

# Using Diffusive Samplers in Vapor Intrusion and Indoor Air Quality Studies

C.R. (Gus) Manning & Maria D.R. Peralta

# My Perspective ... a Diffusive Sampler guy

Diffusive Sampling (Passive Sampling)

a cost-effective and convenient sampling  
method looking for new applications

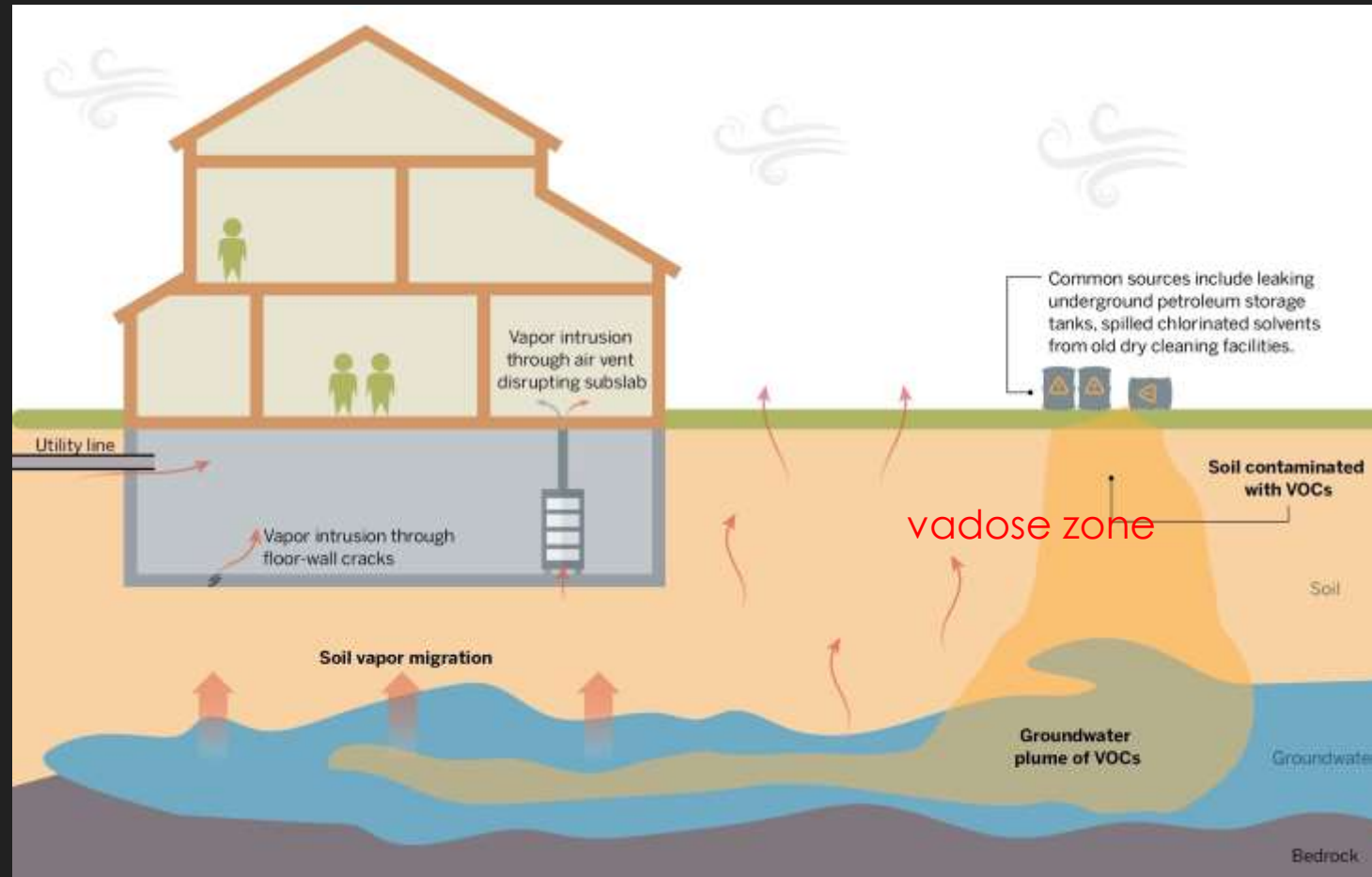
# Vapor Intrusion

involves...

Underground Migration of Volatile Contaminants  
to Indoor Air spaces

# Vapor Intrusion (schematic)

Stored or spilled contaminants can leak into groundwater, then migrate to buildings via diffusion across the vadose (shallow soil) zone



Vapor Intrusion into occupied buildings threatens the health of human occupants.

# Goal of Vapor Intrusion Studies

Anticipate Underground Migration to Indoor Air spaces

- Identify Underground Contaminant Plumes

Typically petroleum hydrocarbons and chlorinated solvents

- Make Contaminant Measurements

Subsurface or Sub-Slab Soil Sampling

Indoor Air Concentrations in affected buildings

# What Sampling Methods Are ...

- Most Popular?
- Practical and Useful?

in Soil Gas Monitoring to Assess Vapor Intrusion

# Soil Vapor Sampling

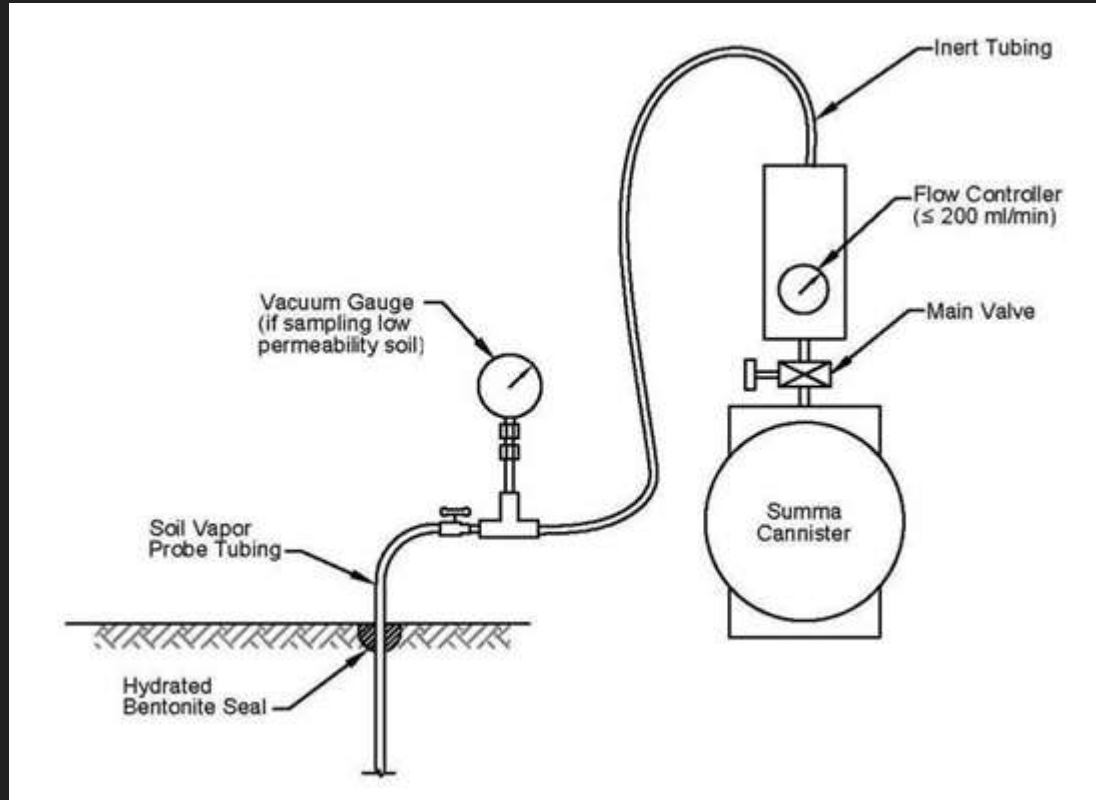
... **Most Popular Method**

Critical Issues when using  
Active Sampling ...

Sampling Rate  
must be < Soil Permeation Rate

Ensure there are no leaks!!

## EPA TO-15 Using Evacuated Cannister

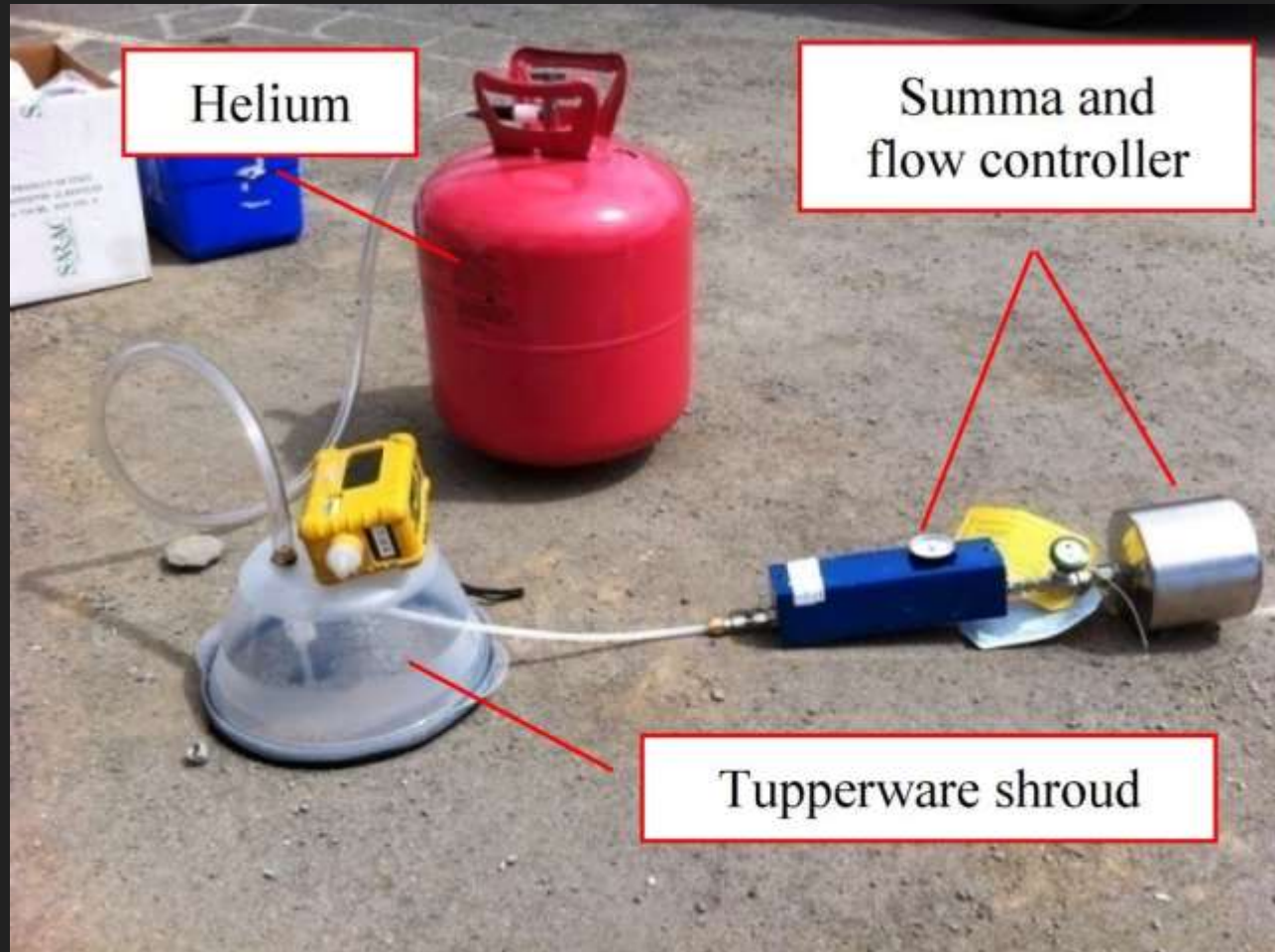




# Soil Vapor Sampling with Helium Displacement

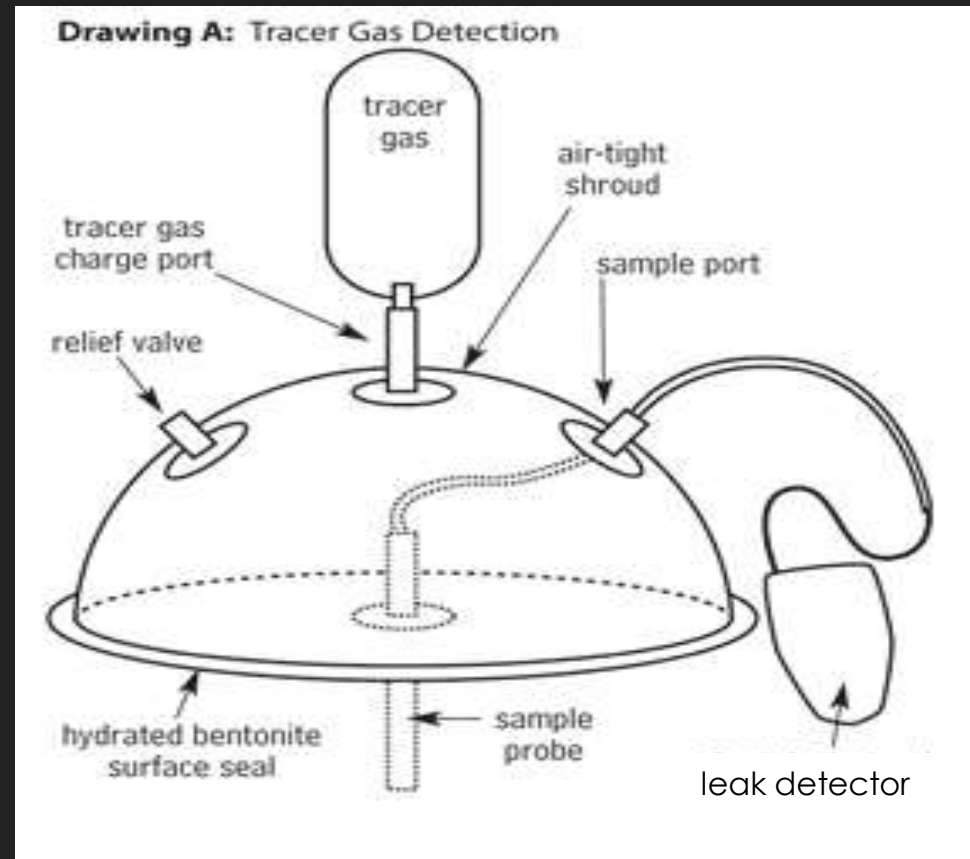
Helium pumped into  
Tupperware shroud  
as a “leak tracer”.

If the yellow detector  
picks up Helium the  
system has leaks.





# Checking for Leaks During Soil Sampling



# Problematic Issues in Soil Vapor Sampling

## ○ Popular Methods

- EPA TO-15 (Evacuated Canister, GC-MS)
- EPA TO-17 (Sampling Pump & Tube, TDA-GC-MS)
- **Expensive Methods** - Designed for ambient Air Sampling

## ○ Soil Resistance to Mass Transport complicates Active Sampling

- Active Sampling perturbs equilibrium between Sub-Surface Air and Soil
- If sub-surface air is removed faster than soil can replenish ...

**Concentration can be Understated**

# Difficulties in using TO-15 & TO-17 for Vapor Intrusion

		EPA TO-15 5-L Steel Canister	EPA TO-17 Pump & Tube
Logistics	→	Bulky	Requires Electricity
Economy, Ease of Use	→	Complicated to Own, Maintain	Complicated To Operate
Soil Gas Sampling	→ →	Active Sampling may Perturb Soil Gas Equilibrium	High Rate Active Sampling will Perturb Soil Gas Equilibrium
Sample Duration		typically 4-24 hr	typically 1-8 hr

# Researchers Recommend Diffusive Samplers as a practical & cost-effective alternative.

Brown, V. M., Crump, D. R. and C. Yu, 1993. Long term diffusive sampling of volatile organic compounds in indoor air. Environmental Technology, Vol. 14, p.771-777.

Brown, V. M. and D.R. Crump, 1998. Diffusive Sampling of Volatile Organic Compounds in Ambient Air. Environmental Monitoring and Assessment, Vol. 52, p. 43-55.

"Passive Sampling", Trends in Analytical Chemistry, 21 (4), p 276. Kuehster, T., D. Folkes & E. Wannamaker, 2004.

PDMS-Based Permeation Passive Samplers for VOC Analysis: Theoretical Considerations and Practical Implications", Pittcon 2007, February 25 – March 1, 2007, Chicago, IL, abstract 1680-3. USEPA, 2002.

Zabiegała, B., M. Partyka, T. Górecki, J. Namieśnik, 2006. "Application of the GC retention index system for the determination of the calibration constants of permeation passive samplers with PDMS membranes", Journal of Chromatography A, 1117 p 19-30.

ASTM D7758 – 17 Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations

# Most Comprehensive Study

## Diffusive Sampling in Vapor Intrusion assessment

### **Quantitative Passive Sampling for Assessing Soil Vapor Intrusion to Indoor Air**

Todd McAlary<sup>1</sup>, Hester Groenevelt<sup>1</sup>, Tadeusz Górecki<sup>2</sup>, Suresh Seethapathy<sup>2</sup>, Paolo Sacco<sup>3</sup>,  
Derrick Crump<sup>4</sup>, Brian Schumacher<sup>5</sup>, Michael Tuday<sup>6</sup>, Heidi Hayes<sup>7</sup>, Paul Johnson<sup>8</sup>; <sup>1</sup>Geosyntec  
Consultants, <sup>2</sup>University of Waterloo, <sup>3</sup>Fondazione Salvatore Maugeri, <sup>4</sup>Cranfield University,  
<sup>5</sup>U.S. Environmental Protection Agency, <sup>6</sup>Columbia Analytical Services, <sup>7</sup>Air Toxics Ltd.,  
<sup>8</sup>Arizona State University

Air Quality Measurement Methods and Technology Conference 2012

# Characteristics of Diffusive Samplers

- Compact, Portable, Disposable, Inexpensive  
No Electric Power Required
- Long Sampling Times (weeks) are practical
- Low Detection Limits  
When Long Sampling Times are Used
- Does Not Perturb Soil Gas Measurement as much As Active Sampling does



# Comparison of Methods for Vapor Intrusion Measurements

TECHNICAL REQUIREMENTS	EPA Methods TO-15 and TO-17	DIFFUSIVE SAMPLERS
Analyze Chlorinated Solvents and Hydrocarbons	Yes	Yes
Sample for 1-14 days	Up to 1 day	0.1-30 days
Measure 1-1000 ppb	Yes	Yes For 7-14 day sample
Ease of Use	Costly & Complicated	Cost-Effective & Convenient

# Styles of Diffusive Samplers



Thermal Desorption  
Tube Sampler



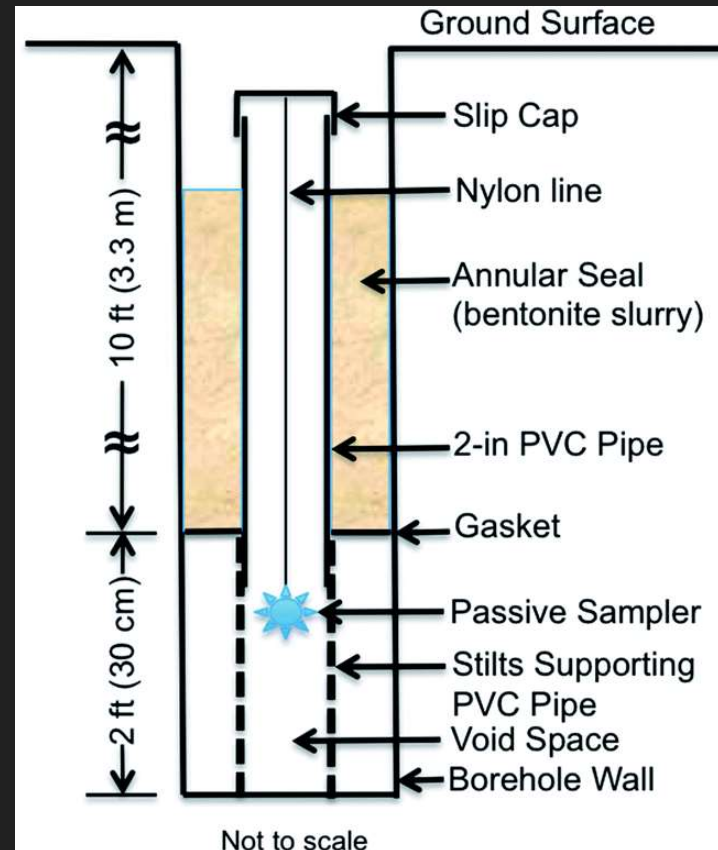
IH Air  
Sampler



Silicone  
Membrane  
Sampler

# Schematic Diagrams

## Soil Sampling with Diffusive Sampler



# ASTM D7758 – 17 Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations

5.2.3 Vapor Intrusion Evaluation—Passive soil gas sampling can be used to identify vapor migration and intrusion, with the data providing a line of evidence on the presence or absence of the compounds in soil vapor, the nature and extent in relation to potential receptors, and whether a vapor pathway is complete. Sorbent samplers can be placed beneath the slab or in close proximity to buildings to collect time-integrated samples targeting VOCs and SVOCs at concentrations often lower than can be achieved with active soil gas sampling methods.

# ASTM D7758 – 17 Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations

5.2.1 Source Identification and Spatial Variability Assessment—Passive soil gas sampling can be an effective method to identify contaminant source areas in the vadose zone and delineate the extent of contamination. By collecting samples in a grid with fewer data gaps, the method allows for an increase in data density and, therefore, provides a high-resolution depiction of the nature and extent of contamination across the survey area.

# ASTM D7758 – 17 Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations

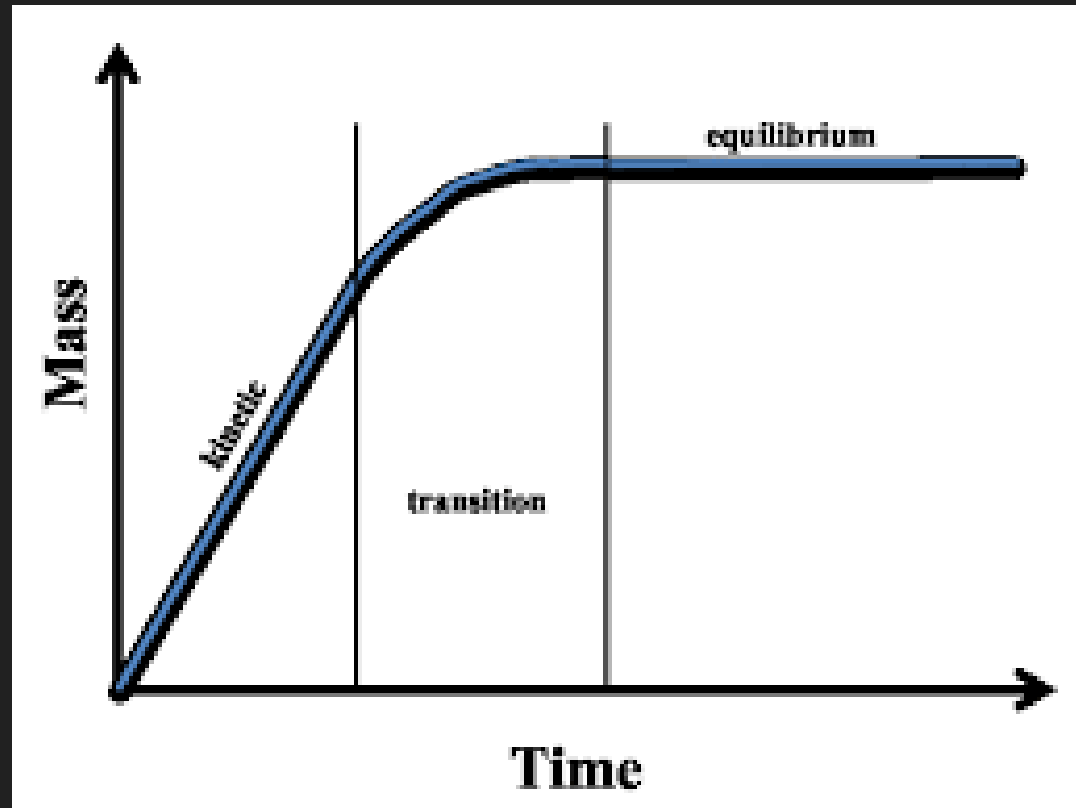
5.2.2 Monitoring—Passive soil gas samplers are used to monitor changes in site conditions. An initial set of data is collected to establish a baseline and subsequent data sets are collected for comparison. The sampling and analytical procedures should remain as near to constant as possible so significant changes in soil gas results can be attributed to those changes in subsurface contaminant levels at the site that will then warrant further investigation to identify the cause.



# Diffusive Samplers ...

## can also measure equilibrium concentrations

Equilibrium may be reached  
after 1 or more weeks  
depending upon  
Sampling Rate  
Sampler Capacity

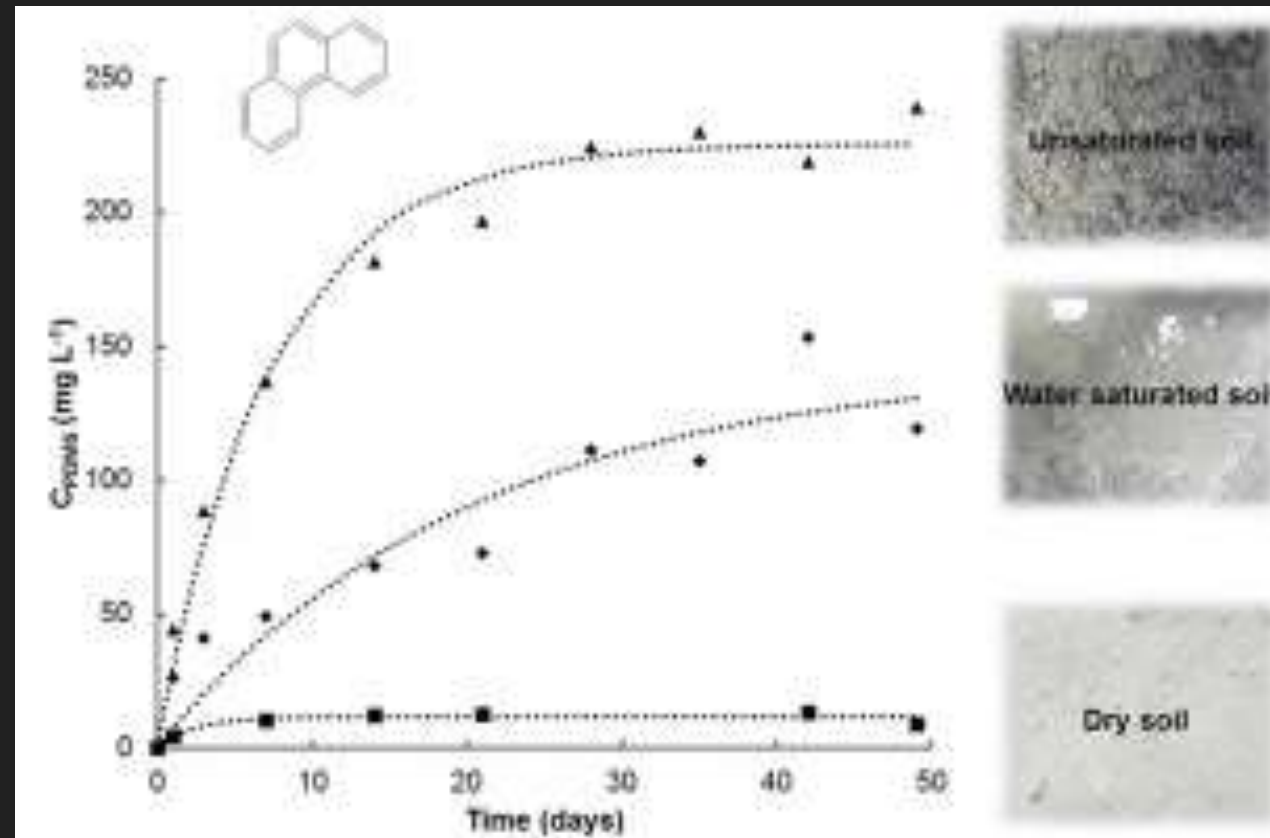


# Diffusive Samplers ...

## can also measure equilibrium concentrations

Pil-Gon Kim, Ji-Yeon Roh,  
Yongseok Hong, Jung-Hwan  
Kwon

Chemosphere, Vol 184,  
October 2017, Pp 86-  
92



# Why Aren't Diffusive Samplers More Popular in Vapor Intrusion ?

- EPA championed the Use of TO-15 & TO-17
  - but does not require their use
- Diffusive Sampler Champions Have Been Absent
- Work Funded by People with Deep Pockets
  - Cost not as important
- Practitioners are Engineering Firms
  - Already happy users of TO-15 & TO-17
  - Used to Complicated & Expensive Stuff

# Summary – Vapor Intrusion

- Diffusive Samplers more Cost-Effective & Convenient
  - compared to TO-15 & TO-17
- Low Sampling Rates & Passive Nature are Advantages
  - Less perturbation of Soil Gas Equilibrium
  - Small & Need no Power Source
  - Can Sample for Days, Weeks, or Months

# Sources of Indoor Air Pollutants

## VAPOR INTRUSION

Halocarbons,  
Petroleum  
Hydrocarbons

## BLDG MATERIALS

Formaldehyde  
Solvents  
Varnishes, Paints

## FURNITURE, GLUES, CLEANERS

Varnishes, Paints  
Acrylics, Isocyanates,  
Formaldehyde

## HEATING/COOLING

CO, Ozone  
Halocarbons

## COOKING

NO<sub>2</sub>, CO, Acrolein  
S & N Compounds

## HUMAN OCCUPANTS

CO<sub>2</sub>, Alcohol,  
Moisture,  
Smoking Products

# Diffusive Samplers





# IAQ Similar to Workplace Sampling except ...

## ■ Workplace

- 1-1000 ppm
- 100's of analytes
- 15 min - 8 hr sampling

## ■ IAQ

- 10 - 1000 ppb
- Dozens of analytes
- 1 hr – 1 week sampling

# Comparison of Methods for Indoor Air Quality Measurements

TECHNICAL REQUIREMENTS	EPA Methods TO-15 and TO-17	DIFFUSIVE SAMPLERS
Analyze 100 Key Analytes	Yes	Yes
Sample for 1-14 days	Up to 1 day	0.1-30 days
Measure 10-1000 ppb	Yes	Yes For 7-14 day sample
Ease of Use	Costly & Complicated	Cost-Effective & Convenient

# Summary – Indoor Air Quality

- Diffusive Samplers more Cost-Effective & Convenient
  - compared to TO-15 & TO-17
- Low Sampling Rates Are OK w/ Long Sampling Times
  - Small & Need no Power Source
  - Can Sample for Days, Weeks, or Months



**Finis**



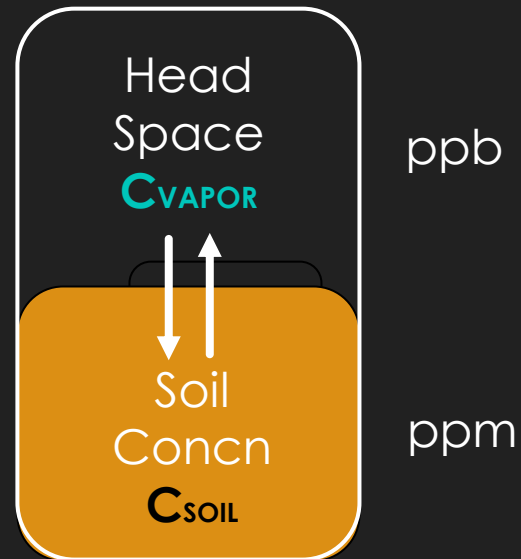
# Vapor Concentration

## Lower than Soil Concentration

### Vapor Concentration

Proportional to...

Soil Concentration  
x Vapor Pressure



### Raoult's Law

$$C_{VAPOR} = vp \times C_{SOIL}$$



# Magnitude of Indoor Air Contamination arising from Underground Contamination

Source:  
Minnesota Pollution  
Control Agency

When chemical vapor pollution is present in soil under houses or buildings, research has shown that vapor levels inside the structure are much lower.

Chemical vapor levels in a house tend to be 100X to 1,000X less than what is present in the soil beneath.

To be safe, the MPCA and MDH assume vapor levels inside the structure would be 33X less than what's measured in the soil beneath.

