

A LOW COST PASSIVE SAMPLING & ANALYSIS SOLUTION FOR AIR QUALITY SAMPLING

Lucas Neil, PhD, Air Quality Scientist
Phil Fellin, MSc, Manager, Air Monitoring & Analysis
Franco DiGiovanni, PhD, Senior Air Quality Modeller
Airzone One Ltd.

222 Matheson Blvd E, Mississauga, ON, L4Z 1X1
ineil@airzoneone.com, 905-890-6957 ext. 111

AirZOne
Comprehensive air quality Services

Typical Sampling Methods for Airborne Volatile Organic Compounds

- Continuous/instantaneous measurement instruments
- Integrative
 - Whole air grab samples
 - Whole air samples with flow controllers
 - Active sampling methods
 - Passive Sampling Devices (PSDs)

Electropolished Canister

- Instantaneous or Integrative
- Precise flow control issues
 - Limiting orifice
 - Canister fill time?
 - Calibration required
- Hysteresis effects (artefacts)
- Time Consuming
 - Costly



Active Samplers



- Requires pump
 - Time consuming calibration procedures
- Require power or limited battery life
- Noise issues
- Thermal Desorption Tubes – Hysteresis effects (artefacts)

Passive Sampling Devices (PSDs)



- No pumps = no calibration
- No pumps = no noise
- Small
 - Unobtrusive
 - Easy to transport
- Low training requirements

- e.g. 3M 3500 Organic Vapour Monitor

Active Samplers & Residential Surveys

- Multi-residence/area surveys are expensive & time consuming
 - Severely limits the number of homes
- Some government agencies recognized these limitations and undertook long term research programs to look at alternative approaches

PSD use in International Studies of Indoor & Outdoor Monitoring

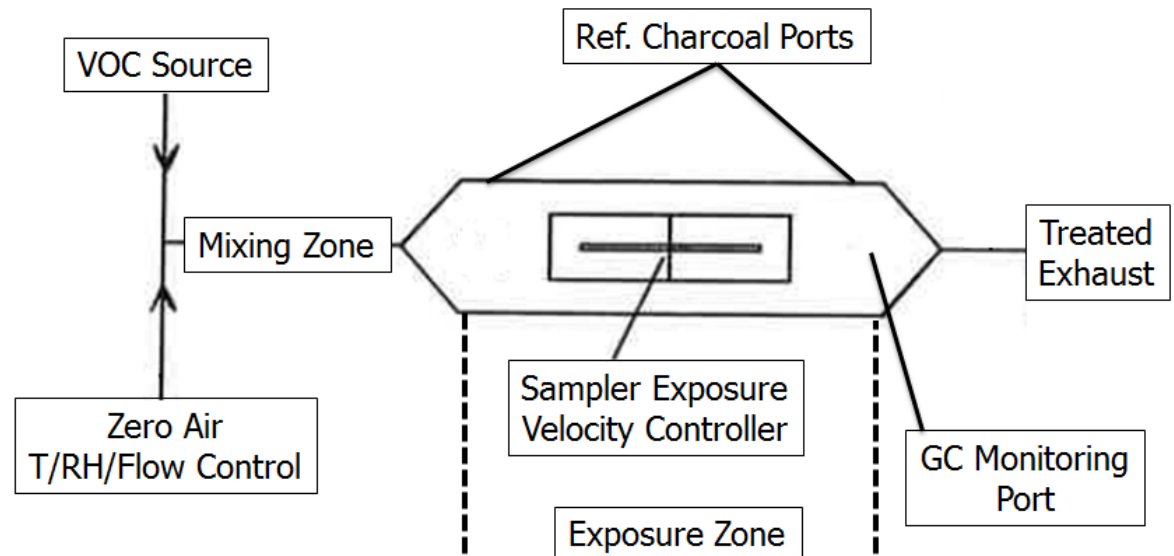
- Health Canada (1992/1993) – national VOC exposure survey (754 homes; 3M OVM 3500)
- Multimedia (air, water & food) exposure studies in Canadian residence and exposure assessment (3M OVM 3500 for VOCs, Ogawa Samplers for NO_x, O₃, SO₂)
- Vehicle exposure studies in urban areas (Winnipeg, Medicine Hat, Windsor, Ottawa & Stockholm [Sweden]) (3M OVM 3500 for VOCs; Ogawa Samplers for NO_x, O₃, SO₂)
- Alberta Cattle Health – 18,000 PSDs for ambient air VOC determination (3M OVM 3500)
- US Forestry Service (inorganic gases) – (Ogawa)
- Ambient air studies in Europe for VOCs & inorganic compounds – (Radiello)
 - MACBETH (Monitoring Benzene in European Towns and Homes)
 - RESOLUTION (high spatial resolution atmospheric monitoring to verify emissions reduction of ozone precursors foreseen by Auto-Oil program),
 - LIFE99ENV/IT/081, LIFE 00 ENV/IT/000005 & ARTEMIDE (High temporal resolution monitoring of VOC's).
- US & in California - (Radiello) for VOCs

Methodology for Development of PSDs

- Initially developed for occupational exposure monitoring in the 70's at ppm or mg/m³ levels
- Of interest for indoor air studies
 - ease of deployment
 - ease of acceptance by typical residents
- Required method improvement and validation

Fellin, Otson & Brice (1989)

- Test Atmosphere Generation System (TAGS)
 - Face velocities = stagnant, 0.5 m/s, 1.8 m/s
 - Concentrations, T, RH, co-pollutants, VOC mix
 - PSDs: 3M OVM 3500 & Pro-Tek G-AA (and others)
 - Co-located with charcoal tubes (reference)

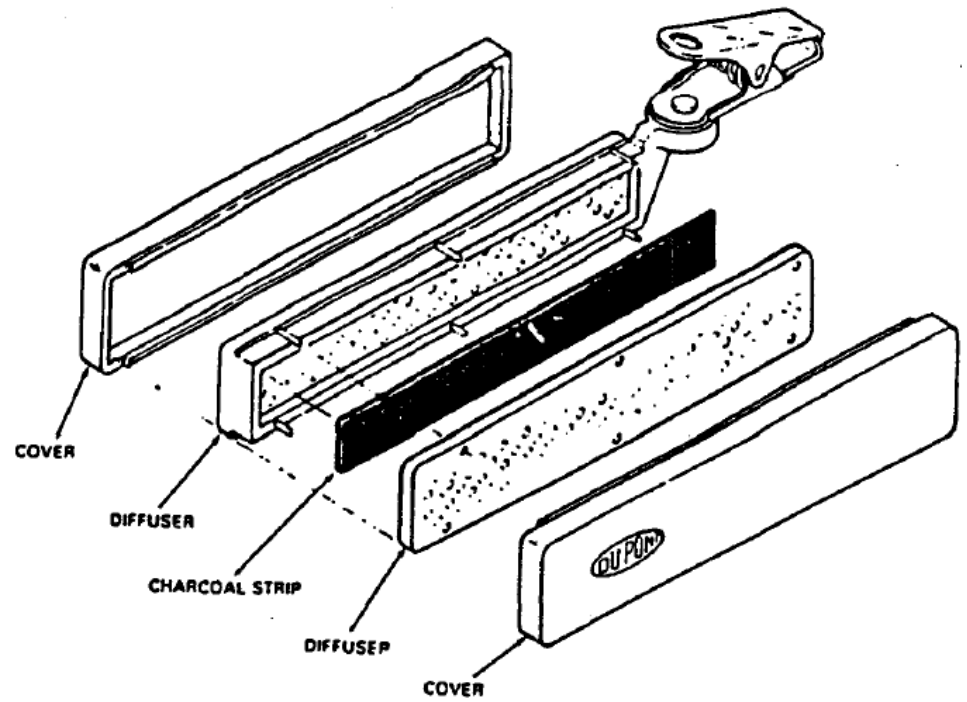


Otson & Fellin (1991)

- Pro-Tek G-AA (& other devices)
 - Sampling Rates increased significantly with face velocity
 - Precision was poorer at high face velocity
- 3M OVM 3500
 - Sampling rates varied by <10% with face velocity
 - $r = 0.95$ correlation coefficient (reference charcoal sorbent tube)

Otson (1990)

- Pro-Tek
 - significant variation in sampling rates with face velocity, T, RH, and analyte concentration
- These effects not seen with 3M OVM 3500
- 3M PSD chosen for full field test



Otson (1990)

- Indoor Field Test
 - 3M OVM 3500 and charcoal tube showed excellent correlation ($r > 0.95$)
 - MDL: 1 to 2 $\mu\text{g}/\text{m}^3$
 - Precision for duplicate determinations
 - +/- 7 to 10 % - 3M OVM 3500
 - +/- 5 to 14% - charcoal

Otson, Fellin & Barnett (1992)

- Duplicate, collocated 3M PSDs & charcoal tubes
 - 17 single family dwellings and 1 office
 - Samples collected in Summer and Winter
- 3M PSDs showed excellent correlation with charcoal reference ($r^2 > 0.96$)
- 3M PSD precision was slightly better than charcoal
- 3M PSD MDL estimated at $2 \mu\text{g}/\text{m}^3$

Development of Passive Sampling Devices

- Contracts with Health Canada to further develop 3M OVM PSDs
- Developments included:
 - Improvements to blank levels and detection limits
 - Improvements to linear dynamic range
 - Testing of performance under broader range of air velocity (< 0.1 to 5 m/s, RH 5 to 95%, concentrations 2 to 5,000 $\mu\text{g}/\text{m}^3$, and co-pollutants [NO_x , SO_2 , O_3])
 - Comparisons with reference methods
 - Solvent extraction & gas chromatography-mass spectrometry

Case Study – Residential Vapour Intrusion Study

- ~ 7,500 indoor samples collected from ~ 500 homes & businesses.
- Compounds of Interest
 - Trichloroethylene (TCE)
 - Perchloroethylene (PCE)
 - 1,1,1-trichloroethane (1,1,1-TCE)
 - 5 potential degradation



Sampling Methodology

- Originally used vacuum canisters with TD/GC/MS
 - Difficult to deploy
 - Issues with flow orifice & uneven filling
 - Reproducibility of duplicate measurements relatively poor
- Cumbersome, costly & long turn-around times

Method Validation for Vapour Intrusion Study

- Sample collected on PSD (3M OVM 3500)
- Replacing canister method with PSD approach required field trials to demonstrate performance
 - QA/QC involved validation vs vacuum canisters, charcoal tubes & thermal desorption tubes
 - Parallel sampling with canisters & thermal desorption tubes by MOECC

Method Validation for VI Study

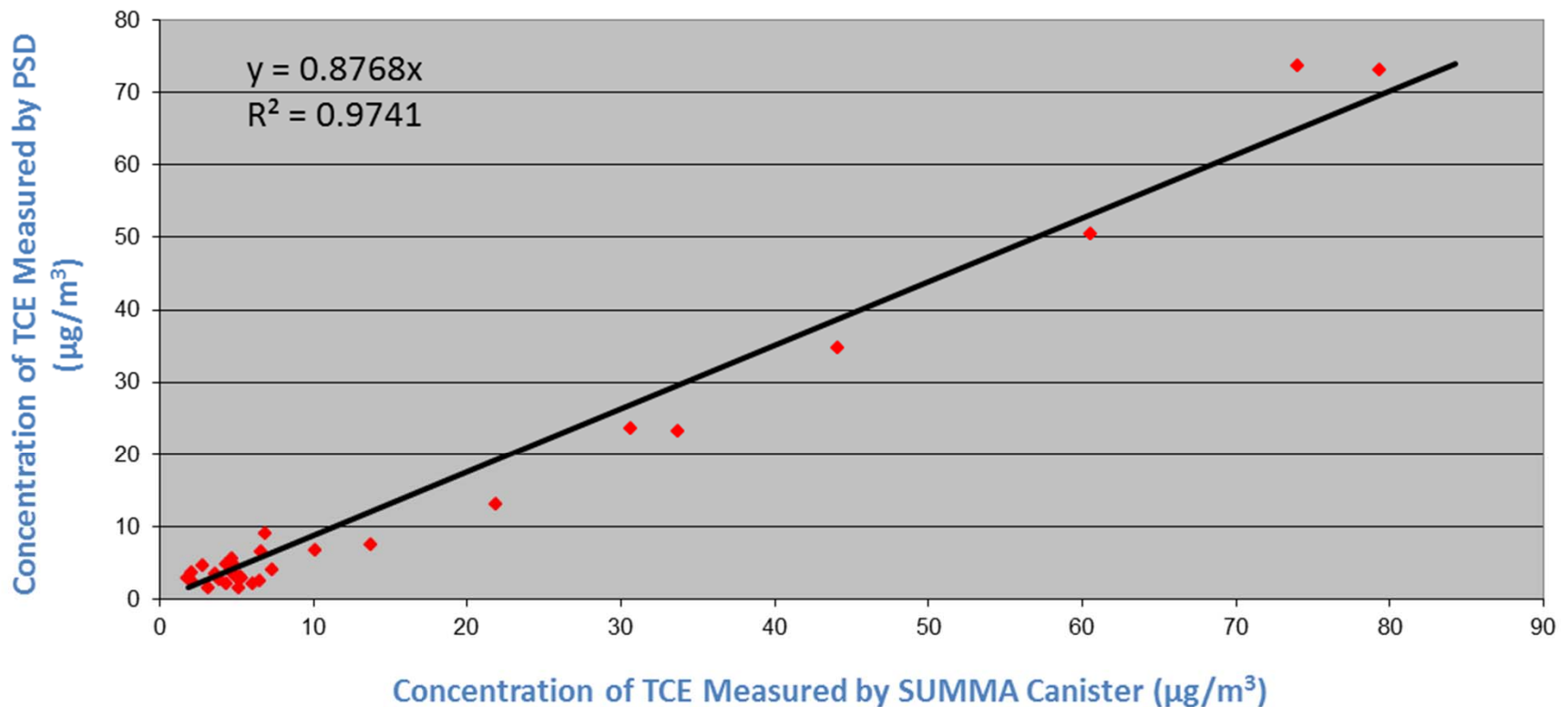
- Detection limit of $0.1 \mu\text{g}/\text{m}^3$
 - $1/5^{\text{th}}$ of target concentration for TCE of $0.5 \mu\text{g}/\text{m}^3$
- Internal QA/QC
 - Field blanks (one per batch of samples)
 - Field duplicates (1 in 10 or one per batch)
 - Lab replicates (1 in 10 and external reference standards)

Precision Based on Duplicate Sampling

Method	# Duplicates	Reproducibility %
3M OVM PSD	258	5.6
Charcoal Tubes	12	11.2
Vacuum Canisters	9	18.6

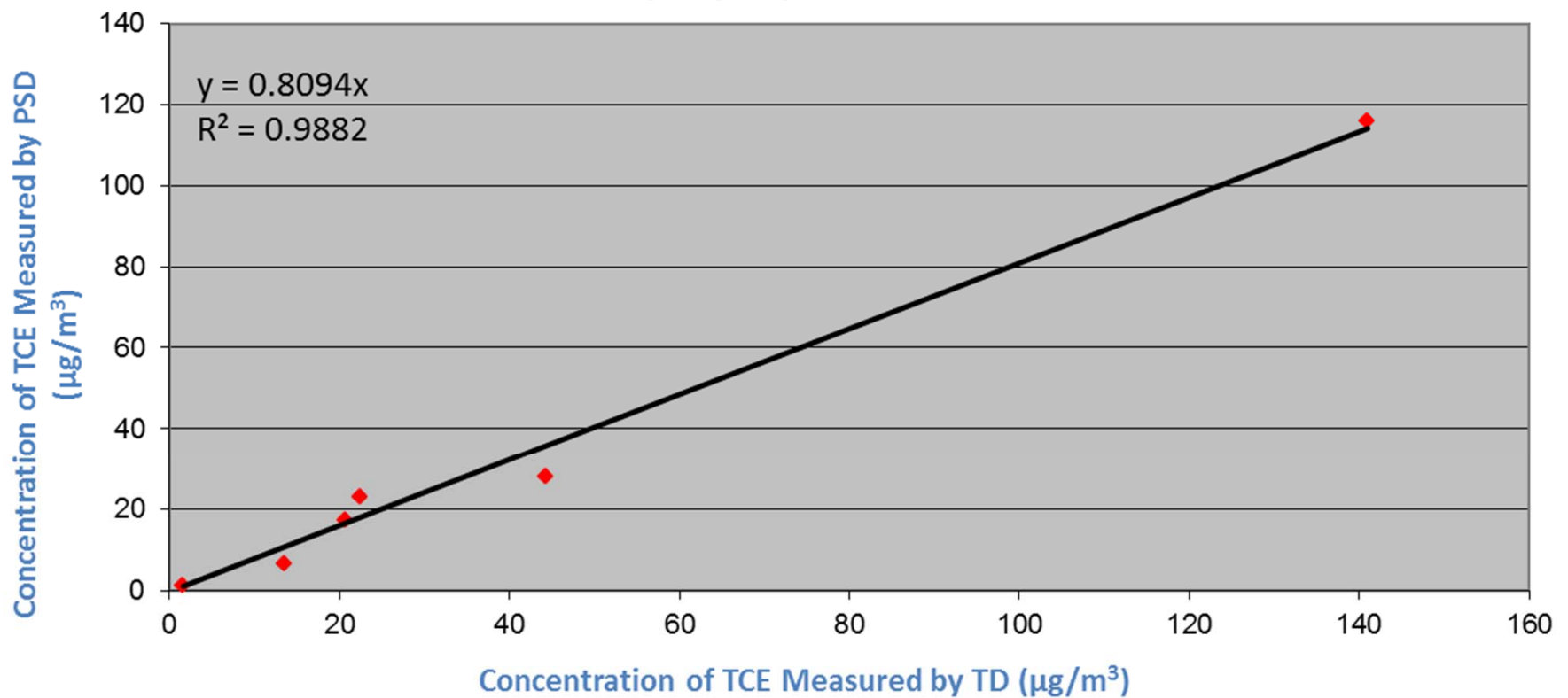
Comparison of 3M PSDs vs Canisters

TCE Concentrations Measured by SUMMA Canisters (Env. Can.) vs PSDs (Airzone)
(n=31 pairs)



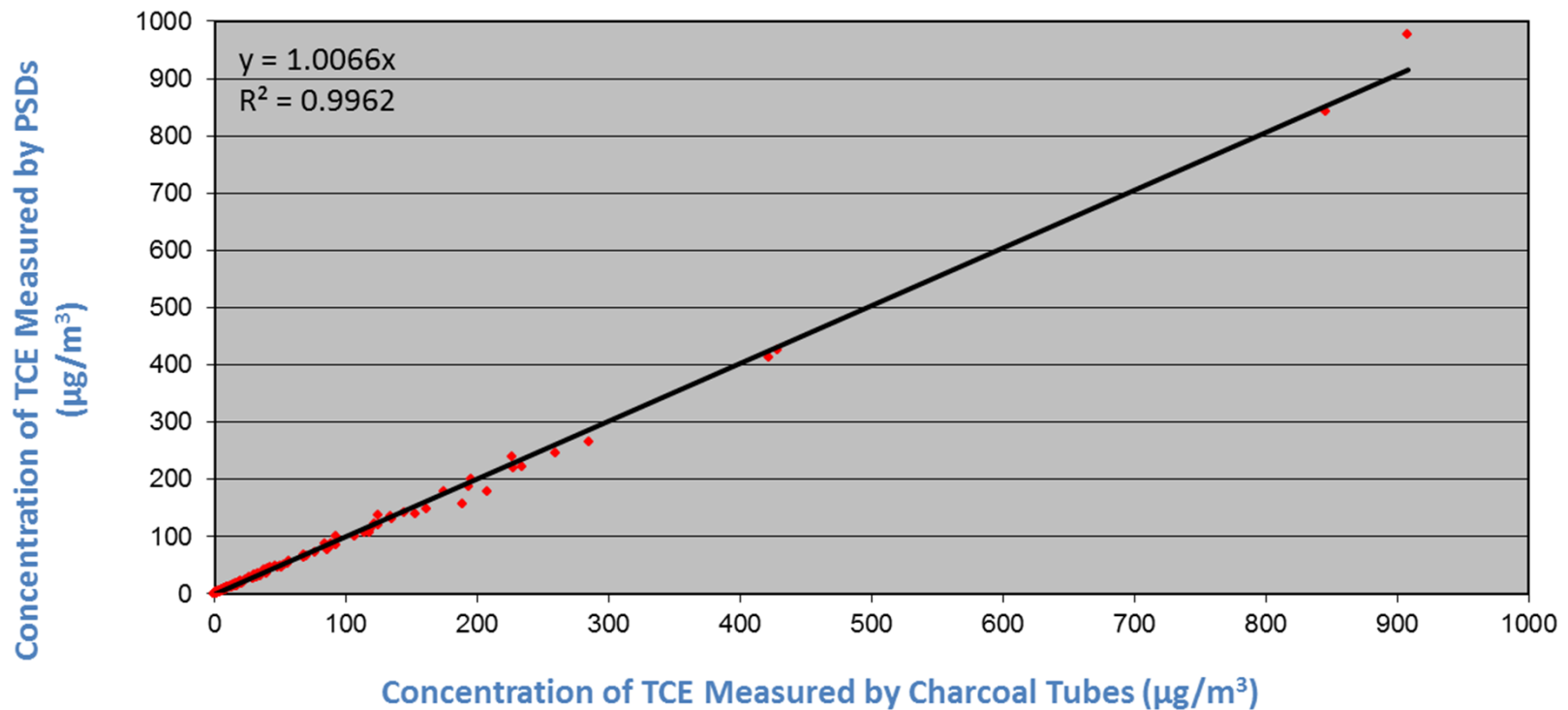
Comparison of 3M PSDs vs Thermal Desorption Tubes

TCE Concentration Measured by TD (MOECC) vs PSD (Airzone)
(n=6 pairs)



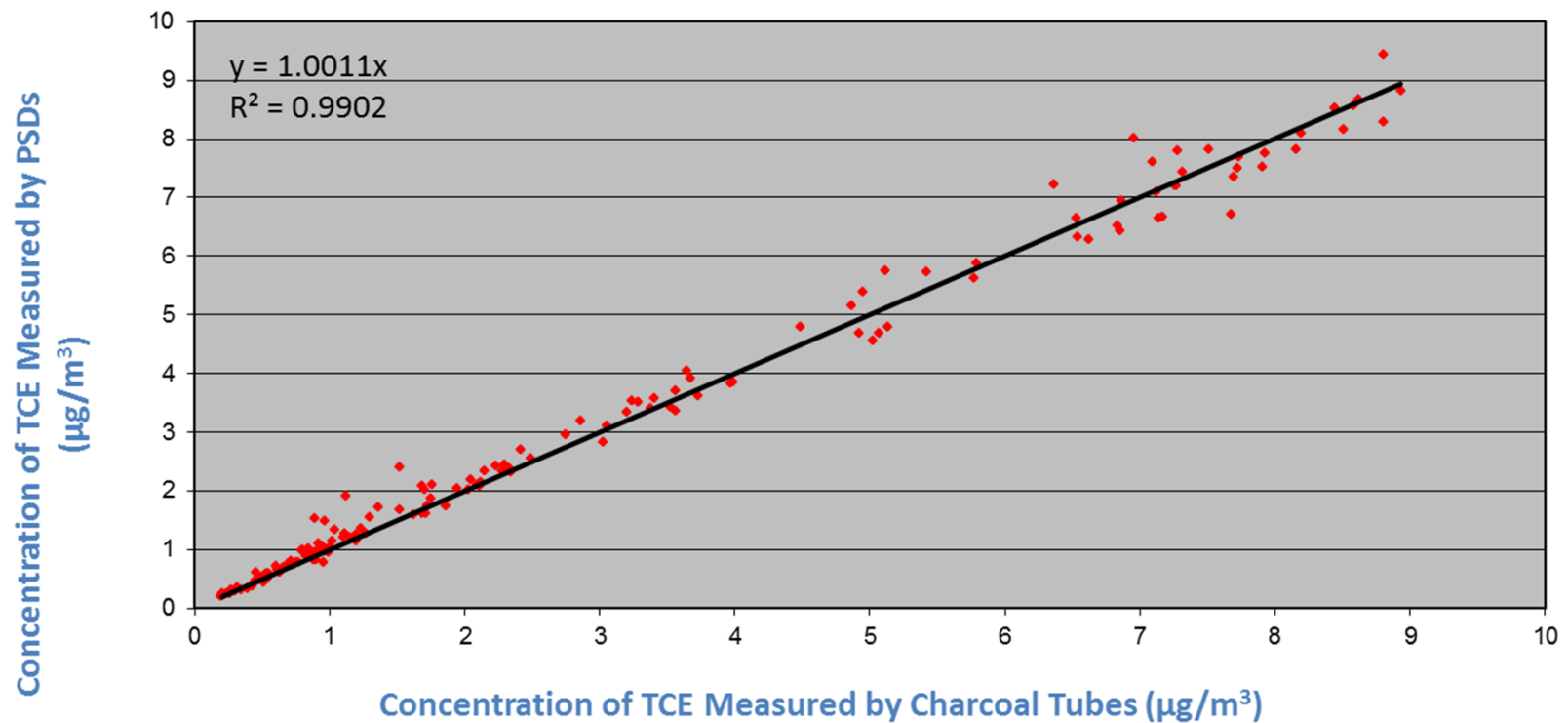
Comparison of 3M PSDs vs Charcoal Tubes Full Range of Measurements

Comparison of the Concentration of TCE Measured by Charcoal Tubes and PSDs
(All data < 1000 $\mu\text{g}/\text{m}^3$, n=247 pairs)



Comparison of 3M PSDs vs Charcoal Tubes Low Range Measurements

Comparison of the Concentration of TCE Measured by Charcoal Tubes and PSDs
($< 10 \mu\text{g}/\text{m}^3$, $n=154$ pairs)



Low Concentration Comparison In Ambient Air Samples

*Airzone charcoal and 3M PSD duplicate samples

TCE in $\mu\text{g}/\text{m}^3$	TD [MOECC]	Canister [Env. Can.]	Charcoal [Airzone*]	3M PSD [Airzone*]
Site 1 [outdoors]	1.46	1.25	1.51/1.55	1.39/1.51
Site 2 [outdoors]	0.060	0.064	<0.1/<0.1	<0.1/<0.1
Site 3 [NAPS outdoors]	0.050	0.038	<0.1/<0.1	<0.1/<0.1
Site 4 [outdoors]	0.060	0.068	<0.1/<0.1	<0.1/<0.1
Site 5 [indoors]	0.76	0.74	0.90/0.88	0.83/0.83
Site 6 [indoors]	0.21	0.21	0.27/0.30	0.32/0.29

Detection Limits

Volatile Organic Compounds	Method Detection Limit (MDL)		
	8 hrs	24 hrs	7 days
	µg/m ³		
Benzene	0.80	0.27	0.04
1,2-Dichloroethane	0.34	0.11	0.02
Ethylbenzene	0.46	0.15	0.02
1,1,2,2-Tetrachloroethane	0.17	0.06	0.01
Tetrachloroethylene	0.29	0.01	0.01
Toluene	0.55	0.18	0.03
Trichloroethylene	0.27	0.09	0.01
Xylene (m- +p-)	0.42	0.14	0.02
Xylene (o-)	0.36	0.12	0.02

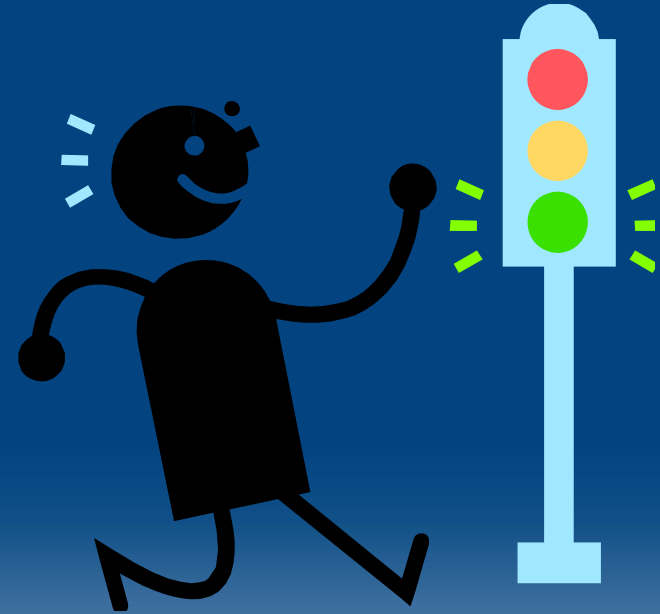
Summary

- PSDs have been accepted by provincial regulatory agencies for use in large scale vapour intrusion and ambient air studies
- PSDs offer several significant advantages
 - Small & unobtrusive
 - Silent & require no power
 - Cost effective
 - Wide range of sampling periods available
- Validation of additional target compounds (e.g., vinyl chloride) still underway
- Detection limits suitable for most applications

References

- Fellin P., R. Otson, D.L. Ernst (1989) A versatile system for evaluation of organic vapour monitoring methods. In Proc. - 8th World Clean Air Cong., L.J. Drasser & W.C. Mulder eds., The Hague, The Netherlands. 3: 675.
- Otson R. (1990) A Health & Welfare Canada program to develop personal exposure monitors for airborne organics at ug/m³. In Proceedings of the 1990 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, A&WMA, Pittsburgh, PA (483-488).
- Otson R., P. Fellin (1991) Effect of air velocity on sampling rates of passive monitors. In Proc. – EPA/AWMA Intern. Sympos. – Measurement of Toxic and Related Air Pollutants, AWMA, Pittsburgh, PA, (291-297)
- Otson R., P. Fellin, S. Barnett (1992) Field testing of a passive monitor for airborne VOCs. In Proc. – AWMA 85th Ann. Meeting, Kansas City. Pittsburgh, PA: (No. 92-80.07, Vol 5)
- Whitmore R.W., S.R. Williams, P. Fellin, R. Otson (1992) Design of a national study of residential air quality in Canada. In Proc. – Statistics and Environ. Of the 1991 Joint Statistical Mathematical Statistics (54th Ann. Meet.), Alexandria, VA
- Otson R., P. Fellin, R.W. Whitmore (1992) A national pilot study on occurrences of airborne VOCs in residences – design and progress. In Proc. – EPA/AWMA Internat. Sympos. – Measurement of Toxic & Related Air Pollutants. AWMA, Pittsburgh, PA (176-183)

The End
Thank You!



Questions/Discussion?

AirZOne
Comprehensive air quality Services