Patented Quantitative passive VOC soil-gas Monitoring with the Waterloo Membrane Sampler™

Thought Leaders Webinar Series

June 24th, 2021

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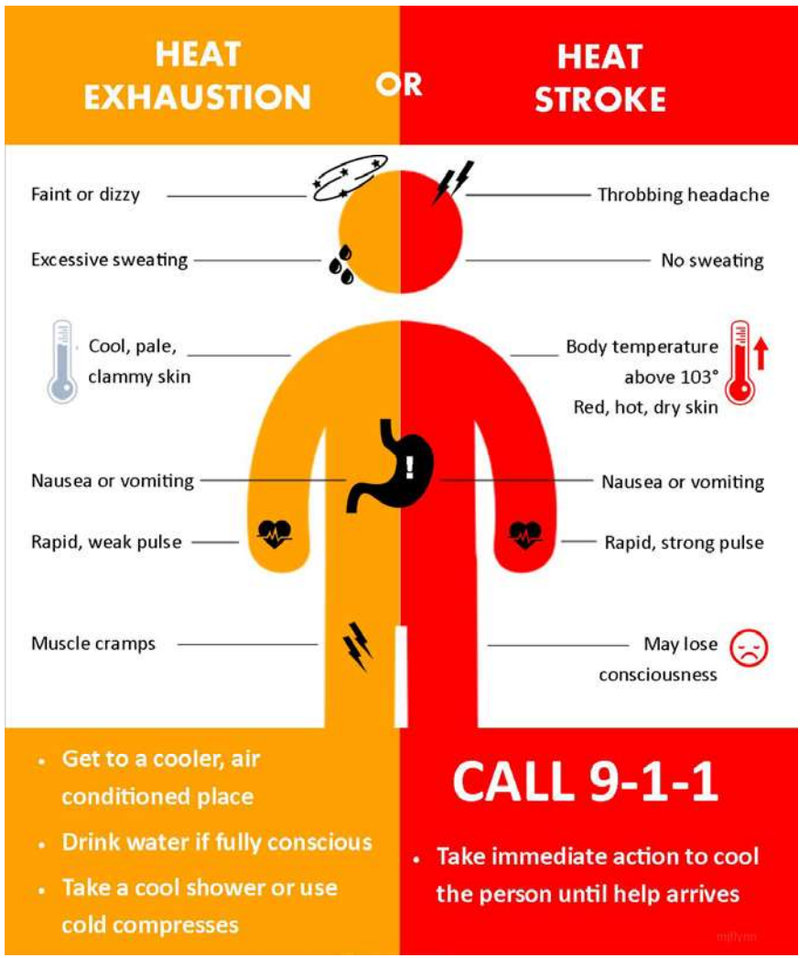
Geosyntec consultants

SiREM

Safety Moment – Working in the Heat

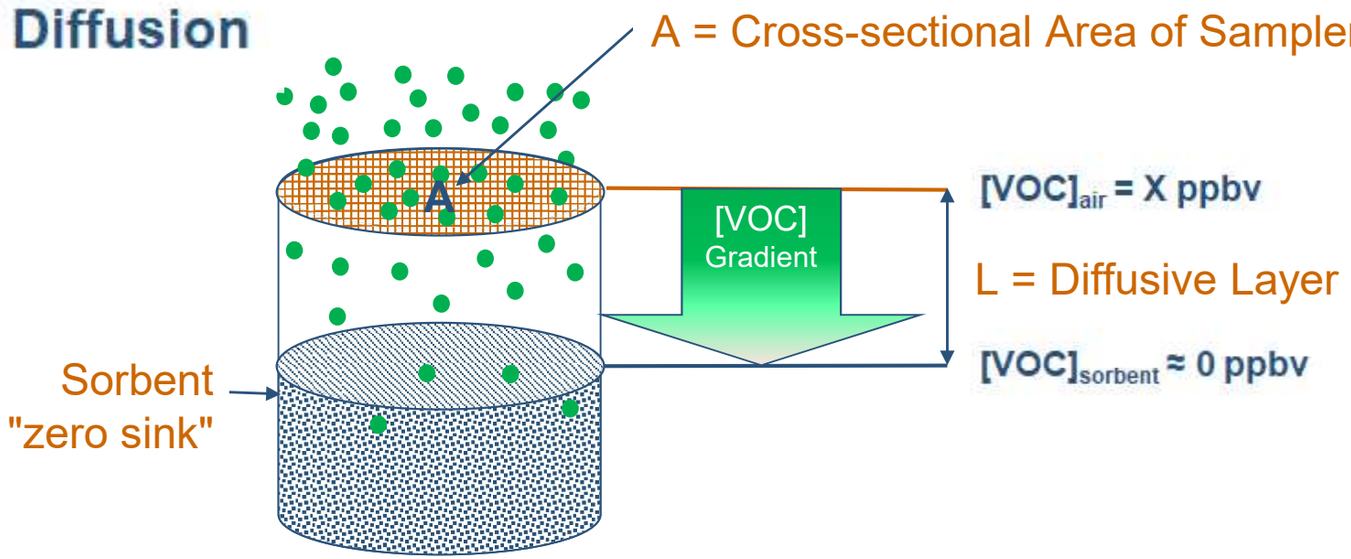


Outline

- Passive Sampling Concepts
- Quantitative Soil Vapor Concentration Determination
- Data Quality and Regulatory Acceptance
- Case Study
- Sewer Gas Monitoring
- Take-Home Messages

Passive Sampling Concepts

Fick's 1st Law of Diffusion

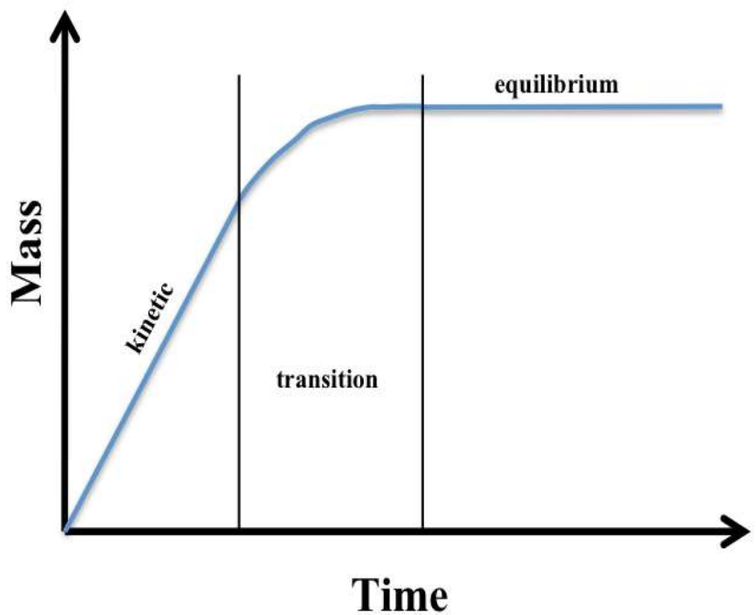


Uptake Rate = Rate at which a chemical vapor passes through opening

$$UR_{ideal} = D^*(A/L)$$

D = Diffusion Coefficient

Passive Sampling Concepts



For Kinetic Samplers

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

Key Point

The mass sorbed (M) and time deployed (t) are both measured accurately. The key is to know the uptake rate (UR).

Calibration

Uptake rates are typically determined by controlled chamber tests

Can also be determined by "field-calibration" using split samples via active sampling

Why Passive Sampling?

EPA TO-15 and TO-17

- Assembly and leak checking protocols required
- Loss of canister vacuum
- Failure of fittings or flow controllers

- Flow calibration and pump operation knowledge required
- Power required
- Changes in flow rate

Passive Sorbent Methods

- No electricity, mechanical parts, connections
- Quick & simple protocols
- Unobtrusive
- Inexpensive to ship

Shipping and Handling

72 six-liter canisters

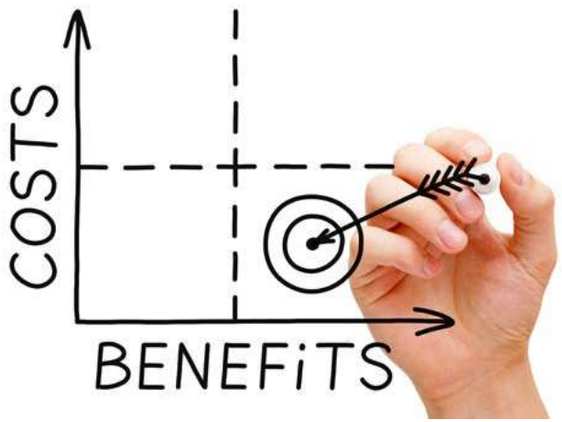
72 passive samplers

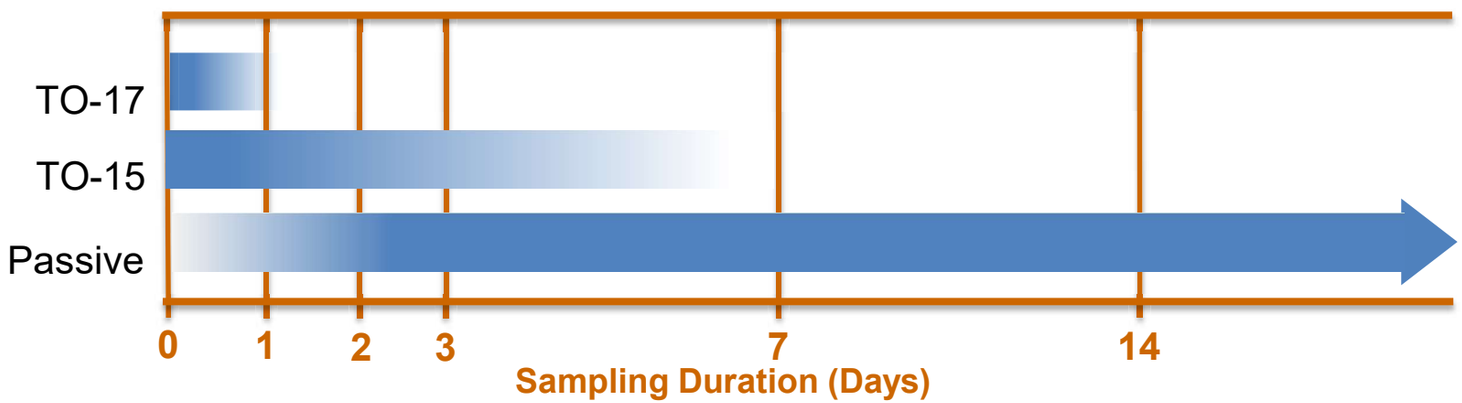
Key Point **Passive samplers are much easier to work with.**

Why Passive Sampling?

Technical Advantages

- Time-integrated sampling
  - Adjustable sensitivity
  - Minimizes sampling variability
- Capable of generating trace level RLs
  - Quantitative results



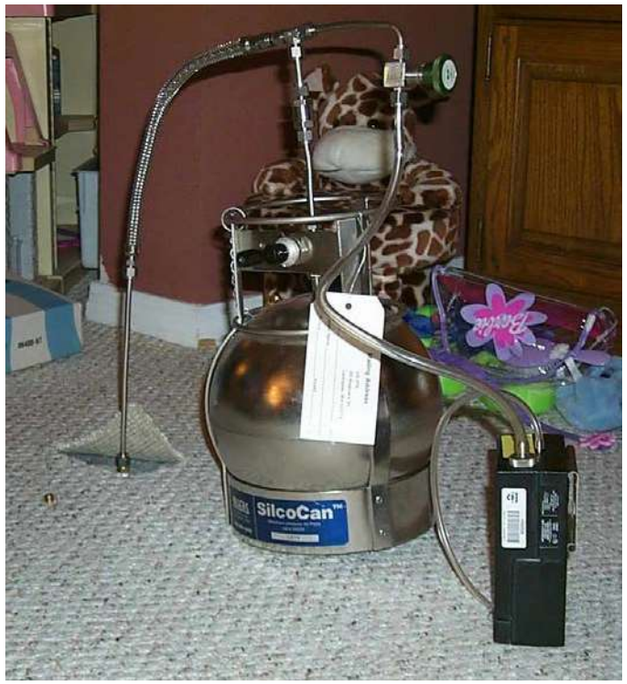


Quantitative Passive Soil Vapor Monitoring with the Waterloo Membrane Sampler™

Geosyntec consultants

SiREM

Conventional Sub-Slab and Soil Gas Sampling



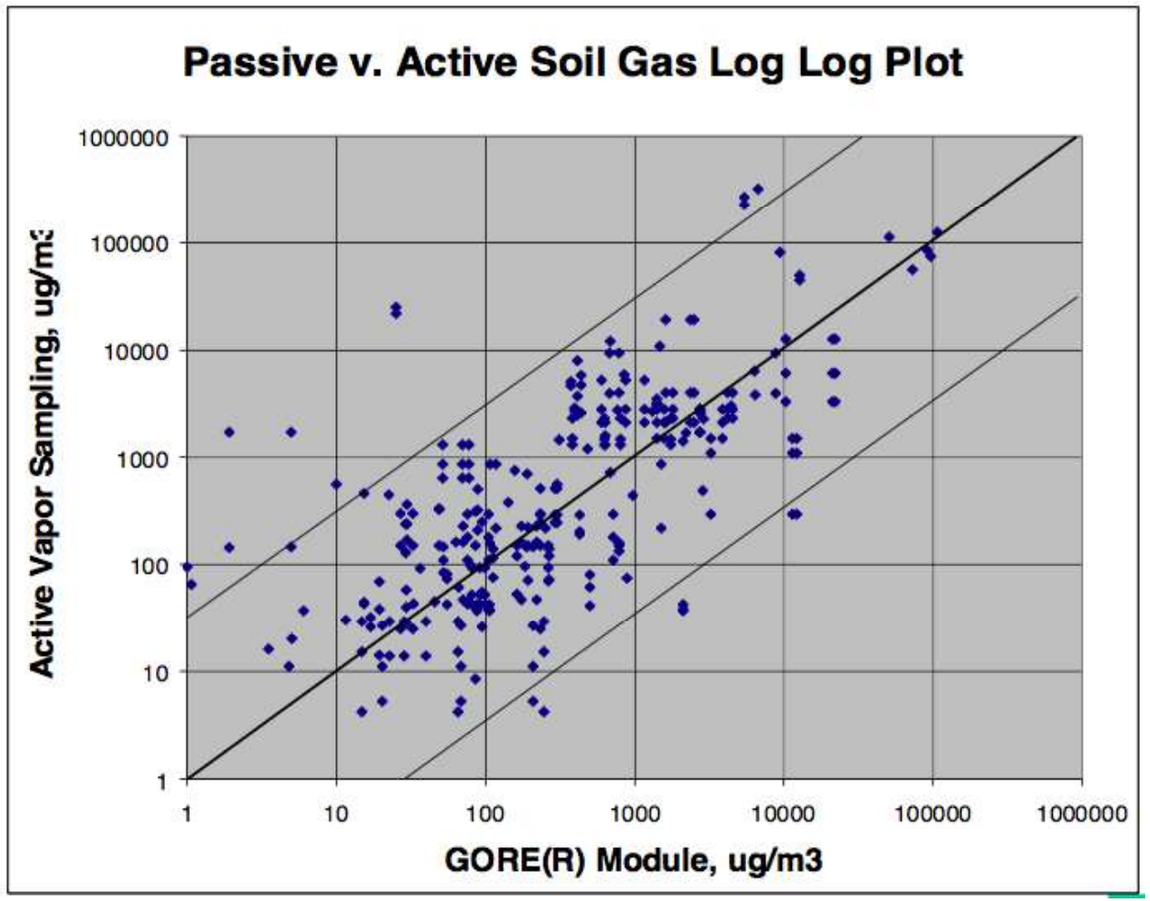
Geoprobe™/Direct Push

QA/QC Considerations

- Inert Materials
- Leak-proof Seals
- Shut-in Test & Helium Tracer Test
- Purging rate, volume
- Vacuum and Permeability
- Field Screening (VOCs, O_2, CO_2, CH_4)
- Sampling (TO-15, TO-17, TO10A, etc.)

Key Point **Labor intensive, multiple fail points, lots of equipment**

Passive Soil Gas Sampling



www.events.awma.org/education/Posters/Final/Whetzel_Poster.pdf

"passive soil gas samples cannot be used to measure the contaminant concentration in soil gas"

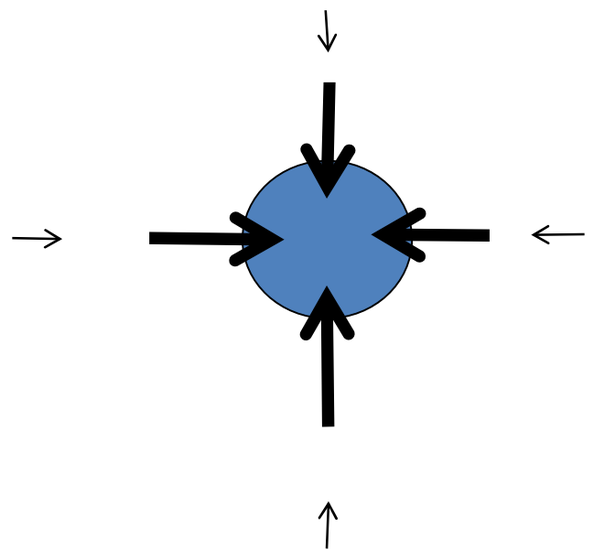
California DTSC, 2011

Key Point

People have been burying sorbents in the ground for 3 decades or more, with limited ability to quantify soil vapor concentrations

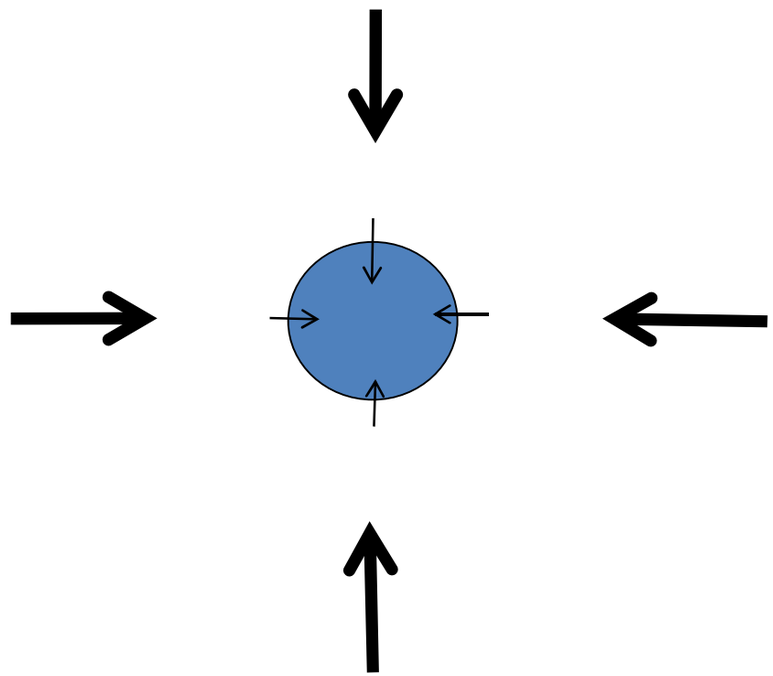
The “Starvation Effect”

Sampler uptake rate is higher than rate of supply of vapors



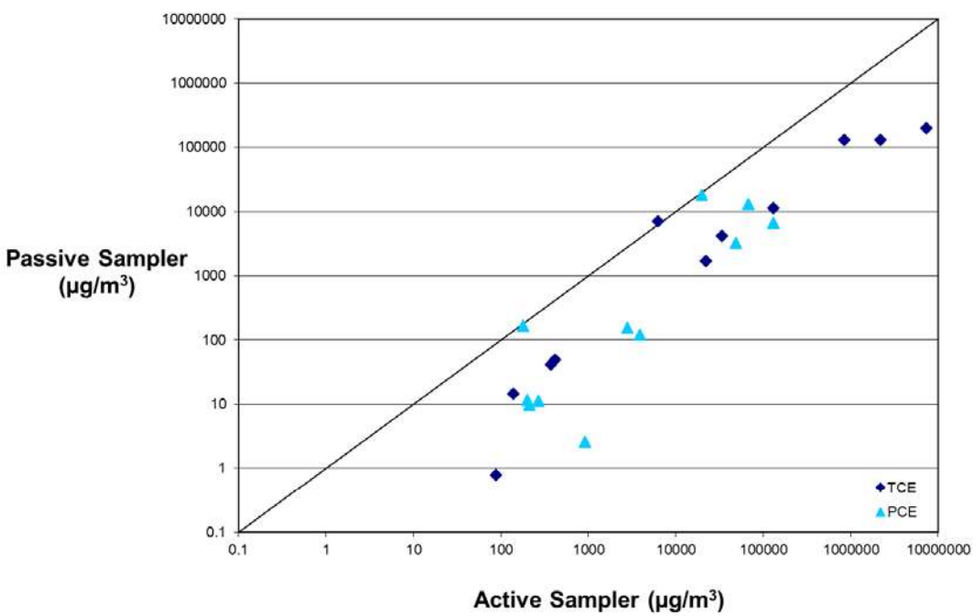
Sampler causes localized depletion in vapor concentrations (“starves” the sampler)

Sampler uptake rate is lower than rate of supply of vapors



No starvation

Developing Quantitative Soil Vapor Sampling



Key Points

In dry soils, vapors diffuse into the borehole quickly (10 min)

In wet soils, it takes longer (~1 day)

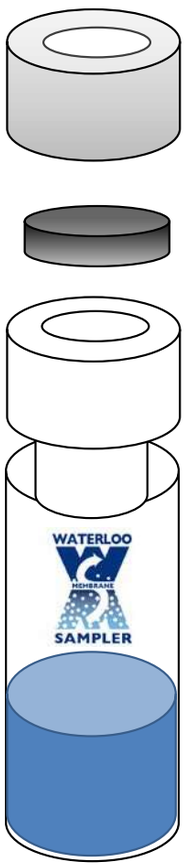
Key Point

Diffusive delivery rate of vapors from soil to the sampler is usually > 1 mL/min, except in very wet soils.

Key Point

In wet soils, a lower uptake rate is needed to avoid the starvation effect, but this can be reasonably predicted.

The Waterloo Membrane Sampler™ (WMS™)



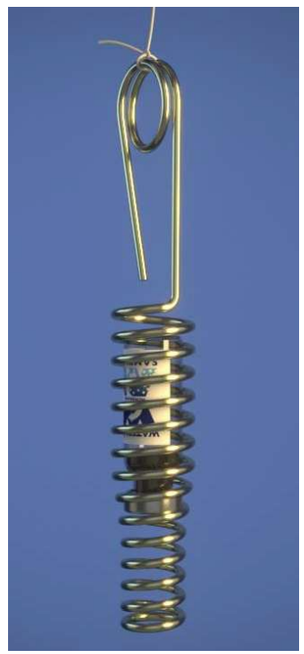
Crimp cap

polydimethylsiloxane (PDMS) membrane

Glass vial

Sorbent

Since 2010

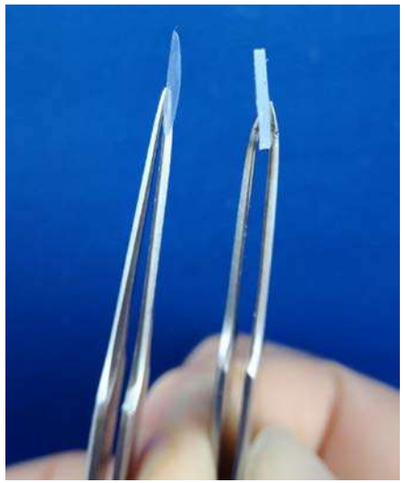


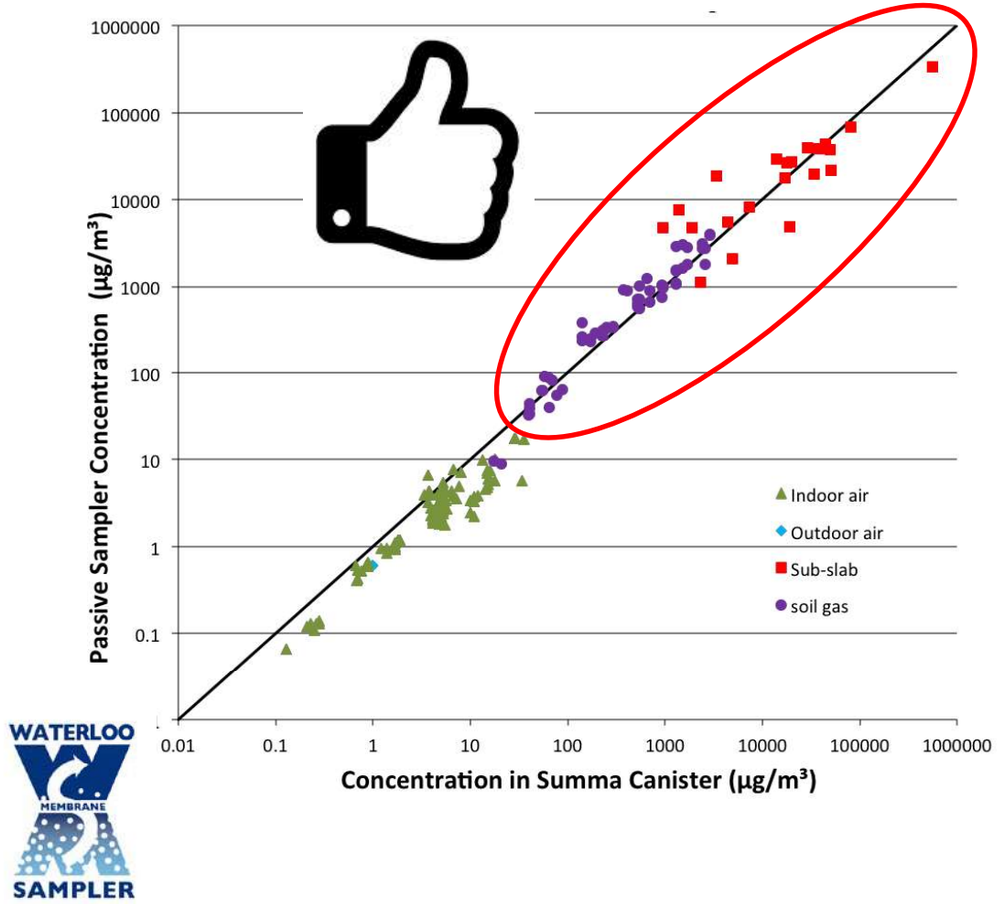
Over 16k units sold!
~10 countries

Open the overpack vial to start sampling
Reseal in overpack vial to stop sampling

https://www.youtube.com/watch?v=J6TAz6aFI-4&feature=youtu.be

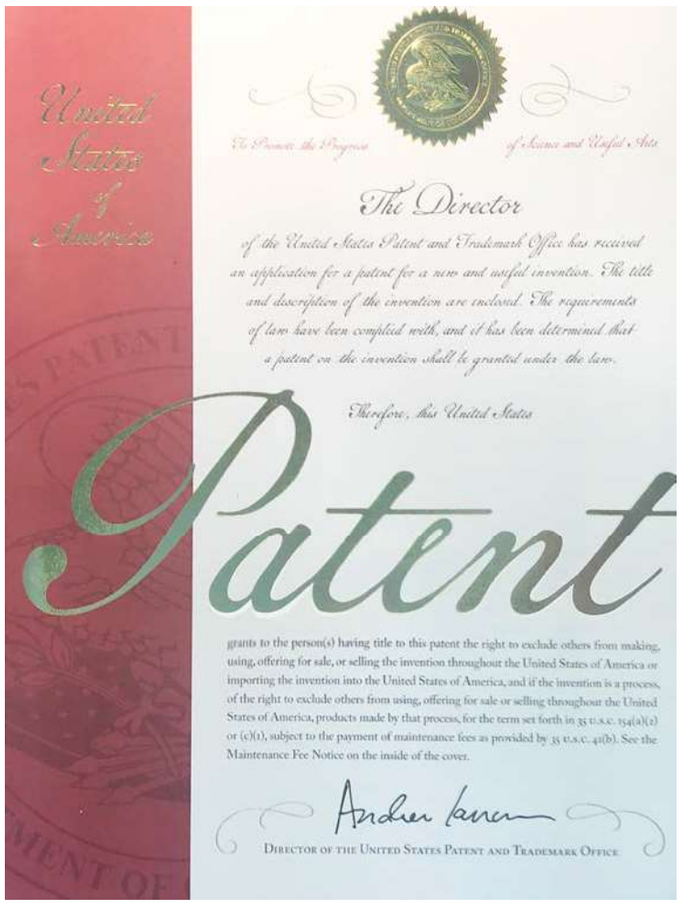
Quantitative Passive Soil Vapor Sampling





WATERLOO MEMBRANE SAMPLER

Patented: Quantitative Soil Vapor Sampling



United States of America

To Promote the Progress of Science and Useful Arts

The Director

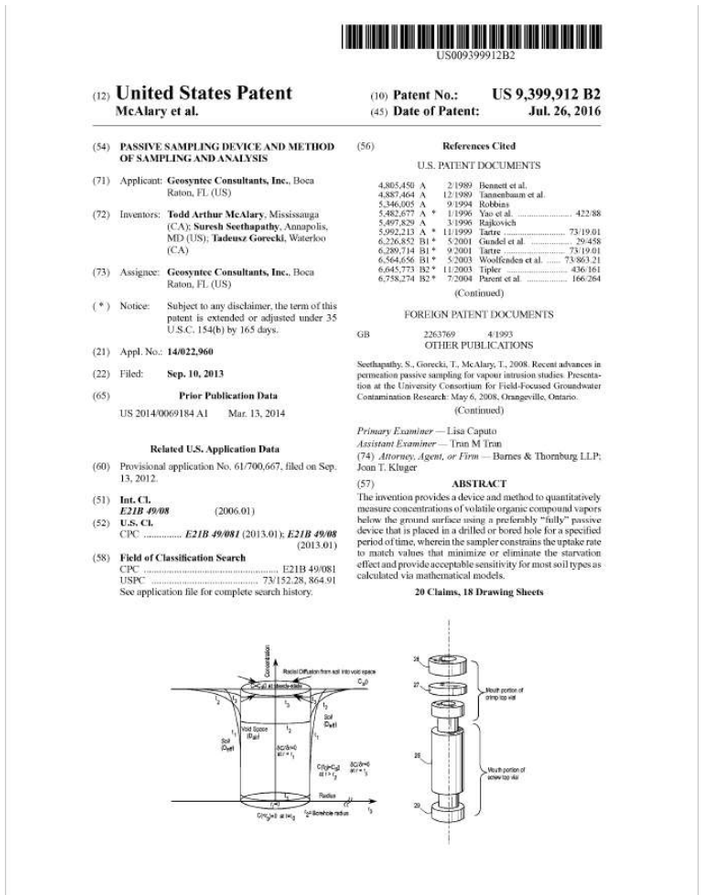
of the United States Patent and Trademark Office has received an application for a patent for a new and useful invention. The title and description of the invention are enclosed. The requirements of law have been complied with, and it has been determined that a patent on the invention shall be granted under the law.

Therefore, this United States

Patent

grants to the person(s) having title to this patent the right to exclude others from making, using, offering for sale, or selling the invention throughout the United States of America or importing the invention into the United States of America, and if the invention is a process, of the right to exclude others from using, offering for sale or selling throughout the United States of America, products made by that process, for the term set forth in 35 U.S.C. 154(a)(2) or (c)(1), subject to the payment of maintenance fees as provided by 35 U.S.C. 41(b). See the Maintenance Fee Notice on the inside of the cover.

Director of the United States Patent and Trademark Office



US009399912B2

(12) **United States Patent**
McAlary et al.

(10) **Patent No.: US 9,399,912 B2**
(45) **Date of Patent: Jul. 26, 2016**

(54) **PASSIVE SAMPLING DEVICE AND METHOD OF SAMPLING AND ANALYSIS**

(71) Applicant: **Geosyntec Consultants, Inc.**, Boca Raton, FL (US)

(72) Inventors: **Todd Arthur McAlary**, Mississauga (CA); **Suresh Seethapathy**, Annapolis, MD (US); **Tadeusz Gorecki**, Waterloo (CA)

(73) Assignee: **Geosyntec Consultants, Inc.**, Boca Raton, FL (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 165 days.

(21) Appl. No.: **14/022,960**

(22) Filed: **Sep. 10, 2013**

(65) **Prior Publication Data**

US 2014/0069184 A1 Mar. 13, 2014

Related U.S. Application Data

(60) Provisional application No. 61/700,667, filed on Sep. 13, 2012.

(51) **Int. Cl.**
E21B 49/08 (2006.01)

(52) **U.S. Cl.**
CPC ***E21B 49/081*** (2013.01); ***E21B 49/08*** (2013.01)

(58) **Field of Classification Search**
CPC E21B 49/081
USPC 73/152.28, 864.91
See application file for complete search history.

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(Continued)

Primary Examiner — Lisa Caputo
Assistant Examiner — Tran M Tran
(74) *Attorney, Agent, or Firm* — Barnes & Thornburg LLP; Joan T. Kluger

(57) **ABSTRACT**

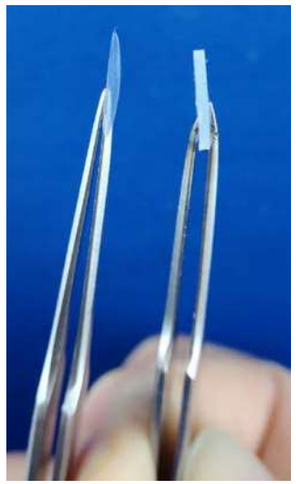
The invention provides a device and method to quantitatively measure concentrations of volatile organic compound vapors below the ground surface using a preferably "fully" passive device that is placed in a drilled or bored hole for a specified period of time, wherein the sampler constrains the uptake rate to match values that minimize or eliminate the starvation effect and provide acceptable sensitivity for most soil types as calculated via mathematical models.

20 Claims, 18 Drawing Sheets

U.S Patents No. 9,399, 912 (July 2016) and 10,060,259 (Aug 2018)

Soil Gas Measurements

- Waterloo Membrane Sampler™ (WMS)™
  - Quantitative soil gas measurements
    - Lower uptake rate to minimize starvation effect
    - Uptake rate: WMS > WMS-LU > WMS-TM



	WMS	WMS-LU	WMS-TM	WMS-TD
Sub-slab, porous fill material	✓			
Standard soil material		✓		
Wet and/or clay material			✓	
SVE Vent Pipe / Sewer Gas	✓			
Indoor/Outdoor Air				✓

Sample Duration

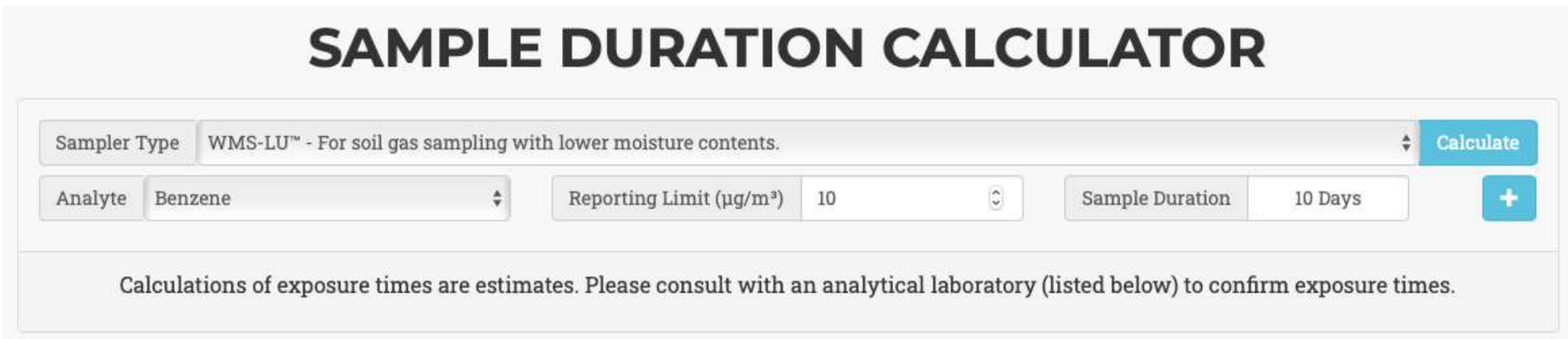
rearrange

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

$$t = \frac{MDL}{(UR \times RBSL)}$$

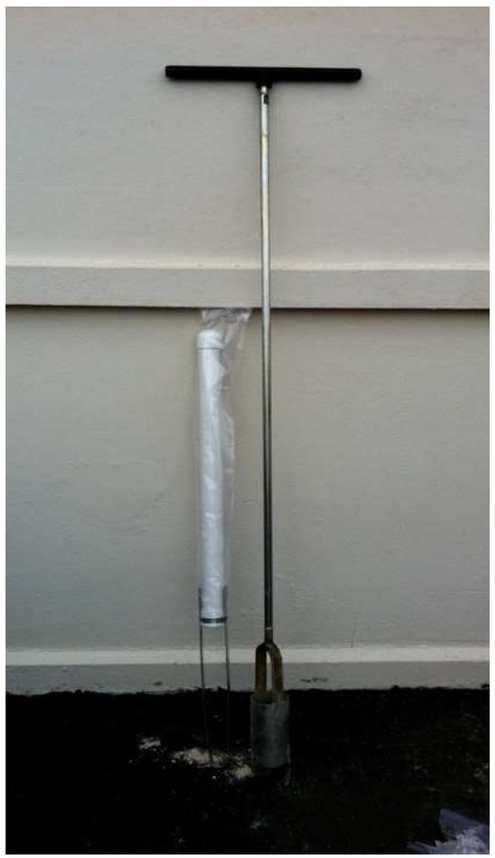
MDL: method detection limit
RBSL: risk-based screening level

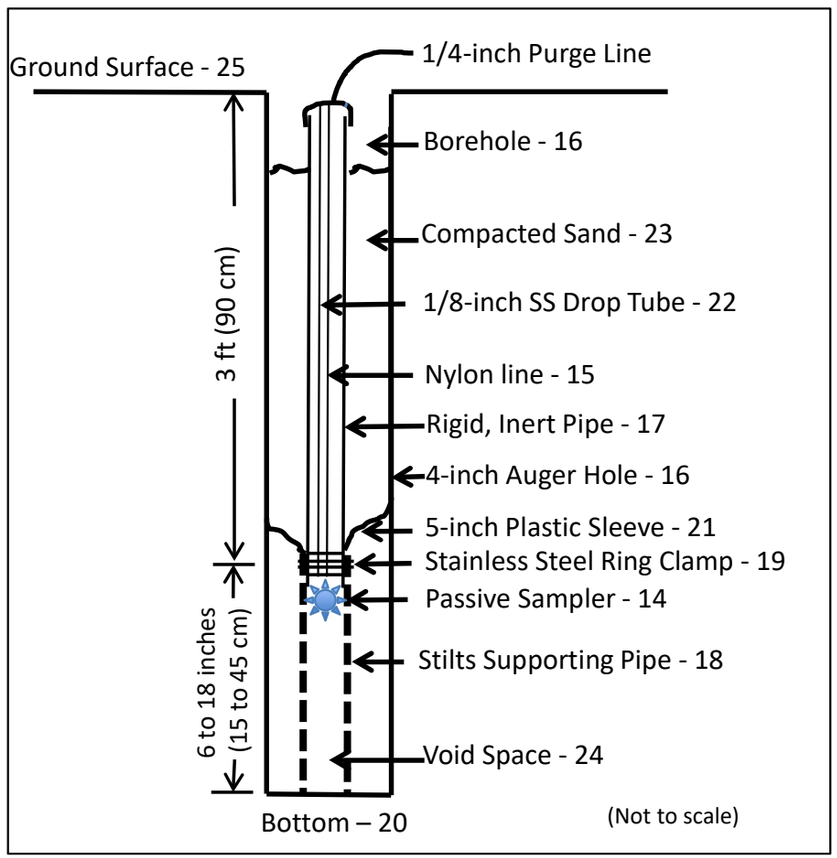
Key Point **Consult with the lab, these are minimum durations**



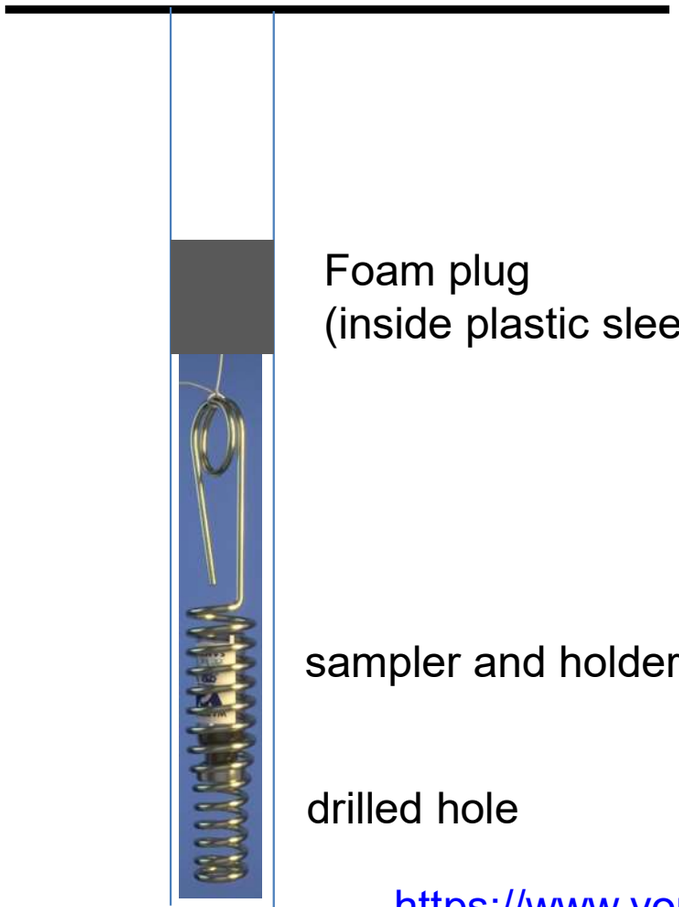
https://www.siremlab.com/waterloo-membrane-sampler-wms/

Sampler Deployment – Soil Gas Well





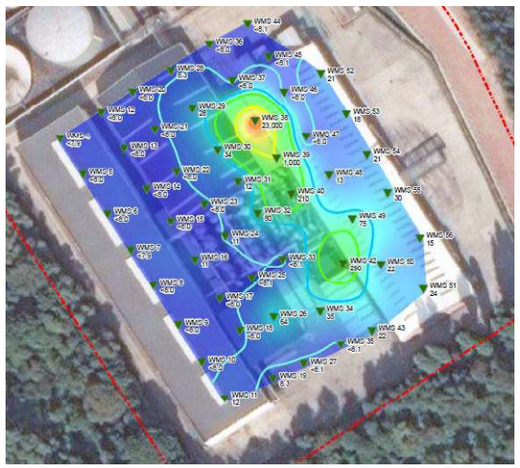
Sampler Deployment – Temporary Probe



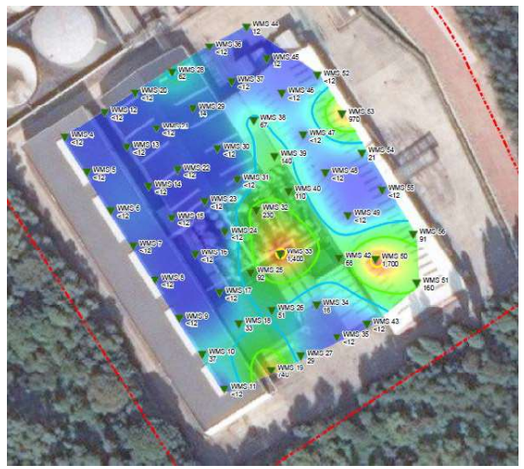
https://www.youtube.com/watch?v=lOrETw9F98w

Soil Gas Sampling – Data Presentation

PCE



TCE



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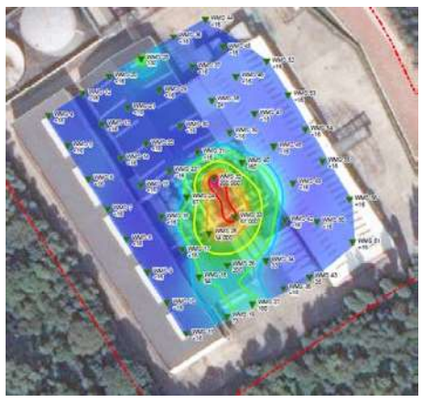
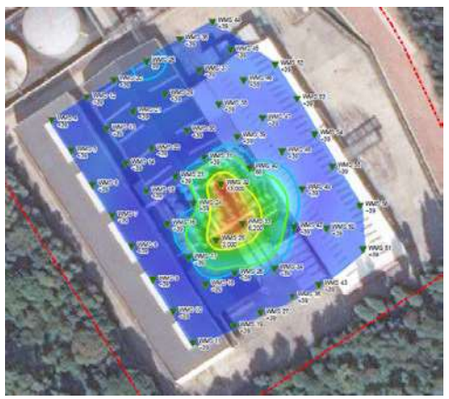


tDCE



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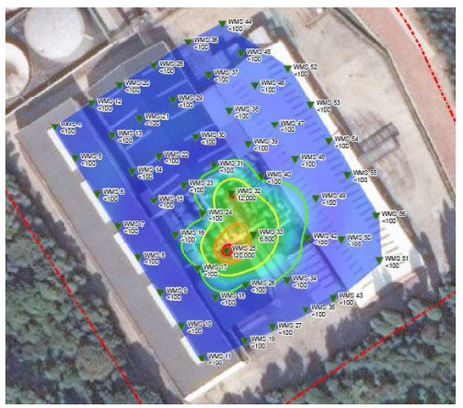


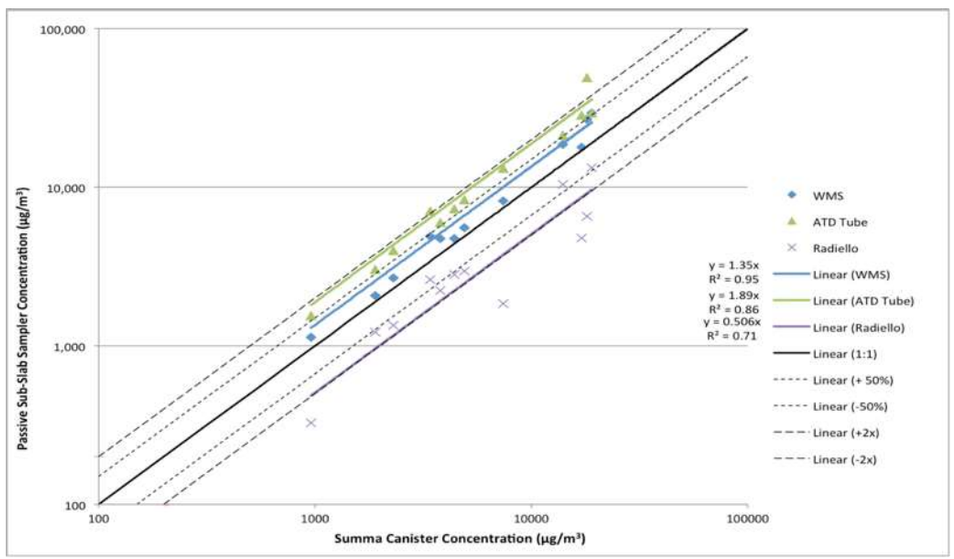
Regulatory Acceptance Case Study WMS™ in Sewer Headspace

Geosyntec consultants

SiREM

Regulatory Acceptance

- Inter-method Split Samples
  - Co-located and coincident
  - Analyzed by conventional method
  - Correlation charts and “field-calibration”



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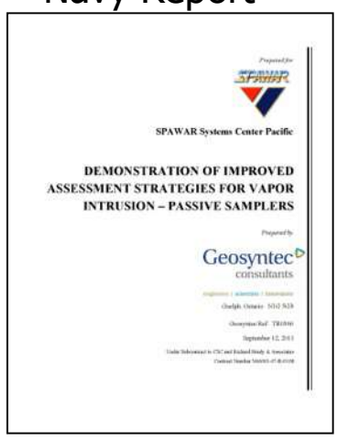
Uptake Rates

ESTCP Report

Navy Report

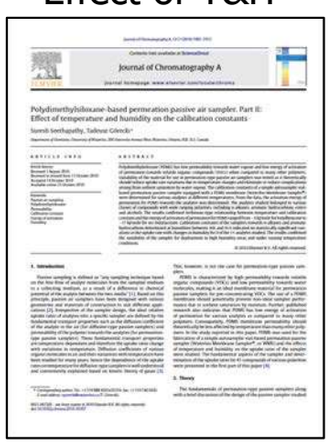


Eng. Issue Paper

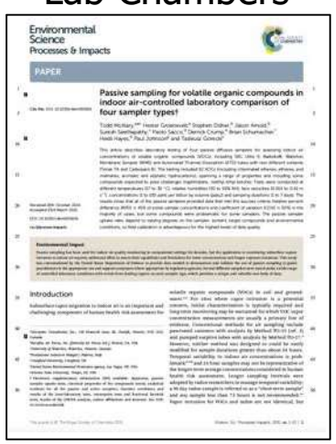
Navy Tech Memo

PhD Thesis

Effect of T&H



Lab Chambers



Soil vapor - #1

Soil vapor - #2

Soil vapor - #3

Soil vapor - #4

Plus ~30 conference presentations

Case Study: Air Force Base, California

Challenges:

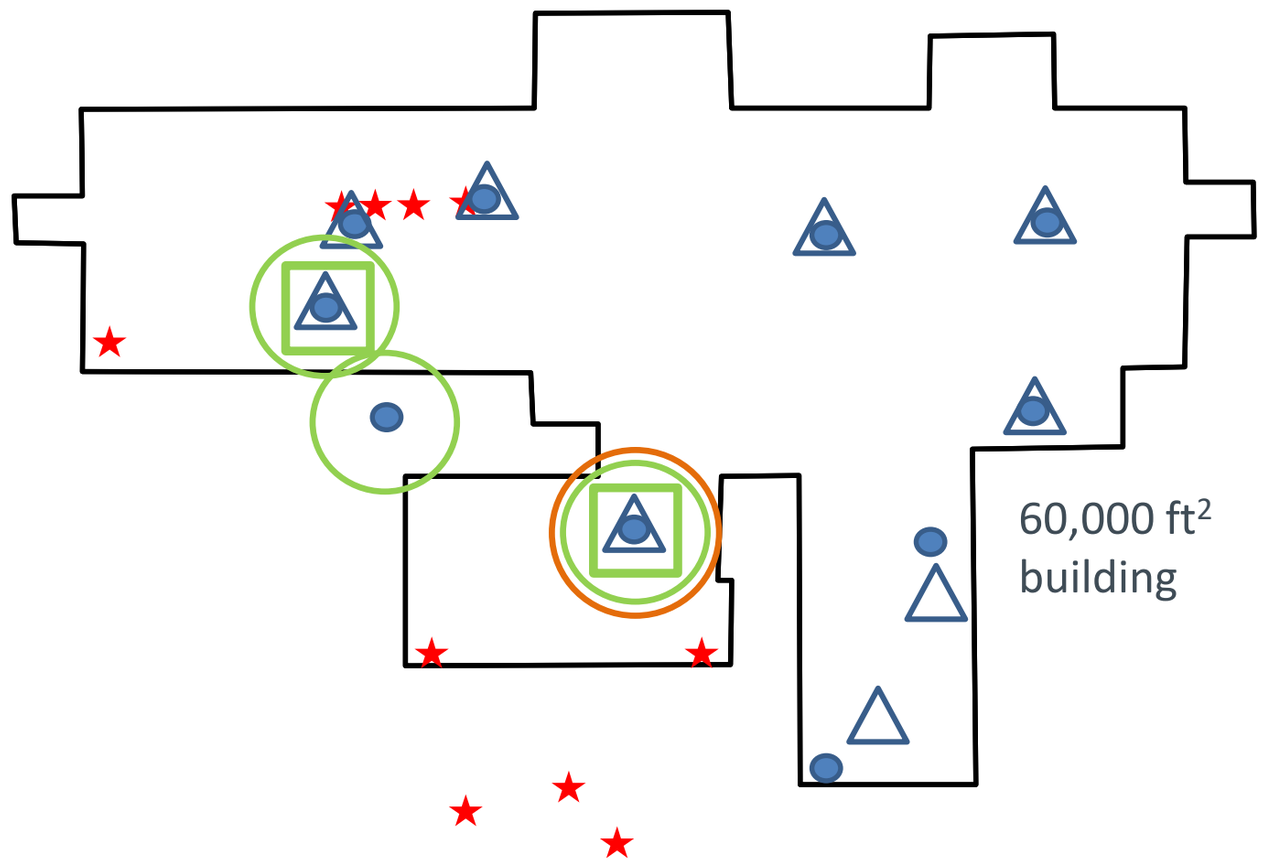
- Multiple regulatory agencies
  Cal EPA, DTSC, Water Board (2 different regions)
- Extremely protective screening levels
- Regulatory policy: reporting limits 1/10th of screening levels
- Mission critical uses/activities inside buildings
- Multiple operable units
- Temporal variability, spatial variability and background sources

Rationale

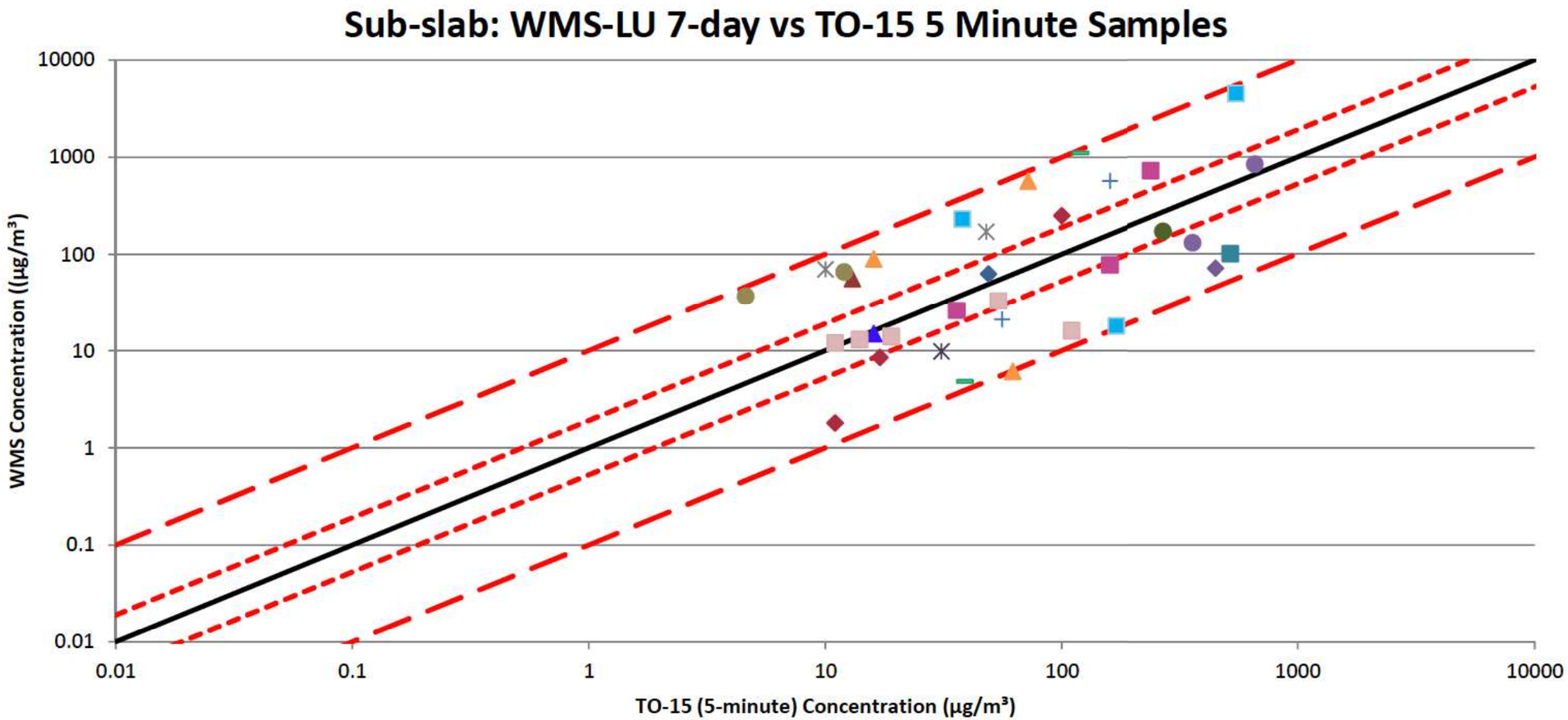
Scope Item	Number	Rationale
Building Survey	11 buildings	Identify interior sources of VOCs to support forensic analysis
Subslab screening via PID, FID, LFG meters	56 locations	Select locations of interest for inter-method duplicate samples
Subslab WMS over 7-day duration	56 locations	Spatial coverage and temporal variability management
Subslab Summa/TO-15 verification samples	13 locations	Field check passive sampler calibration
Indoor and Outdoor air WMS over 7-day duration	76 locations	Spatial coverage and temporal variability management
Indoor Outdoor Summa/TO-15 verification samples	23 locations	Field check passive sampler calibration, provide Level IV Data Validation required for risk assessment
24 hr vs 7-day Summa/TO-15 comparison	11 locations	Assess temporal variability
Cross-slab differential pressure monitoring	11 locations	Assess whether building was inhaling or exhaling
Forensic analysis of background sources	11 buildings	Attribute VOCs to subsurface vs interior sources
Building-specific attenuation factor calculations	11 buildings	Calculate indoor air concentrations for compounds detects in subslab but not in indoor air for assessment of cumulative risks

Example Location Map

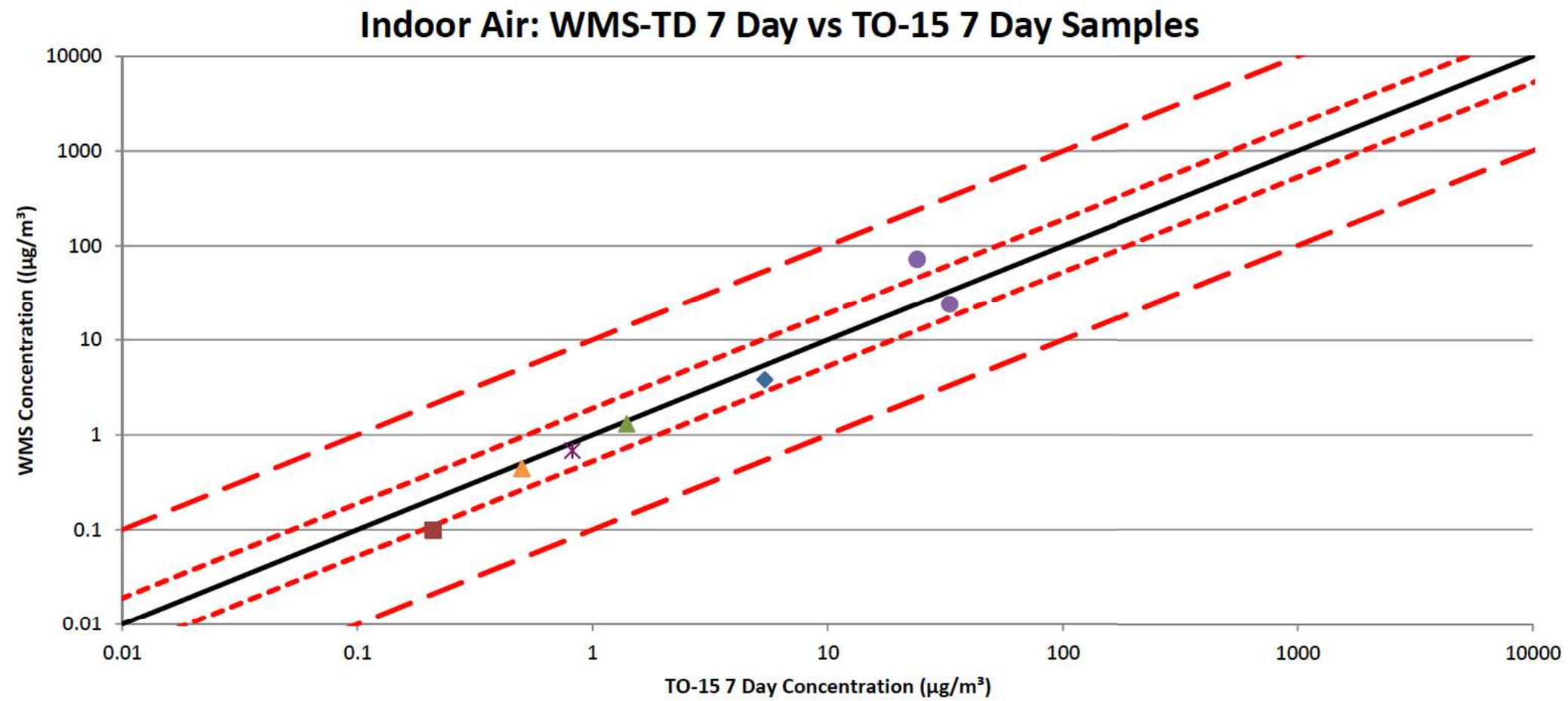
- AOC or SWMU
- WMS 7-day air sample
- WMS 7-day subslab sample
- Summa grab/TO-15 subslab sample
- 24 hr Summa/TO-15 air sample
- 7-day Summa/TO-15 air sample



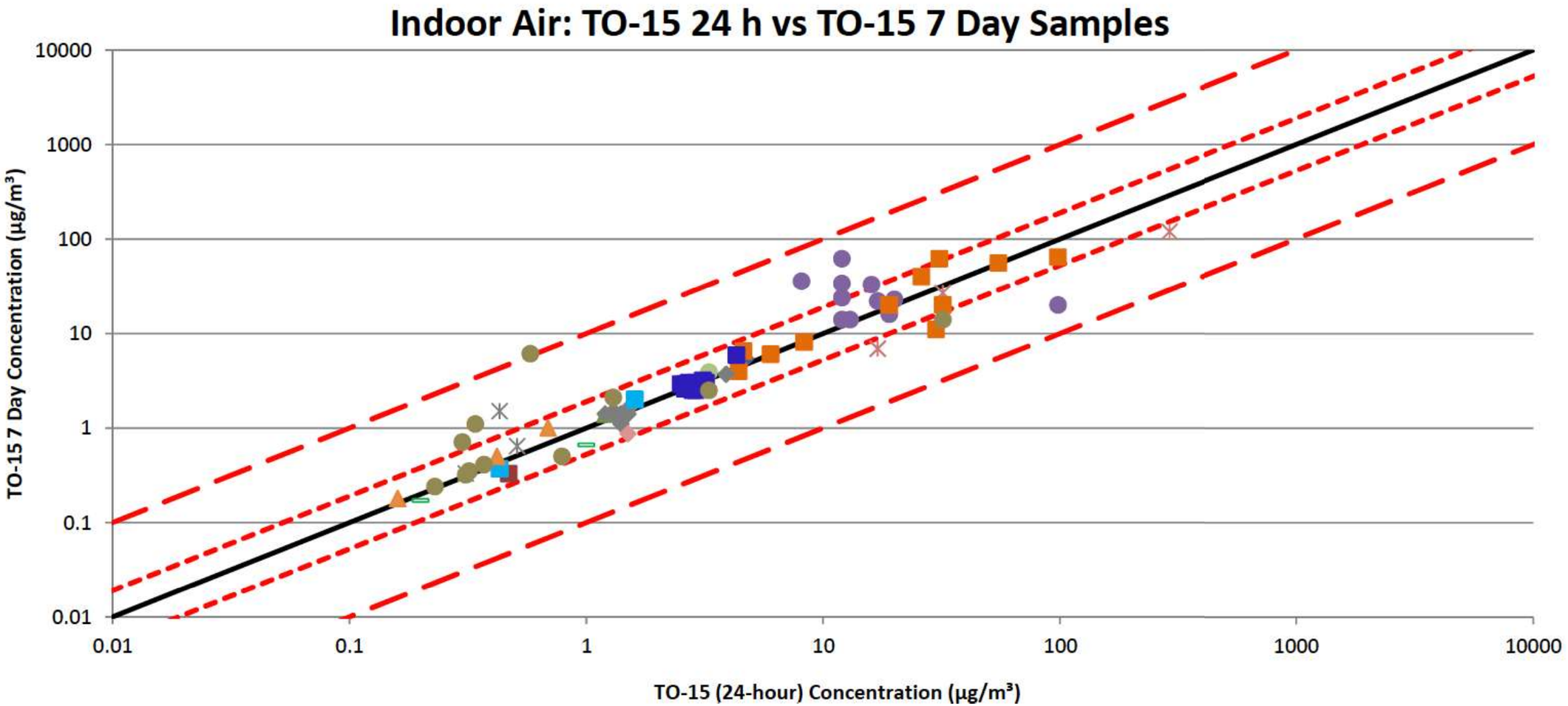
Subslab WMS vs Summa/TO-15



Indoor Air WMS vs Summa/TO-15



24 hr vs 7 day Summa/TO-15



Data Quality Objective: RL < SL

Compound ($\mu g/m^3$)	METHOD	USEPA SSSL	CA SSSL	QAPP PQL	Min RL	Max RL	Frequency of RL > USEPA SSSL	Frequency of RL > CA SSSL	Frequency of RL > PQL
1,1,2,2-Tetrachloroethane	TO-15	7	4.2	7	7.8	65	14/14	14/14	14/14
1,1,2-Trichloroethane	TO-15	26	15	26	6.2	52	1/14(1)	1/14(1)	1/14
1,2,4-Trichlorobenzene	TO-15	290	180	--	34	280	0/14	1/14(1)	--
1,2-Dibromoethane (EDB)	TO-15	0.67	0.4	3.8	8.8	73	14/14	14/14	14/14
1,2-Dichloroethane	TO-15	16	9.4	16	4.6	38	1/14(1)	2/14(1)	1/14
1,2-Dichloropropane	TO-15	40	24	--	5.3	44	1/14(1)	1/14(1)	--
1,3-Butadiene	TO-15	14	1.4	--	2.5	21	1/14(1)	14/14	--
1,4-Dichlorobenzene	TO-15	37	22	--	6.8	57	1/14(1)	1/14(1)	--
3-Chloropropene	TO-15	70	40	--	14	120	1/14(1)	1/14(1)	--
alpha-Chlorotoluene	TO-15	8	5	--	5.9	49	1/14(1)	14/14	--
Benzene	WMS S.E.	53	8.4	53	26	30	0/62	56/62	0/62
	TO-15	53	8.4	53	3.6	30	0/14	1/14(1)	0/14
Bromodichloromethane	TO-15	11	6.6	--	7.6	63	1/14(1)	14/14	--
Carbon Tetrachloride	WMS S.E.	67	5.8	--	8.7	10	0/62	61/62	--
	TO-15	67	5.8	--	7.2	16	0/14	13/14	--
Chloroform	TO-15	18	11	18	5.6	12	0/14	1/14(1)	1/14
cis-1,3-Dichloropropene	TO-15	100	15	--	5.2	43	0/14	1/14(1)	--
Dibromochloromethane	TO-15	15	9	--	9.7	80	2/14(1)	14/14	--
Hexachlorobutadiene	TO-15	19	11	21	49	400	14/14	14/14	14/14
Methylene Chloride	TO-15	40000	240	41000	40	330	0/14	1/14(1)	0/14
Naphthalene	WMS S.E.	12	7.2	12	4.4	5.1	0/62	0/62	0/62
	TO-15	12	7.2	12	10	79	12/14	13/14	12/14
Tetrachloroethene	TO-15	1600	42	1567	7.7	64	0/14	1/14(1)	0/14
trans-1,3-Dichloropropene	TO-15	100	15	--	5.2	43	1/14(1)	1/14(1)	--
Vinyl Chloride	WMS S.E.	93	3.2	93	120	150	62/62	62/62	62/62
	TO-15	93	3.2	93	2.9	24	0/14	3/14	0/14

TO-15 RL > CASSSL for:

- 1122PCA
- EDB
- 13Butadiene
- α-chlorotoluene
- BDCM
- CTET (13/14)
- DBCM
- HCBD
- Naphthalene (13/14)

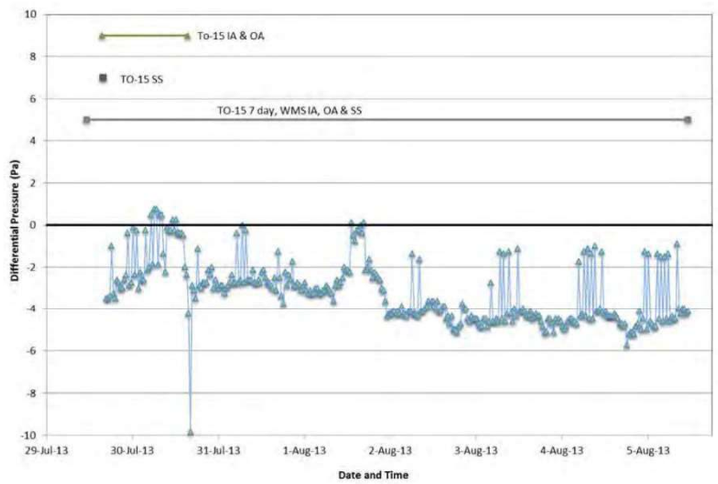
WMS RL > CASSSL for:

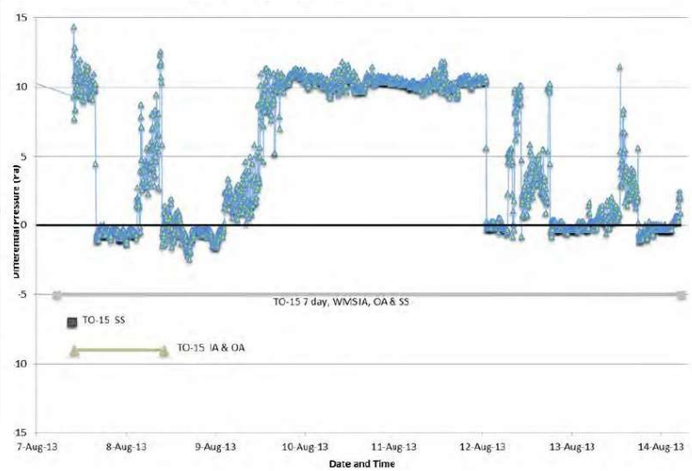
- Benzene
- CTET
- Vinyl Chloride

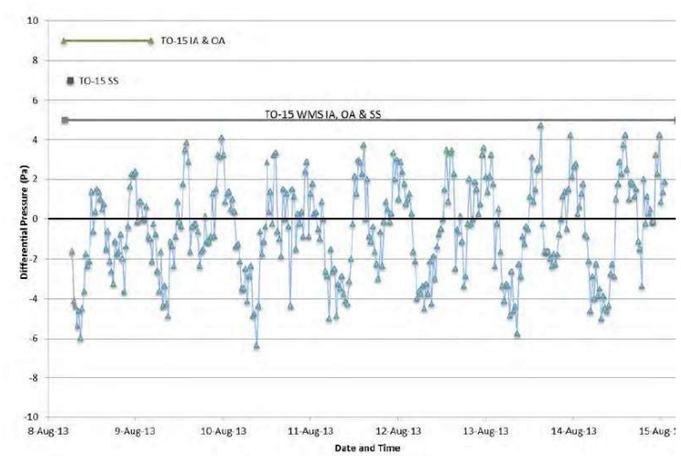
(red also for USEPA SSSL

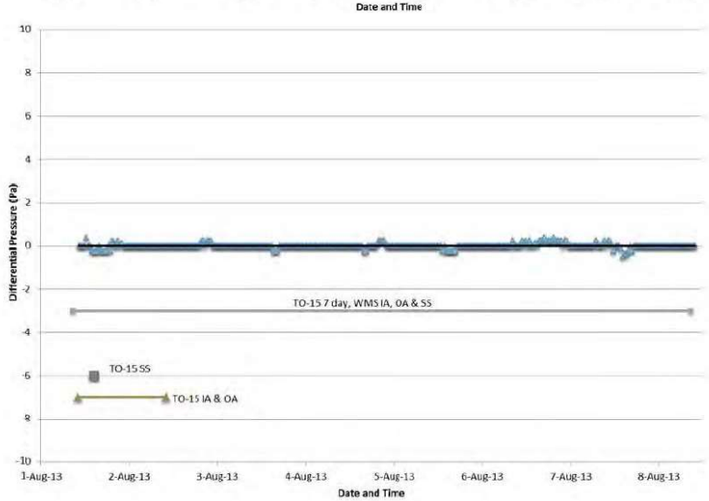
Cross-Slab Differential Pressure

- Negative building pressure
  - Worst case scenario?
- Positive building pressure
  - Temporal variability?
- Cyclic building pressure
  - Representative of long-term?
- Consistently neutral
  - Leaky buildings
  - Leaky floors









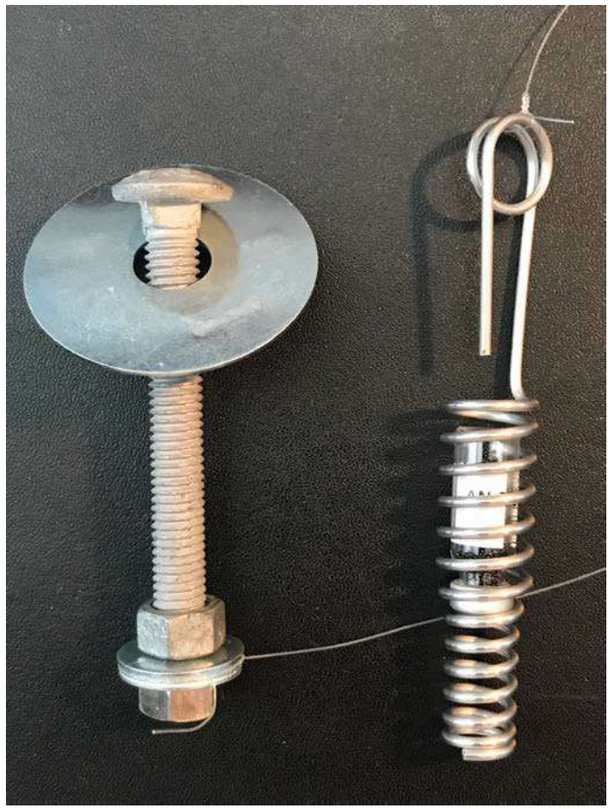
Case Study Summary

- 7-day samples minimize risk of bias from temporal variability
  - Co-located samples demonstrates correlation between passive/active
- There is no silver bullet
  - TO-15 was needed for:
    - vinyl chloride,
    - Level IV data validation
  - WMS was needed for:
    - naphthalene,
    - rapid deployment and retrieval to minimize disruption and cost
    - larger number of locations to minimize risk of false negative outcome from spatial variability
- Accepted by all three agencies in California
  - Took a bit of discussion, but getting easier over time

WMS in Sewer Headspace

Verify depth

Assemble hanger



Deploy

Come back in 7 to 30 days

Take Home Messages

- Passive Sampling simplifies VOC monitoring for soil-gas and vapor intrusion
  - Proven performance
  - Simple protocols, no moving parts, easy shipping
- Manage variability:
  - Integrate over time
  - Minimal operator error
- Benchmarking supports regulatory acceptance
  - 1 of 10 samples collected with a duplicate by Summa/TO-15
- Study design takes some thought
  - Target compounds and screening levels affect sample duration
  - Consider thick membrane for long sample durations
  - Cost savings make it worthwhile

Questions

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SiREM