



Quantitative Passive Diffusive Sampling for Assessing Soil Vapor Intrusion to Indoor Air

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Overview

- Rationale
- Laboratory and Field testing for Indoor Air
- Laboratory and Field Testing for Soil Vapor
- Cost Comparisons

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Passive Samplers



ATD Tubes

SKC Ultra II



3M OVM 3500



Radiello™

The mass (M) and time (t) are measured accurately. Key is to know the uptake rate (k^{-1})

$$C_0 = \frac{M}{k^{-1}t}$$

Waterloo Membrane Sampler™



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

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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

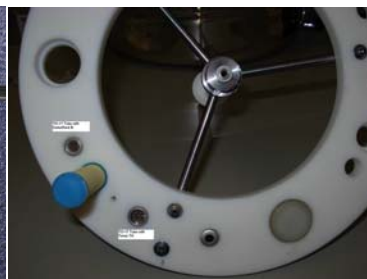
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Laboratory Test Compound List

Analyte	Koc (mL/g)	OSWER indoor conc. at 10^{-6} risk (ppb)	Vapour 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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Experimental Apparatus



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

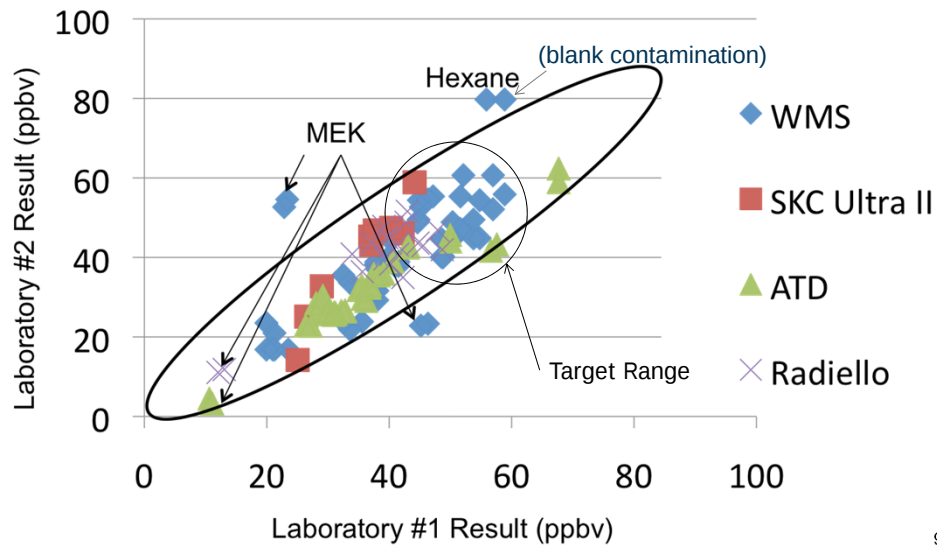
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Inter-Laboratory Testing

Sampler Type	Home Laboratory	Secondary Laboratories	# of Samplers to Each Laboratory
Waterloo Membrane Sampler	University of Waterloo	Air Toxics Ltd Airzone One	2
ATD Tubes with Tenax TA	Air Toxics Ltd	Columbia Analytical Services University of Waterloo	2
ATD Tubes with CarboPack B	Air Toxics Ltd	Columbia Analytical Services University of Waterloo	2
SKC Ultra	Columbia Analytical Services	Air Toxics Ltd Airzone One	2
Radiello	Fondazione Salvatore Maugeri	Columbia Analytical Services Air Toxics Ltd	2

Interlab Test – Youden Plot



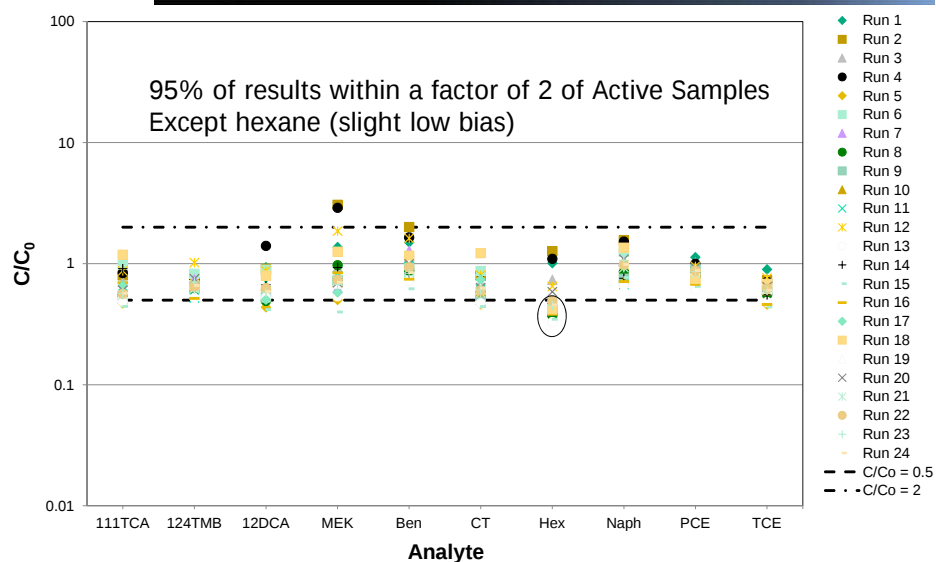
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Fractional Factorial Testing

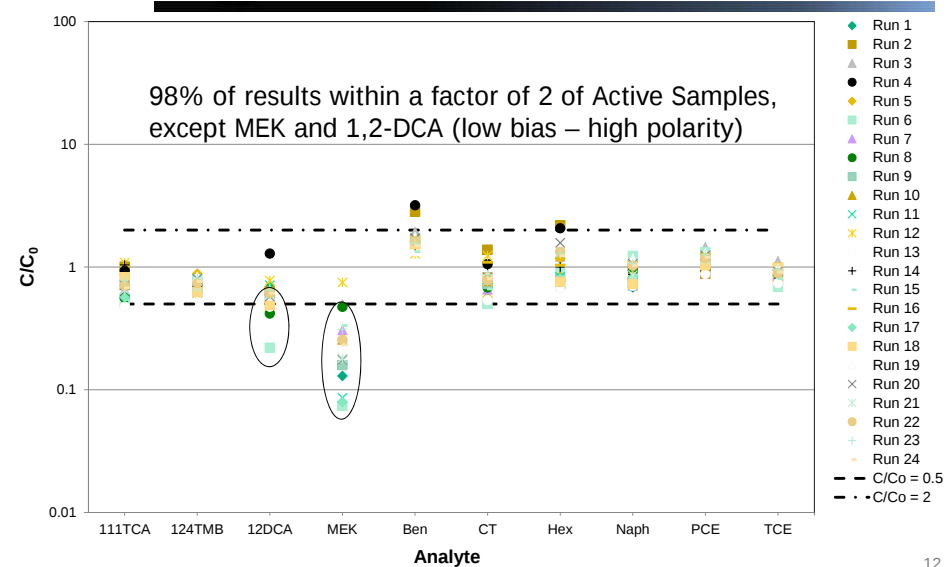
Run #	Approximate Concentration (ppbv)	Approximate Temperature (°C)	Face Velocity (m/s)	Duration (days)	Approximate Humidity (%R.H.)
1	100	17	0.41	1	90
2	1	17	0.014	1	90
3	100	30	0.41	1	30
4	1	30	0.014	1	30
5	100	30	0.41	7	90
6	1	30	0.014	7	90
7	100	17	0.41	7	30
8	1	17	0.014	7	30
9	50	20	0.23	4	60
10	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

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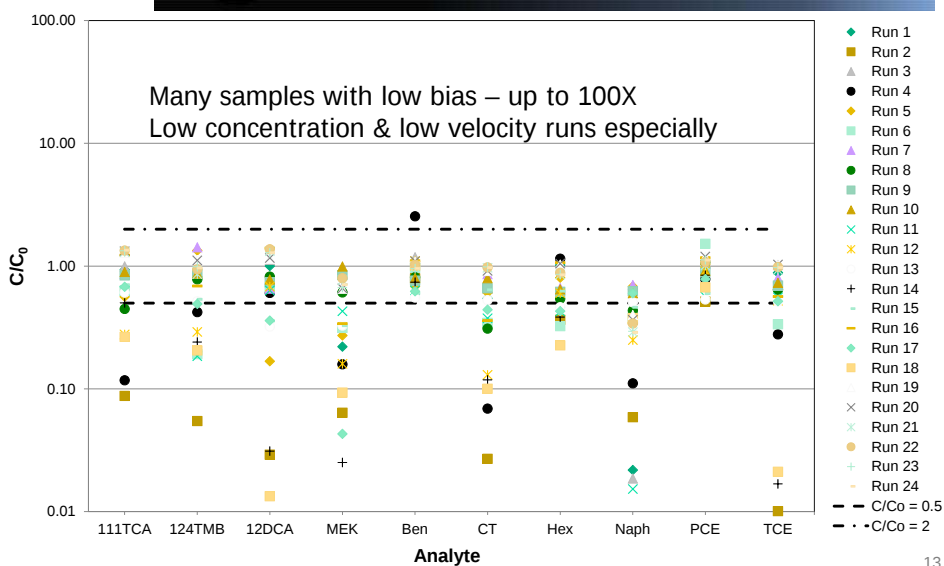
ATD Tenax TA



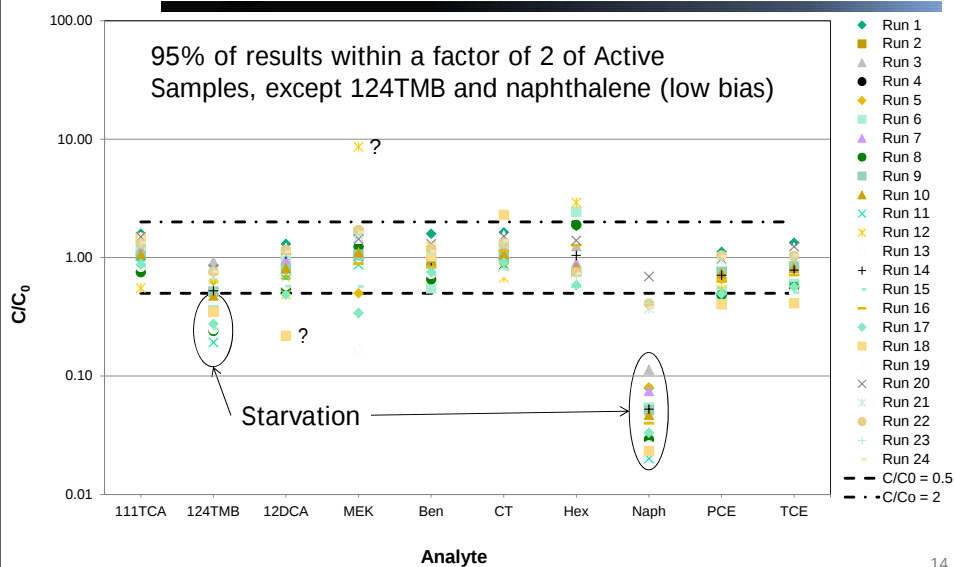
ATD Carboxpack B



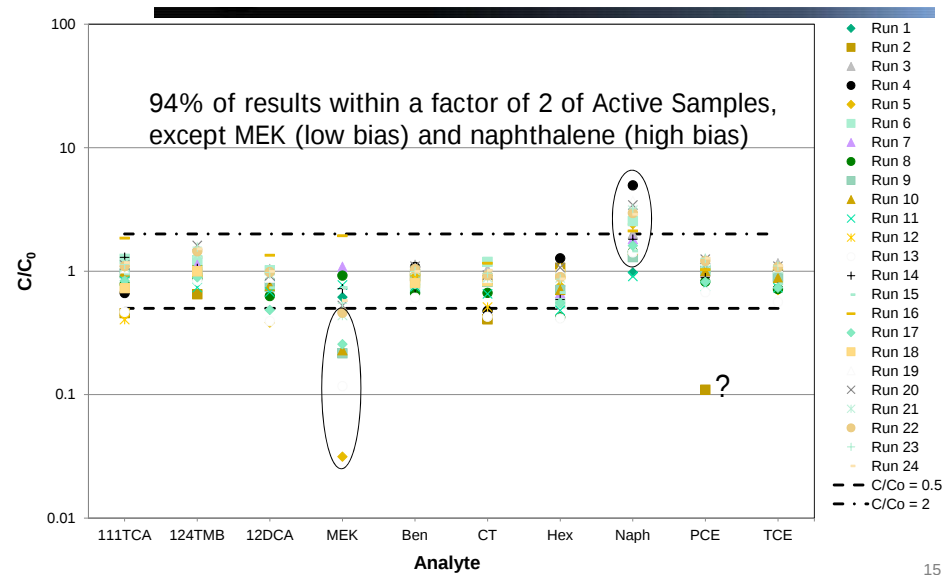
SKC Ultra



Waterloo Membrane Sampler



Radiello



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Table 1: Statistical Significance of the Main Factors in the Fractional Factorial Experiments

Sampler Type	Analyte	Relative Humidity	Temperature	Face Velocity	Exposure Time	Concentration
ATD Carbo-pack	1,1,1-Trichloroethane	0.0778	0.0281	0.0106	0.0003	<.0001
ATD Carbo-pack	1,2,4-Trimethylbenzene	0.3181	0.0009	0.1245	0.5664	0.0011
ATD Carbo-pack	1,2-Dichloroethane	0.0012	0.6819	0.7406	<.0001	0.1371
ATD Carbo-pack	2-Butanone (MEK)	0.0693	0.4097	0.0603	0.7378	0.0119
ATD Carbo-pack	Hexane	0.7999	0.2913	0.4002	0.0272	0.1177
ATD Carbo-pack	Benzene	0.4718	0.2468	0.0547	0.0023	0.0331
ATD Carbo-pack	Carbon tetrachloride	0.0434	0.2975	0.3501	<.0001	<.0001
ATD Carbo-pack	Naphthalene	0.2629	0.6088	0.293	0.007	0.0778
ATD Carbo-pack	Trichloroethene	0.0113	0.2781	0.0002	<.0001	0.9484
ATD Carbo-pack	Tetrachloroethene	0.8513	0.004	0.0071	0.8484	0.0727
ATD Tenax	1,1,1-Trichloroethane	<.0001	0.2715	0.0021	<.0001	<.0001
ATD Tenax	1,2,4-Trimethylbenzene	0.9169	0.8868	0.0121	0.0296	0.2864
ATD Tenax	1,2-Dichloroethane	0.9154	0.8908	0.4733	<.0001	<.0001
ATD Tenax	2-Butanone (MEK)	0.7719	0.0799	0.1479	<.0001	<.0001
ATD Tenax	Hexane	0.6362	0.21	0.6114	<.0001	0.1148
ATD Tenax	Benzene	0.8106	0.0059	0.438	<.0001	0.0442
ATD Tenax	Carbon tetrachloride	<.0001	0.0229	0.0159	<.0001	<.0001
ATD Tenax	Naphthalene	0.311	0.2147	0.565	0.025	0.0347
ATD Tenax	Trichloroethene	0.5875	0.0002	0.0153	<.0001	0.475
ATD Tenax	Tetrachloroethene	0.3221	0.4522	0.11	<.0001	0.9827
RADIELLO	1,1,1-Trichloroethane	0.1005	0.0261	0.003	0.0899	0.0548
RADIELLO	1,2,4-Trimethylbenzene	0.6688	0.0007	<.0001	0.1133	0.0451
RADIELLO	1,2-Dichloroethane	0.0005	0.054	0.0002	0.0327	<.0001
RADIELLO	2-Butanone (MEK)	<.0001	0.5801	0.0003	0.0738	<.0001
RADIELLO	Hexane	0.1795	0.0066	0.0021	<.0001	0.0035
RADIELLO	Benzene	0.0047	0.0496	0.0012	<.0001	0.6113
RADIELLO	Carbon tetrachloride	0.4994	0.0143	0.0513	0.1724	0.9018
RADIELLO	Naphthalene	0.6635	0.0008	0.933	0.1183	0.0005
RADIELLO	Trichloroethene	0.001	0.0032	<.0001	0.0002	0.0169
RADIELLO	Tetrachloroethene	0.2158	0.0023	<.0001	0.3477	0.9109
SKC	1,1,1-Trichloroethane	0.0906	0.1691	0.0055	0.0096	0.0001
SKC	1,2,4-Trimethylbenzene	0.1362	0.3054	0.0012	0.0004	<.0001
SKC	1,2-Dichloroethane	<.0001	0.5187	0.1033	0.9879	0.6424
SKC	2-Butanone (MEK)	<.0001	0.2819	0.3914	0.0073	0.0028
SKC	Hexane	0.0006	0.0398	0.012	0.4921	0.1584
SKC	Benzene	0.0318	0.0551	0.9085	0.0218	0.0125
SKC	Carbon tetrachloride	0.0223	0.2682	0.032	<.0001	<.0001
SKC	Naphthalene	0.1182	0.1437	0.6579	<.0001	0.1122
SKC	Trichloroethene	<.0001	0.9977	0.0306	0.5618	<.0001
SKC	Tetrachloroethene	0.4868	0.0368	0.018	0.0097	0.1261
WMS	1,1,1-Trichloroethane	0.0224	0.9489	0.0042	0.6355	0.4719
WMS	1,2,4-Trimethylbenzene	0.7716	0.7992	<.0001	0.1467	0.0194
WMS	1,2-Dichloroethane	0.7347	0.1749	0.0054	0.0325	0.1887
WMS	2-Butanone (MEK)	0.5881	0.3369	0.14	0.0319	0.0027
WMS	Hexane	0.6198	0.4942	0.022	0.0003	0.0001
WMS	Benzene	0.5712	0.9017	0.0328	0.0012	0.0099
WMS	Carbon tetrachloride	0.0016	0.3838	0.0035	0.0766	0.0553
WMS	Naphthalene	0.9025	0.4298	<.0001	0.5432	0.006
WMS	Trichloroethene	0.6289	0.0325	0.0006	0.8376	0.0124
WMS	Tetrachloroethene	0.5923	0.1477	<.0001	0.9894	0.0074

red highlighted cells indicate statistical significance when alpha=0.05, therefore, p-value<0.05 = significant

ANOVA
Analysis

Highlighted cells are statistically significant at the 5% level.

Need to think about whether “statistically significant” is also “practically significant”

95% within 2X is actually pretty good

If only we could predict the challenging compounds

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Field Testing of Indoor Air



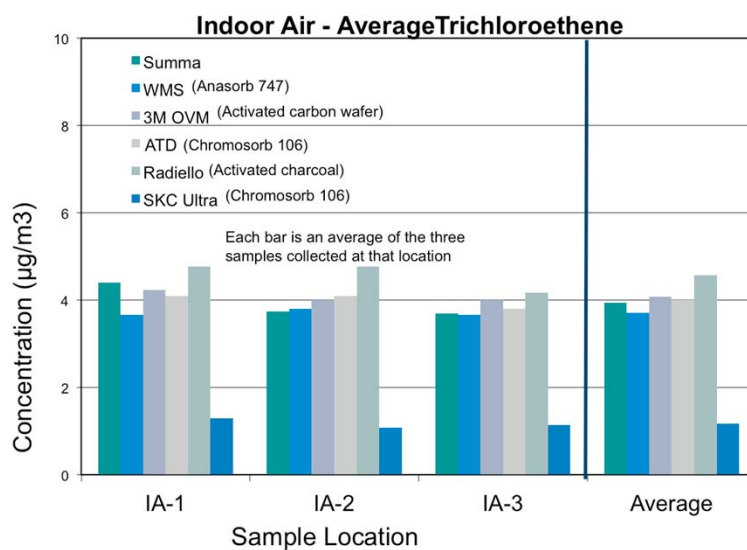
Navy San Diego, CA
Cherry Point, NC
CRREL, NH

3 locations/site
5 passive samplers
Summa cans
Triplicates of each

Thanks to Ignacio Rivera of SPAWAR, Jason Williams of Cherry Point and Louise Parker of CRREL

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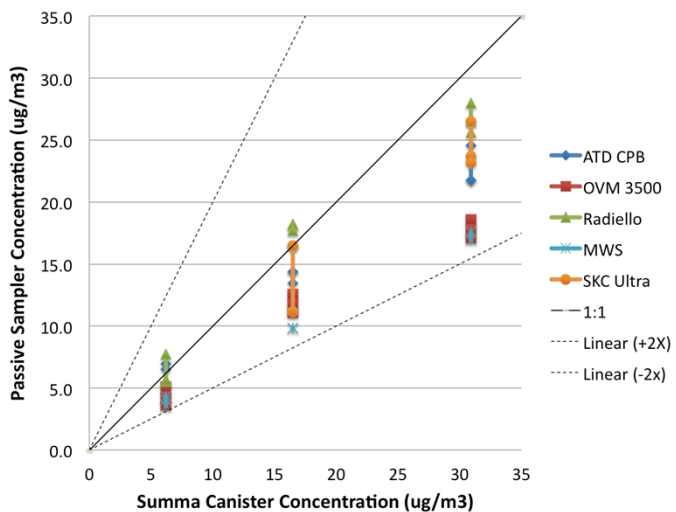
Indoor Air TCE at San Diego



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Indoor Air at CRREL

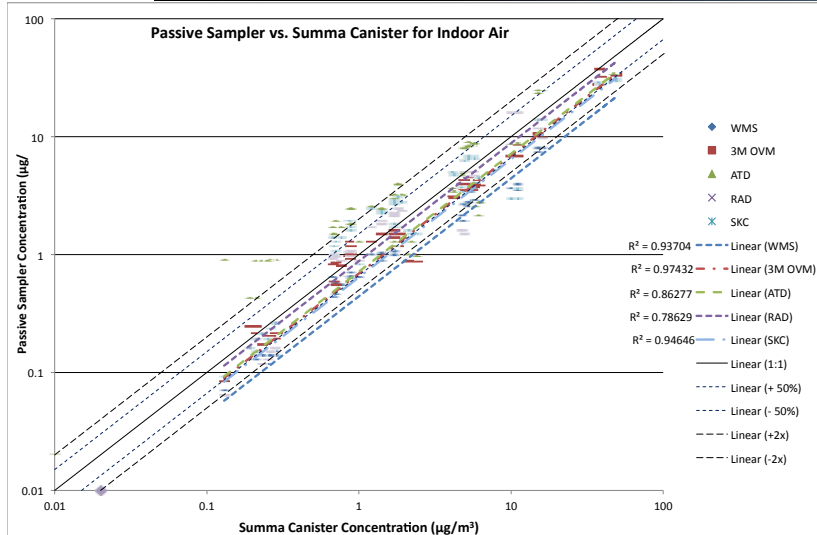
TCE Concentration in Passive Samplers vs Summa Canisters



All passive sampler results were within 2X of Summa canister data for TCE

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Indoor Air VOCs at Cherry Point



Broader range (>100X), but still almost all passive data are within 2X of Summa canisters

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High Concentration Lab Tests

(To mimic soil gas conditions)



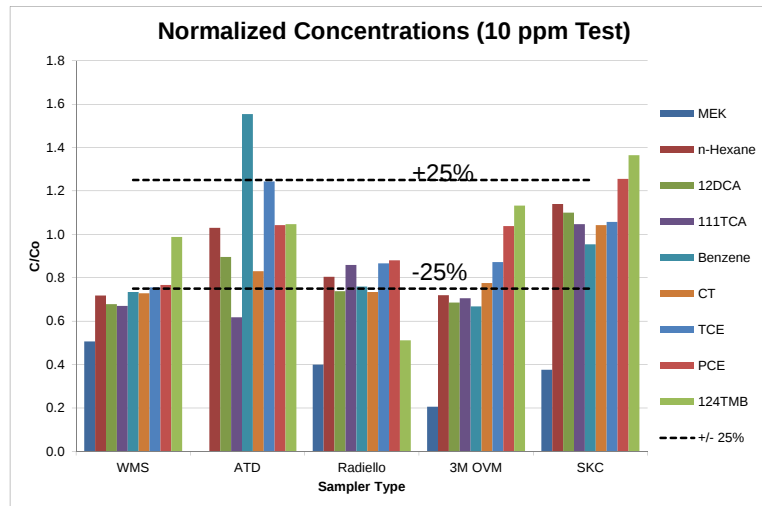
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High Concentration Lab Tests



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High Concentrations Test Results



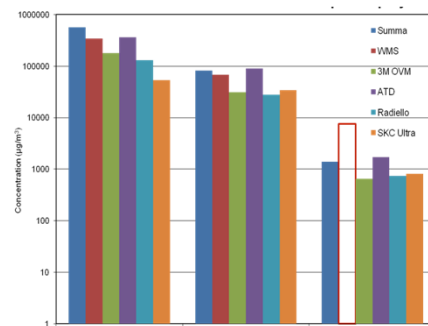
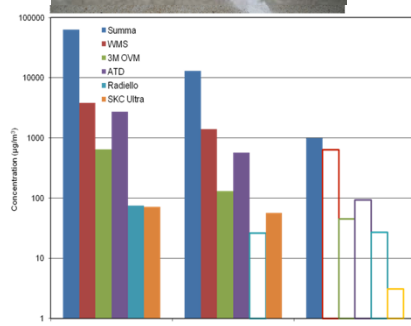
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Sub-Slab – Navy San Diego



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

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



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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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Sorbent Selection

Carbopack B

(Graphitized Carbon Black)
Surface Area: 100 m²/g
Desorption Temperature: 320 °C

	0.2	1	5	10	20	100
Halocarbon 12						
Chloroethane						
Halocarbon 114						
Vinyl chloride						
1,2-Dichloroethane						
Bromochloroethane						
Chloroethane						
Halocarbon 11						
Acrylonitrile						
1,1-Dichloroethane						
Methylene chloride						
3-Chloropropene						
Halocarbon 113						
1,1-Dichloroethane						
cis-1,2-Dichloroethane						
Chloroform						
1,2-Dichloroethane						
1,1,1-Trichloroethane						
Benzene						
Carbon tetrachloride						
1,2-Dichloropropane						
Trichloroethylene						
cis-1,3-Dichloropropene						
trans-1,3-Dichloropropene						
1,1,2-Trichloroethane						
Toluene						
1,2-Dibromochloroethane						
Tetrachloroethane						
Chlorobenzene						
Ethylbenzene						
m & p-Xylene						
Styrene						
1,1,2,2-Tetrachloroethane						
n-Butene						
4-Ethyltoluene						
1,3,5-Trimethylbenzene						
1,2,4-Trimethylbenzene						
1,3-Dichlorobenzene						
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
1,2,4-Trichlorobenzene						
Hexachlorobutadiene						

Performance Key

Adsorption Recovery is less than 20%
Adsorption Recovery is between 21 to 70%
Adsorption Recovery is greater than 71%
Indicates this analyte was strongly adsorbed

SUPELCO

TENAX TA

(Polymer)
Surface Area: 35 m²/g
Desorption Temperature: 300 °C

	0.2	1	5	10	20	100
Halocarbon 12						
Chloroethane						
Halocarbon 114						
Vinyl chloride						
1,2-Dichloroethane						
Bromochloroethane						
Ethyl chloride						
Halocarbon 11						
Acrylonitrile						
1,1-Dichloroethane						
Methylene chloride						
3-Chloropropene						
Halocarbon 113						
1,1-Dichloroethane						
cis-1,2-Dichloroethane						
Chloroform						
1,2-Dichloroethane						
1,1,1-Trichloroethane						
Benzene						
Carbon tetrachloride						
1,2-Dichloropropane						
Trichloroethylene						
cis-1,3-Dichloropropene						
trans-1,3-Dichloropropene						
1,1,2-Trichloroethane						
Toluene						
1,2-Dibromochloroethane						
Tetrachloroethane						
Chlorobenzene						
Ethylbenzene						
m & p-Xylene						
Styrene						
1,1,2,2-Tetrachloroethane						
n-Butene						
4-Ethyltoluene						
1,3,5-Trimethylbenzene						
1,2,4-Trimethylbenzene						
1,3-Dichlorobenzene						
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
1,2,4-Trichlorobenzene						
Hexachlorobutadiene						

Performance Key

Adsorption Recovery is less than 20%
Adsorption Recovery is between 21 to 70%
Adsorption Recovery is greater than 71%
Indicates this analyte was strongly adsorbed

SUPELCO

Soil Gas @ 12 ft – Hill AFB



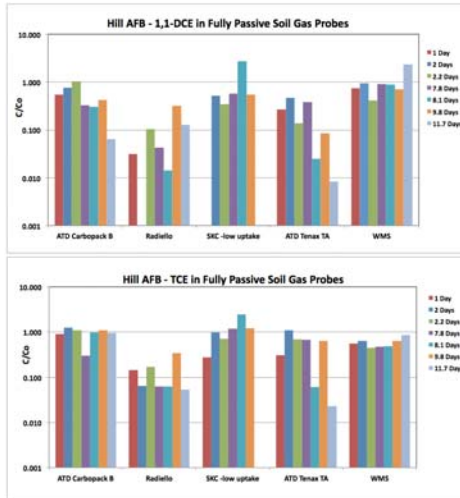
6 probes -12 ft deep

Latin Square Design

1 to 12 day exposures

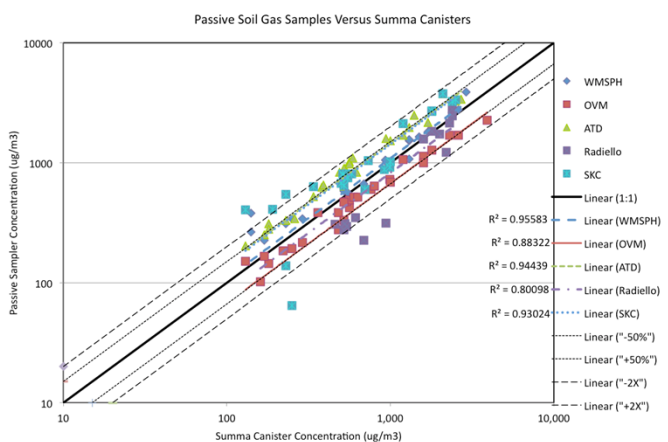
C_0 Measured using combination of Summa and Hapsite GC/MS

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



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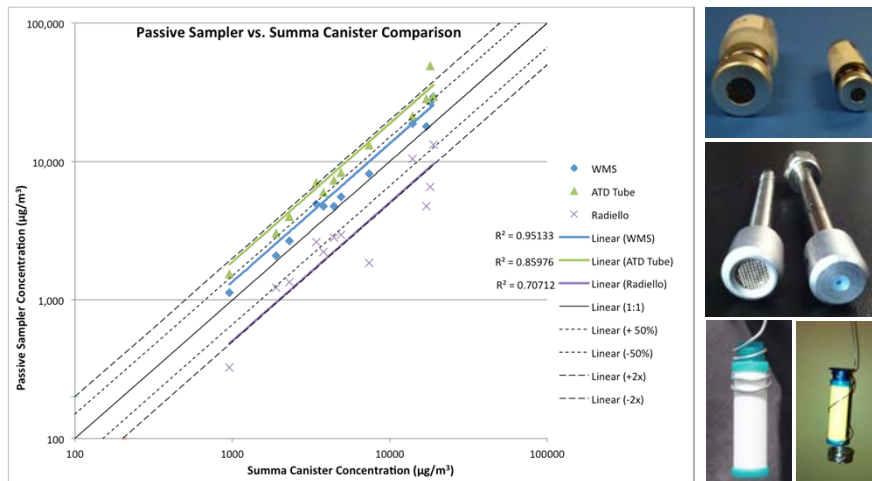
Soil Vapor Sampling – NAS JAX



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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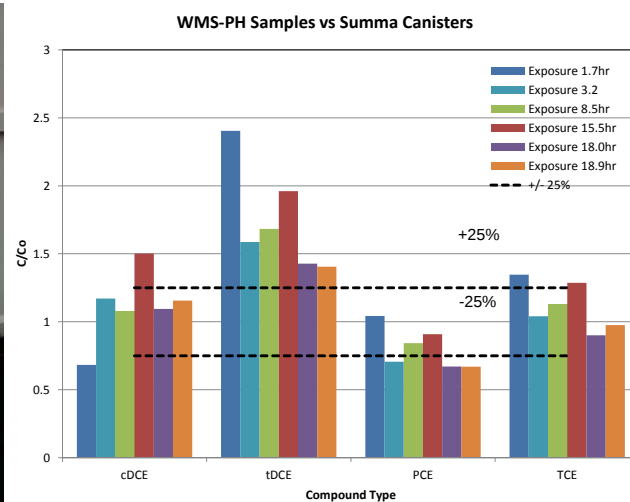
Passive Sub-Slab – NAS JAX



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

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Temporary Passive - NAS JAX

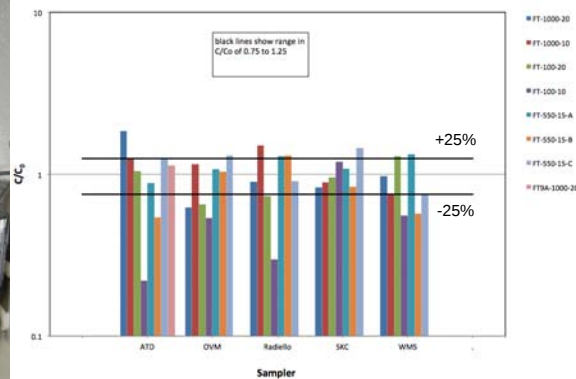


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Flow-Through Cell – CRREL



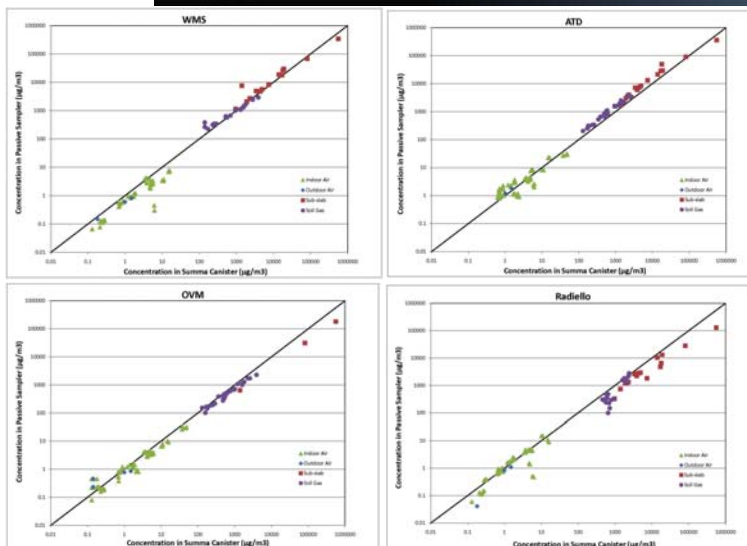
CRREL Sub-Slab Flow-Through Cell - TCE



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

Quantitative results for soil vapor (a breakthrough)

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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

Ballpark 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)

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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Acknowledgments

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Questions/Comments?



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