

Application of SW-846 Method 8261 Model Calculations to Purge and Trap and Static Headspace Analysis of Volatile Organic Chemicals (VOCs)

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Overview of VOC analysis

- VOCs: empirically defined by tendency to partition into gas phase from water, but wide range of physical properties
 - Water Solubility (low mg/L to miscible)
 - Vapor Pressure (0.0001 to > 1 bar)
 - Affinity for organics ($\text{Log } K_{ow} < 0$ to 4+)
- VOC Compound Classes listed in 8260(C):
 - Hydrocarbons
 - Halogenated C_1 - C_4 Alkanes/Alkenes;
 - Substituted Benzenes (C_1 - C_4 , Cl_1 - Cl_3 , Br) and Naphthalene;
 - Oxygenates and Other Water Solubles (THF, 1,4-Dioxane, Alcohols, Nitriles, Ethers, Esters, Aldehydes/Ketones)

Overview of VOC analysis

2 common ways VOCs are measured:

- Aqueous Direct Vapor Partitioning:
 - Aqueous samples analyzed undiluted or after dilution with water
 - 1-5 g soils analyzed after addition of 5-10 mL water, no dilution without compromising container integrity (LOW LEVEL)
 - Physical process: transfer consistent fraction of target VOCs from condensed / solid phases into vapor phase, then into GC with aid of heat, large volume of gas relative to other phases, salt, vacuum
- Organic Solvent Extraction:
 - Solids (soil/sediment) and non-aqueous phase liquids: solvent extraction/dilution (methanol), aqueous dilution (e.g., 100 uL into 5 mL water), then vapor partitioning, resulting in $\geq 50x$ dilution (MEDIUM/HIGH LEVEL)
 - Physical Process: Relative activity of VOCs in solvent is low, re matrix with large amount of organic phase (like likes like), thereby

Synopsis of my talk

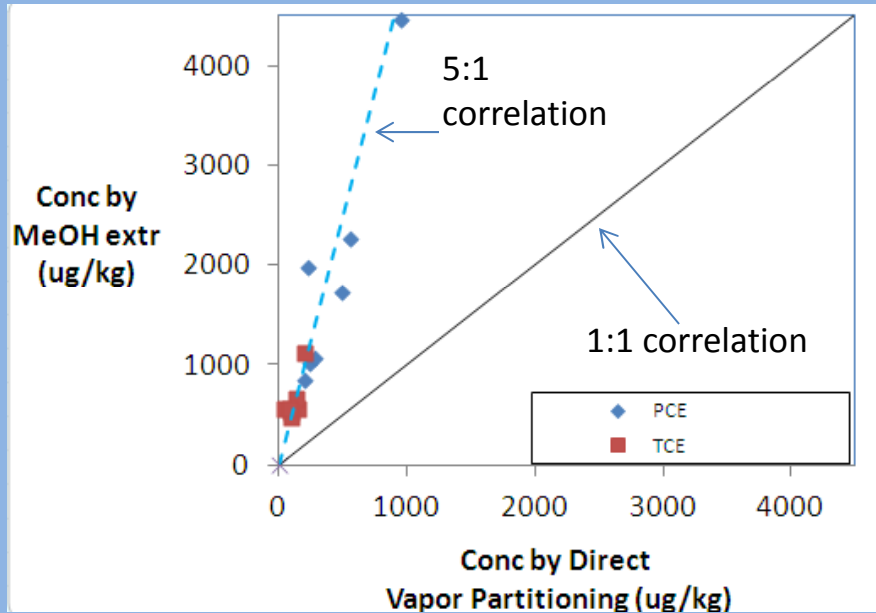
- Direct vapor partitioning VOC measurements can be biased in complex sample matrices relative to solvent extraction. This bias is primarily due to:
 - aqueous activity differences between samples and standards (high salt content, water miscible organic component)
 - sorption to water immiscible phases (oil, soil organic carbon)
- Method 8261 model calculations base target analyte concentration estimates on a system of internal standard recovery corrections that can account for matrix effects in order to provide a better estimate of actual concentration and improves comparability of concentration data particularly for heavier VOCs with solvent extraction

Topics to Follow:

- 1) Problems with comparability between direct vapor partitioning and solvent extraction
- 2) Description of Method 8261 calculation model, SMCReporter
- 3) Overview of method 8261 model comparison for 3 VOC prep techniques

1) Problems with comparability
between direct vapor partitioning and
solvent extraction

Soil Contaminated with PCE, TCE



- Sealable coring devices (~5 g)
- Soils analyzed by direct vapor partitioning and methanol extraction / purge and trap (P&T)
- Concentrations measureable at both levels, enabling comparison

Instrument QC						Matrix spike				
		RRF %RSD	ICV %D	end CCV %D	IS Area (%)	sample LOQ (ug/kg)	sample conc (ug/kg)	matrix spike conc (ug/kg)	measured conc (ug/kg)	% recovery of spike amt
MeOH extraction	TCE	7.9	-3.0	-1.7	92.9- 103.2	220	1100	2800-2900	3640 / 3760	88 / 91
	PCE	8.7	-1.1	-8.2		220	720	2800-2900	3190 / 3300	88 / 89
Low Level (vapor partitioning)	TCE	10.3	10.1	-26.7	86.9- 103.1	4.4	200*	42-44	221* / 215*	52 / 36
	PCE	12.8	9.4	-30.6		4.4	90	42-44	118 / 126	58 / 83

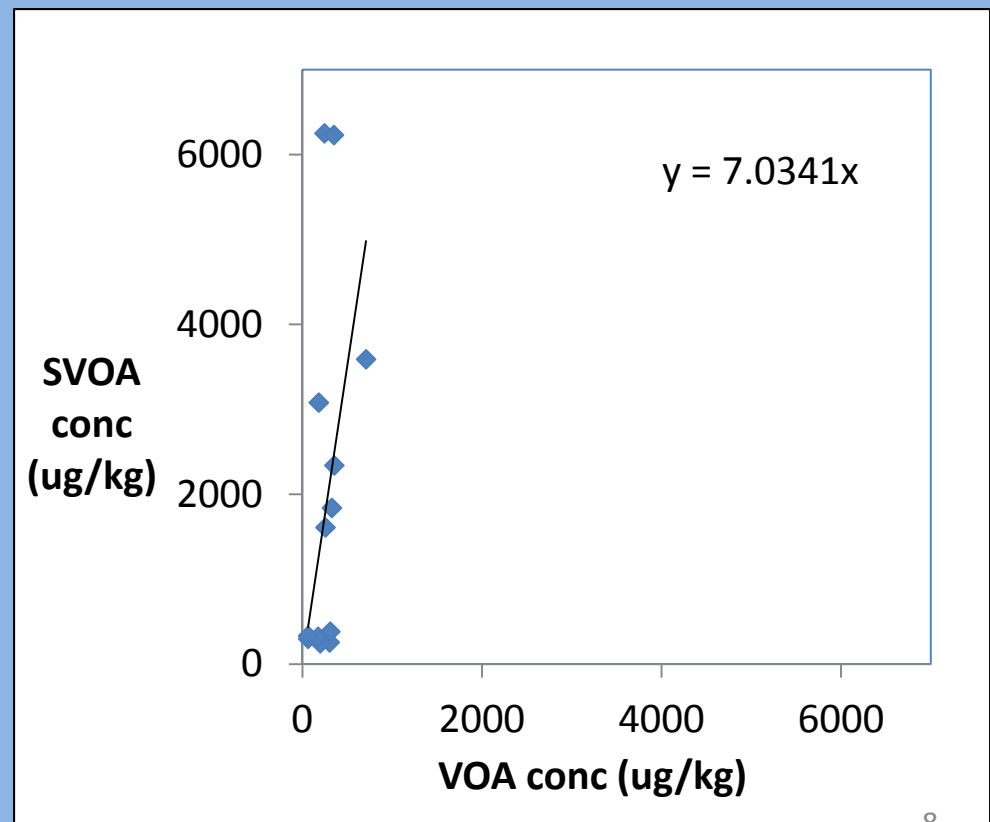
IC: Initial calibration
 RRFAvg: Average relative response factor
 RSD: Relative standard deviation
 ICV: 2° source initial calibration verification standard
 CCV: 1° source continuing calibration verification standard
 LOQ: Limit of quantitation

PCE: Perchloroethylene
 TCE: trichloroethylene
 IS: Internal standard (fluorobenzene)
 %D: % Difference (calc-expected)/expected*100%
 * over calibration range (10-30% above)

Example #2: Naphthalene in Freshwater Sediment

- Soils analyzed for:
 - VOCs by direct vapor partitioning P&T / GCMS (SW-846 methods 5035A/8260C)
 - SVOCs by pressurized fluid extraction / GCMS (SW-846 methods 3545, 1:1 DCM-acetone / 8270D)

Sample #	naphthalene conc (ug/kg)		[SVOA] / [VOA]
	VOA	SVOA	
05-02	62	299	4.8
05-03	244	6250	25.6
05-04	181	3080	17.0
05-05	350	6230	17.8
05-06	302	257	0.9
05-07	309	384	1.2
06-01	708	3590	5.1
06-02	198	247	1.2
06-03	174	323	1.9
14-02	354	2340	6.6
14-03	62	333	5.4
14-04	256	1610	6.3
14-05	327	1840	5.6



Naphthalene in water with high dissolved organics

- Polymer manufacturer process wastewater
 - (high dissolved extractables, high level of vinyl chloride)

Sample #	VOA conc (ug/L)	VOA dil. factor	SVOC conc (ug/L)	SVOC dil. factor	[SVOC] / [VOC]
-01	U (<500)	100x	48.5	10x	-
-02	U (<50)	10x	288	50x	>5
-03	U (<50)	10x	256	50x	>5
-04	U (<100)	20x	673	100x	>5
-05	U (<5)	undil	<1.1	undil	-
-06	U (<25)	5x	342	50x	>10
-07	U (<50)	10x	64	10x	>1.2
-08	U (<50)	10x	975	100x	>10
-09	U (<5)	undil	<1	undil	-
-10	U (<50)	10x	182	100x	>3
-11	U (<1000)	200x	167	100x	>5
-12	U (<25)	5x	668	100x	>20
-13	U (<25)	5x	391	100x	>10
-14	U (<100)	20x	54	10x	-

U = below LOQ

Matrix spike (Sample -14)					
analysis	MS/MSD LOQ (ug/L)	Sample conc (ug/L)	matrix spike conc (ug/L)	MS / MSD meas. conc (ug/L)	% recovery of spike amt
VOC	250	U (<100)	2500	1800 / 1840	72 / 74
SVOC	~10	54	29-33	95 / 97	128 / 140

Recovery of spiked VOCs equilibrated with sample matrix

5 min room temp stirring
after spiking into 5 g soil
+ 5 mL water

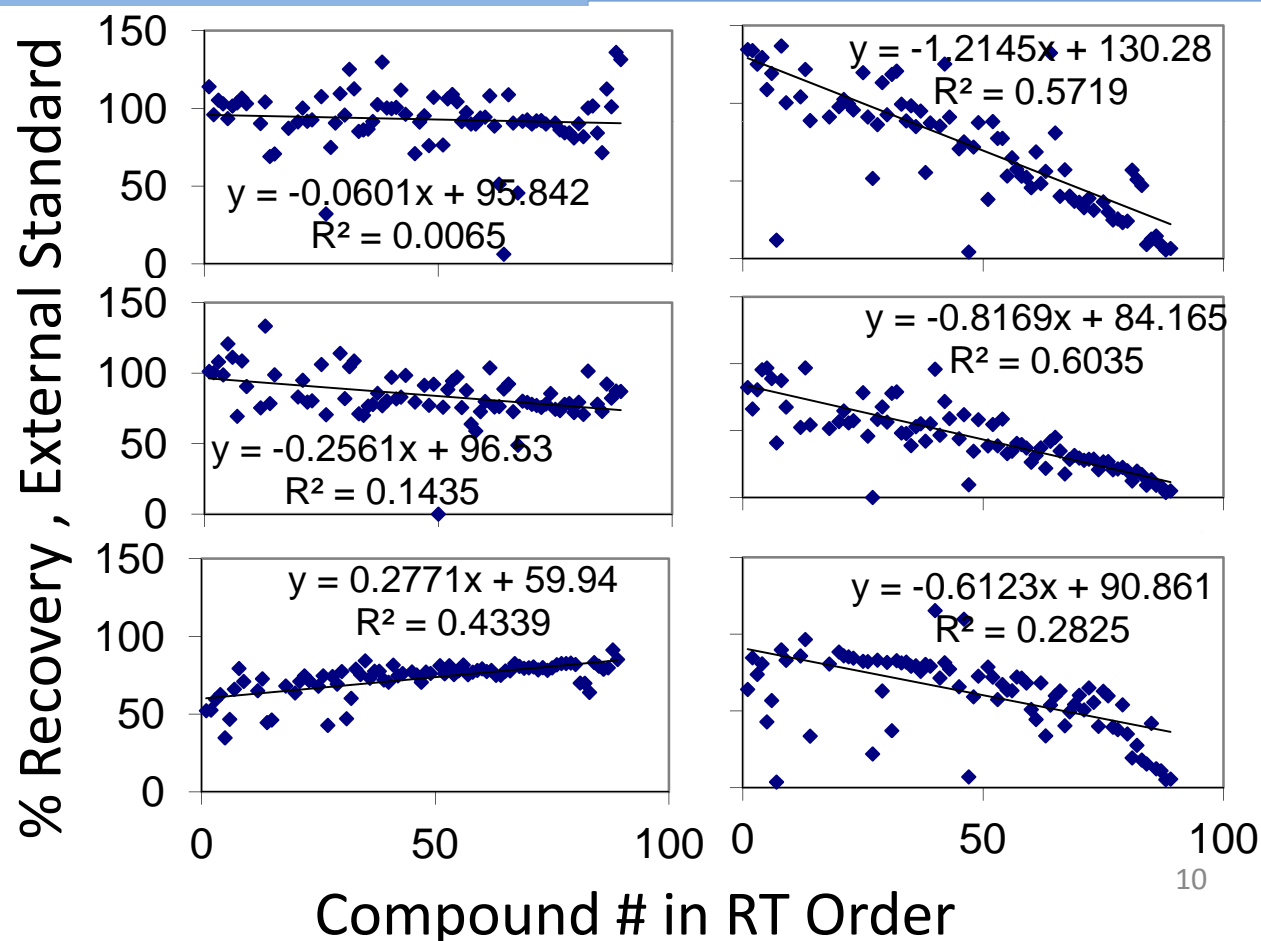
1 cc Static
Headspace

Purge and
Trap

Vacuum
Distillation

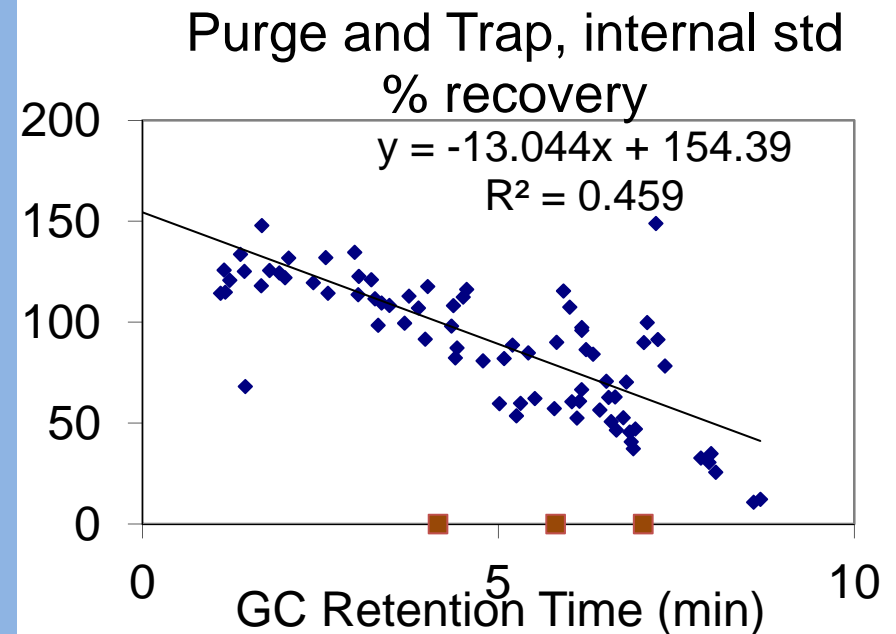
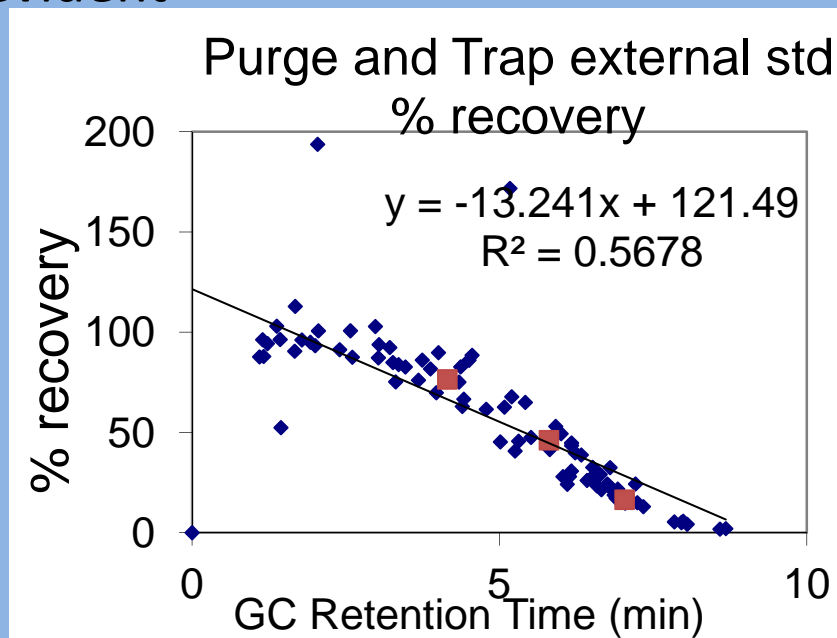
No soil

Jewel Soil, 3.4% O.C.
44:32:25 sand/silt/clay



Equilibrating internal standards with sample does not normalize matrix effect very well

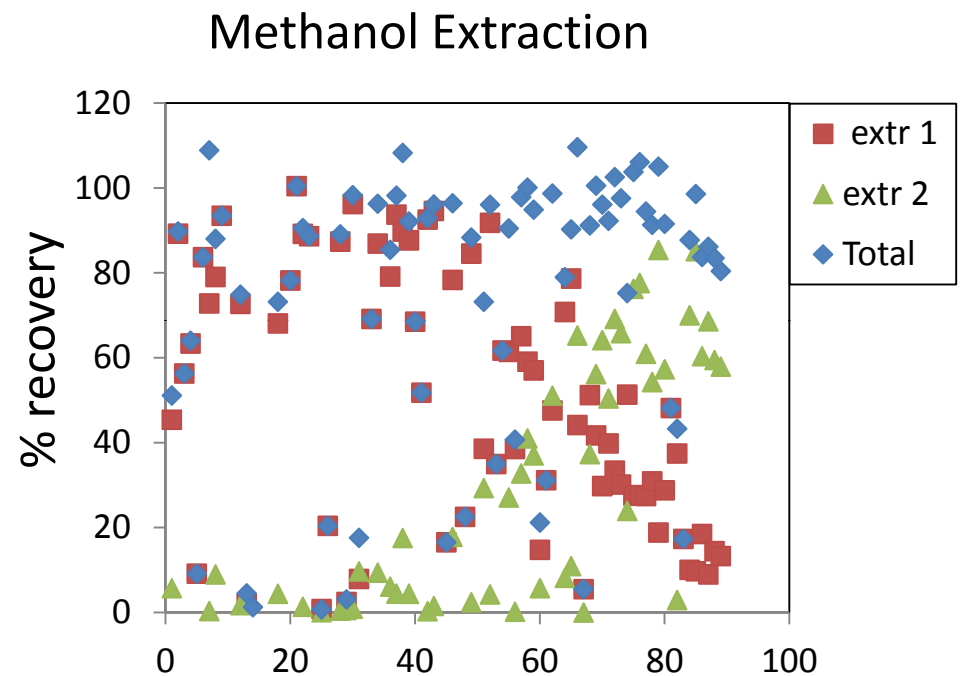
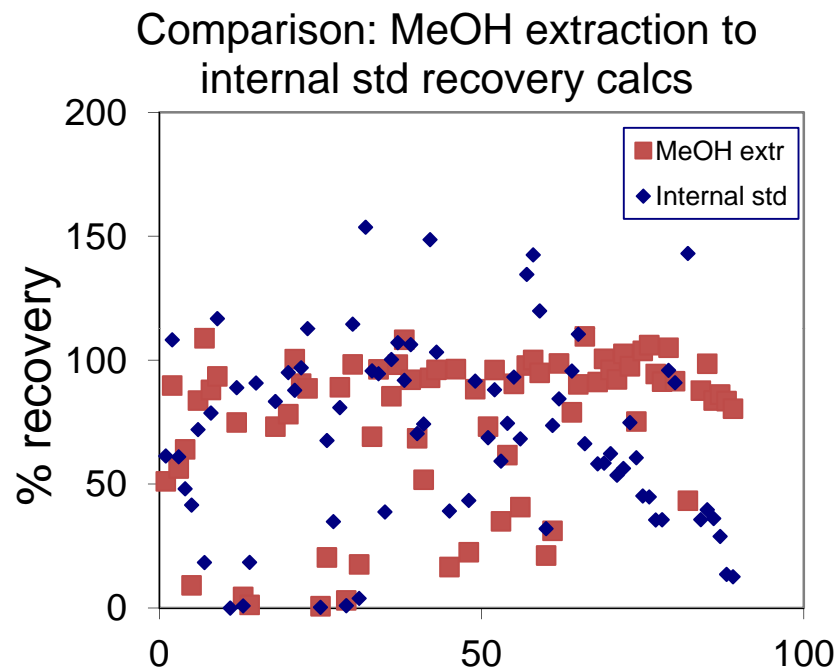
- 8260 recommended ISs: Fluorobenzene, Chlorobenzene-d₅, 1,2-dichlorobenzene-d₄
- Normalize target analyte concentrations to ISs (IS is new “100%”)
- Equil. ISs reduce bias for heaviest targets, but systematic bias still evident



5 min room temp stirring after spiking both targets and ISs into 5 g soil + 5 mL water

Winsconsin soil, 5.8% O.C.
67:21:12 sand/silt/clay

Low recovery of heavy VOCs is not a result of degradation



- Water added to soil, spiked with target VOCs and incubated at room temp for 1 week
- Direct vapor partitioning samples spiked with internal standards and equilibrated overnight prior to analysis
- Methanol extraction (5 mL) performed in triplicate

Winsconsin soil, 2.5 mL water + 5 g soil
(5.8% organic carbon, 67:21:12
sand/silt/clay)

2) Description of Method 8261 calculation model, SMCreporter

Method 8261

System of internal standard recovery corrections developed by Mike Hiatt (ORD-NERL) for use with his vacuum distillation concentrator

Multiple regression model of internal standard recovery vs. two physical properties:

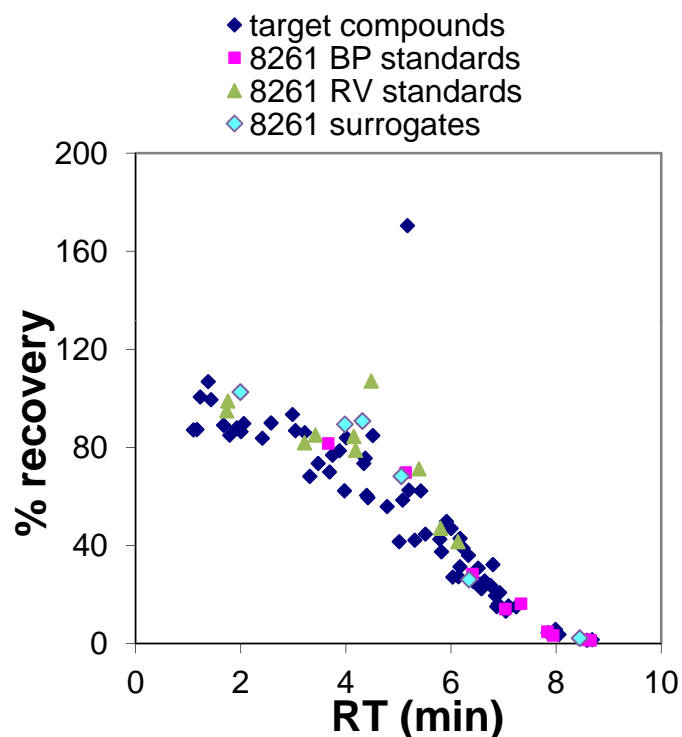
1. Boiling point effects – regression of internal standard recovery vs. STP boiling points (no BP effects modeled below 85°C). Used as a proxy for affinity of chemicals for organics, like K_{oa} (after accounting for relative volatility).
2. Relative volatility effects – effects related to magnitude of water-air partition coefficient. Similar to Henry's Law constant.
3. First pass correction accounts for RV effects in BP standards (uses 3 compounds with BP around 85°C but different relative volatility)



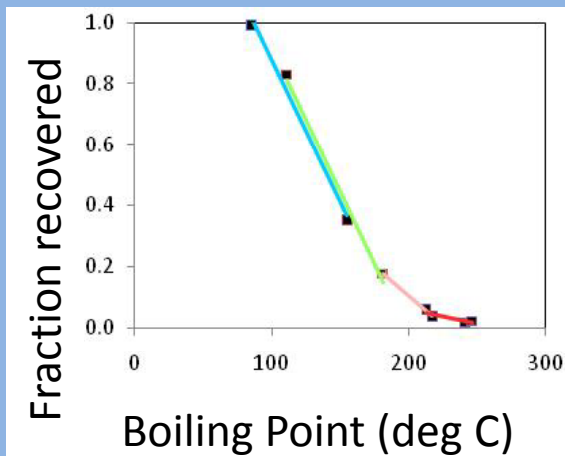
Method 8261

Boiling Point Correction

external standard recovery

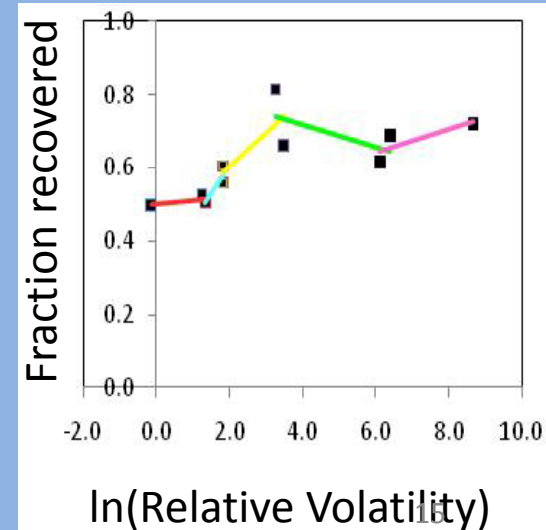


Boiling Point Group	Internal Standard	BP (deg C)	Recovery
1	perfluorobenzene	85	0.990
	toluene-d8	111	0.829
	bromobenzene-d5	155	0.352
2	toluene-d8	111	0.829
	bromobenzene-d5	155	0.352
	1,2-dichlorobenzene-d4	181	0.177
3	1,2-dichlorobenzene-d4	181	0.177
	1,2,4-trichlorobenzene-d3	213	0.059
	naphthalene-d8	217	0.038
4	1,2,4-trichlorobenzene-d3	213	0.059
	naphthalene-d8	217	0.038
	1-methylnaphthalene-d10	241	0.017
	3,5-dibromotoluene	246	0.022



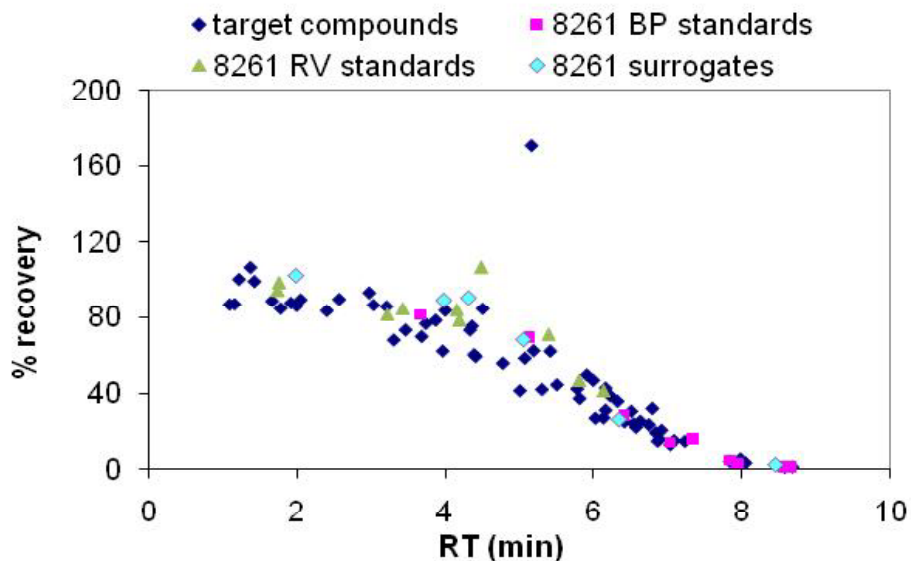
Relative Volatility Correction

Relative Volatility Group	Internal Standard	ln(RV)	Recovery
1	hexafluorobenzene	-0.151	0.499
	fluorobenzene	1.25	0.524
	1,4-difluorobenzene	1.34	0.504
2	1,4-difluorobenzene	1.34	0.504
	o-xylene-d10	1.81	0.605
	chlorobenzene-d5	1.84	0.559
3	o-xylene-d10	1.81	0.605
	chlorobenzene-d5	1.84	0.559
	1,2-dibromoethane-d4	3.26	0.814
4	diethylether-d10	3.48	0.662
	1,2-dibromoethane-d4	3.26	0.814
	diethylether-d10	3.48	0.662
5	tetrahydrofuran-d8	6.12	0.617
	acetone-C13	6.40	0.688
	1,4-dioxane-d8	8.67	0.722



Comparison of 8261 model calculations to 8260

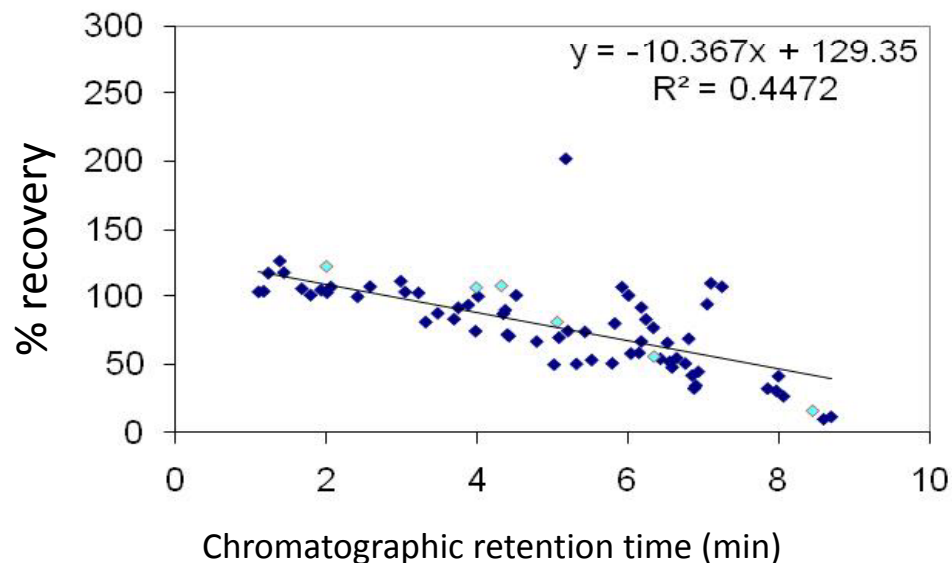
external standard recovery



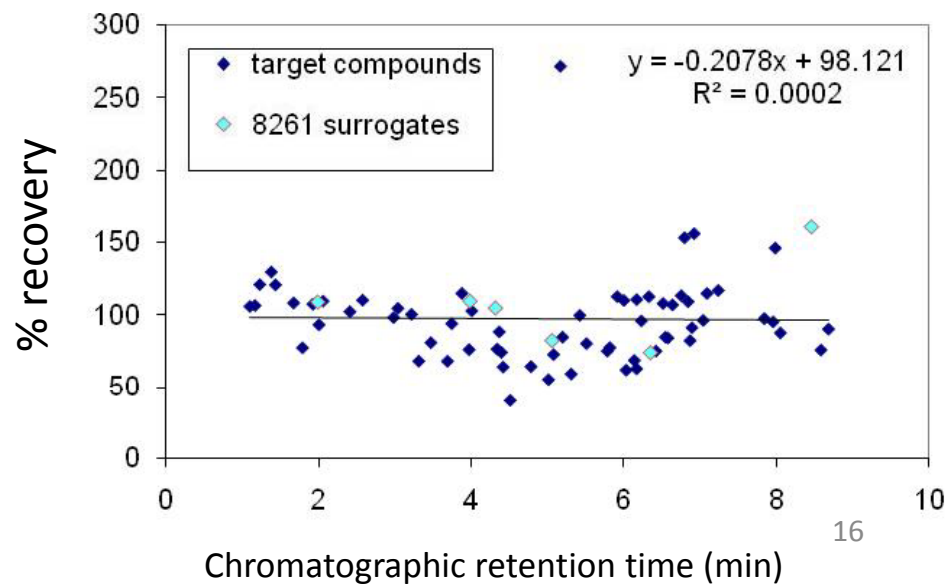
Winsconsin soil, 5.8% organic carbon, 5 g

Analysis Technique	Target Compounds Equilibration	Internal Standards Equilibration
Purge and Trap	spiked into aqueous layer of 5 g soil : 5 mL water slurry; 5 min stirring at room temp	Same as target compounds

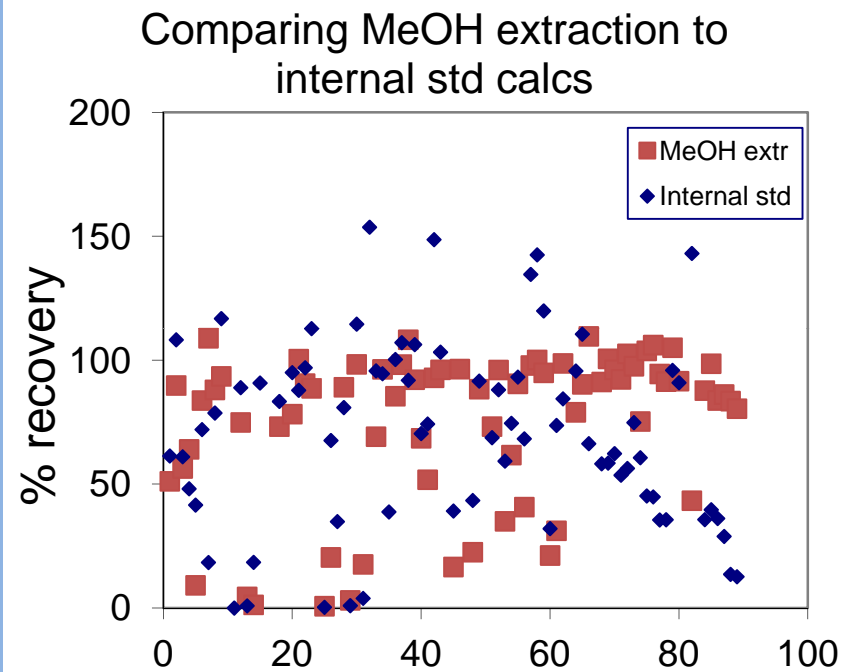
method 8260 internal standard recovery



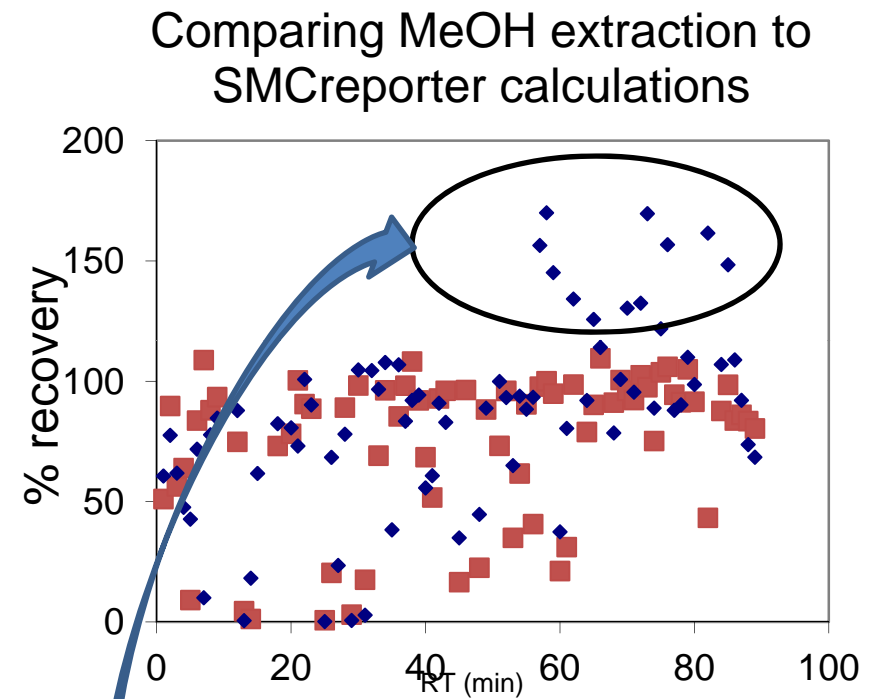
Method 8261 recovery



Comparison of aqueous purge and trap data using 8260 and 8261 model calculations to MeOH extr.



- Spiked with targets and equilibrated at room temp for 1 week
- Direct vapor partitioning samples spiked with internal standards and equilibrated overnight prior to analysis
- Methanol extraction performed in triplicate



Winsconsin soil, 2.5 mL water + 5 g soil
(5.8% organic carbon, 67:21:12 sand/silt/clay)

High bias measurements relative to methanol extraction: alkylbenzenes, 1,2,3-trichloropropane, 1,2-dibromo-3-chloropropane, hexachlorobutadiene

3) Overview of method 8261 model comparison for 3 VOC prep techniques

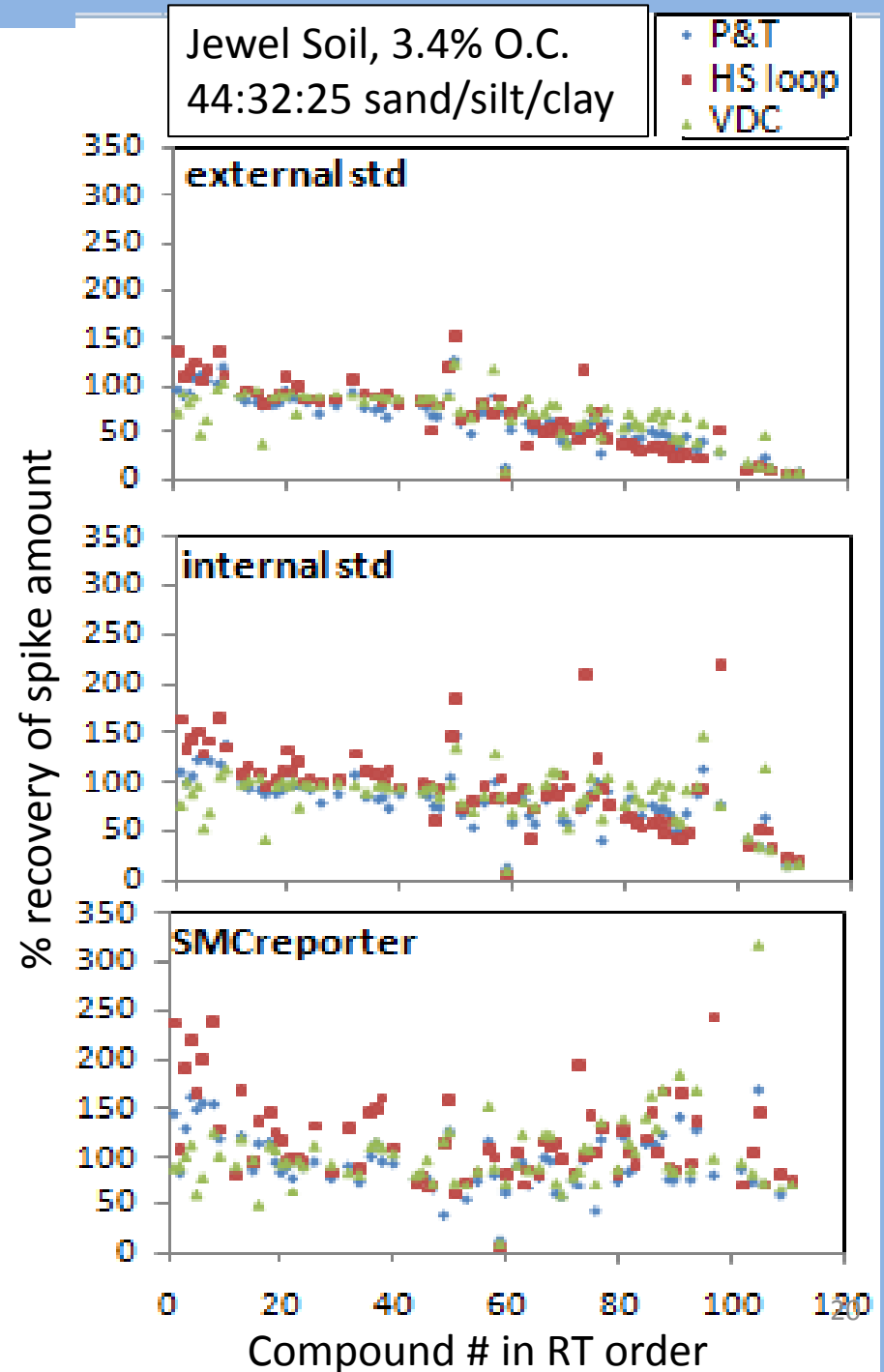
Studies

- Techniques
 - Purge and trap
 - Loop injection static headspace
 - Vacuum distillation
- VOCs tested:
 - Halogenated C1-C4 alkanes/alkenes;
 - Substituted monoaromatics (C1-C4, Cl1-Cl3, Br);
 - Naphthalene + methylnaphthalenes;
 - Water miscibles (nitriles, alcohols, esters, THF, 1,4-dioxane)
 - Ethers
- Matrices:
 - 13 soils, 0.6-22% organic carbon, some clays
 - 5 types of oil (no purge and trap)

Ambient Temp 5 min aqueous spike equilibration in soils

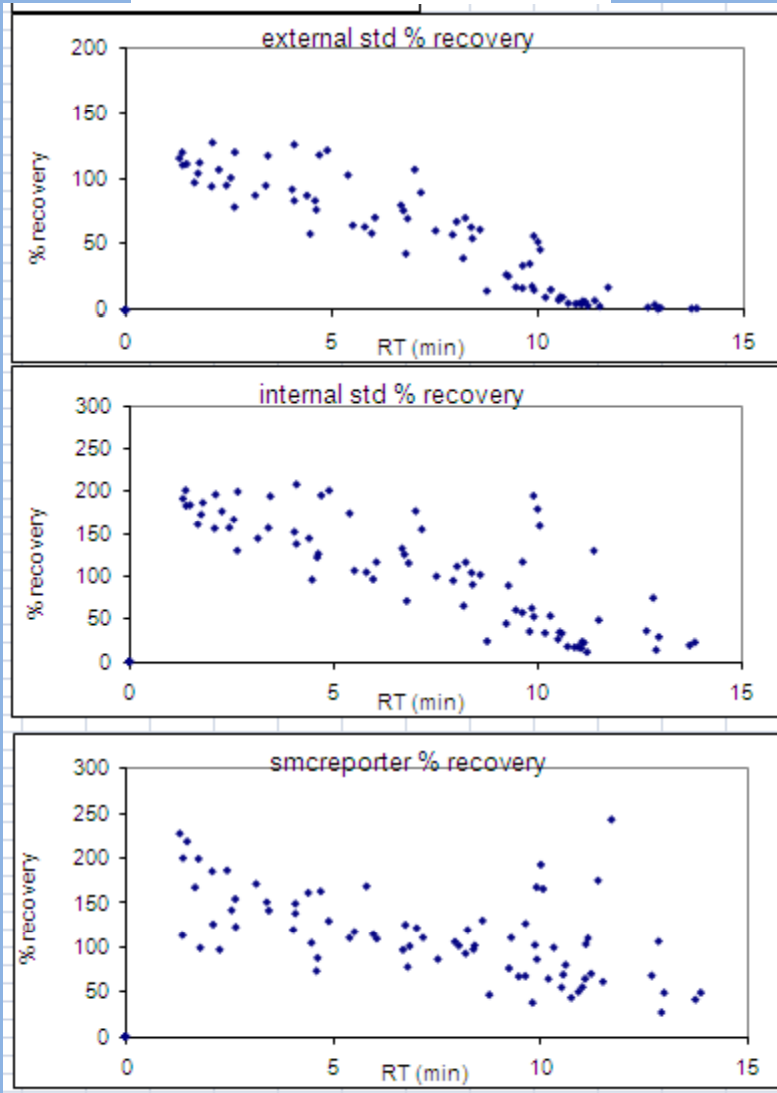
- Add 5 g soil and 5-10 mL water to vial,
- Spike targets and internal standards into water
- Cap and mix for 5 min
- Analyze

- Short contact time, so analyte breakdown is minimized
- Low bias recovery of heavy VOCs greatly reduced for all 3 techniques
- High bias measurement of some analytes increased with SMCreporter, but within a factor of 2 of internal standard model

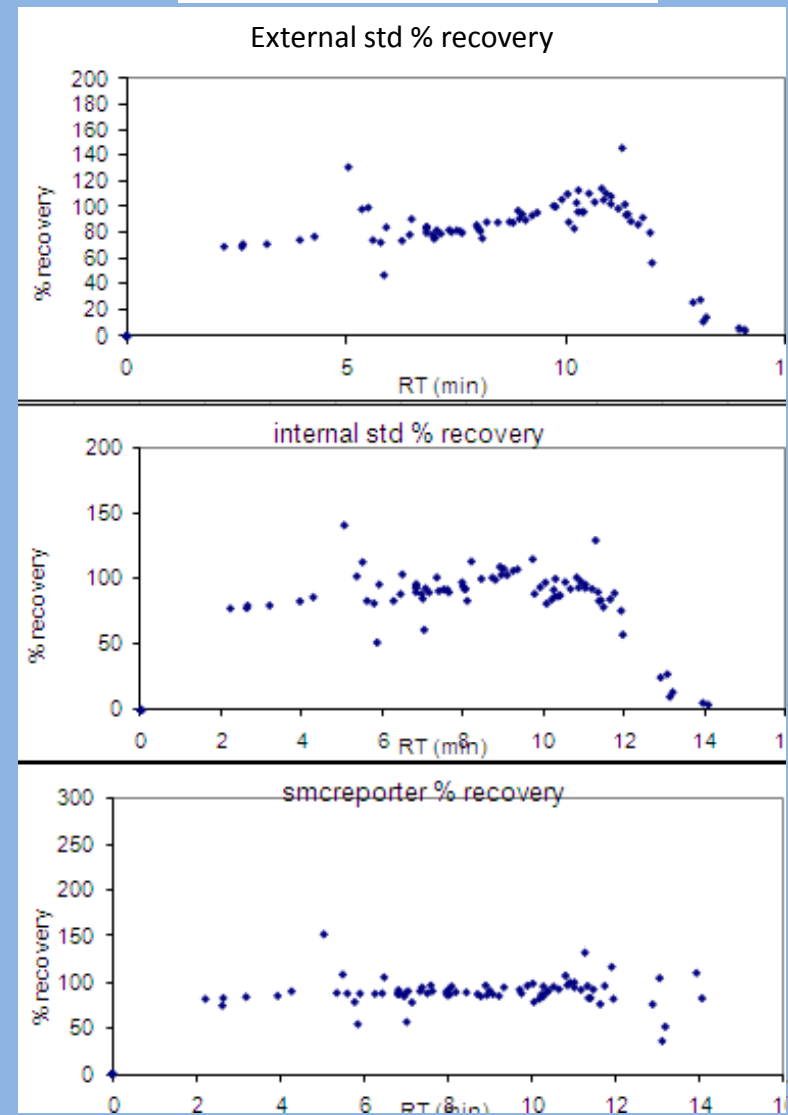


PCB Free transformer oil spike recovery

HS loop

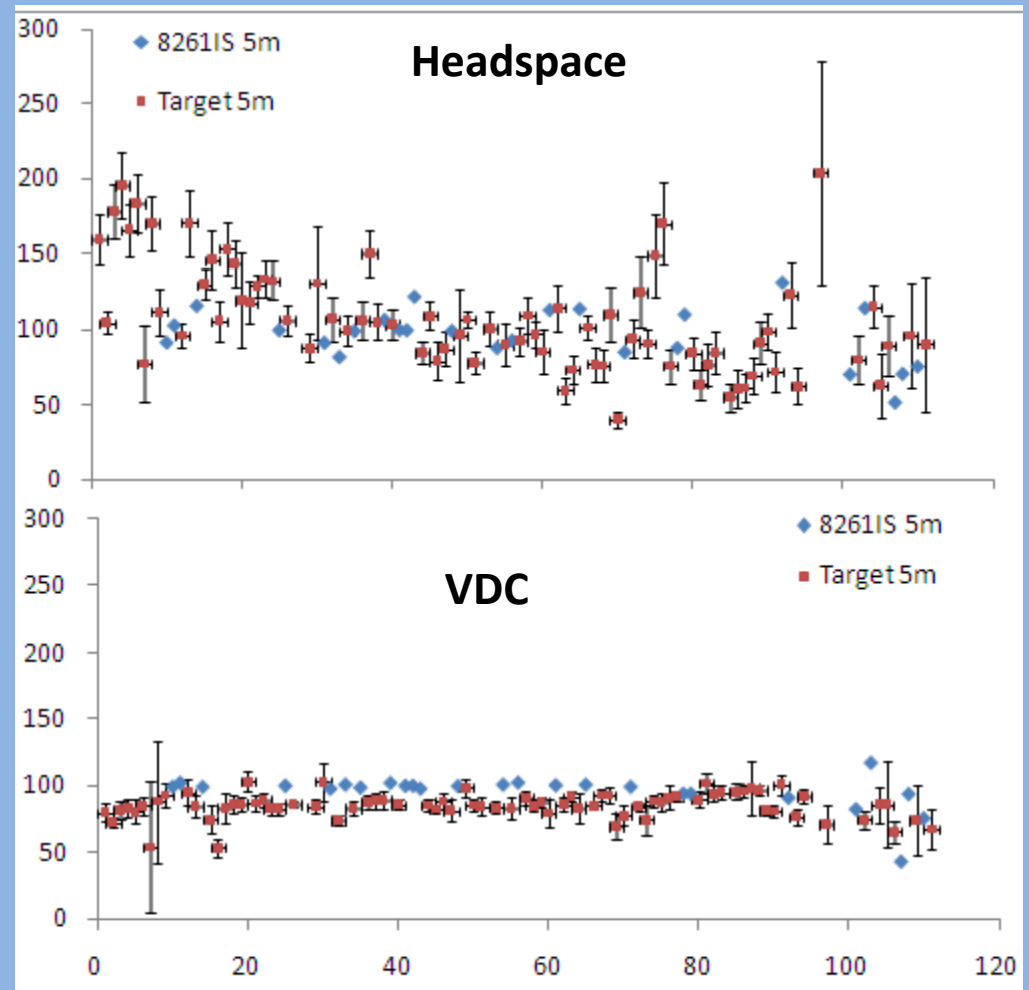


VDC



Spike recovery: 5 oils

- Silicone oil, fish oil, vegetable oil, clean hydrocarbon oil, butter
- 100 mg oil + 5 mL H₂O
- 2.5 mg/kg spike (polars were 10x higher)
- 1 cc static headspace or vacuum distillation



Next steps

- Work on mapping recovery corrections from VDU to headspace and purge and trap to reduce high bias in recovery corrections corrections
 - Apply K_{wa} determined for headspace analysis
 - Use BP recovery corrections below 85 deg C
- Use existing data to describe value added from using surrogates and/or internal standards that bound physical properties of analytes of interest for purge and trap, headspace
- Continue work on low level MeOH extract calibration for solids

Thanks

- RMI project funded by US EPA ORD
- Mike Hiatt
- Interns
- R5 Lab management