Low Volume Sampling Indicates Increased Efficiency in PAH Capture

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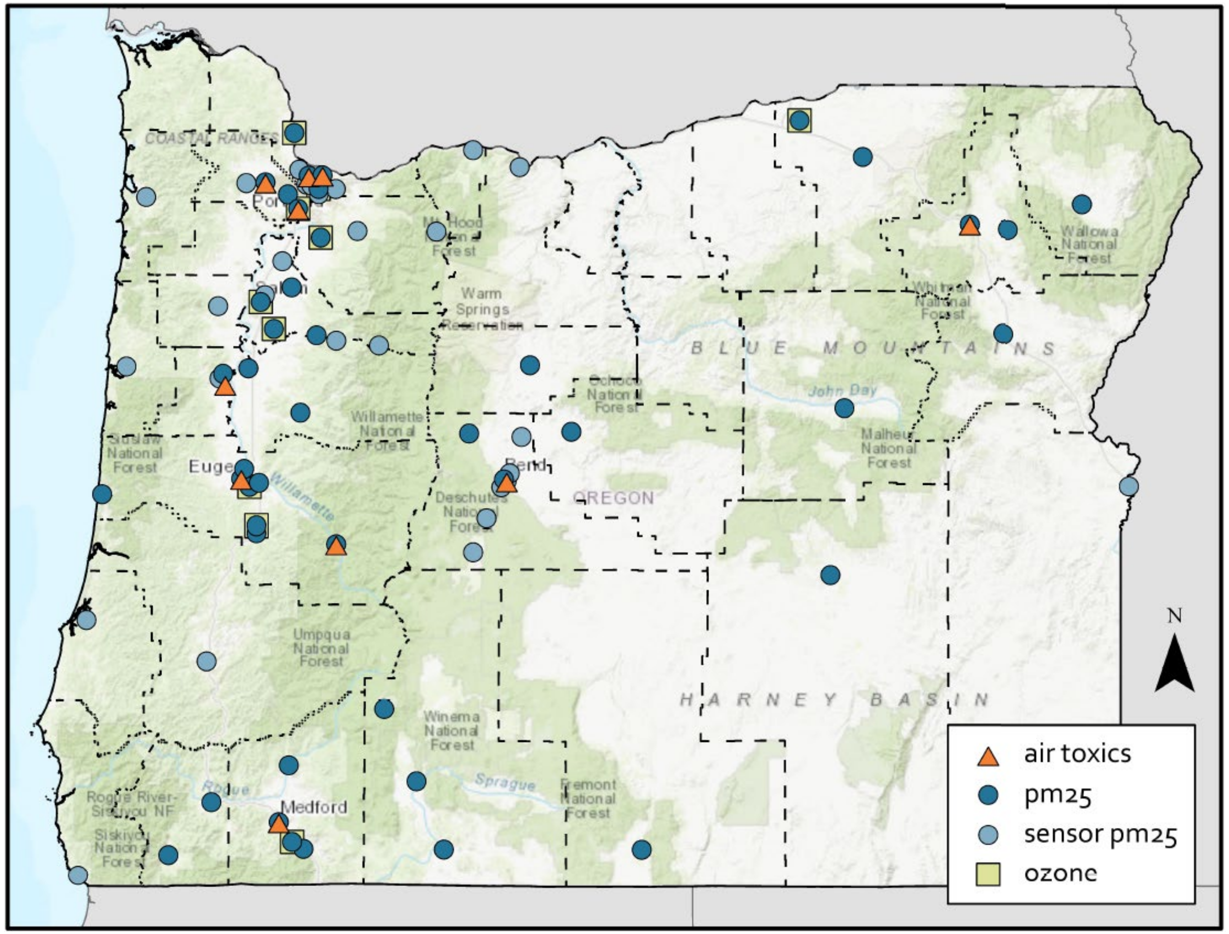
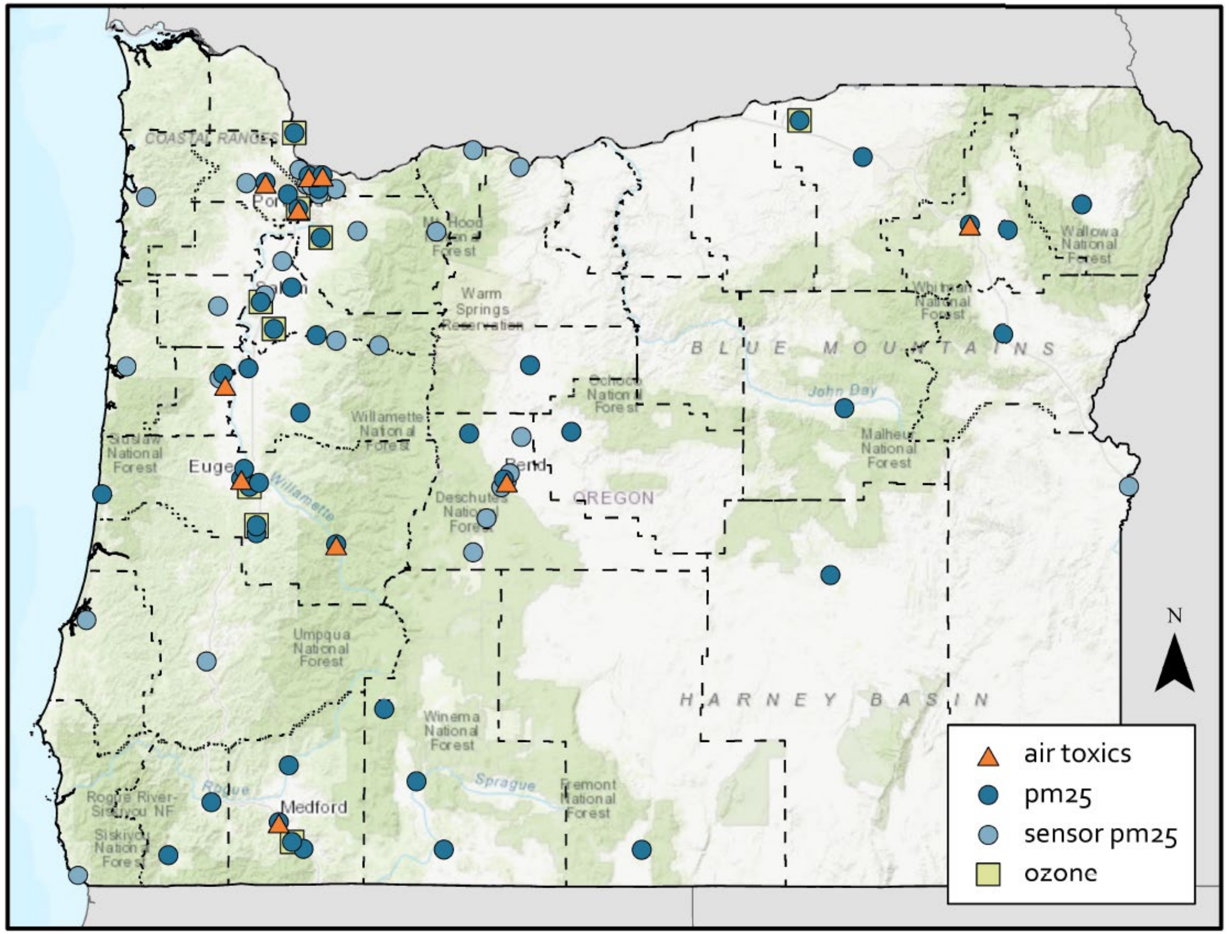
ODEQ monitoring network



- 78 sites
    - 100+ sensors

ODEQ monitoring network



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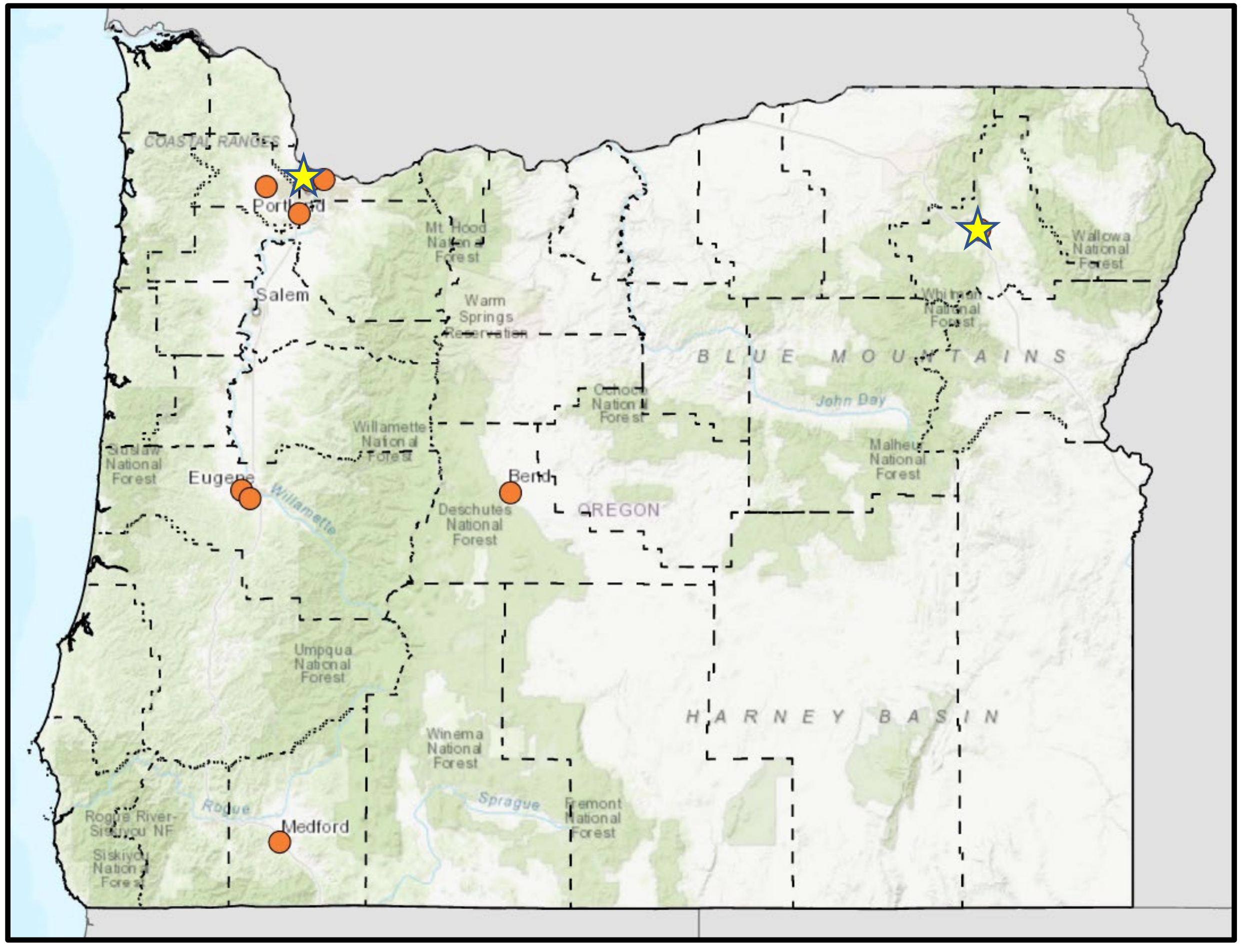

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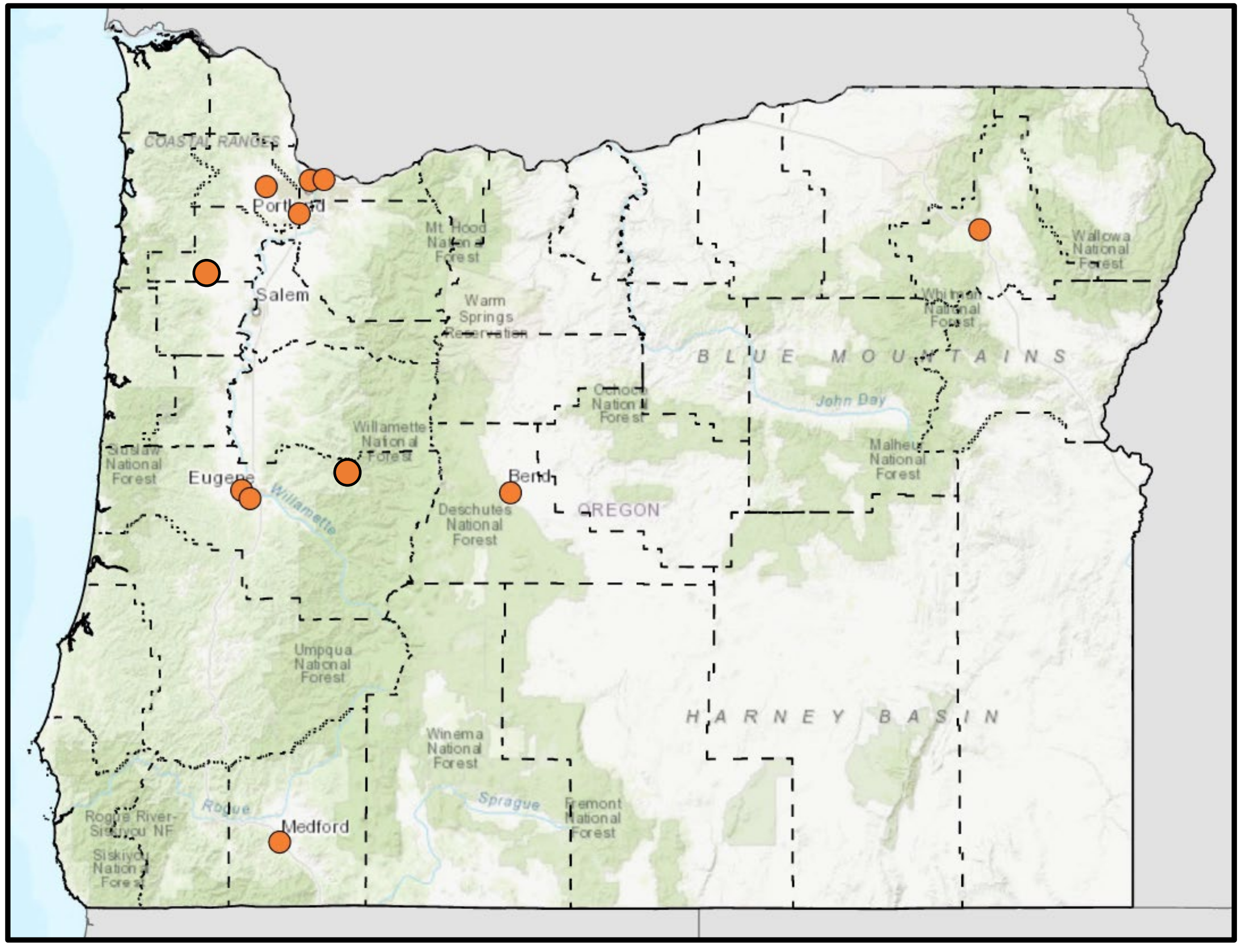

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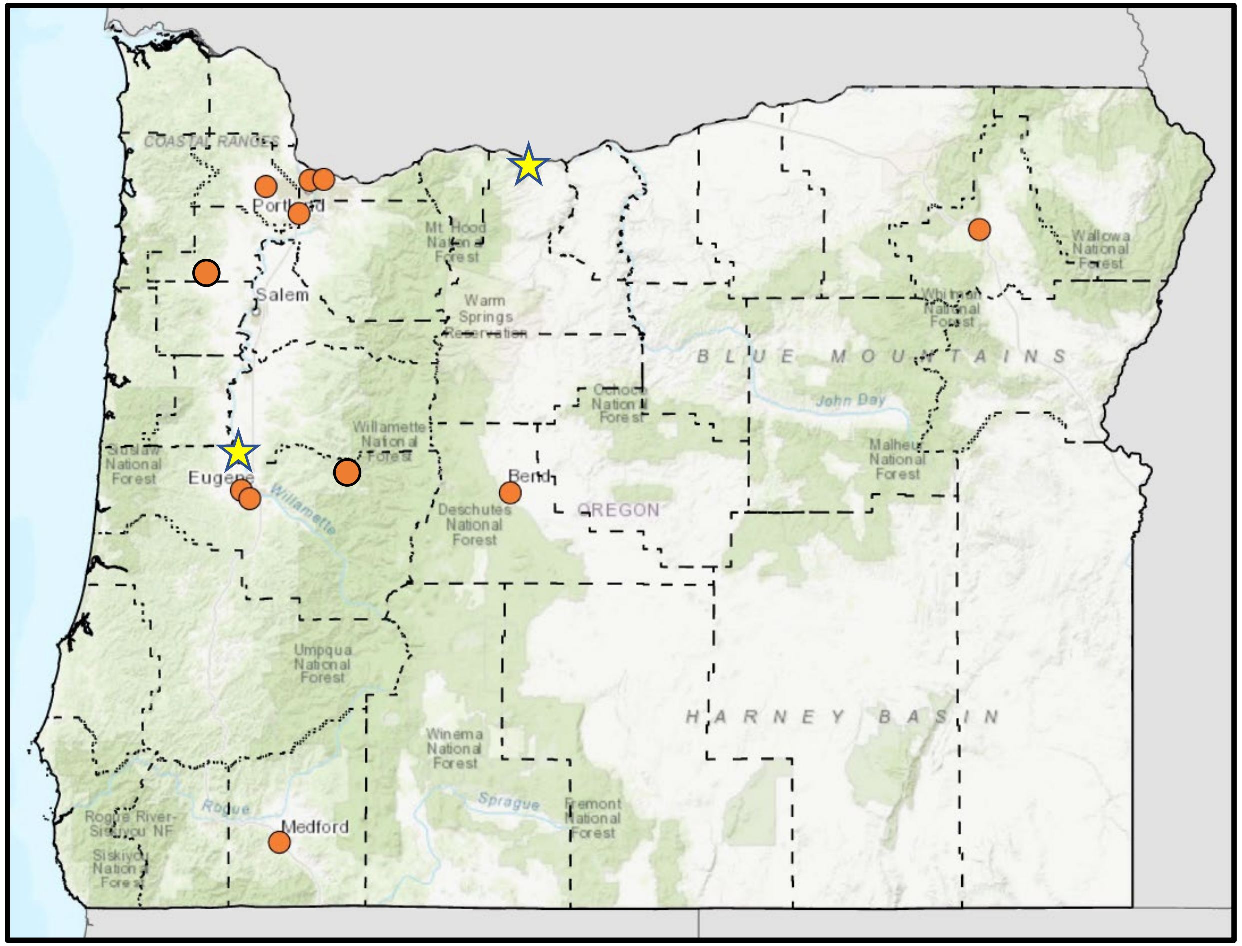
  - LoVol (Cr^{6+})
  - Carbonyl
  - VOC (Summa)
  - HiVol PAH (PUF)

ODEQ monitoring network



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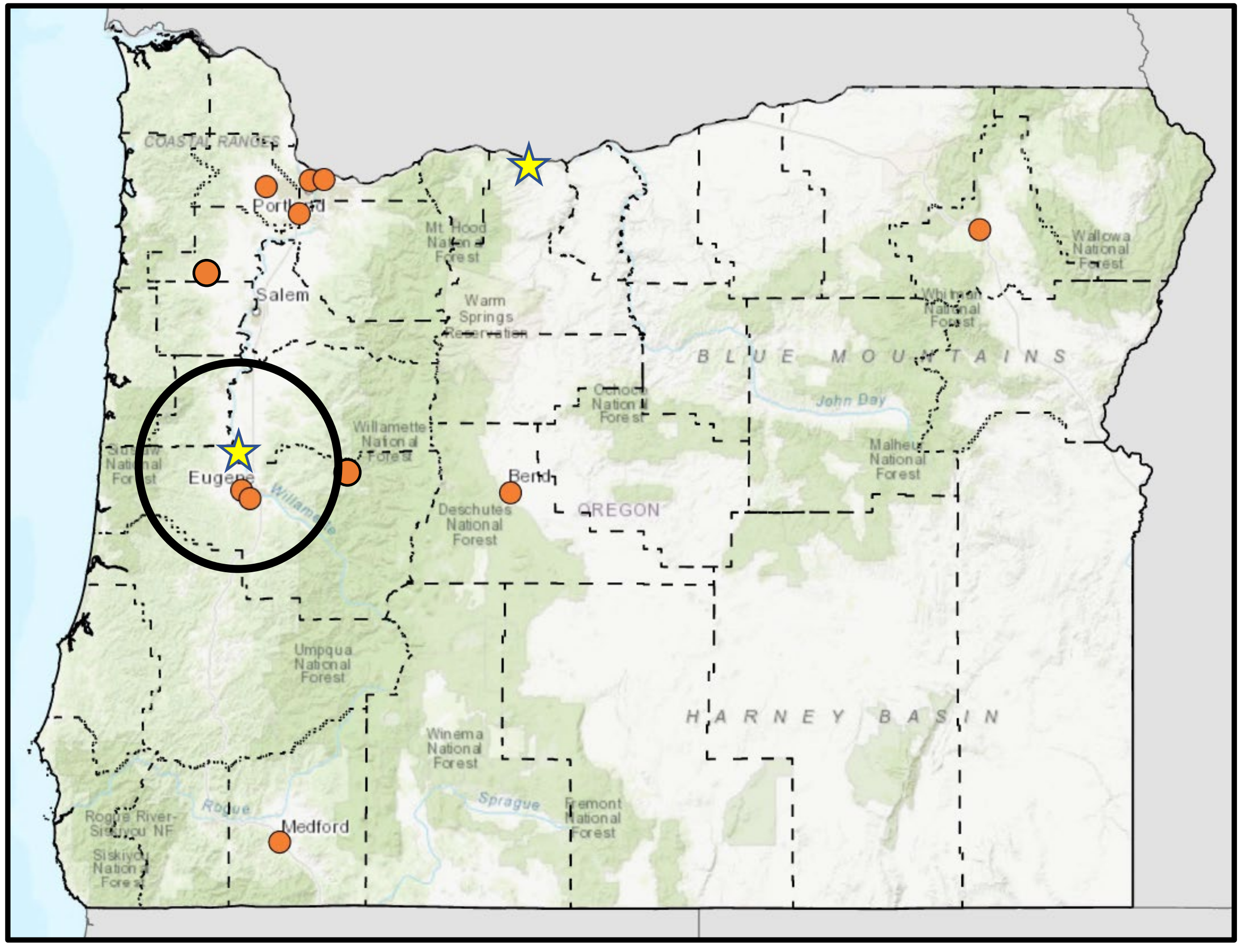

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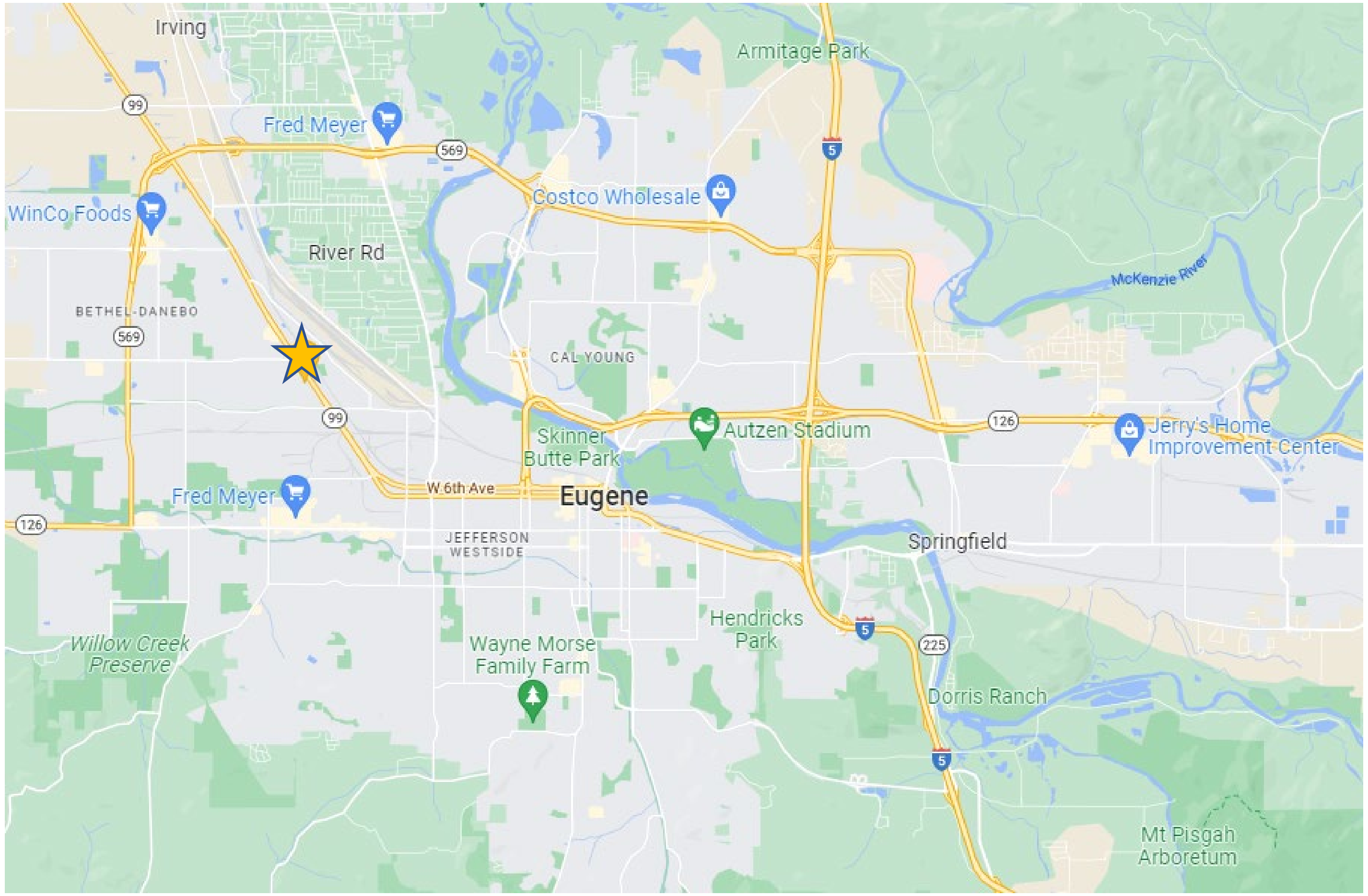
PAH Complaints in Eugene

- Eugene Highway 99
  - Northwest Eugene



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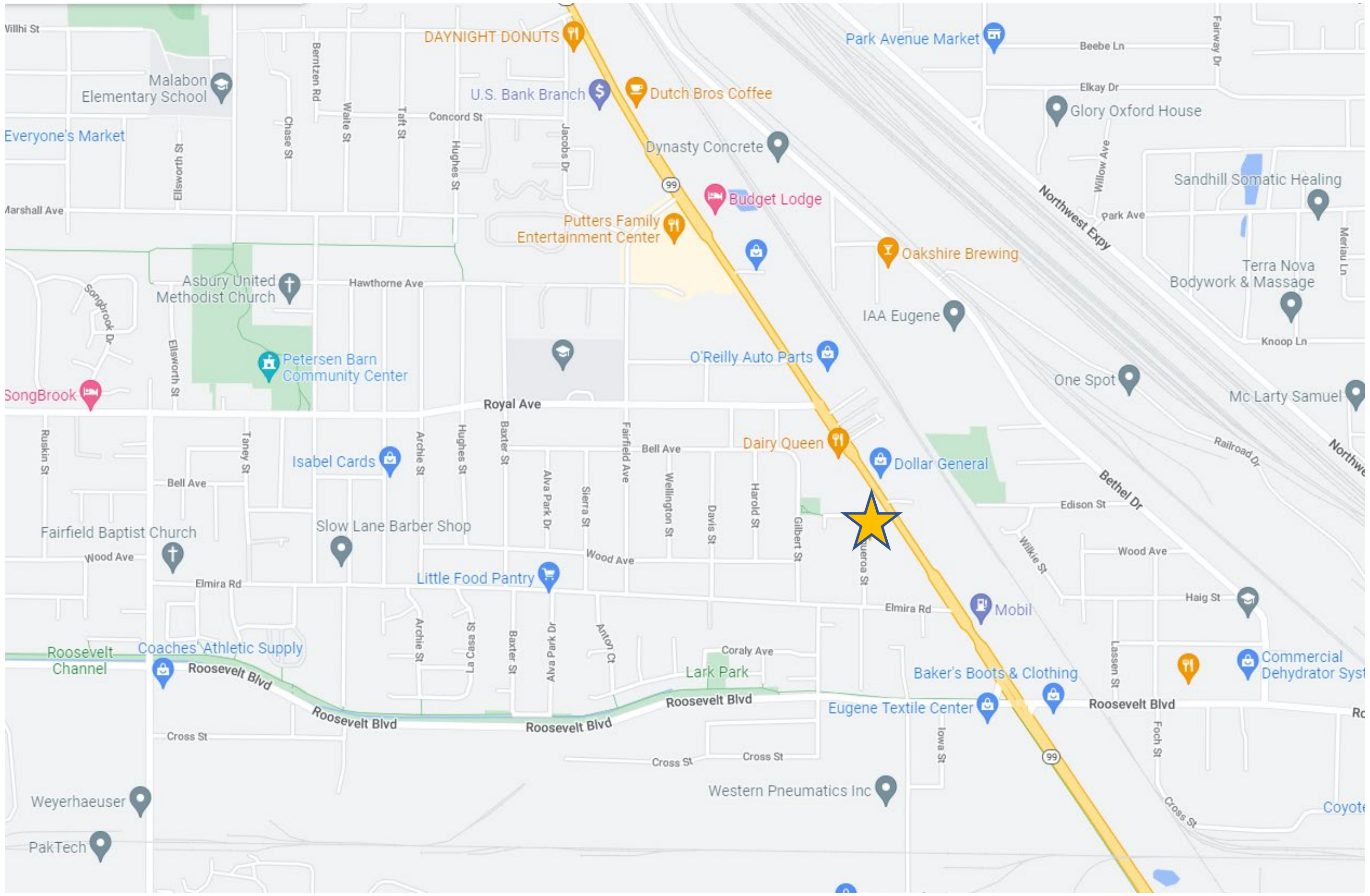
  - On-Road
  - Railroad yard
  - Minor and major Industrial
  - Railyard ties



PAH Complaints in Eugene

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  - On-Road
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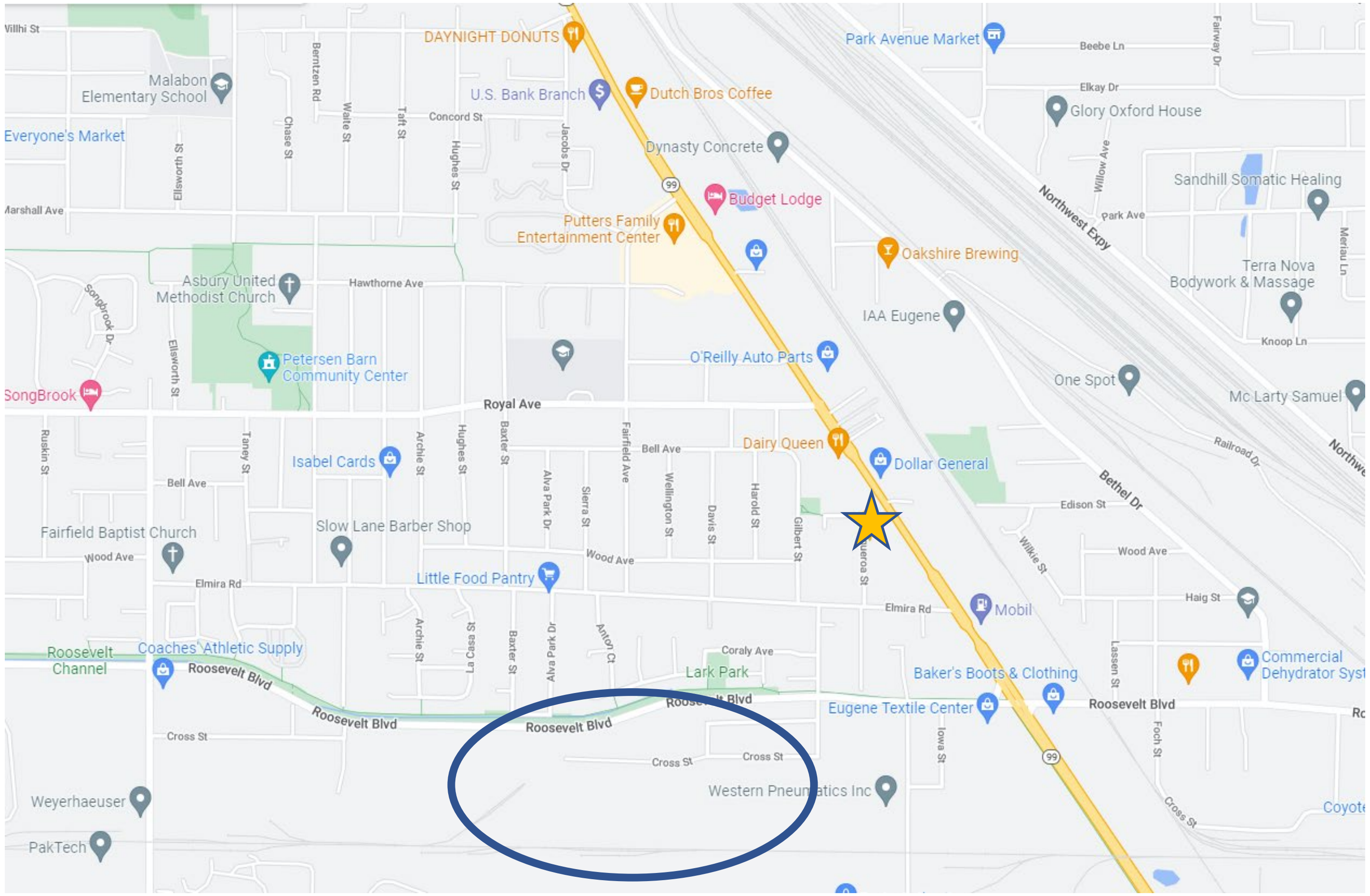
  - Railyard ties
- PAH source
  - J.H.Baxter



Aerosol Science and Technology, 38:972–979, 2004

ISSN: 0278-6826 print / 1521-7388 online
DOI: 10.1080/027868290516790

High-Volume PUF versus Low-Volume PUF Sampling Comparison for Collecting Gas Plus Particulate Polycyclic Aromatic Hydrocarbons

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A yearlong sampling program for $PM_{2.5}$ and semivolatile organic compounds (SVOCs) was conducted in 2000/2001 in Missoula, Montana by The University of Montana, Department of Chemistry. One aspect of this program was to investigate the SVOC fraction of the Missoula Valley $PM_{2.5}$ by evaluating a Federal Reference Method (FRM) $PM_{2.5}$ sampler modified with Polyurethane Foam (PUF) sorbent ($PM_{2.5}$ PUF). In addition, a method of comparison was made between sampling for SVOCs using this modified $PM_{2.5}$ PUF sampler and in using a high-volume PUF sampler (Hi-vol PUF) following EPA protocol. For this comparison, the quartz filter and PUF plugs were extracted together in the analysis of the $PM_{2.5}$ PUF and Hi-vol PUF samples, respectively. Results of this program showed that a trade off between Hi-vol PUF sampling and $PM_{2.5}$ PUF sampling was revealed. During the same sampling periods, the $PM_{2.5}$ PUF measured more of the lighter (smaller molecular weight) SVOCs in a side-by-side comparison with the Hi-vol PUF sampler, with much less volume of sample collected due to a lower flow rate. However, each 24 h Hi-vol PUF sample run provided enough material on which to conduct an SVOC analysis, avoiding the need to aggregate samples (or longer sampling periods) to meet analytical detection limits. In addition, the results presented here also raise important questions about the efficiency of existing PUF samplers (when using quartz filters and PUF sorbent media) in the accurate measurement of lower molecular weight particle and gas-phase SVOCs.

INTRODUCTION

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Particulate organic carbon (OC) consists of thousands of separate compounds, including those that contain more than 20 carbon atoms ($>C_{20}$), such as acids, waxy materials, and ringed structures (Rogge et al. 1993). In Missoula, Montana the organic fraction composes approximately 48% (35% OC, 13% elemental carbon (EC) of the annual $PM_{2.5}$, a number slightly higher than reported in other studies (Rogge et al. 1993; Gebhart and Malm 1994; Hildemann et al. 1994). Some of this organic fraction is composed of polycyclic aromatic hydrocarbons (PAHs) and phenolic compounds. PAHs are carcinogenic compounds that can be formed during the combustion of organic matter, and they consist of two or more fused benzene rings in linear, cluster, or angular arrangements. These compounds are composed of only carbons and hydrogens. Phenolics are compounds that have a hydroxyl group bonded directly to a benzene or benzenoid ring.

Recent $PM_{2.5}$ research has investigated the volatility of compounds that compose fine particles (including nitrate and some OC materials). In these studies, the loss of semivolatile material from particles collected on filters was dominated by the loss of semivolatile organic compounds (SVOCs), which accounts for about half of the total fine particulate organic material. This loss of SVOCs during sampling is known as a "negative" artifact (Eatough et al. 1993, 1995; Tang et al. 1994; Cui et al. 1997, 1998; Ding et al. 2002a). The loss of this mass using single filter Federal Reference Method (FRM) sampling methods and equipment results in the underestimation of $PM_{2.5}$ during sampling (Schaefer et al. 1997; Pang et al. 2002a, 2002b), and could potentially result in biased regulatory issues.

EXPERIMENTAL METHODS

The ambient particle samplers used in this research program were part of a larger sampling program in which $PM_{2.5}$ was collected at two locations in the Missoula Valley to apportion the sources of fine particulate using a chemical mass balance (CMB) model (CMB Version 8.0). Offset from the CMB sampling program schedule (and using the same sampling equipment), a

Received 1 October 2002; accepted 27 July 2004.
The research presented here was supported by the Missoula City—County Health Department, Montana CHEER, Cold Mountains, Cold Rivers, The Native Forest Network, and Smurfit—Stone Container Corporation in Missoula, Montana.
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Tony Ward & Garon Smith (2004) High-Volume PUF versus Low-Volume PUF Sampling Comparison for Collecting Gas Plus Particulate Polycyclic Aromatic Hydrocarbons, Aerosol Science and Technology, 38:10, 972-979

J.H. Baxter wood treatment plant, known for pollution violations, to end operations Monday

Adam Duvernay
Register-Guard

Published 10:13 a.m. PT Jan. 26, 2022 | Updated 3:45 p.m. PT Jan. 26, 2022

View Comments

Neighbors meet along a pedestrian path near the J.H. Baxter & Co. plant in Eugene. *Chris Pietsch/The Register-Guard*

Dioxins found in soil

DEQ announced Jan. 13 that an investigation into the presence of dioxins in soil at and around the plant led to the discovery of those toxic compounds in samples from nearby homes. DEQ is requiring the company pay for soil replacement at those affected homes.

DEQ spokesman Dylan Darling said the agency has not received formal notice the company intends to end its operations, but said an attorney informed them of the plans.

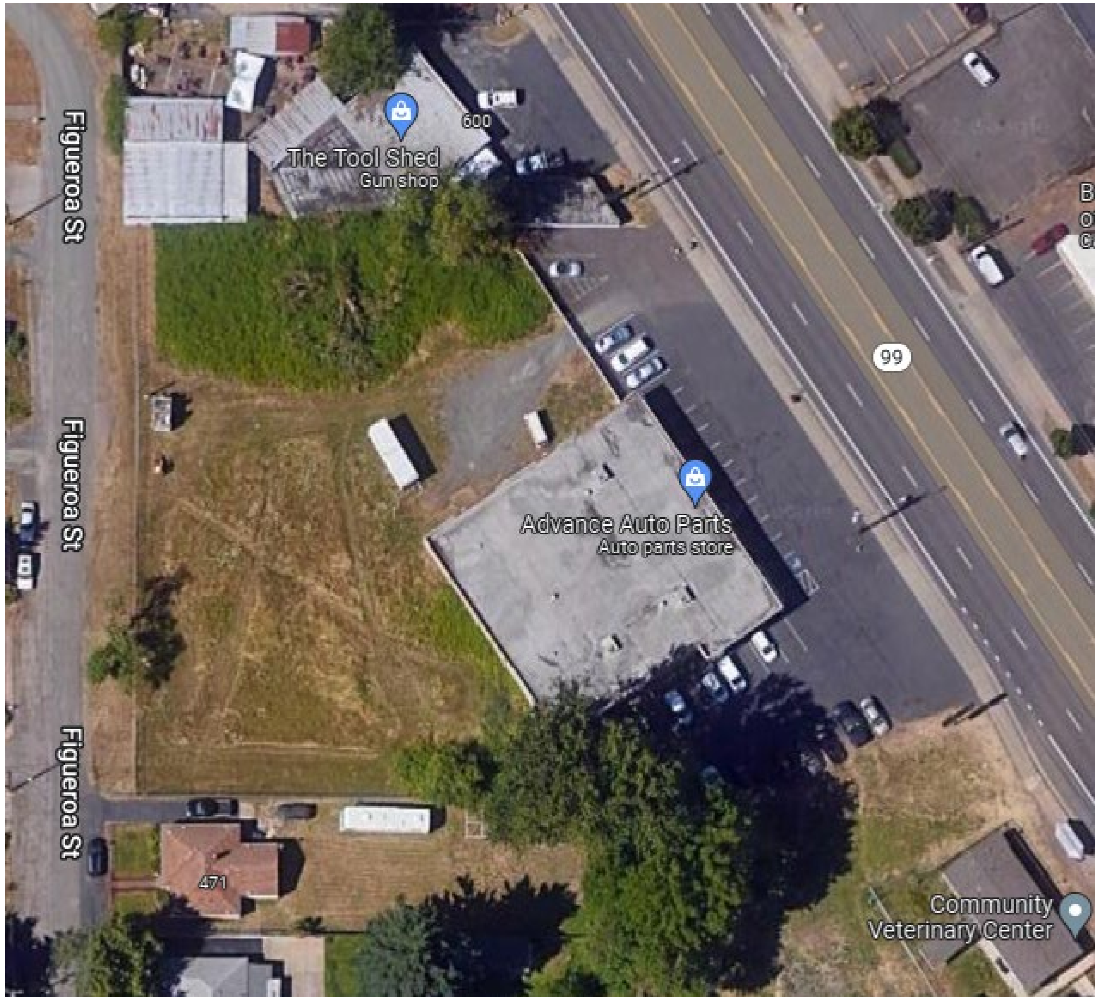
Environment

Months after its closure, a cloud still hangs over J.H. Baxter's Eugene plant

https://www.registerguard.com/story/news/environment/2022/01/26/jh-baxter-plant-shutting-down-eugene-operations-jan-31-history-pollution-dioxins-hazardous-waste/9228050002/

https://www.klcc.org/2022-06-02/months-after-its-closure-a-cloud-still-hangs-over-j-h-baxters-eugene-plant

Eugene E99 site



Experimental Setup

Extraction Setup

Experimental Setup

Method	LoVol	HiVol
Media	XAD-2	Polyurethane/XAD-2
Extraction Method	Dionex ASE 350	Soxhlet
Solvent	Acetone:DCM (1:9 v/v)	10% Et_2O in Hexane
Rotovap	Labconco RapidVap	
Analysis	Agilent 7890 GC with Restek Rxi-5Sil MS and 5975C MSD	

Resulting Statistics

Analyte	LV %Obs>MDL	HV Obs>MDL	average % diff	Stdev of % diff	mean	stdev	RMSE	R2	Slope
Acenaphthene	91	91	31.36%	25.34%	6.51	10.67	12.50	0.92	1.11
Acenaphthylene	41	45	44.21%	44.44%	1.39	3.33	3.61	0.98	1.75
Anthracene	38	40	-0.31%	23.23%	0.05	0.56	0.56	0.96	1.38
Benzo(a)anthracene	12	12	97.77%	72.53%	0.54	0.89	1.04	0.97	1.85
Benzo(a)pyrene	3	3	55.31%	44.31%	0.55	0.89	1.05	0.95	1.79
Benzo(b)fluoranthene	13	13	16.91%	28.47%	0.70	1.51	1.67	0.97	1.73
Benzo(e)pyrene	6	6	48.31%	28.11%	0.53	0.93	1.08	0.99	1.88
Benzo(g,h,i)perylene	5	5	61.43%	44.50%	0.45	0.71	0.84	0.94	2.04
Benzo(k)fluoranthene	4	4	47.30%	20.65%	0.25	0.30	0.39	0.98	1.57
Chrysene	19	21	-2.75%	28.56%	0.35	1.10	1.16	0.97	1.54
Coronene	1	1	31.25%	0.00%	0.03	0.06	0.07	1.00	1.31
Dibenzofuran	91	91	33.02%	22.48%	5.93	7.35	9.45	0.97	1.15
Dibenzothiophene	51	52	16.34%	22.43%	0.24	0.56	0.61	0.92	1.42
Fluoranthene	76	76	9.06%	15.91%	0.28	0.68	0.73	0.98	1.26
Fluorene	91	91	26.63%	21.38%	2.69	3.72	4.59	0.97	1.22
Indeno(1,2,3-cd)pyrene	5	5	64.46%	35.99%	0.66	1.07	1.26	0.98	2.05
Naphthalene	91	91	47.75%	24.25%	59.24	77.41	97.48	0.98	1.32
Phenanthrene	91	91	20.07%	13.97%	2.63	3.73	4.56	0.99	1.30
Pyrene	63	63	4.89%	17.99%	0.10	0.50	0.51	0.92	1.20

355 sample runs

LV > HV = 652

HV > LV = 139

HV ND =490

LV ND = 508

Total HV = 1134

Total LV = 987

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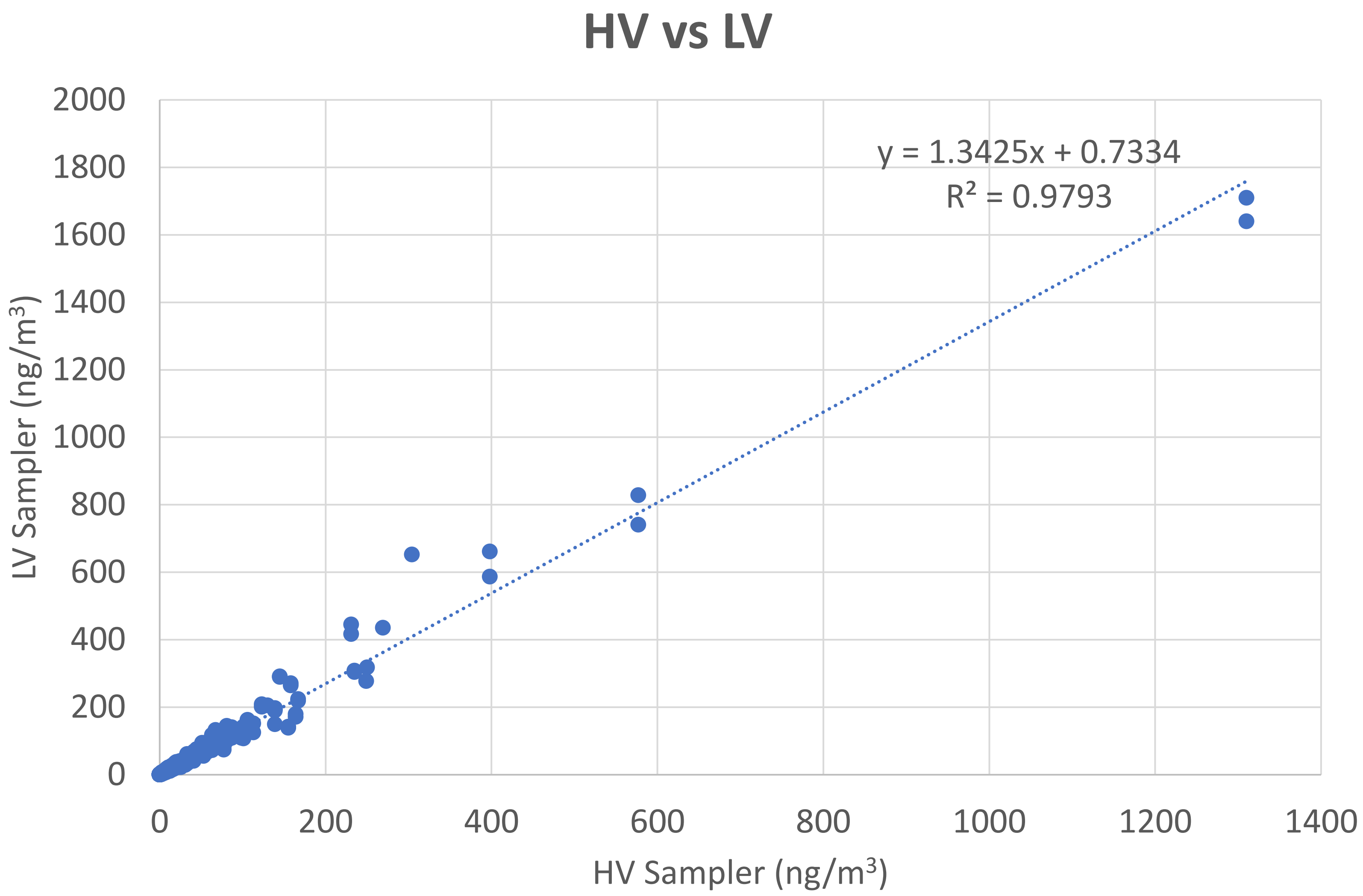

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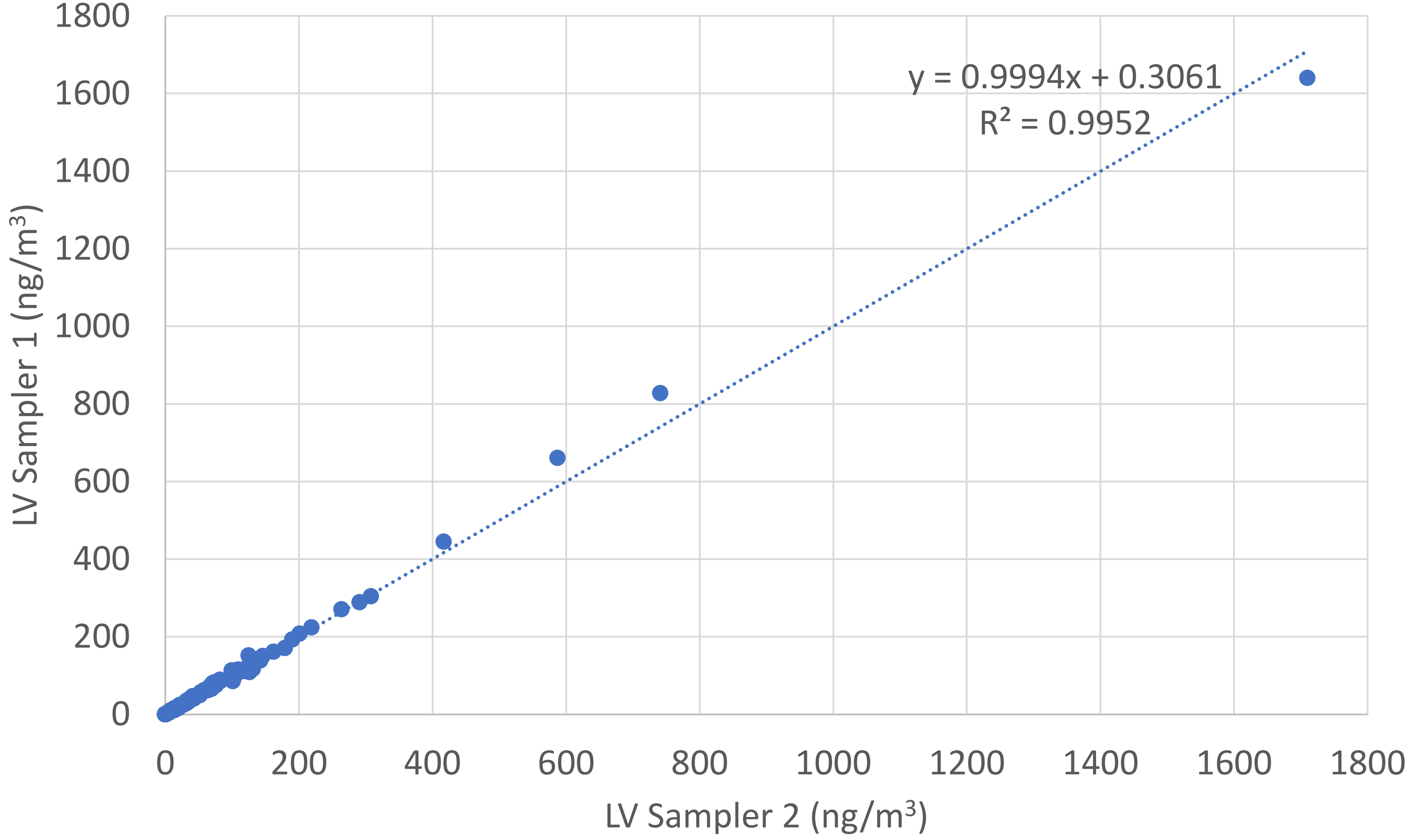
- ~30% higher recovery from LV

Low Volume Duplicate Comparison



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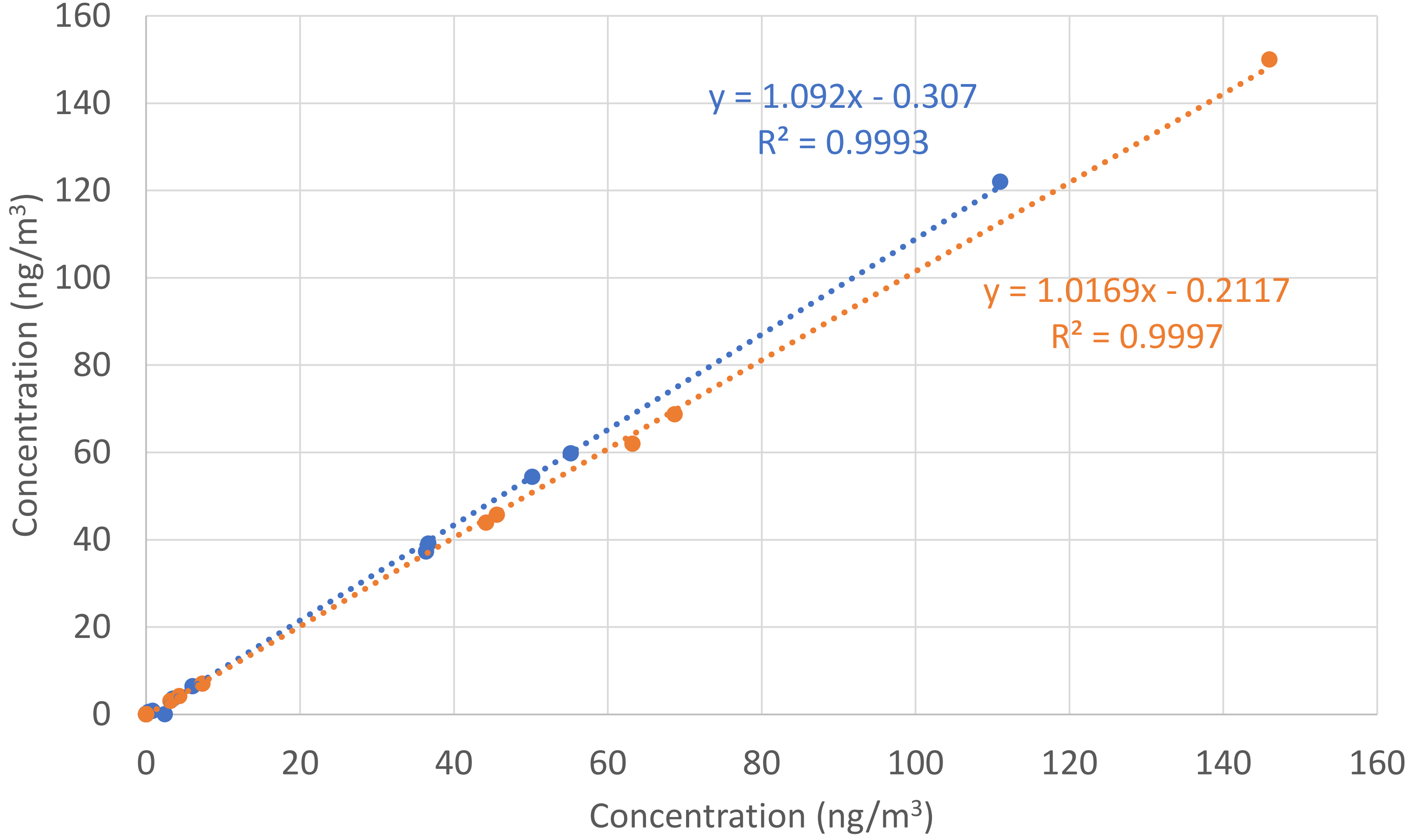
- ~30% higher recovery from LV
- 1:1 for duplicate comparisons

Soxhlet Extraction vs Auto Extraction



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Resulting Statistics

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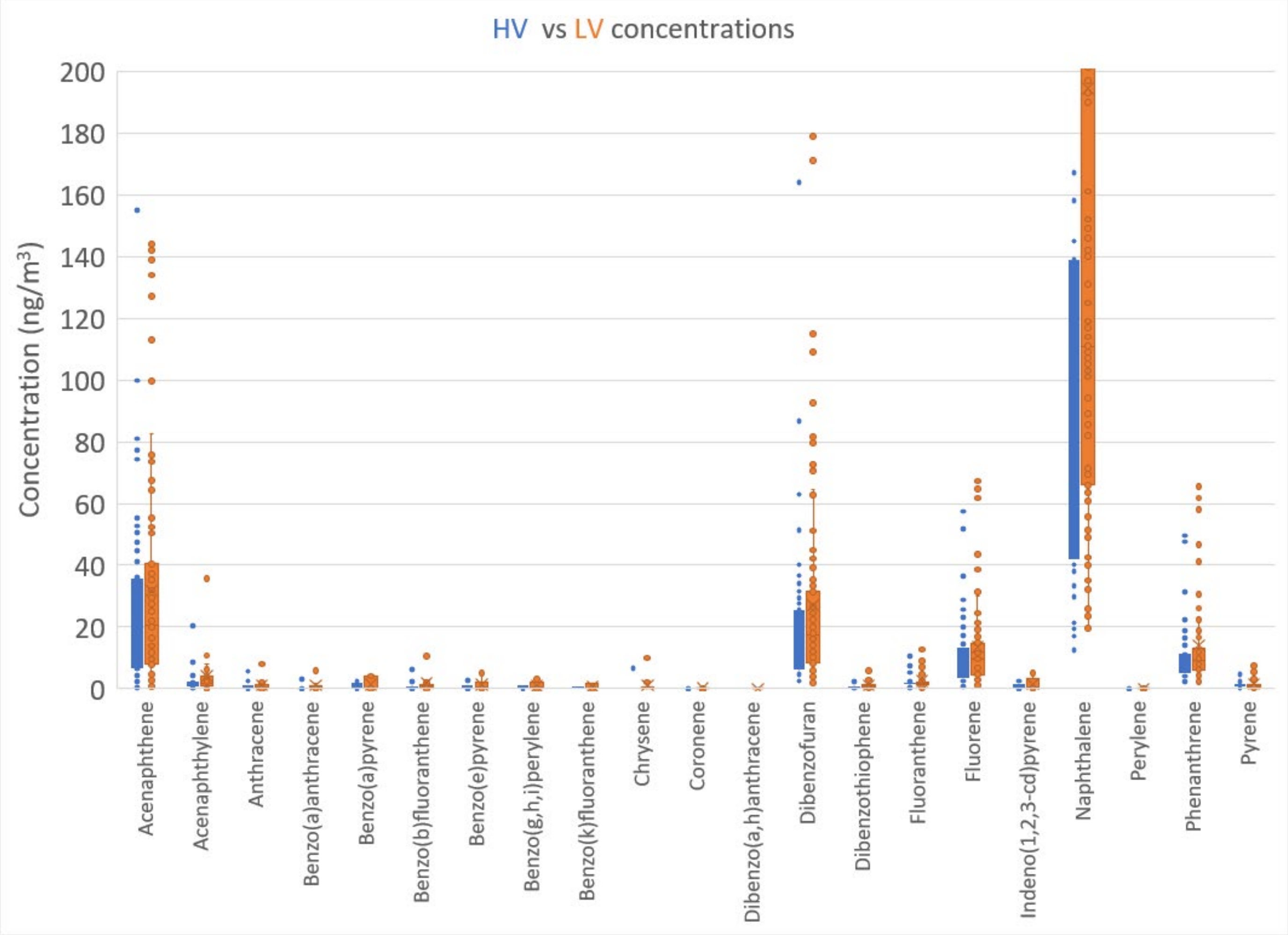
- 1:1 for duplicate comparisons
- ~10% higher recovery for LV in Soxhlet extraction



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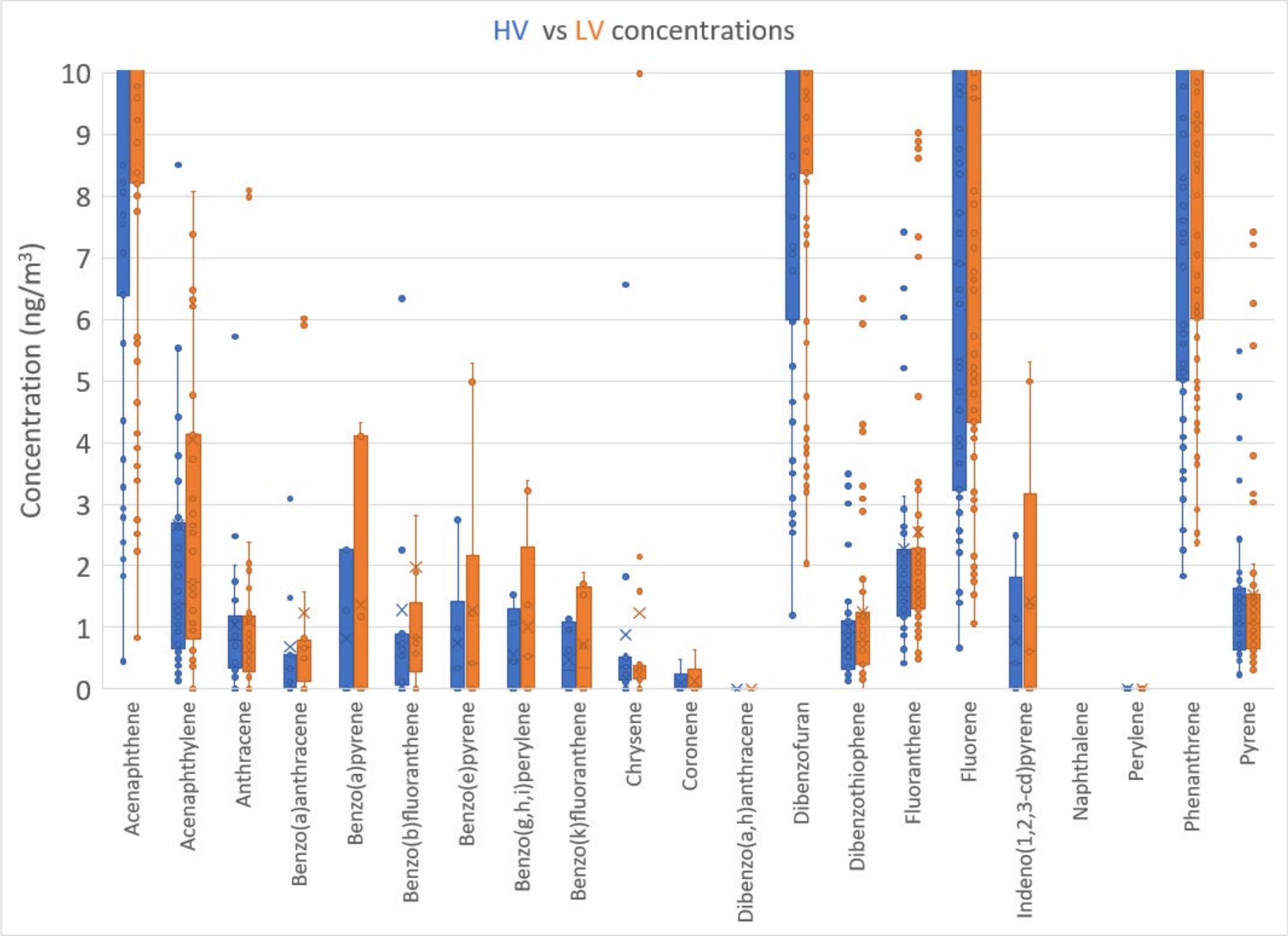

Conclusions

- Setup duplicate LV samplers with HV sampler at E99
- Positive hits on 91 sample events for 5 compounds
- Highest hits for Naphthalene
- Extraction method/solvents show improved recovery
- LV is 30% more efficient on average with Acetone:DCM (1:9 v/v)
- LV is 10% more efficient with 10% Et_2O in Hexane*
- More work needed

Future work

- Expand the network for airshed comparison
- More samples extracted with two solvent systems
- Extract PUF and XAD separately