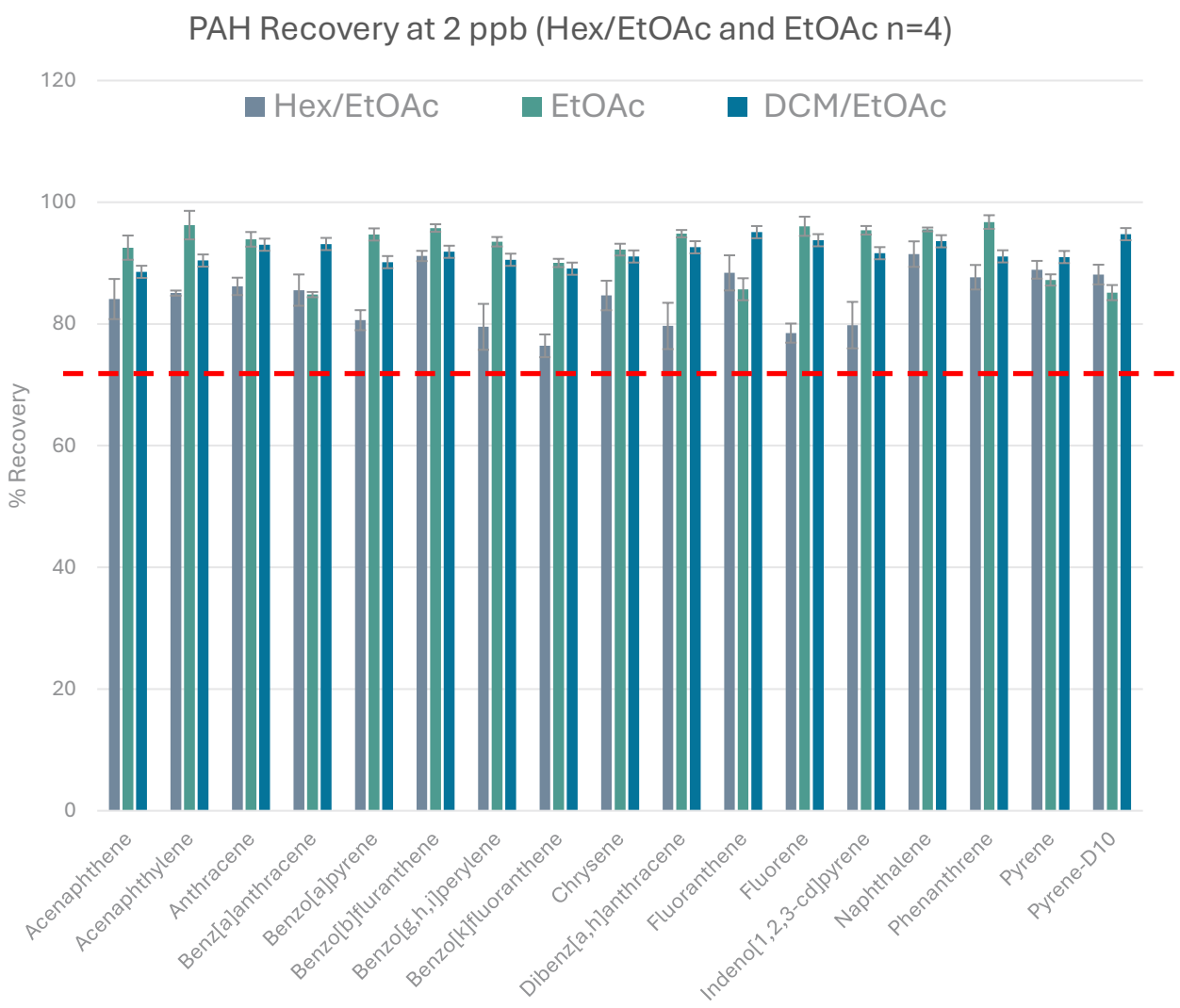

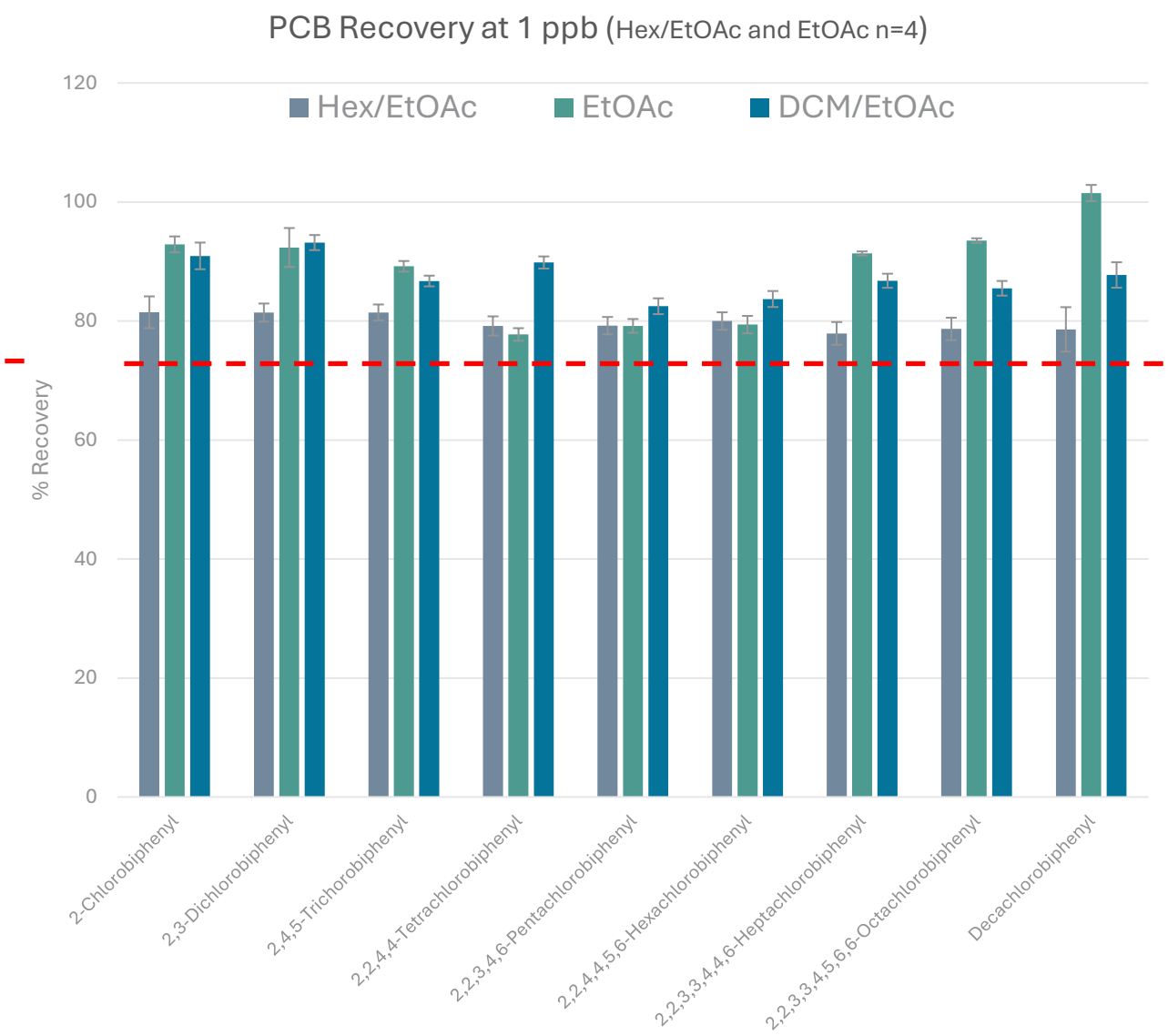

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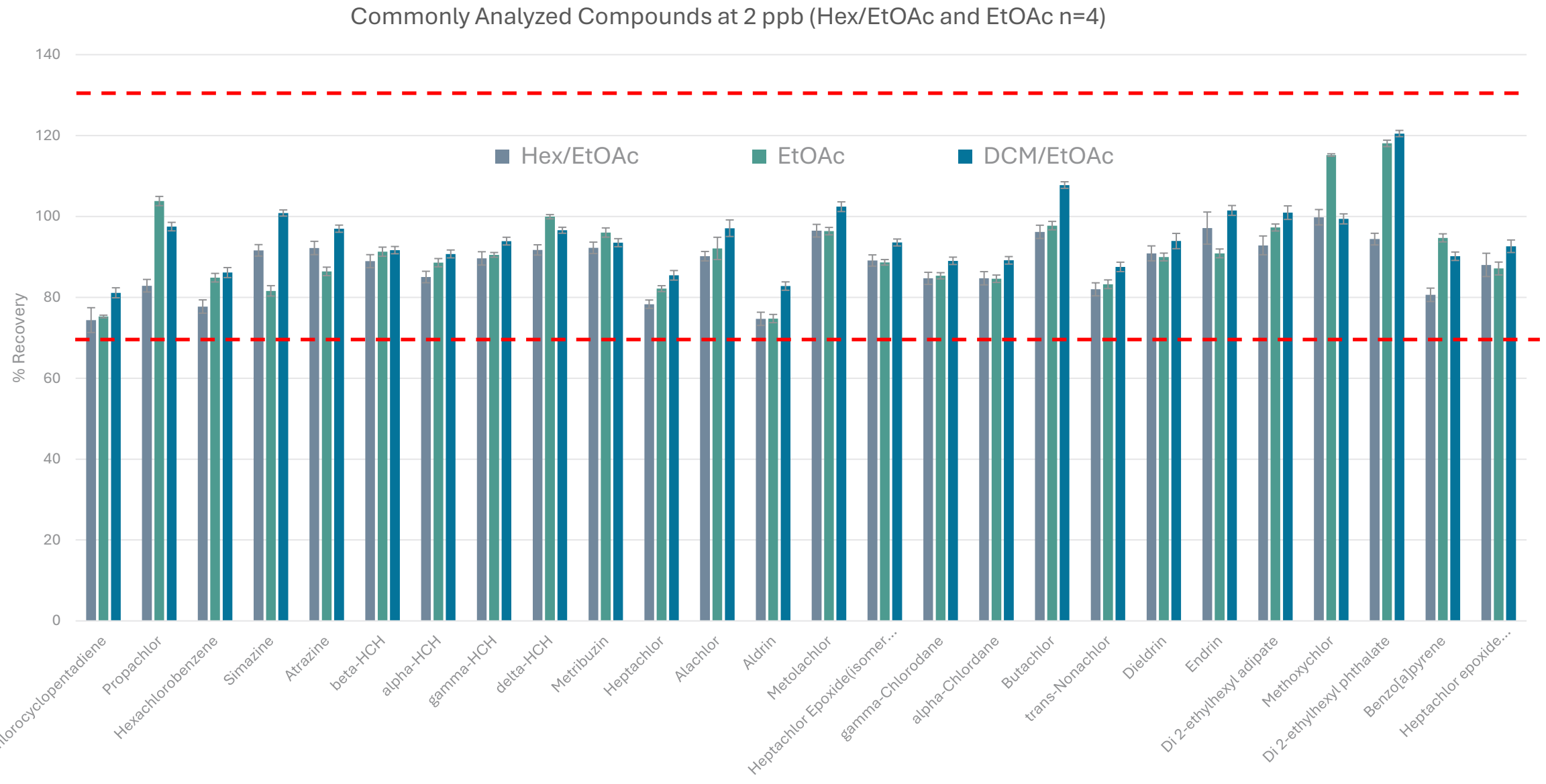

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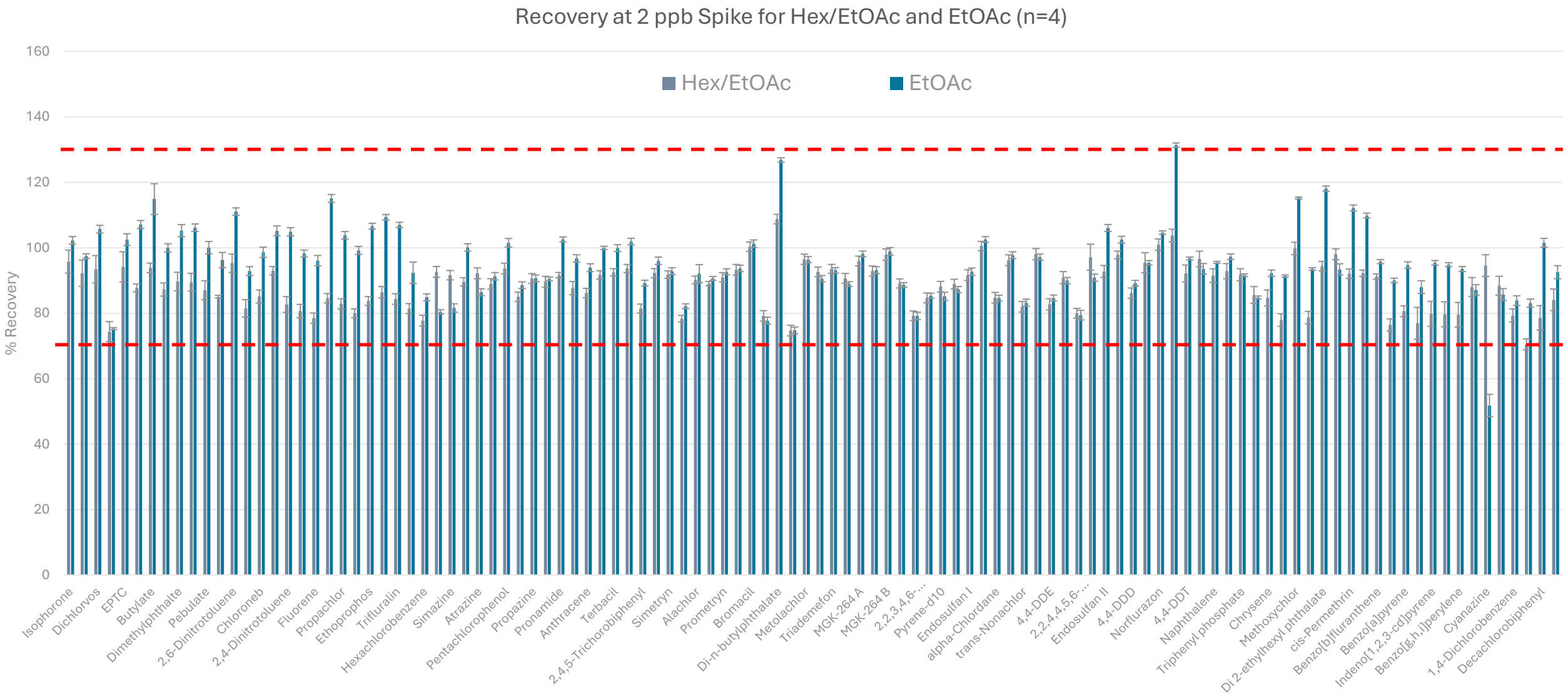
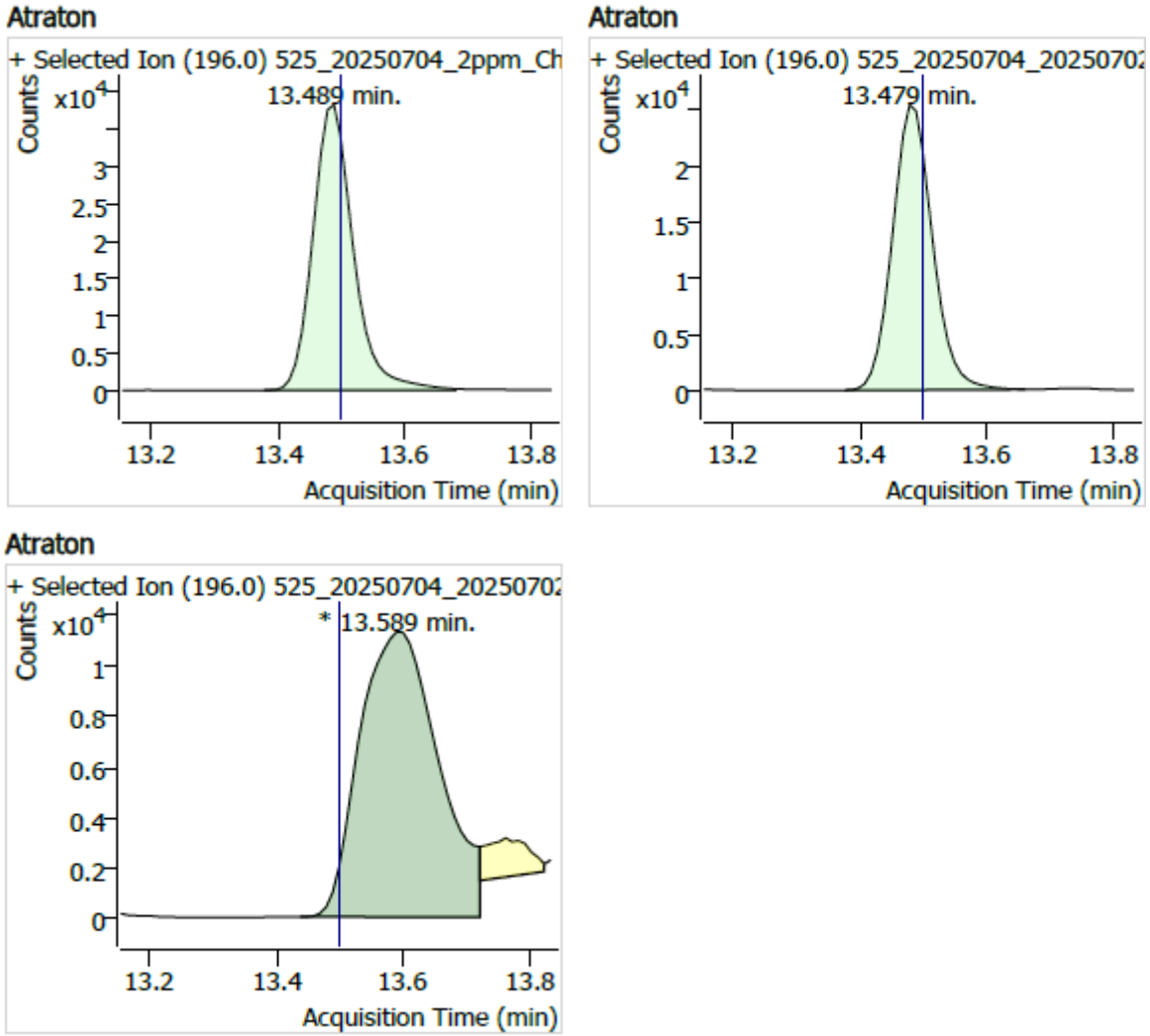


Results – Matrix Effect from EtOAc Extraction

- Some matrix effect observed with EtOAc for Triazine Herbicides (compounds with 1,3,5-Triazine ring)
  - The effect is not observed when samples are acidified to pH 2
- Cyanazine only recovers at 50% using preservatives as per EPA525.3
  - Recovery increases to 80-90% if the sample is acidified to pH 2 without preservatives (as per EPA525.2)
- The EtOAc and Hex/EtOAc data is quantified using DCM/EtOAc MM CAL
  - Improvement is possible using exact MM CAL



Discussion on Using Alternative Solvents

- As a general trend for recovery: DCM/EtOAc ≥ EtOAc > Hex/EtOAc
- Most of compounds for both EtOAc and Hex/EtOAc still recovered within 70-130%
- EtOAc requires 10-20 min additional evaporation time compared to DCM
- Some matrix effects with EtOAc could be improved by using exact Matrix Matched CAL
- Current trial with alternative solvents has room for optimization
  - Final elution volume
  - Adjusting Hex/EtOAc ratio
  - Creating exact Matrix Matched CAL for the specific solvents

Conclusion

- The PromoChrom MD-525-30 Mini-disk in combination with the SPE-03 can effectively extract over 100 SVOCs (plus 4 surrogates)
- This solution along with inline drying columns offer an efficient extraction approach
- Controlled extraction time using positive-pressure pumps further provides laboratories with predictable turnaround times
- Both EtOAc and Hex/EtOAc are promising candidates for replacing DCM

Acknowledgements

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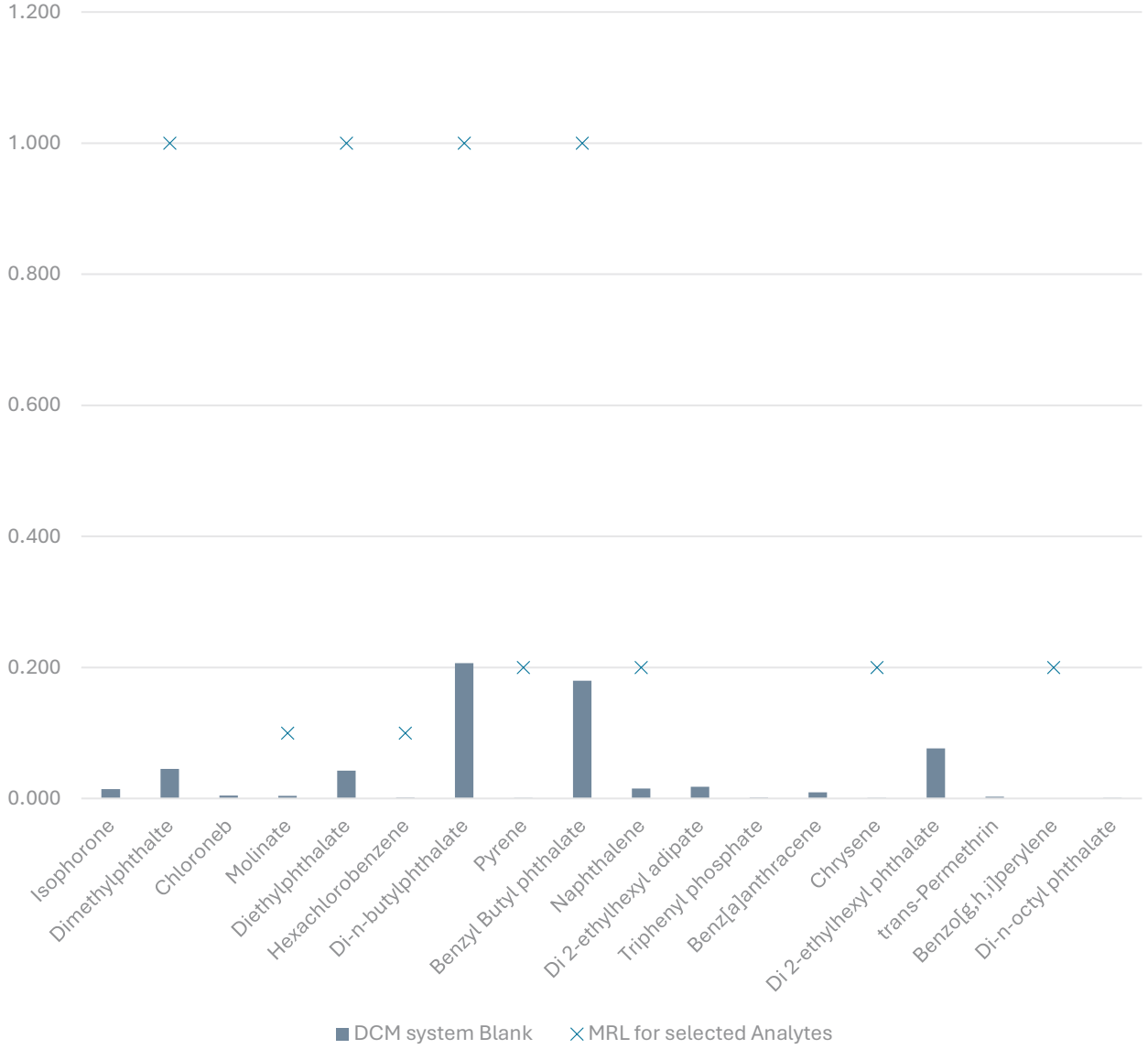
Thank You!

Appendix

System Blank Data



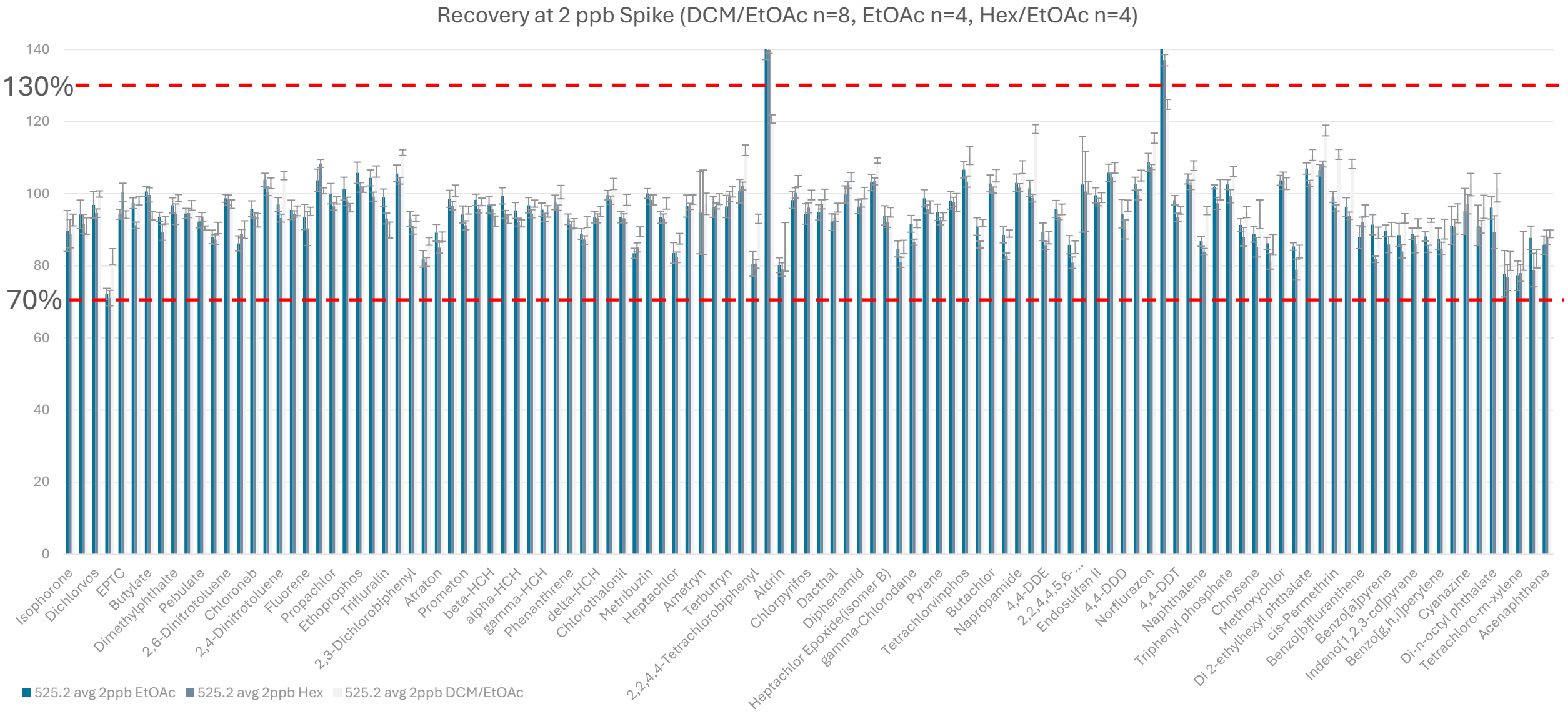
	DCM system Blank (ng/L)	Typical MRL (ng/L)
Isophorone	0.014	
Dimethyl phthalate	**0.045**	1
Chloroneb	0.005	
Molinate	0.004	0.1
Diethyl phthalate	**0.043**	1
Hexachlorobenzene	0.002	0.1
Di-n-butyl phthalate	**0.207**	1
Pyrene	0.001	0.2
Benzyl Butyl phthalate	**0.180**	1
Naphthalene	0.015	0.2
Di 2-ethylhexyl adipate	**0.018**	
Triphenyl phosphate	0.002	
Benz[a]anthracene	0.009	
Chrysene	0.001	0.2
Di 2-ethylhexyl phthalate	**0.077**	
trans-Permethrin	0.003	
Benzo[g,h,i]perylene	0.001	0.2
Di-n-octyl phthalate	**0.001**	

The lab uses bottled drinking water instead of reagent water

Problematic Compounds

	EtOAc 2 ppb spike				Hex/EtOAc 2 ppb spike				DCM/EtOAc 2 ppb (left) 0.2 ppb (right) spike			
Problematic	525.3 avg	525.3 STD	525.2 avg	525.2 STD	525.3 avg	525.3 STD	525.2 avg	525.2 STD	525.3 avg	525.3 STD	525.2 avg	525.2 STD
Carboxin	89.39	2.19	94.05	1.21	87.14	2.81	101.50	1.63	54.40	5.00	127.06	38.87
Diazinon	94.02	1.99	104.79	2.16	83.93	2.35	100.51	1.71	94.44	3.32	93.78	3.05
Disulfoton	96.15	2.48	105.43	1.03	85.41	2.93	100.15	2.12	60.94	4.96	140.28	44.10
Disulfoton Sulfone	104.60	2.41	112.02	1.78	99.95	3.07	114.23	2.52	113.28	3.52	104.63	5.51
Endrin Aldehyde	54.72	1.24	107.64	1.81	92.87	3.28	112.28	2.12	89.39	4.46	67.25	29.32
Endrin Ketone	96.19	2.46	103.31	2.00	91.85	2.84	108.52	2.14	100.79	4.35	107.31	2.98
Fenamiphos	122.30	2.43	119.67	1.48	111.71	3.38	119.01	3.02	140.95	3.47	118.15	9.38
Merphos												
DEF	107.64	1.91	117.55	1.54	105.74	5.42	121.47	3.28	0.00	0.00	95.11	2.04
Methyl paraoxon	108.75	2.36	116.08	2.15	96.58	3.15	110.49	0.84	98.15	1.72	106.85	5.82
Terbufos	99.70	3.44	105.81	4.36	82.38	0.41	95.37	1.60	85.67	1.42	107.83	8.12
Tricyclazole	85.09	3.79	107.77	2.41	96.75	3.17	112.49	2.05	122.39	4.75	106.93	3.94
Fluridone	124.55	2.28	137.60	2.05	99.38	4.39	119.45	3.48	136.46	3.89	116.40	6.06

Results – All Compounds at 2 ppb Spike with 525.2



Results – All Compounds at 2 ppb Spike with 525.2

Recovery of EtOAc and Hex/EtOAc at 2 ppm using 525.2 (Prespike IS DCM/EtOAc n=8, EtOAc n=4, Hex/EtOAc n=4)