Managing Temporal and Spatial Variability in Vapor Intrusion Data

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Environmental Monitoring and Data Quality Workshop
La Jolla, CA
28 March 2012

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **28 MAR 2012**	2. REPORT TYPE	3. DATES COVERED **00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE **Managing Temporal and Spatial Variability in Vapor Intrusion Data**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Geosyntec Consultants, Inc,2002 Summit Blvd, NE Suite 885,Atlanta,GA,30319**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the 9th Annual DoD Environmental Monitoring and Data Quality (EDMQ) Workshop Held 26-29 March 2012 in La Jolla, CA. U.S. Government or Federal Rights License

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**49**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

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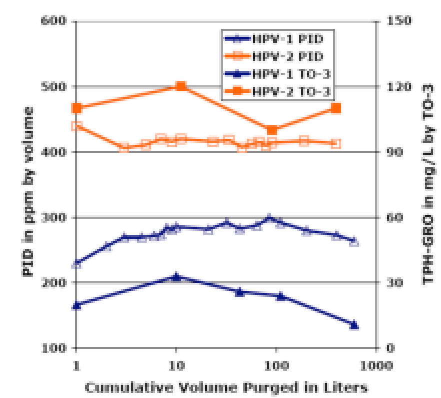
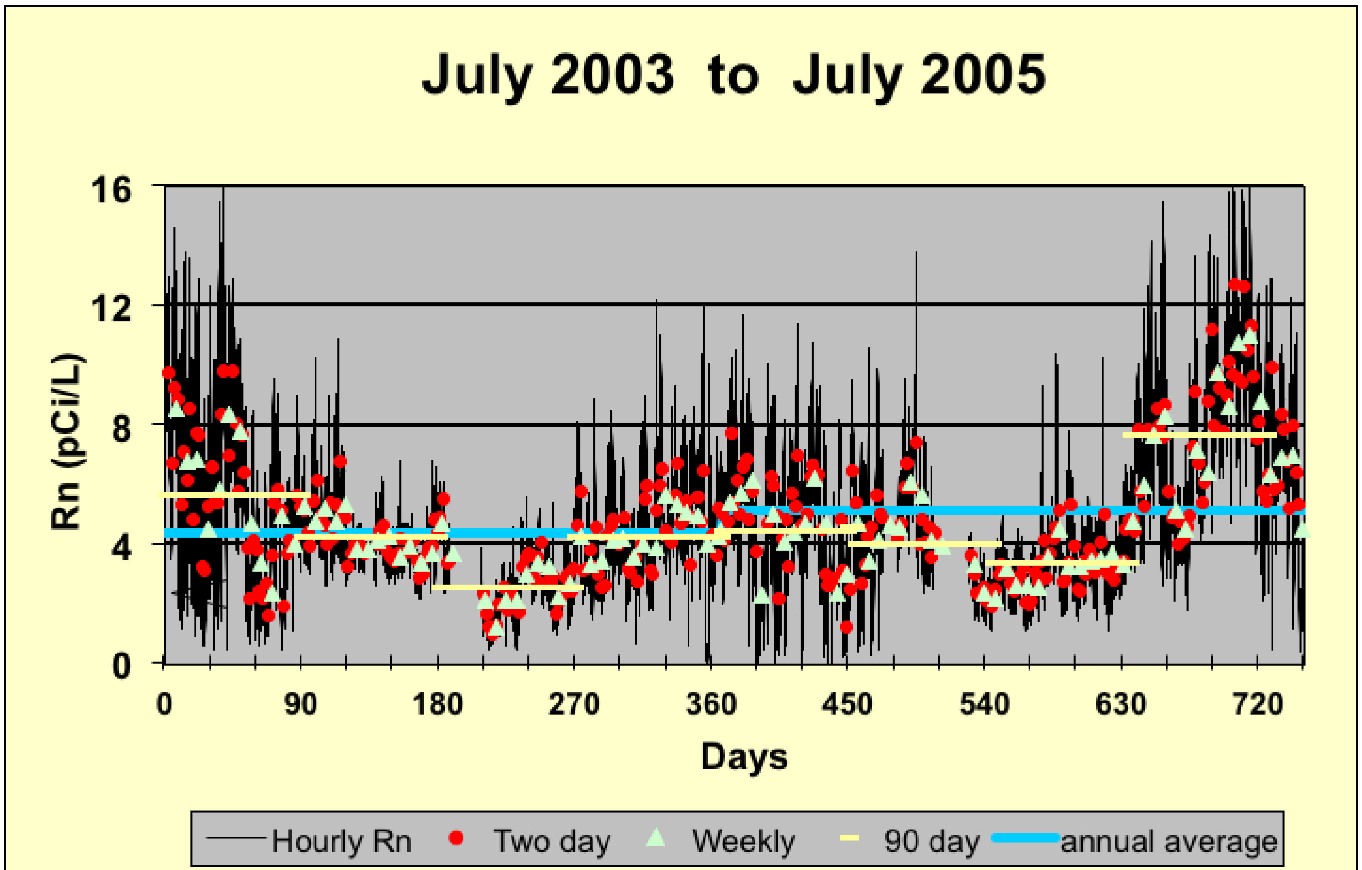
New Sampling Approaches

	Old	New
Temporal Variability	8 to 24-Hour Time Weighted Average 	3 to 30 day Time Weighted Average 
Spatial Variability	1L Volume Weighted Average 	High Purge Volume Sampling 

Temporal Variability (Indoor Air)

Single Day Radon Samples Provide Poor Estimates of Annual Average Radon Concentrations



(Figure from Daniel Steck Ph.D., AEHS San Diego 2011)

Radon guidance recommends longer-term samples to manage temporal variability

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Passive Samplers

3M OVM 3500

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

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

SKC Ultra II

Radiello™

Waterloo Membrane Sampler™

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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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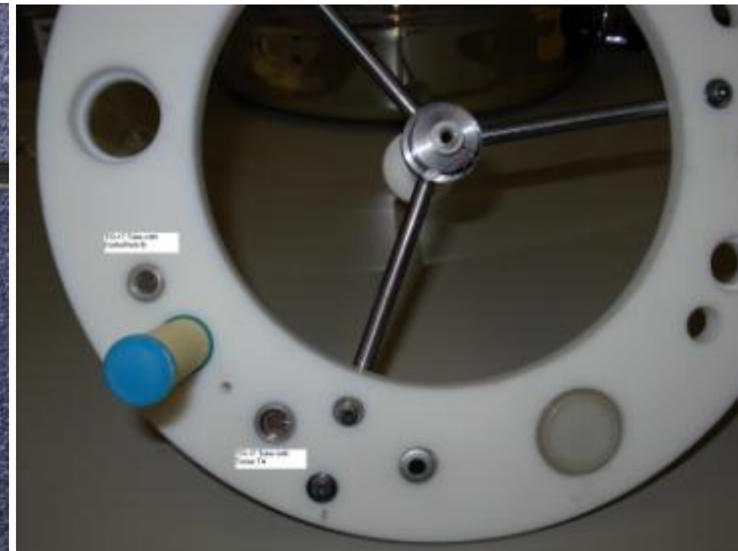
Experimental Apparatus



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


HEMCO

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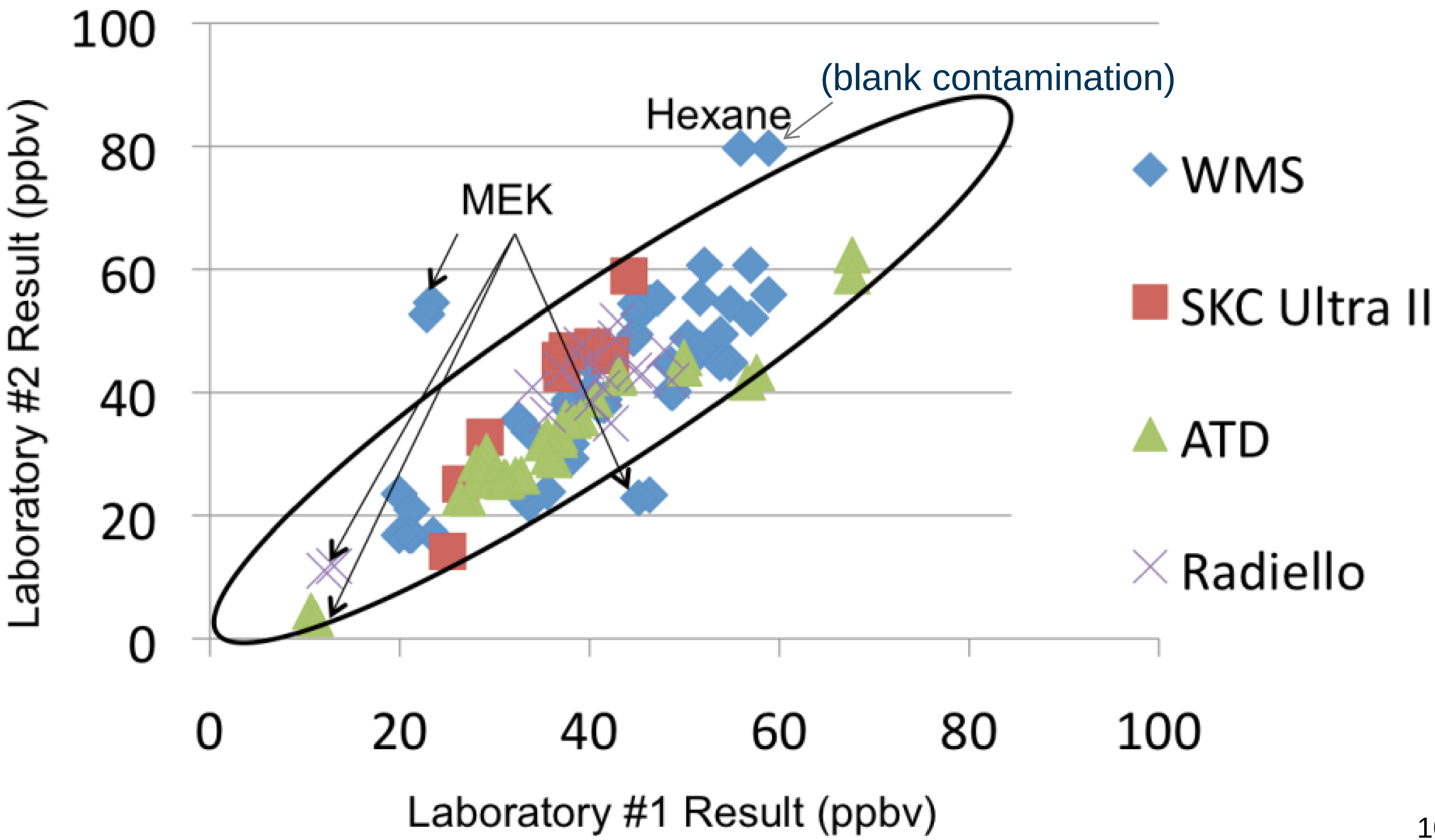
Inter-Laboratory Testing

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



Fractional Factorial Testing

- A series of experiments strategically changing the 5 key factors

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

Concentration

Temperature

Face Velocity

Sample Time

Humidity

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

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ANOVA Analysis of the 5 Factors

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 Carbopack	1,1,1-Trichloroethane	0.0778	0.0281	0.0106	0.0003	<.0001
ATD Carbopack	1,2,4-Trimethylbenzene	0.3181	0.0009	0.1245	0.5664	0.0011
ATD Carbopack	1,2-Dichloroethane	0.0012	0.6819	0.7406	<.0001	0.1371
ATD Carbopack	2-Butanone (MEK)	0.0693	0.4097	0.0603	0.7378	0.0119
ATD Carbopack	Hexane	0.7999	0.2913	0.4002	0.0272	0.1177
ATD Carbopack	Benzene	0.4718	0.2468	0.0547	0.0023	0.0331
ATD Carbopack	Carbon tetrachloride	0.0434	0.2975	0.3501	<.0001	<.0001
ATD Carbopack	Naphthalene	0.2629	0.6088	0.293	0.007	0.0778
ATD Carbopack	Trichloroethene	0.0113	0.2781	0.0002	<.0001	0.9484
ATD Carbopack	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

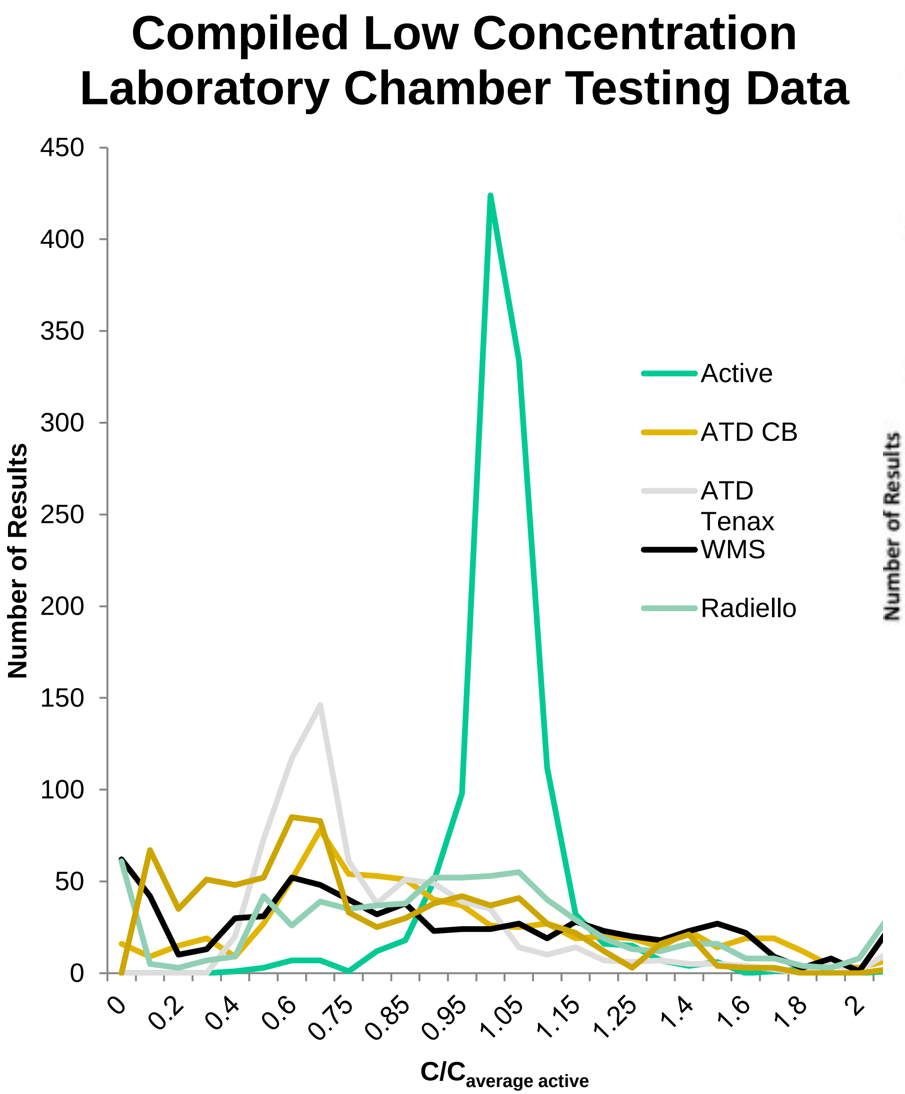
red highlighted cells indicate statistical significance when alpha=0.05, therefore, p-value<0.05 = significant

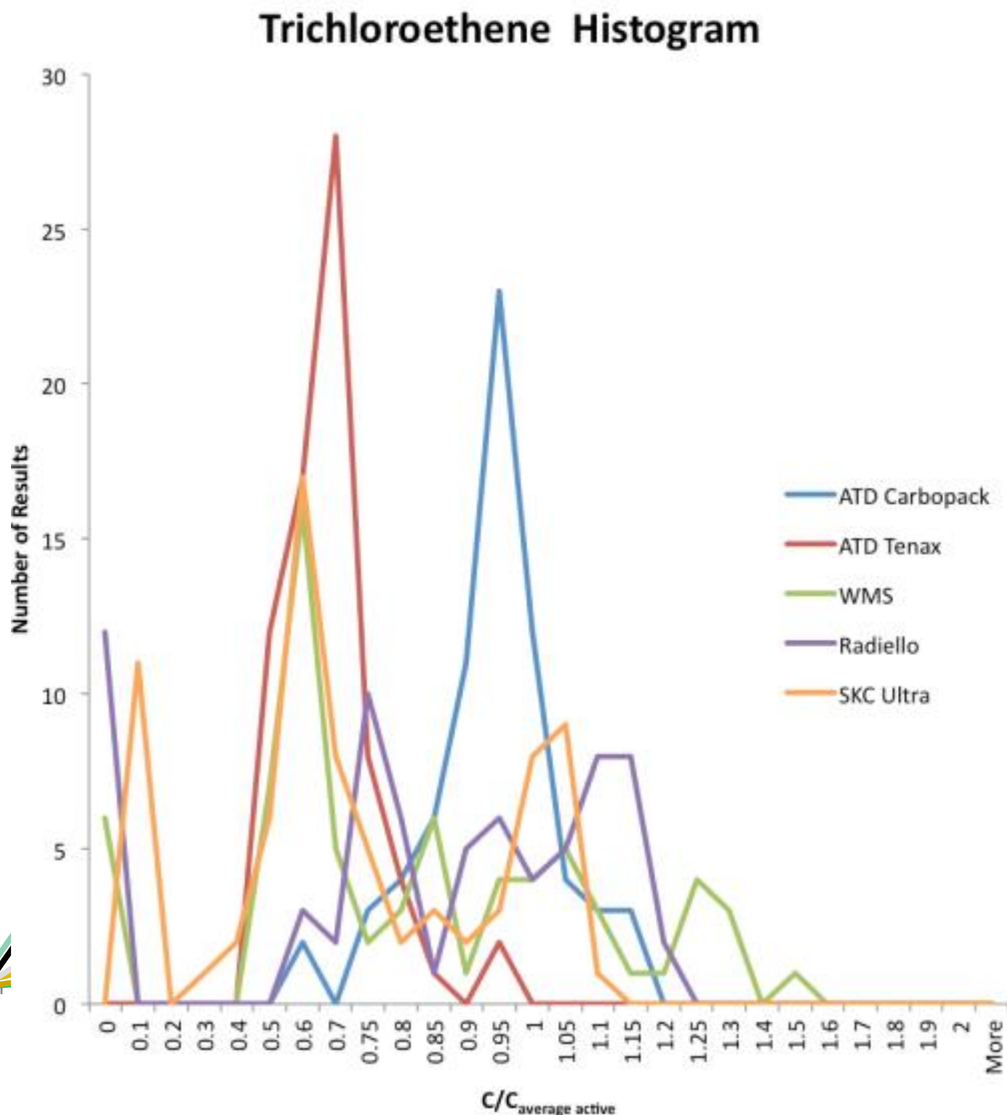
The five factors tested showed statistically significant effects on the concentrations measured with passive samplers.

Need to think about whether "statistically significant" is also "practically significant"

Red cells are significant at 95% level

Low Concentration Lab Tests





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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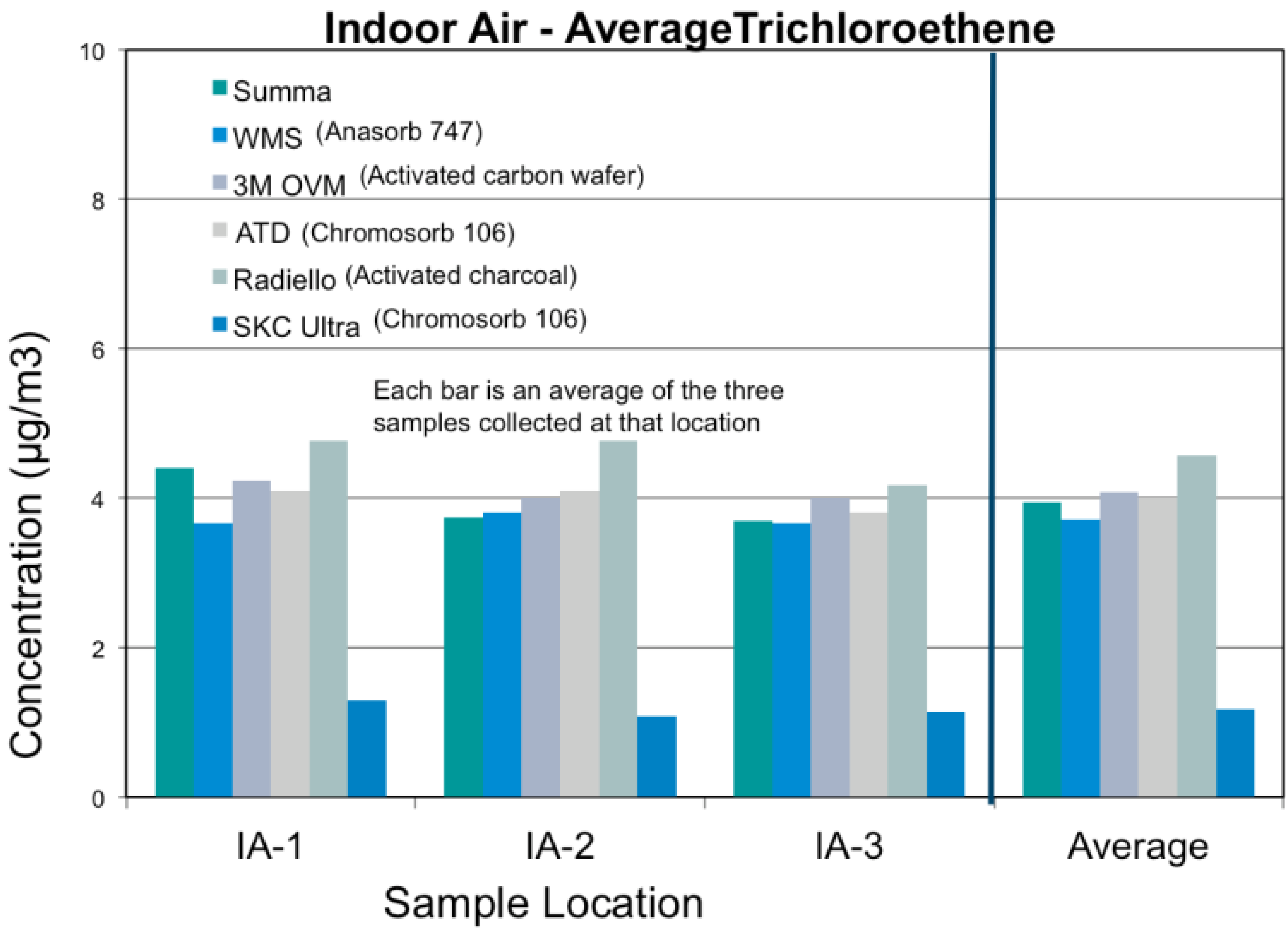
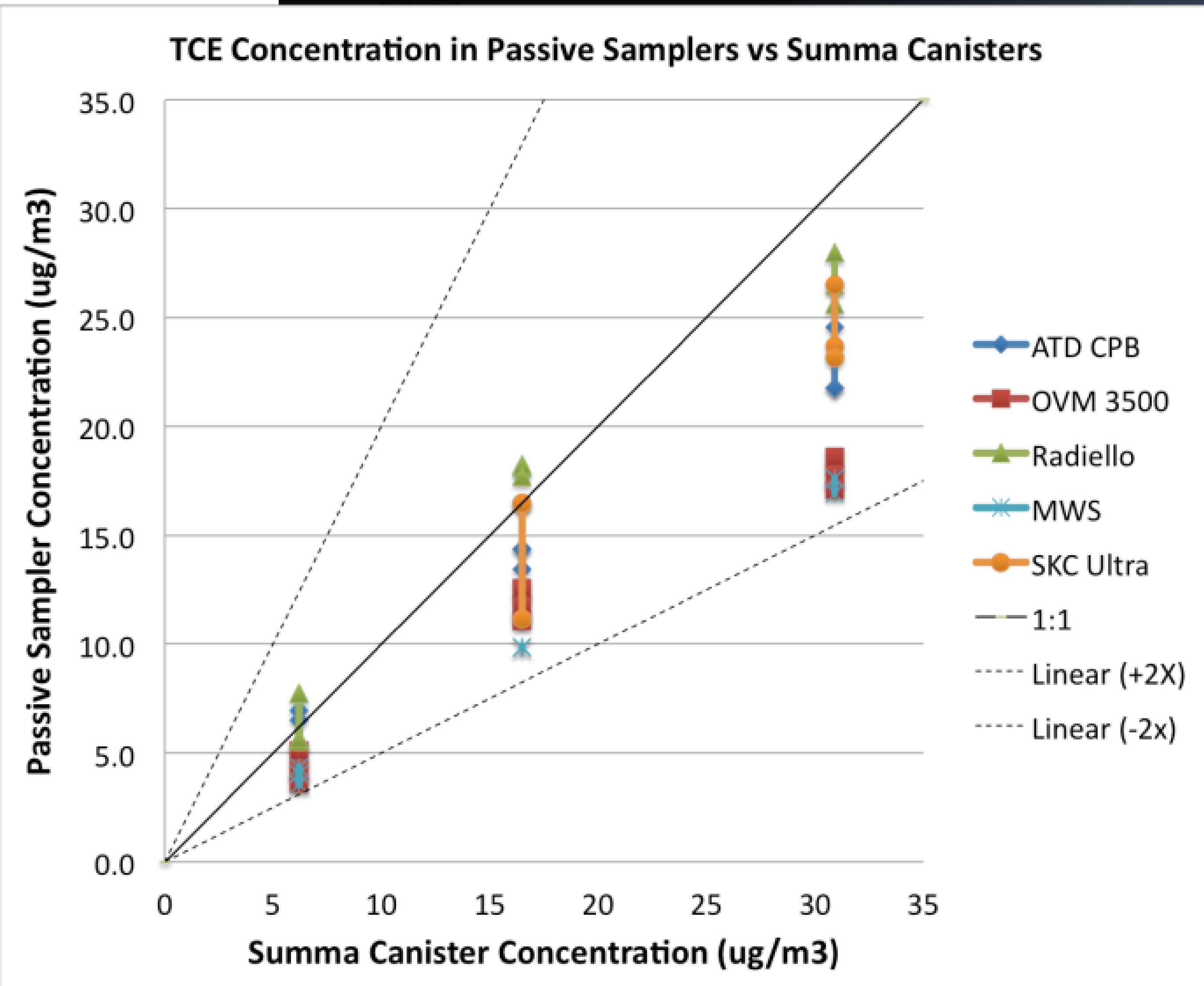
Indoor Air TCE at San Diego

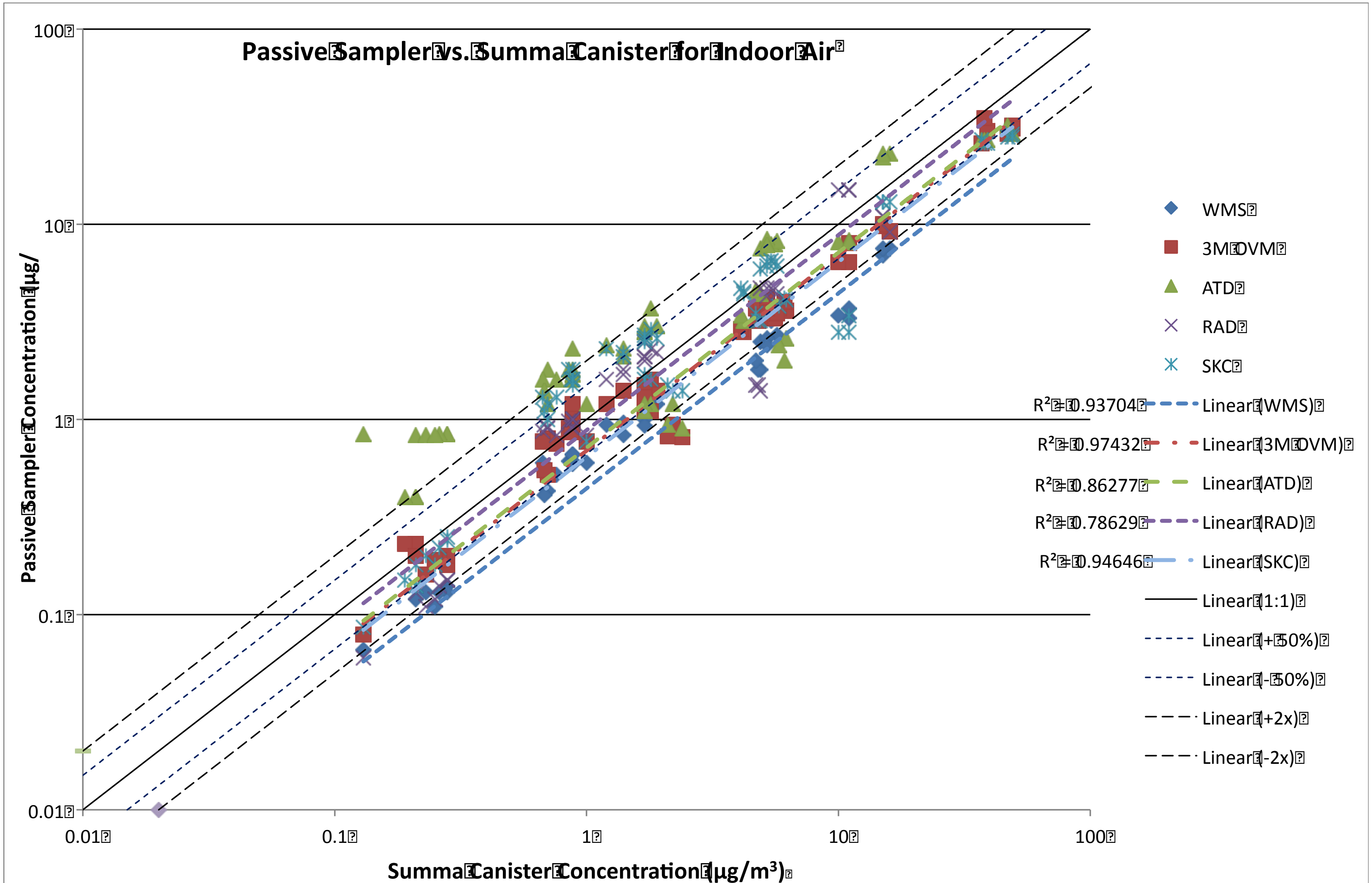


Indoor Air at CRREL



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

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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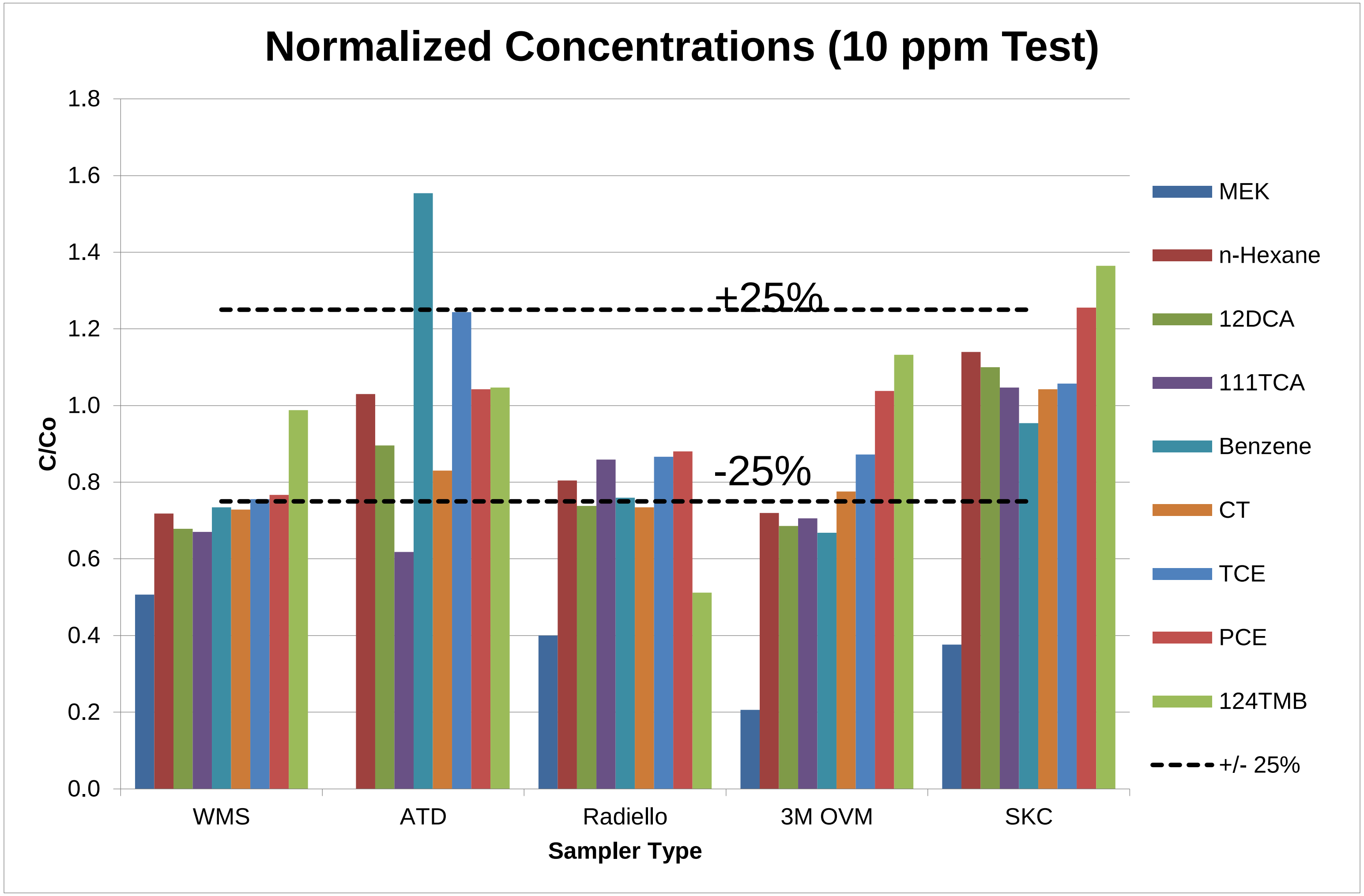
High Concentration Lab Tests

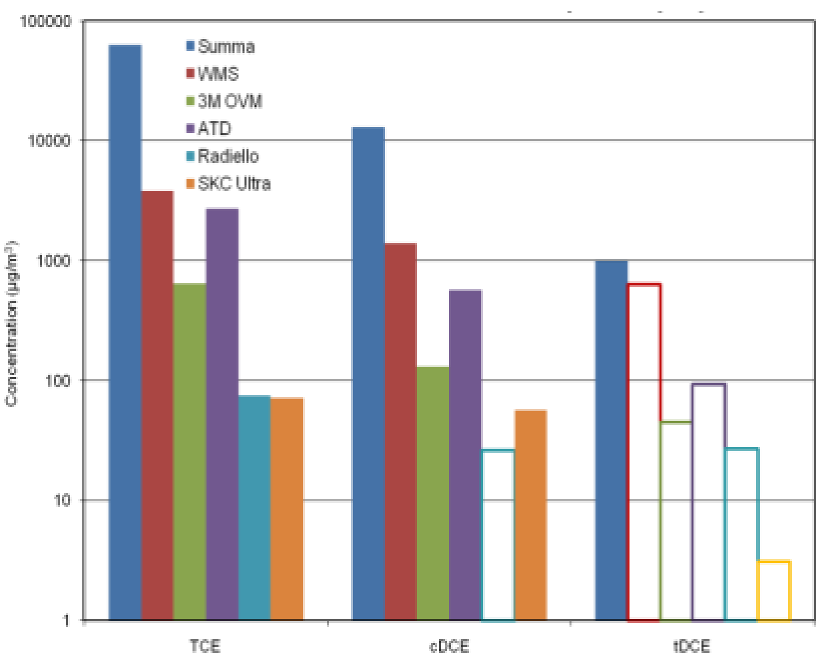
High Concentrations Test Results

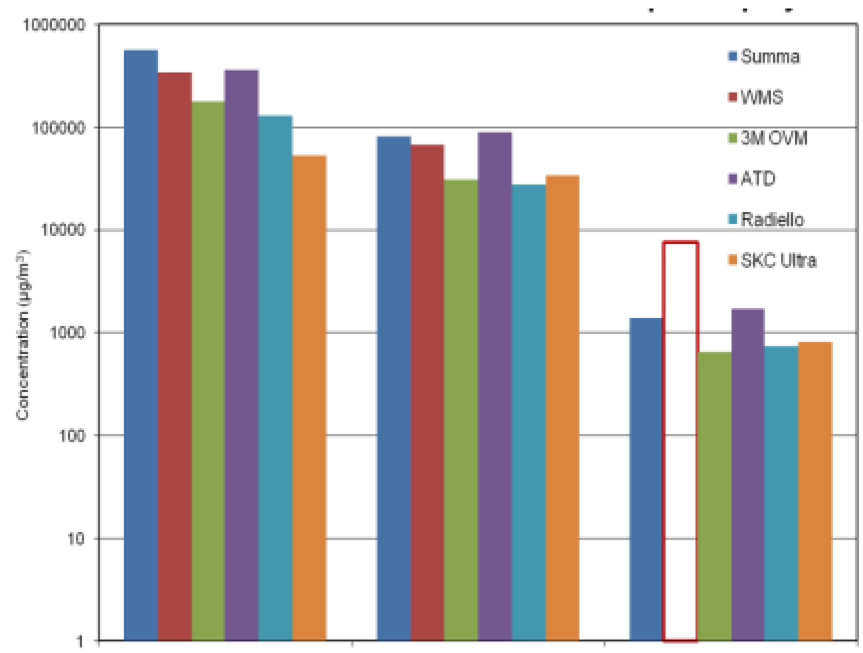


Sub-Slab – Navy San Diego

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

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





Modified Uptake Rates

Lower uptake rate = less starvation

SKC Ultra II and 12-hole Cap

ATD Tube & Pinhole Cap

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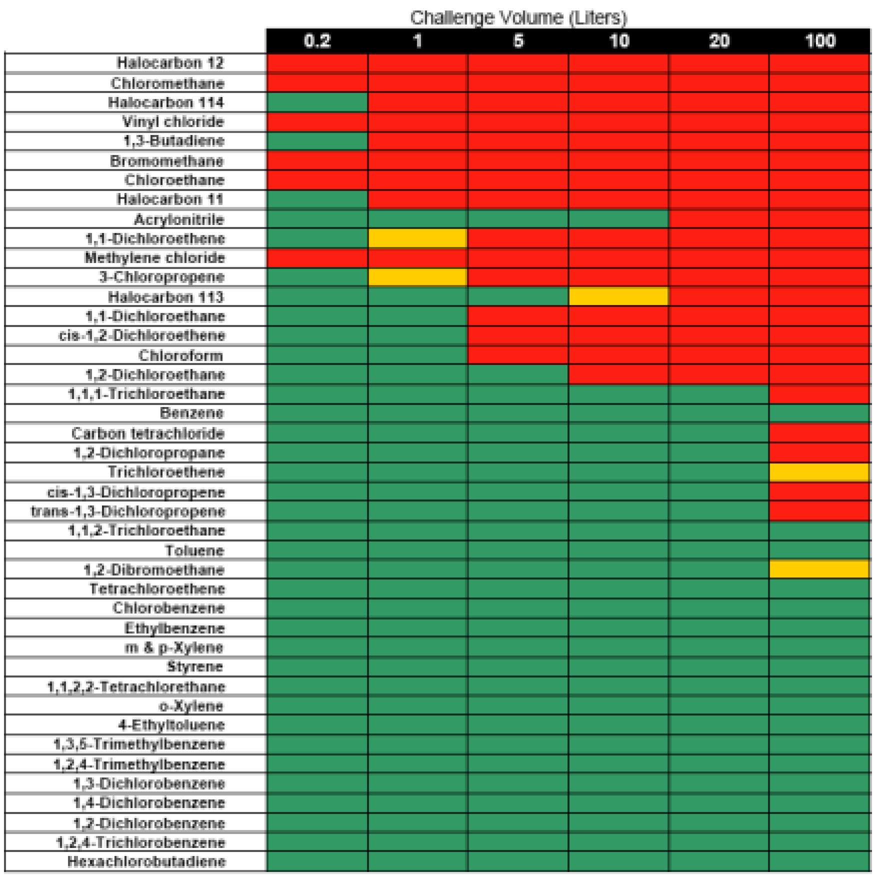
Sorbent Selection

Carbopack B

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

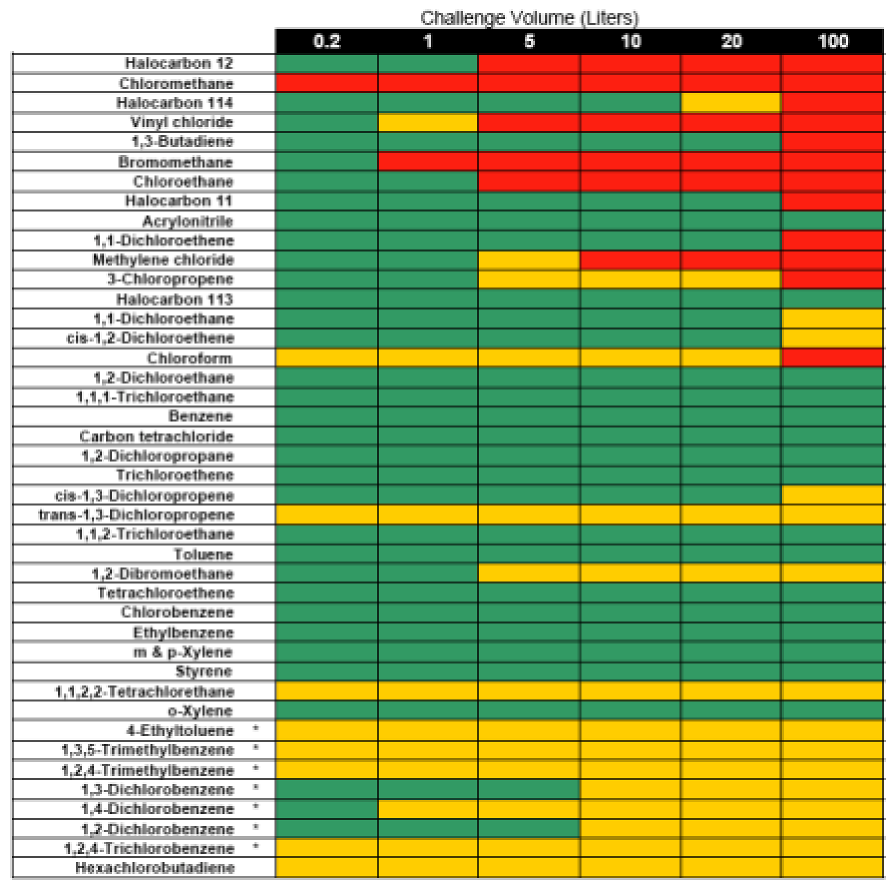


Performance Key
Safe to use: Recovery is greater than 80%
Caution: Recovery is between 21 to 79%
Not Recommended: Recovery is less than 20%
* indicates this analyte was strongly adsorbed

SUPELCO

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

SUPELCO

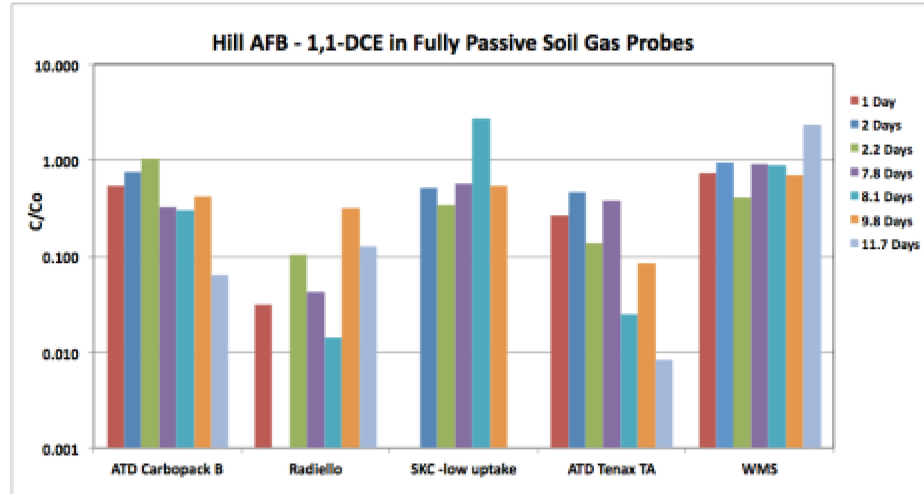
Soil Gas @ 12 ft – Hill AFB

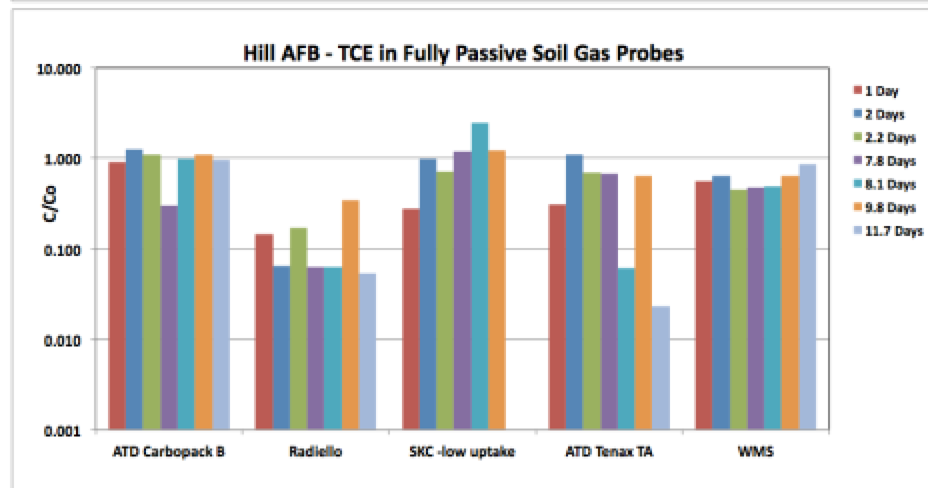
6 probes -12 ft deep

Latin Square Design

1 to 12 day exposures

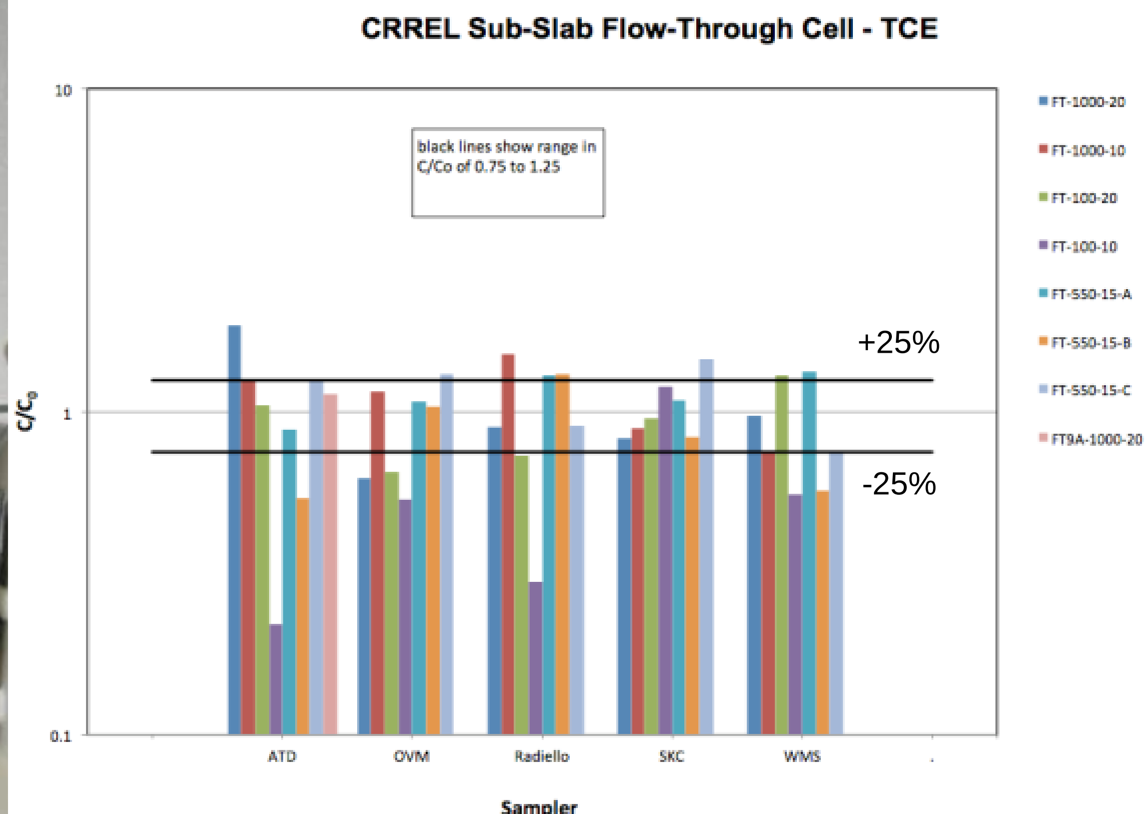
C_o Measured using combination of Summa and Hapsite GC/MS





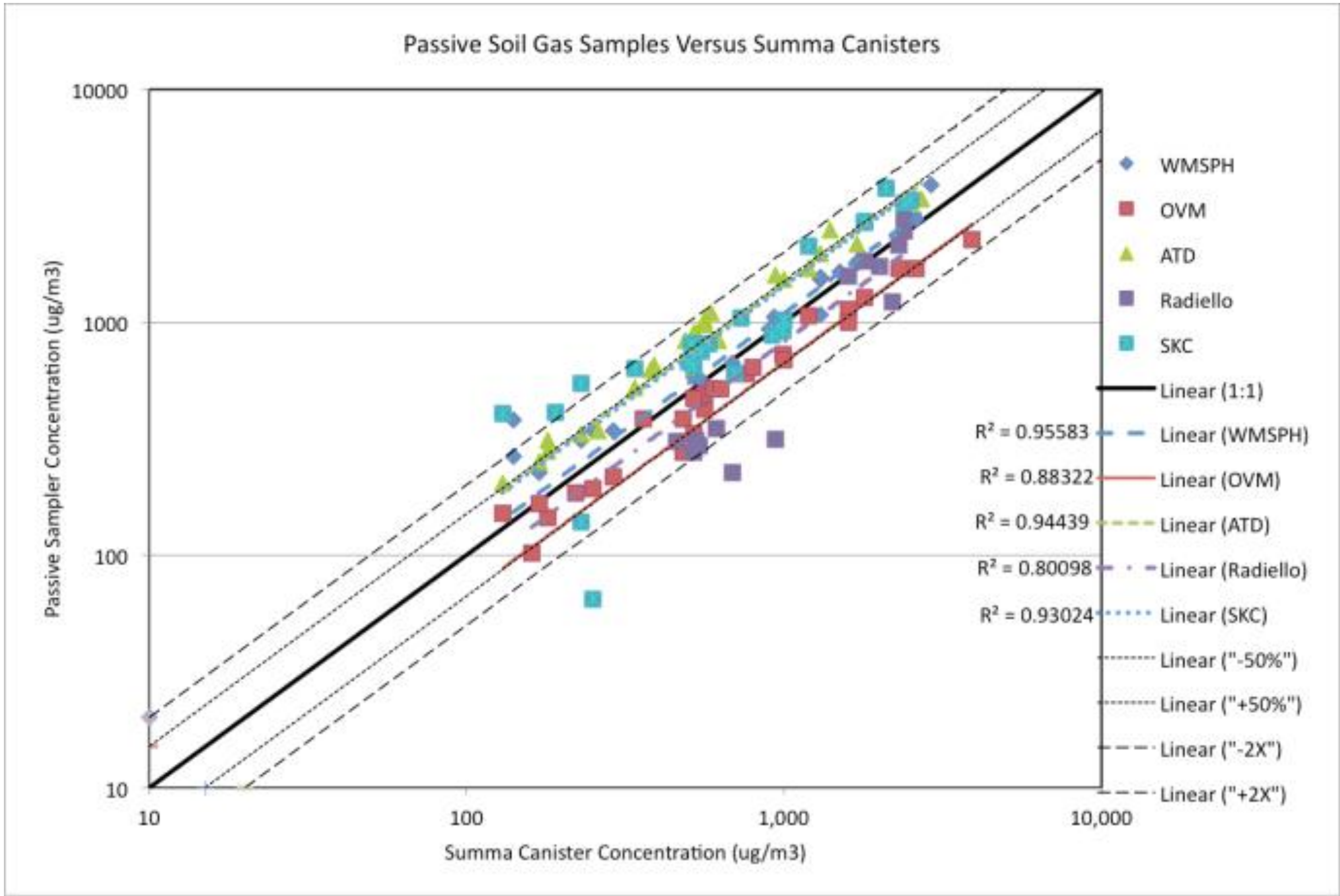
Negative bias for long duration with ATD-Tenax
Negative bias for high uptake rate (Radiello)
Otherwise, encouraging results for TCE and DCE

Flow-Through Cell – CRREL



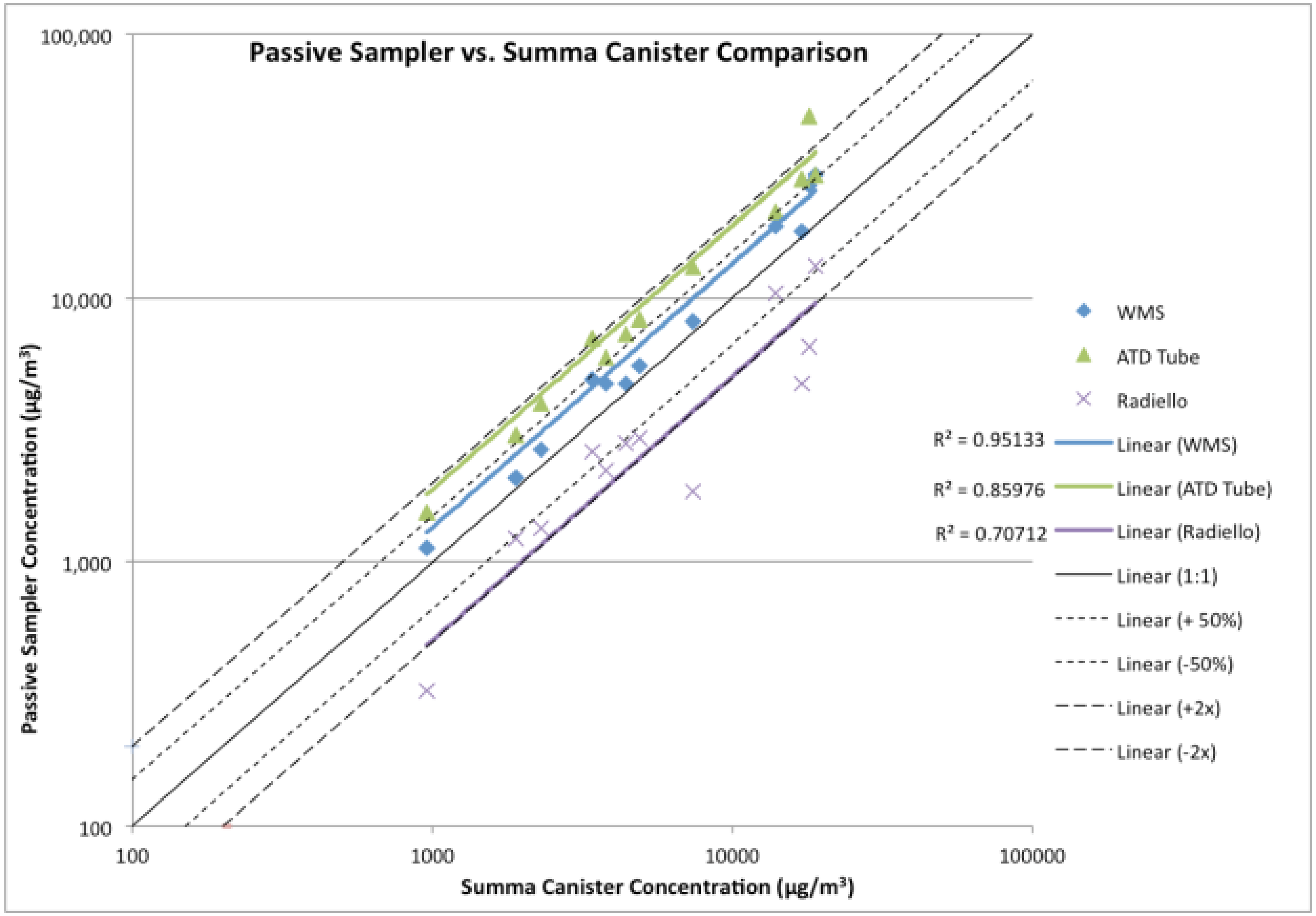
Flow-through cell to avoid starvation by design
No starvation for high-uptake rate samplers
Negative bias only for short duration/low-flow
(insufficient purging)

Soil Vapor Sampling – NAS JAX



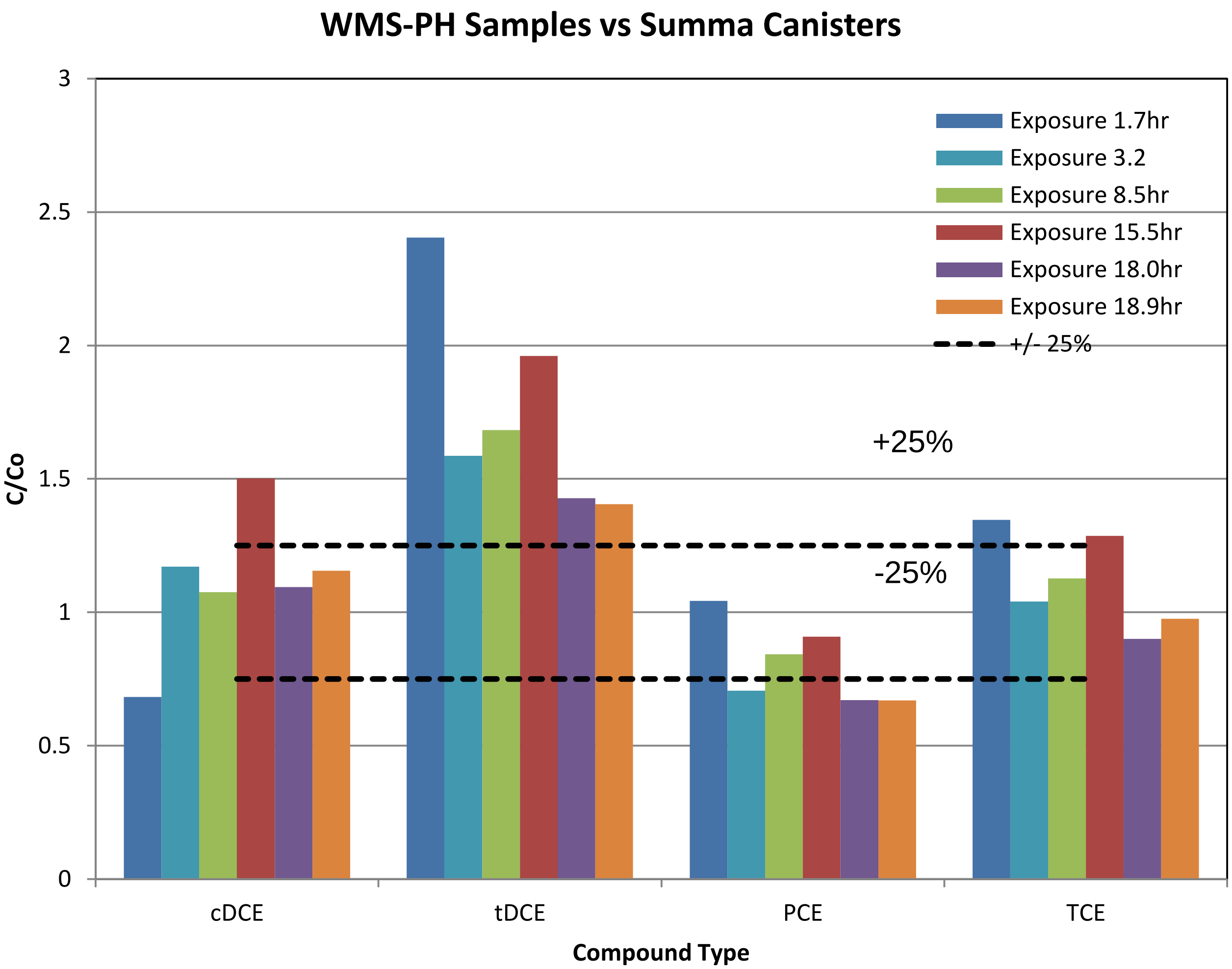
Probes to 3-4 feet deep, exposure durations of 20, 40 and 60 minutes
Strong correlations, regression slopes all near 1.0

Passive Sub-Slab – NAS JAX



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

Temporary Passive - NAS JAX



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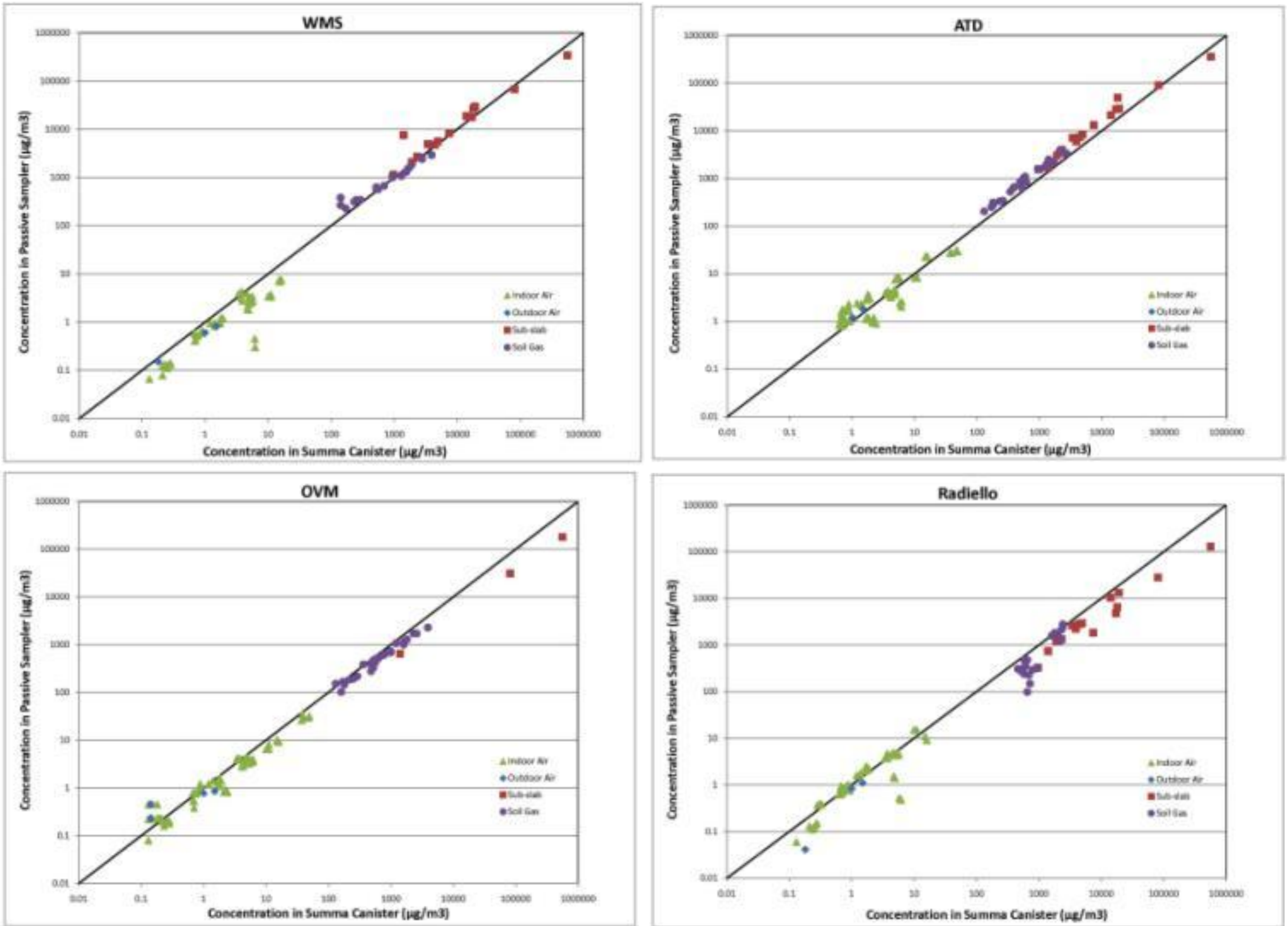
Overall Correlation between Passive and Active Samplers



Strong correlation to conventional samples over 6+ orders of magnitude

Quantitative results for soil vapor (a breakthrough)

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

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)

Case Study – Air Force Base

- TCE concentrations in Area of Interest:
  - Groundwater up to 100,000 ug/L
  - Soil Vapor up to 6,000,000 ug/m^3
- Used Waterloo Membrane Samplers (4 weeks)
  - No VOCs above RBSLs or ambient background
- Open Bay Doors – huge ventilation rate
- Screen out, or reduce to low priority for VI

Even if there is no significant risk, it still needs to be documented

Regulators & occupants often prefer indoor air data

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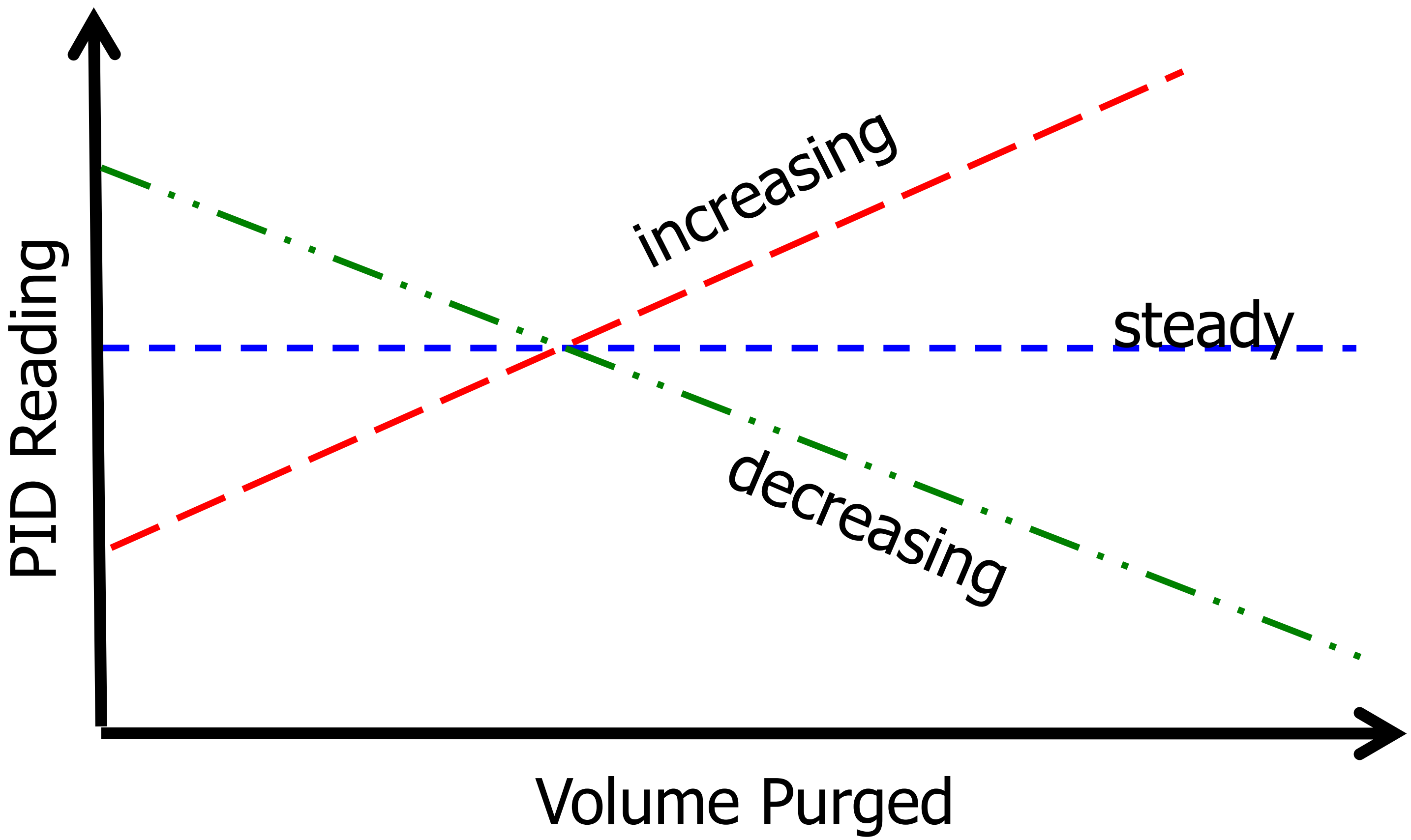
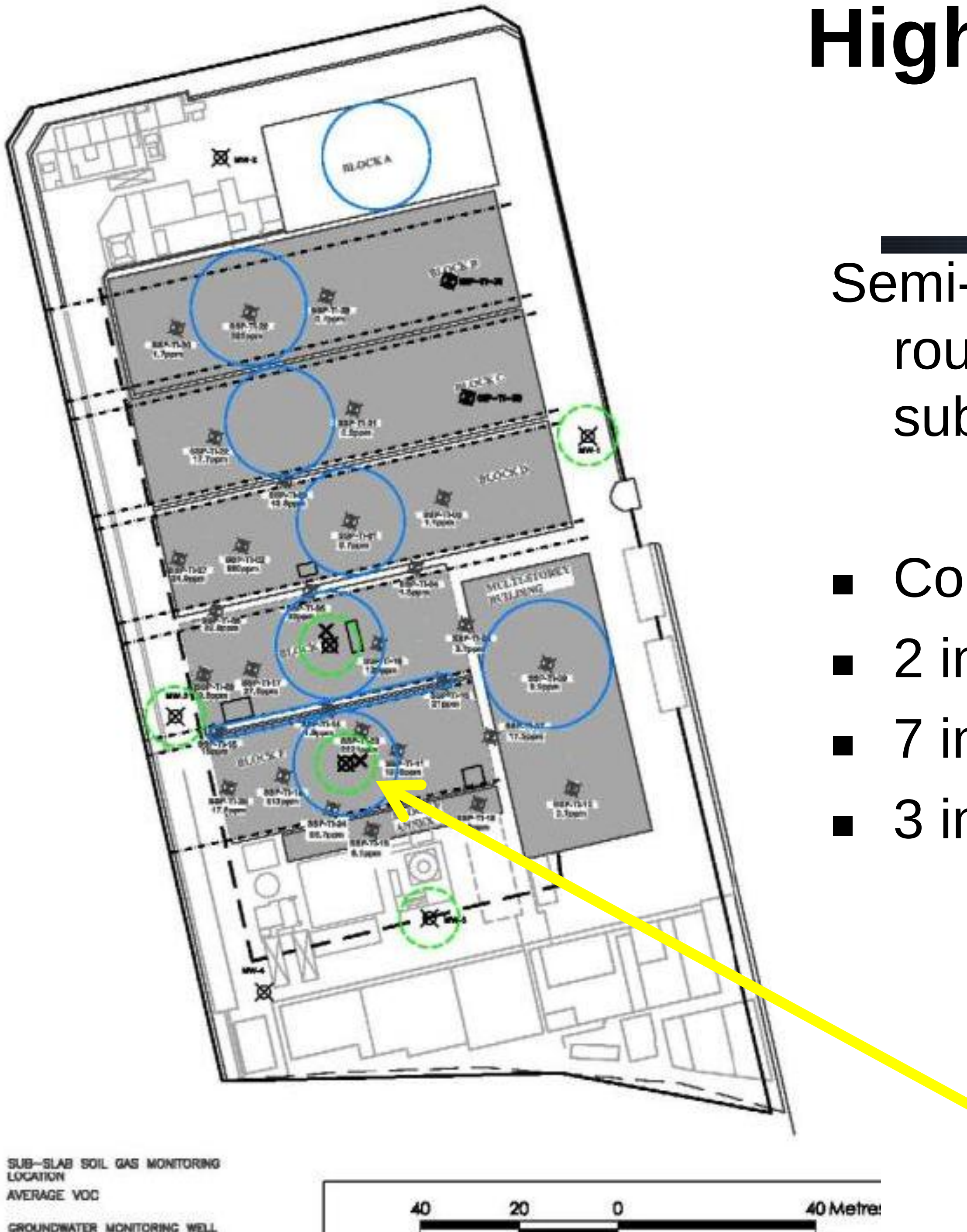
High Purge Volume Sampling

PID Reading vs Volume Purged



Infer concentrations versus distance based on C versus V trend
Minimize risk of missing a localized "hot spot"

High Purge Volume (HPV) Testing



Semi-conductor manufacturer, roughly 100,000 ft^2 (i.e. 100 sub-slab samples?)

- Conducted 12 HPV Tests
- 2 in soil gas probes
- 7 in sub-slab probes
- 3 in monitoring wells

Note "Block F"


17.03.2009

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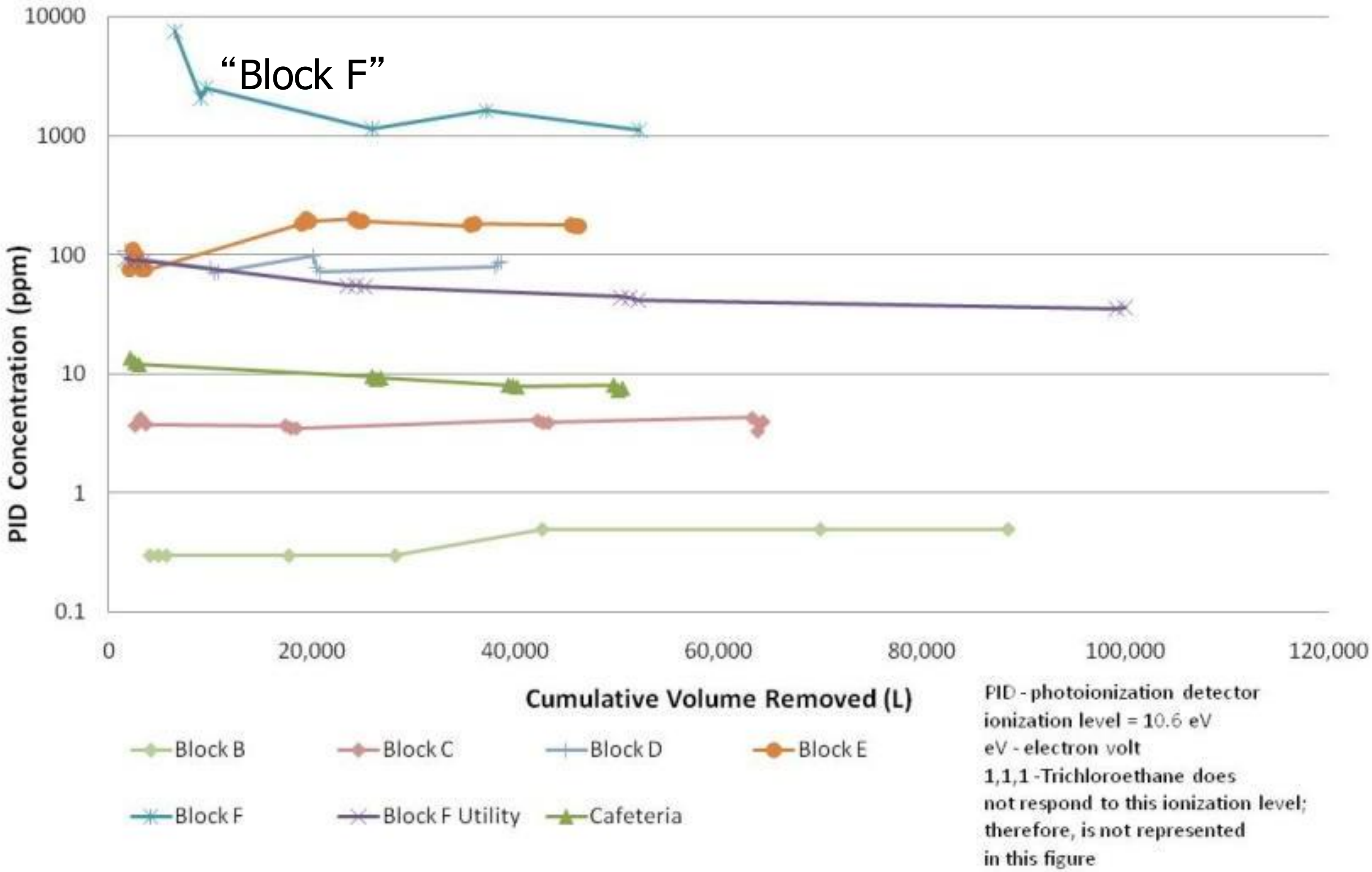
PID versus Volume Purged



What happened to all the spatial variability in sub-slab data?

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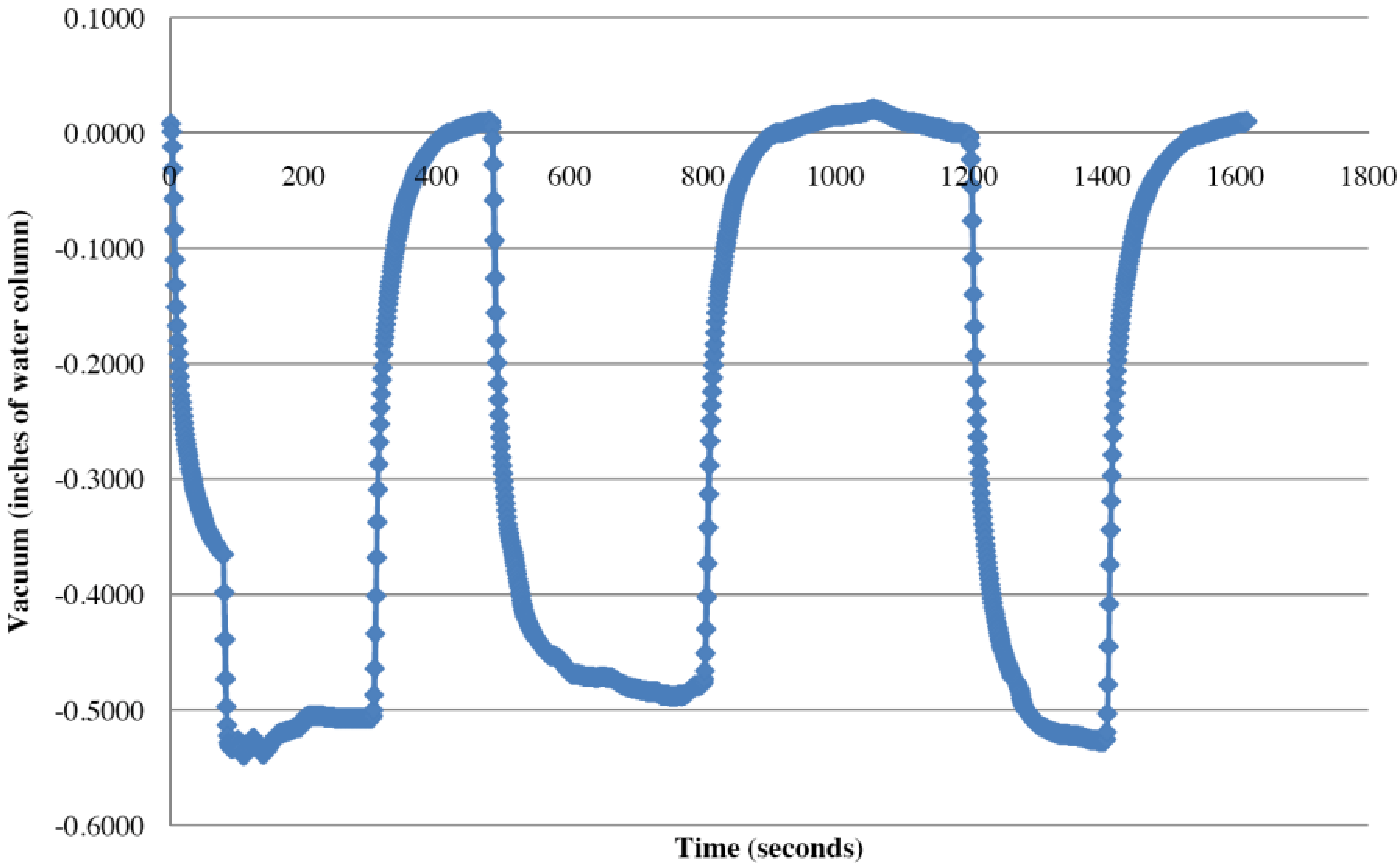
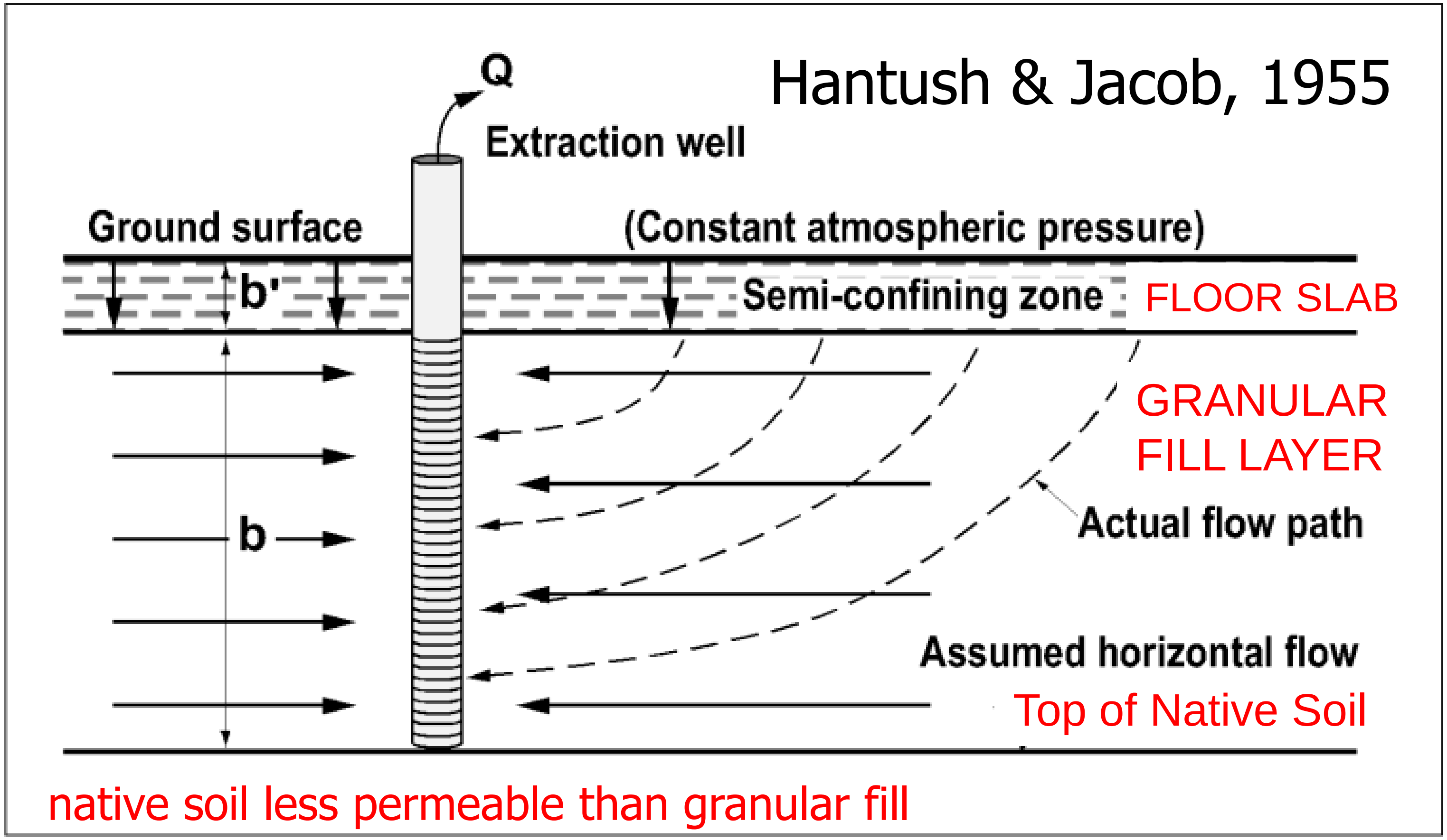
Pressure Transducers / Data Loggers

In just a few minutes, you've got "pump-test" data

Drawdown and Recovery



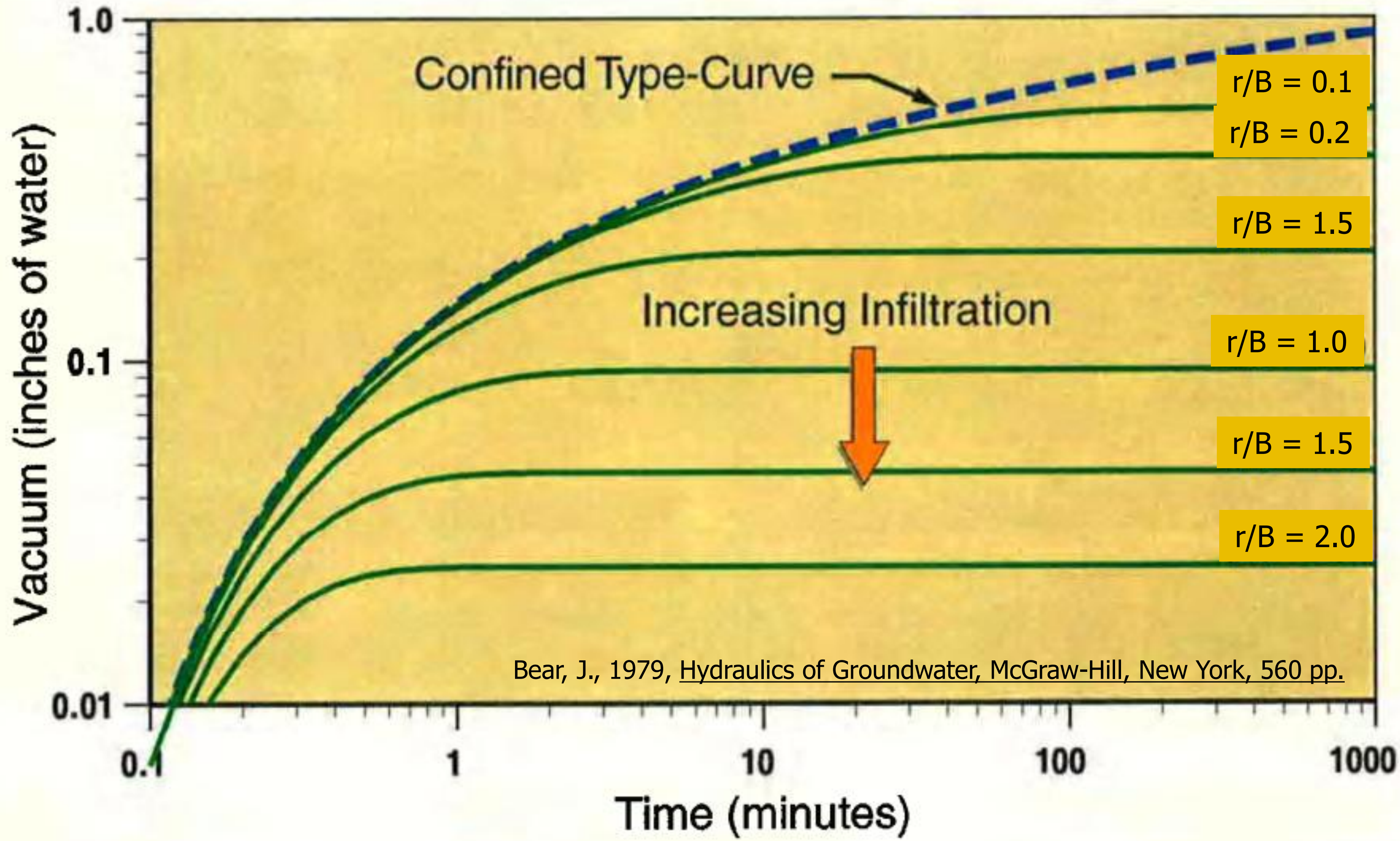
Leaky Aquifer Model for SSD



Thrupp, G.A., Gallinatti, J.D., Johnson, K.A., 1996, "Tools to Improve Models for Design and Assessment of Soil Vapor Extraction Systems", in Subsurface Fluid-flow (Groundwater and Vadose Zone) Modeling, ASTM STP 1288, Joseph D. Ritchey and James O. Rambaugh, Eds., American Society for Testing and Materials, Philadelphia. pp 268-2

Massman, J. W., 1989, "Applying Groundwater Flow Models to Vapor Extraction System Design," J. of Environmental Engineering, Vol. 115, No. 1, pp. 129-149.

Leaky Aquifer Type-Curves



Bear, J., 1979, Hydraulics of Groundwater, McGraw-Hill, New York, 560 pp.

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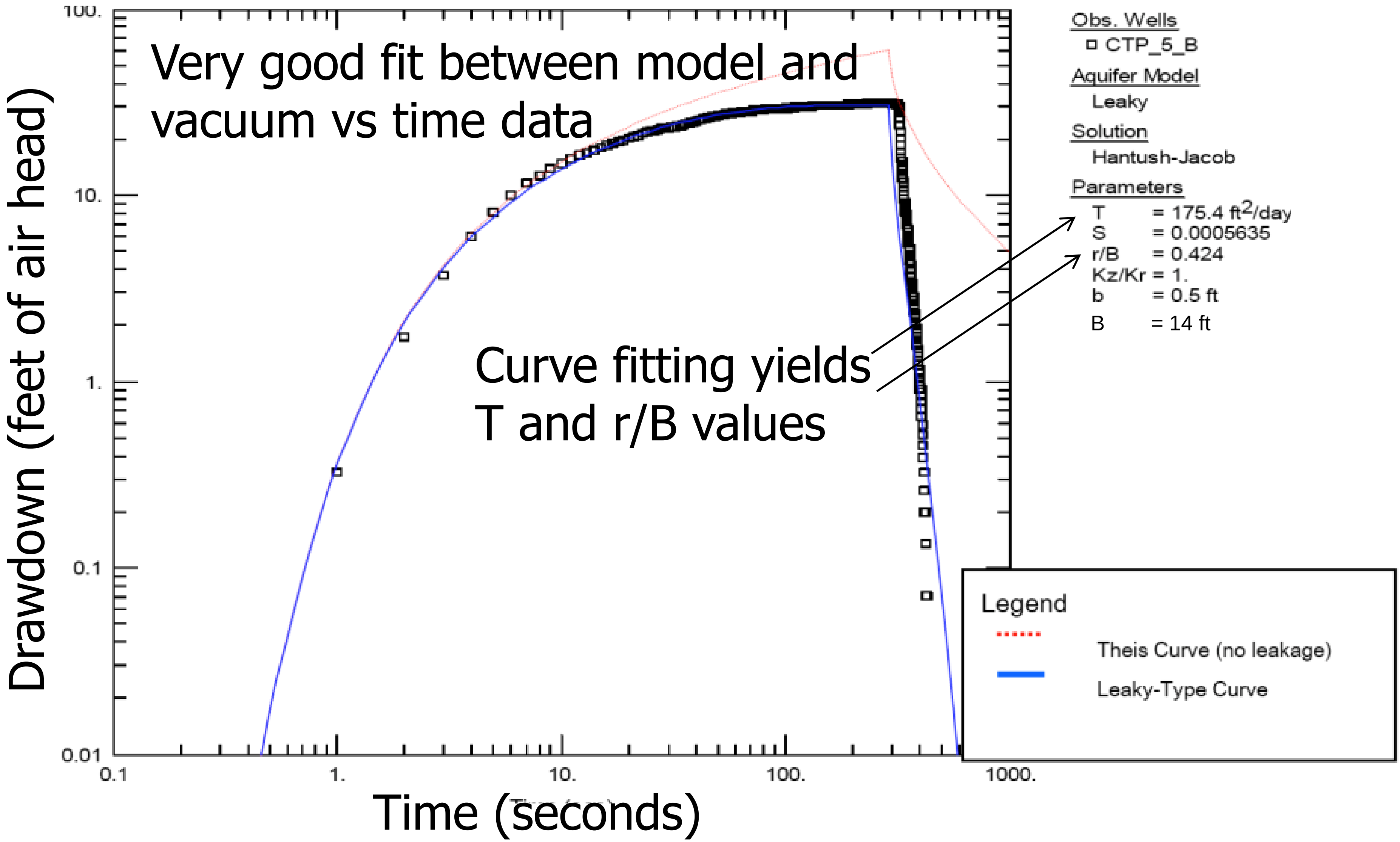
Hantush Jacob Model Fit

Vacuum measurements 6 feet from extraction point



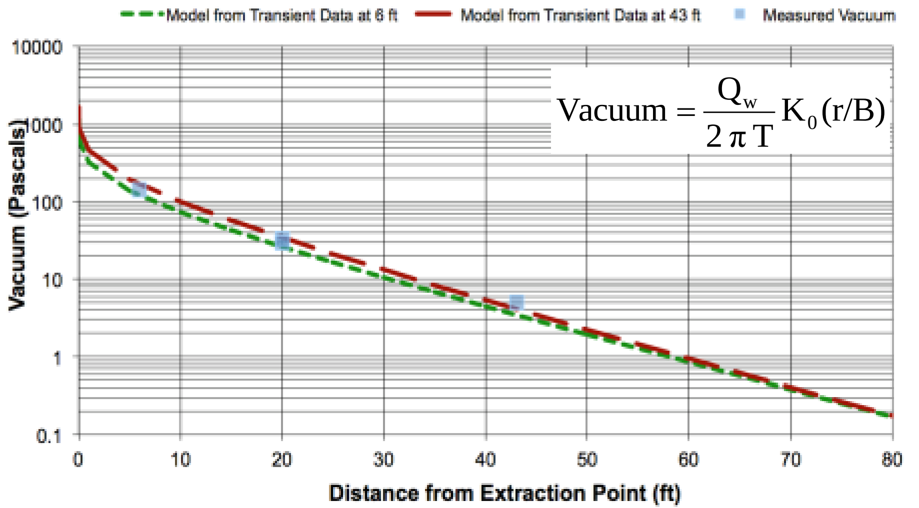
Floor Slab Conductivity

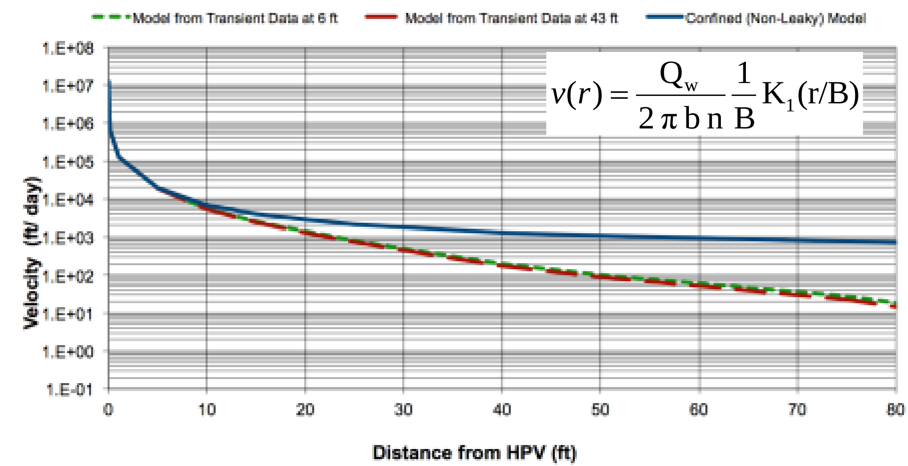
$$K' = \frac{T\,b'}{B^2}$$

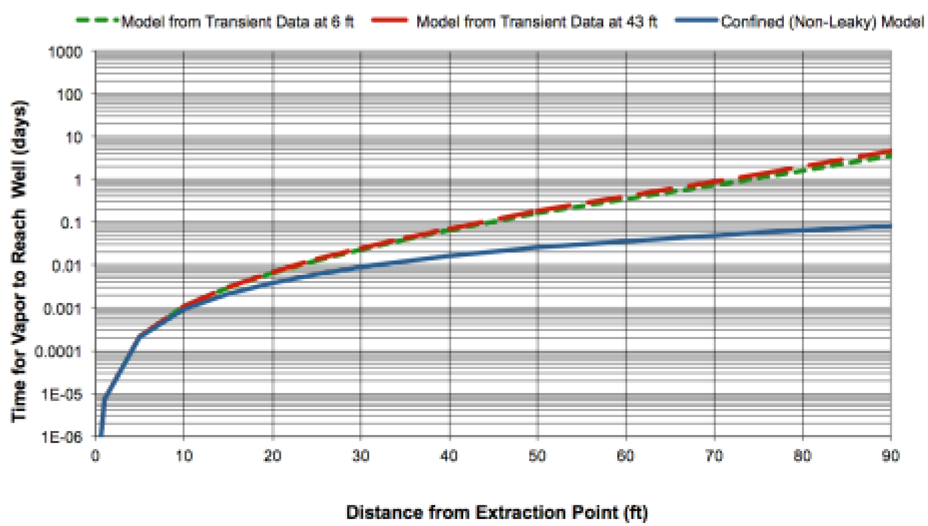
K' = vertical pneumatic conductivity of the floor slab [L/t]
b' = floor slab thickness [L], easily measured
T = transmissivity [L^2/t], a direct output of the model
B = leakance [L], also output from the model

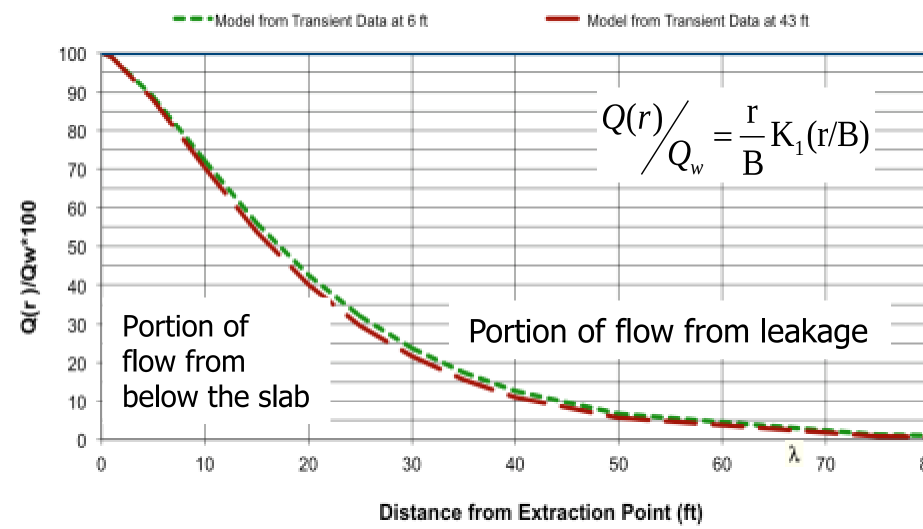
Therefore, if you know b' (slab thickness), you can calculate the vertical pneumatic conductivity of the slab

Calculations









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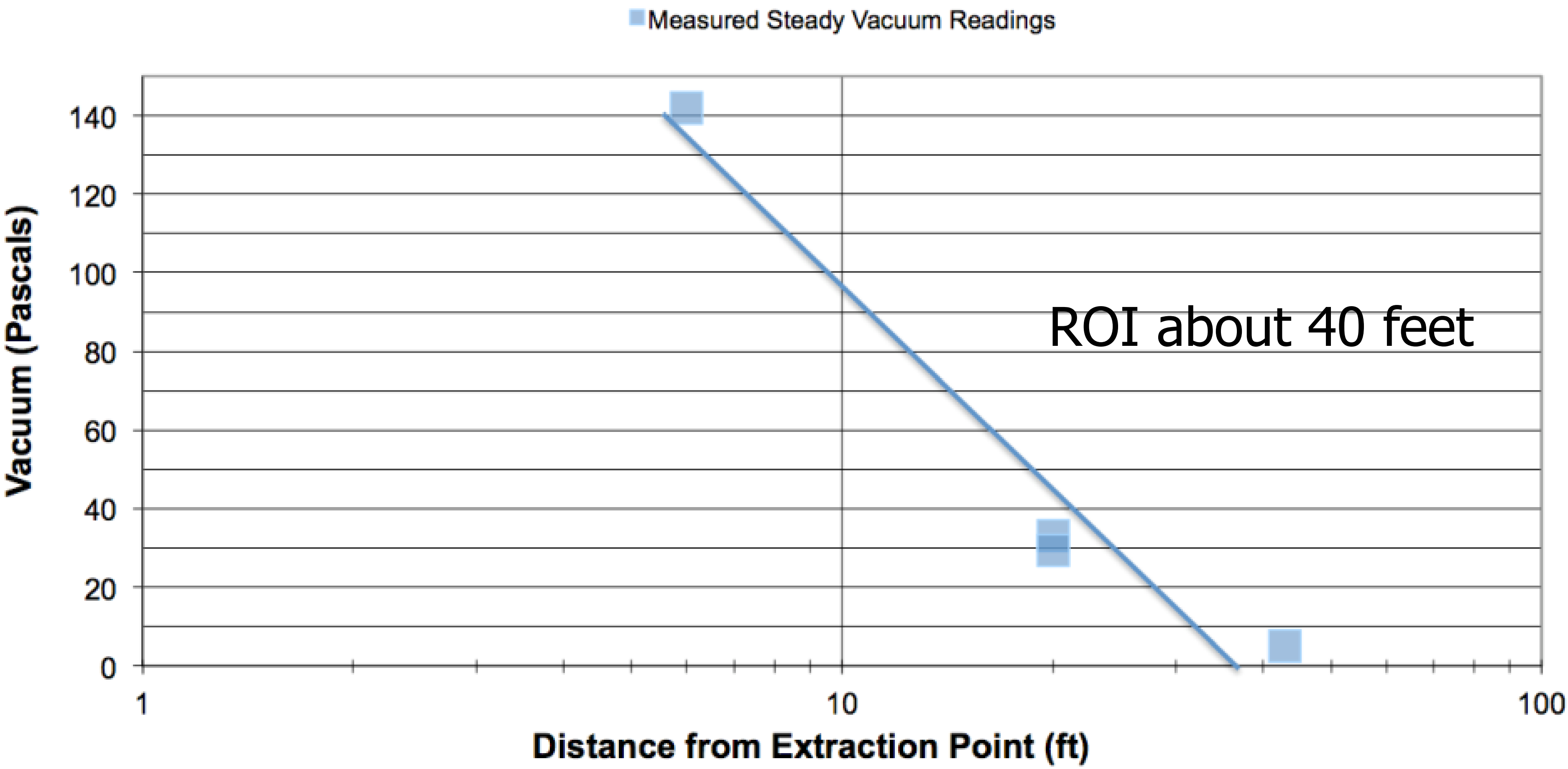
Summary

- Point measurements in space and time are variable
  - We assess risks for a 25 to 30-year exposure scenario
  - Data should be representative and cost effective
- Long-term samples minimize temporal variability
- Large volume samples minimize spatial variability
  - Easy to add pneumatic testing and get design data
- Passive sampling can now give quantitative soil vapor data
- Regulatory acceptance is progressing

Conventional Radius of Influence

Case Study: 100,000 ft^2 commercial building, slab-on-grade



Questions/Comments?

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