Quantitative Passive Diffusive-Adsorptive Sampling Techniques for Vapor Intrusion Assessment

ESTCP Project 08-30


AWMA Specialty Conference – Vapor Intrusion 2010

September 30, 2010
Chicago, IL
Outline

- Challenges with conventional sampling
- Introduction to quantitative passive sampling
- Comparative Studies
  - ESTCP Project 08-30
  - NAVY SPAWAR Project
- Summary of Findings to date
Challenges with Conventional Sampling
Summa Canister and TO-15

Complex procedure, requires special training ($)

Must be cleaned and certified ($)

Bulky ($) to ship and handle

Maximum ~24 hour samples

Costly: $200 to $300/sample, depending on reporting limit

Not useful for analytes heavier than naphthalene (poor recovery)
Automatic Thermal Desorption Tubes / TO-17

Typically customized for each application – high level of training required

Allows longer than 24-hour samples, but the pump must run reliably throughout the sampling period

Capable of a larger list of analytes

Typically <$200/sample, depending on analyte list

Potential for breakthrough and competition in high concentration zones

Challenging to get sufficient sample volume in low permeability soils
Introduction to Quantitative Passive Sampling
Quantitative Passive Sampling

• Expose a sampler for a known time
• Ship to laboratory for analysis of adsorbed mass
• Calculate concentration

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

- \( C_0 \) = concentration of analyte in air (µg/m³)
- \( M \) = mass of analyte collected by the sorbent (pg)
- \( k^{-1} \) = uptake rate (mL/min)
- \( t \) = sampling time (min)

• Uptake rate is unique to each sampler/analyte pair
  • Usually requires expensive controlled experiments
  • Some passive samplers don’t control uptake – qualitative!
Benefits of Passive Sampling

- Simple (minimal training)
- Less expensive
- Low reporting limits with no premium cost
- Time-weighted average concentration (up to a week or a month if needed)
- Smaller – easy to ship, discrete to deploy
- Long history of use in Industrial Hygiene
- Other benefits unique to each sampler
## ESTCP Study Team

<table>
<thead>
<tr>
<th>Organization</th>
<th>Name</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosyntec Consultants, Inc. Guelph (Canada)</td>
<td>Todd McAlary, Hester Groenevelt</td>
<td>Overall project direction &amp; reporting</td>
</tr>
<tr>
<td>US EPA Labs, Las Vegas (NV)</td>
<td>Brian Schumacher, John Nocerino (D)</td>
<td>Experimental Design &amp; Statistics</td>
</tr>
<tr>
<td>Arizona State University (AZ)</td>
<td>Paul Johnson</td>
<td>Practicality for Vapor Intrusion Sites</td>
</tr>
<tr>
<td>University of Waterloo (Canada)</td>
<td>Tadeusz Gorecki, Suresh Seethapathy</td>
<td>PDMS Membrane Sampler</td>
</tr>
<tr>
<td>Cranfield University (UK)</td>
<td>Derrick Crump</td>
<td>ATD Passive and Active Samplers</td>
</tr>
<tr>
<td>Fondazione Salvatore Maugeri (Italy)</td>
<td>Paolo Sacco</td>
<td>Radiello Samplers</td>
</tr>
<tr>
<td>Columbia Analytical Services (CA)</td>
<td>Michael Tuday, Ku-Jih Chen</td>
<td>High Conc. Laboratory Testing Ultra II™ samplers &amp; canisters</td>
</tr>
<tr>
<td>Air Toxics Limited (CA)</td>
<td>Heidi Hayes, Stephen Dishier</td>
<td>Low Conc. Laboratory Testing ATD Passive and Active Samplers</td>
</tr>
</tbody>
</table>

International Team, including the labs most familiar with each of the samplers
Four Different Passive Samplers

Waterloo Membrane Sampler™
(1-D permeation across a membrane, CS$_2$ extraction or thermal desorption)

SKC Ultra II
(Badge sampler, 1-D uptake through porous plate, thermal desorption)

Automated Thermal Desorption (ATD) Tubes
(1-D diffusion through air, thermal desorption)

Radiello™
(Radial uptake through porous cylinder, thermal desorption or solvent extraction)

Geosyntec consultants
Desorption Methods

Thermal desorption

Solvent desorption

Solvent
Sorbent
## Sorbent Media Selection

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Description</th>
<th>Sampling Properties</th>
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</thead>
<tbody>
<tr>
<td>Anasorb 747</td>
<td>Beaded active carbon</td>
<td>High capacity for VOCs, solvent desorption</td>
</tr>
<tr>
<td>Tenax TA</td>
<td>Porous polymer</td>
<td>Low capacity, medium to high boiling compounds, thermal desorption</td>
</tr>
<tr>
<td>Carbopack B</td>
<td>60/80 mesh graphitized carbon black</td>
<td>Non-porous, high capacity for VOCs, thermal desorption</td>
</tr>
</tbody>
</table>

There are many, many more sorbents available.
Laboratory Analyte List

<table>
<thead>
<tr>
<th>CAS #</th>
<th>Target Analyte</th>
<th>ORNL 2009 Indoor Air Residential Screening Level at 10⁻⁵ risk (ppbv)</th>
<th>Organic Carbon Partitioning Coefficient, Koc (mL/g)</th>
<th>Vapor Pressure (atm)</th>
<th>Water Solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71-55-6</td>
<td>1,1,1-Trichloroethane</td>
<td>40,000</td>
<td>110</td>
<td>0.163</td>
<td>1.33</td>
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<tr>
<td>95-63-6</td>
<td>1,2,4-Trimethylbenzene</td>
<td>62</td>
<td>472</td>
<td>0.00197</td>
<td>0.0708</td>
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<tr>
<td>107-06-2</td>
<td>1,2-Dichloroethane</td>
<td>1.1</td>
<td>174</td>
<td>0.107</td>
<td>8.52</td>
</tr>
<tr>
<td>78-93-3</td>
<td>2-Butanone (MEK)</td>
<td>75,000</td>
<td>134</td>
<td>0.1026</td>
<td>~256</td>
</tr>
<tr>
<td>71-43-2</td>
<td>Benzene</td>
<td>5</td>
<td>59</td>
<td>0.125</td>
<td>1.75</td>
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<tr>
<td>56-23-5</td>
<td>Carbon Tetrachloride</td>
<td>1.3</td>
<td>174</td>
<td>0.148</td>
<td>0.793</td>
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<tr>
<td>91-20-3</td>
<td>Naphthalene</td>
<td>0.68</td>
<td>2,000</td>
<td>0.000117</td>
<td>0.031</td>
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<td>110-54-3</td>
<td>n-Hexane</td>
<td>8,800</td>
<td>43</td>
<td>0.197</td>
<td>0.0128</td>
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<td>127-18-4</td>
<td>Tetrachloroethene</td>
<td>3.1</td>
<td>155</td>
<td>0.0242</td>
<td>0.2</td>
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<tr>
<td>79-01-6</td>
<td>Trichloroethene</td>
<td>12</td>
<td>166</td>
<td>0.0948</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Selected to span a range of compounds of interest for vapor intrusion studies
Chlorinated ethenes, ethanes, methanes, and VOCs of differing solubility and sorptive properties
Low Concentration Tests:
To Mimic Indoor and Outdoor Air Conditions

Concentration: 1, 50 and 100 ppbv
Temperature: 22, 25, 28 °C
Humidity: 30, 60 and 90% RH
Face velocity: 0.01, 0.2 and 0.4 m/s
Exposure time: 1, 4 and 7 days

High Concentration Tests:
To Mimic Soil Gas Conditions

Concentration: 1, 10 and 100 ppmv
Temperature: ambient
Humidity: 90-100%
Face velocity: very low (5x10^{-5} m/s)
Exposure time: 30 minutes
Exposure Chamber

- Conditioned gas enters at bottom and flows past samplers
- Samplers rotate on a carousel to control face velocity
- Baffles help to minimize turbulence
- All surfaces passivated to minimize adsorption
Exposure Chamber (cont’d)

Off the shelf glassware, modified by glass-blower

All surfaces passivated

Surrounded by tube of circulating fluid and insulated for temperature control
## Inter-Laboratory Testing

<table>
<thead>
<tr>
<th>Sampler Type</th>
<th>Home Laboratory</th>
<th>Secondary Laboratories</th>
<th># of Samplers to Each Laboratory</th>
</tr>
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<tbody>
<tr>
<td>Waterloo Membrane Sampler</td>
<td>University of Waterloo</td>
<td>Air Toxics Ltd</td>
<td>2</td>
</tr>
<tr>
<td>ATD Tubes with Tenax TA</td>
<td>Air Toxics Ltd</td>
<td>Columbia Analytical Services</td>
<td>2</td>
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<tr>
<td>ATD Tubes with CarboPack B</td>
<td>Air Toxics Ltd</td>
<td>University of Waterloo</td>
<td></td>
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<tr>
<td>SKC Ultra</td>
<td>Columbia Analytical Services</td>
<td>Air Toxics Ltd</td>
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<td>Radiello</td>
<td>Fondazione Salvatore Maugeri</td>
<td>Columbia Analytical Services</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Air Toxics Ltd</td>
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</tr>
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</table>
Most results show good agreement between labs. MEK was problematic.
ANOVA Testing

Set the five factors at their midpoints, and run test multiple times to determine variance from experimental procedures

<table>
<thead>
<tr>
<th>Factor</th>
<th>Units</th>
<th>Center Value</th>
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<tbody>
<tr>
<td>Concentration</td>
<td>ppb</td>
<td>50</td>
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<tr>
<td>Temperature</td>
<td>° C</td>
<td>20</td>
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<tr>
<td>Gas Flow Velocity</td>
<td>m/s</td>
<td>0.2</td>
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<tr>
<td>Sampling Duration</td>
<td>days</td>
<td>4</td>
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<tr>
<td>Relative Humidity</td>
<td>%</td>
<td>60</td>
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</table>
# Fractional Factorial Testing

A series of experiments strategically changing the 5 key factors:

- Concentration
- Temperature
- Face Velocity
- Sample Time
- Humidity

<table>
<thead>
<tr>
<th>Run #</th>
<th>Approximate Concentration (ppbv)</th>
<th>Approximate Temperature (°C)</th>
<th>Face Velocity (m/s)</th>
<th>Duration (days)</th>
<th>Approximate Humidity (%R.H.)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>17</td>
<td>0.41</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>17</td>
<td>0.014</td>
<td>1</td>
<td>90</td>
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<tr>
<td>3</td>
<td>100</td>
<td>30</td>
<td>0.41</td>
<td>1</td>
<td>30</td>
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<tr>
<td>4</td>
<td>1</td>
<td>30</td>
<td>0.014</td>
<td>1</td>
<td>30</td>
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<tr>
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<td>100</td>
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<td>7</td>
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<tr>
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<td>1</td>
<td>30</td>
<td>0.41</td>
<td>1</td>
<td>90</td>
</tr>
</tbody>
</table>
Chamber Test Results to Date

ATD Tenax

Analyte

C/C₀
Chamber Test Results to Date

ATD Carbopack B

![Graph showing Chamber Test Results to Date with various analytes and run numbers.](image)

- Analytes: 111TCA, 124TMB, 12DCA, MEK, Ben, CT, Hex, Naph, PCE, TCE
- Runs shown with different marker types and colors

(low bias)
Chamber Test Results to Date

WMS

(1-day)

(Blank)

(Calculated Uptake Rate)

Analyte

111TCA  124TMB  12DCA  MEK  Ben  CT  Hex  Naph  PCE  TCE
Chamber Test Results to Date
Chamber Test Results to Date

SKC Ultra

Analyte

111TCA  124TMB  12DCA  MEK  Ben  CT  Hex  Naph  PCE  TCE

\( \frac{c}{c_0} \)

- Run 1
- Run 3
- Run 4
- Run 5
- Run 6
- Run 7
- Run 8
- Run 9
- Run 10
- Run 11
- Run 12
- Run 19
- Run 20
- Run 21
- Run 22
- Run 23
- Run 24

Geosyntec consultants
Field Testing (SPAWAR/NESDI)
Comparative sampling of indoor air, outdoor air, and soil vapor

Indoor Air:
- ATD Tubes
- 3M OVM 3500
- Radiello
- SKC Ultra II
- Waterloo Membrane

Versus

6-day Summas
With
3 Replicates

Acknowledgements to Ignacio Rivera and Bart Chadwick of SPAWAR for Support
The low bias for SKC is believed to be due to sorbent selection (Chromosorb 106 worked well for ATD, but SKC has 20X higher uptake rate). TCE was the dominant compound.
Sub-Slab Sampling

Two types:

1) Fully passive (drop and cork for 24 hours)

2) Semi-passive (drop and purge with PID for 10 minutes)
Fully Passive samples (left) showed “Starvation Effect” in proportion to uptake rate.

Much less “starvation” when PID used to purge gas from hole during 10 min sampling interval.
Starvation Factor vs Uptake Rate

Starvation Factor = Summa conc’n
Passive conc’n

Consider a custom “low-uptake” sampler
Modified Uptake Rates

WMS Sampler

ATD Tube & Pinhole Cap

SKC Ultra II and 12-hole Cap

Reduce the uptake rate by reducing the area

Lower uptake = less starvation
Passive Soil Gas – Utah House

- Screw for hanging samplers
- PVC pipe
- Bentonite seal
- Gasket for retaining bentonite
- Passive sampler (e.g., SKC Ultra)
- Void space

Geosyntec consultants
6 Passive Samplers

- ATD tube (Tenax)
- ATD tube (Carbopack)
- Radiello
- WMS
- WMS pin hole
- SKC (Cap)

Uptake rates: 0.01 to 75 mL/min

Void space was larger than SPAWAR sub-slab sampling
6 Passive Probes + 1 Conventional

Modified Latin Square Test
Added one Duplicate
Tested 1 to 12 day exposures
Drop the sampler/Purge 3 PV
Fully Passive – Deep 2-inch Probes

C/Co = Passive data divided by Mean of all Hapsite data
All but about 3 of these measurements are within a half order of magnitude
Longer samples with weaker sorbent show losses (Tenax)
Fully Passive – Deep 2-inch Probes

Longer samples show losses with both Carbopack and Tenax for ATD Tubes
Consistent with theory for incomplete retention
(11DCE is 3X less sorptive than TCE)
Starvation Factor Versus Uptake Rate

After removing artifacts of weak sorbent, trend is encouraging.
Why worry about starvation at all?
Just purge soil gas past the sampler at a modest rate
Comparable to groundwater “Low Flow Sampling Protocol”
Flow-through cell neutralizes the starvation effect
Variability about 1 order of magnitude, but so did Summa cans
Interim Conclusions

- Encouraging results to date
  - No samplers eliminated
  - Challenges with highly sorptive or highly soluble compounds
  - Challenges with very high humidity or long exposures for some sampler/sorbent combinations
  - Much better understanding of how to avoid starvation for soil gas sampling – quantitative results are likely feasible

- Modifications can overcome some of the limitations
  - Custom sorbents and uptake rates
  - Based on theory & data

- This is roughly the “half-way” point – stay tuned!