Passive Sampling Demonstration/Validation for Vapor Intrusion Assessments

Todd McAlary and H. Groenevelt, Geosyntec Consultants, Inc.,
T. Gorecki and S. Seethapathy, University of Waterloo,
D. Crump, Cranfield University,
P. Sacco, Fondazione Salvatore Maugeri,
H. Hayes, Air Toxics Limited,
M. Tuday, Columbia Analytical Services,
B. Schumacher, USEPA,
P. Johnson, Arizona State University

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Benefits of Passive Sampling

- Simple (minimal training, less risk of leaks)
- Time-weighted average concentration
  (up to a week or a month if needed)
- Low reporting limits with no premium cost
- Smaller – easy to ship, discrete to deploy
- Long history of use in Industrial Hygiene
- Less expensive
- Other benefits unique to each sampler

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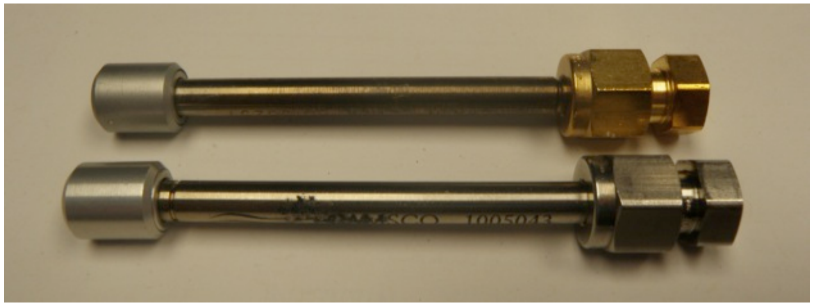
Passive Samplers Tested



ATD Tubes

3M OVM 3500

The mass (M) and time (t) are measured accurately. Key is to know the uptake rate (UR)

$$C_0 = \frac{M}{UR\ t}$$

Equivalent Sample Volume → $UR\ t$

Waterloo Membrane Sampler™

SKC Ultra II

Radiello™

Differences: size, uptake rates, sorbents, medium of uptake, method of analysis

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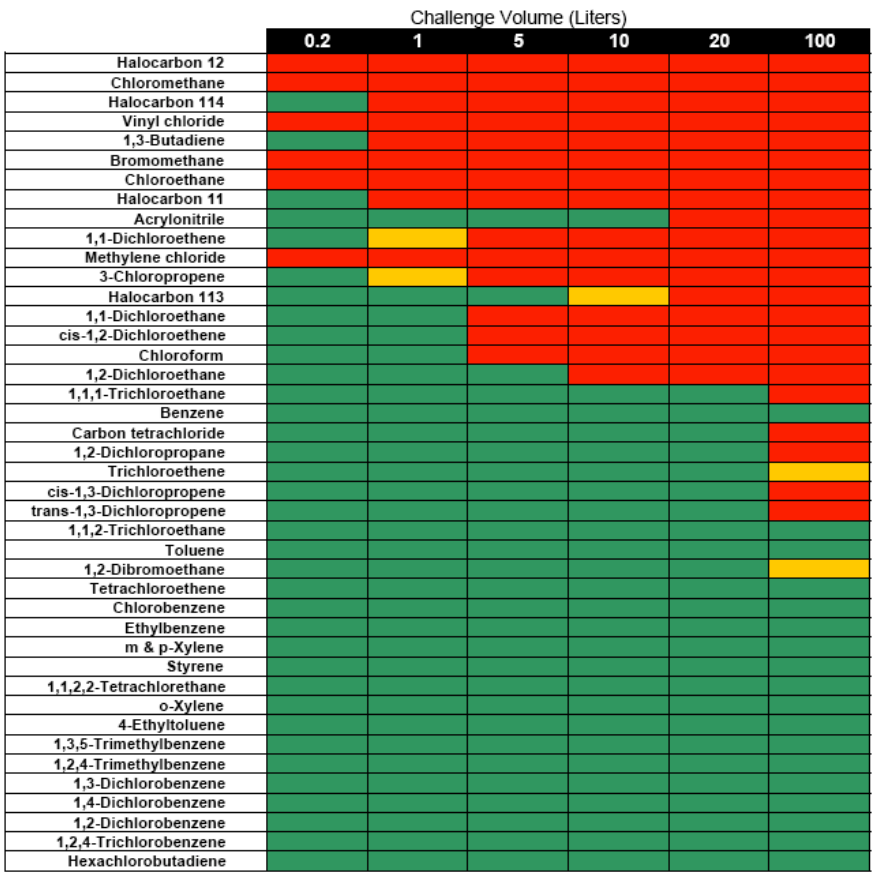
TO-17 Sorbent Selection

Carbopack B

(Graphitized Carbon Black)
Surface Area: 100 m^2/g
Desorption Temperature: 330 °C



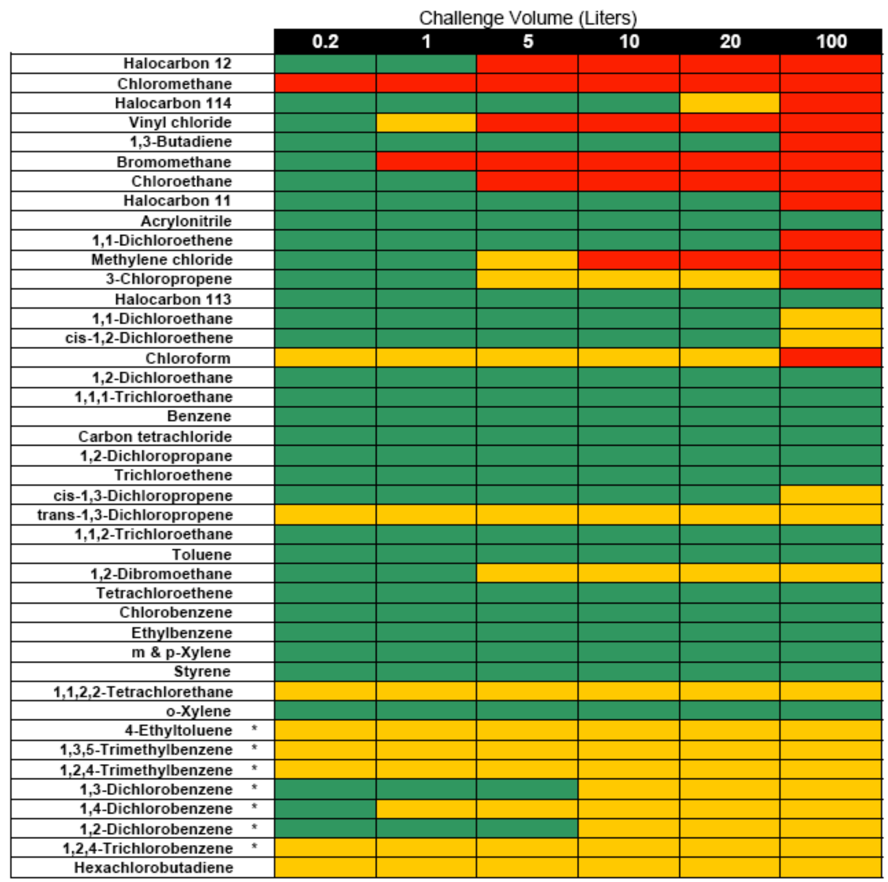
Performance Key

Safe to use: Recovery is greater than 80%
Caution: Recovery is between 21 to 79%
Not Recommended: Recovery is less than 20%

** indicates this analyte was strongly adsorbed*

Carbopack X

(Graphitized Carbon Black)
Surface Area: 240 m^2/g
Desorption Temperature: 330 °C



Performance Key

Safe to use: Recovery is greater than 80%
Caution: Recovery is between 21 to 79%
Not Recommended: Recovery is less than 20%

** indicates this analyte was strongly adsorbed*

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Laboratory Test Compound List

Analyte	Koc (mL/g)	OSWER indoor conc. at 10^{-6} risk (ppb)	Vapor pressure (atm)	Water solubility (g/l)
1,1,1-Trichloroethane	**110**	400	0.16	1.33
1,2,4-Trimethylbenzene	**472**	1.2	0.00197	0.0708
1,2-Dichloroethane	**174**	0.023	0.107	8.52
2-Butanone (MEK)	**134**	340	0.1026	~ 256
Benzene	**59**	0.10	0.125	1.75
Carbon tetrachloride	**174**	0.026	0.148	0.793
Naphthalene	**2,000**	0.57	0.000117	0.031
n-Hexane	**3,000**	57	0.197	0.0128
Tetrachloroethene	**155**	0.12	0.0242	0.2
Trichloroethene	**166**	0.22	0.0948	1.1

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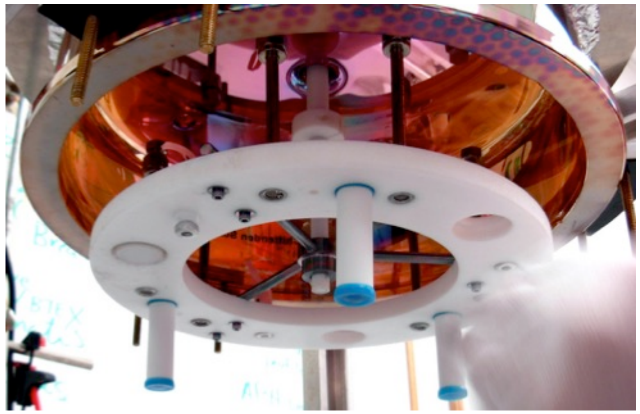
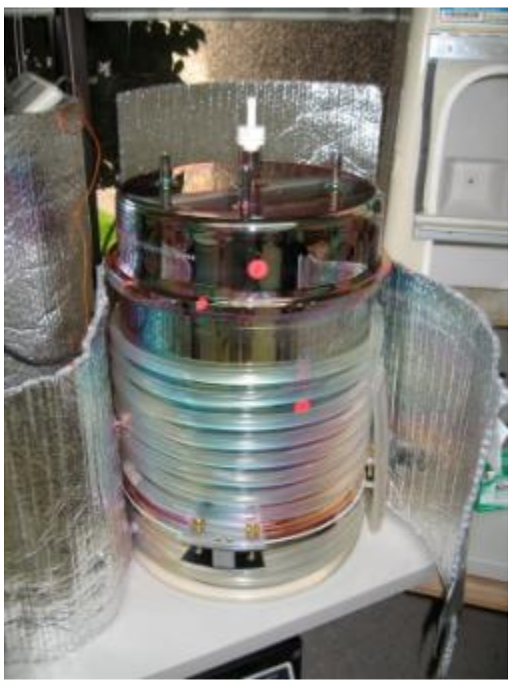
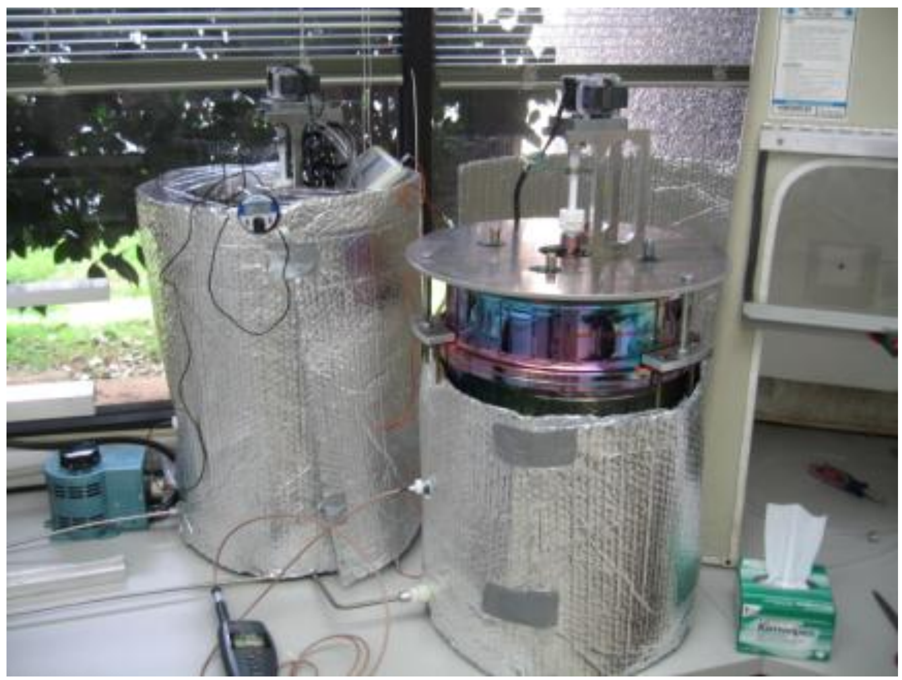
Passive Sampler Calibration



Testing included:
5 samplers in triplicate
10 Compounds
High, Medium and Low:
- Concentration,
- Face Velocity,
- Temperature,
- Relative Humidity,
- Duration





24 chambers x
5 sampler types x
3 replicates x
10 chemicals
= 3600 data points


HEMCO

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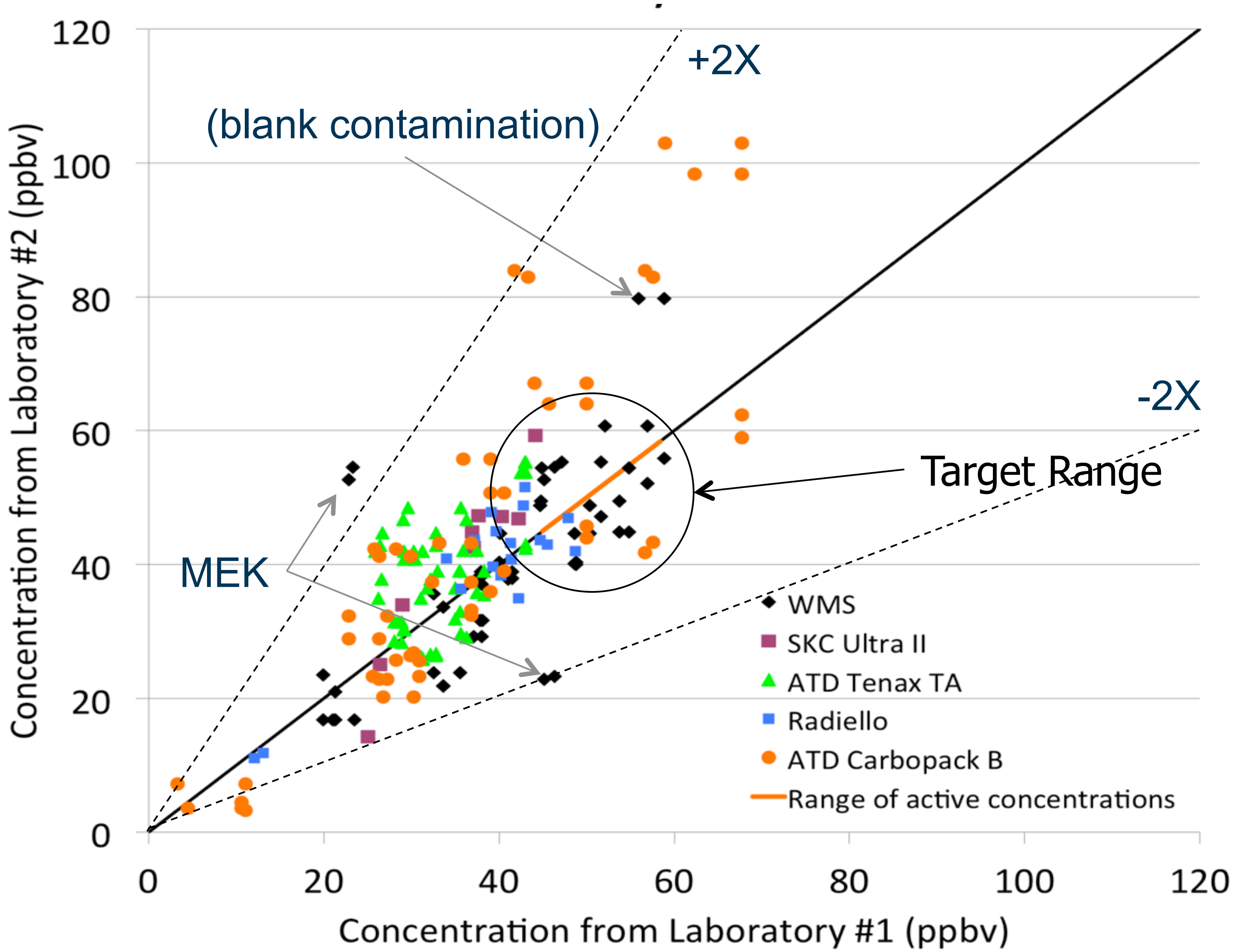
Inter-laboratory Test



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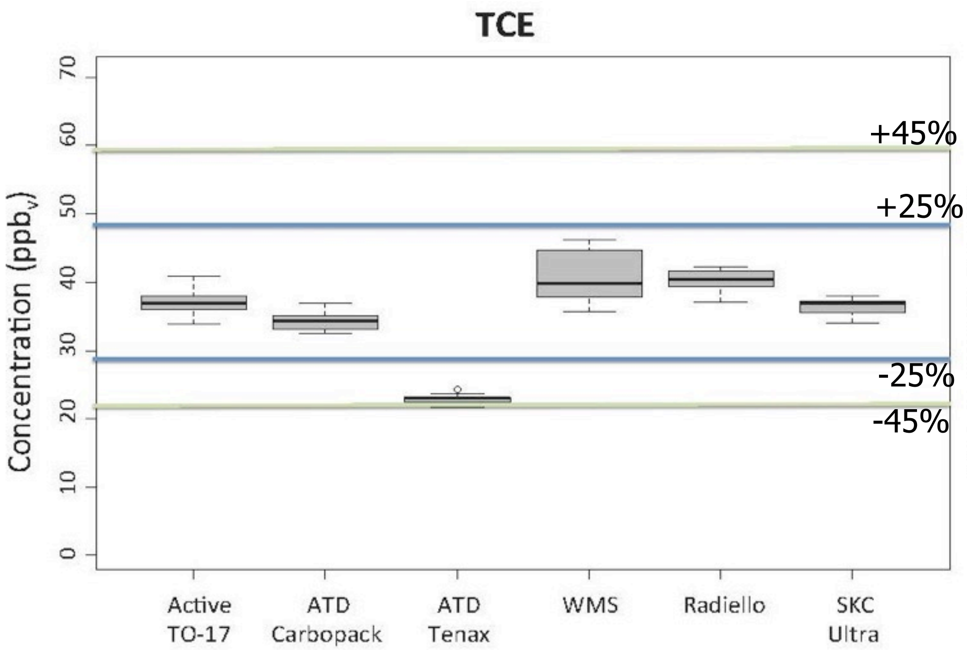
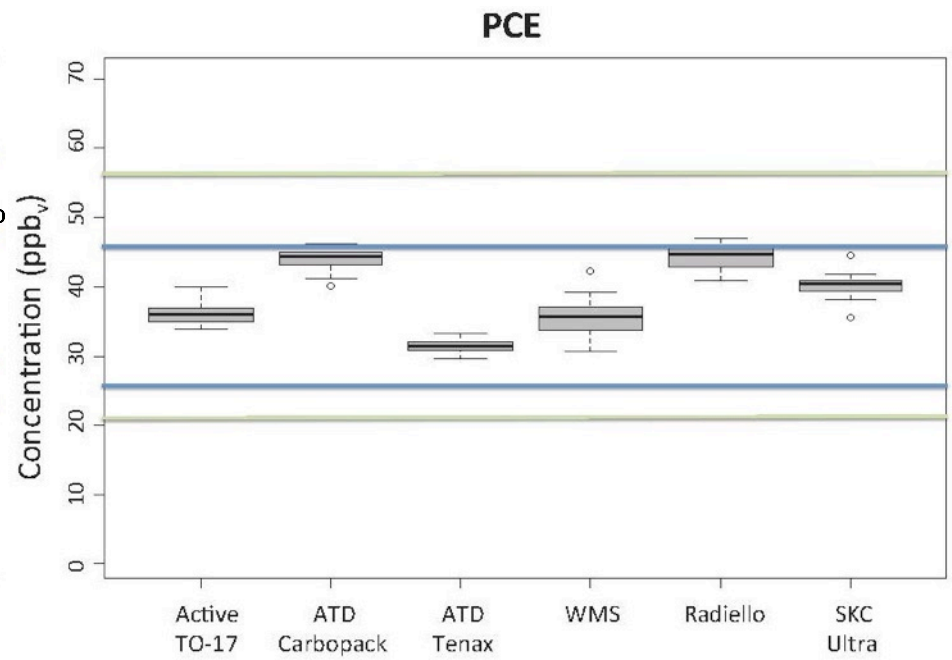
Fractional Factorial Testing

Run #	Approximate Concentration (ppbv)	Approximate Temperature (^oC)	Face Velocity (m/s)	Duration (days)	Approximate Humidity (%R.H.)
1	100	17	0.41	1	90
2	1	17	0.014	1	90
3	100	30	0.41	1	30
4	1	30	0.014	1	30
5	100	30	0.41	7	90
6	1	30	0.014	7	90
7	100	17	0.41	7	30
8	1	17	0.014	7	30
9	50	20	0.23	4	60
10	50	20	0.23	4	60
11	100	17	0.014	1	30
12	1	17	0.41	1	30
13	100	17	0.014	7	90
14	1	17	0.41	7	90
15	100	30	0.014	7	30
16	1	30	0.41	7	30
17	100	30	0.014	1	90
18	1	30	0.41	1	90

Center-Point Results

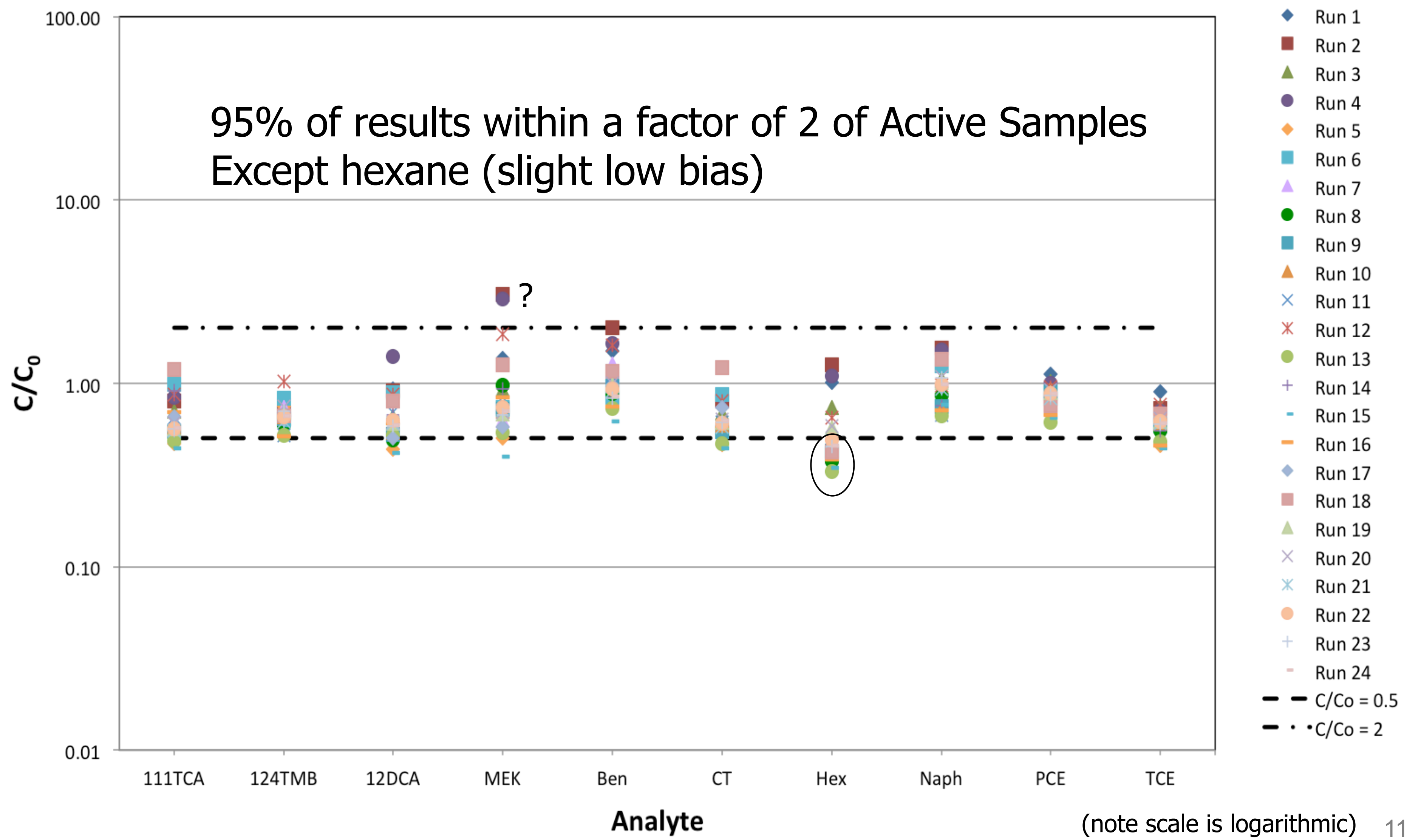




Results only for the center-point tests (all factors at middle of ranges)

(note scales are linear)

ATD Tenax TA



(note scale is logarithmic)

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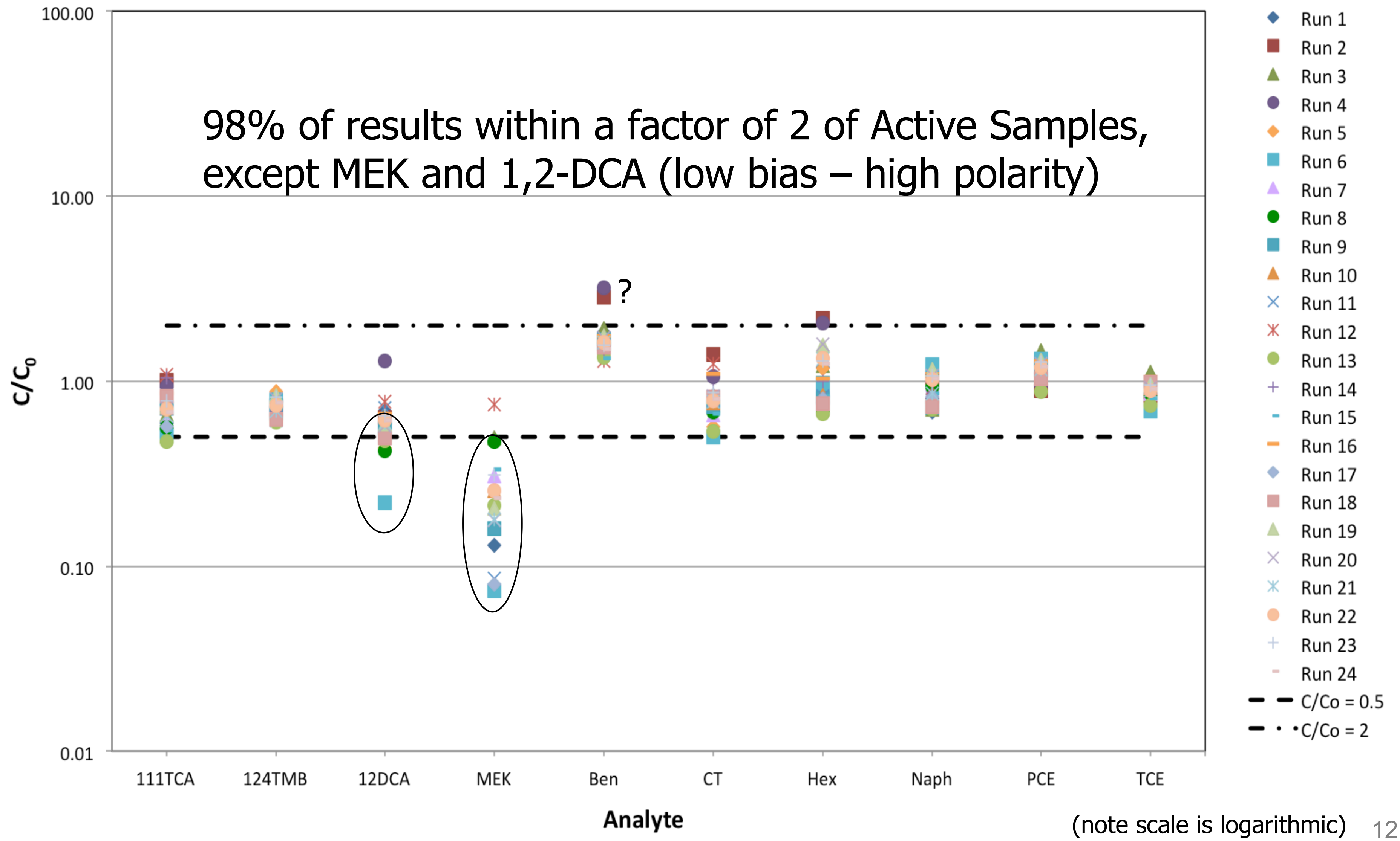
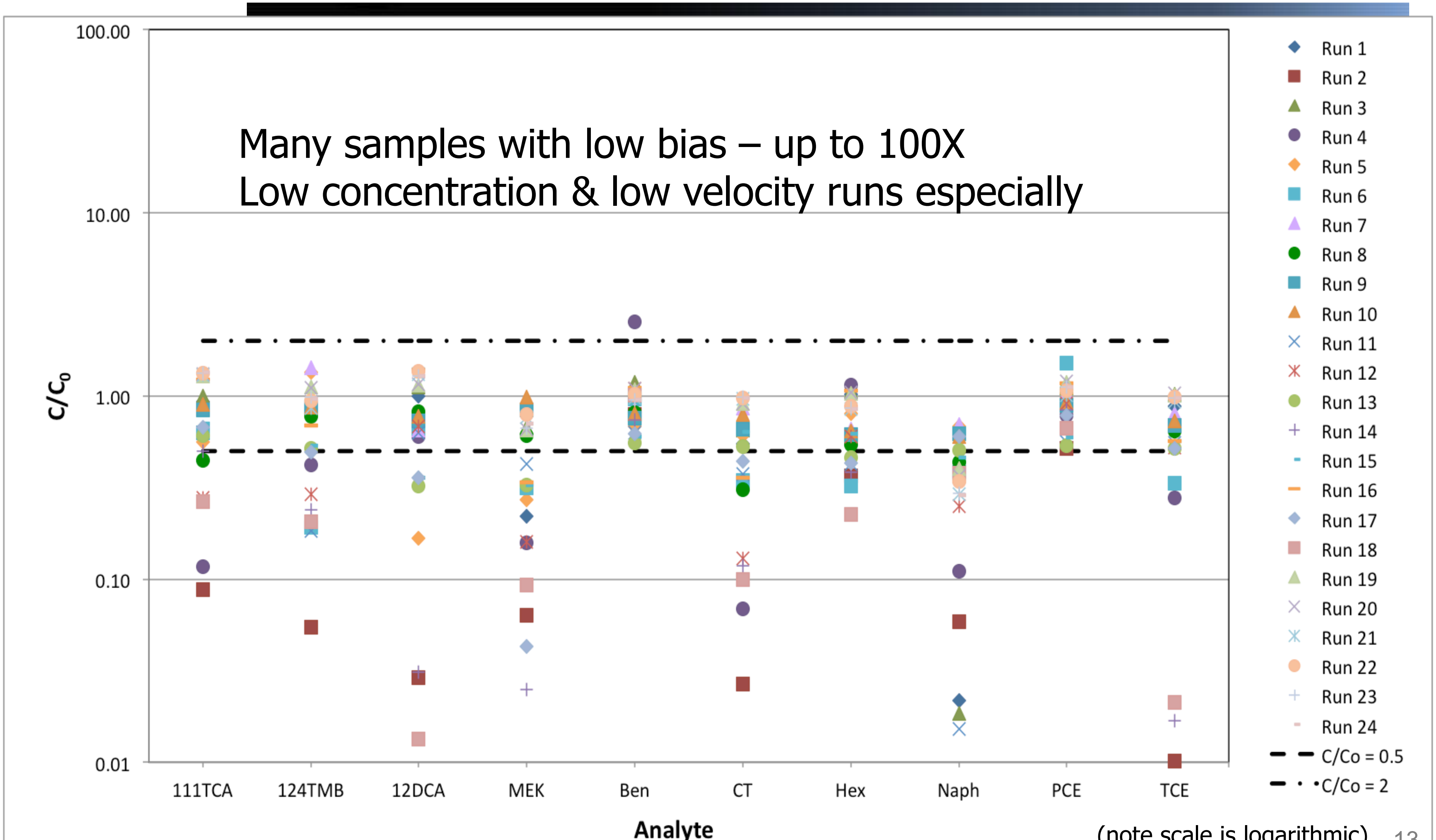
ATD Carbopack B



(note scale is logarithmic)

SKC Ultra



(note scale is logarithmic)

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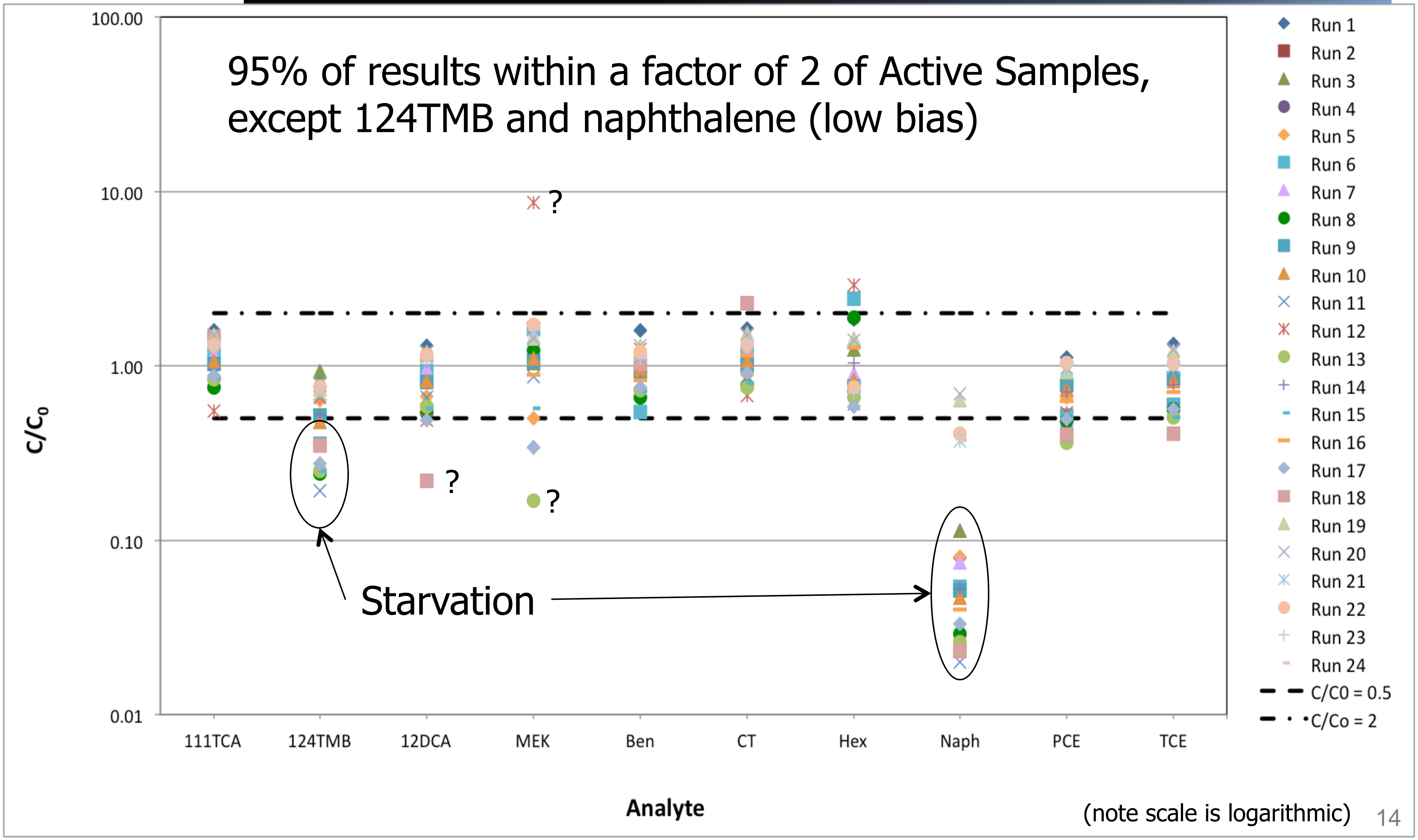
Waterloo Membrane Sampler



(note scale is logarithmic)

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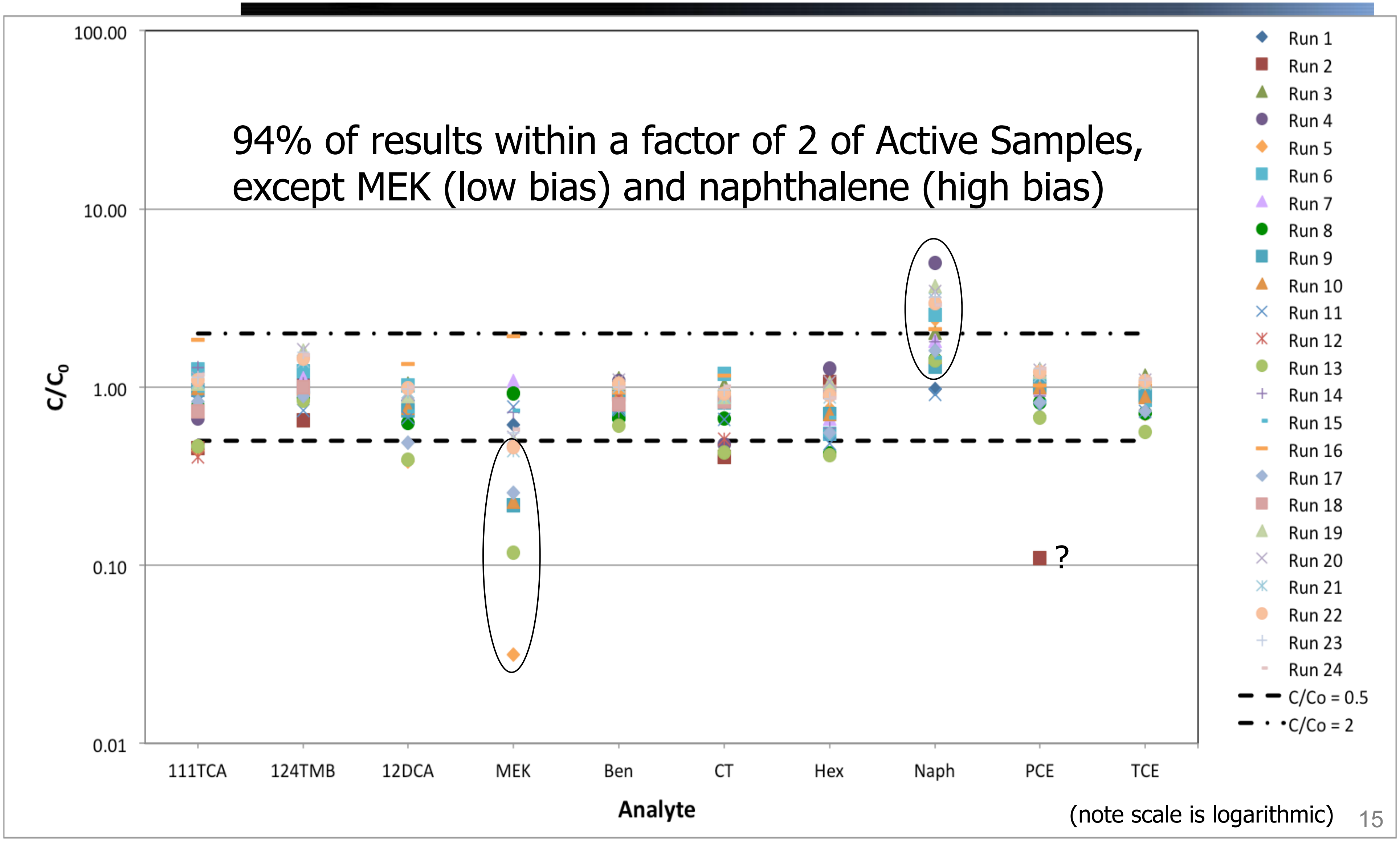
Radiello



Inter-Chamber Precision

Compound	Mean Intra-Chamber Coefficient of Variation (COV)					
	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active ATD/ Calculated
111TCA	**7%**	**3%**	**7%**	**5%**	**14%**	13%
124TMB	**5%**	**5%**	**7%**	**4%**	**22%**	7%
12DCA	**8%**	**3%**	**6%**	**4%**	**12%**	9%
MEK	47%	**5%**	**13%**	**11%**	**23%**	15%
CT	**4%**	**6%**	**8%**	**4%**	**8%**	12%
HEX	**7%**	**2%**	**7%**	**7%**	**16%**	7%
BENZ	**5%**	**6%**	**12%**	**3%**	**10%**	6%
NAPH	**6%**	**12%**	**7%**	**6%**	**16%**	7%
PCE	**2%**	**3%**	**6%**	**3%**	**6%**	5%
TCE	**3%**	**2%**	**5%**	**3%**	**16%**	5%

Mean intra-chamber COV is the average of 24 COV values, from three replicates in each chamber

Bold: COV value meeting the success criterion (< 30%)

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Intra-Chamber Precision

Mean inter-chamber COV	Mean Inter-Chamber Coefficient of Variation (COV)					
	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active ATD/ Calculated
111TCA	**24%**	**27%**	**26%**	35%	51%	18%
124TMB	**12%**	**16%**	42%	**25%**	55%	17%
12DCA	31%	32%	35%	**28%**	61%	23%
MEK	88%	69%	116%	70%	65%	19%
CT	**25%**	**26%**	31%	**28%**	59%	19%
HEX	37%	45%	56%	**28%**	39%	27%
BENZ	**25%**	31%	**26%**	**16%**	40%	19%
NAPH	**18%**	**25%**	128%	46%	58%	17%
PCE	**13%**	**14%**	34%	**27%**	**26%**	18%
TCE	**11%**	**17%**	34%	**30%**	51%	16%
Inter-chamber COV is the COV of 24 average C/C_0 values, one from each chamber test						
Bold: COV value meeting the success criterion (< 30%)						

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Accuracy

Compound	Mean C/C_0 (passive/active)					
	ATD: Carbopack B	ATD: Tenax	WMS	Radiello	SKC	Active/ Calculated
111TCA	**0.72**	**0.67**	**1.15**	**0.95**	**0.80**	0.79
124TMB	**0.73**	**0.69**	0.54	**1.13**	**0.69**	0.89
12DCA	0.60	**0.67**	**0.86**	**0.83**	**0.75**	0.87
BEN	1.71	**1.07**	**0.99**	**0.90**	**0.95**	0.72
CT	**0.82**	**0.67**	**1.18**	**0.81**	0.55	0.98
HEX	**1.12**	0.55	**1.15**	**0.80**	**0.70**	0.86
MEK	0.21	**1.00**	**1.12**	0.62	0.46	1.33
NAPH	**0.90**	**0.98**	0.17	2.26	0.36	0.82
PCE	**1.15**	**0.85**	**0.72**	**1.02**	**0.98**	0.94
TCE	**0.91**	0.62	**0.80**	**0.91**	**0.87**	0.91
Mean C/C_0 is the mean of 24 passive/active concentration ratios (one for each chamber test)						
Bold: average C/C_0 values within the 0.63 to 1.58 range, meeting the success criterion (RPD < +/-45%)						
Active ATD tube data compared to concentrations calculated from standard gas dilution						

High Concentration Lab Tests

(To mimic soil gas conditions)

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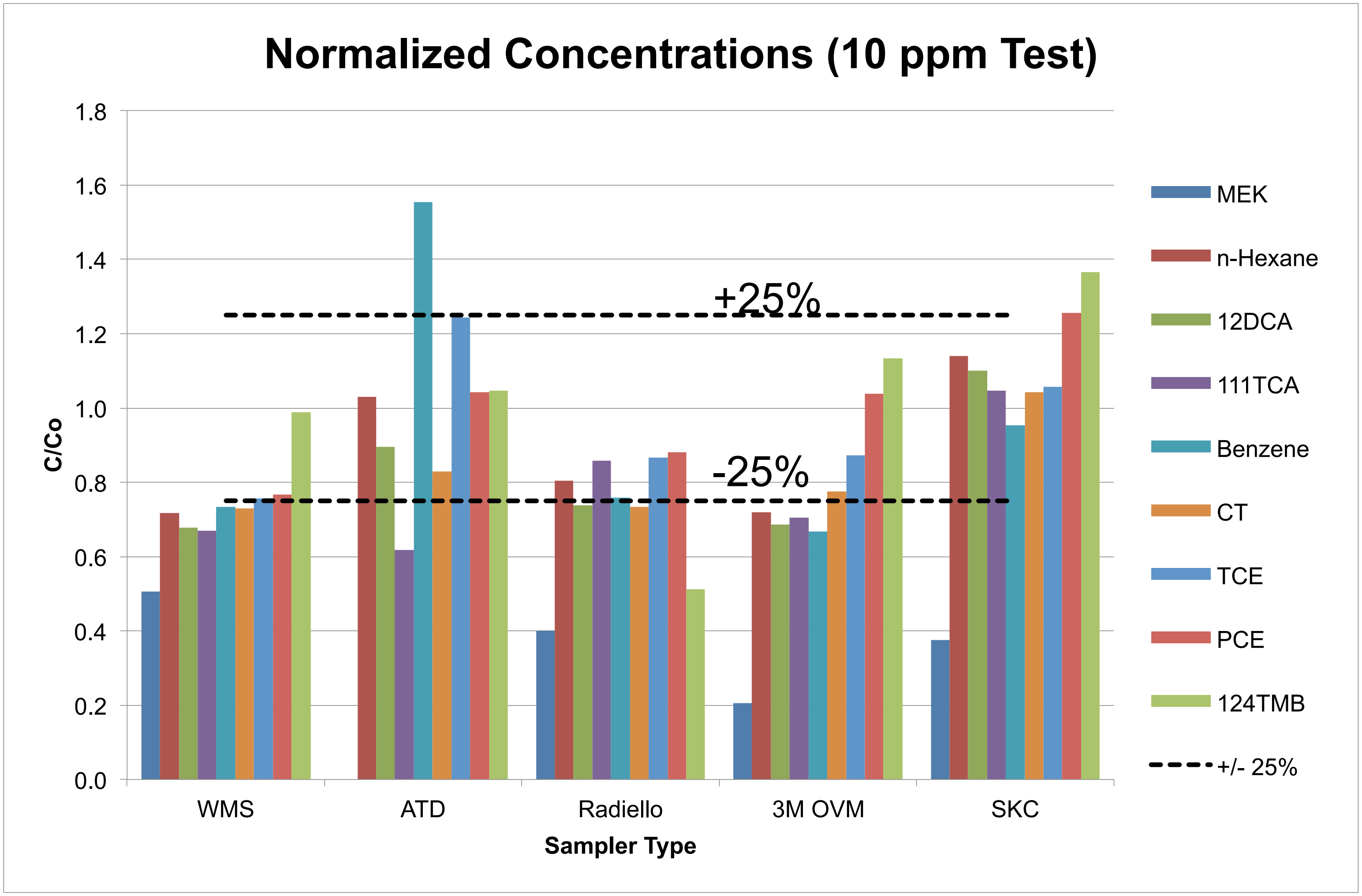
High Concentration Lab Tests

High Concentrations Test Results



Field Testing

Indoor and Outdoor Air

Soil Gas

Sub-slab

Acknowledgements to Ignacio Rivera and
Bart Chadwick of SPAWAR for Support

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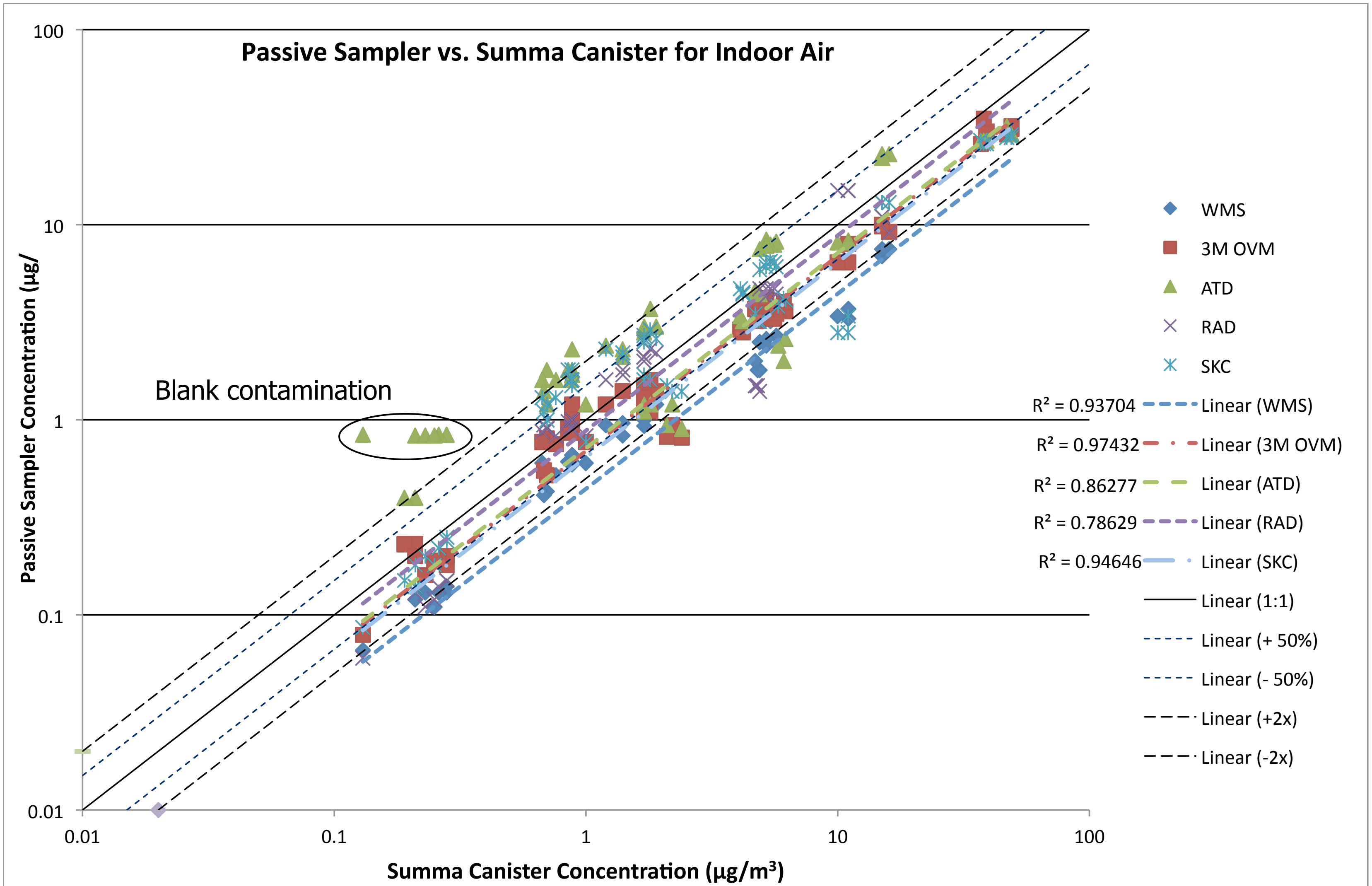
Indoor Air VOCs at Cherry Point

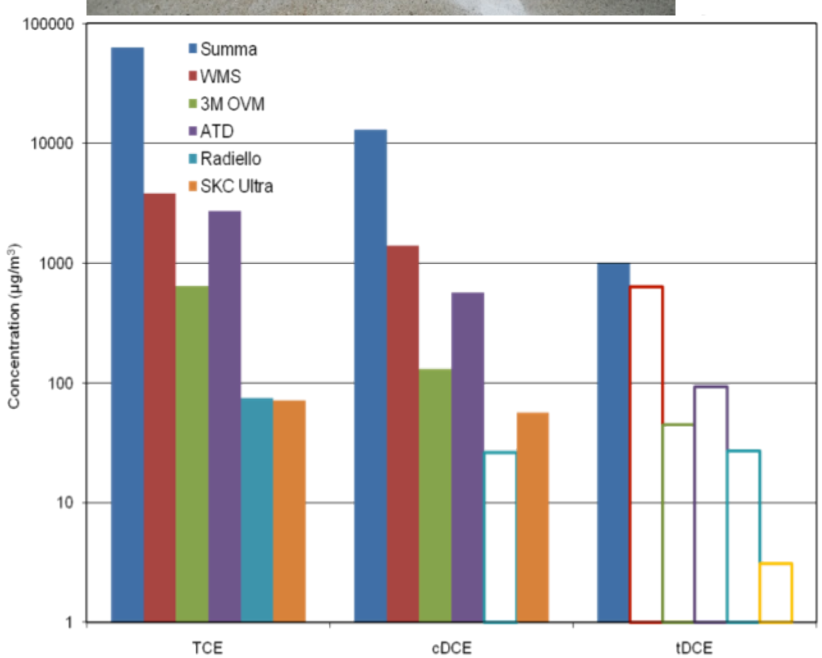


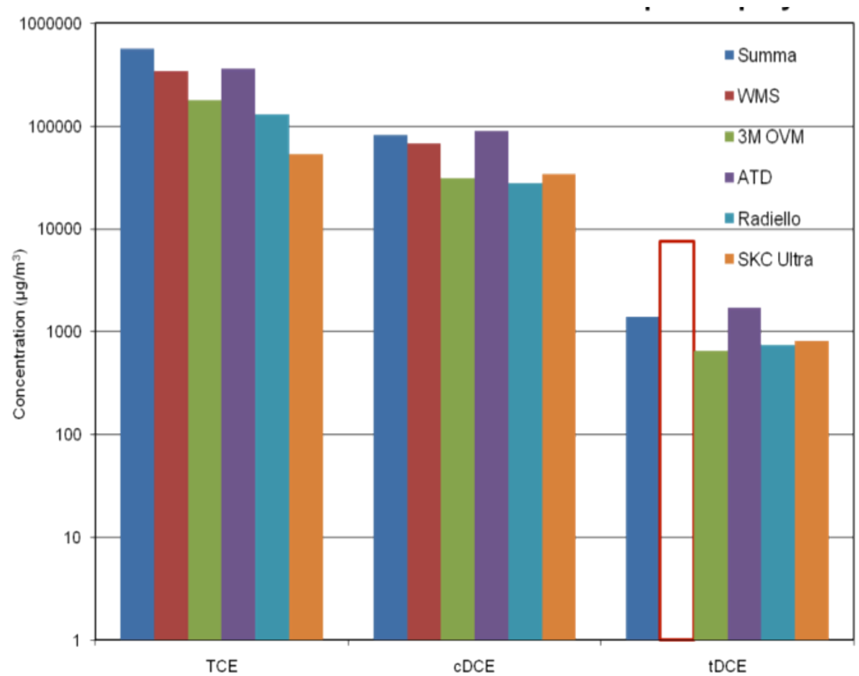
Excludes compounds for which equivalent sample volume was greater than Safe Sample Volume

Sub-Slab – Navy San Diego

Sub-slab samples only
Fully-passive and with PID purging (flow-through)

Starvation proportional to uptake rate
Less starvation for semi-passive samples





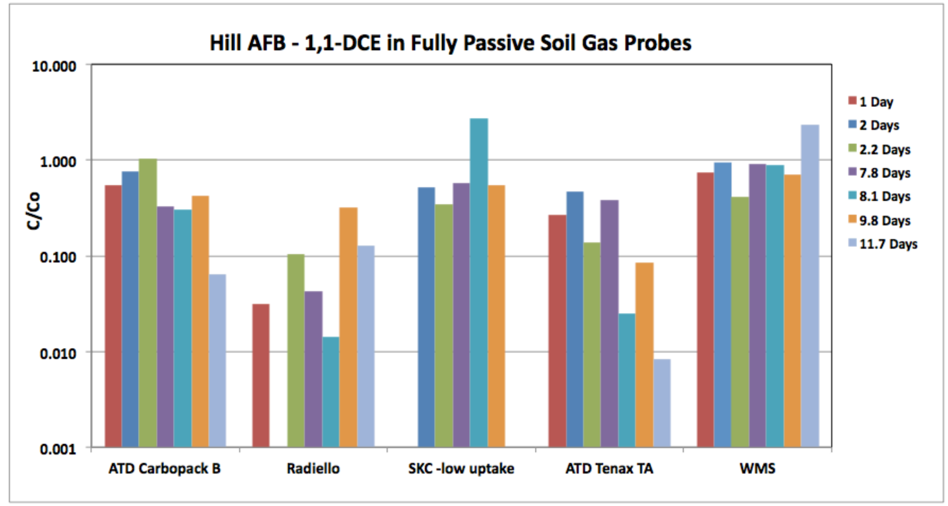
Soil Gas @ 12 ft – Hill AFB

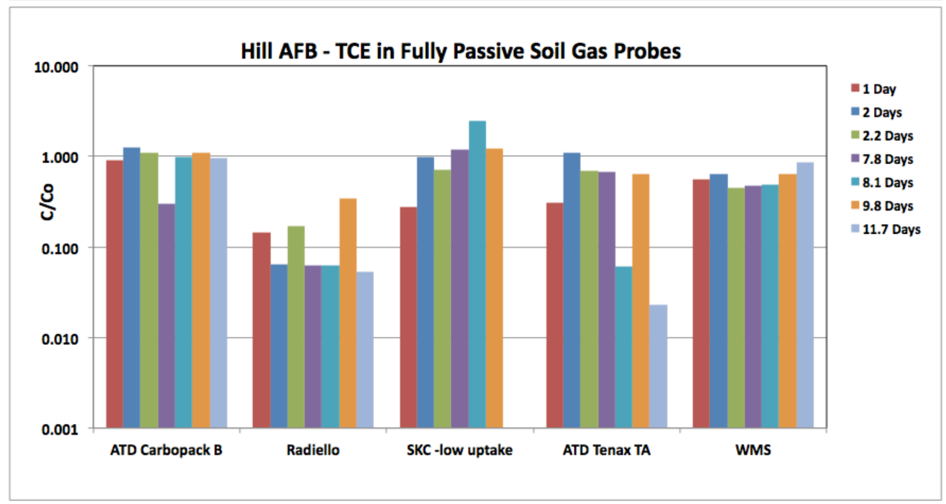
6 probes -12 ft deep

Latin Square Design

1 to 12 day exposures

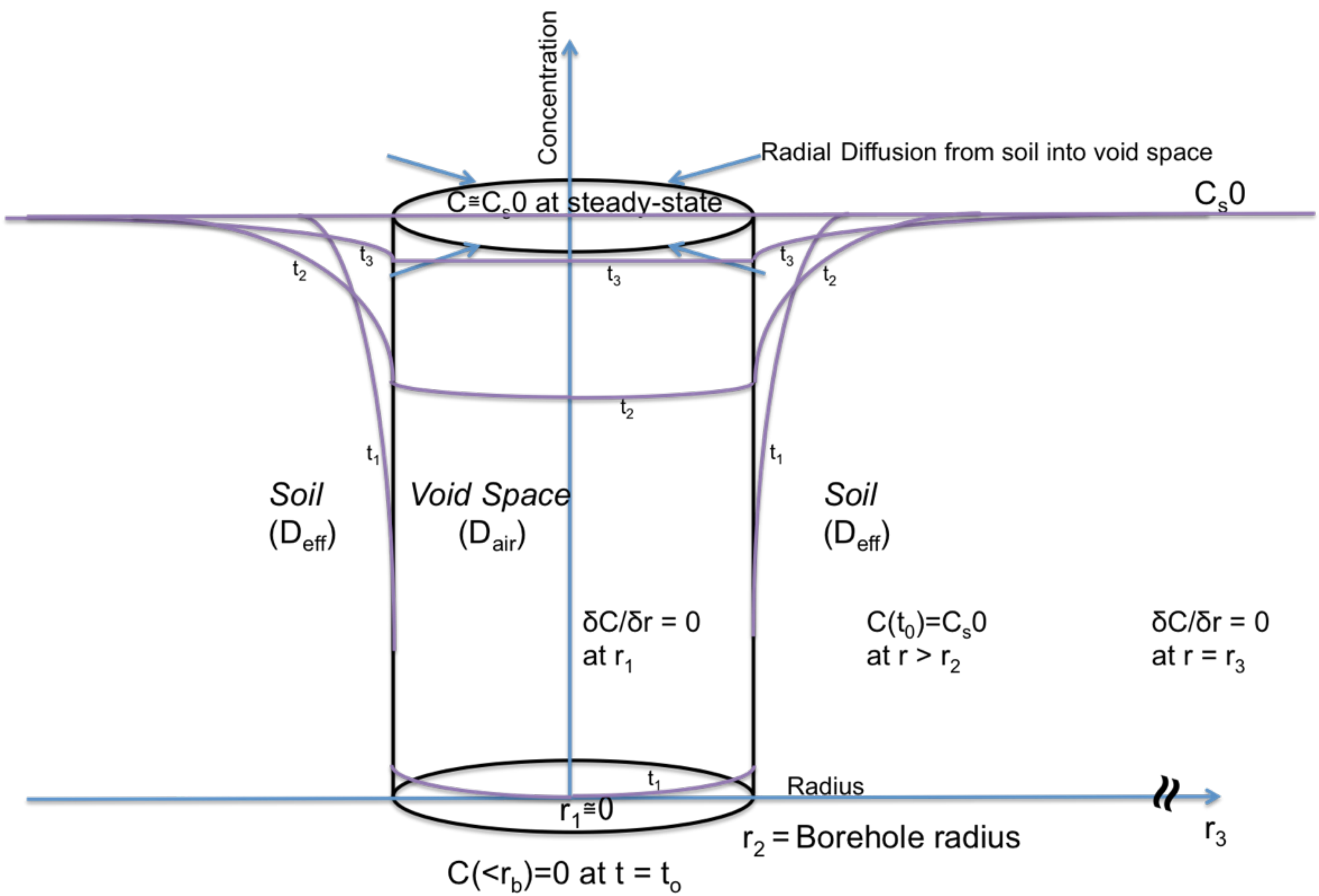
C_o Measured using combination of Summa and Hapsite GC/MS





Negative bias for long duration with ATD-Tenax
Negative bias for high uptake rate (Radiello)
Otherwise, encouraging results for TCE and DCE

Mathematical Modeling

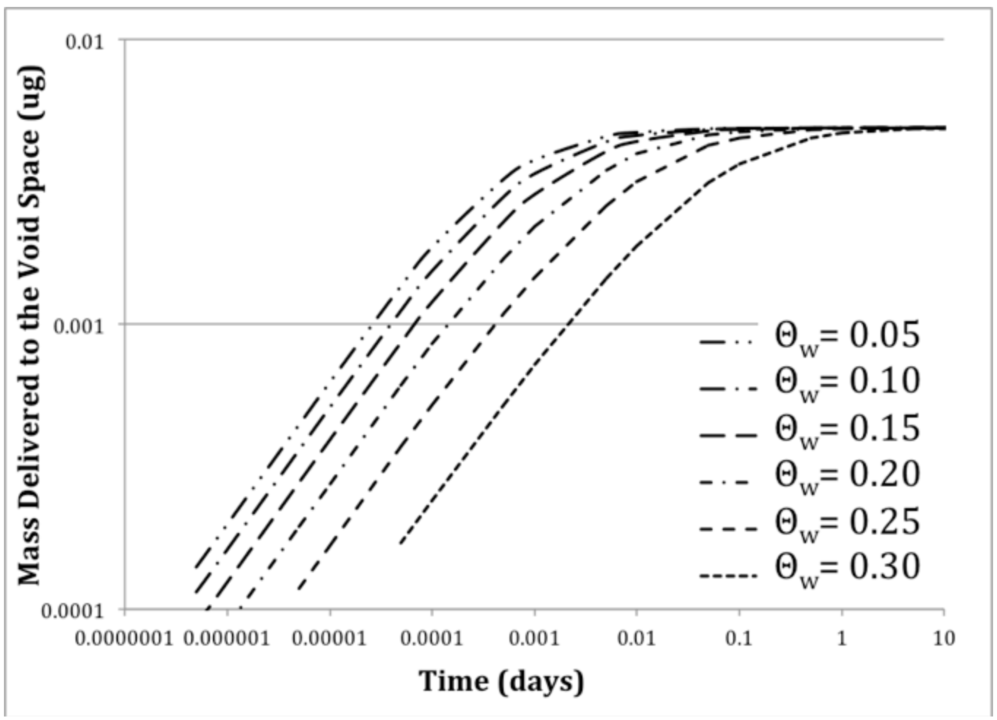


Transient and Steady-State Modeling

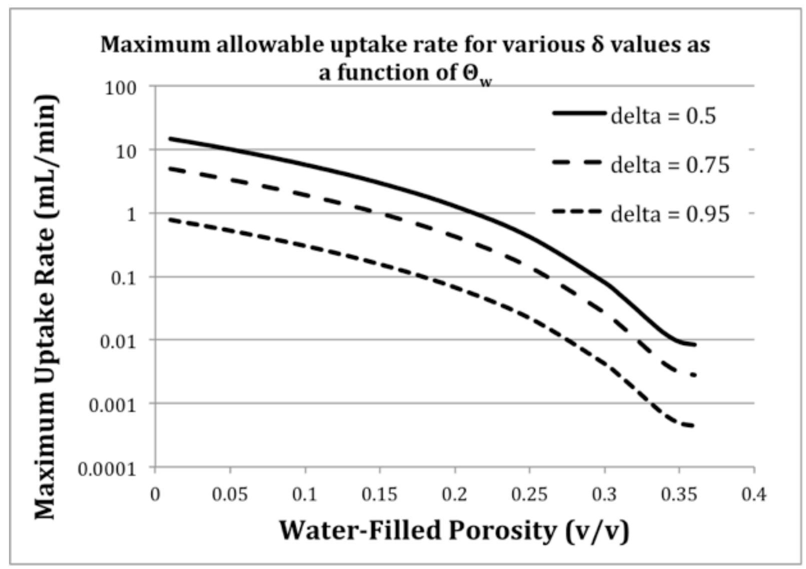
$$\bar{M}(p) = \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5} \frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2)\right]$$

$$I_\alpha(x) = i^{-\alpha} J_\alpha(ix) = \sum_{m=0}^{\infty} \frac{1}{m!\,\Gamma(m+\alpha+1)} \left(\frac{x}{2}\right)^{2m+\alpha}$$

$$K_\alpha(x) = \frac{\pi}{2}\frac{I_{-\alpha}(x) - I_\alpha(x)}{\sin(\alpha\pi)} = \frac{\pi}{2} i^{\alpha+1} H_\alpha^{(1)}(ix) = \frac{\pi}{2}(-i)^{\alpha+1} H_\alpha^{(2)}(-ix)$$



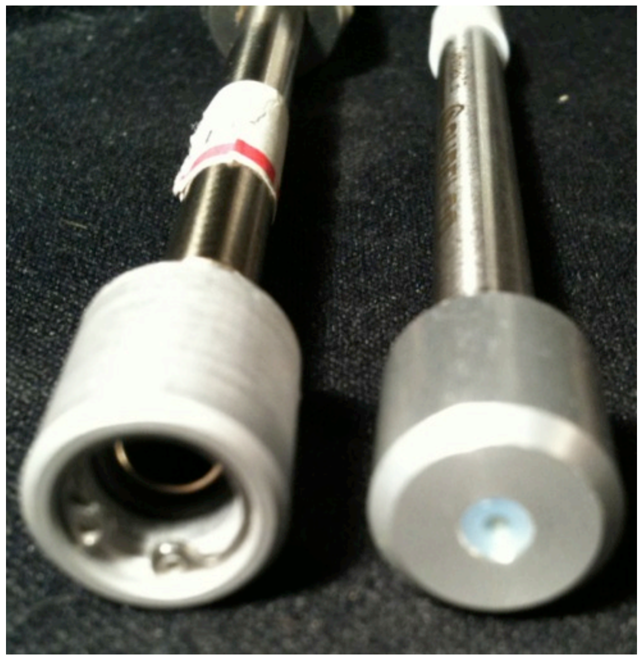
$$UR\left[\frac{mL}{min}\right] = \frac{2\pi h[cm] D_{eff}[\frac{cm^2}{s}](1-\delta)}{\ln\left(\frac{r_3}{r_2}\right)\delta}\ x\ 60[s/min]$$



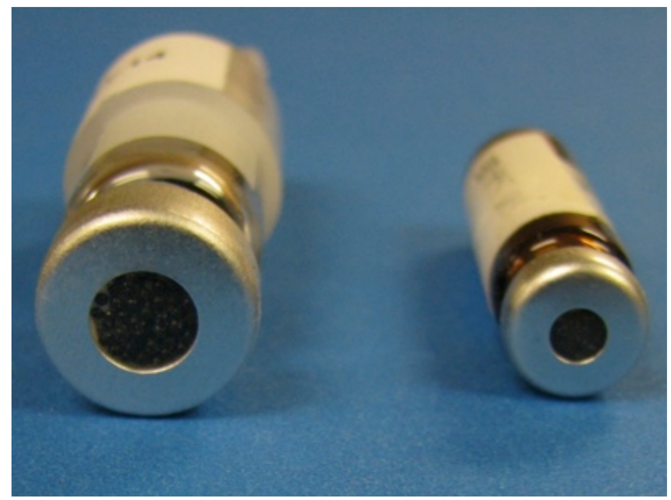
Modified Uptake Rates

Lower uptake rate = less starvation

SKC Ultra II and 12-hole Cap



ATD Tube & Pinhole Cap



WMS and Low-Uptake WMS

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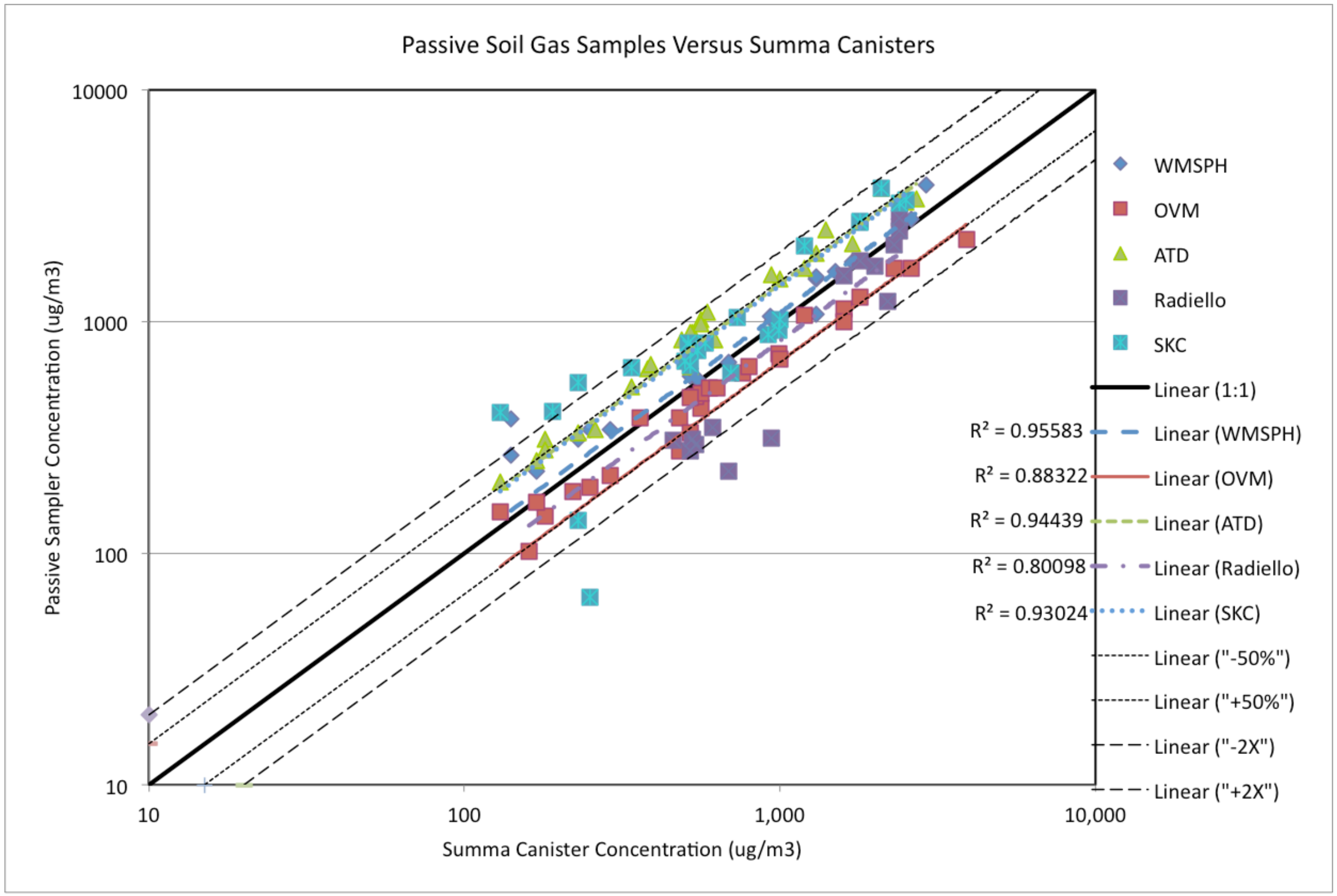
Soil Vapor Sampling – NAS JAX



Probes to 3-4 feet deep, exposure durations of 20, 40 and 60 minutes
Strong correlations, regression slopes all near 1.0

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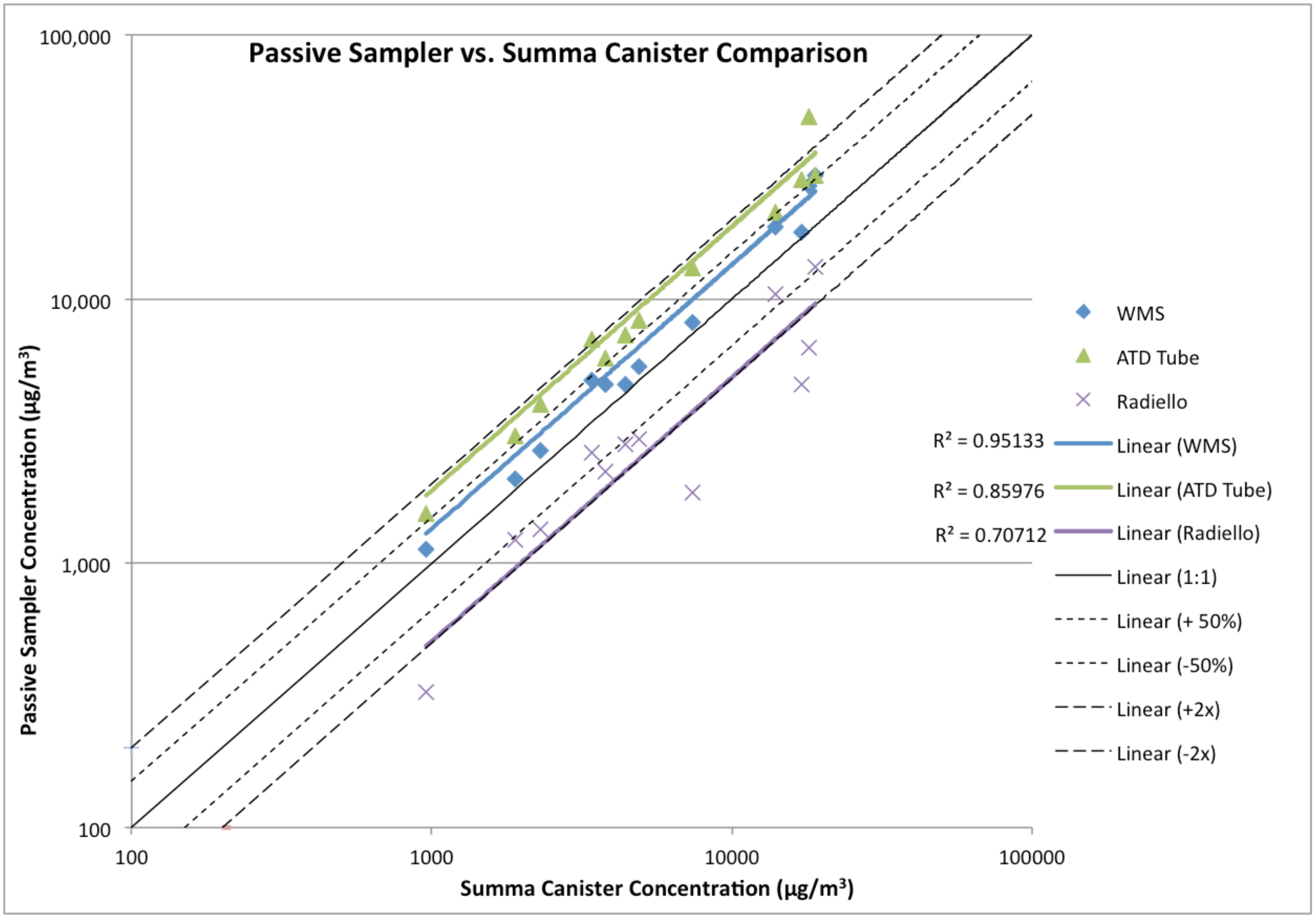
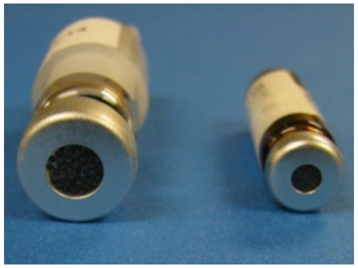
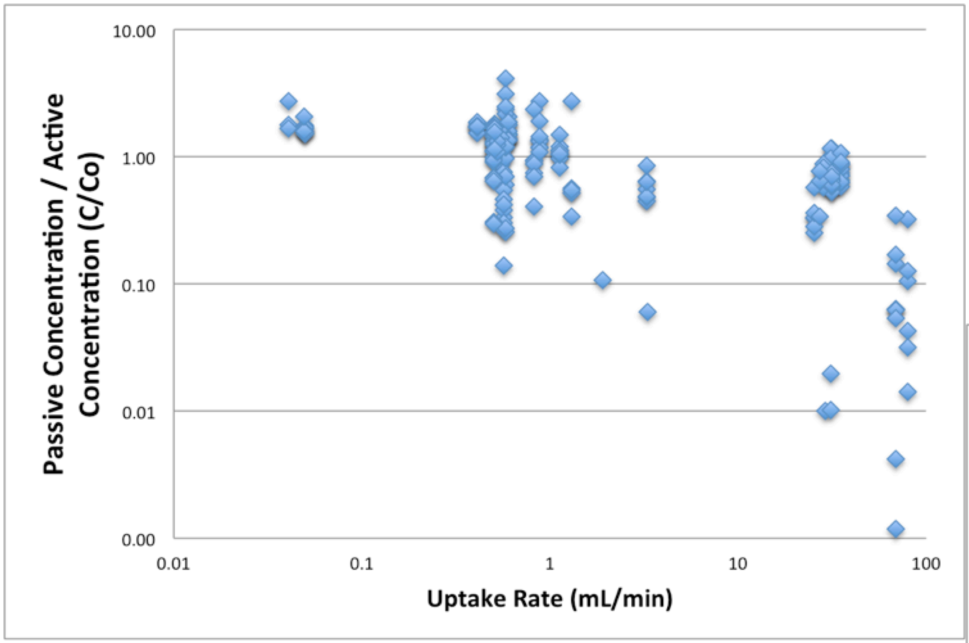
Passive Sub-Slab – NAS JAX



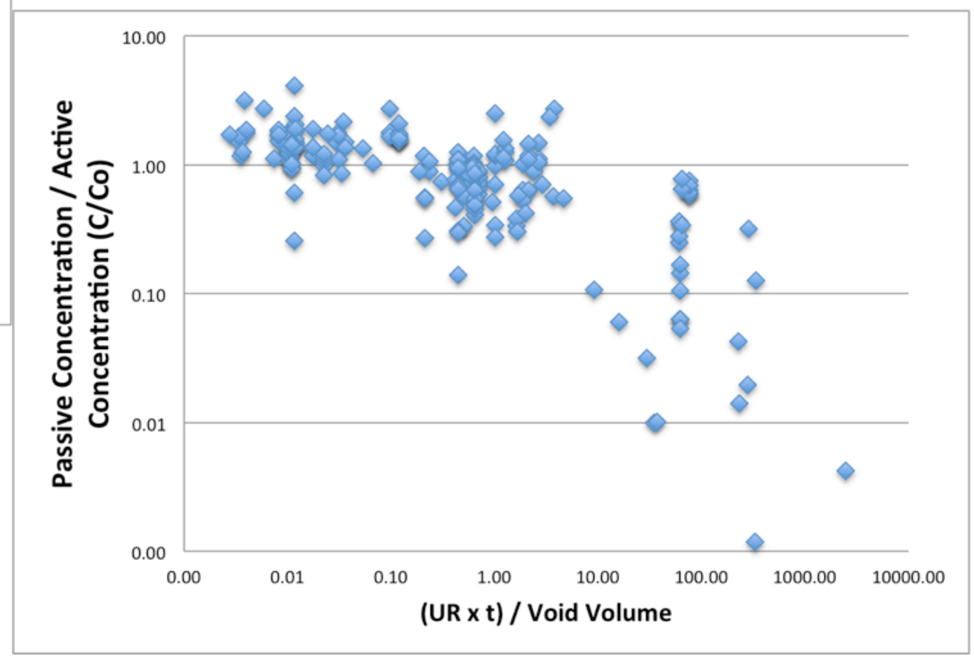


Limited to 1-inch diameter or less – Low-Uptake Rate Samplers

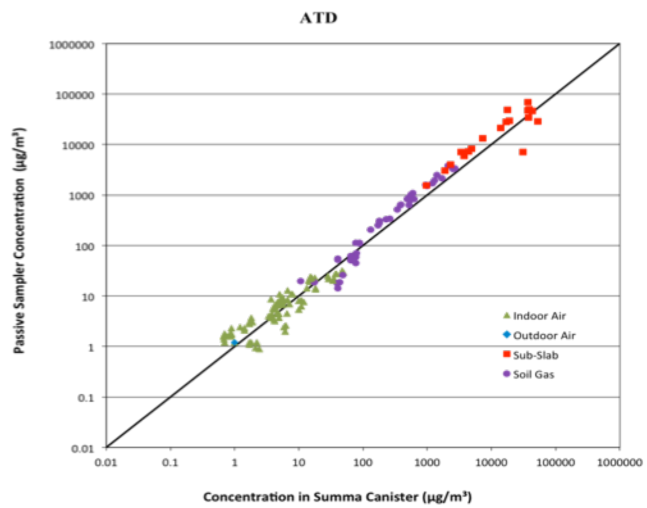
Starvation and Retention

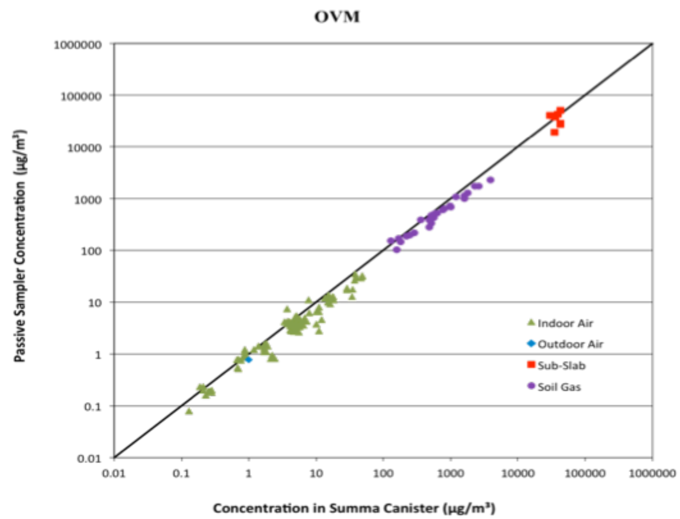


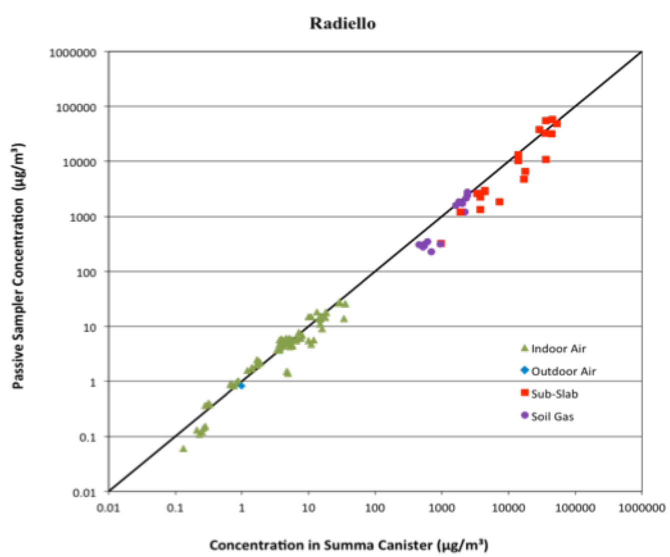
Two important considerations
1) Starvation = f (uptake rate)
2) Equivalent Sample Volume (UR x t) vs void volume (V V)

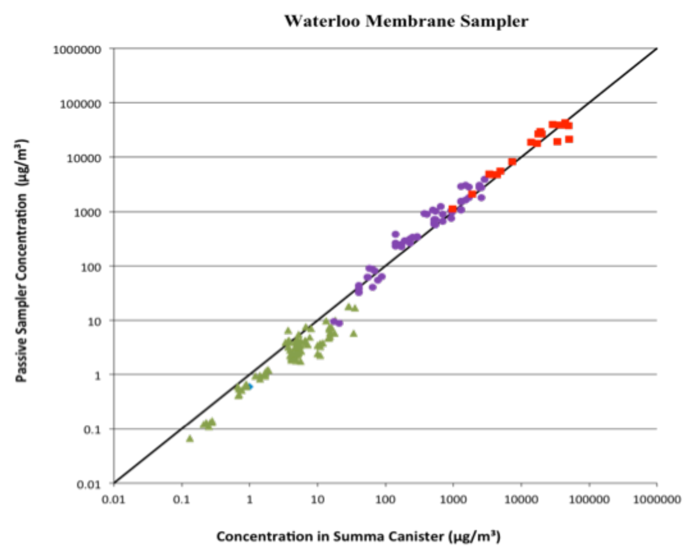


Overall Correlation between Passive and Active Samplers









Strong correlation to conventional samples over 6+ orders of magnitude

Quantitative results for soil vapor (a breakthrough)

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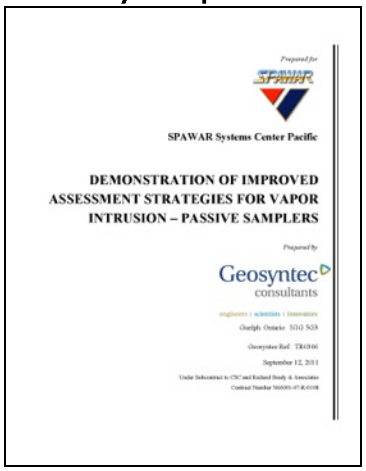
Performance Assessment

- Accuracy
  - Met criterion in most cases, except:
    - (UR x t) > Safe Sample Volume (poor retention)
    - UR > Diffusive Delivery Rate and (UR x t) > Void Volume (starvation)
    - Blank contamination (rare)
  - Some compounds posed challenges for some conditions
    - E.g., MEK on charcoal with high humidity
- Precision
  - Excellent within replicates (often better than TO-15 or TO-17)
  - More sensitive to conditions during sampling
- Ease of use
  - Comparable or better than TO-15 and TO-17
- Cost
  - Savings increase with size of the sampling program

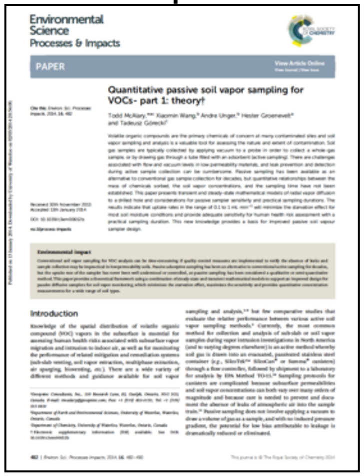
Reports and Articles

ESTCP Report

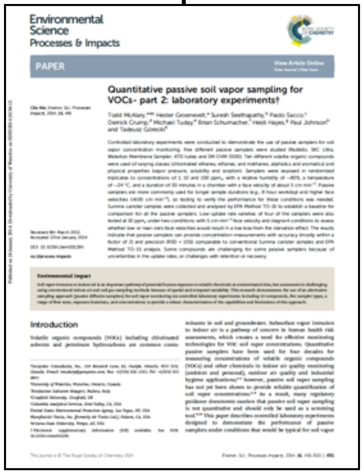
Navy Report



Soil Vapor - #1



Soil Vapor - #2



Soil Vapor - #3

Soil Vapor - #4

U.S. Pat Pending

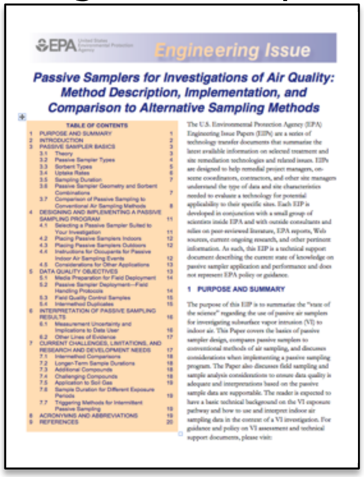
Quantitative Passive Soil Vapor Sampling

U.S. Pat Pending

Method for Deployment of Passive Soil Vapor Samples

Lab Chambers

Eng. Issue Paper



Plus ~30 conference presentations

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Take-Home Messages

- Passive Sampling is a valid option for many VOCs
  - Integrate over time to manage temporal variability for indoor air
  - Simpler protocols for soil gas sampling – less operator error
  - Easier to ship, handle and deploy – lower overall cost
  - Precision and accuracy mostly comparable to active samplers
- Five Potential Biases
  - Retention, starvation, calibration, contamination, recovery
  - All avoidable through careful sampler/sorbent selection, QA/QC
- Benchmarking is recommended for highest confidence
  - 1 of 10 samples collected with a duplicate active sample
  - Accounts for site-specific conditions, challenging compounds

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Acknowledgments

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  - ESTCP ER0830
  - U.S. Navy Environmental Sustainability Development to Integration (NESDI) Program
  - In-kind contributions from Geosyntec Consultants, Inc.

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Questions/Comments?

tmcalary@geosyntec.com