Passive Samplers for Vapor Intrusion Monitoring: Update on EPA's Technical Support Document and Research Results

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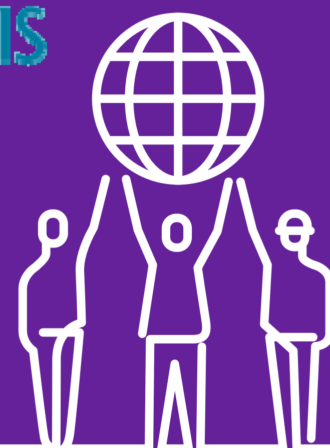
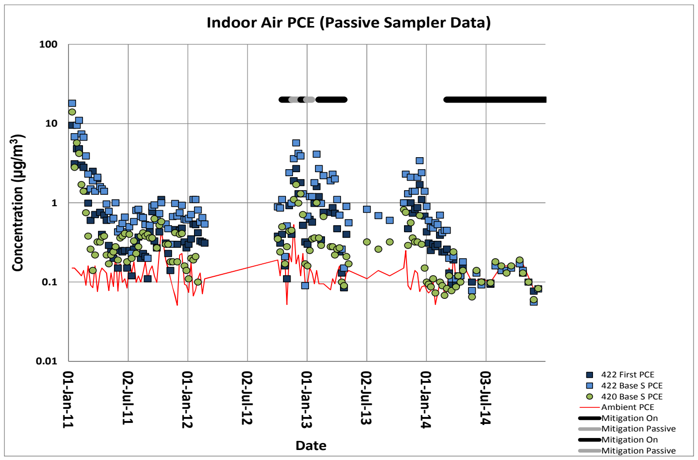
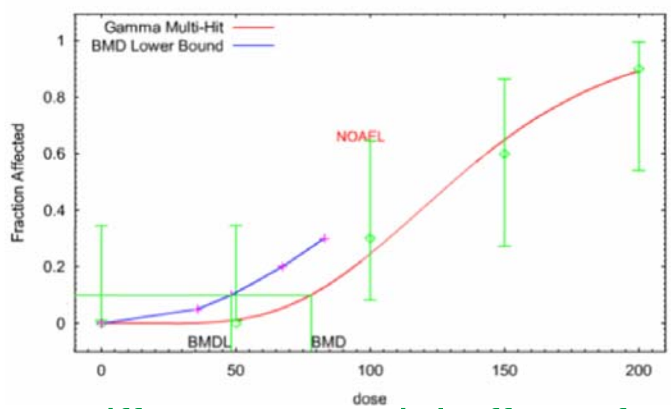


Innovation that Provides Sustainable Solutions to Complex Local Challenges, Worldwide

Indoor Air Temporal Variability at VI sites. A small fraction of the time contributes the most to chronic exposure. Timescales of variation; diurnal, seasonal and climatic.



Zimmerman, 2015; Lutes, Johnson, Truesdale 2013



Example Challenge: "A Perfect Storm"

TCE from VI is currently regulated in various jurisdictions based on 8 hour, 24 hour, 21 day and/or 26 year exposures.
(Lowe, 2014)

A perfect storm for risk management decisions
Gillay, 2014

Different potential effects from short-term and long-term exposures but a similar concentrations

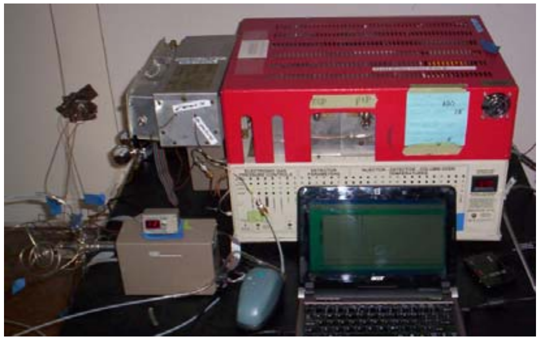
Current/Historic U.S. Practice

Summa™ Canisters

- Still the predominant tool, well known.
- Method TO-15 laboratory analysis
- Often $200-$400 per sample
- Suitable for 8 to 24 hour durations, can be used to 72 hours with some reliability problems.
- Research underway to demonstrate controllers capable of 14 day sampling.

Field Portable GC or GC/MS (HAPSITE, FROG, Hartman etc.)

- Currently expensive
- Down to 15 min resolution
- Commonly used for initial investigation
- Not in routine use for long term exposure monitoring



Passive Sampling

Practical Advantages

- Reliable deployment with little training of field staff required
- Unobtrusive
- Inexpensive to ship

Technical Advantages

- Range of sampling durations from days to weeks can be accommodated.

Limitations

- Some information on the target compounds and expected concentration ranges needed for selecting the sampler.
- Expertise and skill is required to select the right passive geometry and sorbent type for a given application.
- Sampler uptake rate must be known for the compound/sampler combination

U.S. Regulatory Acceptance ?

- EPA 2013 Draft Guidance: *"Although passive diffusion samplers have been less commonly used to quantify indoor air concentrations, their use may grow as a result of recent demonstrations that they can yield results comparable to those obtained using evacuated canisters …..and a recognition that they may be less intrusive for some building owners and occupants and more convenient for field staff"*
- Region IX – December 2013: "*EPA Region 9 supports the use of longer-term passive samplers to help assess the temporal variability of indoor air vapor intrusion-related contaminant concentrations."*
- NC DENR 2014 "*The use of passive samplers allows the collection of indoor air samples over a longer time, up to 30 days, thereby providing an average indoor air concentration over a longer exposure period.".* Commonly used by dry cleaning fund contractors.
- Common for occupational monitoring for high concentrations, <24 hour Well developed for BTEX Environmental level monitoring in Europe, EU standard methods exist, has now been tested for CAHs indoors in US
- EPA Engineering Issue, expected in 2015

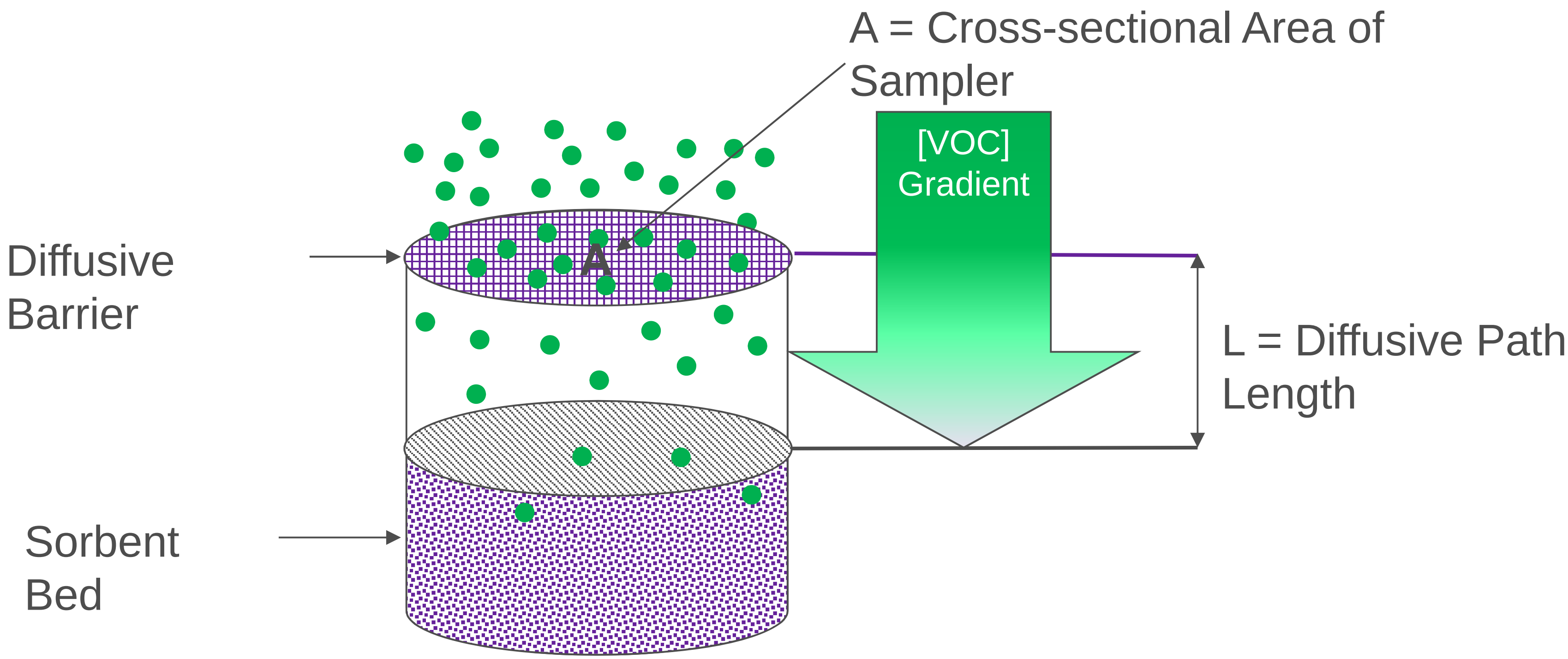
EPA Engineering Issue: Content Highlights

Standard Methods Availability

- Not from EPA for VOCs (analytical portions of TO-17 apply) – exception is new Method 325 for VOCs in ambient air using tube type samplers
- ISO Method ISO 16017-2: Designed for tube type samplers and TCD: *VOCs including hydrocarbons, halogenated hydrocarbons, ketones and alcohols; 8 hours to four weeks exposure*
- United Kingdom Method MDHS 88 - method mentions badge, tube, and radial geometries. Uptake rates are tabulated for four different major manufacturer samplers covering tube, badge, and radial geometries
- European Standards EN13528 -Tube, badge, and radial samplers are mentioned with both TD and solvent extraction
- ASTM D6196-3 covers ambient and indoor VOC sampling using *either* pumped or diffusive methods. Both tube and radial geometries of passive sampling are specifically discussed.
- ASTM D6306-10 focuses on placing and using diffusive samplers in the indoor environment

Passive Sampling Concepts

Fick's 1st Law of Diffusion



Uptake Rate = Rate at which VOC vapors pass through opening

Uptake Rate α A/L

Passive Sampling: What Goes into Calculating Your Concentration?

Measured in lab

$$\text{Concentration } (\mu g/m^3) = \frac{\text{Analytical Result } (\mu g) \times \frac{1000 \text{ mL}}{1 \text{L}} \times \frac{1000 \text{ L}}{m^3}}{\text{Uptake Rate (mL/min)} \times \text{Sampling duration (min)}}$$

Sampler Geometry specific

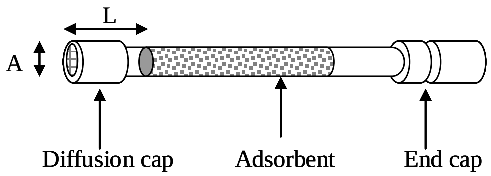
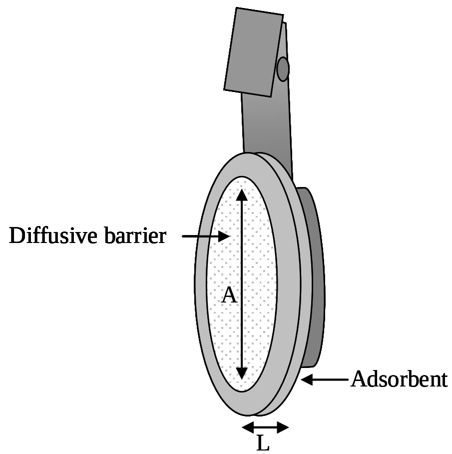
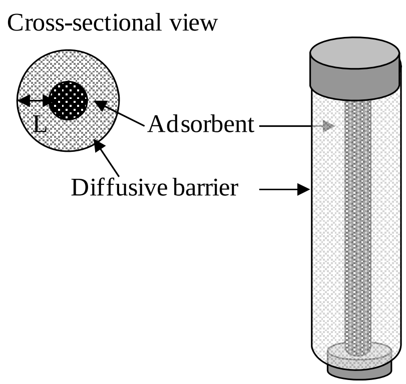
Chemical specific

Temperature Dependent

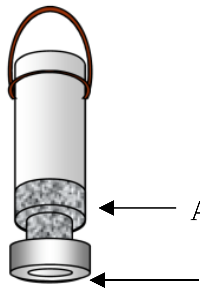
Tabulated values/equations available

Recorded in the field

Passive Sampler Types

Type	Schematic	Uptake Rate	Examples
Tube (Axial)		Low	ATD Tubes (Markes, Perkin Elmer, Supleco, CAMSCO) ORSA (Draeger)
Badge (Axial)		Medium	OVM 3500 (3M) Ultra Series, 575 (SKC) 521 Organic Vapor Badge (Assay Technologies)
Radial		High	Radiello (Fondazione Salvatore Maugeri)

Passive Sampler Types

Type	Schematic	Uptake Rate	Examples
Permeation (Axial)		**Low (Between the tube and badge-styles)**	**Waterloo Membrane Sampler (SiREM)**

Permeation Design: VOCs dissolve in and diffuse through a nonporous, hydrophobic membrane.

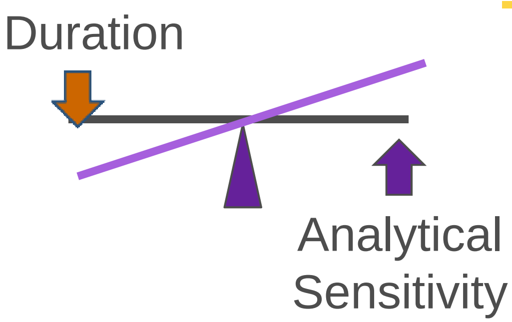
Sorbent Types

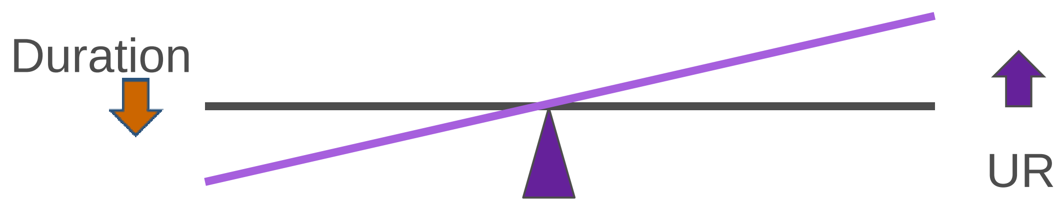
	Charcoal-based	Thermally-Desorbable
Examples	Activated charcoal, Anasorb 747	Tenax TA, Carbopack, Carbograph, Carboxen
Performance	Strong VOC Retention	Weaker VOC Adsorption
Capacity	High surface area	Relatively less capacity
Prep Method	Solvent Extraction (SE)	Thermal Desorption (TD)
Analytical Sensitivity	Low: ~0.1 µg	High: ~0.01 to 0.001 µg

Sorbent must effectively retain compounds of interest during sample collection while efficiently releasing the compound at the time of analysis.

Passive Sampler Selection

	Sampler Geometries			
Sorbent	**Tube**	**Permeation**	**Badge**	**Radial**
Thermal Desorption	**ATD**	**WMS-TD**	**SKC Ultra**	**Radiello 145**
Solvent Extraction	**ORSA 5**	**WMS-Charcoal**	**SKC 575,Ultra 3M OVM 521 Assay**	**Radiello 130**





Passive Sampling Program Design

1) Target Chemicals – What are your compounds of interest?

   - List of compounds most likely to contribute to inhalation risk by comparing soil gas or groundwater concentrations to risk-based screening levels (RBSLs).
   - Compounds that exceed RBSLs by greatest margin will most likely dominate risk.
   - Select passive sampler configuration based on these target chemicals.

2) Passive sampler selection – how many of target compounds have calibrated uptake rates?

   - Published rates
   - Estimated rates
   - Field Calibrated rates

Passive Sampling Program Design

3) Reporting Limits and Sampling Duration – What target reporting limits are needed and how does that influence the duration?

- Calculated sample duration should be compared to project goals and practical constraints.
- Product of uptake rate and duration (UR x t) should be compared to recommended safe sampling volume (SSV).
  - Ideal (UR x t) is << SSV to minimize the potential of back diffusion during period.
  - Verify that the selected sorbent exhibits good desorption efficiency.

Laboratory's analytical chemist can assist with sorbent selection based on project needs.

Passive Sampler Selection Example

Trichloroethene Indoor Air Reporting Limits* (µg/m³)
Assume C_{RBSL} = 0.48 µg/m³

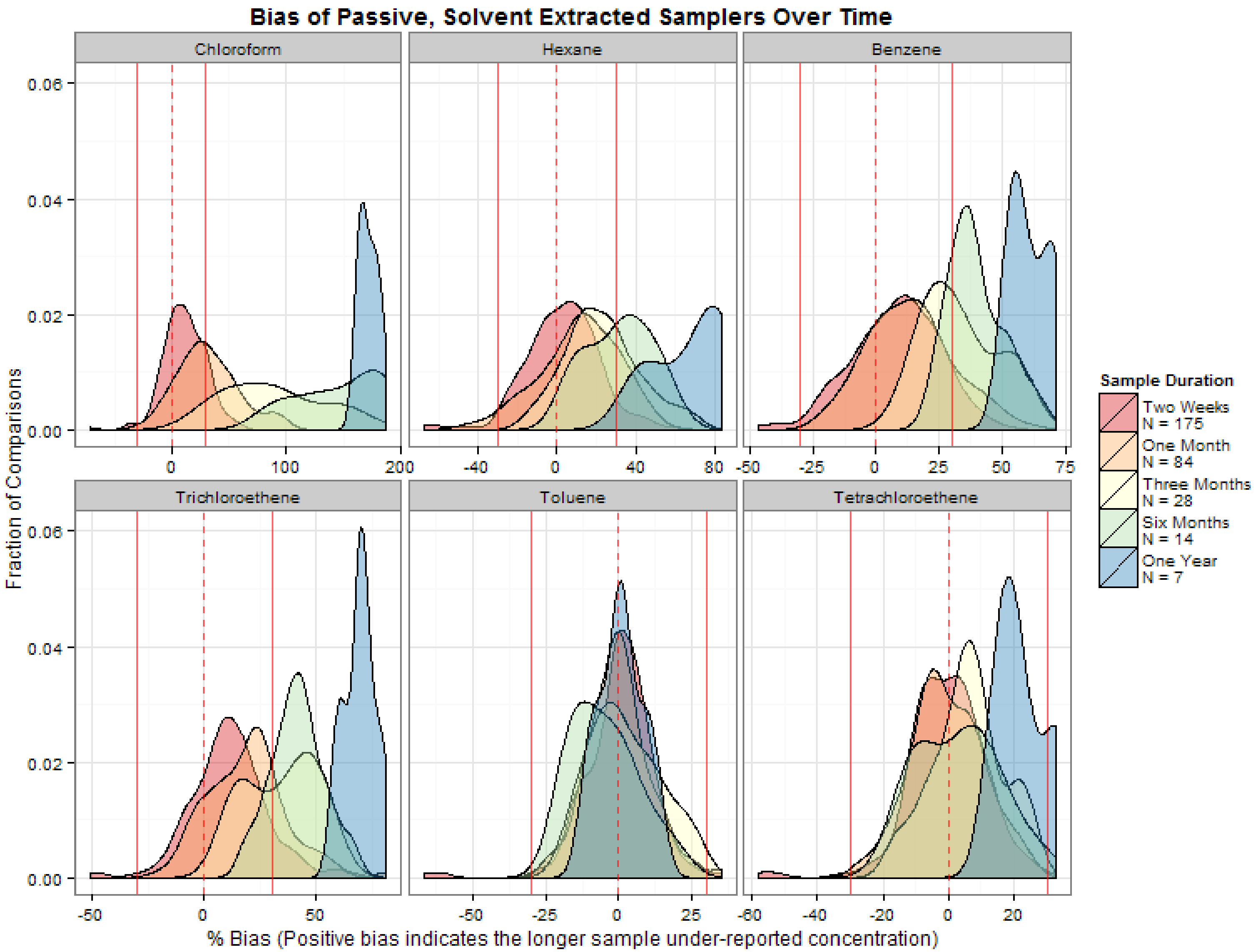
Type	Sorbent	1 day	3 days	7 days	14 days	30 days
Radial	TD	0.064	0.021	0.0092	0.0046	0.0021
Badge	TD	0.15	0.050	0.017	0.0083	0.0039
Permeation	TD	0.57	0.19	0.082	0.040	0.019
Radial	SE	1.0	0.34	0.14	0.072	0.034
Badge	SE	6.1	2.0	0.86	0.43	0.20
Permeation	SE	11	3.5	1.5	0.76	0.35

*Actual RLs will vary depending on specific laboratory capabilities. Values presented are representative of methods. Duration of TD methods depends on specific sorbent selected.

Implementation

- Indoor Air Placement
  - Avoid stagnant air spaces (starvation effect – low bias)
  - Avoid turbulence such as near vents (high bias)
  - Avoid high humidity locations such as bathrooms
- Field QC samples
  - Field Blanks – Critical in identifying and quantifying artifacts due to sorbent background or handling/storage issues.
  - Field Duplicates
- Inter-method Duplicates
  - % of Collocated samples (TO-15 or TO-17)
  - Provide verification of passive performance
  - Or used to generate site specific uptake rates
- Concurrent passive samplers at subintervals

EPA Research – Long Term Sampler Performance



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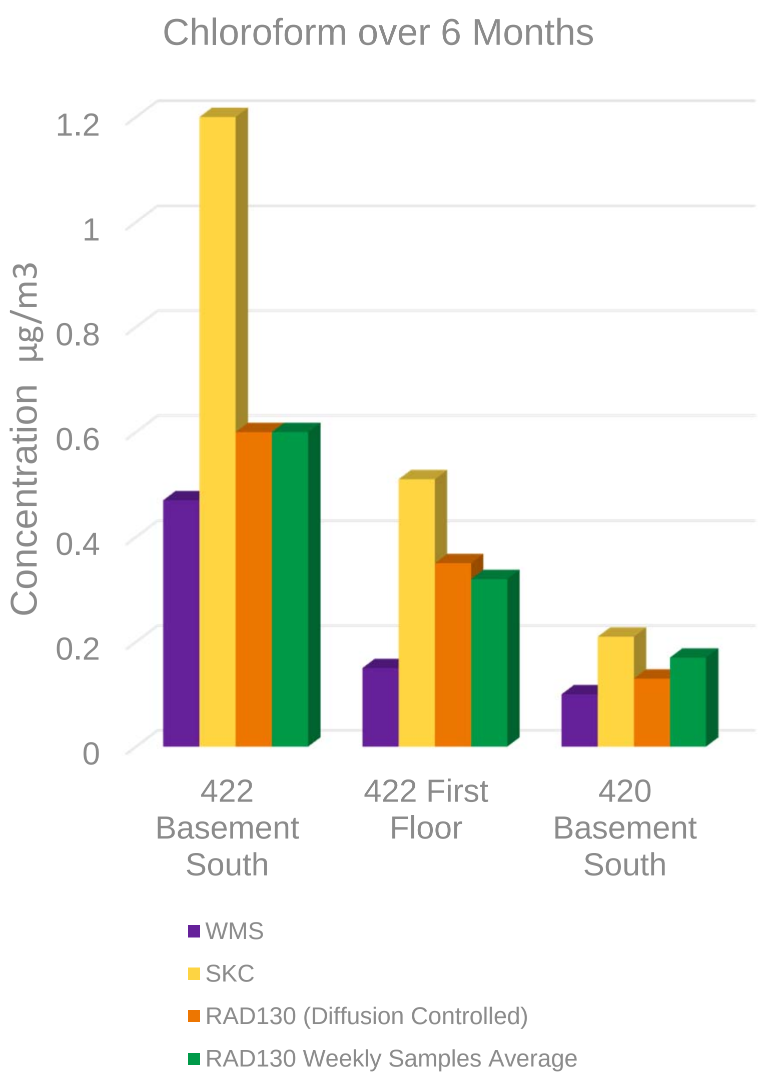
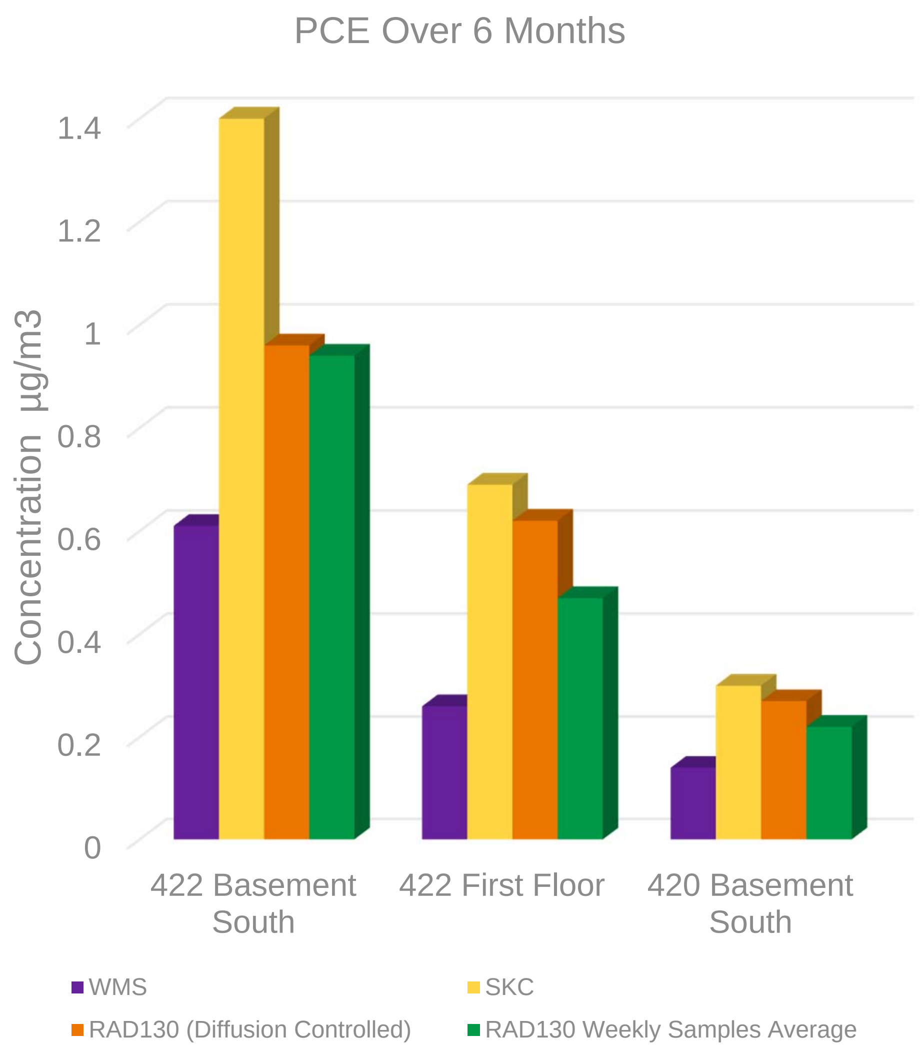
Performance of Three Passive Samplers Over 6 Months vs. Short Duration Passive Gold Standard





Research and Development Needs

Additional Compounds

- Determination of applicability of a broad list of compounds using passive sorbent methods

Challenging Compounds

- Quantitative passive solution for high vapor pressure, low molecular weight compounds such as Vinyl chloride
- Optimization and evaluation of passive sorbent samplers for compounds with very low RBSLs, requiring long exposures to meet targeted reporting limits

Variable Exposure Periods

- Identification and evaluation of a set of cost-effective sampling tools to assess short-term acute and subchronic health effects and long-term chronic effects
- How best to employ passive samplers in conjunction with conventional air methods and field sensors?

Intermittent Passive Sampling

- Can passive samplers be designed such that a "trigger" initiates sample collection?

Thank You

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