G-040, in K.A. Fields and G.B. Wickramanayake (Chairs), *Remediation of Chlorinated and Recalcitrant Compounds—2010.* Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2010). ISBN 978-0-9819730-2-9, Battelle Memorial Institute, Columbus, OH, **www.battelle.org/chlorcon**.

Long-Term Integrated Samplers for Indoor Air and Subslab Soil Gas at VI Sites

Christopher C. Lutes (Christopher.Lutes@arcadis-us.com) and Robert Uppencamp
(ARCADIS U.S., Inc., NC, USA)
Heidi Hayes (Air Toxics Ltd., Folsom, CA, USA)
Ronald Mosley and Dale Greenwell (U.S. EPA, Research Triangle Park, NC, USA

Vapor intrusion (VI) site assessments are plagued by substantial spatial and temporal variability that makes exposure and risk assessment difficult. Most risk- based decision making for volatile organic compound (VOC) exposure in the indoor environment is based on sub-chronic or chronic health benchmarks (toxicity values). However the most common approach to indoor air assessment in the industry is comparison of a limited number of one day integrated Summa Canister (Method TO-15) data to benchmarks based on 1 to 30 years of exposure.

In the region closest to a structure, VI is controlled by advective flow through foundation cracks. In many cases, the pressure driven entry flow rate is directly proportional to the differential pressure across the slab. Numerous studies of differential pressure across building slabs, including the one discussed in this presentation, show variance across several different time scales (transient, diurnal and seasonal) driven by occupant activities, heating ventilation & air conditioning (HVAC) cycles, frontal passage and climatic variations. Thus passive sorbent systems that provide a 2-week integrated measurement of volatile organic compound (VOC) concentrations may be a superior VI assessment tool. Studies were recently conducted at two sites in which the performance of passive samplers were compared to Summa canister measurements. Radiello samplers (both solvent extracted and thermally desorbed) as well as Chromosorb 106 passive tubes were tested. Comparisons between VOC sampling methods comparing relative cost, sample duration, sensitivity and dynamic range will be provided in this presentation.

Subslab soil gas sampling methods for VOCs normally collect small volume samples actively over 2 to 15 minutes (rarely 24 hour periods). The variance in differential pressure alters the flow direction across the slab, potentially dramatically changing the concentration in the immediate subslab region near cracks. Existing passive soil gas sampling methods are not considered to be quantitative because of the difficulty of establishing diffusion and thus uptake rates when the sampler is in direct contact with the soil. Proof of concept experiments have been conducted at two sites on an innovative subslab soil gas sampler. This sampler couples passive media that give good performance in indoor environments with a simple chamber refreshed by a continuous flow of subslab soil gas. The sampler integrates both over time and space. The performance of this innovative integrating subslab sampler will be compared to established methods of analysis, including on-line monitoring, for both VOCs and radon.

Long-term Integrated Samplers for Indoor Air and Sub-slab Soil Gas at VI Sites

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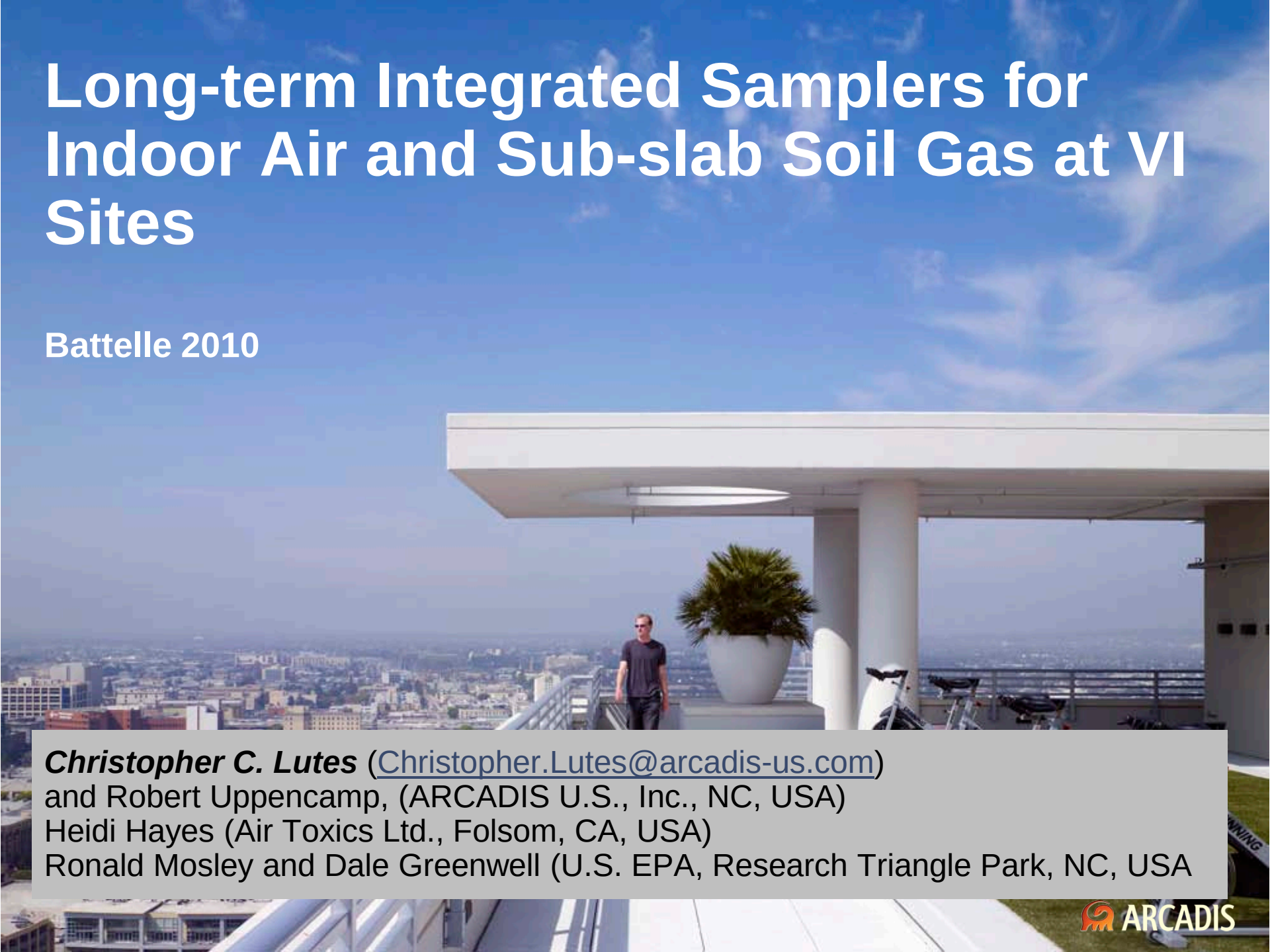

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Introduction to Passive, Diffusive, Sorbent Samplers

- Does not require a pump or flow meter so is easy to use
- Extensive literature/well accepted for occupational monitoring for relatively high concentrations, <24 hour durations
- Well developed for BTEX Environmental level monitoring in Europe, EU standard methods exist, less well tested for CAHs indoors
- Analytical extraction can either be thermal, or with a solvent like carbon disulfide

For more information see Brown, J. Environ Monit, 200, 2, 1-9.

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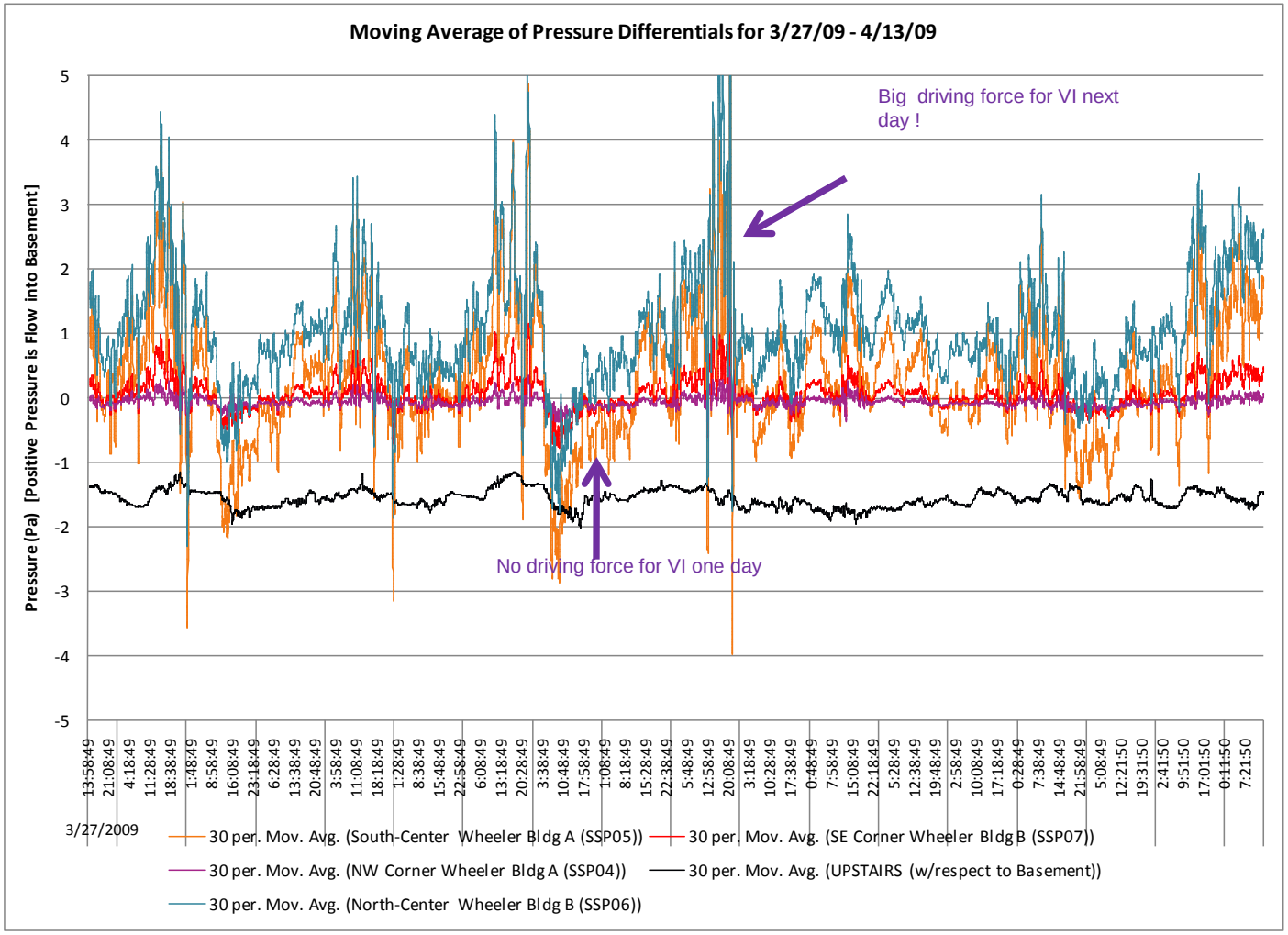
How Do Passive Samplers Work? Uptake Rates of Passive, Diffusive, Sorbent Samplers

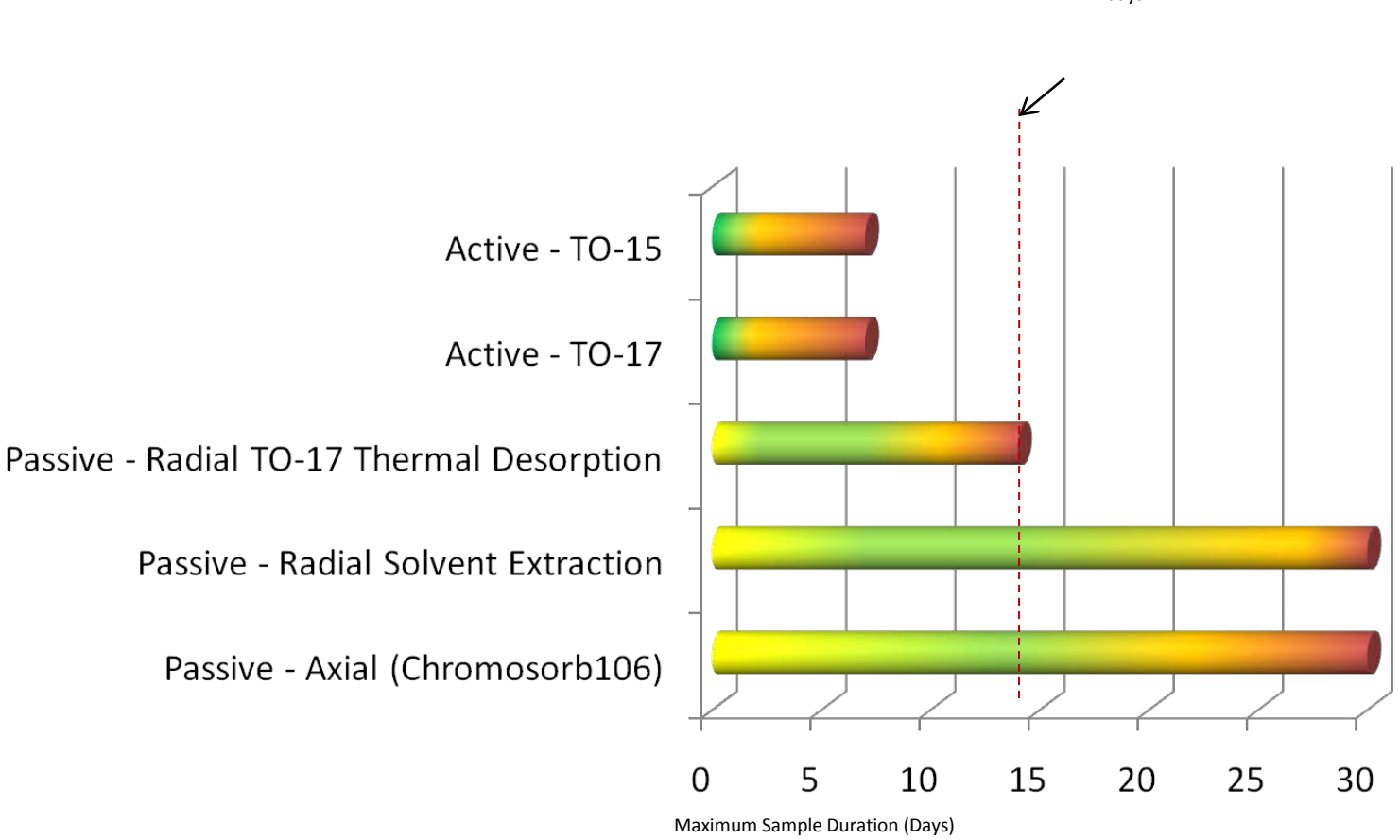
- Uptake rate = effective sampling volumetric flow rate
- Uptake rate is proportional to difference between the concentration of the analyte in the atmosphere outside the sampler and the concentration at the end of the diffusive path (ideally zero).
- Uptake rate also dependent on sampler geometry and face velocity.
- A decrease in the effective uptake rate can occur due to back-diffusion or from the analyte having a residual vapor pressure off the sorbent surface

For more information see Brown, J. Environ Monit, 200, 2, 1-9.

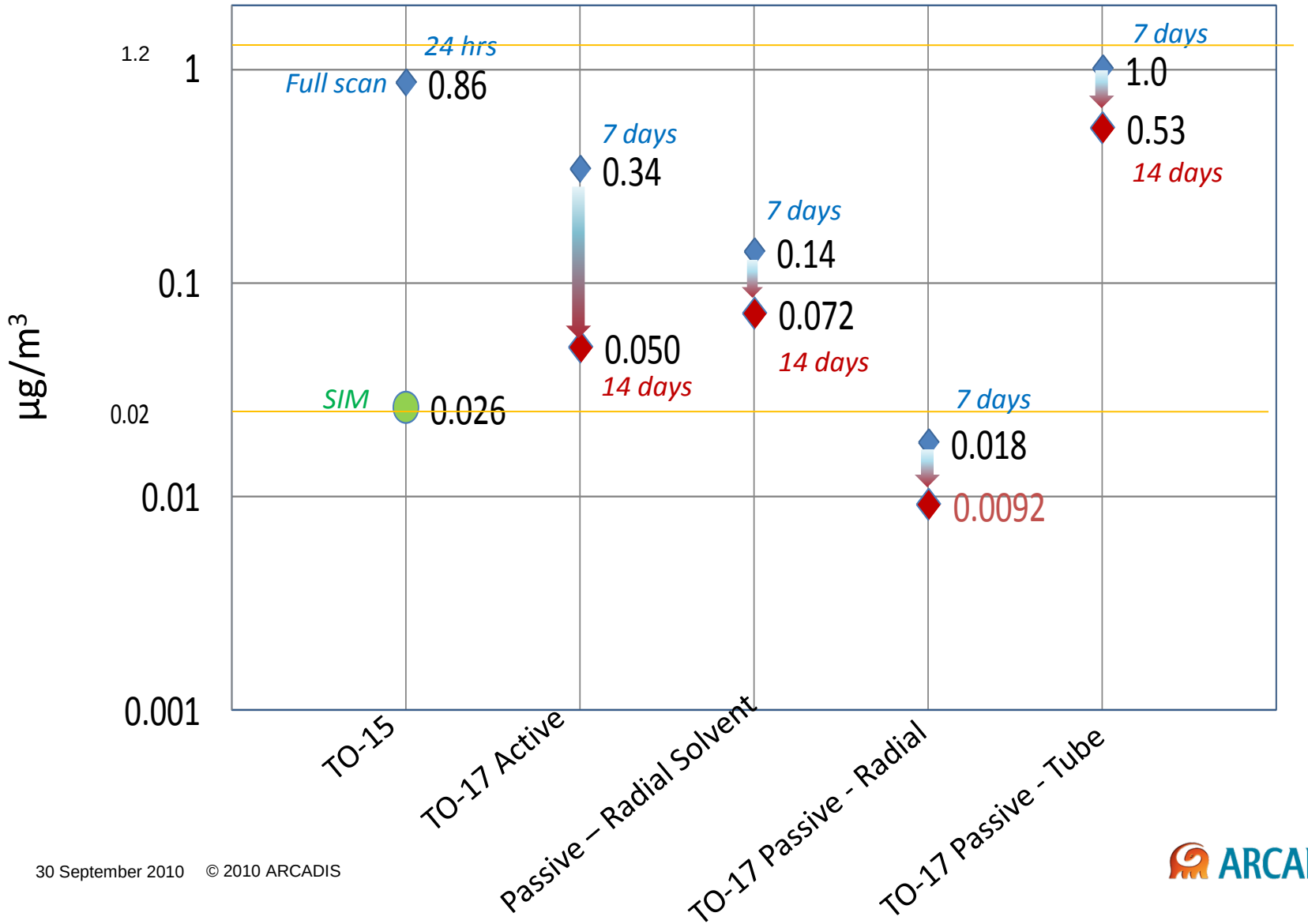
Why Use Long Term Integrated Samples? Differential Pressure Data Shows Why



Method Performance Comparison – Sample Collection Duration (TCE)



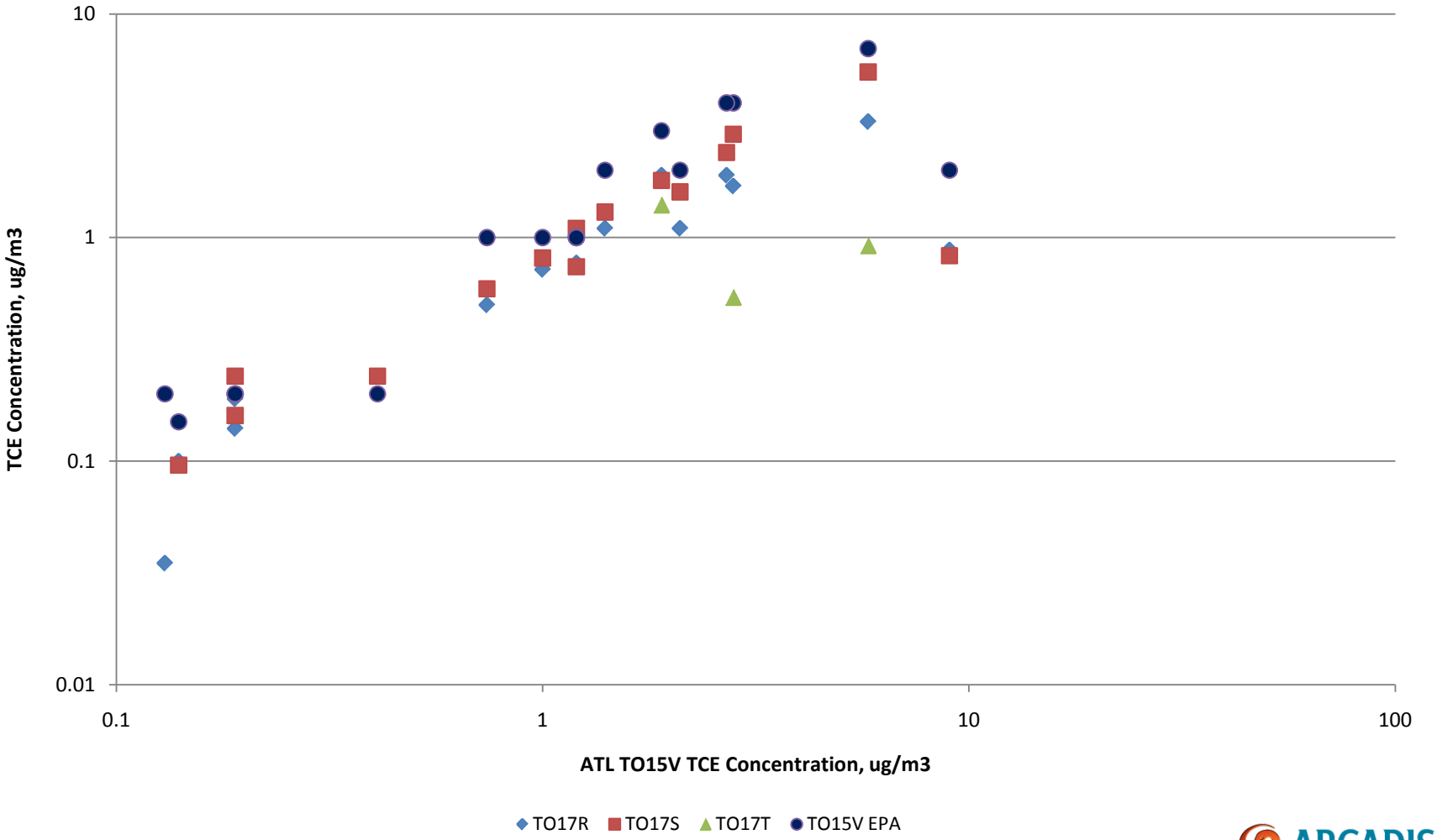
Method Performance Comparison – Reporting Limit (TCE) (In the Absence of Interferences)



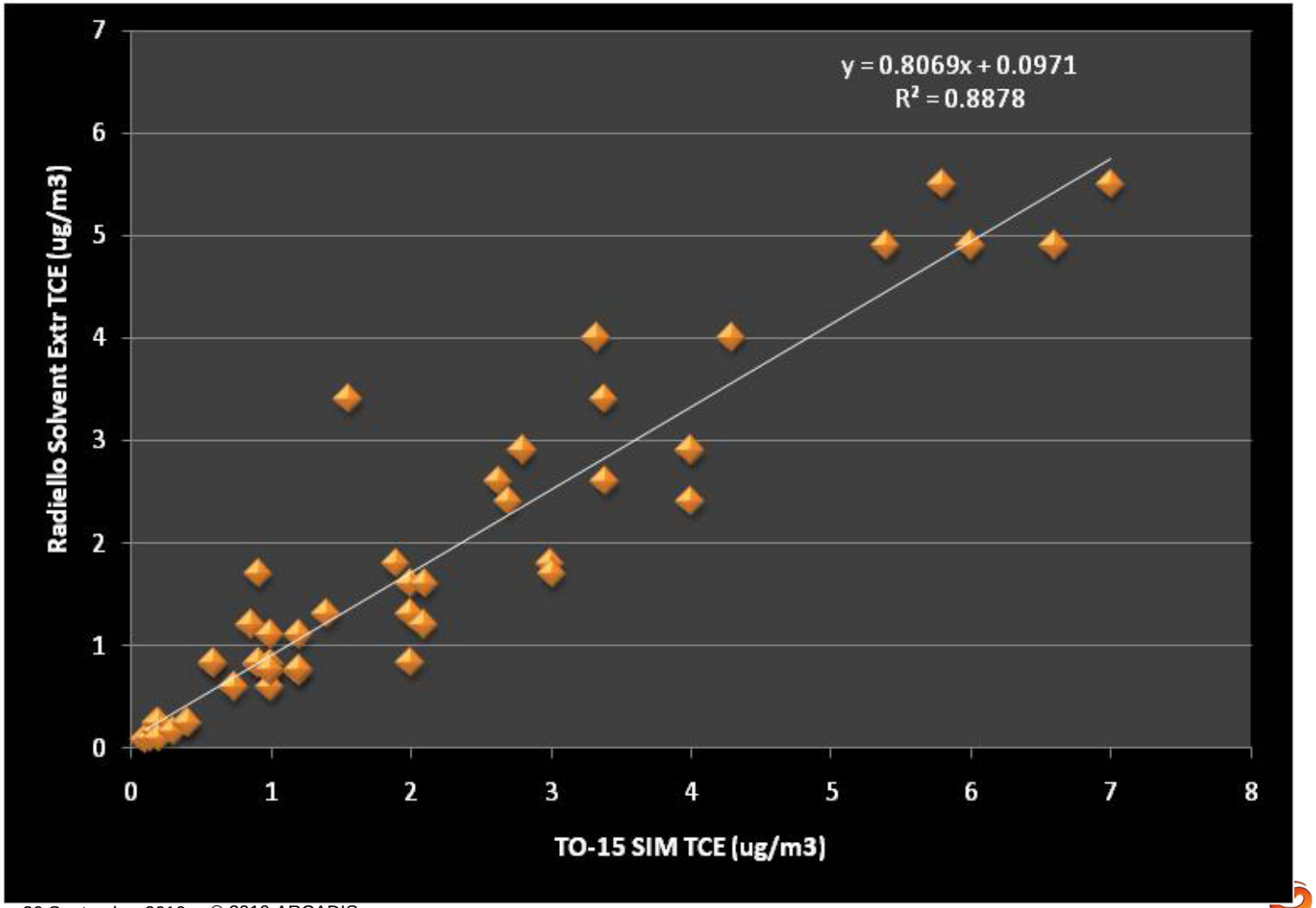
Moffett Field CA Testing – Indoor Air - Experimental Design

- Unoccupied, essentially matched, residential townhouse units, over a groundwater plume. TCE main constituent of concern
- Phase I – 20 units:
  - 14 day integrated in each unit, Three samplers solvent and thermal Extracted Radiellos, plus Tube
  - Compared to 2 short term TO-15 Summa samples in each unit, beginning and end
- Phase II – 8 units
  - 14 day integrated Solvent and Thermal Extracted Radiellos
  - Compared to 2 short term TO-15 samples

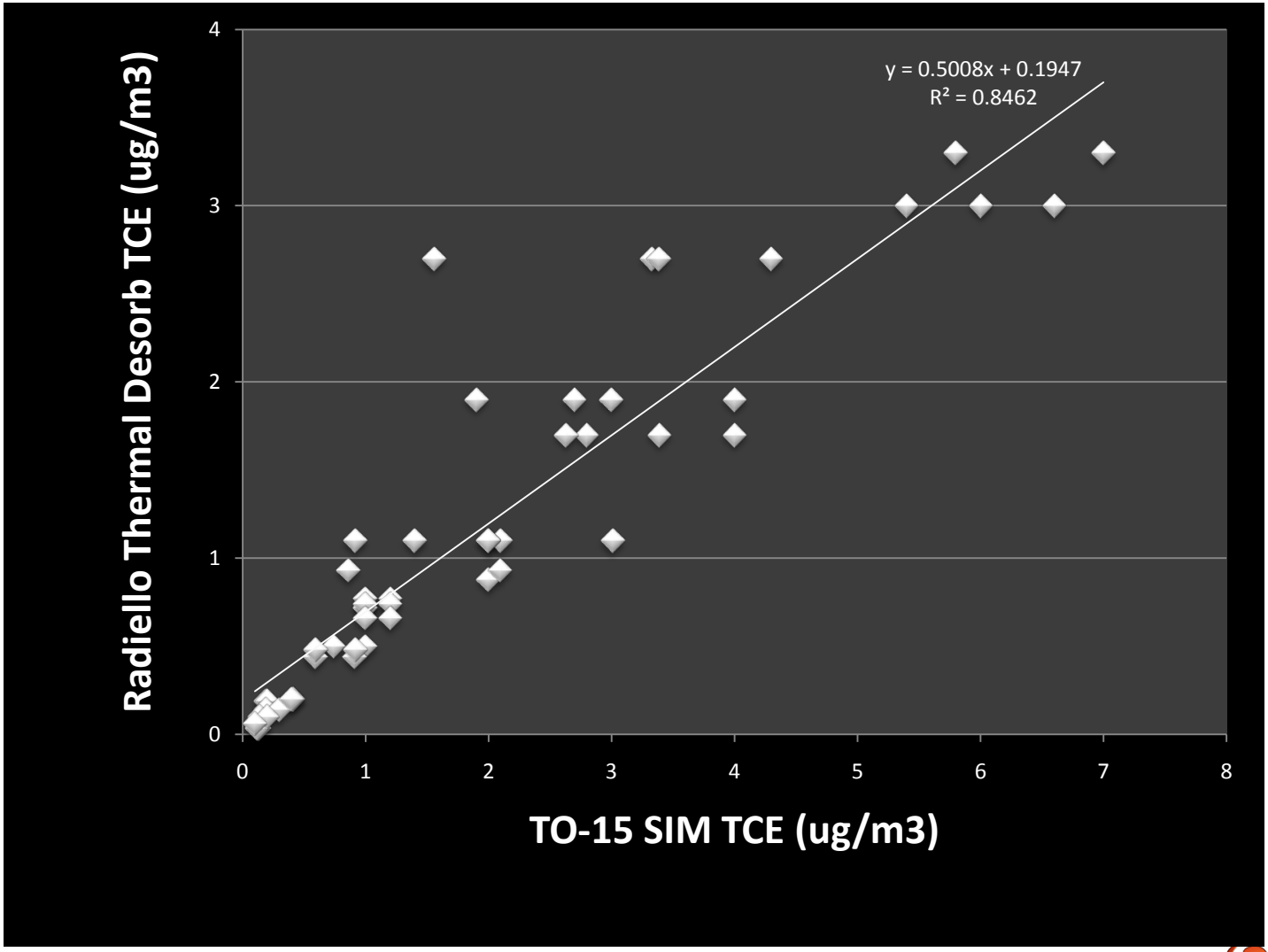
Moffett Field Phase I:
Air Toxics TO-15 TCE vs. Passive Methods and Alternate TO-15 Lab



Moffett Field Phases I and II: TO-15 Summa vs. Passive Radiello Solvent Extracted (some outliers not shown)

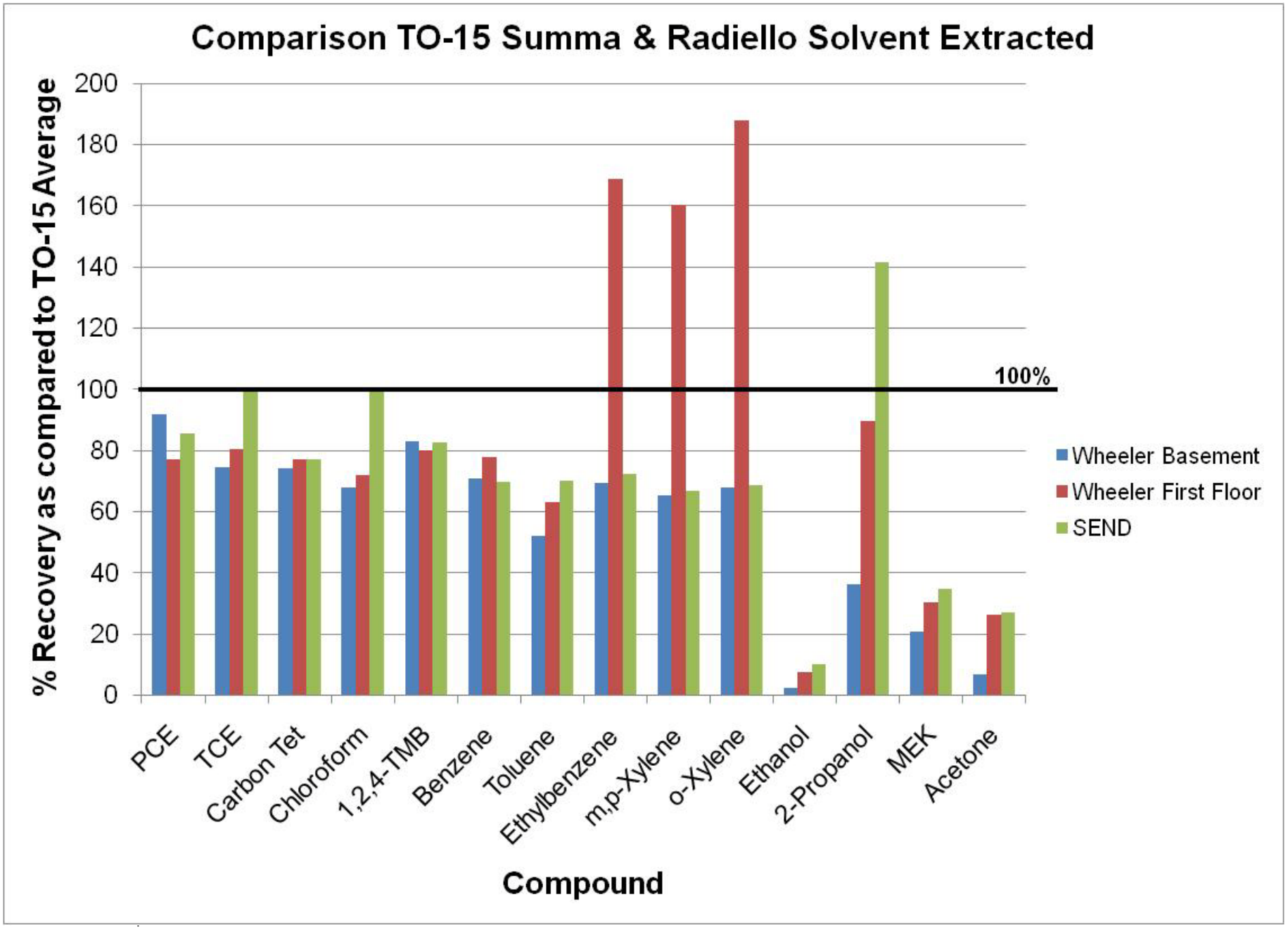


Moffett Field Phases I and II: TO-15 Summa vs. Radiello Thermal (some outliers not shown)



Wheeler Building, Indianapolis, Indoor Air Testing – Experimental Design

- Occupied mixed residential, office and art building; historic industrial building.
- Soil, groundwater and indoor sources of multiple volatile compounds
- Three sampling locations. Two week duration
- Solvent extracted Radiellos (duplicated at two locations)
- During those two weeks, three 24 hour Summa canisters at each location – beginning, middle and end


Comparison TO-15 Summa & Radiello Solvent Extracted
% Recovery as compared to TO-15 Average
200
180
160
140
120
100
80
60
40
20
0
100%
PCE
TCE
Carbon Tet
Chloroform
1,2,4-TMB
Benzene
Toluene
Ethylbenzene
m,p-Xylene
o-Xylene
Ethanol
2-Propanol
MEK
Acetone
Compound
Wheeler Basement
Wheeler First Floor
SEND

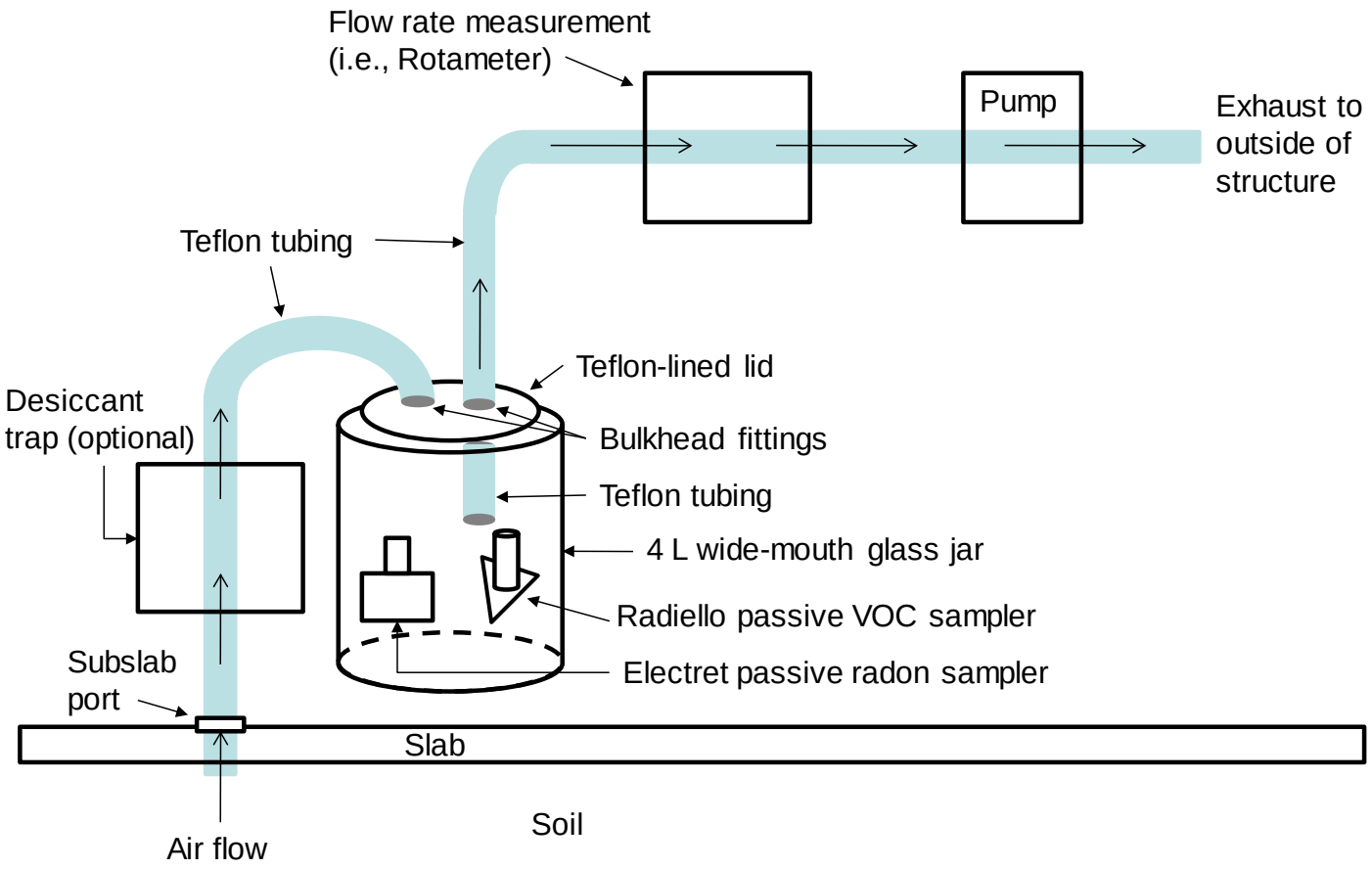
Indoor Air Testing Conclusions

- Radiello solvent extracted showed good agreement to TO-15 and precision at both sites for chlorinated compounds
    - Tends to give slightly lower concentrations
- Agreement poor for polar compounds – ethanol, MEK, MIBK and acetone
- Radiello thermal desorption correlated well with Summa TO-15 but gave noticeably lower concentrations – probably two weeks is too long
- Agreement poorer for tube type passive sampler

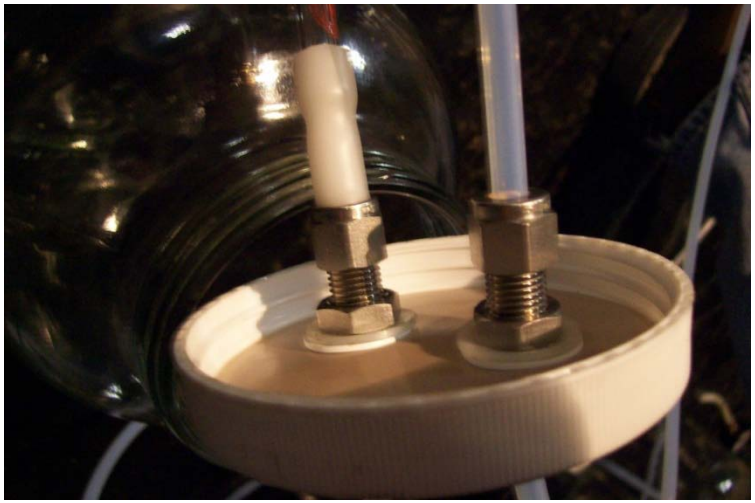
Current Tools for Subslab Soil Gas Sampling

- Most practitioners use TO-15 Summa canisters typically sampled at <200 ml/min for 5-30 min. In contrast risk assessment focuses on exposure periods from 24 hours to 30 years
- TO-17 active sorbent samplers also used typically with short collection times < 1 hour
- Existing passive soil gas methods give mass collected, but are not generally considered quantitative for concentration due to uncertainties about diffusion rates in varying soils (ITRC, 2007, page D-17)

Schematic Diagram of Integrating Sublab Sampler



Integrating Subslab Sampler – Mark I



Multiple Rounds of Testing of Integrated Subslab Sampler - Radon

Site	Dates	Experimental Design features	Radon Concentration, Standard Protocol (pCi/L)	Analytes	Radon Passive Result (% Recovery)
Moffett Field CA	9/16/08-9/30/08	Four separate ports sampled with one electrets sampler each. Compared to Pylon.	286-460	Radon and VOCs in the same jar	65-109 (Average 89%)
Indianapolis IN	9/16/2009-9/20/2009	Duplicate electrets in four parallel jars on same port, compared to Alphaguard; pairs with and w/o desiccant	3263	Radon sampler only	92-167% (Average 117%)
Indianapolis IN	10/1/2009 – 10/5/2009	Four samplers on one port – 2 w/desiccant 2 w/o desiccant duplicate samples per jar	3259	Radon and VOCs samplers in same jar	88 to 110 (Average 95)

Multiple Rounds of Testing of Integrated Subslab Sampler - TCE

Site	Dates	Experimental Design features	TCE TO-15 Concentration (ug/m3)	Analytes	TCE Passive Result (% Recovery)
Moffett Field CA	9/16/08-9/30/08	Four separate ports sampled with one sampler each, each sampler had one Radiello.	11 -1622	Radon and VOCs in the same jar	53-87% average 67%
Indianapolis IN	10/1/2009 – 10/5/2009	Four samplers – 2 w/desiccant 2 w/o duplicate samples per jar	5483	Radon and VOCs samplers in same jar	41 to 57
Indianapolis IN	11/10/09-11/13/09	Four radiello samplers in parallel one per jar	3250	VOC only	63 to 80
Air Toxics Ltd. laboratory	1/17/2010	Two Radiello samplers in one jar, test run for only 2 hours, compared to TO-15 Tedlar bags	4650	VOC only	95 to 120 average 107

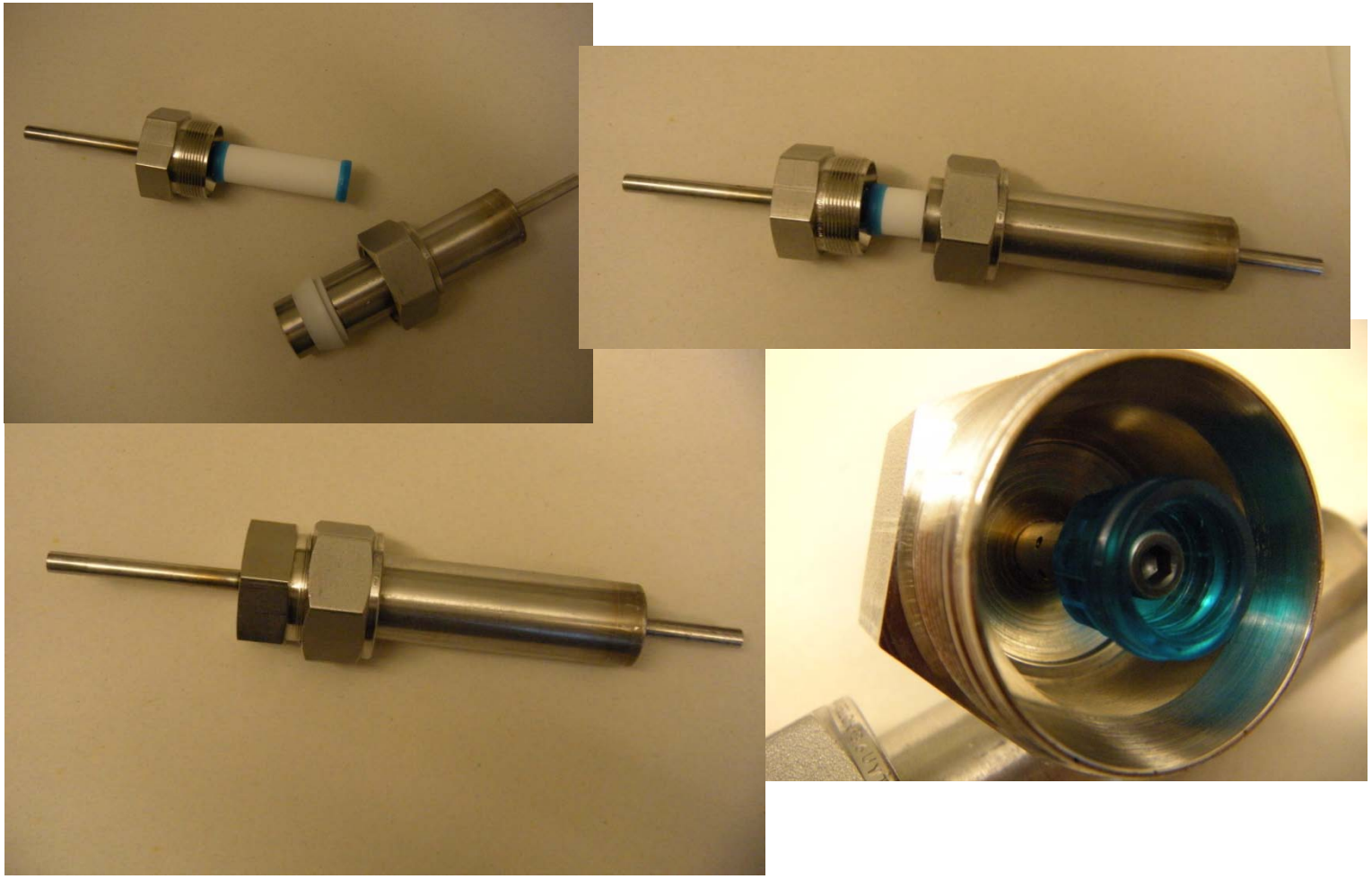
Conclusions of Integrating Subslab Sampler Test – Part 1

- Integrating subslab sampler using electret for Radon show good precision.
- Radon results agree well with alpha spectroscopy and Pylon scintillation cells
- Integrating Radiello samples for TCE showed good precision, but recoveries lower then method TO-15
- Lower recoveries for VOCs at moderately high humidity and high VOC concentrations are consistent with the literature on uptake rates.

Conclusions of Integrating Subslab Sampler Test – Part 2

- Separate static experiments were performed that showed VOC Radiello recoveries were considerably lower when radon Electret sampler was present.
- Electret chambers are constructed with carbon fiber filled polypropylene , probably causing VOC sorption. VOC and radon should be sampled separately
- Low face velocity may decrease uptake rate in Mark I design.
- We are also carefully reviewing the rotometer measurement of flow rate achieved through the Mark I sampler, which could be another source of error.

Alternate – “Mark II” Integrated Subslab Sampler Designed and Built



Comments –Comparing Passive Integrating Samplers as Compared to Summa Canisters

- It is difficult to accurately control Summa canister flows for >24 hour sampling times
- Uptake rates for passive samplers can vary at extended time intervals and high concentrations
- Flow rate variance with Summa's effects the representativeness over the exposure period but not the absolute concentration directly
- Uptake rate variance directly effects concentration for passive samplers
- Analytical errors similar for each method
- Passive generally somewhat lower cost
- Two week samples are a more realistic exposure measure

How Significant are Uptake Rate and other Method Errors Compared to Variations Expected in the True Value in VI Measurements?

- Schuver and Mosley reviewed the literature on radon sampling intervals
- “There are many known, but hard-to-predict variables that influence….variability in indoor air”
- “In general, the range of temporal variability decreases when using longer duration samples”
- “The vast majority of the short term (> 2 day) data lie within a factor of three (3x) of the long term (e.g. annual) average concentration
- For BTEX the change in uptake rate is 10-15% as sampling time goes from 1 to 4 weeks

Schuver and Mosley
http://secure.awma.org/presentations/VaporIntrusion09/Papers/Keynote.pdf

Also Brown, Diffusive Monitor #10 , page 4, 1998.

How Significant are Uptake Rate Variations for Passive Samplers vs. Analytical Uncertainty for Summa Canisters?

- For BTEX the change in uptake rate is 10-15% as sampling time goes from 1 to 4 weeks

- For comparison, in two recent TO-15 interlaboratory comparisons administered by ERA the acceptance range for tetrachloroethylene results were:
  - 4.31-22.3 ppbv (July -Sept 2009 study)
  - 31.6-74.1 ug/L (October – November 2007 study)

- For comparison in a 2007 TO-14/TO-15 study conducted by Scott Specialty Gasses the reported values for Toluene reported by 12 labs varied from 3.1-18.6 ppb

Overall conclusions –Comparing Passive Integrating Samplers as Compared to Summa Canisters

- Passive samplers agree well with Summa Canisters for Indoor concentrations for TCE and other chlorinated compounds
- Radillo solvent extracted samplers don’t agree as well for some polar compounds in our experiment
- Consider both sampling error and measurement error in selecting methods.

Acknowledgements

- Alana Lee, Katherine Baylor, Matthew Plate and Penny Reddy of EPA Region IX in conducting the Moffett field studies and analyzing data.
- Access provided by the US Army, Navy and NASA to that site
- The support of the staff of SEND, Mark Stewart, president as well as the residents of the Wheeler Arts Building in conducting studies in that building
- Ray Cody of US EPA Region I for information regarding the Raymark studies is also appreciated
- Kim Engler, Carl Singer and Lilian Abreu, ARCADIS


Imagine the result