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Quantitative Passive Soil Vapor Sampling for VOCs

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Quantitative Passive Samplers

ATD Tubes

3M OVM 3500

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

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

SKC Ultra, Ultra II

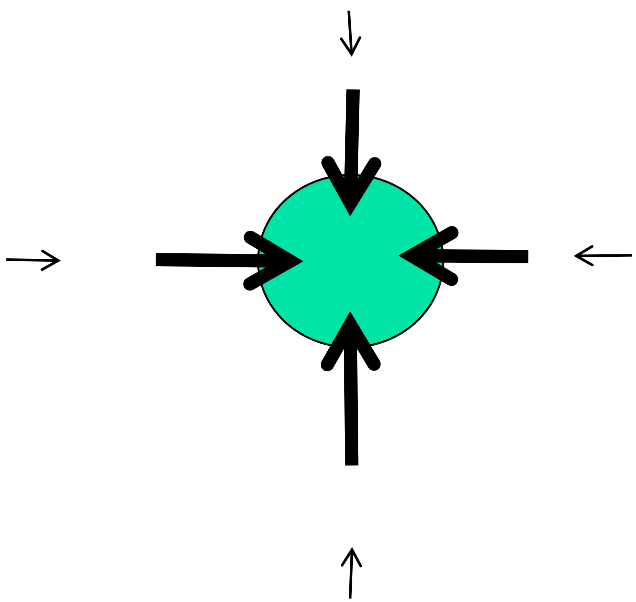
Radiello™

Waterloo Membrane Sampler™

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

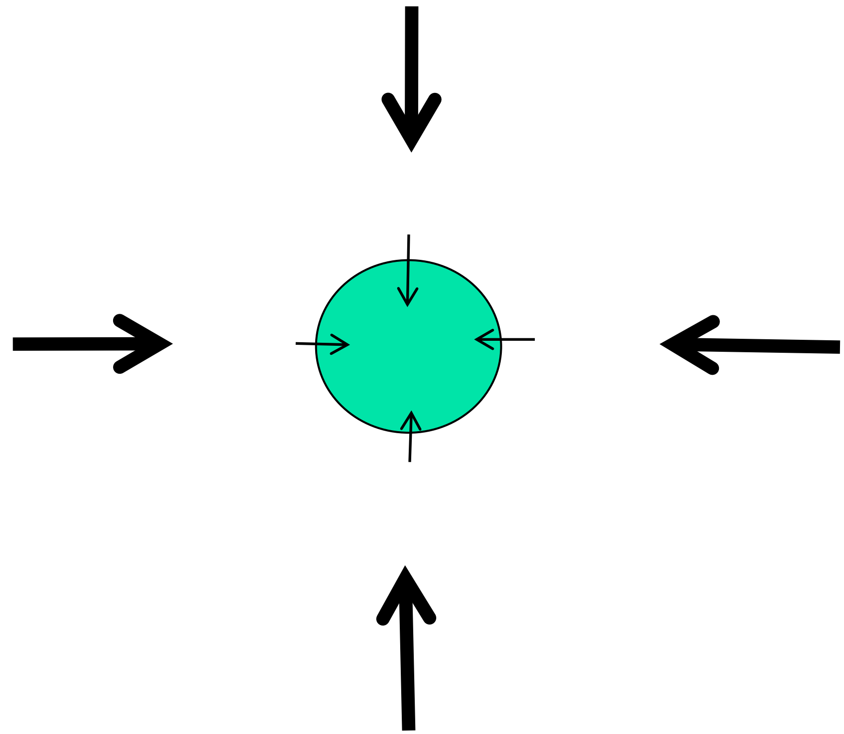
The “Starvation Effect”

Sampler uptake rate is higher than rate of supply of vapors



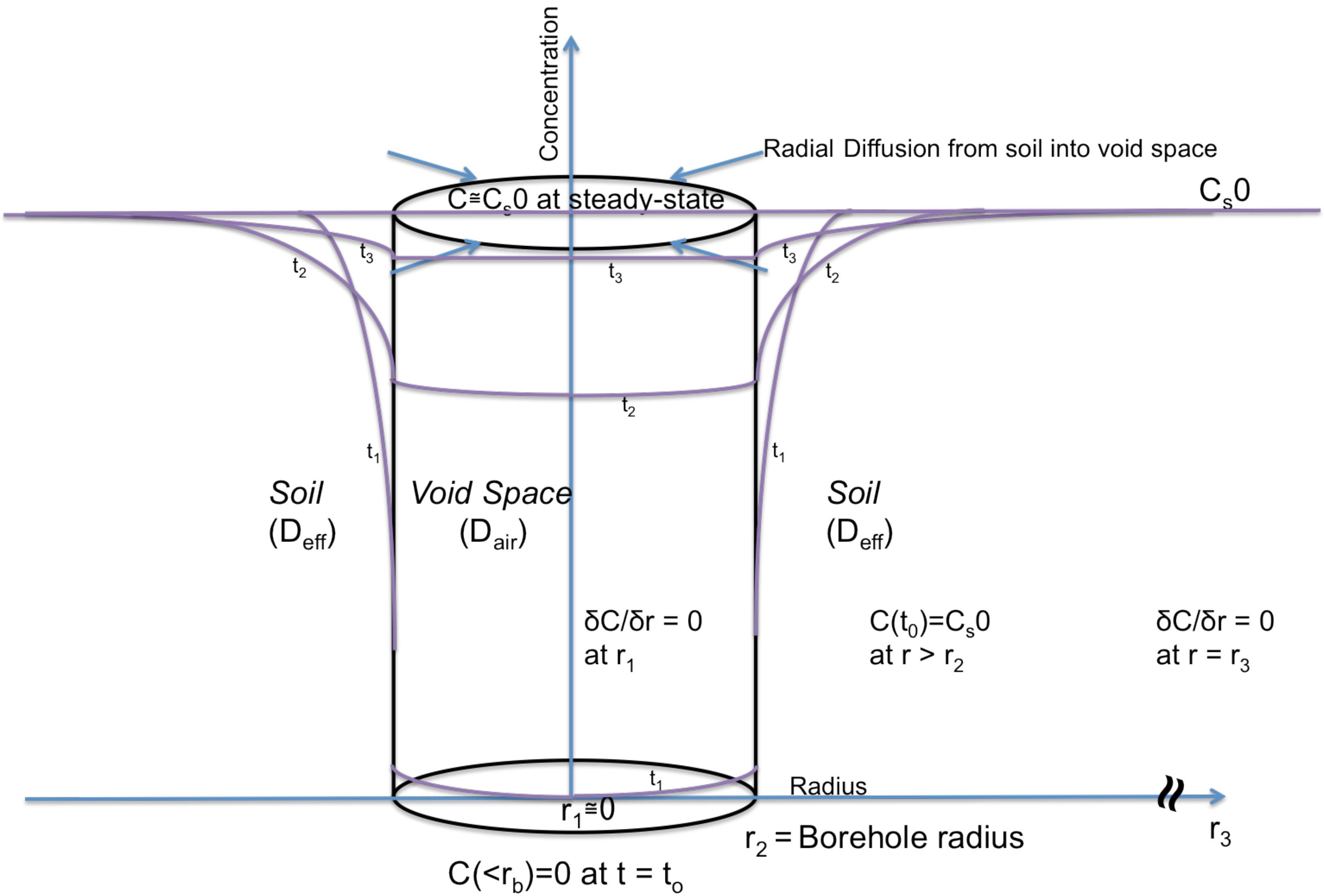
Sampler causes localized depletion in vapor concentrations (i.e., “starves” the sampler)

Sampler uptake rate is lower than rate of supply of vapors

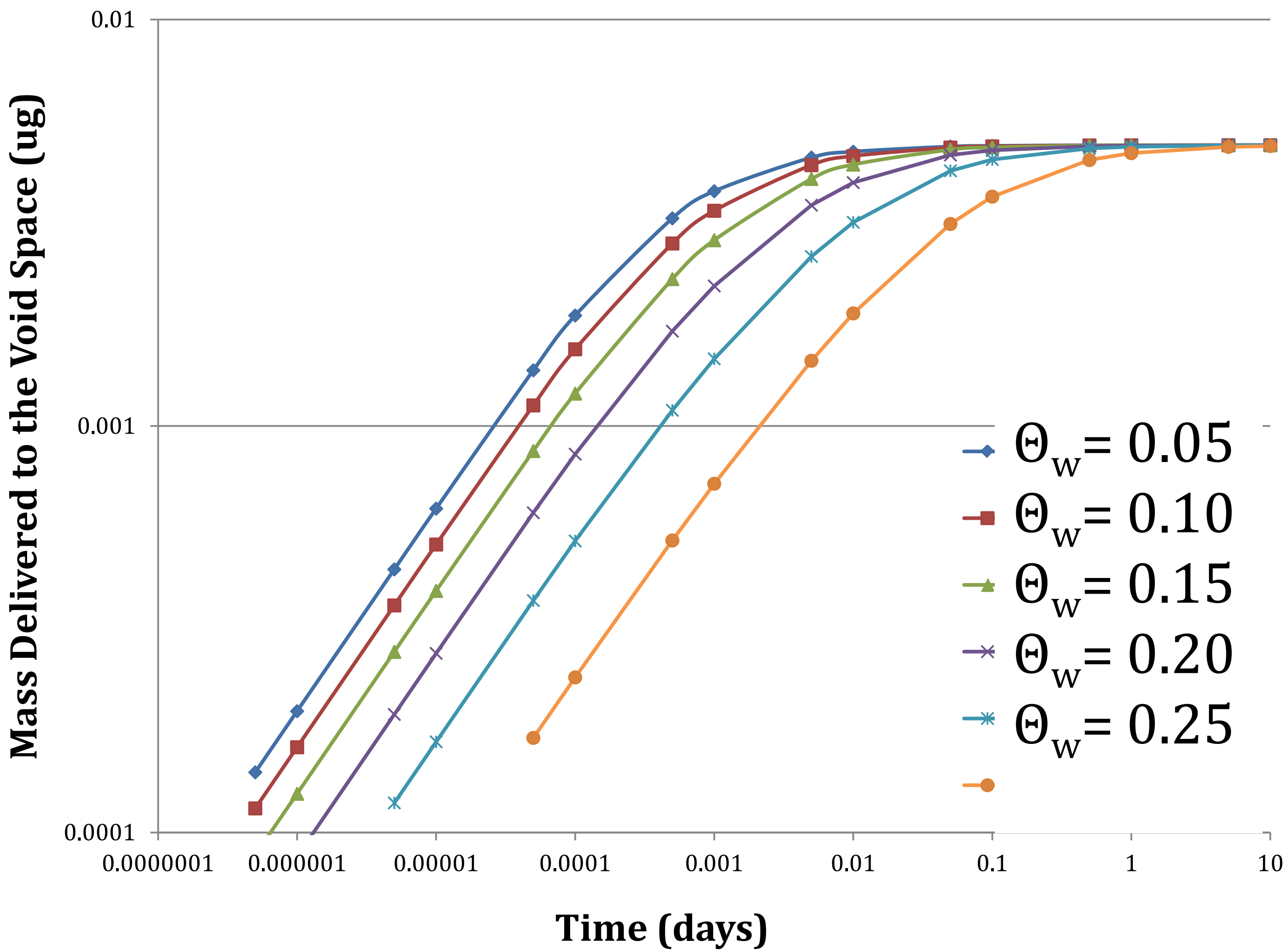


No starvation

Transient Mathematical Model



Time to Steady-State



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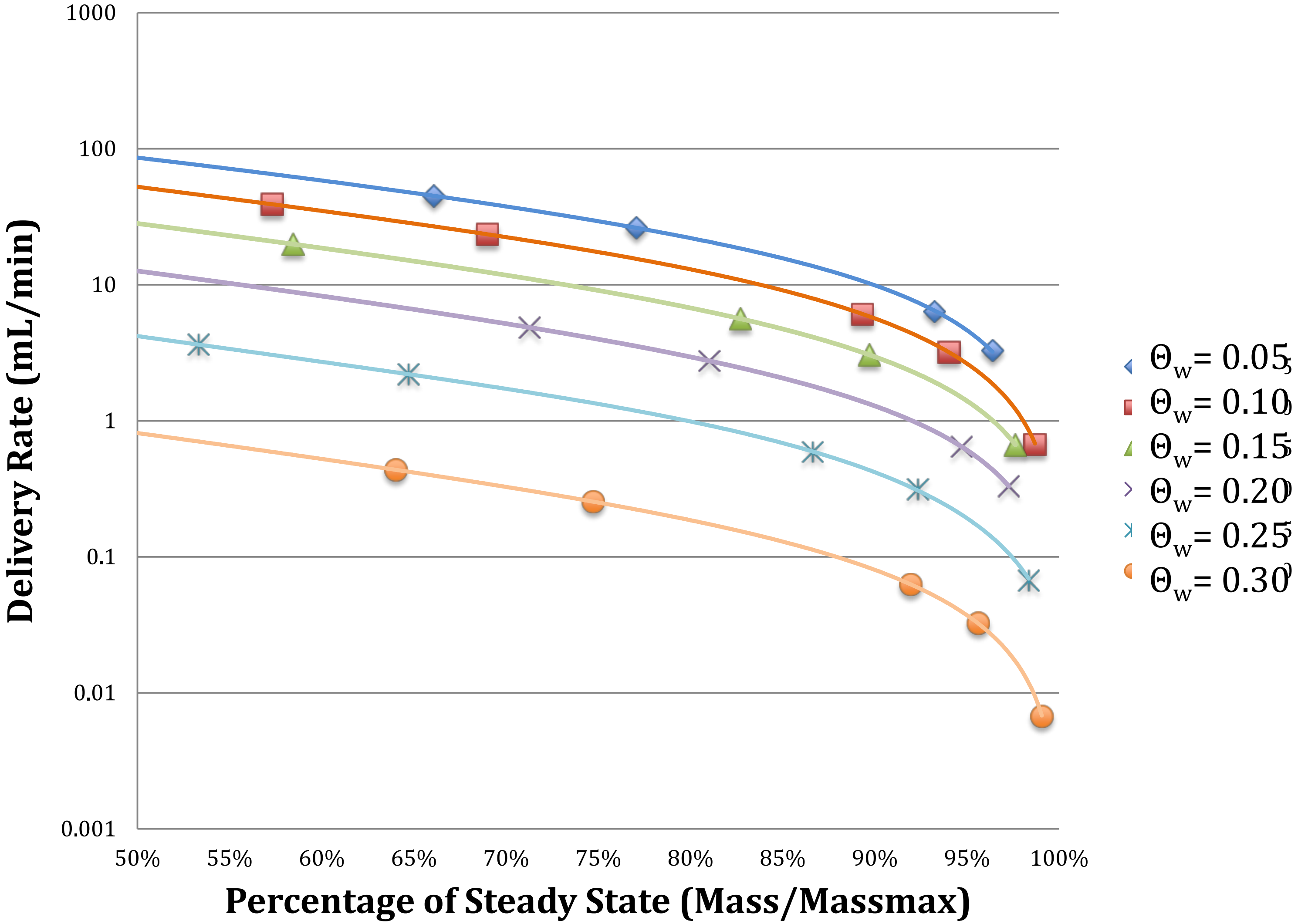
Delivery Rate of Vapors



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Steady-State Model

The rate of mass delivery into the borehole $M1 = \frac{2\pi D_{eff}(C_{sg} - C_{bh})}{\ln(\frac{r_1}{r_2})}$

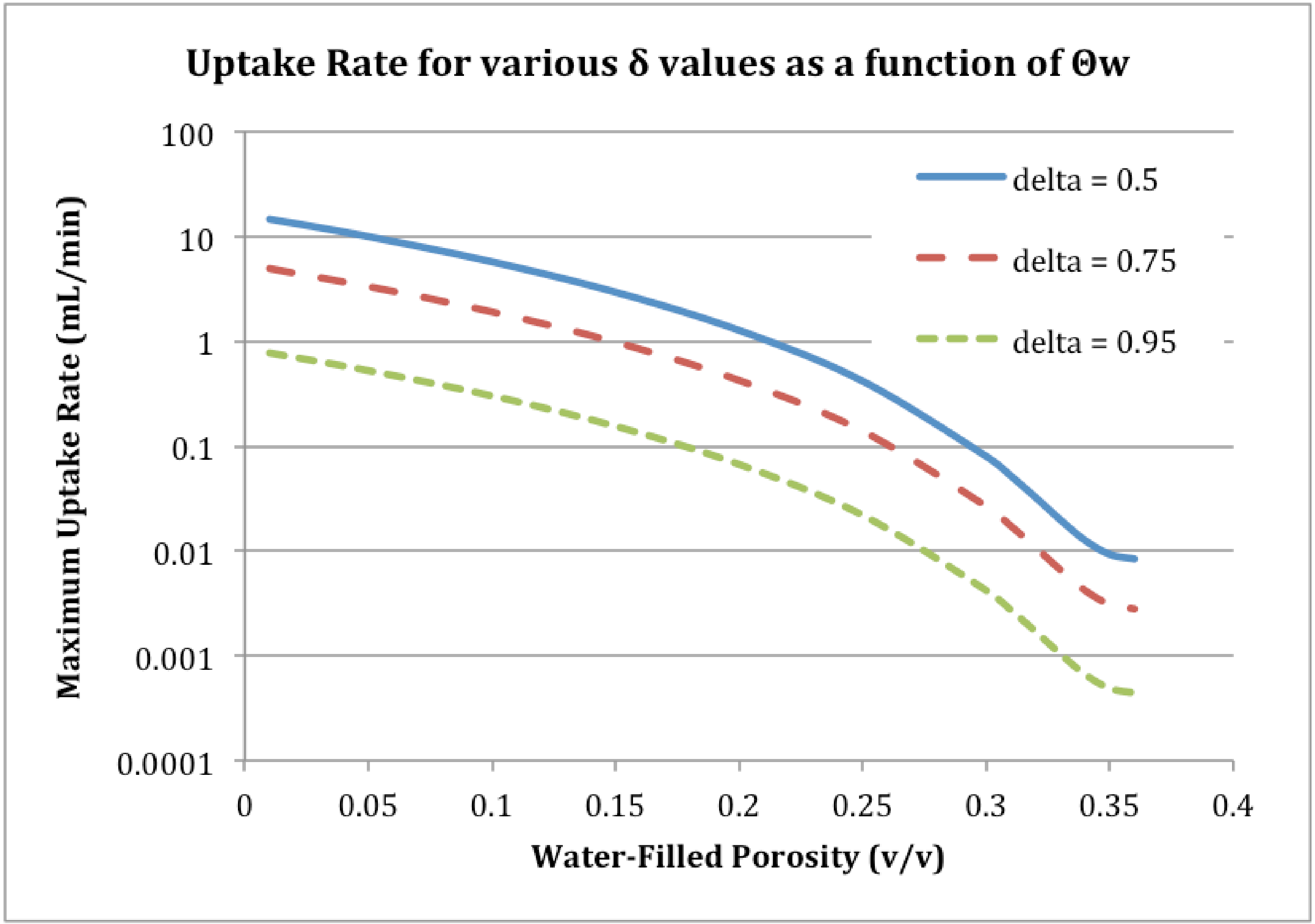
The rate of mass uptake by the sampler $M2 = C_{bh} \; x \; UR$

Setting M1 = M2 gives:

$$UR\left[\frac{mL}{min}\right] = \frac{2\pi h[cm] D_{eff}[\frac{cm^2}{s}](1-\delta)}{\ln(\frac{r_2}{r_1})\delta} \; x \; 60[s/min]$$

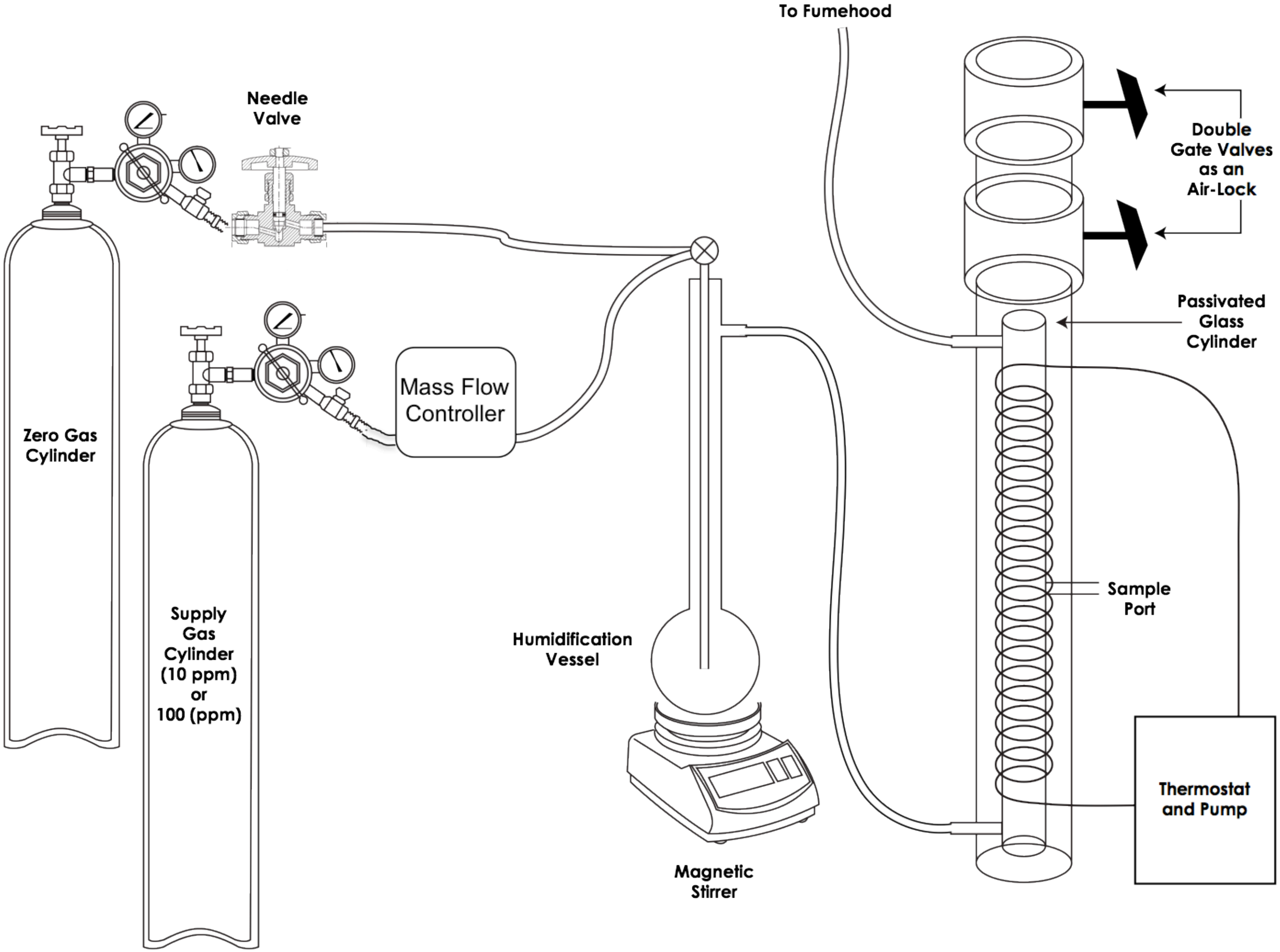
Delta = vapor concentration inside borehole / vapor concentration in surrounding soil

Steady-State Model Results



Delta = vapor concentration inside borehole / vapor concentration in surrounding soil

Laboratory Testing Apparatus



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Laboratory Testing Apparatus

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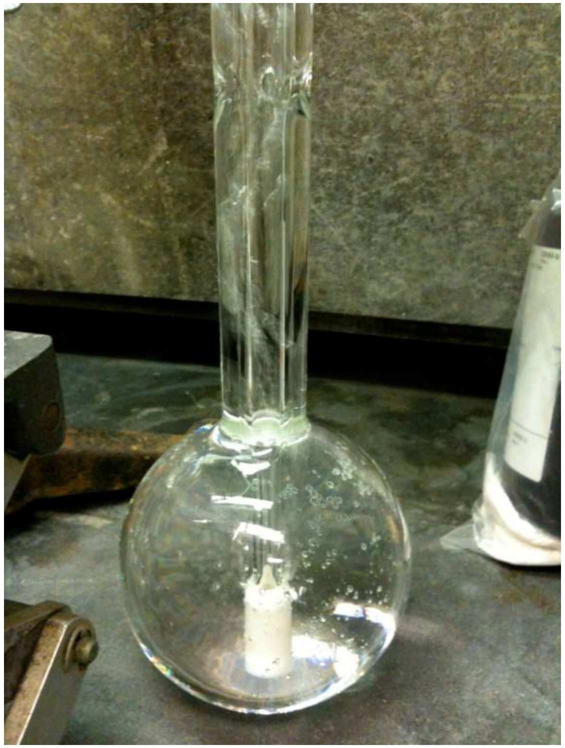

Concentration: 1, 10, and 100 ppmv

Temperature: ambient

Humidity: 90-100%

Face velocity: very low ($5x10^{-5}$ m/s)

Exposure time: 30 minutes

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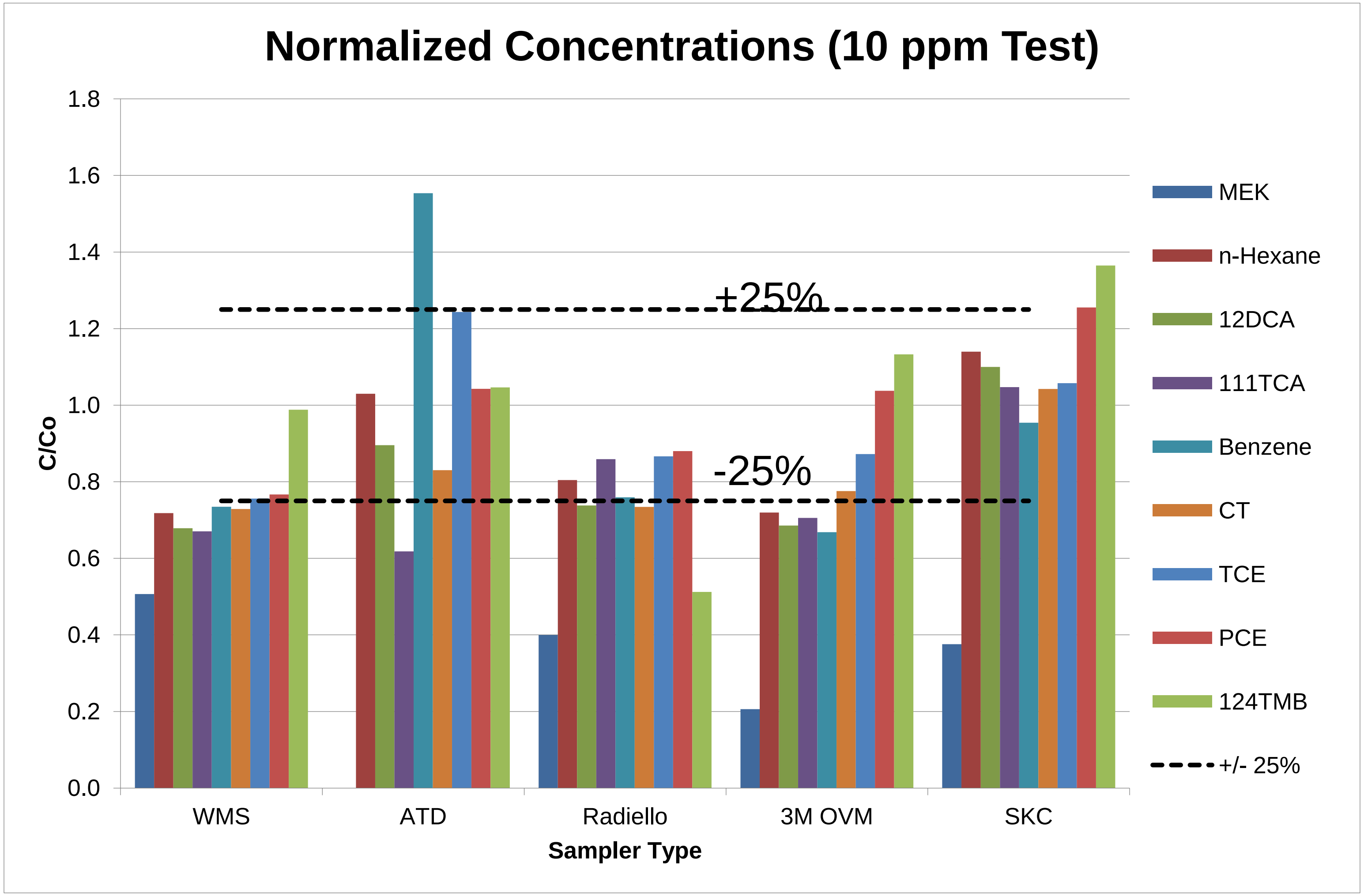
Laboratory Test Compound List

Analyte	Koc (mL/g)	Henry's Law Constant @ 25 °C (dim)	Vapor pressure (atm)	Pure Component Maximum Vapor Concentration (ppmv)	Water solubility (g/L)	OSWER Target Deep Soil Gas Conc'n (10-5 risk, AF = 0.01) (ppmv)
1,1,1-Trichloroethane (111TCA)	43	0.70	0.16	160,000	1.3	40
1,2,4-Trimethylbenzene (124TMB)	614	0.25	0.0020	2,000	0.057	0.12
1,2-Dichloroethane (12DCA)	39	0.048	0.11	110,000	8.6	0.023
2-Butanone (MEK)	4.5	0.0023	0.10	100,000	220	34
Benzene (BENZ)	146	0.23	0.13	130,000	1.8	0.098
Carbon tetrachloride (CTET)	43.9	1.1	0.15	150,000	0.79	0.026
Naphthalene (NAPH)	1540	0.18	0.00012	120	0.031	0.057
n-Hexane (NHEX)	132	74	0.20	200,000	0.0095	5.7
Tetrachloroethene (PCE)	94.9	0.72	0.024	24,000	0.21	0.12
Trichloroethene (TCE)	61	0.40	0.095	95,000	1.3	0.0041

High Concentrations Test Results



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Laboratory Testing Results

Accuracy: passive sampler concentration / Summa concentration

Overall Average C/Co	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.67	0.98	0.74	0.69	0.76	0.73	0.82	0.84	0.69	0.24	0.72
ATD Tenax TA	1.04	1.14	0.96	0.75	2.00	0.88	1.49	1.22	0.71	1.22	1.14
Radiello Charcoal	0.49	0.90	0.87	0.99	0.92	0.84	1.01	0.99	0.31		0.81
3M OVM 3500	0.24	0.74	0.72	0.75	0.79	0.77	0.92	1.06	0.79	0.46	0.72
SKC Carbograph	0.88	1.03	1.05	0.99	1.00	0.92	1.00	1.16	0.87	1.11	1.00

Precision: standard deviation divided by the mean (COV)

Overall Average	MEK	NHEX	12DCA	111TCA	BENZ	CTET	TCE	PCE	124TMB	NAPH	Average
WMS Anasorb 747	0.11	0.15	0.04	0.06	0.07	0.05	0.03	0.04	0.05	0.15	0.07
ATD Tenax TA	0.05	0.04	0.04	0.07	0.05	0.08	0.03	0.04	0.08	0.09	0.06
Radiello Charcoal	0.11	0.10	0.09	0.09	0.10	0.08	0.10	0.13	0.19	NA	0.11
3M OVM 3500	0.03	0.07	0.07	0.05	0.09	0.07	0.07	0.07	0.07	0.07	0.07
SKC	0.11	0.13	0.09	0.11	0.05	0.11	0.11	0.11	0.12	0.14	0.11
Summa Canister	0.11	0.07	0.09	0.08	0.09	0.08	0.09	0.14	0.22	0.26	0.12

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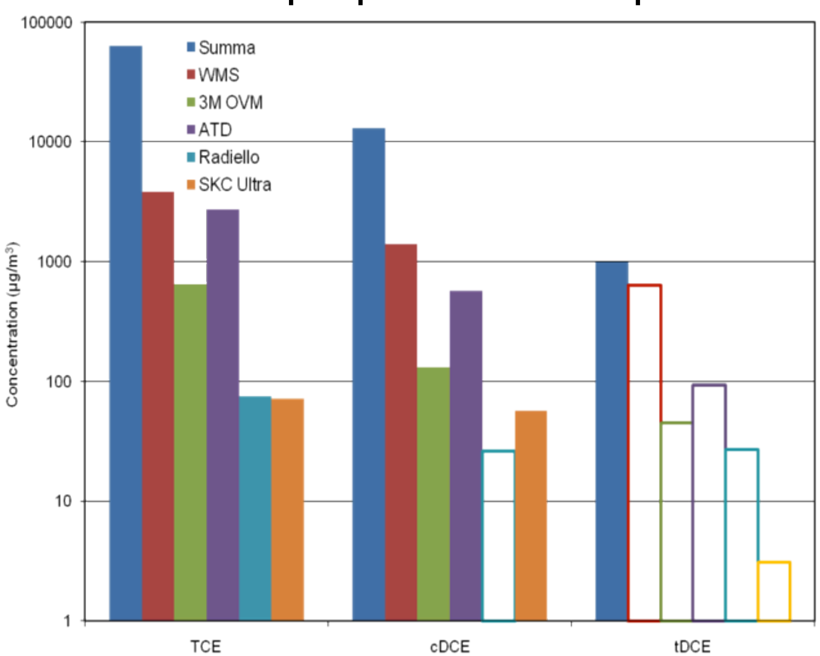
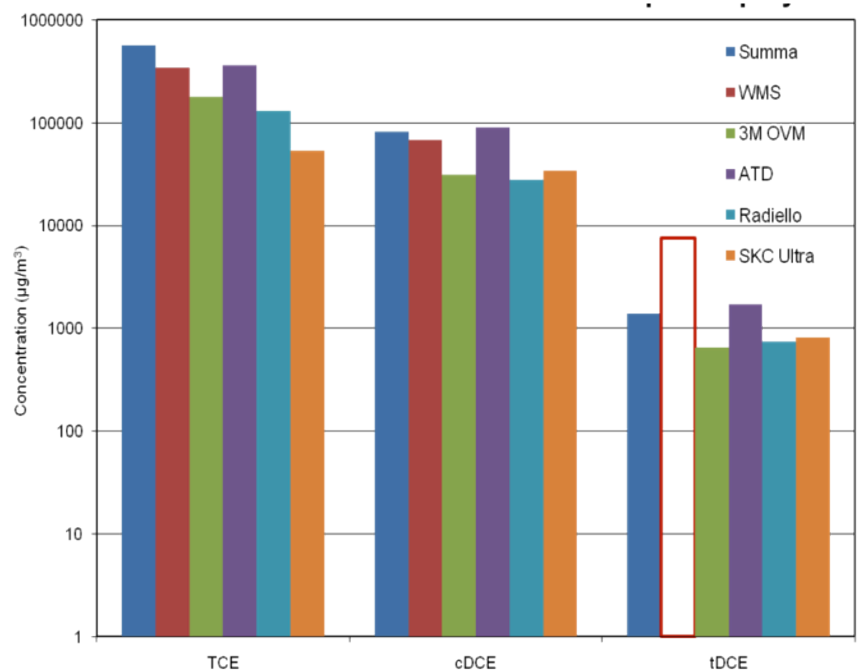
Sub-Slab – Navy San Diego

Fully-Passive Samples
Starvation proportional to uptake rate



Sampling with continuous purging
Less starvation for semi-passive samples



Modified Uptake Rates

Lower uptake rate = less starvation

SKC Ultra II and 12-hole Cap

ATD Tube & Pinhole Cap

WMS and Low-Uptake WMS

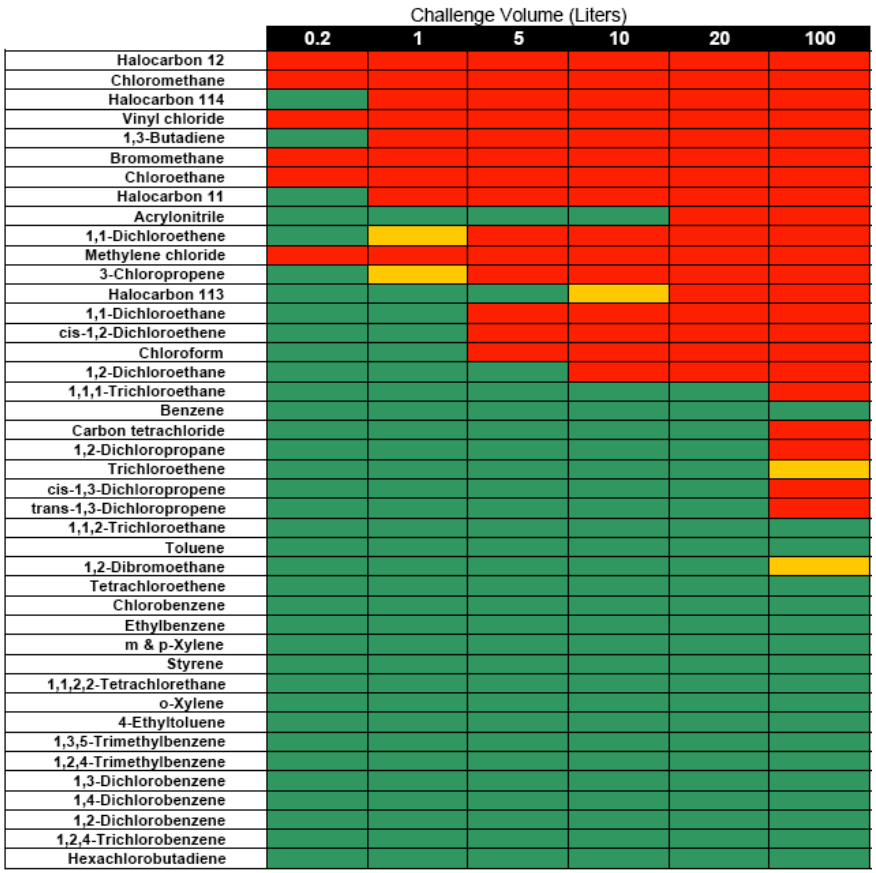
Sorbent Selection

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%

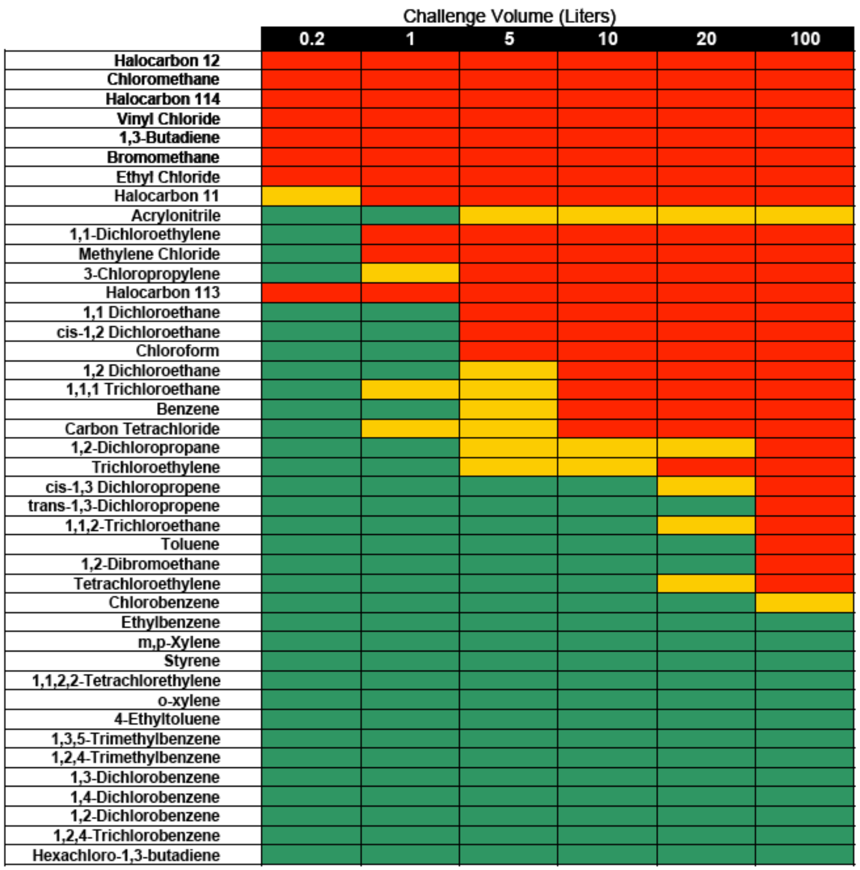
** indicates this analyte was strongly adsorbed*

TENAX TA

(Polymer)

Surface Area: 35 m^2/g

Desorption Temperature: 300 °C



Performance Key

Safe to use: Recovery is greater than 80%

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Not Recommended: Recovery is less than 20%

** indicates this analyte was strongly adsorbed*

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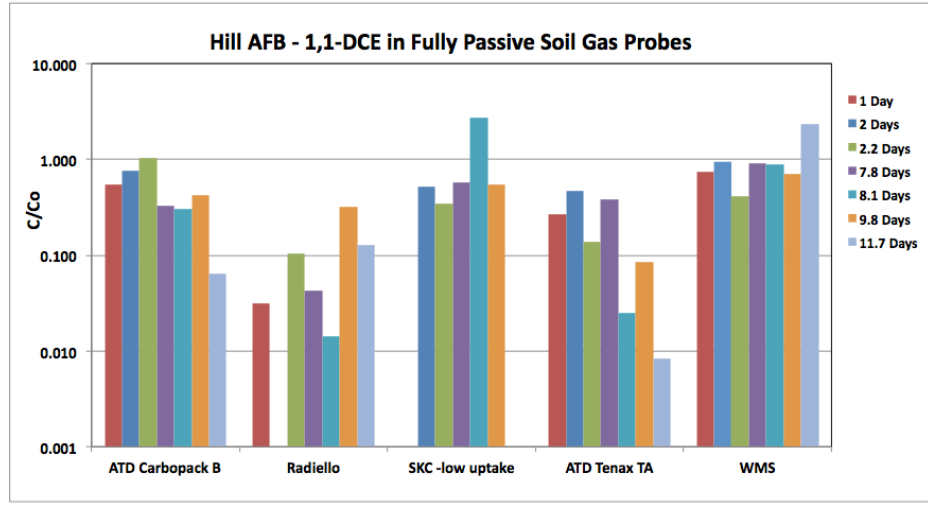
Soil Gas @ 12 ft – Hill AFB

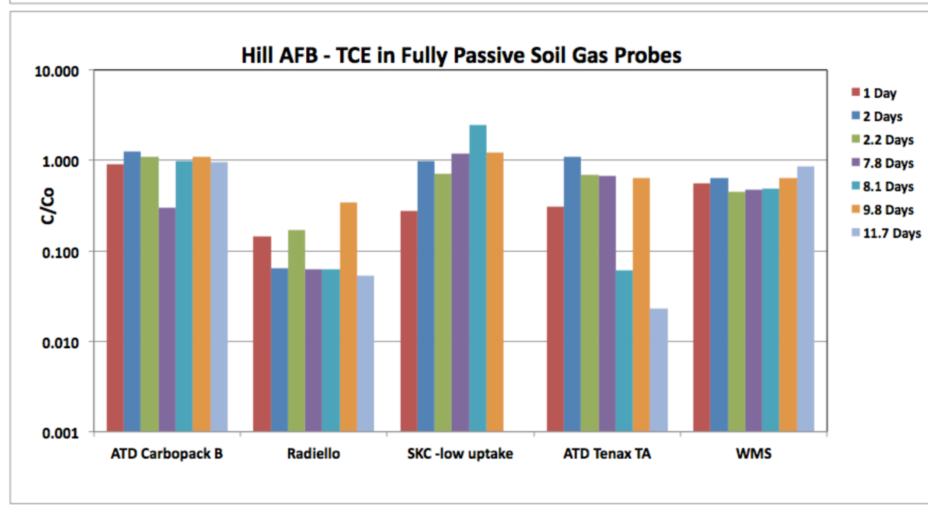
6 probes -12 ft deep

Latin Square Design

1 to 12 day exposures

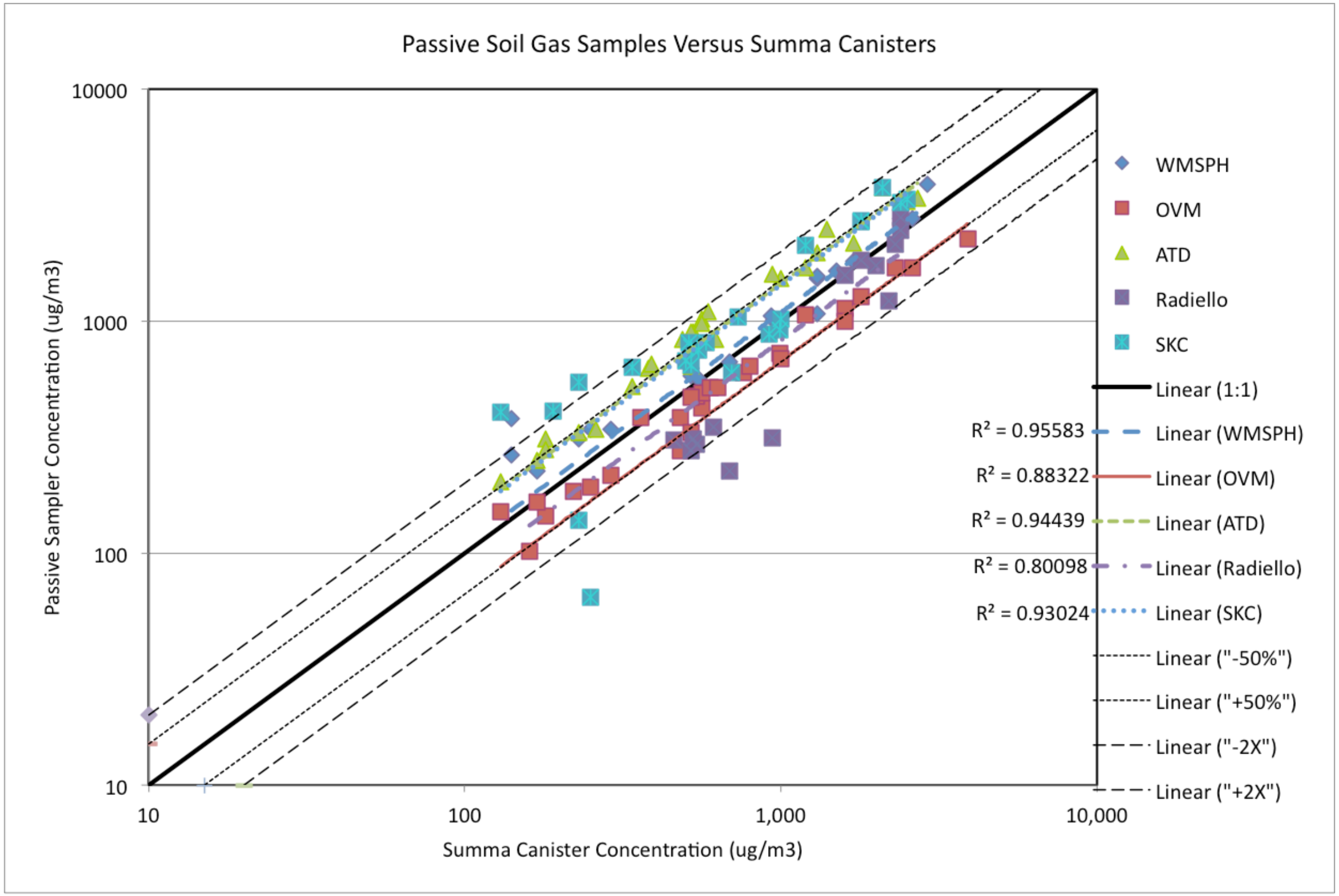
C_o Measured using combination of Summa and Hapsite GC/MS





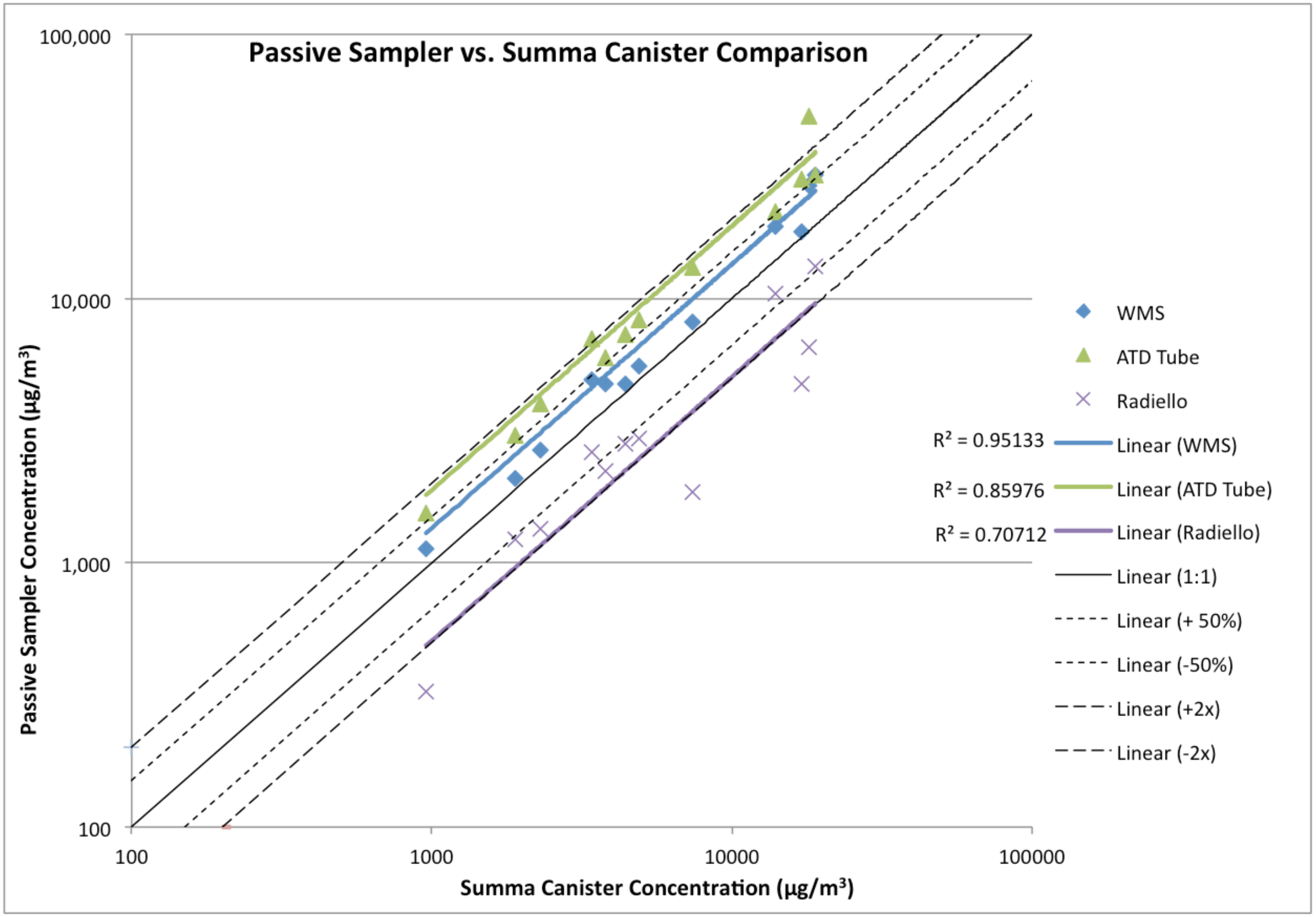
Negative bias for long duration with ATD-Tenax
Negative bias for high uptake rate (Radiello)
Otherwise, encouraging results for TCE and DCE

Soil Vapor Sampling – NAS JAX



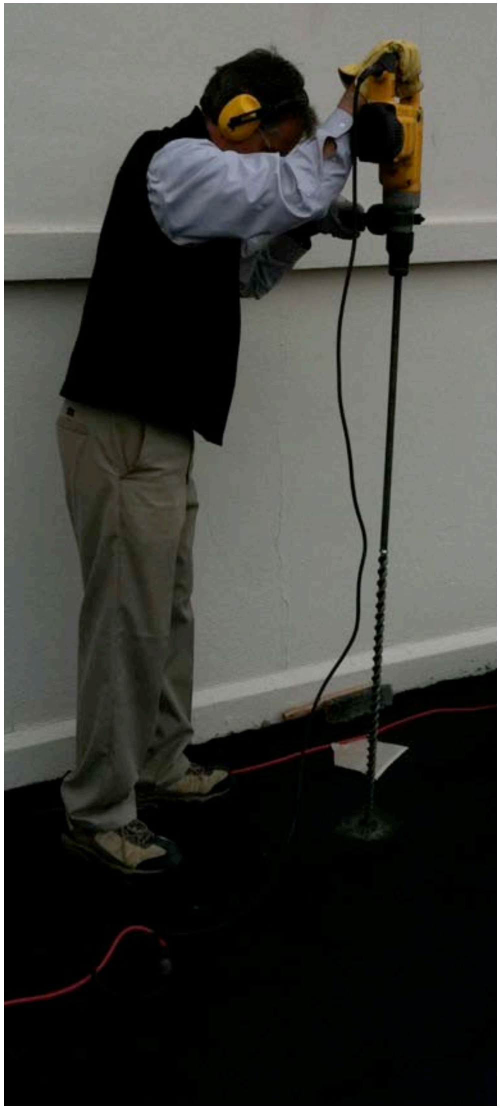
Probes to 3-4 feet deep, exposure durations of 20, 40 and 60 minutes
Strong correlations, regression slopes all near 1.0

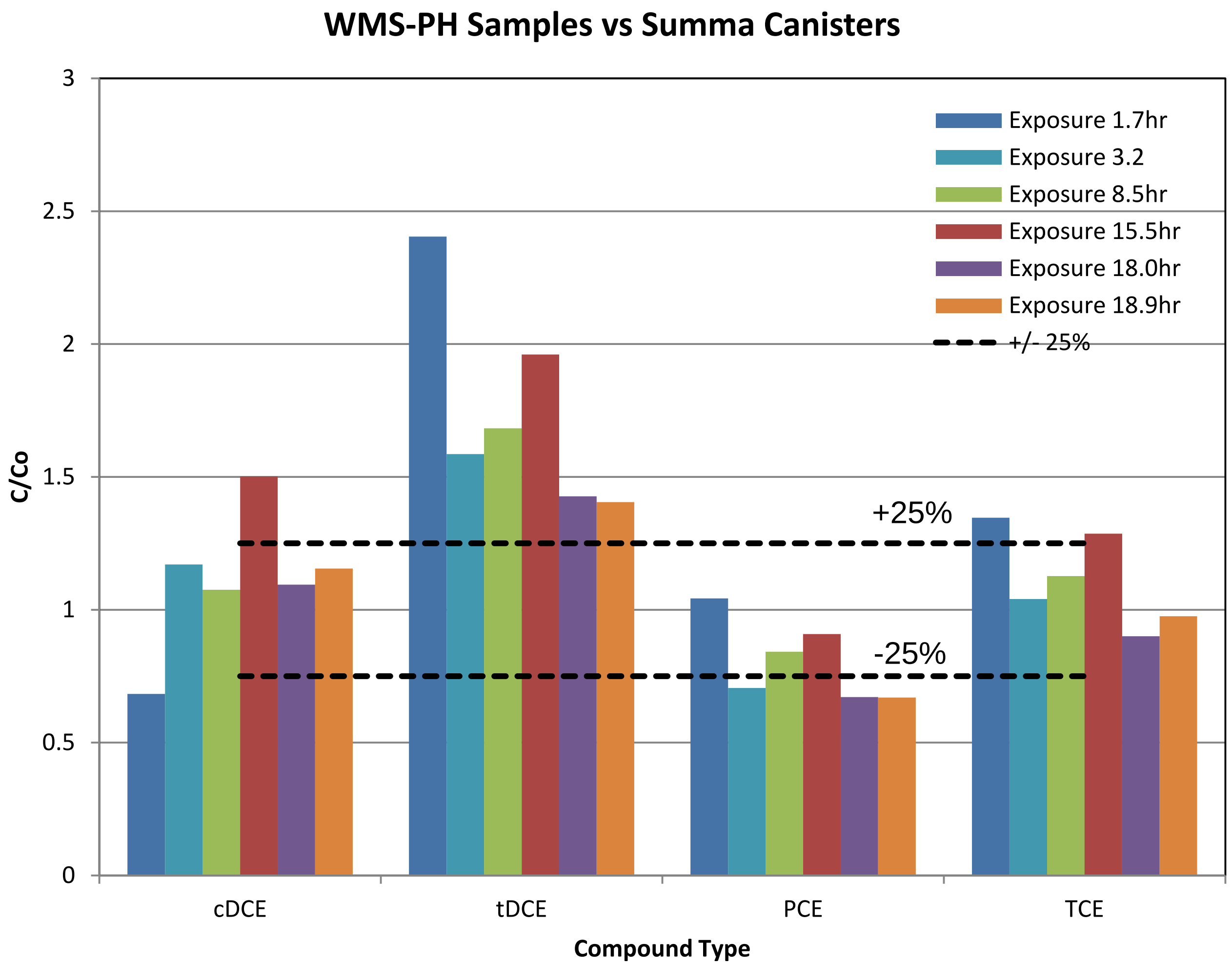
Passive Sub-Slab – NAS JAX



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

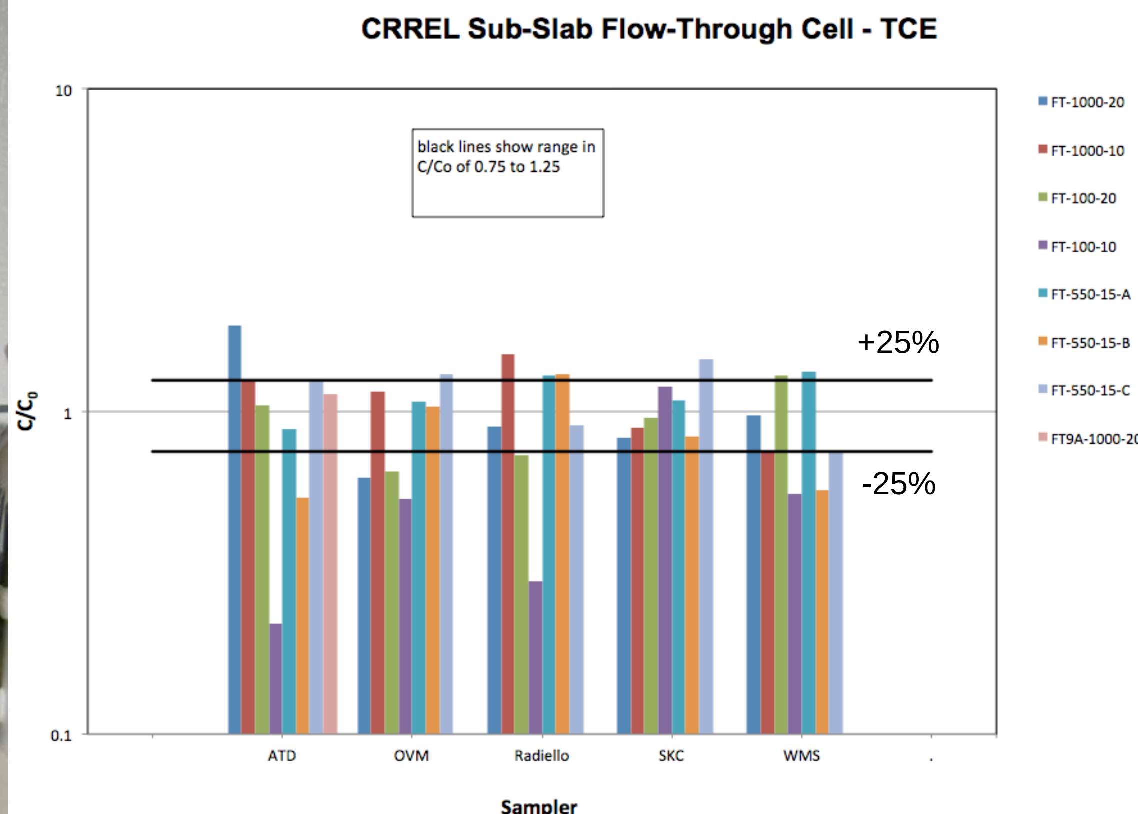
Temporary Passive - NAS JAX





23 of 24 results were within 2X of Summa/TO-15 Results

Flow-Through Cell – CRREL



Flow-through cell to avoid starvation by design
No starvation for high-uptake rate samplers
Negative bias only for short duration/low-flow (insufficient purging)

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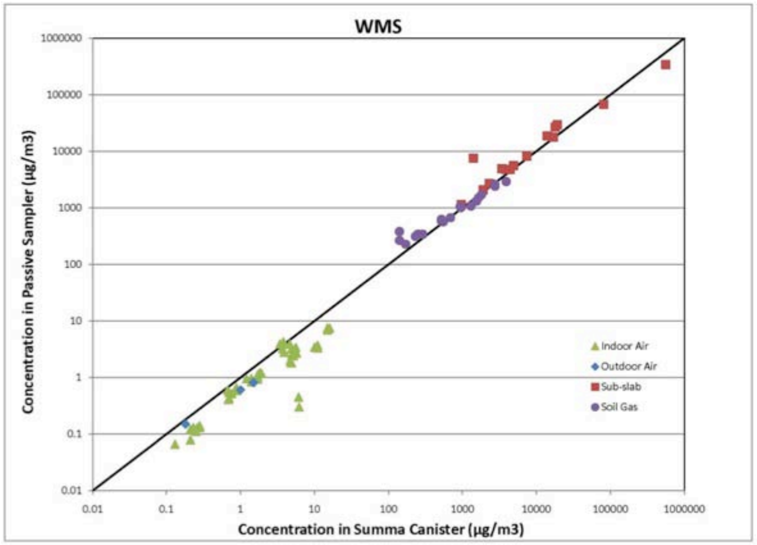
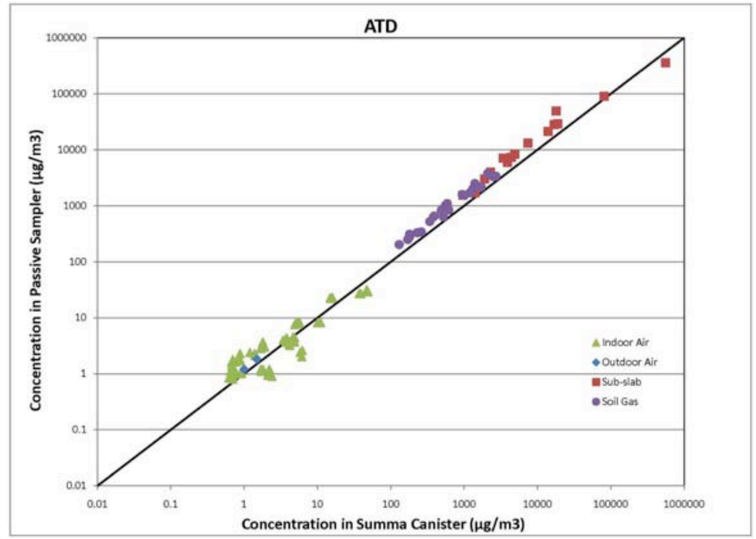
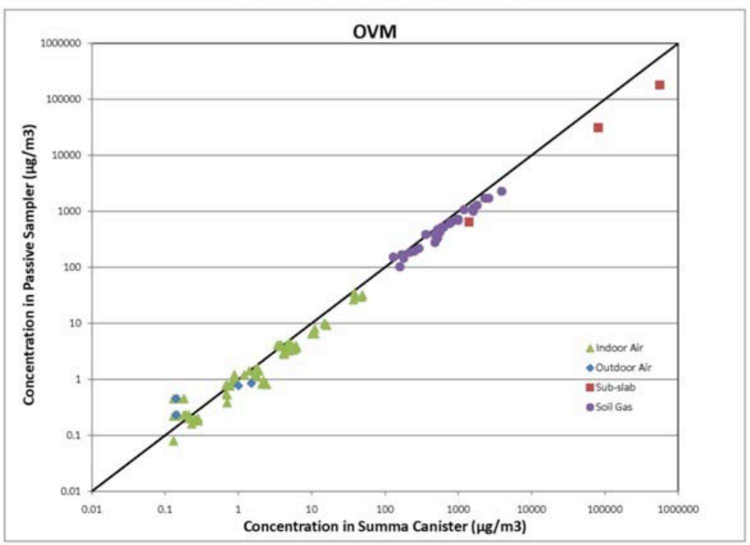
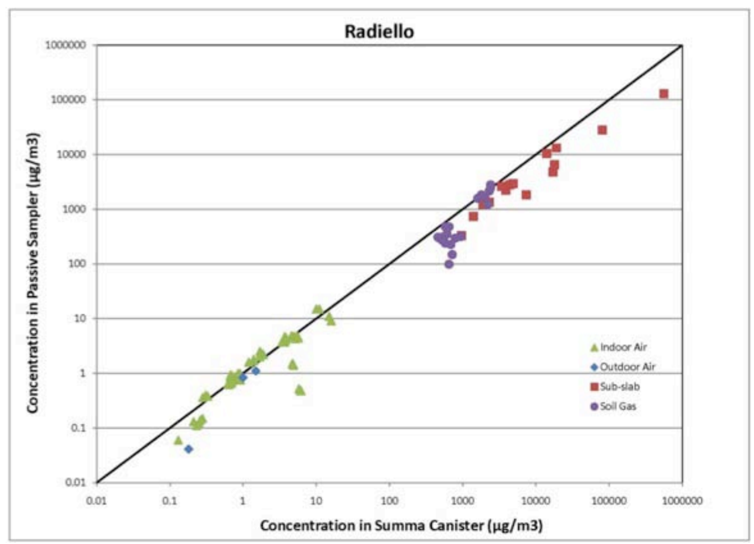
Overall Correlation between Passive and Active Samplers









Strong correlation to conventional samples over 6+ orders of magnitude

(charts include indoor and outdoor air samples)

Maybe we don't need to be using so many Summa Canisters

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Cost Comparison

Simple comparison:

6 indoor samples
2 outdoor samples
6 sub-slab samples

Summa	WMS	Radiello	ATD	3M OVM	SKC
$6,810	$3,670	$3,590	$3,590	$3,610	$4,100

Approx. 50% cost for passive samplers versus Summa cans

(even with some side-by-side Summa cans for benchmarking, you can still save a lot of money)

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Benefits of Passive Sampling

- Simple (minimal training, less risk of leaks)
- Low reporting limits with no premium cost
- Smaller – easy to ship
- Long shelf-life and hold-time
- Long history of use in Industrial Hygiene
- Less expensive overall
- Other benefits unique to each sampler

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Take-Home Messages

- Passive Sampling is becoming a reality for VI assessment
  - Strong positive correlation with Summa cans
  - Generally good consistency, but sensitive to wind, rain, temp.
- Minimize variability:
  - Integrate over time to manage temporal variability for indoor air
  - Simpler protocols for soil gas sampling – less operator error
- Benchmarking is recommended in the near-term
  - 1 of 10 samples collected with a duplicate by Summa/TO-15
  - Accounts for site-specific conditions, challenging compounds
- Study design takes a little more thought
  - Different samplers have different pros and cons
  - Cost savings make it well worthwhile

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Questions/Comments?

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