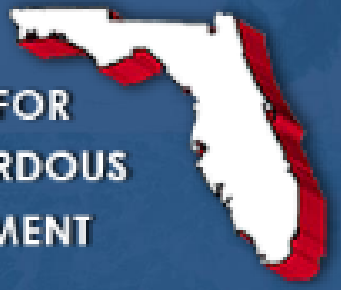
UF Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

HINKLEY CENTER FOR SOLID AND HAZARDOUS WASTE MANAGEMENT



Understanding the Environmental Impacts of Reclaimed Asphalt Pavement

End of Project

Technical Advisory Group Meeting

May 31st, 2022

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE

THE HINKLEY CENTER FOR SOLID AND HAZARDOUS WASTE MANAGEMENT

HINKLEY CENTER FOR SOLID AND HAZARDOUS WASTE MANAGEMENT

https://www.hinkleycenter.org/

Past HC Projects

- Leaching of Pollutants from Reclaimed Asphalt Pavement (Brantley & Townsend, 1999)

- Contribution of Asphalt Products to Total and Bioaccessible Polycyclic Aromatic Hydrocarbons (Su et al., 2013)

Contribution of Asphalt Products to Total and Bioaccessible Polycyclic Aromatic Hydrocarbons

Jing Su[1] · Peng Gao[2] · Steven James Laux[1] · Lena Qiying Ma[2] · Timothy Glyndon Townsend[1]

Received: 11 September 2018 / Revised: 9 March 2019 / Accepted: 5 April 2019 / Published online: 15 April 2019
© University of Tehran 2019

Abstract
Soil-like waste products such as construction and demolition debris fines, street sweepings and catch basin sediments often contain elevated concentrations of polycyclic aromatic hydrocarbons (PAHs) resulting from anthropogenic activities. Previous research suggested that small pieces of asphalt may contribute to PAHs in these wastes. The objective of this research was to investigate this idea by analyzing total PAHs concentrations in various asphalt products to assess their contribution to PAHs in these wastes. Five types of asphalt products (new and used asphalt shingles, new asphalt pavement, reclaimed asphalt pavement [RAP], and bitumen) were selected. PAHs concentrations were relatively low in most of the asphalt products except for RAP. The benzo[a]pyrene-equivalent (BaP-equivalent) concentrations in two RAP samples exceeded both Florida and EPA risk thresholds. PAHs bioaccessibility tests were conducted using a mild solvent extraction method on asphalt product samples of several different samples sizes (< 0.5 cm and < 250 μm); bioaccessibility was measured at < 10% for most samples. When asphalt products were mixed with clean sand to mimic soil-like waste, PAHs concentrations and bioaccessibility for most products decreased with decreasing asphalt percentages. Though PAHs sources for asphalt products are petrogenic, the few detected diagnostic ratios did not indicate a clear petrogenic source for these materials, suggesting that caution be taken when using diagnostic ratios for source apportionment related to these materials.

Article Highlights

- **Polycyclic aromatic hydrocarbon (PAH) in asphalt products were analyzed.**
- **Asphalt products have been a suspected source of PAH in soil-like wastes.**
- **PAH concentrations were found to be low in most asphalt products.**
- **Asphalt does not appear to be a significant source of PAH in soil-like wastes.**

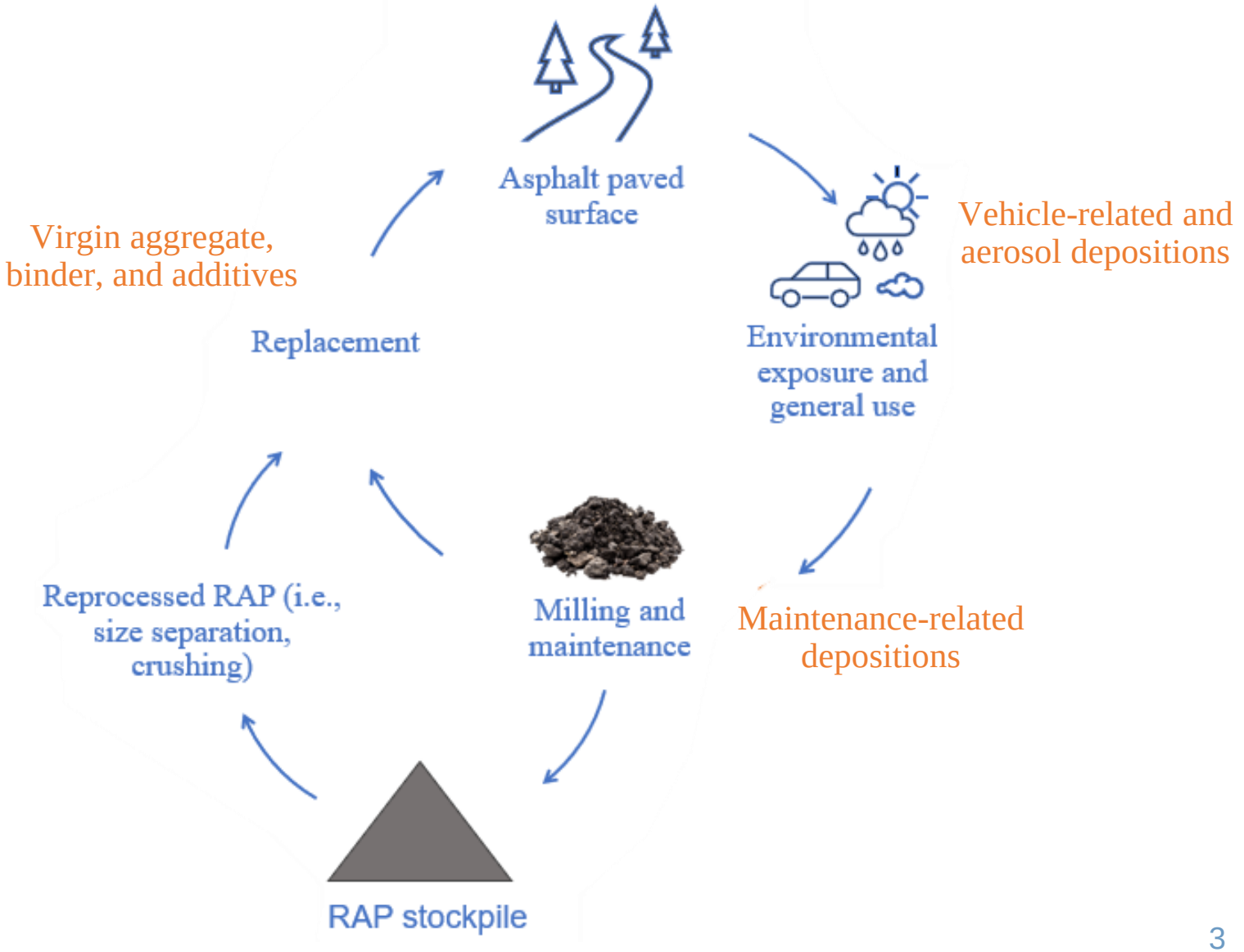
Background Recap

Background

- **Reclaimed Asphalt Pavement (RAP):** Granular pieces of asphalt pavement removed during roadway maintenance or replacement for later reuse

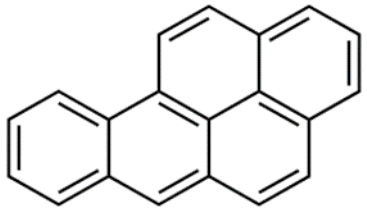
Three primary substances:

1. Aggregate
2. Binder
3. Depositions



Polycyclic Aromatic Hydrocarbons (PAHs)

- Class of 100+ compounds
- Present in coal, crude oil, and gasoline
- Sometimes carcinogenic
- Toxic
- Mutagenic



Benzo(a)pyrene

EPA 16 Priority PAHs

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

Benzo(a)pyrene Equivalents (TEF)

- Associated toxicity of PAHs can be assessed using BaP TEF

$$BaP = (1.0)[BaP] + (0.1)[BaA] + (0.1)[BbF] + (0.01)[BkF] + (0.001)[CH] + (1.0)[DahA] + (0.1)[IP]$$

[BaP] = Benzo(a)pyrene
[BaA] = Benzo(a)anthracene
[BbF] = Benzo(b)fluoranthene
[BkF] = Benzo(k)fluoranthene
[CH] = Chrysene
[DahA] = Dibenzo(a,h)anthracene
[IP] = Indeno(1,2,3-cd)pyrene

- Only accounts for carcinogenicity, not all PAHs have BaP TEFs

Concerns regarding RAP

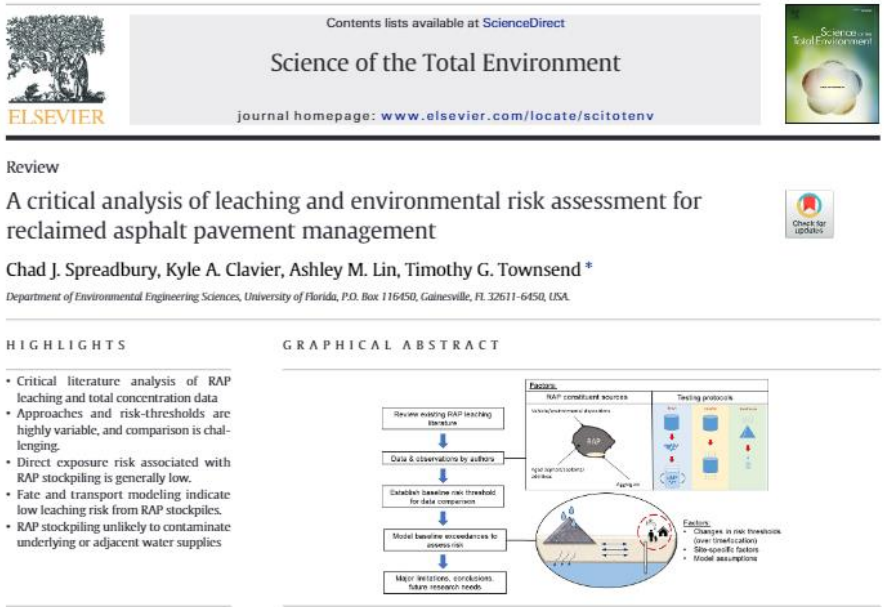
- Thurston County, WA – Herrera report
- Uncertainty on human/environmental risks → inconsistencies in management among agencies
- Variability in data? Is there cause for concern?

A critical analysis of leaching and environmental risk assessment for reclaimed asphalt pavement management

Spreadbury et al., 2021

- Existing literature on constituent leaching from RAP
  - 17 studies identified
  - 14 at the bench scale
  - 3 at the full scale
- Applied IWEM fate and transport simulation
- Key findings
  - Limited analysis of PAHs, only EPA 16 priority PAHs
  - After considering dilution and attenuation, lead and naphthalene were the only constituents above EPA RSLs
  - Existing data is dominated by TCLP and batch testing

NATIONAL ASPHALT PAVEMENT ASSOCIATION



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

ELSEVIER

Review

A critical analysis of leaching and environmental risk assessment for reclaimed asphalt pavement management

Chad J. Spreadbury, Kyle A. Clavier, Ashley M. Lin, Timothy G. Townsend *

Department of Environmental Engineering Sciences, University of Florida, P.O. Box 116450, Gainesville, FL 32611-6450, USA.

HIGHLIGHTS

- Critical literature analysis of RAP leaching and total concentration data
- Approaches and risk-thresholds are highly variable, and comparison is challenging.
- Direct exposure risk associated with RAP stockpiling is generally low.
- Fate and transport modeling indicate low leaching risk from RAP stockpiles.
- RAP stockpiling unlikely to contaminate underlying or adjacent water supplies

GRAPHICAL ABSTRACT

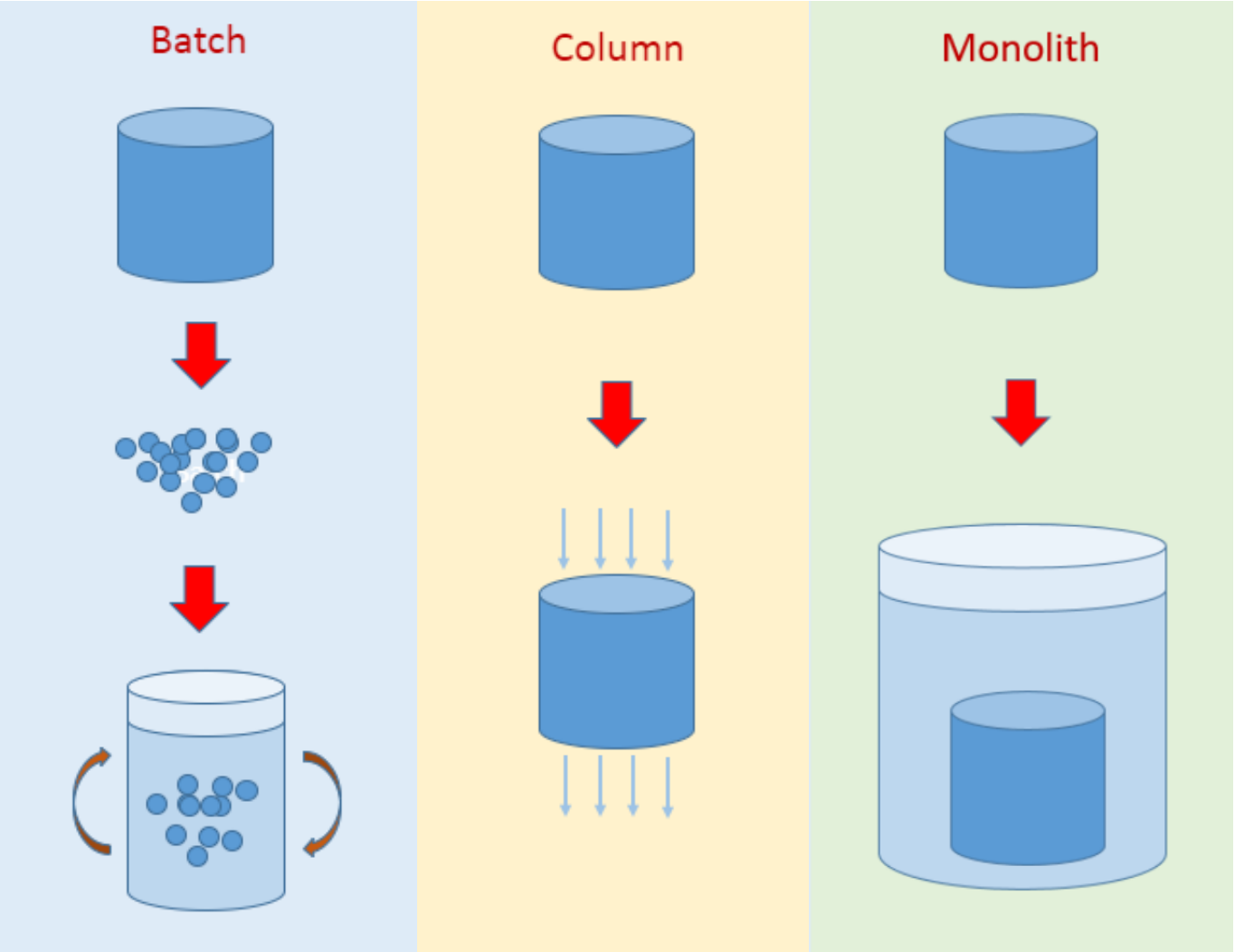
Leaching Procedure Types

Traditional EPA Methods

- 1311 Toxicity Characteristic Leaching Procedure (**TCLP**)
- 1312 Synthetic Precipitation Leaching Procedure (**SPLP**)

Leaching Environmental Assessment Framework (LEAF)

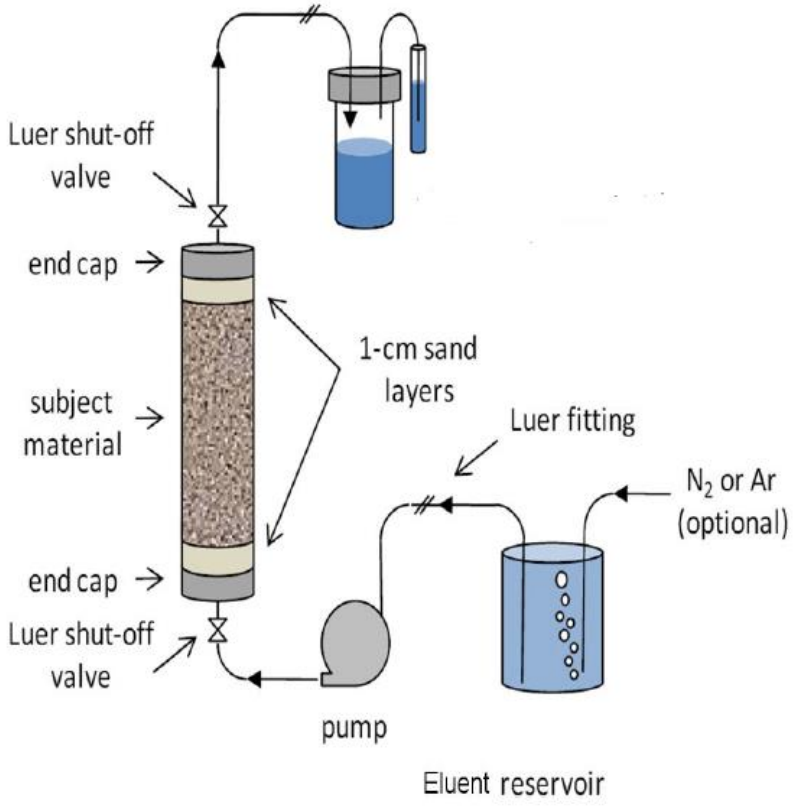
- 1313 Liquid Solid Partitioning as a Function of Extract pH
- **1314 Liquid Solid Partitioning using Up-Flow Percolation column**
- 1315 Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials
- 1316 Liquid Solid Partitioning as a Function of L/S



Leaching Procedure Types

Leaching Environmental Assessment Framework (LEAF)

- 1314 Liquid Solid Partitioning using Up-Flow Percolation column



SCHEDULE OF ELUATE FRACTIONS FOR COLLECTION WITH EXAMPLE VOLUMES

Interval Label	End Point ΣL/S (mL/g-dry)	Fraction L/S (mL/g-dry)	Example Fraction Volume (mL)
T01	0.2 ± 0.1	0.2	60
T02	0.5 ± 0.1	0.3	90
T03	1.0 ± 0.1	0.5	150
T04	1.5 ± 0.2	0.5	150
T05	2.0 ± 0.2	0.5	150
T06	4.5 ± 0.3	2.5	750
T07	5.0 ± 0.2	0.5	150
T08	9.5 ± 0.3	4.5	1350
T09	10.0 ± 0.2	0.5	150
B01	Eluent		100

NOTE: Example fraction volumes based on assumed packing mass of 300 g-dry

2021 Hinkley Center Project

Project Objectives

1. Measure the total and leachable pollutants in RAP using methodologies realistic to RAP reuse scenarios
2. **Expand analyzed PAHs beyond EPA 16 priority PAHs**
3. Implications for RAP stockpiling and reuse management

Polycyclic Aromatic Compounds, 35:330–354, 2015
Published with license by Taylor & Francis
ISSN: 1040-6638 print / 1563-5333 online
DOI: 10.1080/10406638.2014.991042

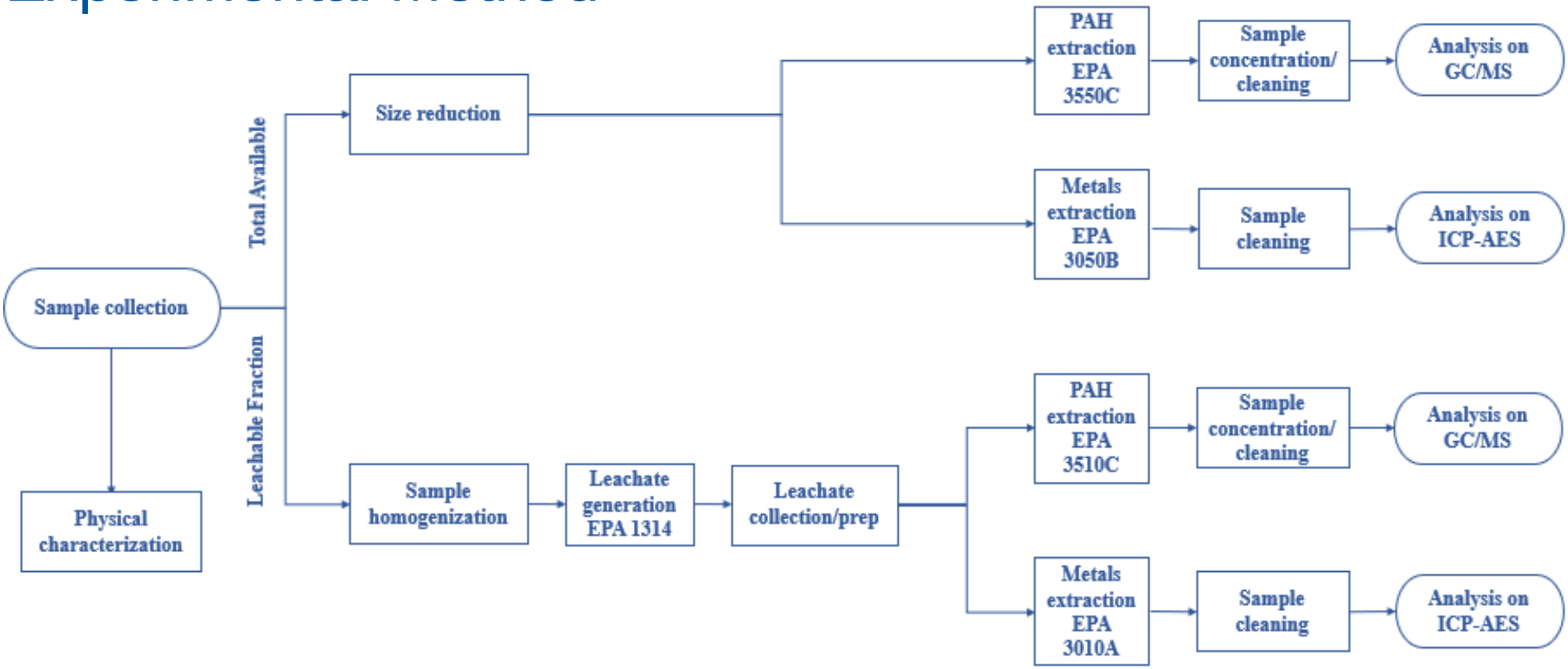
Taylor & Francis
Taylor & Francis Group

Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes

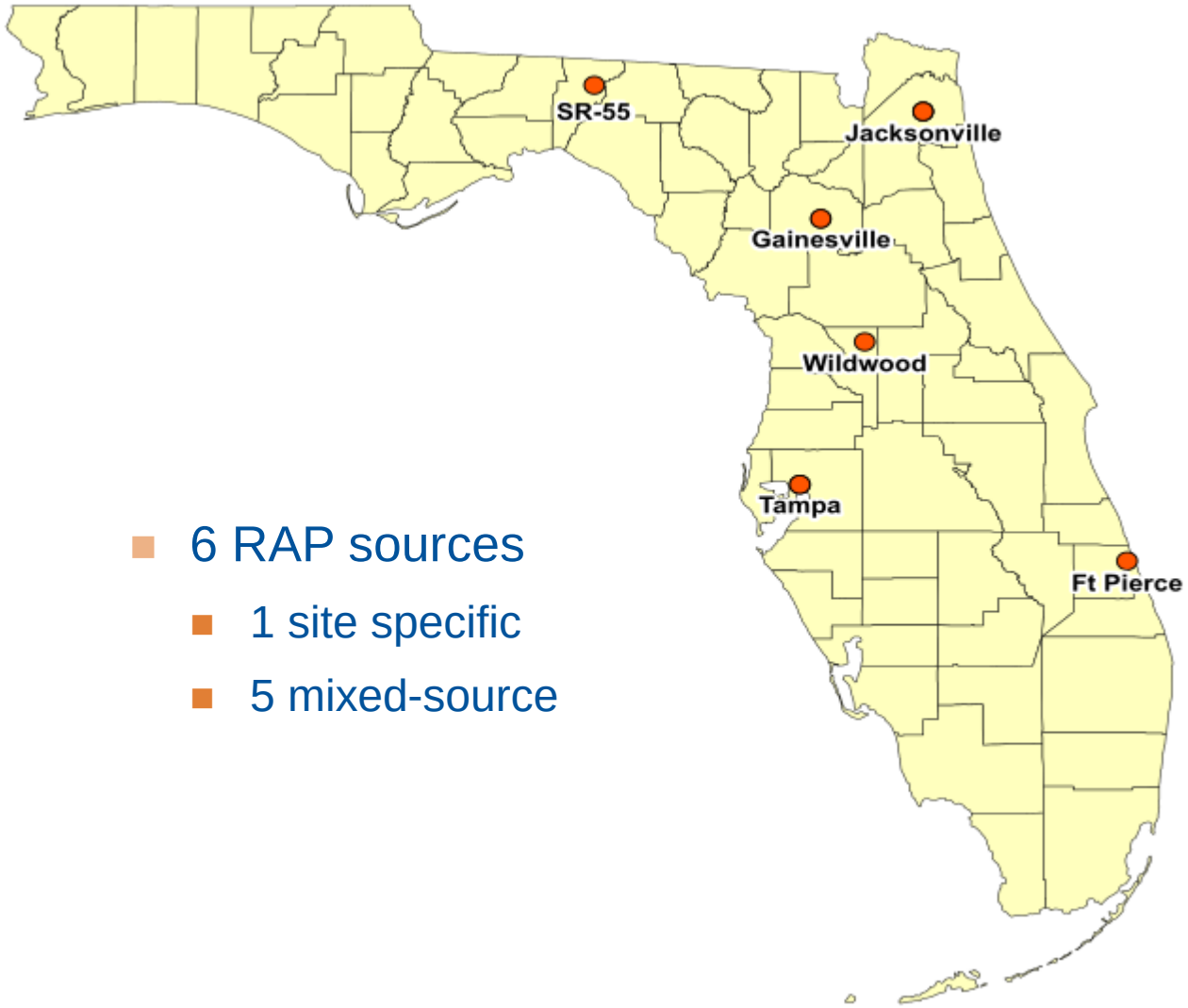
Jan T. Andersson[1] and Christine Achten[2]

[1]Institute of Inorganic and Analytical Chemistry, University of Muenster, Muenster, Germany
[2]Institute of Geology and Palaeontology – Applied Geology, University of Muenster, Muenster, Germany

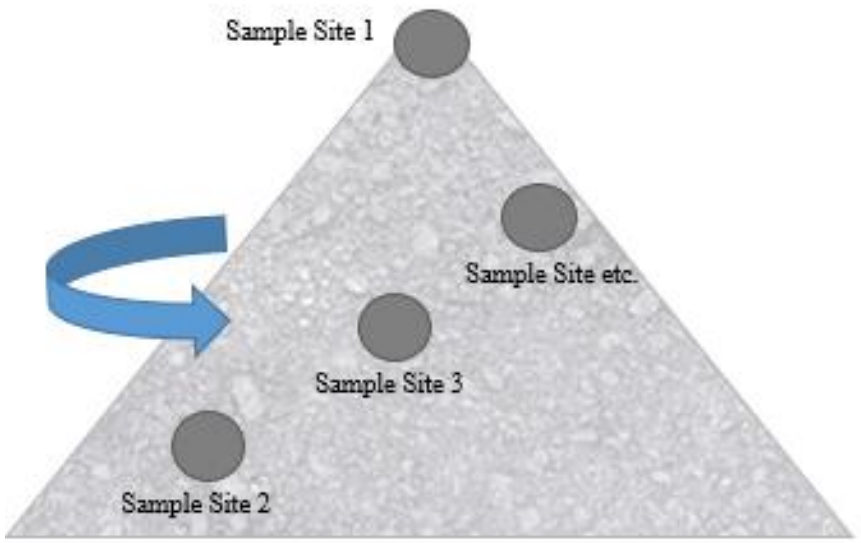
Experimental Method

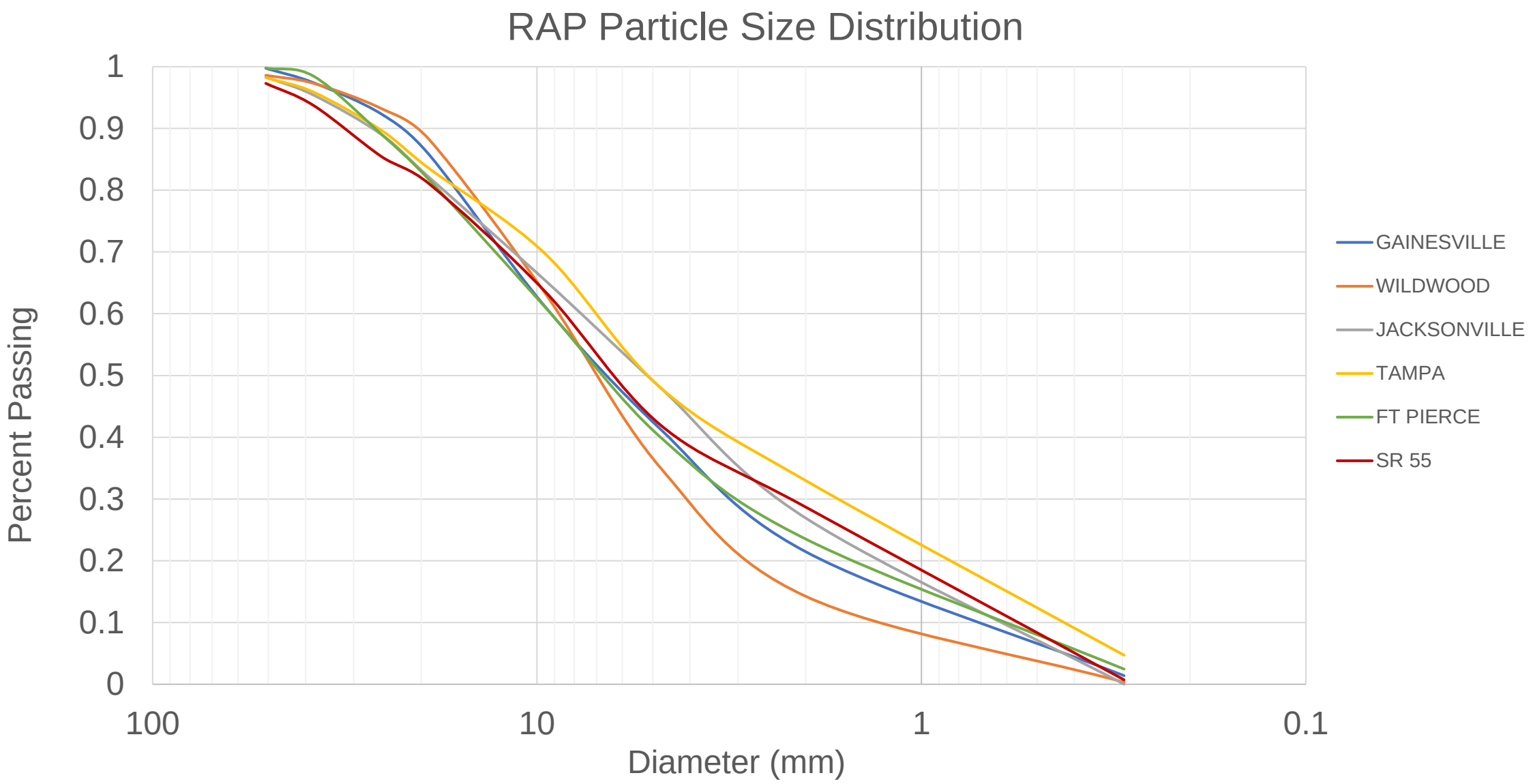


Sample Collection

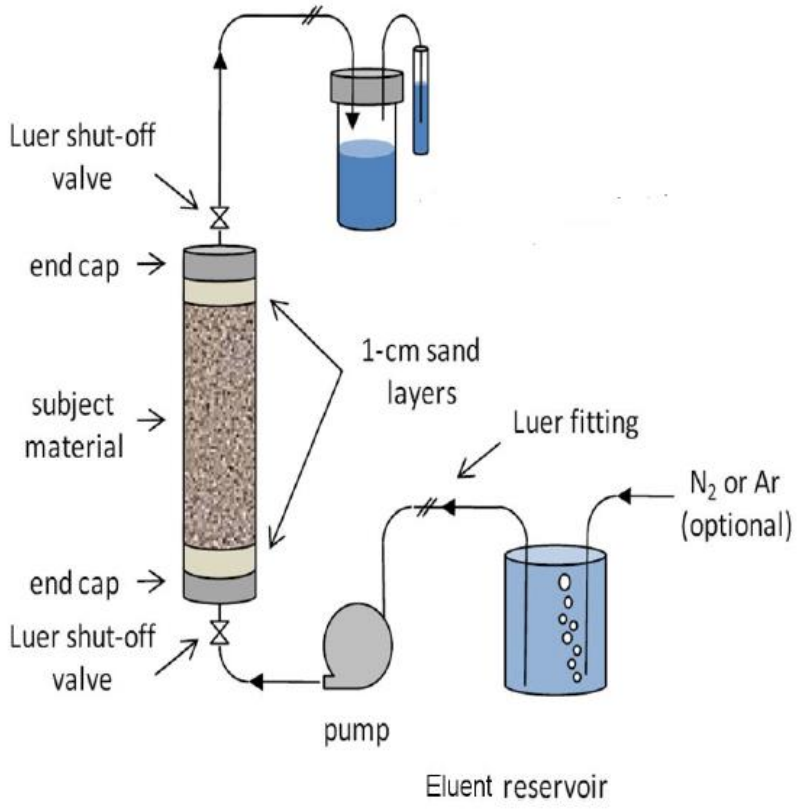


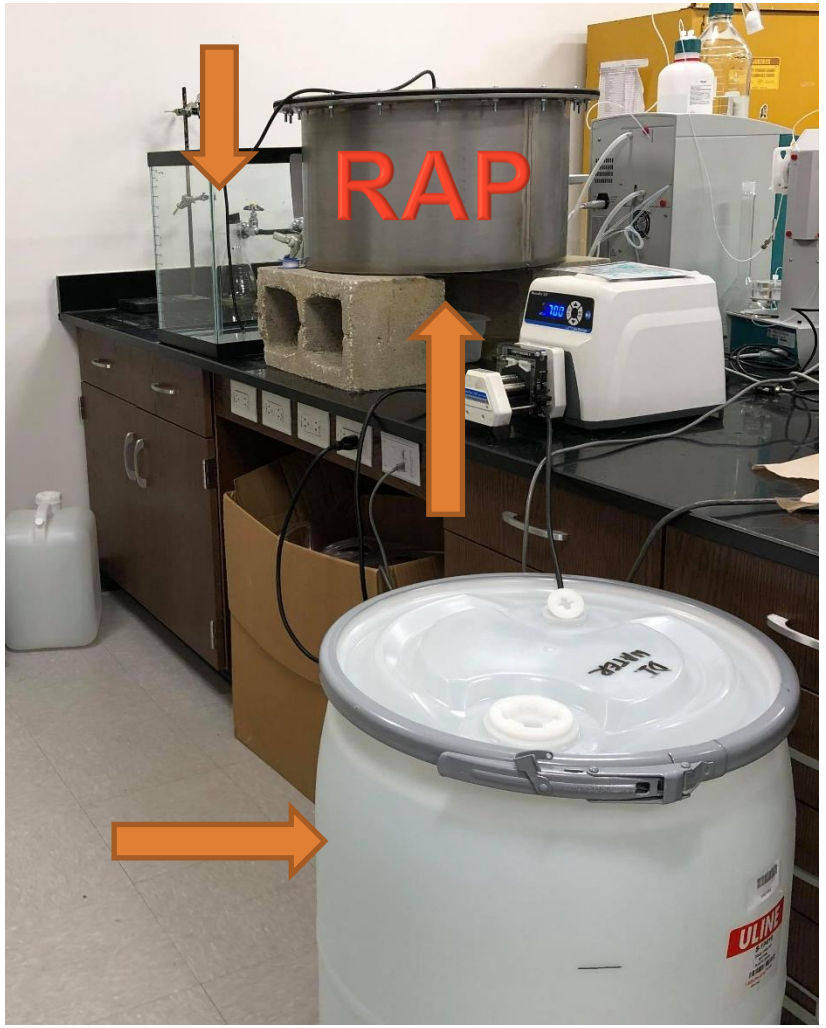
- 6 RAP sources
  - 1 site specific
  - 5 mixed-source




RAP Particle Size Distribution
Percent Passing
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
10
1
0.1
Diameter (mm)
GAINESVILLE
WILDWOOD
JACKSONVILLE
TAMPA
FT PIERCE
SR 55

Modified EPA Method 1314 – Leaching Apparatus





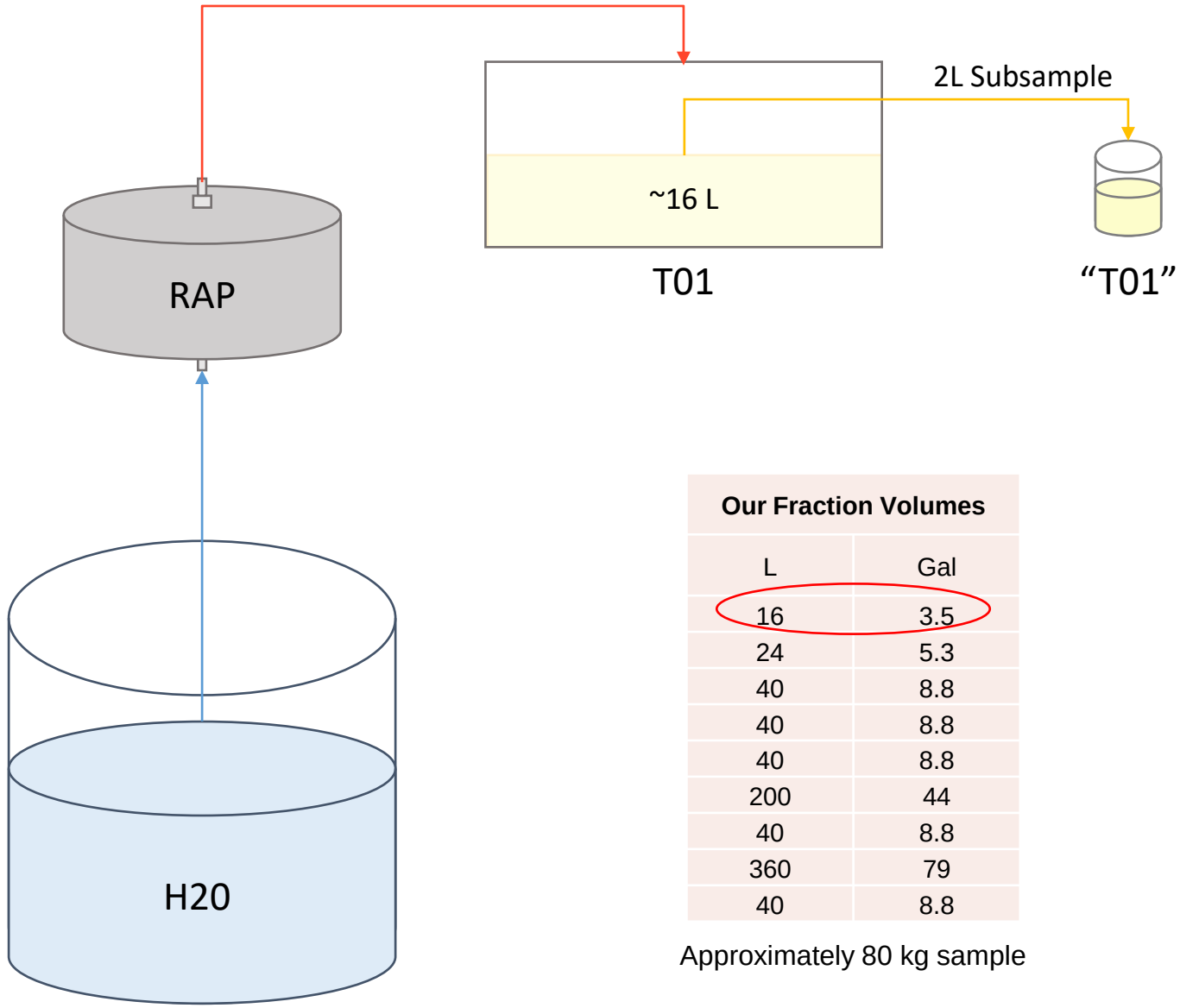
EPA Method 1314

SCHEDULE OF ELUATE FRACTIONS FOR COLLECTION WITH EXAMPLE VOLUMES

Interval Label	End Point ΣL/S (mL/g-dry)	Fraction L/S (mL/g-dry)	Example Fraction Volume (mL)
T01	0.2 ± 0.1	0.2	60
T02	0.5 ± 0.1	0.3	90
T03	1.0 ± 0.1	0.5	150
T04	1.5 ± 0.2	0.5	150
T05	2.0 ± 0.2	0.5	150
T06	4.5 ± 0.3	2.5	750
T07	5.0 ± 0.2	0.5	150
T08	9.5 ± 0.3	4.5	1350
T09	10.0 ± 0.2	0.5	150
B01	Eluent		100

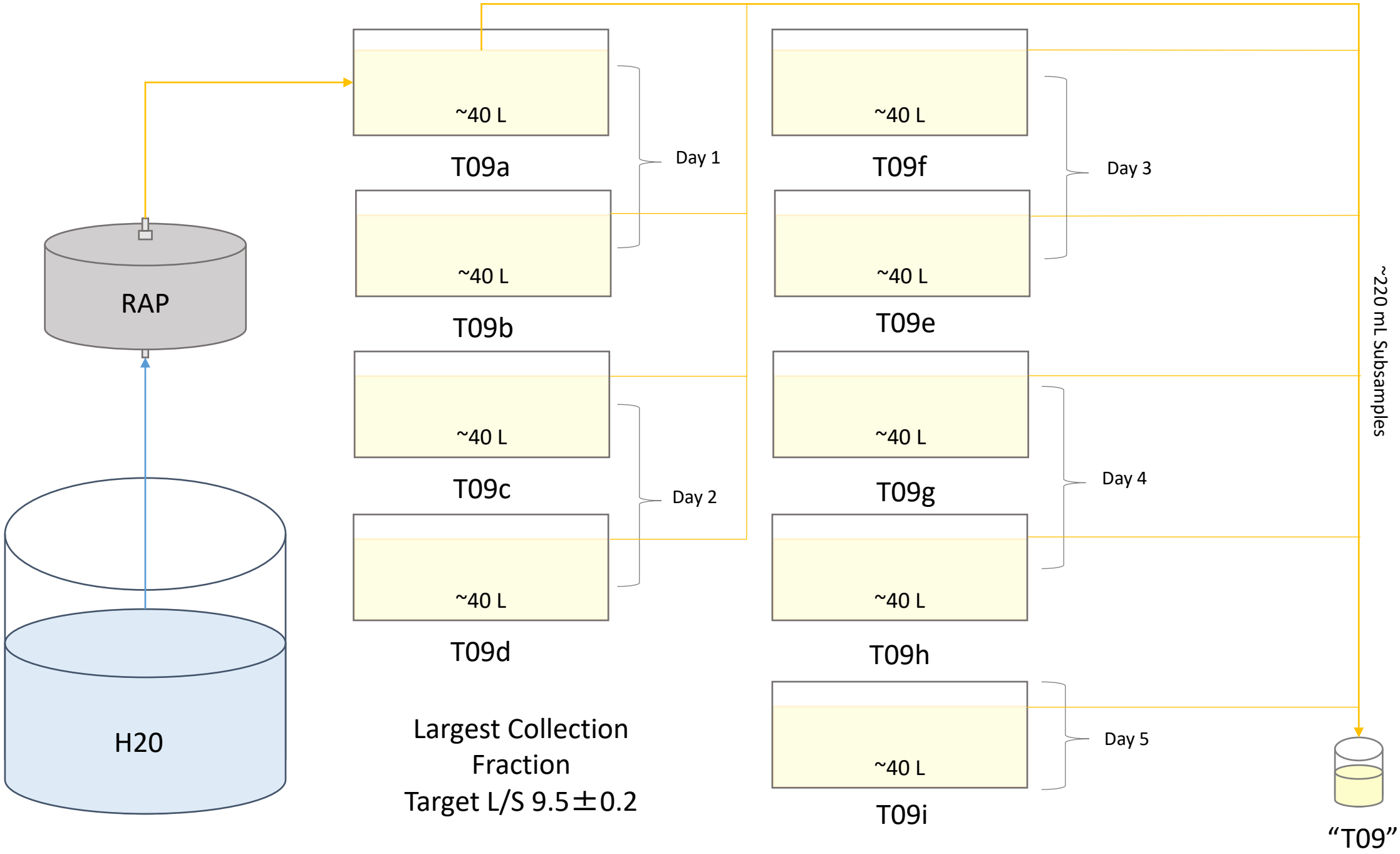
NOTE: Example fraction volumes based on assumed packing mass of 300 g-dry

Smallest Collection Fraction
Target L/S 0.2±0.1



Our Fraction Volumes	
L	Gal
16	3.5
24	5.3
40	8.8
40	8.8
40	8.8
200	44
40	8.8
360	79
40	8.8

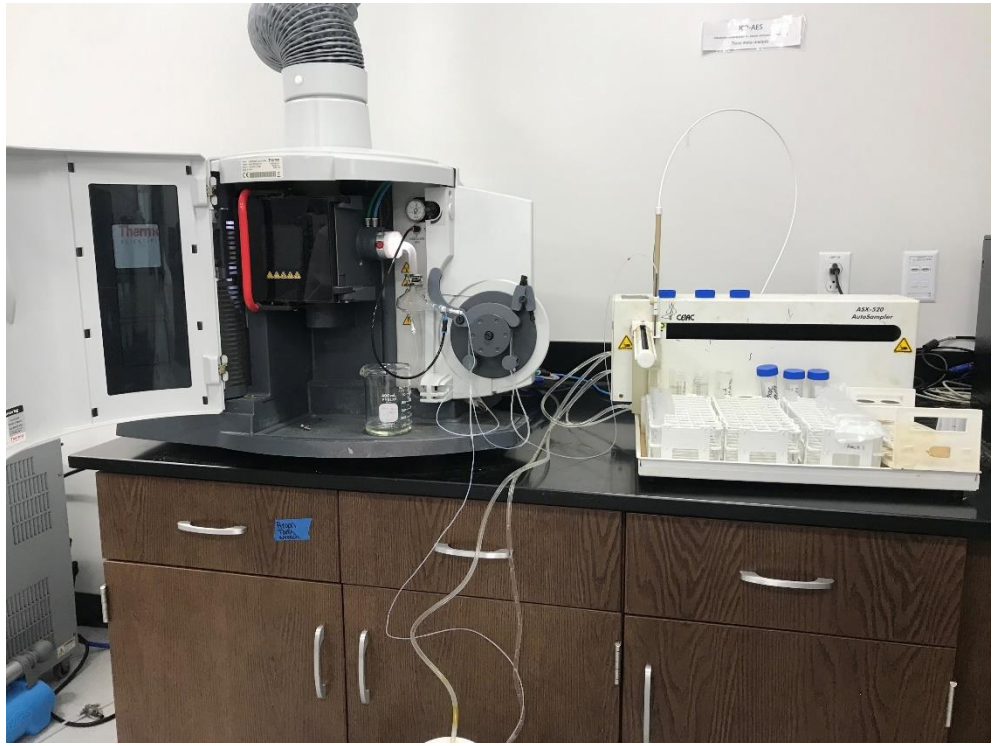
Approximately 80 kg sample


RAP
H20
~40 L
T09a
~40 L
T09b
~40 L
T09c
~40 L
T09d
Day 1
Day 2
~40 L
T09f
~40 L
T09e
~40 L
T09g
~40 L
T09h
~40 L
T09i
Day 3
Day 4
Day 5
~220 mL Subsamples
Largest Collection Fraction
Target L/S 9.5±0.2
“T09”

Metals Analysis

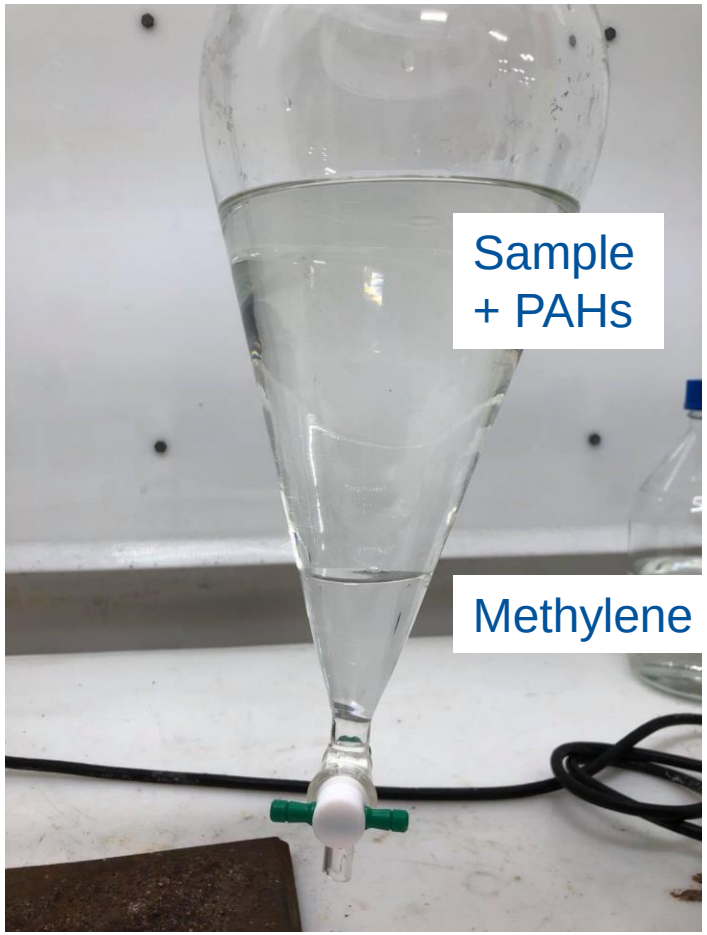
50mL subsample

Digestion and Prep

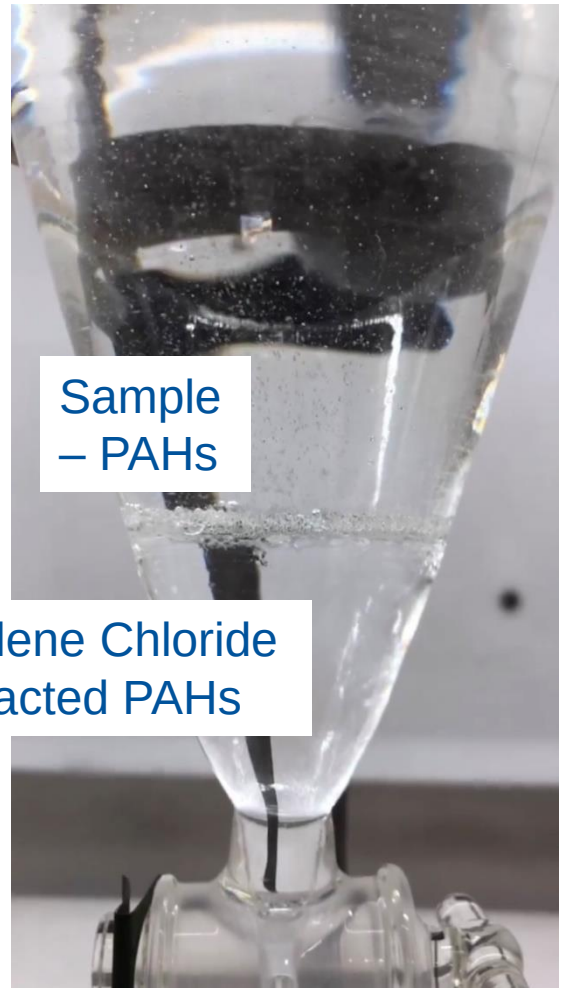


ICP-AES

PAH Extraction



X 3



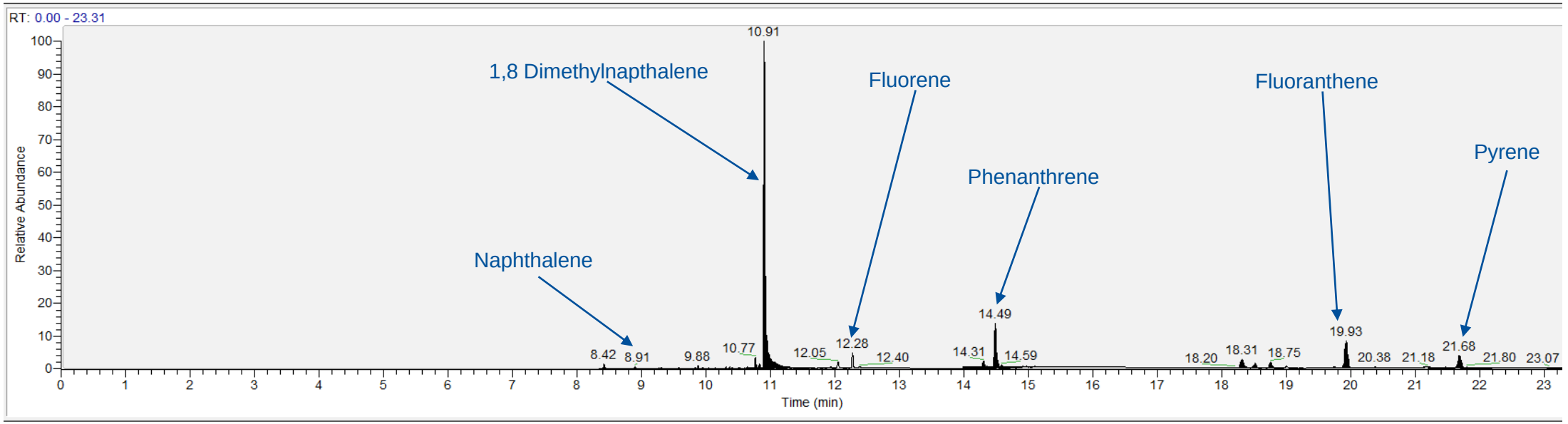
PAH Concentration

180mL Methylene Chloride + PAHs

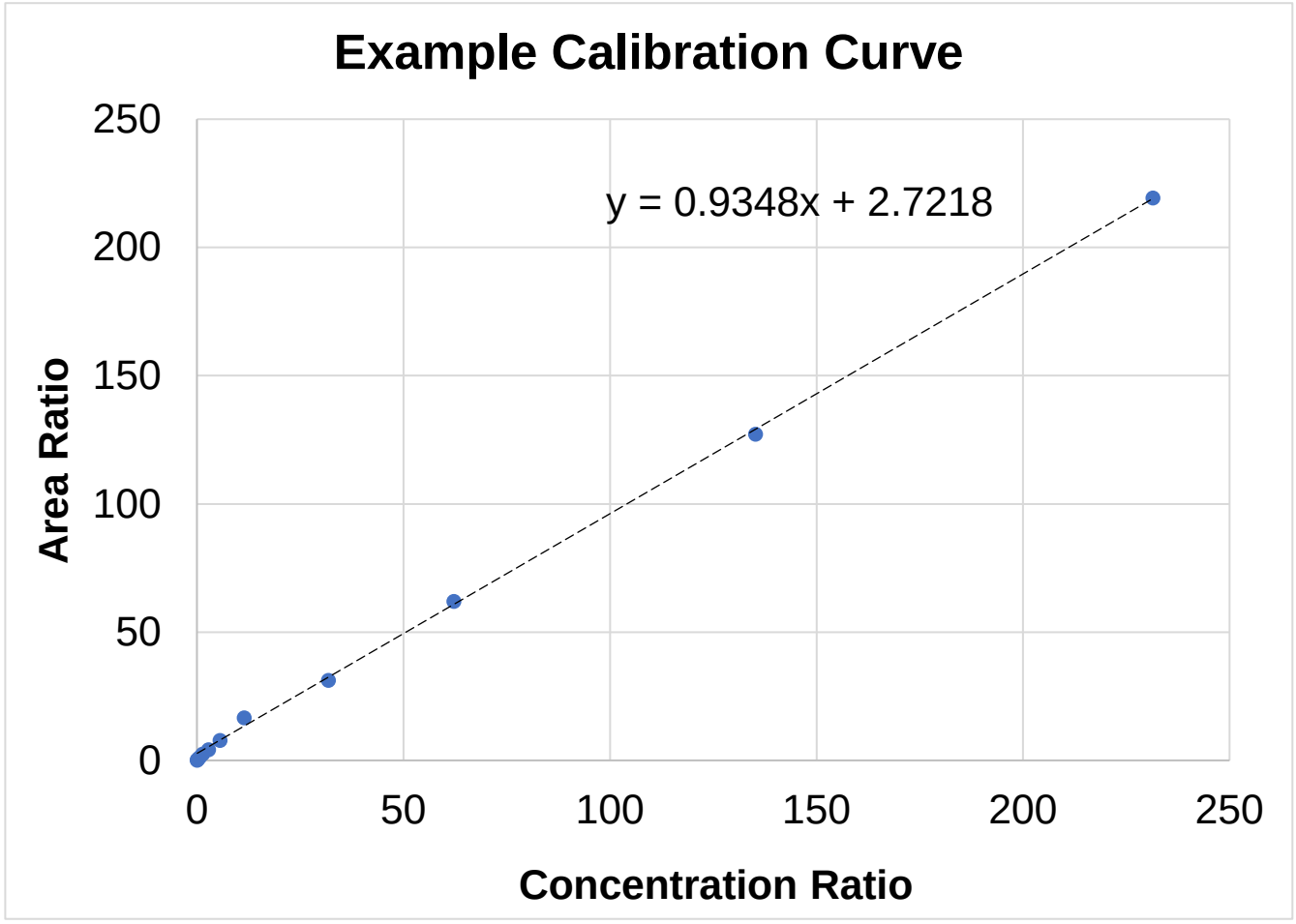
1mL Methylene Chloride + PAHs

GC/MS Triple Quadrupole

Example GC/MS Output

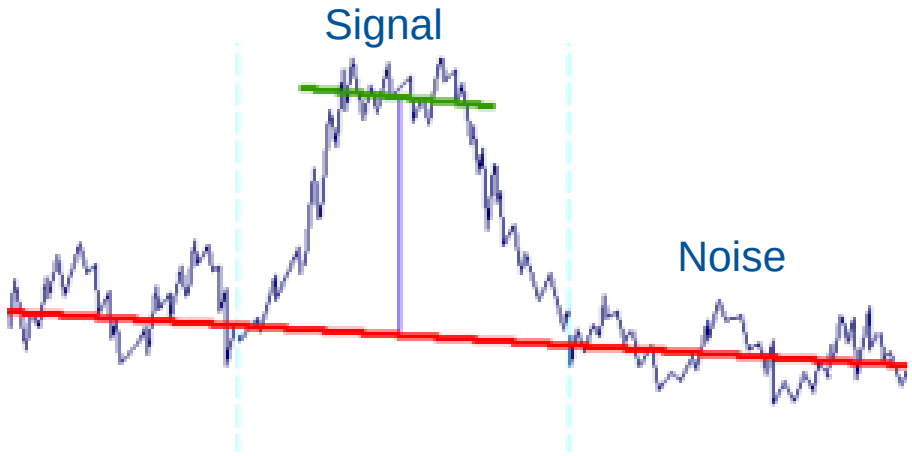


PAH Quantitation Simplified



- Integrate peaks and compare to calibration curve
- Target range: 0.01 ug/L to 80 ug/L

Limit of Detection = Signal > 3x Noise



PAHs

Study	EPA 16 PAHs	Emerging PAHs
Kriech, 1991	X	X (+13)
Brantley & Townsend, 1999	X	
Morse et al., 2001		
Norin & Stromvall, 2004	X	
Legret et al., 2005	X	
Birgisdottir et al., 2007	X	
Kang et al., 2005		
Shedivy et al, 2012	<	X (+2)
Townsend et al., 2013	<	
Hoy et al., 2016		
Roque et al., 2016		
Aydilek et al., 2017		
Mehta et al., 2017	<	X (+2)
Yang et al., 2020	<	
Mijic et al., 2020		
This study, 2022	X	X (+23)

Our 39 PAHs of Interest

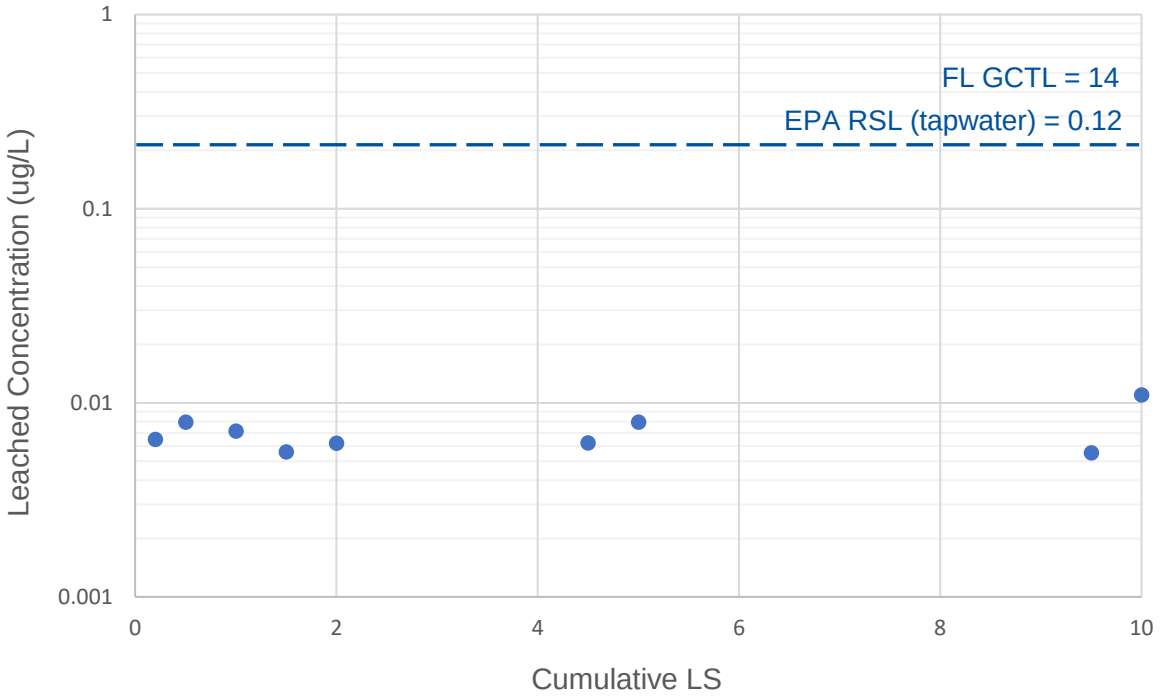
Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

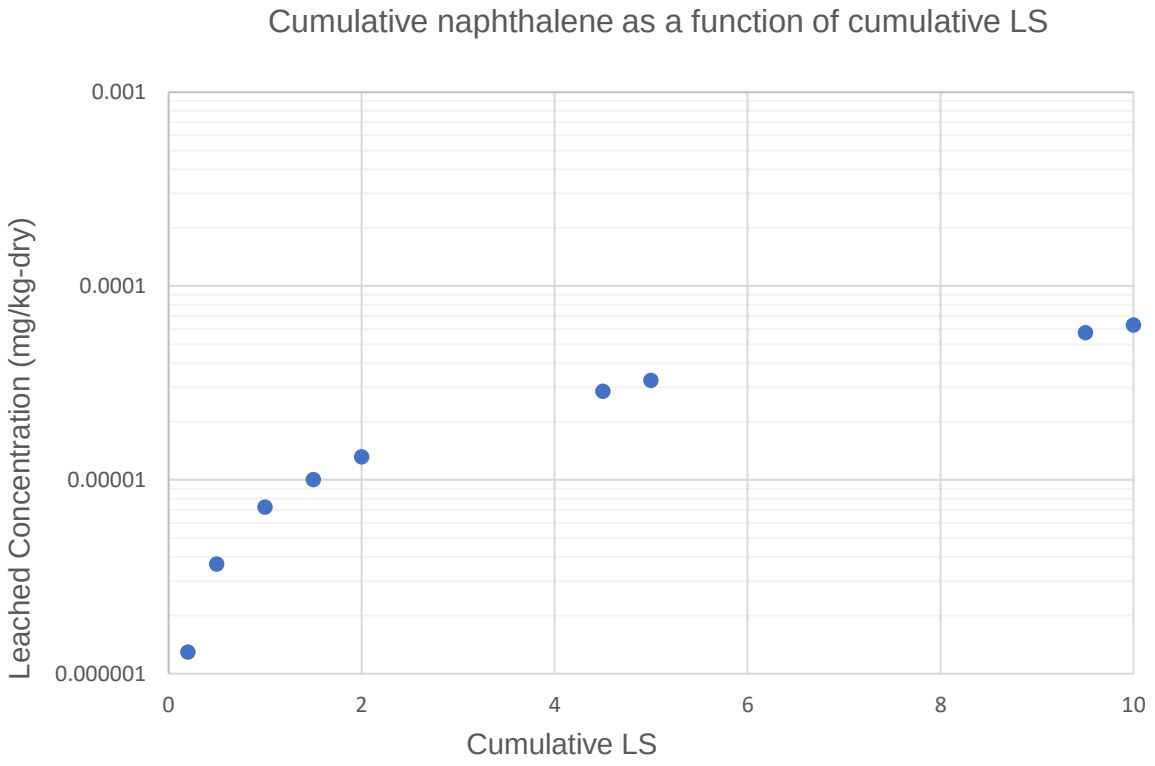
1-Methylnaphthalene
2-Methylnaphthalene
1,2-Dimethylnaphthalene
1,6-Dimethylnaphthalene
2,6-Dimethylnaphthalene
1,7-Dimethylphenanthrene
1-Methylfluoranthene
3-Methylfluoranthene
1-Methylpyrene
4-Methylpyrene
Retene
3-Methylchrysene
6-Methylchrysene
Biphenyl
Perylene

Benzo[e]pyrene
Benzo[j]fluoranthene
Benzo[c]phenanthrene
Dibenz[a,j]acridine
Dibenzo[a,l]pyrene
5-Methylchrysene
1,8-Dimethylnaphthalene
9-Chloroanthracene

EPA 16

1314 Leaching as a Function of L/S – Example Data Jacksonville





$$Weighted\ Leached\ Concentration = C_{0.2LS} * \left(\frac{0.2}{10}\right) + C_{0.5LS} * \left(\frac{0.3}{10}\right) + C_{1LS} * \left(\frac{0.5}{10}\right) + \cdots$$

This Sample	Highest Observed (ug/L)	Weighted Average Concentration (ug/L)
Naphthalene	0.011	0.0063

EPA 16 Exceedances

Existing studies:

- Most below detection limits
- Some exceedances seen for naphthalene, benz(a)anthracene, benzo(a)pyrene, dibenz(a,h)anthracene

Sample	Exceedance of EPA RSL?	Exceedance of FL GCTL?
Ft Pierce	-	-
Gainesville	-	-
Jacksonville	-	Dibenz(a,h)anthracene, <LOD (0.016)
SR-55	-	Dibenz(a,h)anthracene, <LOD (0.016)
Tampa	-	-
Wildwood	-	-

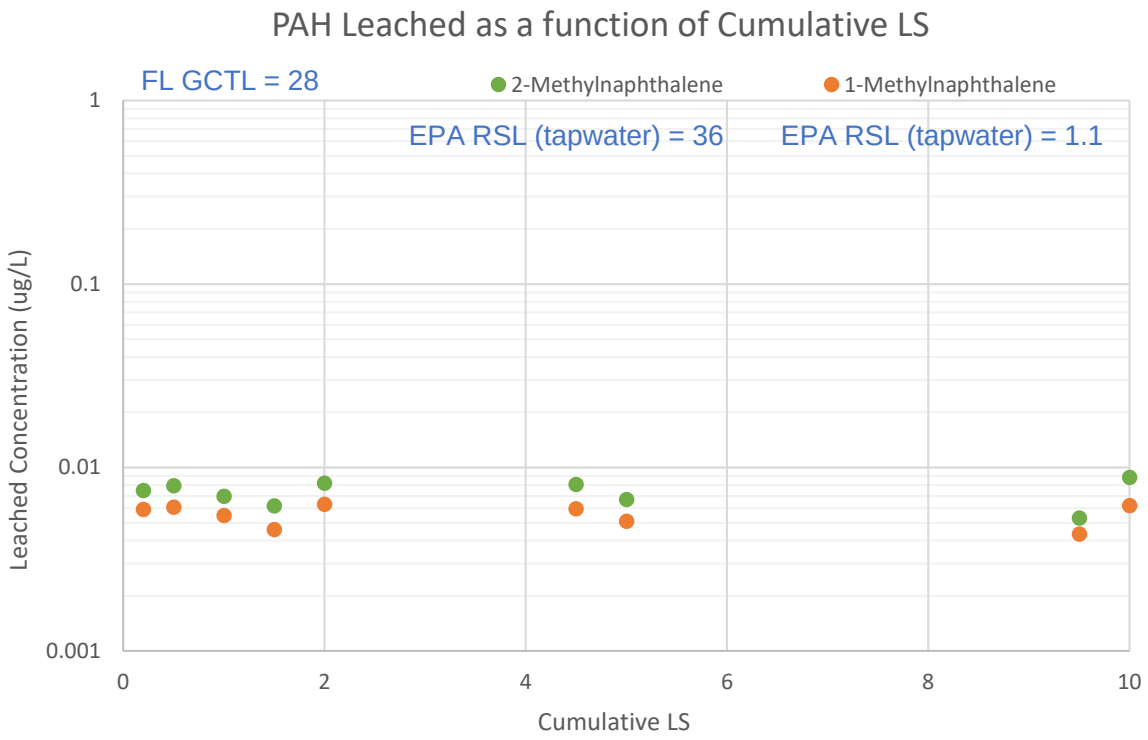
*Using highest concentration leached

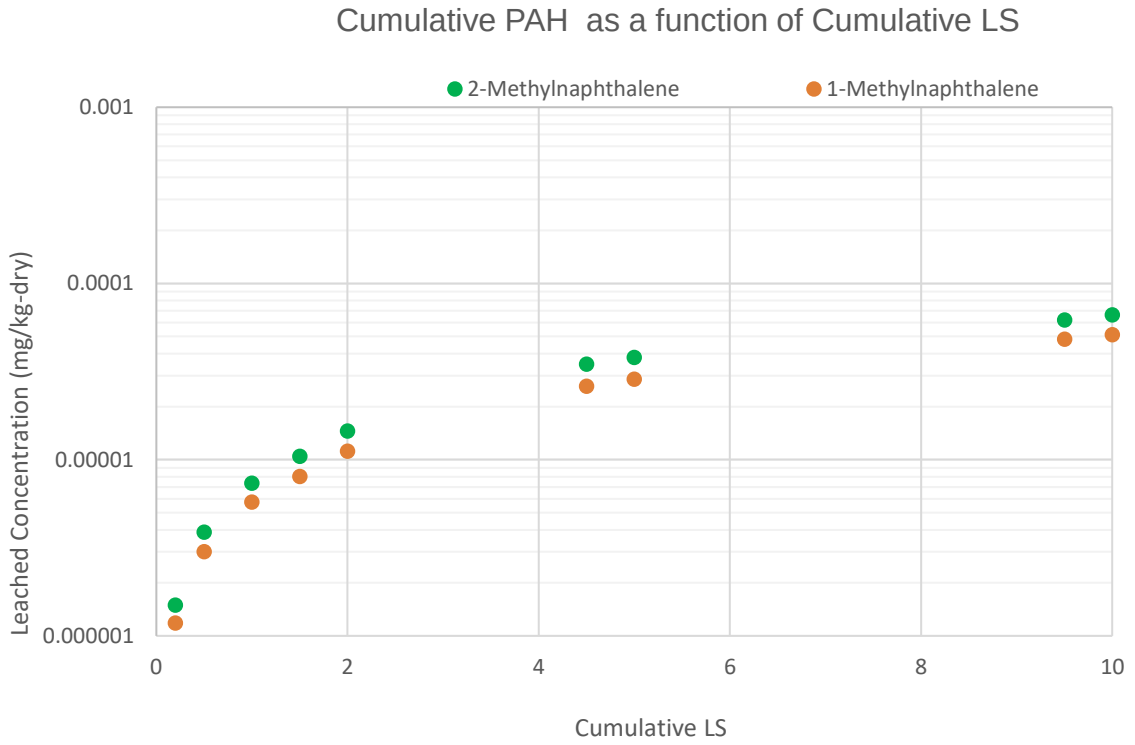
Exceedance comparison to existing column studies

Compounds	This study, DI	Legret et al., DI	Birgisdottir et al., DI	Brantley & Townsend, SPLP	Townsend et al., SPLP	Yang et al., Acidified Solution	Norin & Stromvall, Acidified Solution
Acenaphthene							
Acenaphthylene							
Anthracene							
Benz(a)anthracene			X				
Benzo(a)pyrene							
Benzo(b)fluoranthene							
Benzo(g,h,i)perylene							
Benzo(k)fluoranthene							
Chrysene							
Dibenz(a,h)anthracene	?	X	X				X
Fluoranthene							
Fluorene							
Indeno(1,2,3-cd)pyrene							
Naphthalene			X				X
Phenanthrene							
Pyrene							

Emerging PAHs

1314 Leaching as a Function of L/S – Example Data Jacksonville





This Sample	Highest Observed (ug/L)	Weighted Average Concentration (ug/L)
2-Methylnaphthalene	0.0088	0.0066
1-Methylnaphthalene	0.0063	0.0051

Emerging PAHs – Context to Associated Risks

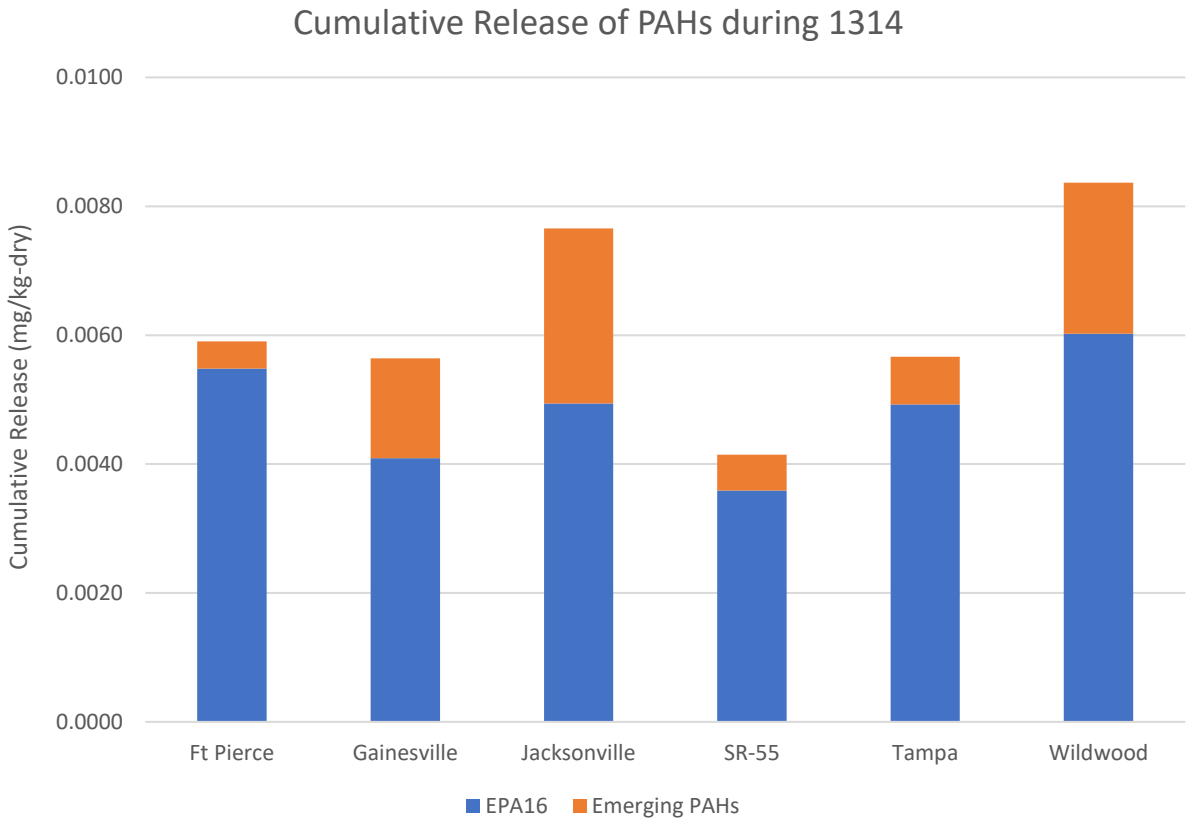
- Five emerging PAHs in our analysis with EPA RSLs were below thresholds
- Six of the other 18 emerging compounds have BaP equivalents in the literature

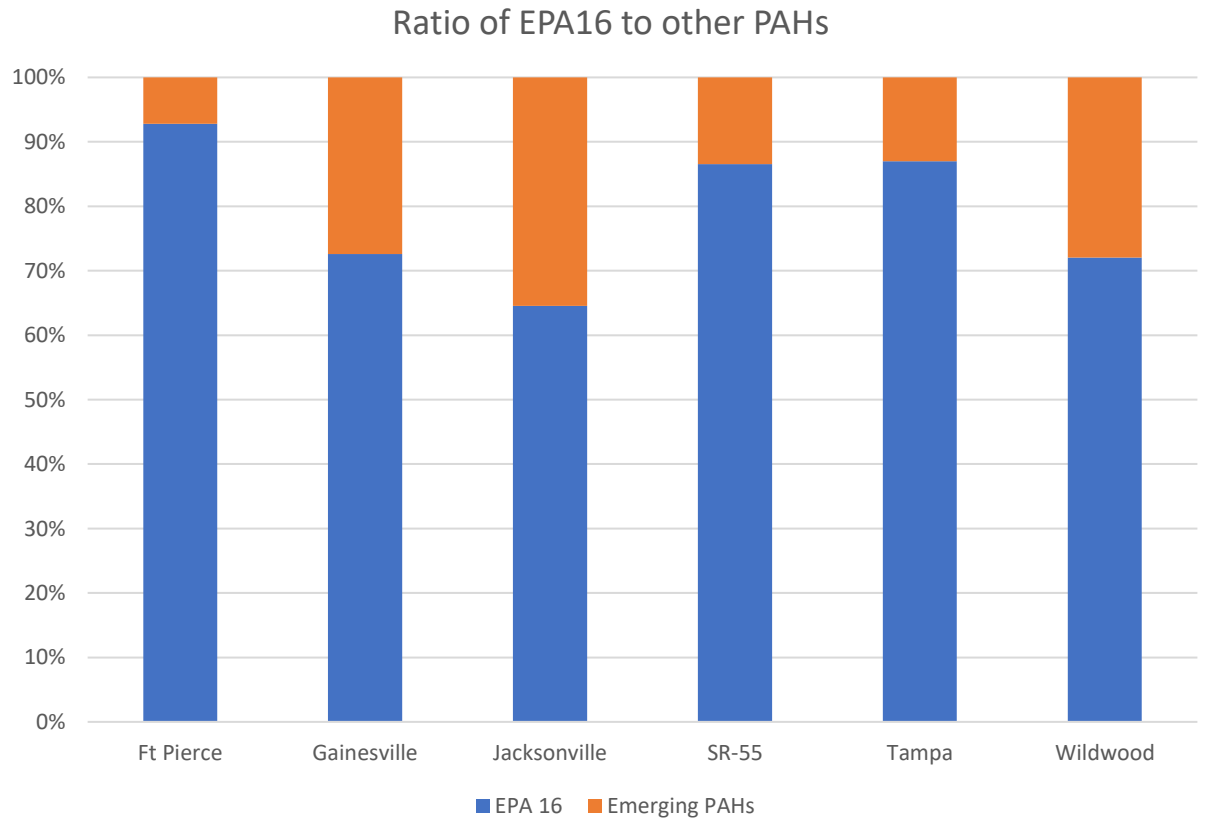
	BaP Toxic Equivalence Quotient (TEQ)	Converted to "EPA RSL" (ug/L)	Exceedance in any sample?
7H-Benzo(c)fluorene	20	0.00125	2, < LOD (0.063 ug/L)
1-Methylpyrene	0.1	0.25	-
Benzo(j)fluoranthene	0.1	0.25	-
Dibenz(a,j)acridine	0.1	0.25	-
Anthanthrene	0.1	0.25	-
Dibenzo(a,l)pyrene	10	0.0025	-

Richter-Brockmann & Achten, 2018

- Among the remaining 12 emerging compounds, 5 naphthalene-related compounds were found above LOD

PAH contributions – EPA 16 & Emerging

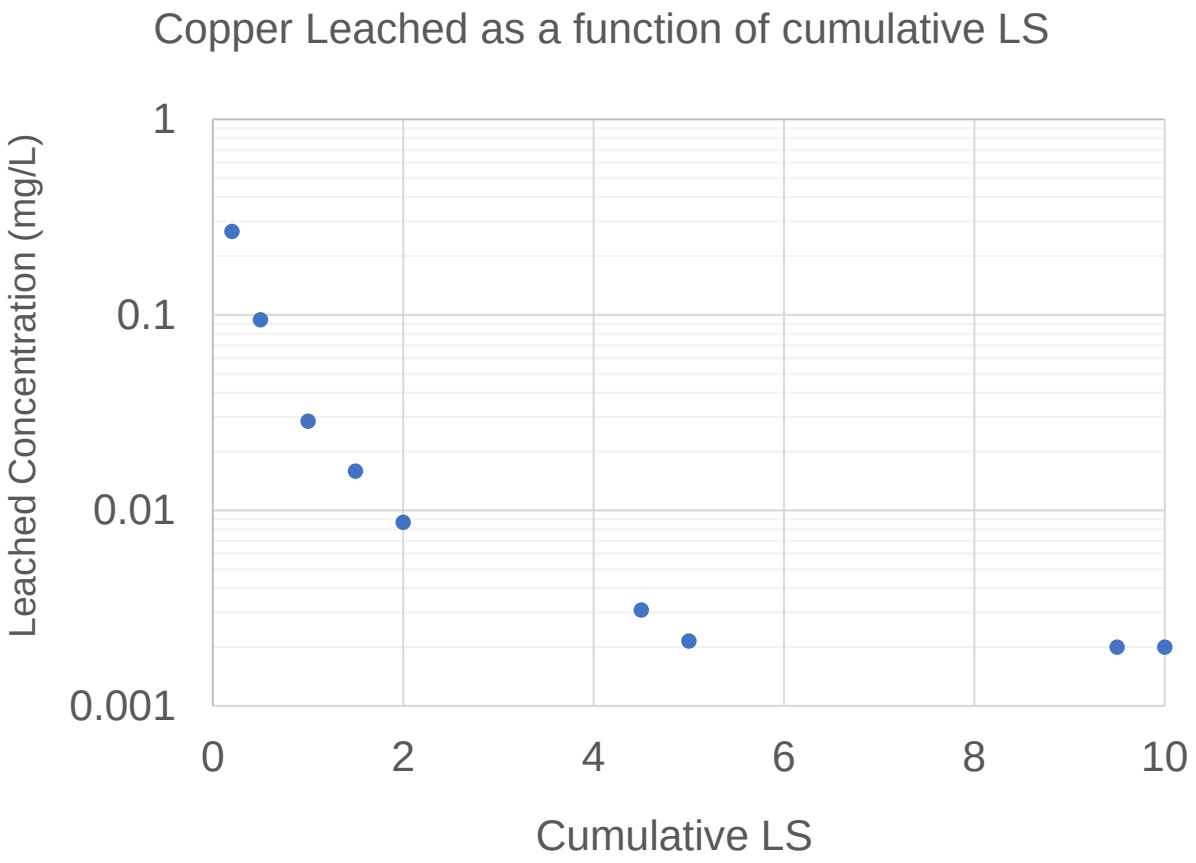


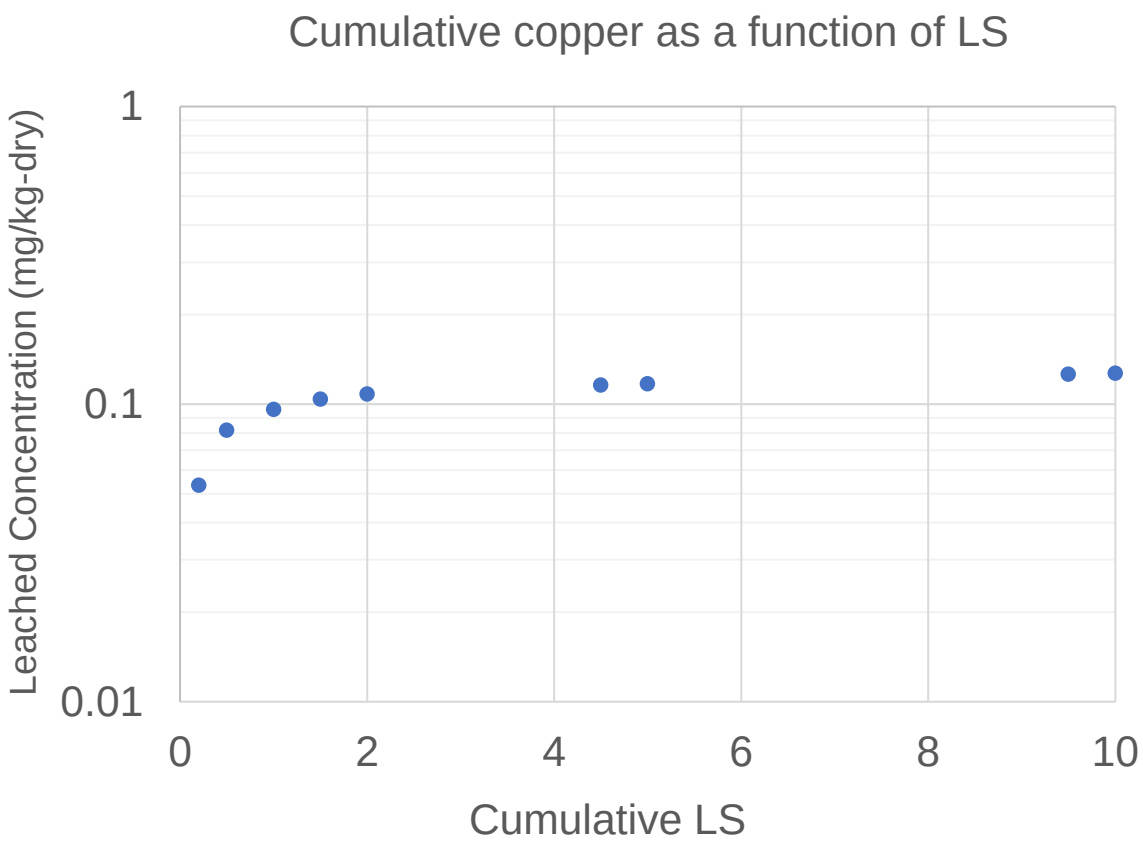


* Assuming LOD concentrations for compounds below quantitation levels

Metals

1314 Leaching Results – Example Data Jacksonville





Threshold Exceedances – FL GCTL

	Ft Pierce	Jacksonville	SR-55	Tampa	Wildwood
Aluminum	**X**			**X**	
Arsenic		X			
Antimony					
Barium					
Boron					
Cadmium					
Chromium					
Copper					
Iron					
Lead					
Manganese					
Molybdenum		X		X	
Nickel		X			
Selenium					
Silver					
Vanadium		**X**			

*Table using highest concentration leached, Vanadium & Aluminum still in exceedance considering weighted concentration

Implications & Future Work

Conclusions

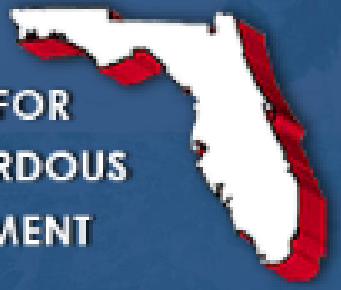
- PAHs Overall
  - EPA 16 PAHs are dominant in leachate
  - Comparing emerging compound concentrations in leachate versus totals analysis
    - <1% leachability
- EPA 16:
  - No PAH exceedances were observed, except for dibenz(a,h)anthracene (FL GCTL), where concentrations were below detection limits
- Emerging 23:
  - No exceedances of EPA RSLs were observed, except for 7H-benzo(c)fluorene (theoretical EPA RSL), where concentrations were below detection limits
- Metals (average leached concentrations), exceedances in aluminum and vanadium
- **Using the most representative leaching method, EPA 1314, and the most expansive PAH analysis – leaching data does not differ meaningfully from previous studies; data continue to suggest that PAH and metals leaching from RAP stockpiles are unlikely to result in exceedances of risk-based limits in groundwater**

Looking ahead

- Hinkley Center report
  - Target: June 10th to TAG for review
- Semi-quantitative analysis of < LOD compounds
- Questions?

UF Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

HINKLEY CENTER FOR SOLID AND HAZARDOUS WASTE MANAGEMENT



Thank you

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE