PAHs and Phthalate Monitoring at Urban Waters Summer-Winter 2011

Justin P. Miller-Schulze, Ph.D.
Research Associate
Baker Laboratory/Center for Urban Waters
December 20 2011

Welcome

- Introduction
- Sampling
- Analysis
- Data
- Future Work

Objective (s)

- Wanted to get some preliminary data on PAHs & phthalates/**get analytical laboratory 'up and running**'
- Initial project funding to purchase sampling equipment to study phthalate deposition
  - Atmospheric deposition and surface runoff are significant source of these species in Puget Sound

Quick Background-PAHs

- Polycyclic Aromatic Hydrocarbons (PAHs) known to be both carcinogenic and mutagenic
- PAHs are also employed as markers of combustion processes
- Part of the Puget Sound Partnerships‘s Action Agenda is to ‘Reduce the Source of Toxic Chemical Entering Puget Sound’
  - PAH levels in fish explicitly stated as part of this goal

Quick Background-Phthalates

- Phthalates primarily used as plasticizers in products such as PVC (poly vinyl chloride) piping[1]
  - BBP (benzyl butyl) predominant stain-resistant plasticizer in PVC
  - DBP (di *n*-butyl) plasticizer in nail polish, explosives, rocket propellant
  - Etc….
- Most significant (or studied) route of exposure seems to be ingestion (food, cosmetics, toys)
  - Not much data on outdoor concentrations, as indoor exposures assume to be much more prevalent
- Primary health concern is with reproductive health and/or fetal development

Sampling

- TISCH Corp Hi-Vol Air Sampler located on roof of Center for Urban Waters
  - Approximate height of sampler = **16.8 m** above sea level
- Two Phases of Samples Collected:
  - Total suspended particulate (TSP) w/ quartz filters for particulate-phase species
  - Gas-phase w/ polyurethane foam (PUF) media for gas-phase species

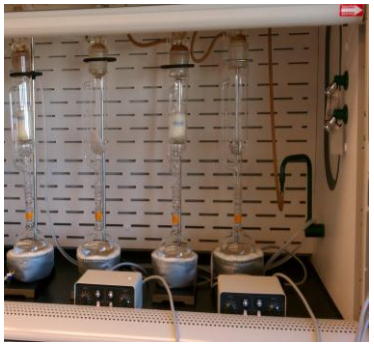
Sampling

- Sampling done on EPA's 1-in-6 day sampling schedule
- Flow rate = ~180 L/min
- Samples collected are 24-hour integrated samples
  - Total volume sampled= ~ 275 m^3
- Meteorological data collected on w/ 0.5 hour resolution at co-located met station

Sampling/Analysis

Step 1: Air Sampling
EPA 1-in-6 Day
Schedule

Step 2: Soxhlet
Extraction



Step 3:
Evaporation/Concentration
(Rotovap)

Step 4:
Evaporation/Concentration
(Turbovap)

Step 5: Analysis via
GCMS

Spike with Recovery
(Surrogate) standards here

Spike with quantification
(Internal) standards here

Quantification of Analytes

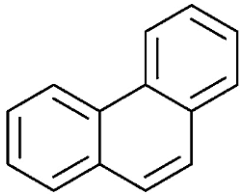
- Sequence specific calibration curves used to calculate mass of analytes/sample
  - 1/X weighting employed due to linear range issues
- Limit-of-Detection (LOD) calculated as:

$$LOD = CONC_{AVG\ (methodblank)} + 3x\ (Std\ Dev_{methodblank})$$

- Different blanks used for filter and PUF samples

	Gas-Phase (PUF)			Particulate-Phase (Filter)		
	Surrogate % Recovery (RSD)	LOD Nominal Air Concentration (ng/m³)	% Above Limit of Detection	Surrogate % Recovery (RSD)	LOD Nominal Air Concentration (ng/m³)	% Above Limit of Detection
1-Methyl Naphthalene	28 (90)	0.283	**90**	18 (111)	0.160	6
2-Methyl Naphthalene	28 (90)	0.129	**90**	18 (111)	0.069	6
Acenaphthylene	58 (48)	0.023	**90**	54 (24)	0.009	41
Acenaphthene	58 (48)	0.088	**95**	54 (24)	0.014	35
Phenanthrene	77 (42)	0.178	**95**	86 (12)	0.039	**88**
Anthracene	77 (42)	0.062	**95**	86 (12)	0.131	29
Fluoranthene	77 (42)	0.080	**100**	86 (12)	0.057	**76**
Pyrene	77 (42)	0.063	**100**	86 (12)	0.035	**82**
Benzo (a) Anthracene	65 (44)	0.004	**62**	59 (38)	0.067	29
Chrysene	65 (44)	0.089	**57**	59 (38)	0.147	35
Benzo (a) Pyrene	65 (44)	0.183	0	59 (38)	0.066	12
Indeno (1,2,3-c,d) Pyrene	65 (44)	0.038	0	59 (38)	0.086	29
Dibenz (a,h) Anthracene	65 (44)	0.015	10	59 (38)	0.341	0
Benzo (g,h,i) Perylene	65 (44)	0.026	0	59 (38)	0.085	35
Dimethyl Phthalate	58 (48)	0.121	**100**	54 (24)	0.016	**100**
Diethyl Phthalate	58 (48)	4.020	0	54 (24)	0.422	**100**
Di-n-Butyl Phthalate	65 (44)	11.178	14	86 (12)	3.410	**100**
Butyl Benzyl Phthalate	65 (44)	0.178	33	59 (38)	0.233	**59**
Di-ethylhexyl Phthalate	65 (44)	3.098	10	59 (38)	1.621	**94**
Di-n-Octyl-Phthalate	65 (44)	0.097	38	59 (38)	0.782	12

PAHs	GAS-PHASE (PUF) (n=21)				PARTICULATE PHASE (FILTER) (n=17)			
	AVG (ng/m^3)	Median (ng/m^3)	Std Dev	% Above LOD	AVG (ng/m^3)	Median (ng/m^3)	Std Dev	% Above LOD
1-Methyl Naphthalene	4.85	1.69	7.48	**90**				6
2-Methyl Naphthalene	2.04	0.91	2.98	**90**				6
Acenaphthylene	0.86	0.20	1.37	**90**				41
Acenaphthene	1.78	1.20	1.50	**95**				35
Phenanthrene	11.8	10.5	7.61	**95**	0.092	0.099	0.054	**88**
Anthracene	7.08	1.05	12.9	**95**				29
Fluoranthene	2.49	2.06	1.36	**100**	0.121	0.099	0.098	**76**
Pyrene	1.19	1.20	0.75	**100**	0.094	0.075	0.091	**82**
Benzo (a) Anthracene	0.02	0.02	0.02	**62**				29
Chrysene	0.13	0.1	0.13	**57**				35



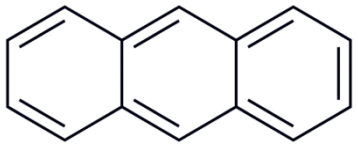
Phenanthrene	GAS-PHASE (PUF) (95% >LOD) G.Mean (ng/m³)	Range	PARTICULATE PHASE (FILTER) (88%>LOD) G.Mean (ng/m³)	Range
CUW	**8.46**	**<0.178-30.6**	**0.076**	**<0.039-0.220**
Baltimore-Winter[a]	12.2	8.3-18	5% Total on Filter	
Baltimore-Summer[a]	>7.5	NA		
<u>Buffalo, NY</u>				
Marina-Winter	2.8	0.90-38		
Marina-Summer	15	3.6-59		
Residential-Winter	3.7	1.4-42		
Residential-Summer	57	19-118		
Highway-Winter	3.6	1.1-26		
Highway-Summer	16	7.9-30		
Seattle (Duwamish)[b]	MAX = 69			

<u>References:</u>

a: Bamford, H.E., Baker, J.E. “Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region”, *Atmos. Environ.,* **2003** (37) 2077-2091

b:Minegishi, T. *Characterization of PAH Composition Patterns in Diesel Emission,* Master’s Thesis, **2006**, University of Maryland, College Park, MD.

c: Puget Sound Clean Air Agency and The University of Washington,“Tacoma and Seattle Area Air Toxics Evaluation” **2010**



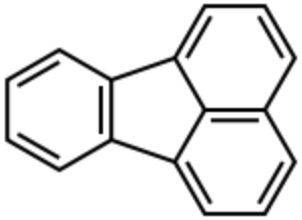
	GAS-PHASE (PUF) (95%>LOD)		PARTICULATE PHASE (FILTER) (29%>LOD)	
Anthracene	G.Mean (ng/m^3)	Range	G.Mean (ng/m^3)	Range
CUW	**1.40**	**<0.03-42.0**		
Baltimore-Winter[a]	0.93	0.330-1.14	8% Total on Filter	
Baltimore-Summer[a]	0.750	0.213-0.4	4% Total on Filter	
Buffalo, NY				
Marina-Winter	0.17	ND-44		
Marina-Summer	0.93	0.27-3.4		
Residential-Winter	0.39	ND-4.8		
Residential-Summer	3.8	1.1-10		
Highway-Winter	0.27	ND-2.9		
Highway-Summer	1.2	0.65-2.7		
Seattle (Duwamish)[b]	0.250 (AVG)			

References:

a: Bamford, H.E., Baker, J.E. “Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region”, *Atmos. Environ.,* **2003** (37) 2077-2091

b:Minegishi, T. *Characterization of PAH Composition Patterns in Diesel Emission,* Master’s Thesis, **2006**, University of Maryland, College Park, MD.

c: Puget Sound Clean Air Agency and The University of Washington,“Tacoma and Seattle Area Air Toxics Evaluation” **2010**



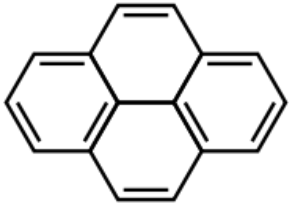
	GAS-PHASE (PUF) (100%>LOD)		PARTICULATE PHASE (FILTER) (76%>LOD)	
Fluoranthene	G.Mean (ng/m^3)	Range	G.Mean (ng/m^3)	Range
CUW	**2.14**	**0.54-5.54**	**0.089**	**<0.057-0.396**
Baltimore-Winter[a]	3.5	2.5-5.74	24% on Filter	
Baltimore-Summer[a]	9.5	7.28-13.5	2% on Filter	
Buffalo, NY[b]				
Marina-Winter	0.53	ND-2.1		
Marina-Summer	6.1	3.1-18		
Residential-Winter	0.85	0.40-2.1		
Residential-Summer	28	13-61		
Highway-Winter	0.74	0.35-1.9		
Highway-Summer	5.7	2.1-23		
Seattle (Duwamish)[c]	MAX = 11			

References:

a: Bamford, H.E., Baker, J.E. “Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region”, *Atmos. Environ.,* **2003** (37) 2077-2091

b:Minegishi, T. *Characterization of PAH Composition Patterns in Diesel Emission,* Master’s Thesis, **2006**, University of Maryland, College Park, MD.

c: Puget Sound Clean Air Agency and The University of Washington,“Tacoma and Seattle Area Air Toxics Evaluation” **2010**



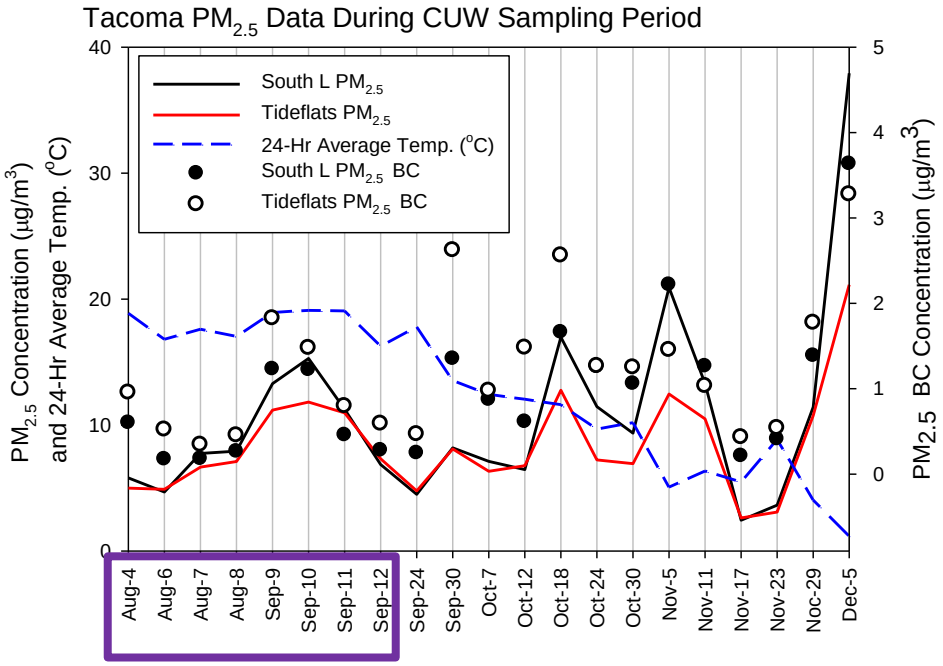
Pyrene	GAS-PHASE (PUF) (100%>LOD) G.Mean (ng/m³)	Range	PARTICULATE PHASE (FILTER) (82%>LOD) G.Mean (ng/m³)	Range
CUW	**1.00**	**0.22-3.73**	**0.066**	**0.028-0.389**
Baltimore-Winter[a]	3.4	2.24-6.00	23% Filter	
Baltimore-Summer[a]	5.8	3.94-6.75	2% Filter	
Buffalo, NY				
Marina-Winter	0.38	0.20-1.4		
Marina-Summer	2.9	1.6-7.5		
Residential-Winter	0.57	0.29-1.3		
Residential-Summer	11	5.3-24		
Highway-Winter	0.56	0.26-0.4		
Highway-Summer	2.8	1.3-9.6		
Seattle -Duwamish[b]	MAX = 7			

References:

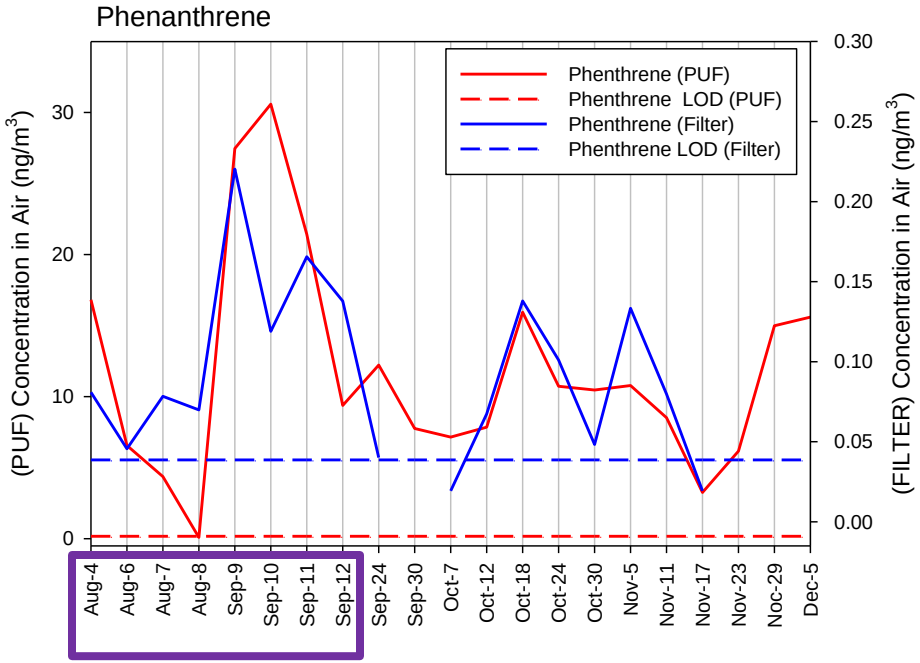
a: Bamford, H.E., Baker, J.E. “Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region”, *Atmos. Environ.,* **2003** (37) 2077-2091

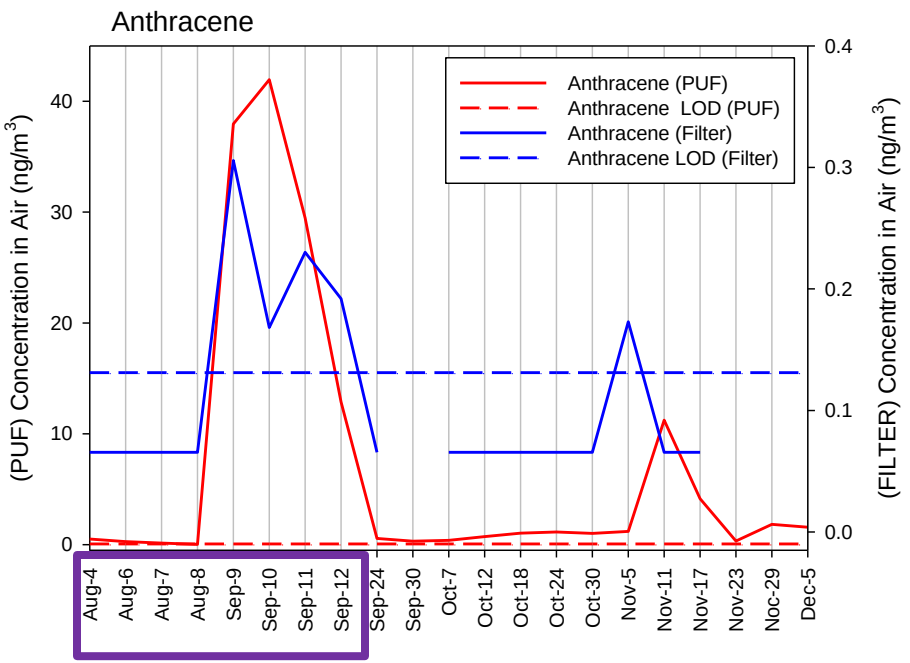
b:Minegishi, T. *Characterization of PAH Composition Patterns in Diesel Emission,* Master’s Thesis, **2006**, University of Maryland, College Park, MD.

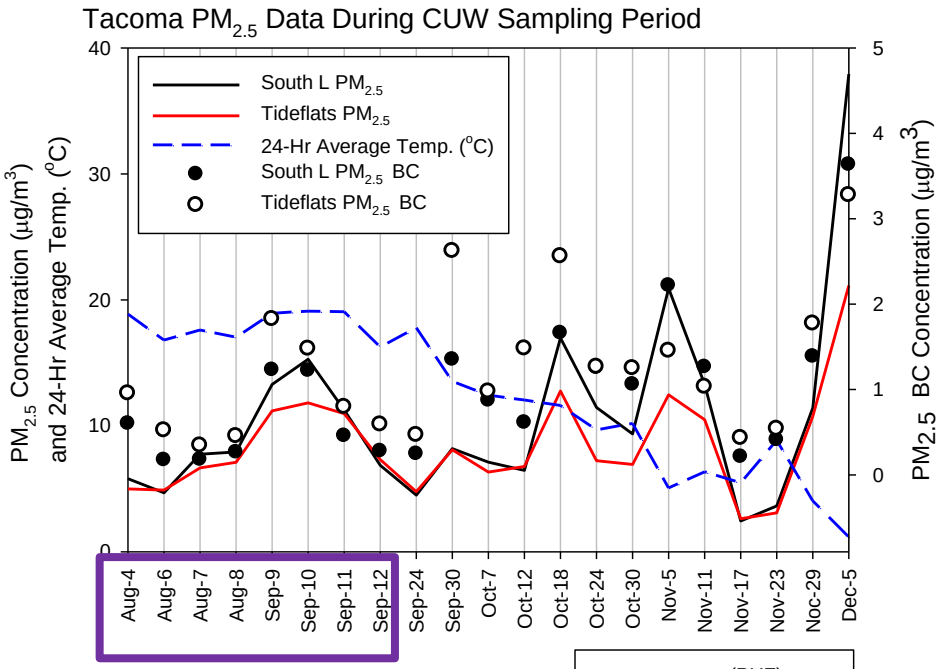
c: Puget Sound Clean Air Agency and The University of Washington,“Tacoma and Seattle Area Air Toxics Evaluation” **2010**



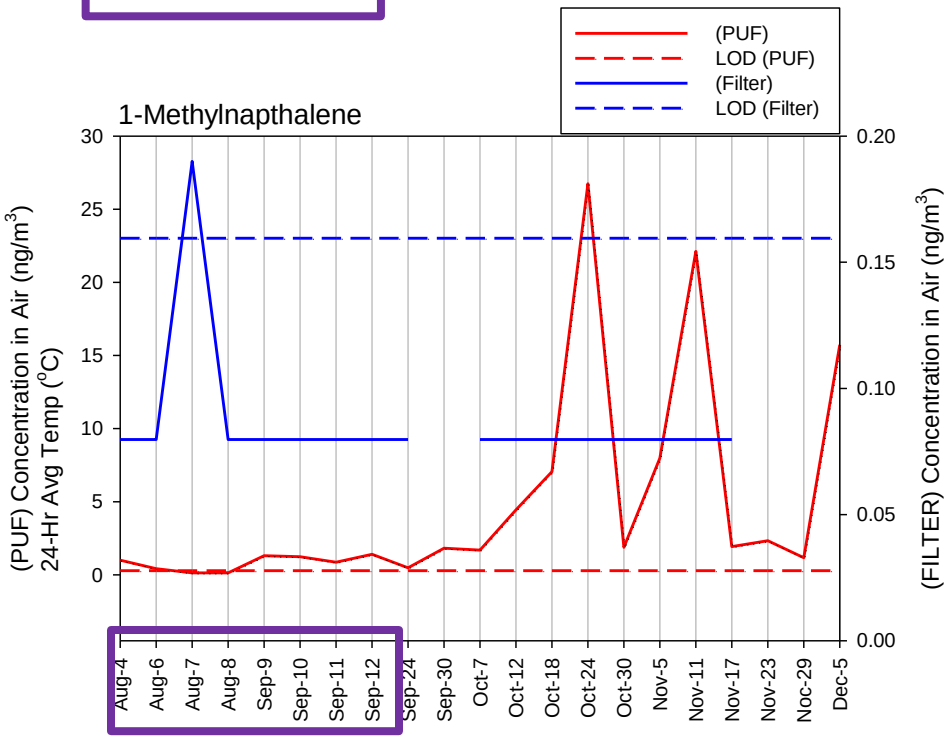
- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data

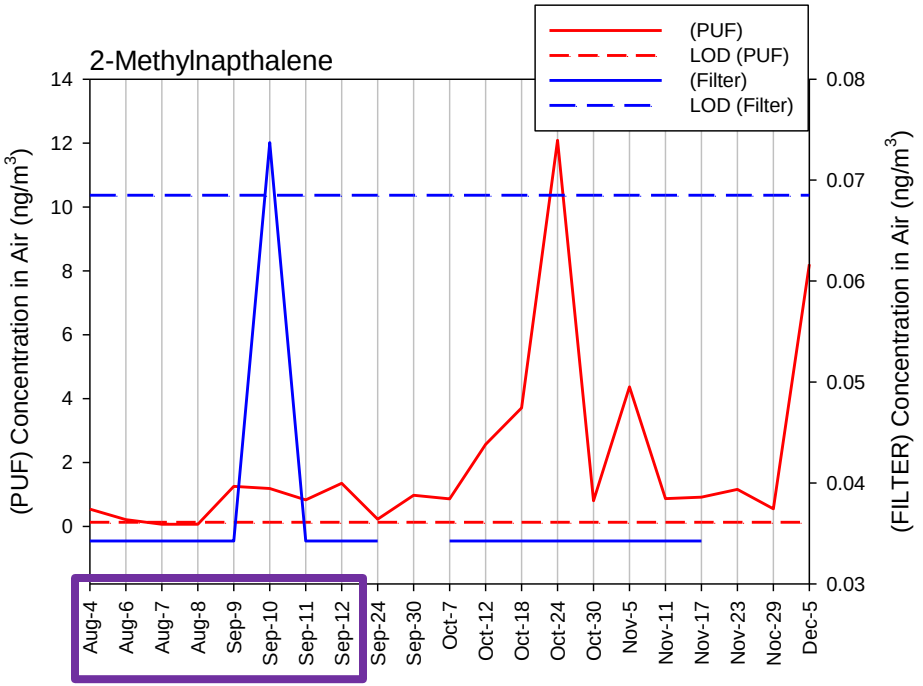


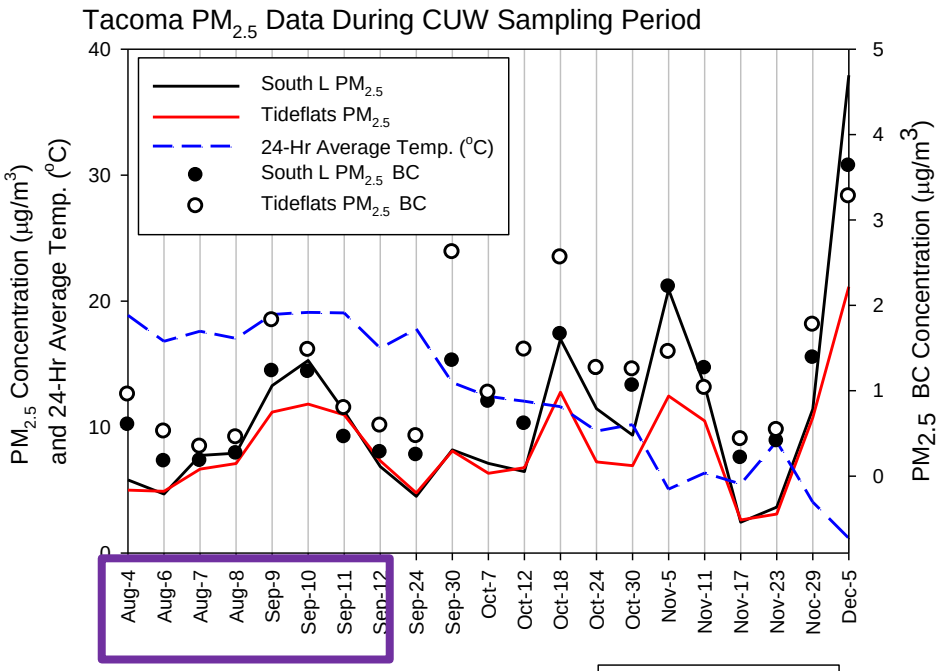




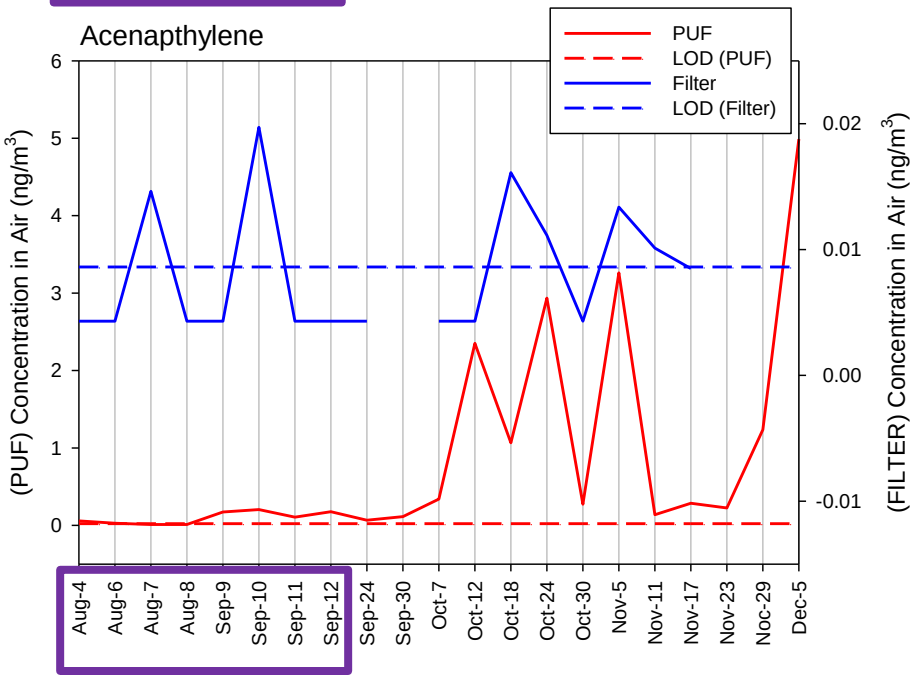
- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data

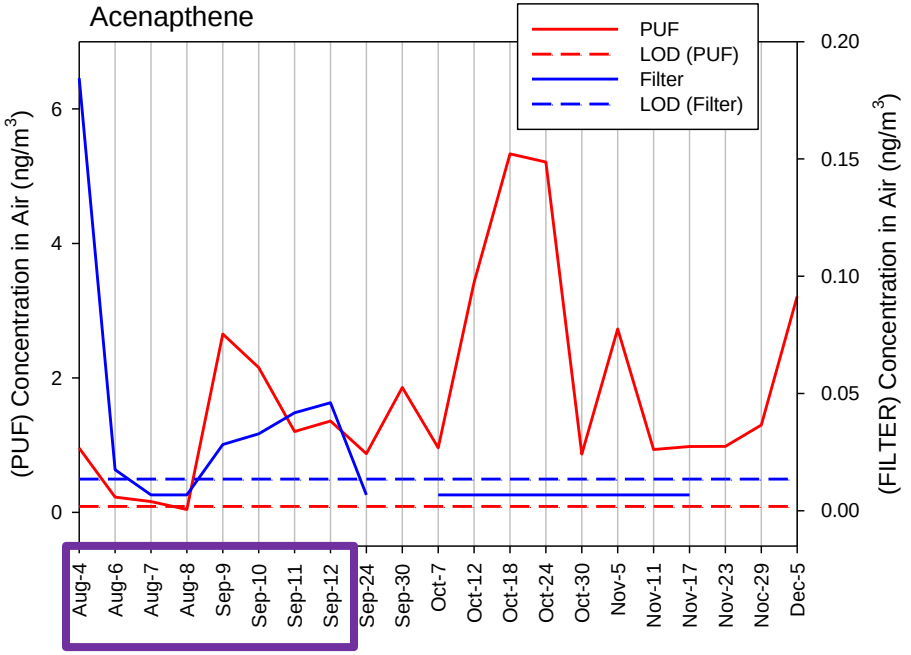


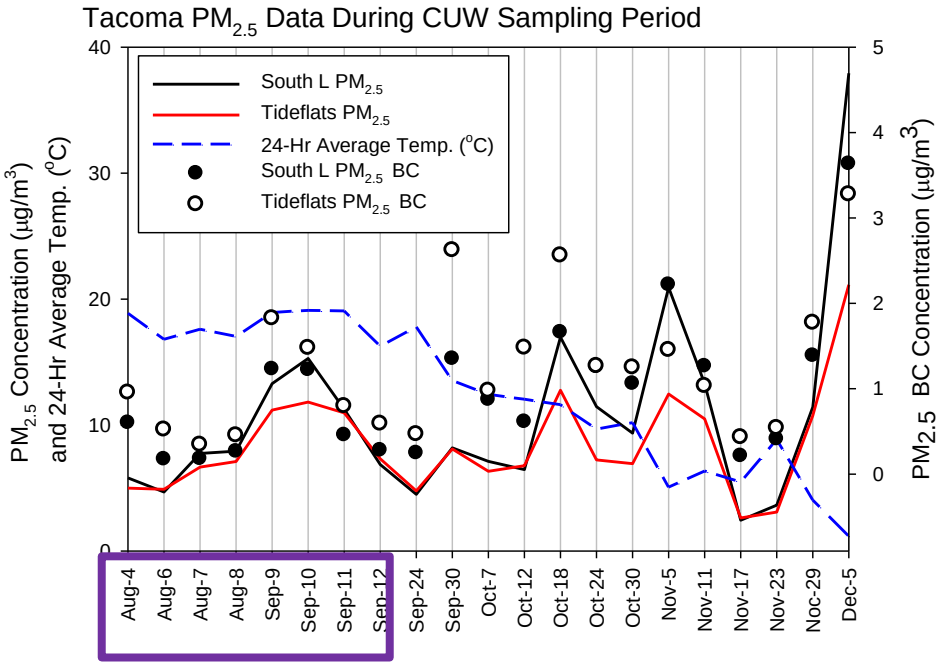




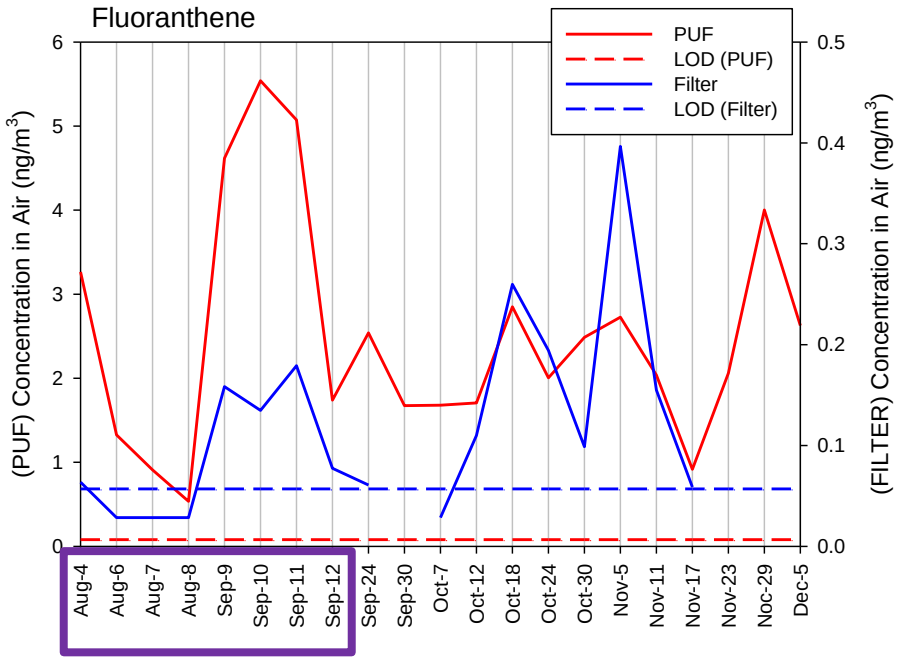
- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data

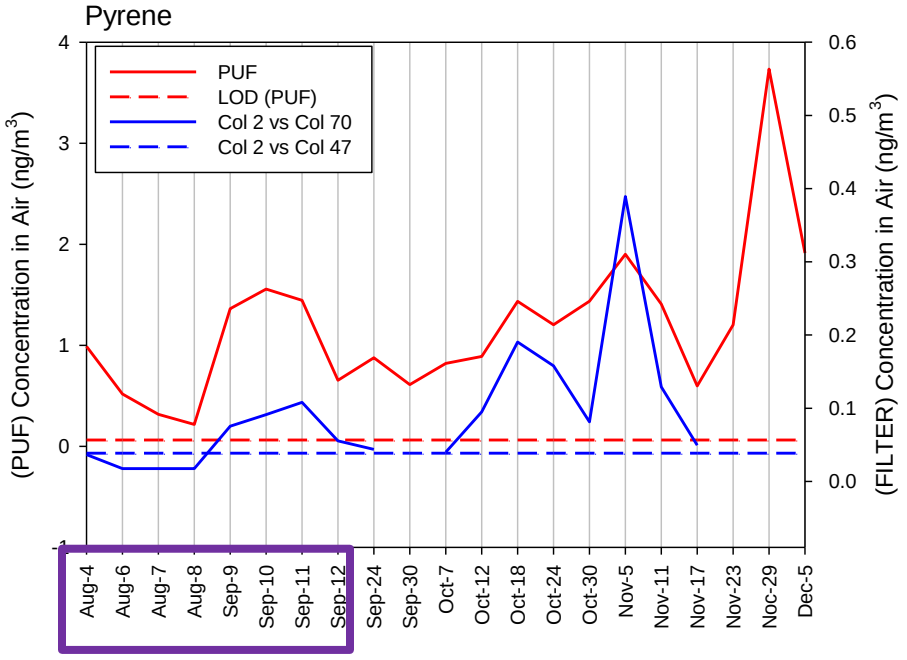


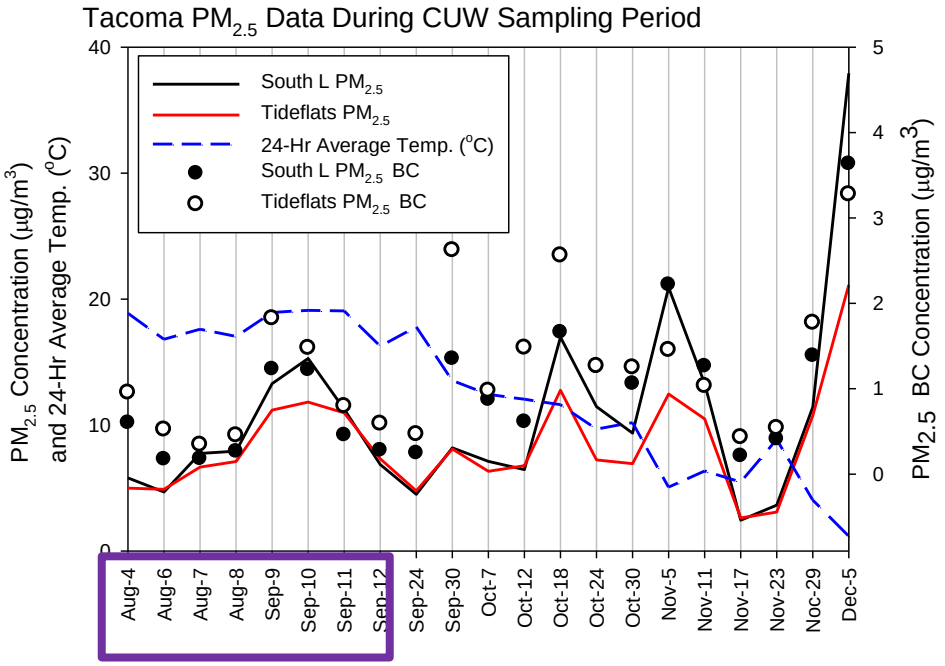




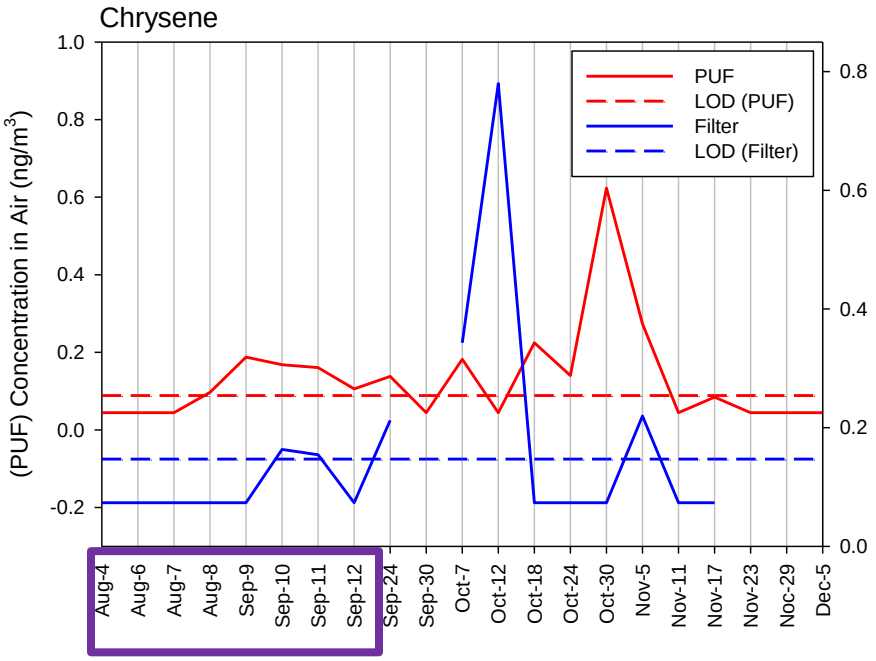
- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data

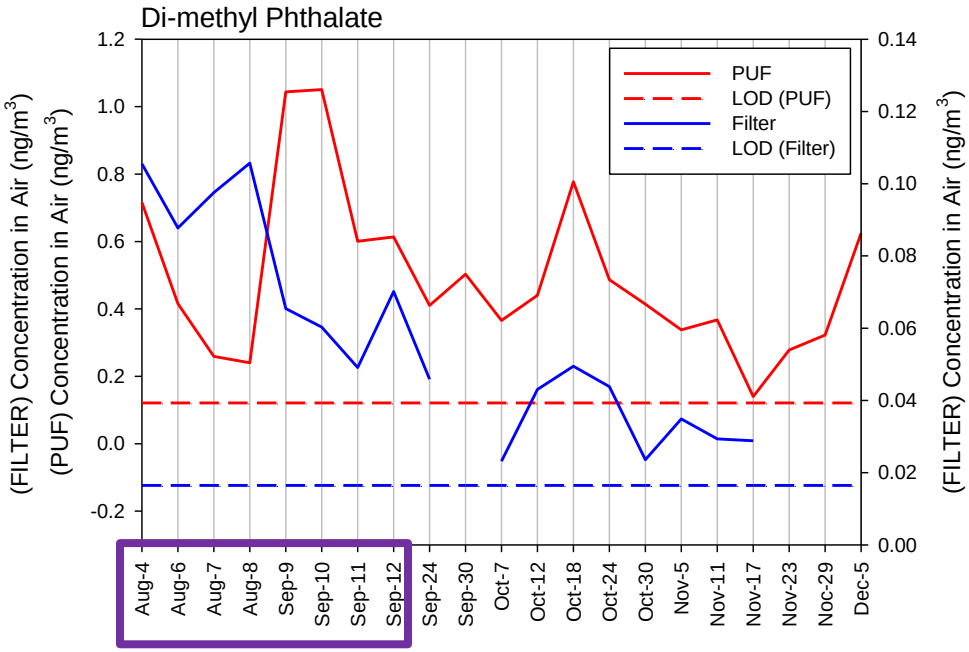


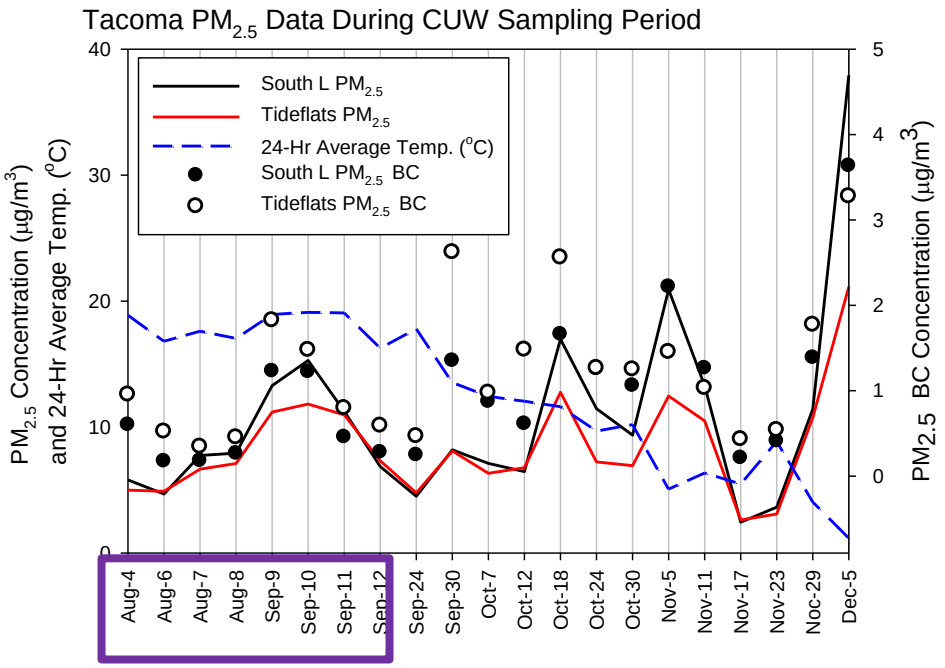




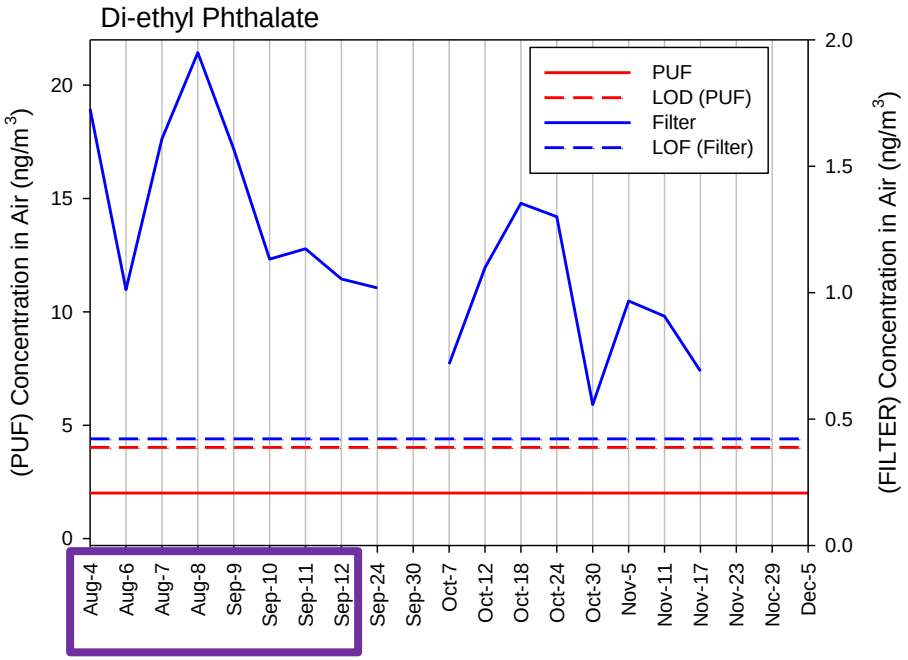
- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data

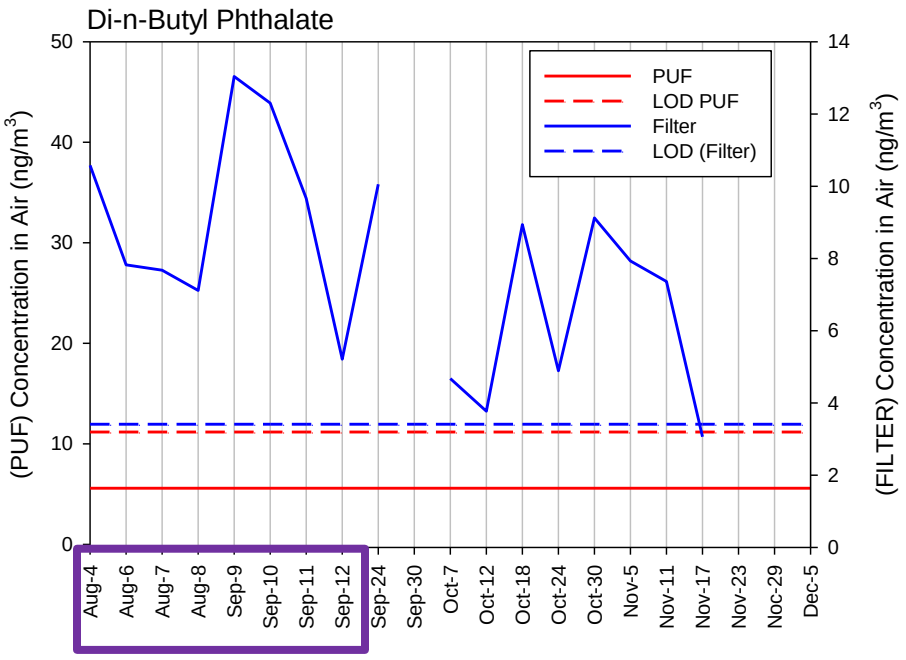


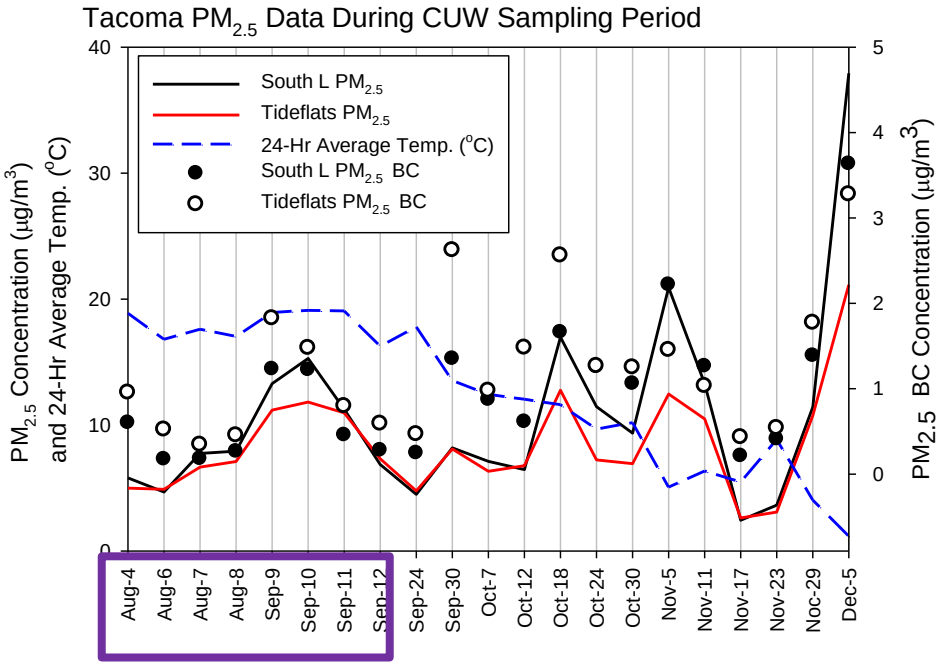




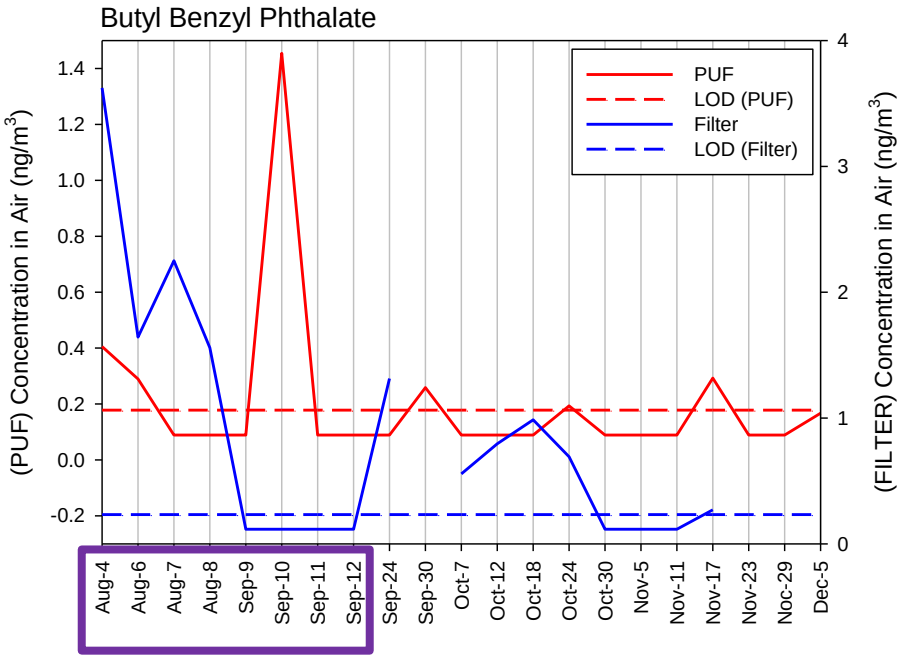
- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data

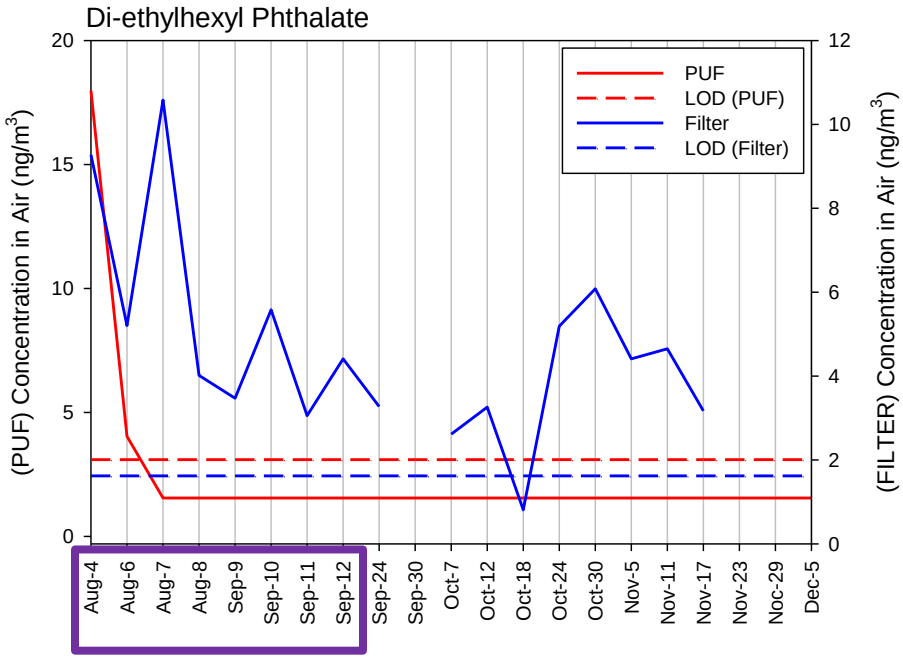






- Purple Boxes around dates: Intensive (daily) sampling in Aug/Sep
- Red Data in PAH/Phthalate plots: PUF data
- Blue Data in PAH/Phthalate plots: Filter Data





Summary/Conclusions

- Out of 14 PAHs, 8 detected reliably above LOD in either gas or particulate phase
  - Chrysene, benzo(a) anthracene >50%
  - Heavy PAHs problematic due to high blanks/low sensitivity
- Concentrations of what was detected reliably in-line with data from Baltimore, Buffalo
- Out of 6 phthalate esters, 4 detected reliably detected above (high) LODs
  - All but di-methyl phthalate in particulate phase

Future Work

- Questions:
  - What is the variability and source strength of specific sources of PM?
  - Now that we have begun to estimate ambient concentrations of PAHs and phthalates, what is the extent of deposition due to precipitation?
- First step: quantification of additional PAHs that in GCMS method that are tracers for specific combustion types (retene/soft wood burning, coronene/gasoline exhaust)
  - Optimization of method and driving down of LODs in parallel with above

Future Work

- Currently archiving filters collected starting November to enable sectioning (punching) for additional analyses
  - Planning extract punches for levoglucosan and nitro-PAHs
- Levoglucosan will be analyzed via derivitization and GC-MS
  - Levoglucosan is a well-defined marker for woodsmoke emissions
- Nitro-PAHs by GC-MS or LC-MS/MS
  - 1-nitropyrene (and 3-nitrofluoranthene) are markers for diesel exhaust
  - Other nitro-PAHs (2-nitropyrene, 4-nitropyrene, 2-nitrofluoranthene) are markers for secondary formation processes
    - Both techniques and methods exist in-house at CUW

Future Work

- Atmospheric Deposition:
  - Beginning of rainwater collection and analyses for similar analytes as described in this presentation

Acknowledgements

- Shristi Prakash
  - Sampling, Extraction, GCMS analysis
- Puget Sound Clean Air Agency
  - Sampling advice
- City of Tacoma Staff
  - GCMS technical support

References

1. US EPA, “Phthalate Action Plan” **2009**
2. Bamford, H.E., Baker, J.E. “Nitro-polycyclic aromatic hydrocarbon concentrationsand sources in urban and suburban atmospheres of the Mid-Atlantic region”, *Atmos. Environ.,* **2003** (37) 2077-2091
3. Minegishi, T. *Characterization of PAH Composition Patterns in Diesel Emission,* Master’s Thesis, **2006**, University of Maryland, College Park, MD.
4. Puget Sound Clean Air Agency and The University of Washington,“Tacoma and Seattle Area Air Toxics Evaluation” **2010**