What Does the EPA Method 625.1 Round Robin Data Really Tell Us?

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OUTLINE

- General Overview
- Some data
- Concluding Remarks
- What's Next
- Q&A

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When Did It Start?

- First reference in literature to the use of SPE
  - So the people grumbled at Moses, saying, "What shall we drink?" Then he cried out to the LORD, and the LORD showed him a tree; and he threw it into the waters, and the waters became sweet. Exodus 15: 24 and 25

Method 625.1 Acceptance Limits

- Table 6
  - Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.

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Method 625.1 Acceptance Limits (con't.)

- Table 7
  - Precision and recovery as a function of concentration w/ footnote that says "Regressions based on data from Reference 2"
  - "EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides," EPA 600/4-84-053, National Technical Information Service, PB84-206572, Springfield, Virginia 22161, June 1984.

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Method 625.1 Acceptance Limits (con't.)

- Method 625
  - Two different columns
    - 1 for acids/ 1 for base neutrals
  - Two separate calibrations
  - Packed columns
  - Separatory funnel extraction

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Method 625.1

- Acceptance Criteria based on 625
  - Only 6 compounds with lower limit ≥ 50%
  - Best lower acceptance limit 60%
    - 2-chloronaphthalene

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Labs from Method 625

- Acurex Corporation
- California Analytical Laboratories, Inc.
- Envirodyne
- Environmental Research Group, Inc.
- Environmental Science and Engineering, Inc.
- Foremost-McKesson
- GCA Corporation
- Mead CompuChem

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Labs from Method 625

- Pedco
- Rockwell International
- Rocky Mountain Analytical
- Spectrix
- Stewart Labs
- The University of Utah Research Institute
- West Coast Technical Service, Inc.

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The Studies

- 6 or 7 Suppliers
- Acceptance criteria
  - Method 625
  - TNI
- Each SPE product was tested in at least three laboratories

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The Studies

- Phase 1
  - Spiked DI water (LCS)
  - ASTM Synthetic Wastewater
    - Flat light beer
    - Flour
    - Sea salts
    - Kaolin
    - Triton X-100
    - DI water

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The Studies

- Phase 2
  - LCS
  - TCLP acetate buffer solution
    - Glacial acetic acid
    - 1N NaOH
    - DI water
  - Limited ASTM WW

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The Studies - Data

- Phase 1
  - Data from 17 labs, but no correlation between supplier and lab was provided

The Studies

- Phase 2
  - 24 labs
    - Supplier 1 Labs 1-3
    - Supplier 2 Labs 4-6
    - Supplier 3 Labs 7-9
    - Supplier 4 Labs 10-15
    - Supplier 5 Labs 16-18
    - Supplier 6 Labs 19-21
    - Supplier 7 Labs 22-24

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The Studies - Assumptions

- The samples prior to extraction were all prepared the same from lab to lab.
- Each supplier provided the same SPE product(s) to each of their laboratories.
- Each laboratory for a supplier implemented that specific-SPE system in the same manner.

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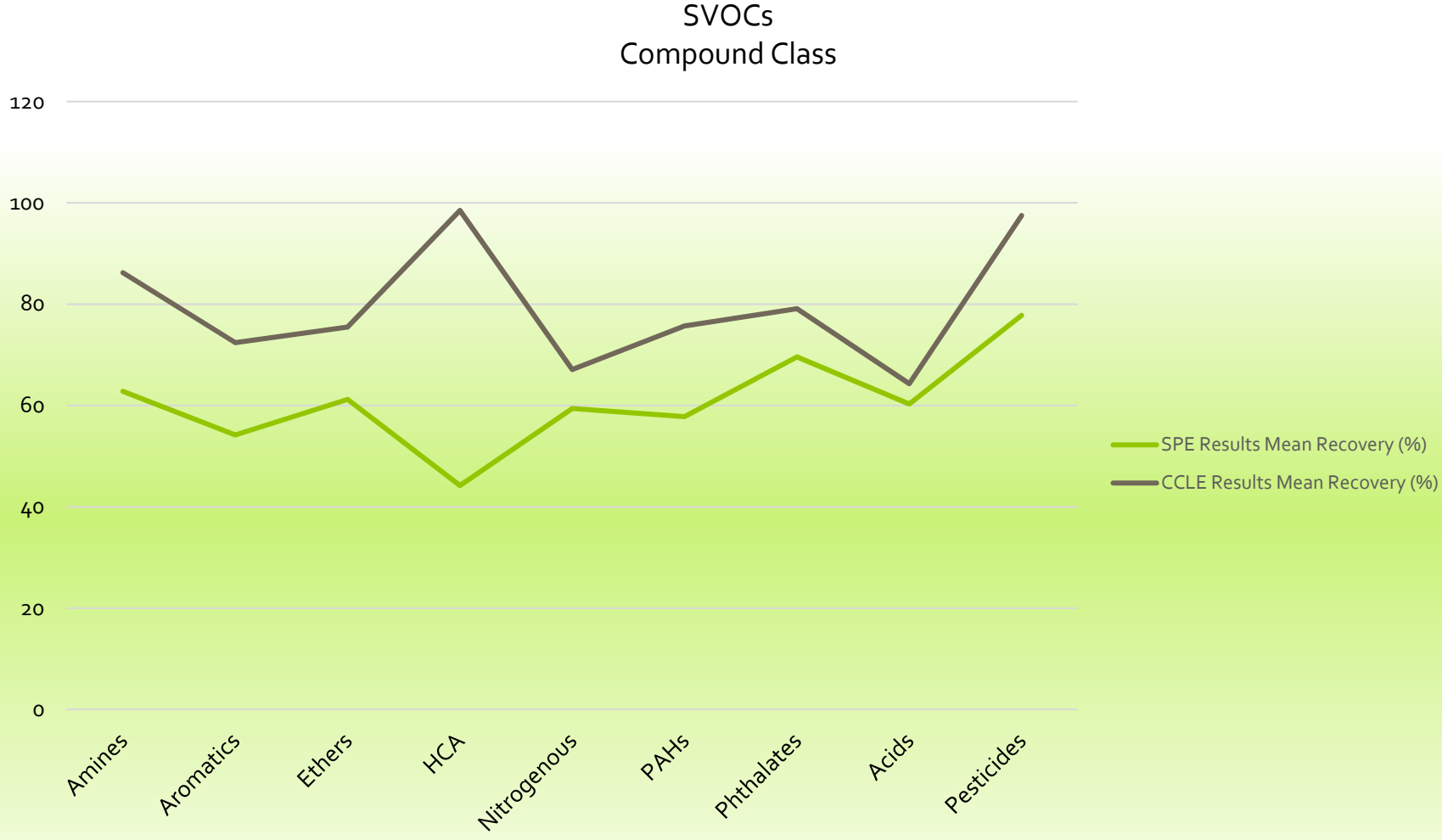
Data - Phase 1 – LCS (%R)



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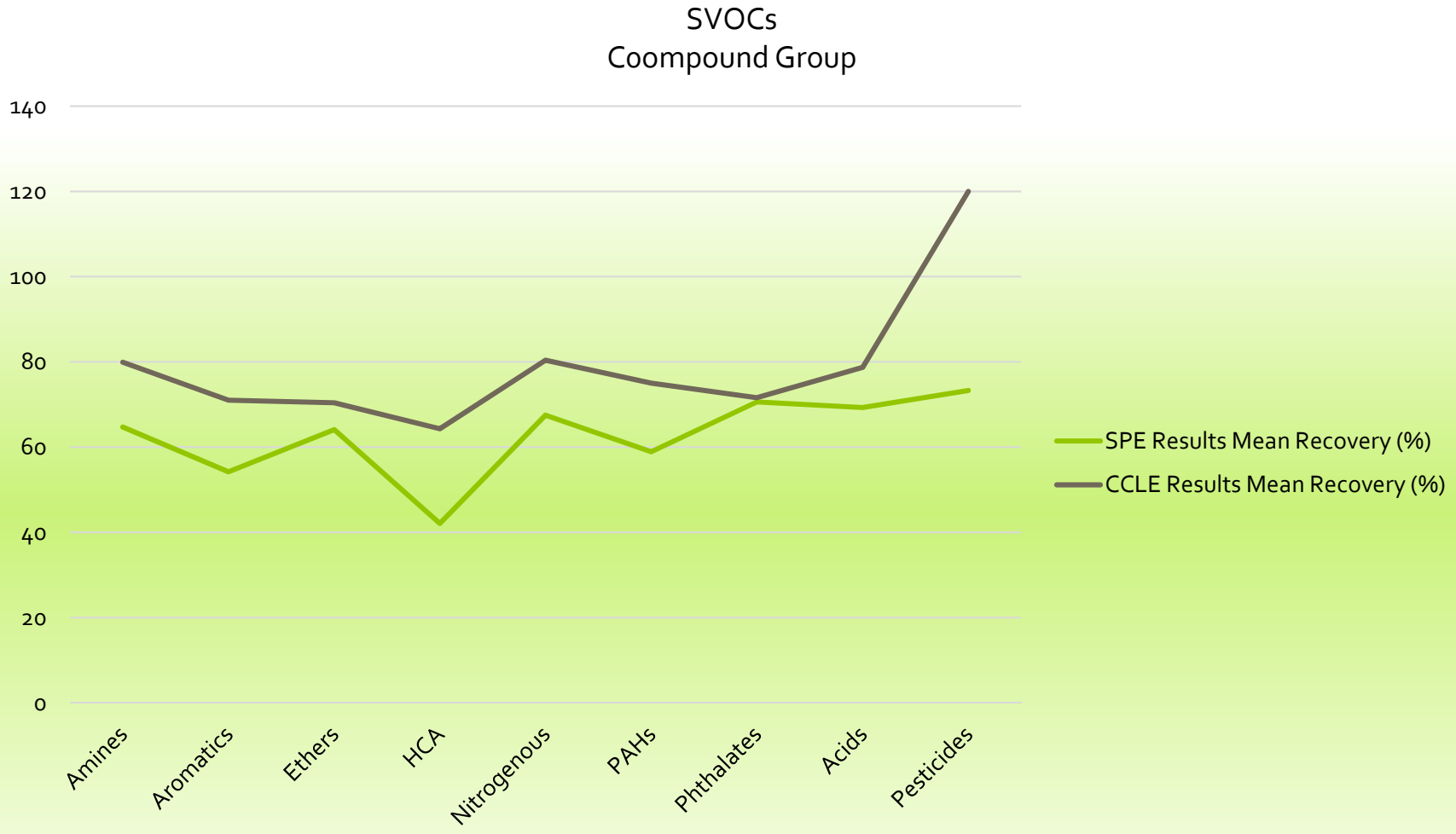
Data - Phase 1 – ASTM (%R)



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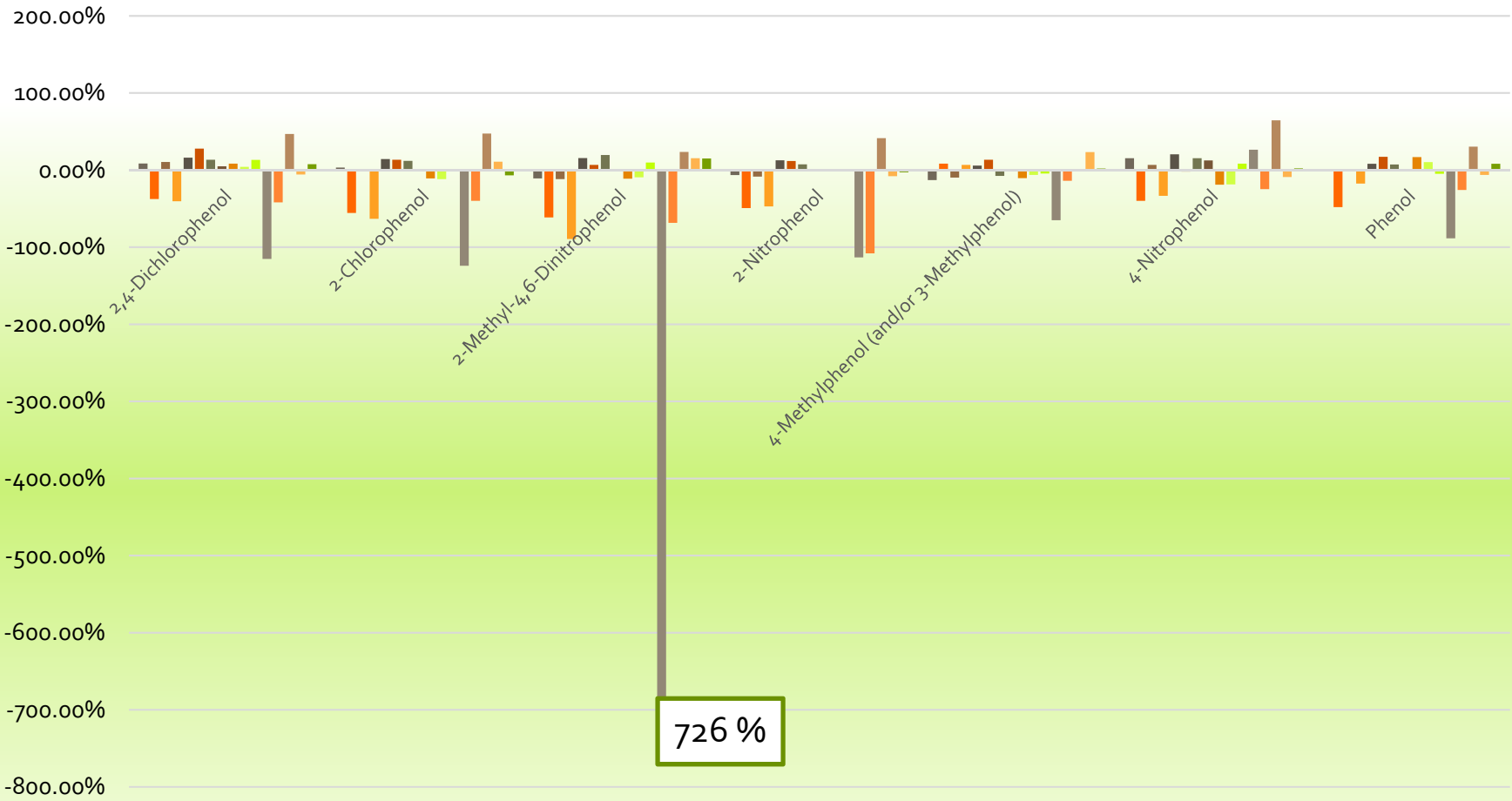
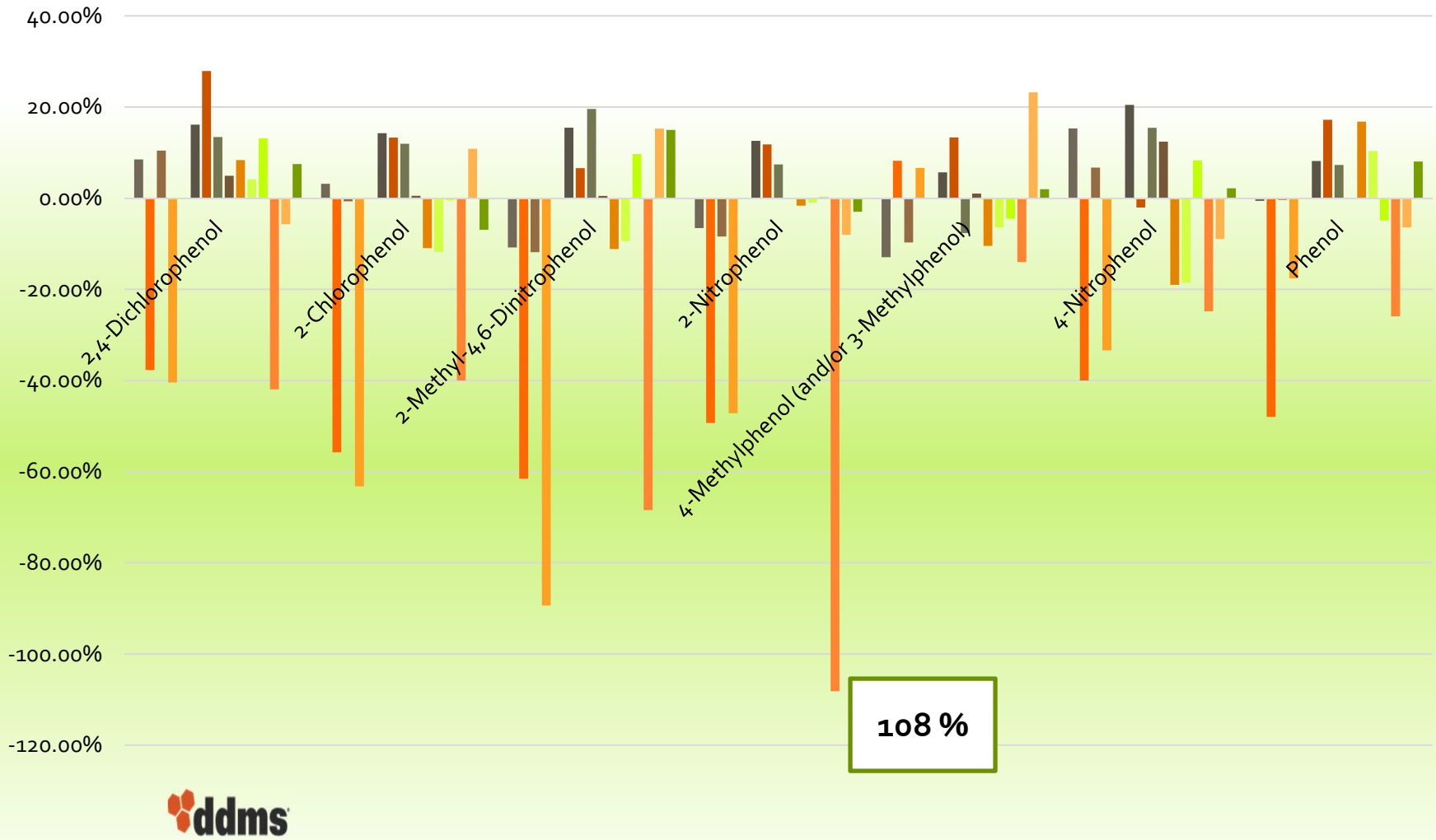
Data - Phase 2 LCS Acids

%R Delta –Unlabeled vs. Labeled



Data - Phase 2 LCS Acids

%R Delta –Unlabeled vs. Labeled



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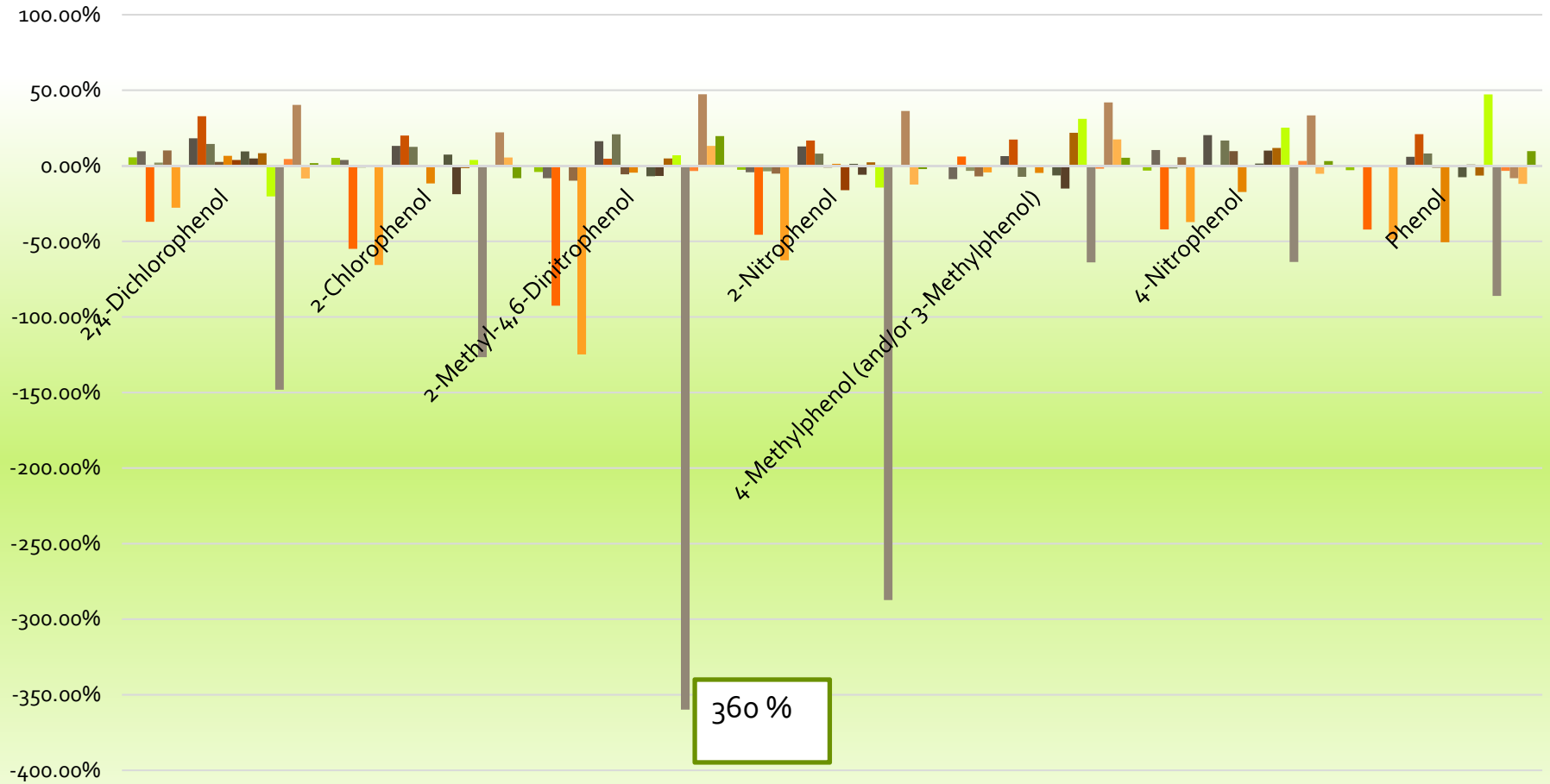
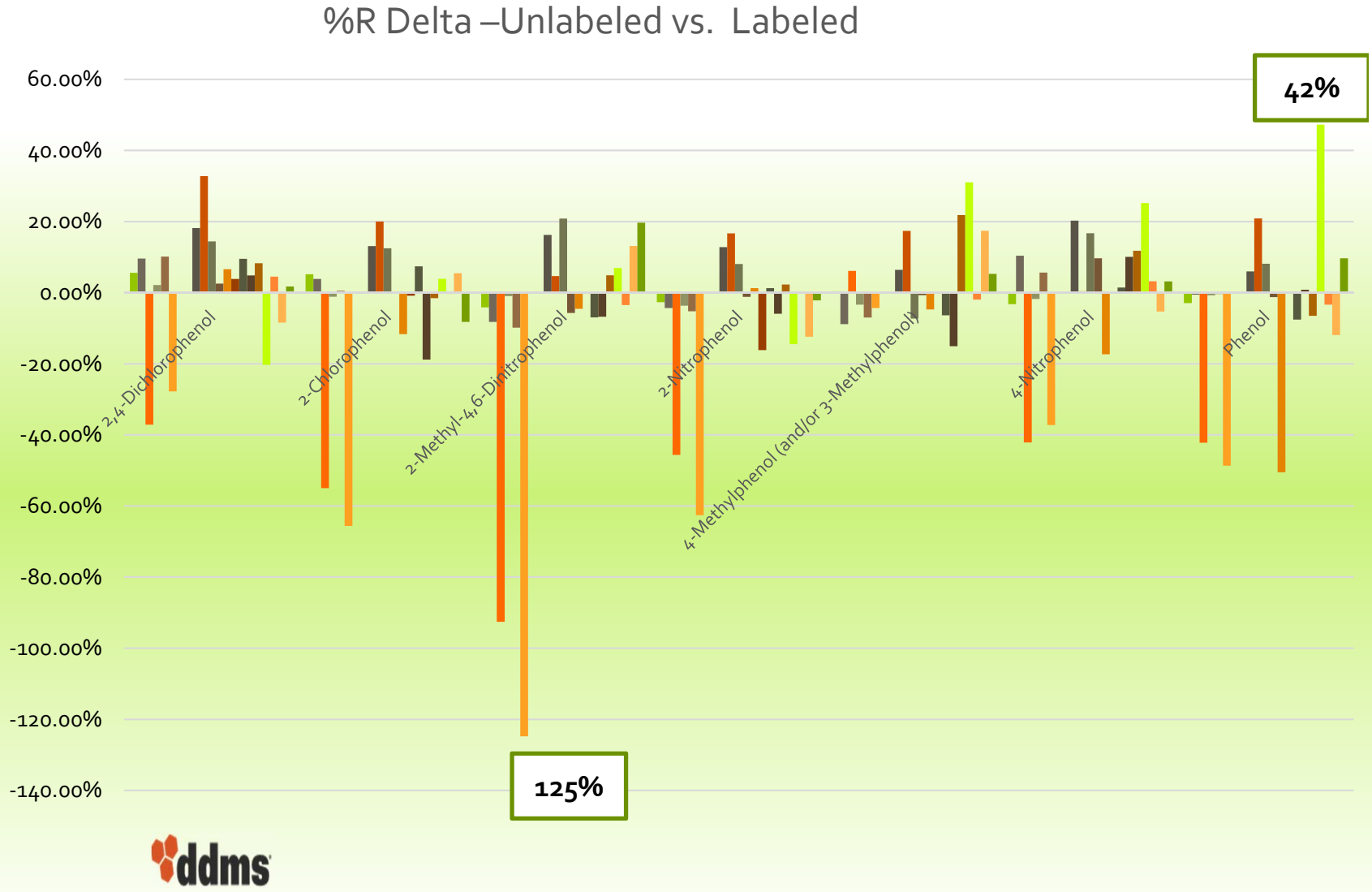
Data - Phase 2 TCLP Acids

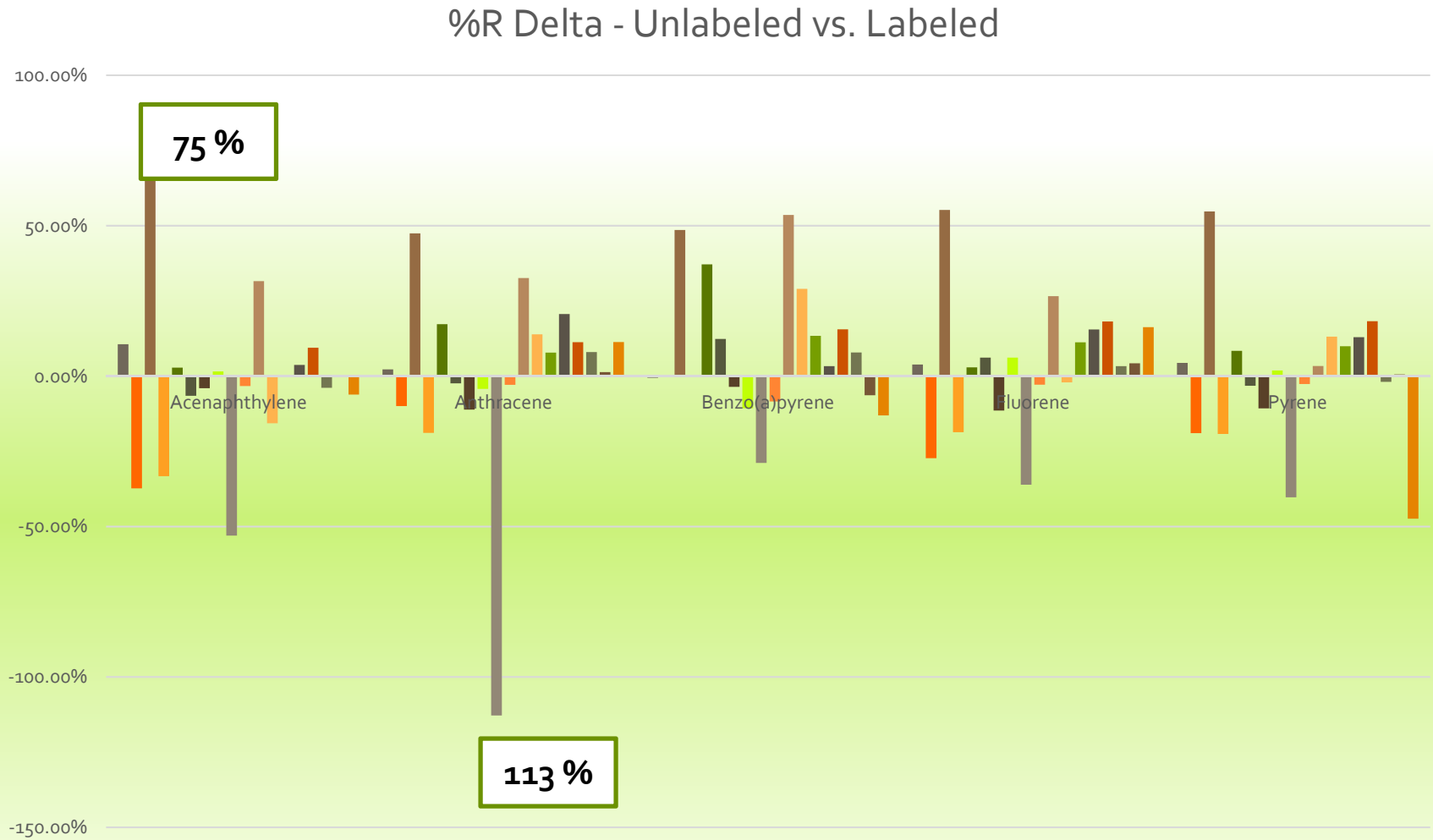
%R Delta –Unlabeled vs. Labeled



Data - Phase 2 TCLP Acids



The Data – Phase 2 LCS PAHs



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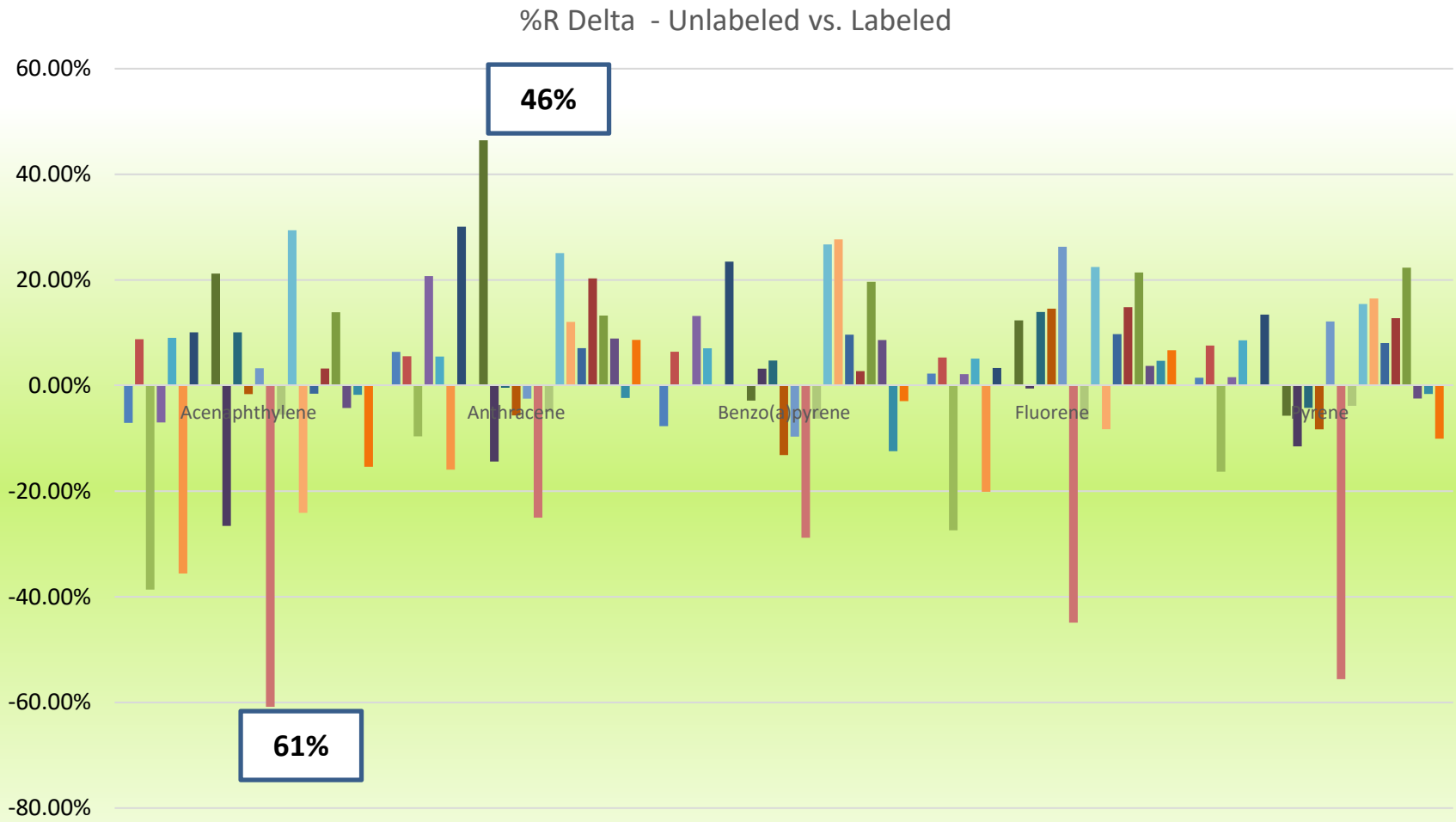
Data – Phase 2 TCLP PAHs



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Acids – Phase 2

Compound	LCS Average	LCS SD	LCS Min	LCS Max	TCLP Average	TCLP SD	TCLP Min	TCLP Max	ASTM WW Average	ASTM WW SD	ASTM WW Min	ASTM WW Max
2,4,5-Trichlorophenol	83.37%	37.87%	16.63%	162.77%	89.75%	51.25%	17.06%	249.36%	61.52%	28.20%	16.93%	97.44%
2,4,6-Trichlorophenol	90.04%	45.59%	15.75%	206.64%	101.75%	62.94%	26.73%	279.65%	58.88%	24.61%	23.73%	89.68%
2,4-Dichlorophenol	78.19%	45.64%	14.68%	200.63%	78.81%	40.97%	19.92%	212.11%	47.53%	18.30%	19.69%	67.08%
2,6-Dichlorophenol	77.35%	50.52%	0.00%	152.61%	77.09%	49.47%	0.00%	163.82%	44.16%	34.73%	0.00%	89.87%
4-Chloro-3-methylphenol	86.04%	46.23%	13.90%	194.38%	85.41%	41.20%	20.90%	208.76%	63.02%	26.64%	18.91%	92.96%
2-Chlorophenol	75.70%	46.21%	14.65%	191.35%	73.51%	37.83%	21.56%	177.07%	44.70%	17.73%	20.66%	64.10%
2,4-Dimethylphenol	86.09%	46.13%	20.97%	196.44%	82.44%	36.55%	20.55%	186.67%	51.81%	20.38%	23.63%	71.01%
2-Nitrophenol	82.82%	51.78%	20.43%	207.99%	89.04%	65.14%	23.23%	347.21%	41.66%	15.13%	21.70%	57.99%
2-Methyl-4,6-Dinitrophenol	151.62%	252.20%	10.75%	1108.16%	96.68%	109.58%	0.00%	544.56%	46.57%	16.78%	13.64%	62.37%
Pentachlorophenol	127.72%	187.44%	12.60%	836.86%	93.66%	81.80%	0.00%	362.53%	46.43%	25.43%	12.58%	89.77%
2-Methylphenol	65.37%	27.98%	22.10%	138.40%	63.98%	28.87%	0.00%	117.49%	49.48%	21.03%	19.31%	78.35%
4-Methylphenol (and/or 3-Methylphenol)	67.73%	28.26%	18.06%	134.60%	60.56%	27.85%	0.00%	115.58%	46.82%	17.20%	24.10%	64.54%
2,4-Dinitrophenol	65.98%	62.41%	0.00%	239.71%	66.12%	86.24%	0.00%	430.33%	29.07%	17.36%	0.00%	50.32%
4-Nitrophenol	67.42%	28.79%	16.66%	118.42%	64.50%	33.87%	0.00%	132.73%	46.51%	19.73%	17.49%	72.89%
Phenol	54.34%	38.92%	6.28%	158.33%	No data				36.80%	15.65%	14.67%	53.66%
Average	83.99%	57.02%	16.62%	272.87%	80.23%	48.66%	19.33%	240.79%	47.66%	17.00%	18.71%	61.37%

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Acids – Phase 2 LCS

Compound	LCS Average	LCS SD	LCS Min	LCS Max	LCS Delta Min/Max
2-Methyl-4,6-Dinitrophenol	151.62%	252.20%	10.75%	1108.16%	1097.41%
4-Nitrophenol	67.42%	28.79%	16.66%	118.42%	101.76%

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Acids – Phase 2 TCLP

Compound	TCLP Average	TCLP SD	TCLP Min	TCLP Max	TCLP Delta Min/Max
2-Methyl-4,6-Dinitrophenol	96.68%	109.58%	0.00%	544.56%	544.56%
4-Methylphenol	60.56%	27.85%	0.00%	115.58%	115.58%

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Acids – Phase 2 ASTM WW

Compound	ASTM WW Average	ASTM WW SD	ASTM WW Min	ASTM WW Max	ASTM WW Delta Min/Max
2,6-Dichloro-phenol	44.16%	34.73%	0.00%	89.87%	89.87%
2-Nitrophenol	41.66%	15.13%	21.70%	57.99%	36.29%

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PAHs – Phase 2 LCS

Compound	LCS Average	LCS SD	LCS Min	LCS Max	LCS Delta Min/Max
Phenanthrene	76.12%	48.81%	12.63%	242.68%	230.05%
Fluorene	65.95%	24.39%	12.54%	94.17%	81.62%

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PAHs – Phase 2 TCLP

Compound	TCLP Average	TCLP SD	TCLP Min	TCLP Max	TCLP Delta Min/Max
Indeno(1,2,3-cd)pyrene	71.72%	41.04%	5.88%	222.05%	216.17%
Acenaphthene	71.60%	24.62%	17.33%	103.02%	85.69%

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PAHs – Phase 2 ASTM WW

Compound	ASTM WW Average	ASTM WW SD	ASTM WW Min	ASTM WW Max	ASTM WW Delta Min/Max
Pyrene	61.04%	38.11%	11.98%	117.00%	105.02%
Dibenzo(a,h)anthracene	36.72%	14.67%	10.89%	52.37%	41.48%

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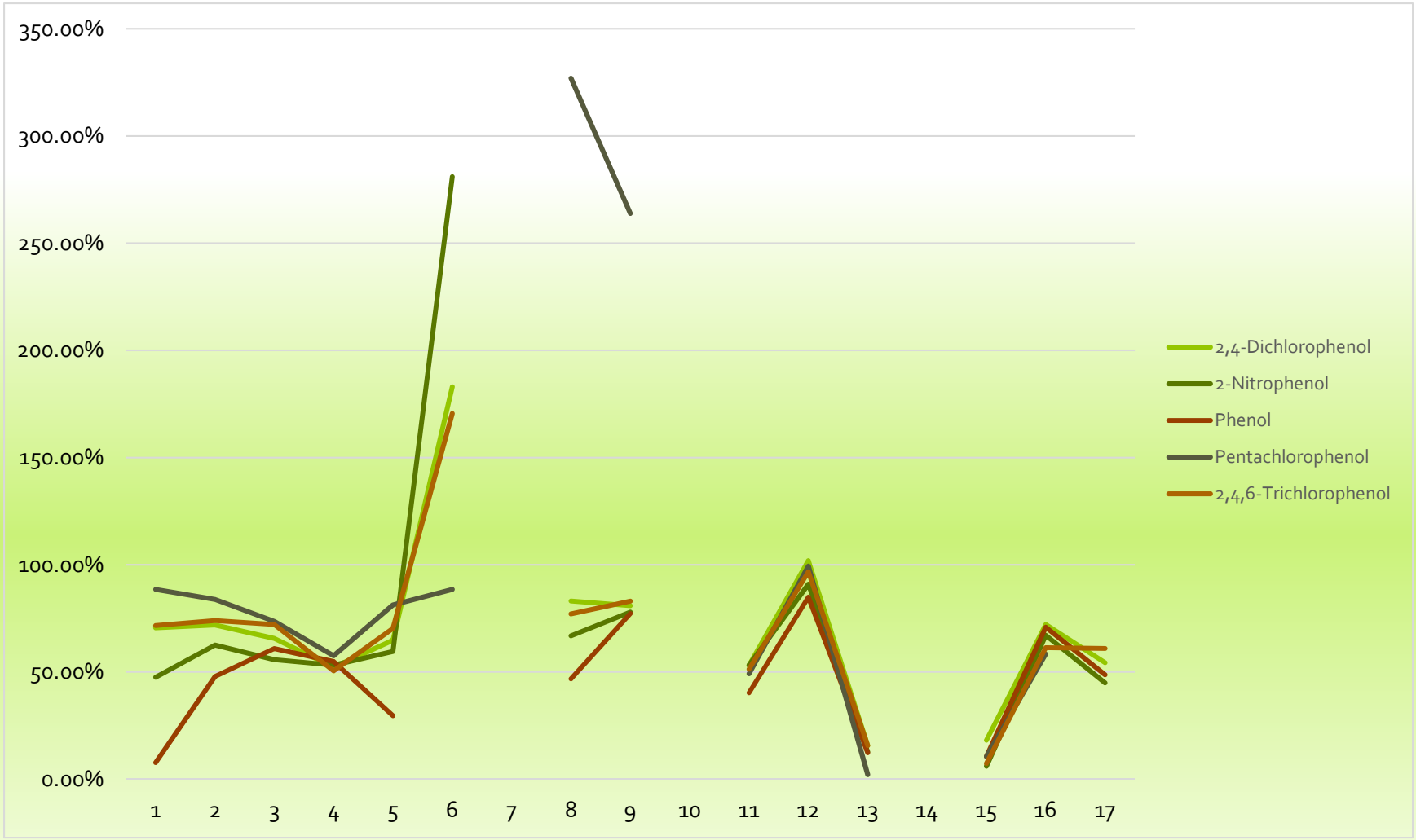
Acids - Potential Environmental Impact

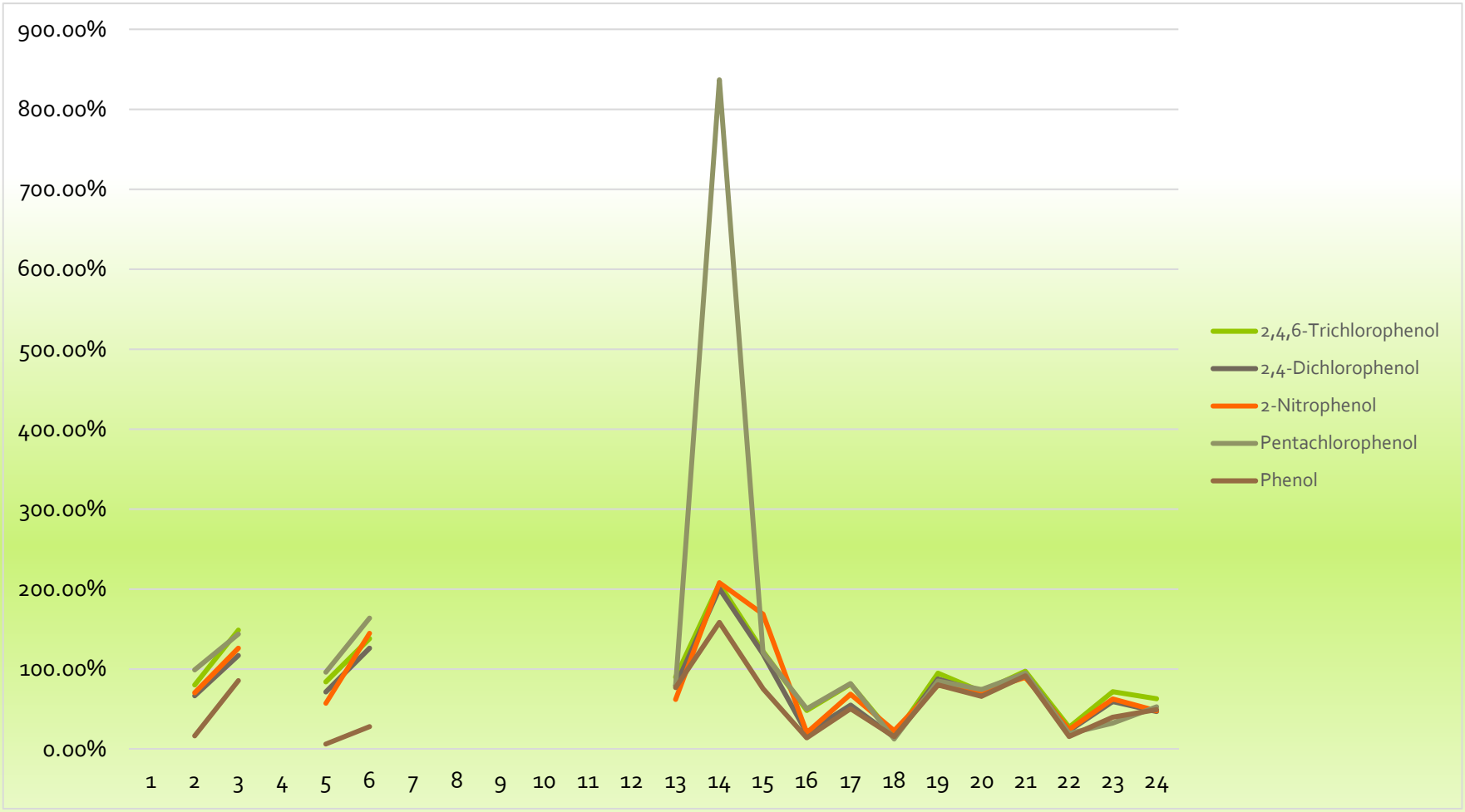
- Phenol
- 2-Nitrophenol (2-NP)
- 2,4-Dichlorophenol (2,4-DCP)
- 2,4,6-Trichlorophenol (2,4,6-TCP)
- Pentachlorophenol (PCP)

ddms

Acids – Phase 1 LCS



Acids – Phase 2 LCS



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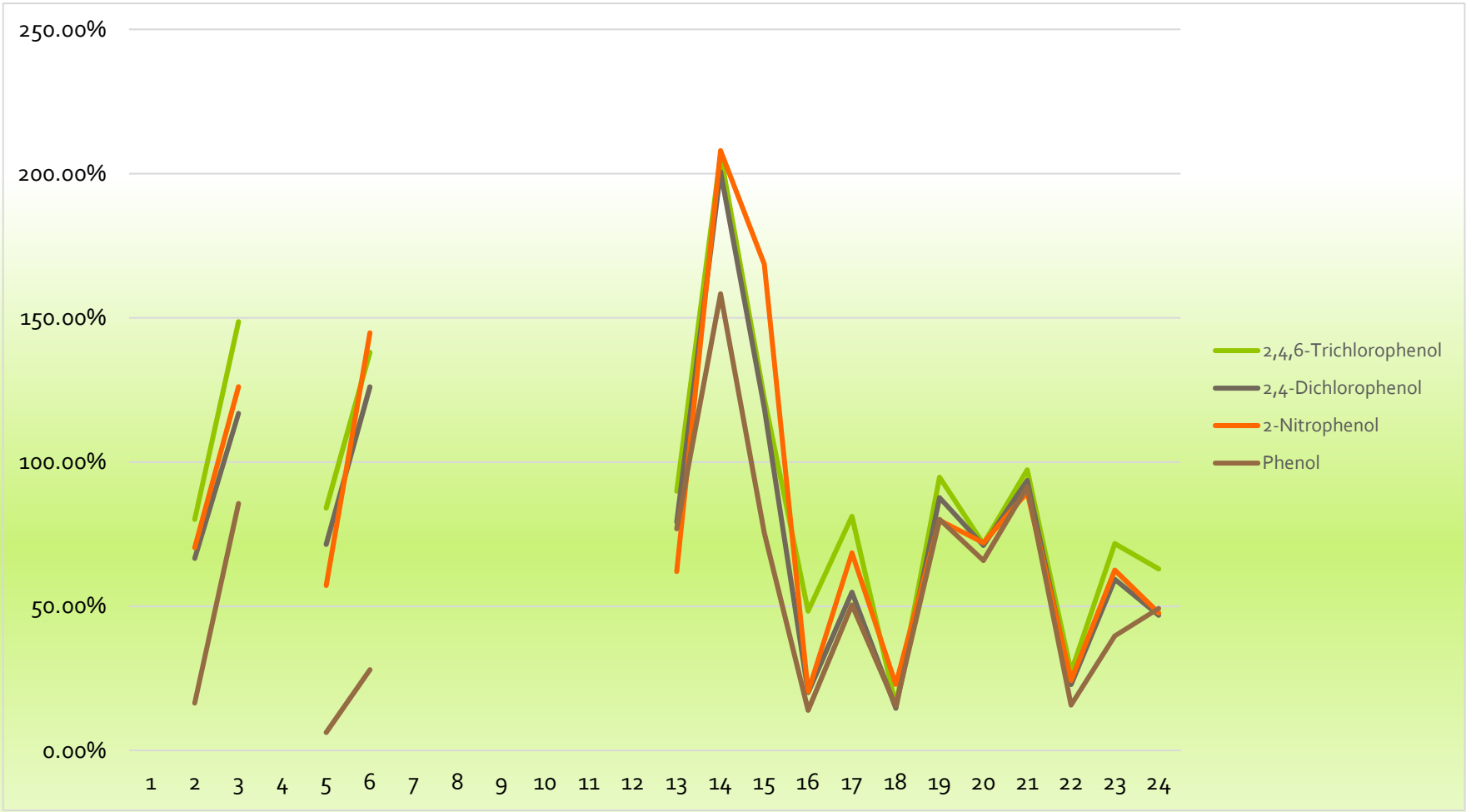
Acids – Phase 2 LCS



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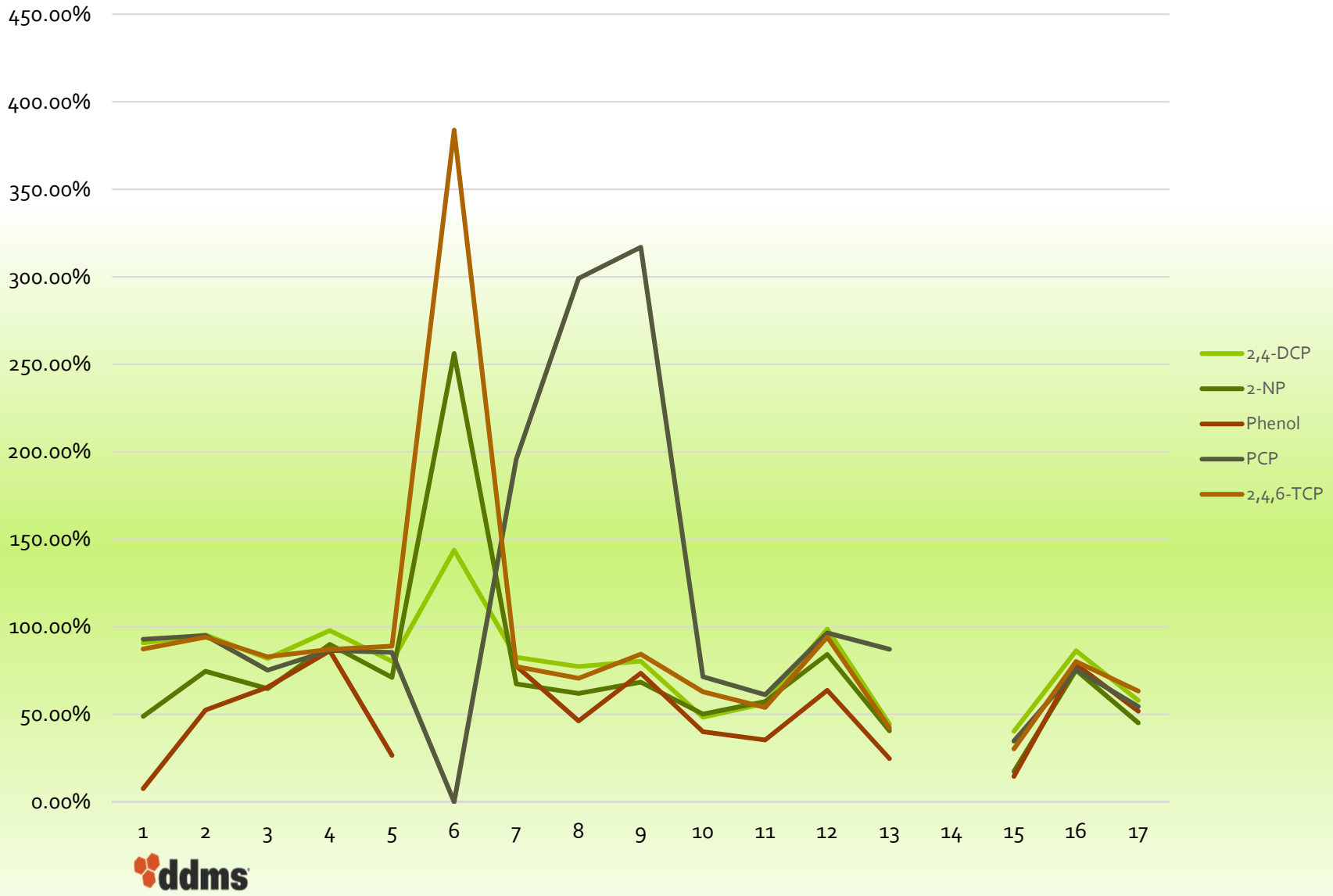
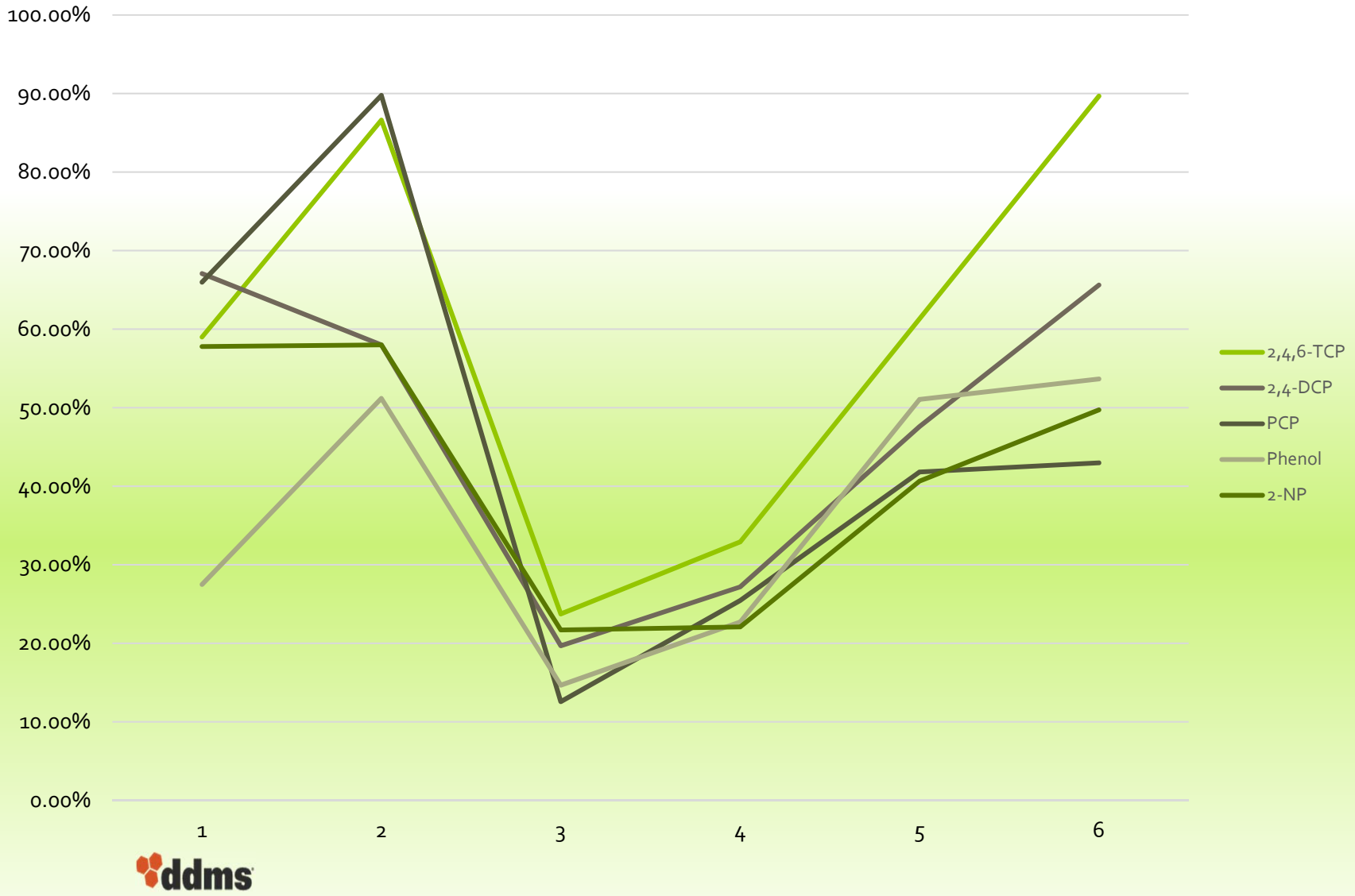
Acids – Phase 1 ASTM WW



Acids – Phase 2 ASTM WW



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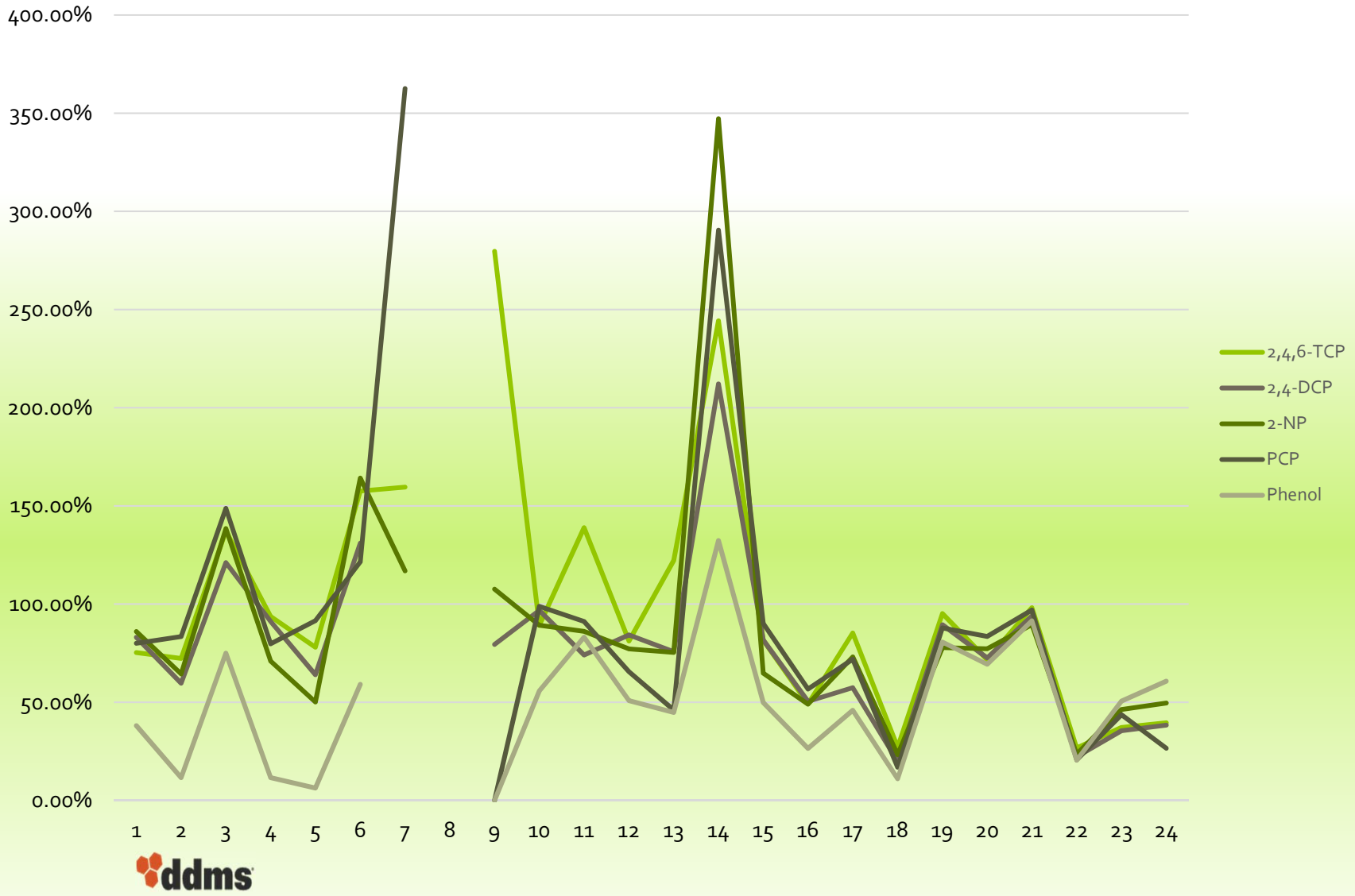
Acids – Phase 2 TCLP



PAHs with TEF

- Benzo(a)pyrene [BaP]
- Benzo(a)anthracene [BaA]
- Benzo(b)fluoranthene [BbF]
- Benzo(k)fluoranthene [BkF]
- Chrysene [Chry]
- Dibenzo(a,h)anthracene [DahA]
- Indeno(1,2,3cd)pyrene [I(123cd)P]

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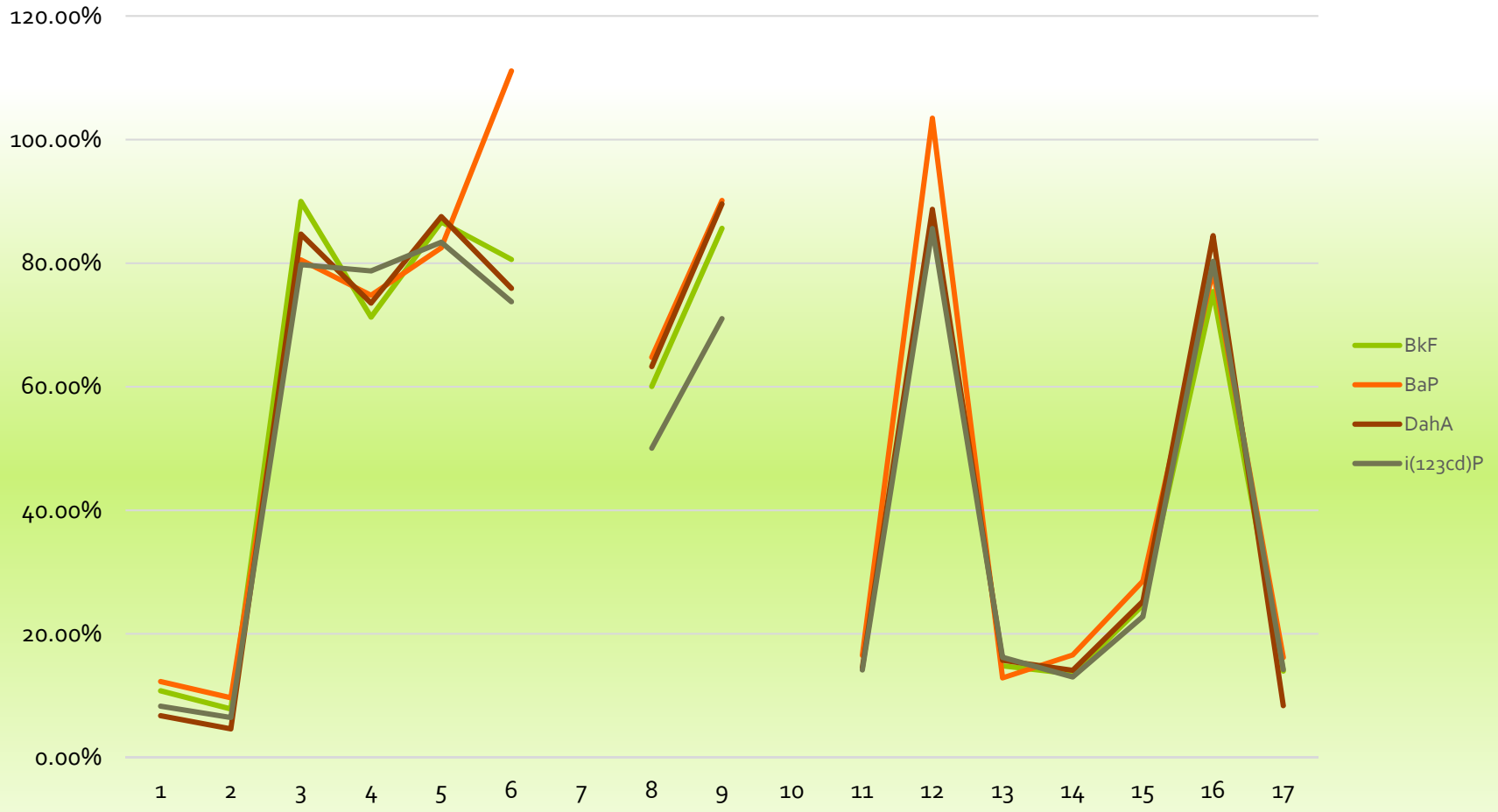
PAHs – Phase 1 LCS



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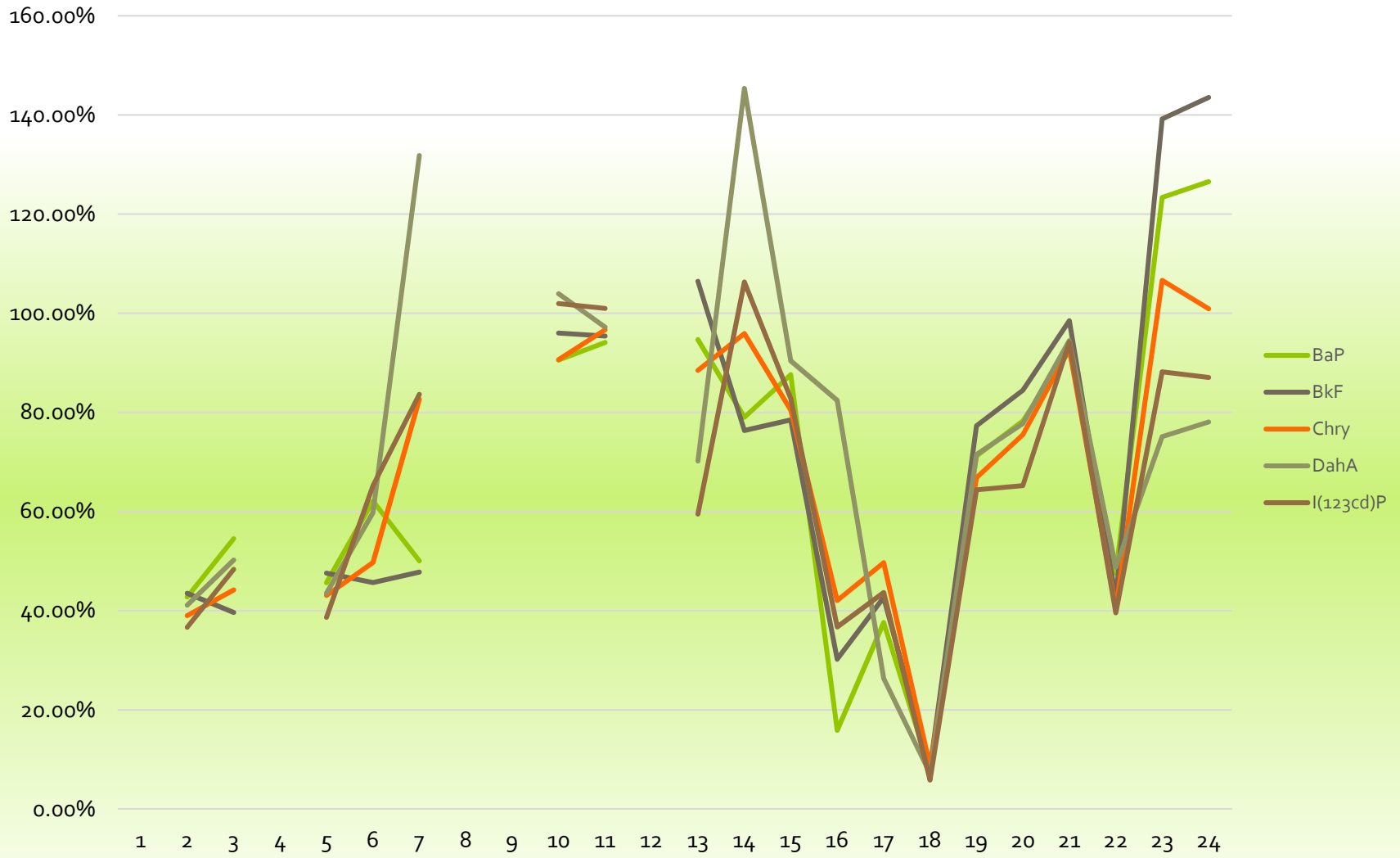
PAHs – Phase 2 LCS



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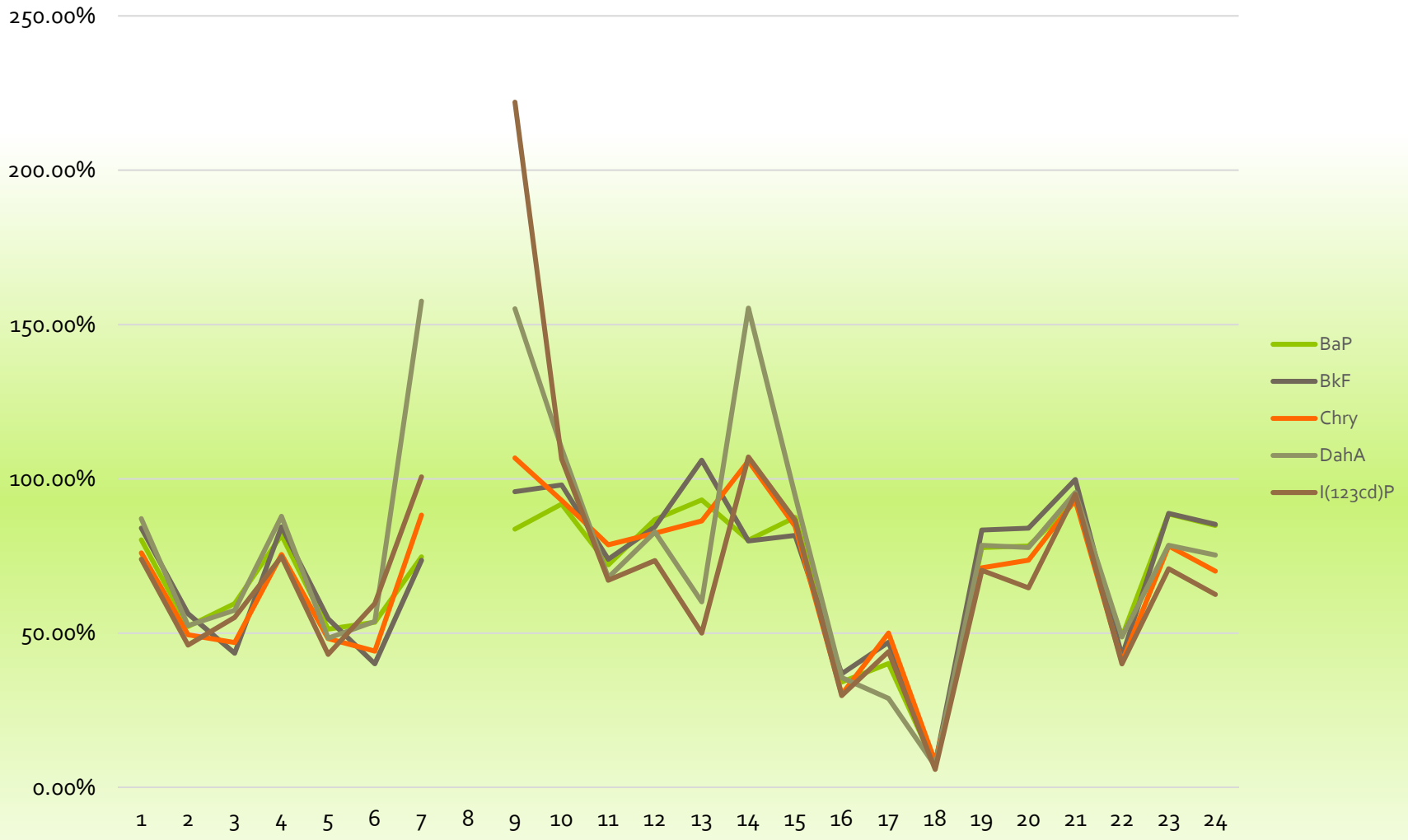
PAHs – Phase 2 TCLP



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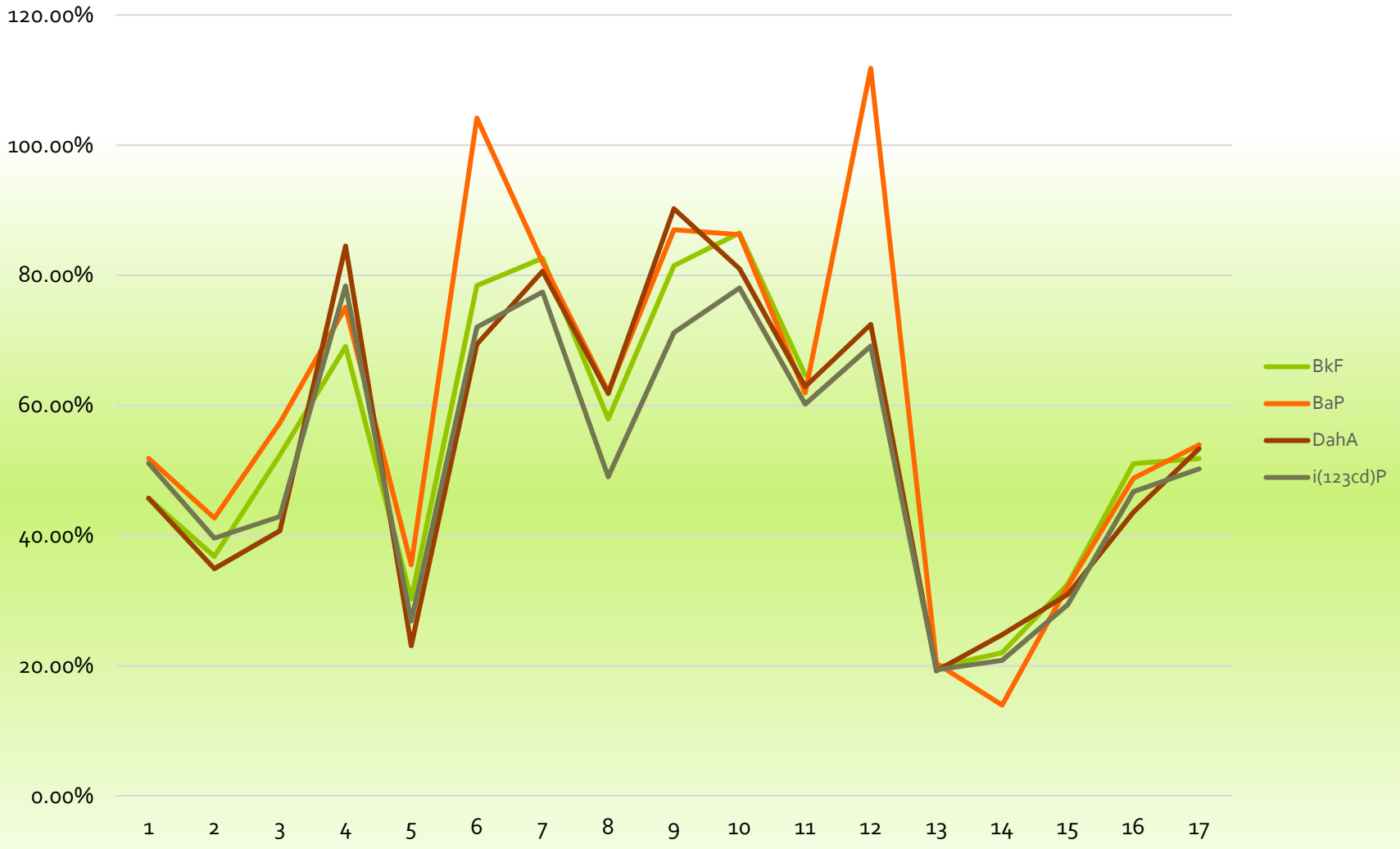
PAHs – Phase 1 ASTM WW



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PAHs – Phase 2 ASTM WW

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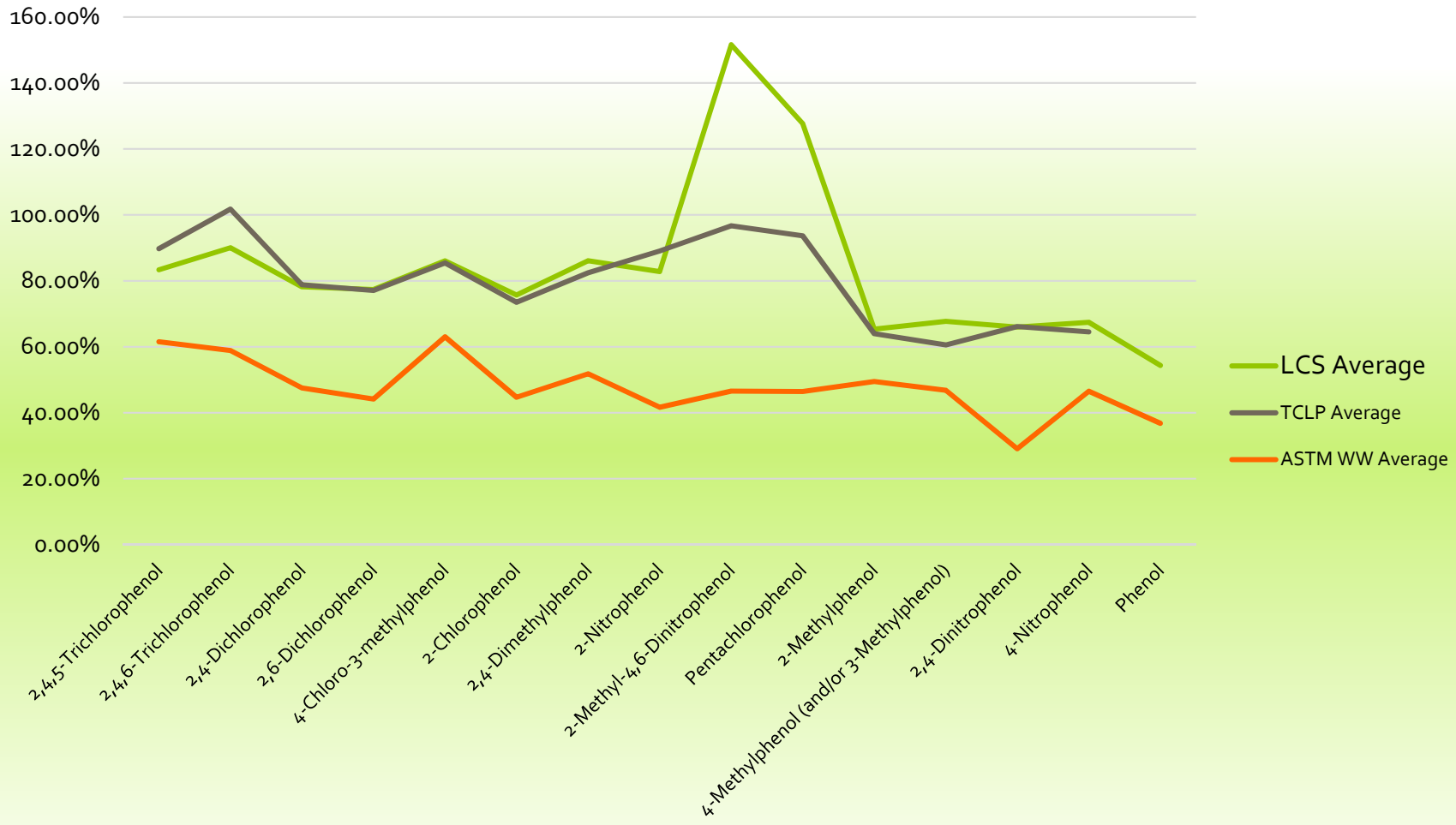
Acids – Phase 2 Avg %R



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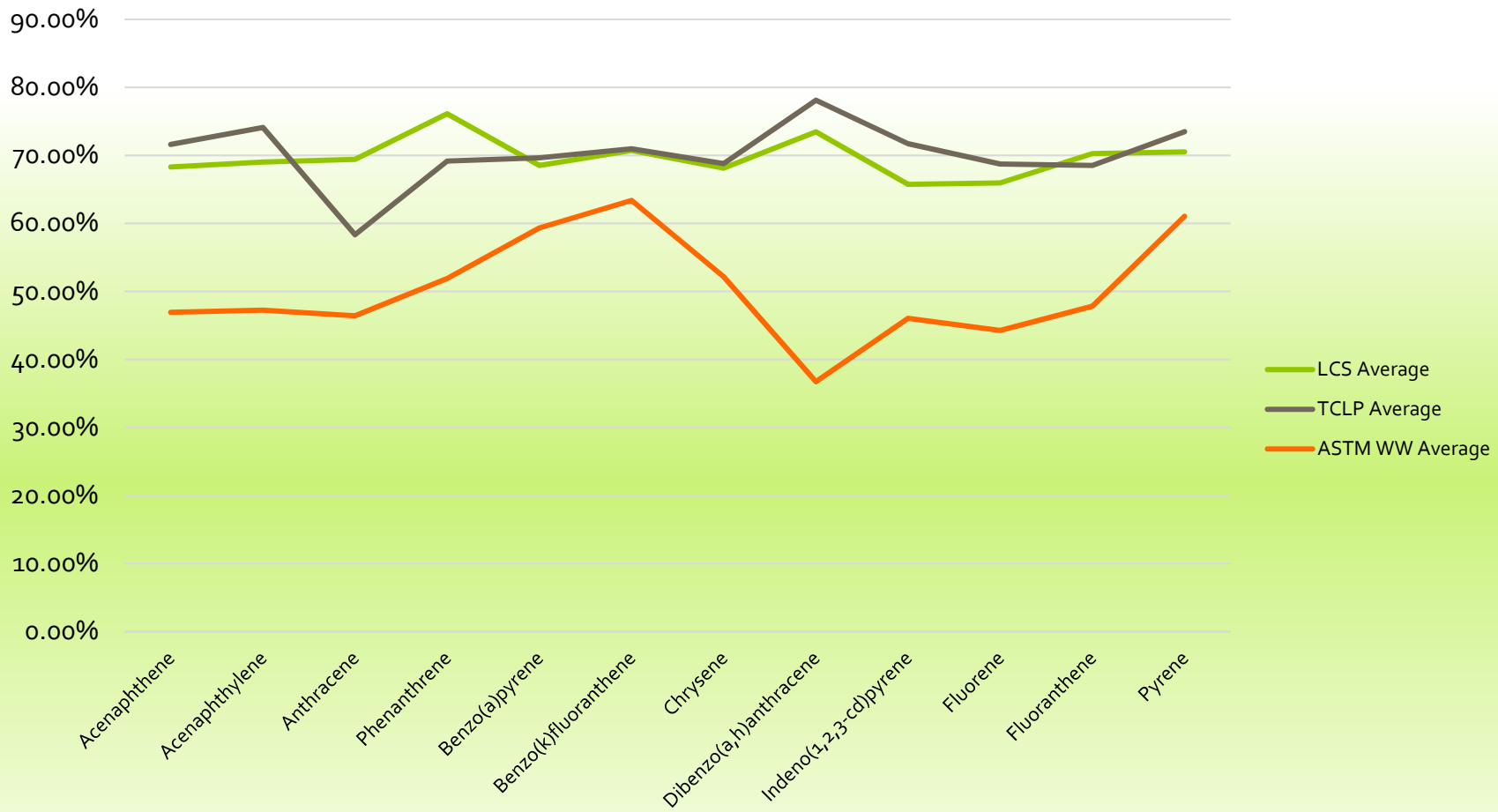
PAHs – Phase 2 Avg. %R



Finally

- Averaging
- Data variability
  - Large SDs
  - Orders of magnitude – Min vs. Max
- Method 625.1 or TNI acceptance criteria
- Waste water

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What's Next?

- Inconsistent compounds reported from Phase 1 to Phase 2.
- Verify SPE products for both phases
  - Spin bars
  - Disks
  - Cartridges
- Pair up labs from Phase 1 to Phase 2
- Data gaps

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What's Next?

- Issues with matrices
- Extractions
- Conventional liquid – liquid extraction
- Other lab QC
- Lab specific excursions
  - Labeled vs. unlabeled
  - %Rs

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What's Next?

- Extract clean ups
- Apply tighter limits to the existing data
- Compare recoveries of classes of compounds

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Facts do not cease to exist because they are ignored.

- Aldous Huxley- author of Brave New World

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We are scientists!

We can all figure this out, right?

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References

- "EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides," EPA 600/4-84-053, National Technical Information Service, PB84-206572, Springfield, Virginia 22161, June 1984.
- Phase 1 Data
- Phase 2 Data

Acknowledgements

- NEMC and TNI
- You, the audience for your patience and attention
- Colleagues, past and present

DISCLAIMER

The views and opinions expressed in this presentation are those solely of the presenters and do not reflect the opinions, official policy, or position of any client or regulatory agency.

The Studies – SPE Products and Vendors

Agilent Technologies, Inc. 2850 Centerville Road Wilmington, DE 19808	Bond Elut C18, 6ml, 1 gm, P/N 12256001 and Bond Elut ENV, 6ml, 500 mg, P/N 12255011
Fluid Management Systems 580 Pleasant Street Watertown, MA 02472	Mixed mode cartridge with a coconut charcoal 2nd cartridge, automated system
Gerstel Corp. 701 Digital Drive; Suite J Lithicum, MD 21090	GERSTEL Twister, PDMS Phase, 10mm x 0.5mm, P/N 011222-001-00
Horizon Technology Inc. 16 Northwestern Drive Salem, NH 03079	SPE-DEX® 4790 Automated Extractor with One-Pass kit and Envision Controller 47-mm disk holder (Part number 50-0807-01) for 100-mL volume samples and EZ-flow holder for 1-L samples (Part number 50-2767) Atlantic® One-pass disk (Part number 47-2346-11) Max Detect Carbon cartridge (Part number 9-2620-01) DryDisk® (Part number 40-705-HT) used with either the manual drying glassware (Part number SDS-101-19/22) or the DryVap in-line drying and evaporation system

The Studies – SPE Products and Vendors

Phenomenex Corp. 411 Madrid Avenue Torrence, CA 90501	Strata™-XL-C 2g/20mL Giga tube (P/N 8B-S044-KEG), Polymer-Based Mixed Mode Strong Cation-Exchange & Reverse Phase,100µm particle size, 300Å pore size
UCT, Inc. 2731 Bartram Road Bristol, PA 19007-6893	UCT Enviro-Clean 8270 (p/n: EC8270-KIT or EC8270-KIT1L)

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Thank you!

Any Questions?

Contact Information

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