

# **REPORT ON:**

# Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion into Buildings

Submitted to: The Ministry of Environment May 2011

Submitted by: Science Advisory Board For Contaminated Sites in British Columbia

> Prepared under contract by Golder Associates Ltd. Burnaby, British Columbia



# **Soil Vapour Intrusion Guidance**

# Acknowledgements and Disclaimer

#### I. Acknowledgements

The report herein on *Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion into Buildings* is presented for the information and benefit of the Contaminated Sites community in British Columbia. It is hoped that it will be of interest to practitioners in other jurisdictions as well.

The work was supervised by the SABCS through a Task Force chaired by Dr. Ian Hers, SABCS Director. Golder Associates Ltd. were contracted to prepare the report and appendices. The Task Force was comprised of SABCS members Will Gaherty and Dr. Tiona Todoruk, and Eric Nickel of Shell Canada Ltd., and Colm Condon and latterly Peter Kickham of the BC Ministry of Environment. Dr. Glyn Fox was the BC Ministry of Environment liaison for the soil vapour intrusion project as a whole which included other reports. Special recognition is given to Dr. Ian Hers for his tireless efforts in bringing the work to completion. The SABCS has benefitted from his widely recognized expertise in the field of soil vapour intrusion.

The SABCS appreciates the review comments of the BC Environmental Laboratory Technical Advisory Committee chaired by Mark Hugdahl.

The SABCS acknowledges with appreciation grant funding from the government of British Columbia through the Ministry of Environment that has made this work possible.

# II Disclaimer

Practitioners and others with interests in contaminated sites should be aware that this report including the appendices has not been adopted in whole or in part by the Ministry of Environment of British Columbia. While every effort has been made to incorporate the best available science, it should be used solely as scientific review and commentary by the reader and applied in practice solely at the readers discretion and responsibility. This disclaimer is consistent with SABCS Policy. See also the disclaimer included in the main report (which also applies to the appendices) that is endorsed by the SABCS.

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#### **IV Request for Comments**

The Science Advisory Board for Contaminated Sites in British Columbia is soliciting comment on the documents, which together constitute a report to the BC Ministry of Environment on recommendations for the development of guidance on soil vapour intrusion into buildings for practitioners in British Columbia. Comments will be reviewed and compiled by the SABCS, and will be much appreciated.

Please send your comments to the Science Advisory Board for contaminated Sites by email or email attachment to <u>pwest@uvic.ca</u>. Comments received by June 30, 2011 will be most useful in further refinement of this work. However, comments at any time on SABCS work are always welcome.

May 12, 2011

# **REPORT ON**

# Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion into Buildings

Submitted to: Science Advisory Board for Contaminated Sites in British Columbia P.O. Box 3065, Stn. C University of Victoria Victoria, BC V8X 3V6

Submitted by: Golder Associates Ltd. 500 – 4260 Still Creek Drive Burnaby, BC V5C 6C6

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Science Advisory Board for Contaminated Sites



REPORT

# PREFACE

This report, prepared by Golder Associates Ltd. (Golder) for the Science Advisory Board for Contaminated Sites in British Columbia (SABCS), provides guidance on site characterisation for evaluation of soil vapour intrusion into buildings. As part of an initial project, Golder prepared soil vapour guidance for SABCS that was published in 2006; this document is a much needed update to that guidance that responds to recent advances in the science and new methods for soil vapour characterization. Soil vapour characterization remains highly relevant given the recent regulatory changes in British Columbia, where soil vapour standards and soil vapour technical guidance are now in-place, and in many other jurisdictions where vapour intrusion is considered an important exposure pathway.

The purpose of this guidance is to describe the framework, approach and methods for sampling, chemical analysis and data interpretation that should be considered when undertaking site characterization programs at contaminated sites where information obtained is used to evaluate potential human health risk from inhalation of soil vapour migrating into indoor air.

The guidance begins with an overview of the conceptual site model for soil vapour intrusion into buildings followed by approaches and methods for sampling and analysis of soil vapour and indoor air. While the focus of the guidance is characterisation of soil vapour and indoor air, the sampling and analysis of soil and groundwater media and collection of ancillary data in the context of vapour intrusion studies are also addressed. The guidance concludes with recommendations for data interpretation and analysis, including consideration of quality assurance/quality control issues.

This guidance for soil vapour and indoor air characterization is based on the current state of the science. As the practice of site characterization and risk assessment advances, there will be new developments for methods described in this guidance. These new advances should be incorporated in future updates to the guidance, as warranted.

This document was authored by Ian Hers, Ph.D., Eric Hood, Ph.D. and Jeanette Southwood of Golder Associates Ltd. Valuable technical advice, input and external peer review was provided by Dr. Paul Johnson of Arizona State University (2006 report), Dr. Matt Lahvis of Shell Research and Mr. Todd McAlary of Geosyntec Consultants. We also acknowledge the guidance of Dr. Paul West, Chairman of the SABCS, and very helpful input and review provided by the SABCS Task Groups that were established for each project, consisting of Mr. Scott Hannam, ALS Environmental, Inc. (Chair); Dr. Jean Cho; Dr. Glenn Harris; BC Ministry of Environment and Mr. John Lambert (Roster Steering Committee representative) for the 2006 guidance, and Mr. Will Gaherty, Pottinger Gaherty, Mr. Eric Nickel, Shell Canada, Mr. Colm Condon, BC Ministry of Environment, Mr. Peter Kickham, BC Ministry of Environment, and Dr. Tiona Todoruk, WorleyParsons for the update. There are also many unnamed individuals who have contributed to an improved understanding of soil vapour characterization whose input is gratefully acknowledged.

# DISCLAIMER

This report provides a scientific review and guidance on site characterization for evaluation of soil vapour intrusion into buildings and has been prepared by Golder Associates Ltd. for the Science Advisory Board for Contaminated Sites (SABCS) in British Columbia. Any use that a third party may make of this report, or any reliance on or decisions made based on it, are the responsibility of the third parties. We disclaim responsibility or consequential financial effects on site management, or requirements for follow-up actions and costs. This report should not be construed to represent BC Ministry of Environment policy on soil vapour intrusion.

The services performed as described in this report were conducted in a manner consistent with the level of care and skill normally exercised by other members of the science professions currently practicing under similar conditions, subject to the time limits and financial and physical constraints applicable to the services. This report provides professional opinions and, therefore, no warranty is expressed, implied, or made as to the conclusions, advice, and recommendations offered in this report. This report does not provide a legal opinion regarding compliance with applicable laws or regulations.

# TABLE OF CONTENTS

SECTION PAGE						
1.0 INTRODUCTION						
	1.1 Purpose					
	1.2	Soil Vapour Intrusion Pathway	1			
	1.3	Scope	1			
	1.4	Background and Need for Guidance				
	1.5	Report Structure	2			
	1.5	References	3			
2.0	CONCEPTUAL SITE MODEL FOR SOIL VAPOUR INTRUSION					
	21	Contamination Sources				
	2.1	Chemical Transfer to Vanour Phase (Volatilization)	6			
	2.2	Vadose Zone Fate and Transport Processes				
	2.5	2 3 1 Diffusion	0 8			
		2.3.1 Diffusion	Q			
		2.3.2 Vadose Zone / Advection	9 9			
		2.3.4 Riodegradation	10			
	2.4	Near-Building Processes for Soil Vapour Intrusion	10			
	2.1	Summary	10			
	2.5	Resources References and Links	11			
	2.0	Pafaranaas	11			
2.0		VIDEACE CUADACTEDIZATION FOD EVALUATION OF SOUL VAL				
5.0	SUBSURFACE CHARACTERIZATION FOR EVALUATION OF SOIL VAPOU					
	2 1	Contact Durnasa and Saana				
	2.1	Study Objectives	23			
	5.2 2.2	Makinla Lines of Friday of Content				
	3.3					
	3.4	Soil Vapour Sampling Approach and Design				
		3.4.1 Overview of Sampling Strategy				
		3.4.2 Considerations for Sampling Locations				
		3.4.3 Recommendations for Sampling Locations				
	2.5	3.4.4 When to Sample and Sampling Frequency				
	3.5	Soli Gas Probe Construction and Installation				
		3.5.1 Probes Installed in Boreholes				
		3.5.2 Probes Installed Using Direct Push Technology				
		3.5.3 Driven Probes				
		3.5.4 Use of water Table Monitoring wells as Soll Gas Probes				
		3.5.5 Subsido Soli Gas Probes				
	26	5.5.0 Probe Materials				
	3.0	2 C 1 Seil Ces Envillentier				
		3.6.1 Soll Gas Equilibration				
		2.6.2 Flow and Vacuum (Probe Performance) Uneck	45 15			
		2.6.4 Dependent of Sampling Equipment	43 10			
		2.6.5 Testing of Drohog and Someling Train for Looks and Short C				
		5.0.5 Testing of Probes and Sampling Train for Leaks and Short Cr	rcuiting48			

#### **Golder Associates**

		3.6.6	Sample Probe Purging and Sampling	49		
	3.7	Soil Ga	as Analytical Methods	52		
		3.7.1	Selection of Method	52		
		3.7.1	Field Detectors	53		
		3.7.2	Field Laboratory Analysis	53		
		3.7.3	Fixed Laboratory Analysis	56		
	3.8	Quality	Assurance / Quality Control Considerations	61		
		3.8.1	Data Quality Objectives	61		
		3.8.2	Detection Limits	61		
		3.8.3	Duplicate Samples	62		
		3.8.4	Field Quality Control Tests	62		
	3.9	Soil an	d Groundwater Characterisation	64		
		3.9.1	Groundwater Data	64		
		3.9.2	Soil Data	65		
	3.10	Ancilla	ary Data	65		
	3.11	Resour	ces and Weblinks	68		
	3.12	Referen	nces	68		
4.0	INDO	OR AIR	QUALITY TESTING FOR EVALUATION OF SOIL VAPOUR			
	INTR	USION	`	74		
	4.1	Contex	t, Purpose and Scope	74		
	4.2	Concer	ptual Site Model for Indoor Air	76		
		4.2.1	Background Indoor Air Concentrations			
		4.2.2	Building Foundation Construction			
		4.2.3	Building Ventilation	79		
		4.2.4	Building Depressurization and Weather Conditions	80		
		4.2.5	Mixing of Vapours Inside Building	81		
		4.2.6	Vapour Depletion Mechanisms	82		
	4.3	Develo	opment of Indoor Air Quality Study Approach and Design	82		
		4.3.1	Define Study Objectives	82		
		4.3.2	Identify Target Compounds	83		
		4.3.3	Develop Communications Program	85		
		4.3.4	Conduct Pre-Sampling Building Survey	86		
		4.3.5	Conduct Preliminary Screening.	86		
		4.3.6	Identify Immediate Health or Safety Concerns	87		
		4.3.7	Define Number and Locations of Indoor and Outdoor Air Samples.	87		
		4.3.8	Define Sampling Duration	88		
		4.3.9	Define Sampling Frequency	88		
		4.3.10	Preparing the Building for Sampling and Conditions During Sampli	ng91		
	4.4	Indoor	Air Analytical Methods	92		
		4.4.1	Air Analysis Using USEPA Method TO-15	93		
		4.4.2	Air Analysis using Passive Diffusive Samplers	93		
	4.5	Resour	ces and Weblinks	95		
	4.6	6 References				
5.0	DATA INTERPRETATION AND ANALYSIS					
	5.1	Data O	rganization and Reporting	.100		
	52	Data O	Puality Analysis	101		
		X				

#### **Golder Associates**

	5.3	Data Consistency Analysis	)2	
	5.4	Methods for Discerning Contributions of Background from Indoor Sources . 103		
		5.4.1 Further Evaluation	)9	
	5.5	References	)9	
6.0	ACRO	JYMS	11	
7.0	CLOSU	/RE	13	

# LIST OF TABLES

- Table 3.1
   Comparison of Different Media for Vapour Intrusion Investigations
- Table 3.2
   Comparison of Soil Vapour Measurement Locations
- Table 3.3Soil Gas Sampling Containers and Devices
- Table 3.4
   Summary of Common Soil Vapour Sampling and Analysis Methods
- Table 4.1
   Dominant Sources of VOCs in Residential Indoor Air
- Table 4.2Compilation of Indoor Air Quality Data from Canadian Studies
- Table 4.3Analyte List Recommended by CSAP Task Group
- Table 5.1
   Lines-of-Evidence for Evaluating Contribution of Background Indoor Air

   Sources
   Sources

# LIST OF FIGURES

Figure 2.1	Example of a Conceptual Site Model for Vapour Intrusion into a Residential
	Building
Figure 2.2	Fresh Water Lens
Figure 2.3	Interface Plume Development
Figure 2.4	Falling Water Table
Figure 2.5	Lateral Diffusion and Preferential Pathway
Figure 2.6	Conceptual Model for Aerobic Biodegradation
Figure 2.7	Stack and Wind Effect on Depressurization
Figure 3.1	Comparison of Deep and Shallow Soil Vapour Concentrations Measured at Casper Site
Figure 3.2	Temporal Soil Vapour and Groundwater Data for Endicott Site
Figure 3.3	Subslab Soil Vapour TCE Concentrations at Cortlandville House
Figure 3.4	Comparison of External and Sub-slab Soil Vapour Concentrations
Figure 3.5	Results of 3-D Oxygen-Limited Soil Vapour Transport Modeling for High
	Concentration Source (Cg = $100 \text{ mg/L}$ ) and Moderate Concentration Source (Cg = $20 \text{ mg/L}$ ) (from Abreu and Johnson, 2005)
Figure 3.6	Lateral Transect Concept
Figure 3.7	Soil Vapour Sampling Locations and Vertical Profile Concept
Figure 3.8	USEPA (2004) Recommended Design for Subslab Soil Gas Probes
Figure 4.1	Framework for IAQ Sampling and Analysis Program
Figure 4.2	Indoor Air Monitoring at Lowry AFB Site
Figure 4.3	Indoor Air Monitoring at Wall Township Site
Figure 4.4	1,1-Dichloroethylene Groundwater-Air Attenuation Factor at Redfield Site
Figure 5.1	Subslab Vapour to Indoor Air Attenuation Factors for Trichloroethylene –
	USEPA and Health Canada Database
Figure 5.2	Tri-Linear Plot Comparing Soil Vapour and Indoor Air Data from Petroleum
	Contaminated Site.
Figure 5.3	Evaluation of possible background influence using concentration ratios for
	Redfield site (N=344, data provided by Jeff Kurtz, Envirogroup)

# LIST OF EXHIBITS

- Exhibit 2.1 Conceptual Site Model Scenarios
- Exhibit 3.1 Lessons Learned from Extensively Monitored Sites
- Exhibit 3.2 Considerations for Cold Weather Sampling
- Exhibit 4.1 Indoor air Variability at Soil Vapour Intrusion Sites
- Exhibit 4.2 Preparation of Building for IAQ Sampling

# LIST OF APPENDICES

- Appendix A Checklist for Vapour Intrusion Conceptual Site Model
- Appendix B Modeling Study of Soil Vapour Sampling
- Appendix C Considerations for Shut-in Vacuum Testing
- Appendix D MGD-2002 Helium Detector Methane Interference Testing
- Appendix E Selected Laboratory Analytical Methods
- Appendix F Overview of Analytical Approaches for Hydrocarbon Fractions for Soil Vapour and Indoor Air
- Appendix G Field Instruments and Possible Interferences
- Appendix H Considerations for Cold-Weather Sampling
- Appendix I Duplicate Soil Vapour Sampling Methodology
- Appendix J Examples Indoor Air Quality Testing Program Building Surveys
- Appendix K Review of Passive Diffusive Sampler Method of Analysis
- Appendix L Suggested Operating Procedures

# 1.0 INTRODUCTION

#### 1.1 Purpose

As part of human health risk assessment, the soil vapour intrusion pathway is now commonly evaluated at contaminated sites where buildings are located near to subsurface volatile chemicals. The soil vapour intrusion pathway, unlike other potential exposure pathways, often requires that contaminant concentrations in soil vapour, and in some cases, indoor air be characterized as part of the risk assessment process. The purpose of this guidance is to describe the framework, approach and methods for sampling, chemical analysis and data interpretation that should be considered when undertaking site characterization programs at contaminated sites where information obtained is used to evaluate potential human health risk from inhalation of soil vapour migrating into indoor air.

# 1.2 Soil Vapour Intrusion Pathway

Soil vapour intrusion is the migration of volatile or semi-volatile chemicals from contaminated groundwater or soil into nearby buildings. When chemical releases occur near buildings, the subsequent volatilization of chemicals from the subsurface contamination can result in the intrusion of vapour-phase contaminants into indoor air. If the soil vapour intrusion pathway is complete, there may be the potential for unacceptable health risks to building occupants as a result of inhalation of vapours.

# 1.3 Scope

The focus of this guidance is sampling and analysis of soil vapour and indoor air, although other media and ancillary data are also addressed and only limited guidance on characterization of soil and groundwater quality at contaminated sites is provided. It is important that a sufficiently detailed investigation be completed such that an initial conceptual site model describing the soil vapour intrusion pathway can be developed prior to site characterization for soil vapour risk assessment purposes. While the context for this guidance is characterization of soil vapour intrusion, the concepts and methods described are applicable for any site assessment where soil vapour sampling is conducted.

The characterization methods described in this guidance are designed to provide the information needed to evaluate potential chronic health risks due to long-term exposure to vapours. The guidance does not address characterization to evaluate potential hazardous accumulation of gases and explosion or other safety risks. If the results of the soil gas sampling program indicate that there is an immediate safety concern, then emergency response or interim actions should be implemented, as required under provincial and/or federal regulations.

# 1.4 Background and Need for Guidance

Characterization of sites for evaluation of soil vapour intrusion can be relatively complex and may involve sampling of multiple media from different locations between the contamination source and the building. The development of technically defensible characterization programs requires an adequate conceptual site model, understanding of fate and transport processes, and knowledge of sampling methods and analytical protocols (where protocol is used in this document to refer to a test method or procedure it is not intended to have a legal meaning). There have been only a few comprehensive guidance documents that provide background information on science and a thorough evaluation of procedures (*e.g.*, API, 2005; EPRI, 2005; ITRC, 2007; TSERAWG, 2008; Golder, 2008). There continue to be new advances and methods for soil vapour characterization, which are important to reflect in the latest guidance. In British Columbia, soil vapour standards (that apply to air) were enacted under the Contaminated Sites Regulation (CSR) and Technical Guidance (TG) 4: Vapour Investigation and Remediation was issued in 2010. For details on soil vapour characterization, TG 4 refers practitioners to the SABCS guidance on soil vapour characterization.

To meet these needs, comprehensive guidance on sampling design and methods, chemical analysis and data interpretation is provided in this document. To provide the context for sampling programs, a significant focus of the guidance is the background needed for understanding of fate and transport processes and conceptual site model development. The guidance attempts to balance prescription of methods, where appropriate and needed, with description of a range of approaches and methods, recognizing that soil vapour characterization is an emerging field and that there may be multiple methods that will yield acceptable results. Several checklists and exhibits are included to provide practical tools for practitioners working in this area.

# 1.5 Report Structure

The report is organized as follows:

- Chapter 2 describes the conceptual site model for soil vapour intrusion and fate and transport processes for soil vapour; specific conceptual site scenarios are also provided for a range of possible site conditions;
- Chapter 3 provides guidance on soil vapour characterization, which includes sampling design, sampling methods and analytical protocols;
- Chapter 4 provides guidance on indoor air quality characterization, and includes specific aspects of the conceptual site model relevant to indoor air, preparatory tasks that are undertaken prior to indoor air sampling, indoor air sampling approaches and methods and analytical protocols, and;
- Chapter 5 describes the data organization, quality review and interpretation process.

#### 1.6 References

- American Petroleum Institute (API) (2005). Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface Vapour-to-Indoor-Air Migration Pathway at Petroleum Hydrocarbon Sites. November 2005.
- Electric Power Research Institute (EPRI), 2005. Reference Handbook for Site-Specific Assessment of Subsurface Vapor Intrusion in Indoor Air. Palo Alto, California, 1008492.
- Golder Associates Ltd. (Golder), 2008. Draft Guidance Manual for Environmental Site Characterization in Support of Human Health Risk Assessment (Volumes 1-3), prepared for Health Canada, September. Interstate Technology and Regulatory Council (ITRC). 2007. The Vapor Intrusion Pathway: A Practical Guide (VI-1) and Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios (VI-2). January http://www.itrcweb.org/Documents/VI-1.pdf. http://www.itrcweb.org/Documents/VI-1A.pdf
- Tri-Services Environmental Risk Assessment Working Group (TSERAWG) 2008. *Tri-Services Handbook for the Assessment of the Vapor Intrusion Pathway*. Rev. 4.0, 15 February (U.S. Air Force, U.S. Navy, U.S. Army).

# 2.0 CONCEPTUAL SITE MODEL FOR SOIL VAPOUR INTRUSION

A conceptual site model (CSM) is a visual representation and narrative description of the physical, chemical, and biological processes occurring, or that have occurred, at a contaminated site. The CSM should be able to tell the story of how the site became contaminated, how the contamination was and is transported, where the contamination will ultimately end up, and whom it may affect.

A well developed CSM provides decision makers with an effective tool that helps to organize, communicate and interpret existing data, while also identifying areas

#### **Conceptual Site Model (CSM)**

This chapter describes the CSM for soil vapour intrusion, starting with basic fate and transport processes. Using this understanding, several different CSMs are described in an illustrative manner in Exhibit 2.1. The outline and corresponding sections in the chapter are:

- Contamination sources (2.1),
- Chemical transfer to vapour phase (2.2),
- Vadose zone fate and transport processes (2.3),
- Near-building processes for soil vapour intrusion (2.4).
- A CSM checklist is provided in Appendix A.

where additional data is required. The CSM should be considered dynamic in nature and should be continuously updated and shared as new information becomes available (USEPA, 2002).

A CSM used for evaluating the risks associated with soil vapour at a contaminated site should provide a summary of the following:

- The source and distribution of contamination (history of contamination, present conditions, and potential future conditions);
- The receptors that could be exposed to the contamination (under both present and future land use scenarios); and;
- The fate and transport pathways between the contamination and the receptors (under both present and future land use scenarios).

An example of a CSM for soil vapour intrusion is shown in Figure 2.1 below.



# 2.1 Contamination Sources

Common contaminants of potential concern (COPCs) for soil vapour intrusion comprise a range of organic chemicals including petroleum hydrocarbons from fuel products, coal-tar or creosote, and chlorinated solvents.

Petroleum hydrocarbons are associated with fuels such as gasoline, jet fuel and diesel and are mixtures of hundreds of compounds. While often the focus of risk assessments are benzene, toluene, ethylbenzene and xylenes (BTEX), these compounds only represent a small fraction of hydrocarbon vapours and there may be other specific compounds of interest such as hexane, decane, trimethylbenzenes and naphthalene, depending on the fuel type. Typically, analytical tests for hydrocarbon vapours will also include hydrocarbon fractions based on carbon chain length (*e.g.*, F1 and F2 as defined in CCME (2008) or VPHv as defined by BC MoE (2009)) and aromatic and aliphatic fractions.

Coal-tar, associated with former manufactured gas plants (MGP), and creosote, associated with wood preservation, have similar organic contaminants of potential concern composed of monocyclic aromatic hydrocarbons, such as BTEX, and polycyclic aromatic hydrocarbons (PAHs). There is significant variation in the volatility and mobility of PAH compounds ranging from naphthalene, considered a semi-volatile, to five- and six-ring PAHs, which are essentially non-volatile. While some of the heavier PAH compounds are identified as COPCs for the vapour intrusion pathway based on conservative screening approaches, their vapour concentrations are relatively low and organic carbon partitioning coefficient (K<sub>oc</sub>) tend to be higher. As a consequence, the mobility of heavier molecular weight PAHs via soil vapour transport is limited and, for practical purposes, is not of potential concern for vapour intrusion. Similar considerations apply to other heavier molecular weight organic chemicals with similar properties.

Common chlorinated solvents include tetrachloroethylene or perchloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA), and associated breakdown products of biodegradation or abiotic transformation (*e.g.*, cis- and trans-1,2-dichloroethylene (cis-1,2-DCE), 1,1-dichloroethylene (1,1-DCE) and vinyl chloride). Chloroform is also relatively commonly detected in soil vapour, and is in some cases associated with anthropogenic sources (*e.g.*, leaking water mains) or natural sources. Most chlorinated solvents are relatively mobile and persistent within the unsaturated zone due to their relatively low solubility, high volatility and their resistance to degradation under aerobic conditions.

Inorganic chemicals such as mercury may also pose a potential vapour inhalation risk since elemental mercury has a high vapour pressure and mercury vapours are relatively toxic.

Soil gases such as methane, carbon dioxide and, in some cases, hydrogen sulphide, may be generated as a by-product of the anaerobic decomposition of organic chemicals such as petroleum fuels, waste material (*e.g.*, refuse) and/or native organic matter (*e.g.*, peat). The presence of these gases may represent a potential safety hazard through explosion or asphyxiation. Methane is explosive in the range of 5 to 15 percent by volume in air. Gas produced by microbiological activity may generate pressure gradients that enhance subsurface vapour migration through advection. Another source of pressure-driven gas is leaking natural gas lines. The CSM subsequently described in this chapter does not directly address assessment of sites where there is potential for significant pressure-driven gas flow.

# 2.2 Chemical Transfer to Vapour Phase (Volatilization)

Chemical transfer to the vapour phase may occur through partitioning of non-aqueous phase liquid (NAPL) present above the water table into soil gas ("vapourisation") or partitioning of dissolved chemicals in soil-water above the water table into soil gas ("volatilization"). The NAPL is referred to as a *primary source* of vapours while a dissolved phase plume is referred to as a *secondary source*. Soil contamination within the unsaturated zone also represents a potential source of vapours.

The distribution of NAPL relative to the water table will have a large influence on its potential to volatilize and migrate to indoor air. If the NAPL is situated below the water table, then volatilization will be relatively limited since, as subsequently discussed in this chapter, the mass

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transport through groundwater is relatively slow due to the low diffusion rate in water, and since vertical dispersion tends to be limited.

For a secondary source where chemicals are present only as a dissolved phase in groundwater, their distribution below the water table will also determine their potential to volatilize. If volatile chemicals are present near the surface of the water table, volatilization will readily occur. In contrast, if there is a layer of "clean" groundwater above contaminated water, then the rate of volatilization will decrease.

Equilibrium partitioning models are typically used to estimate the distribution of chemicals between different phases. Where NAPL is present above the water table, a two-phase model based on the vapour pressure of the chemical is used to estimate the soil vapour concentration. Raoult's Law accounts for partitioning for a multi-component mixture of chemicals, which is a function of the mole fraction and vapour pressure, as follows:

$$C_{v} = \frac{1000M_{W}XV_{P}}{RT}$$
[2-1]

where  $C_v$  is the soil vapour concentration (mg/m<sup>3</sup>),  $M_W$  is the molecular weight (g/mole), X is the mole fraction (dimensionless),  $V_P$  is the vapour pressure (atm), R is the gas constant (m<sup>3</sup>-atm/K-mole), T is the temperature (K), and 1000 is a unit conversion factor (mg/g).

For dissolved chemicals in groundwater, the Henry's Law constant is typically used to estimate the soil vapour concentration ( $C_v$ ) in equilibrium with water, as follows:

$$C_v = 1000C_g H'$$
 [2-2]

where  $C_g$  is the groundwater concentration (mg/L), H' is the dimensionless Henry's Law constant, and 1000 is a unit conversion factor (L/m<sup>3</sup>). Since it is not possible to obtain a soil gas sample at the water table (*i.e.*, due to the capillary transition zone), the measured soil vapour concentration should be lower than that predicted using the Henry's Law constant. This is because there will be attenuation of chemical concentrations by diffusion (and possibly biodegradation) within the capillary fringe and transition zone between the water table and region where there are continuous gas-filled soil pores. The attenuation within the capillary zone has implications for soil vapour intrusion modeling and comparison of measured and predicted soil vapour concentrations.

Where there is soil contamination, but no NAPL, a three phase model<sup>1</sup> for partitioning between sorbed, aqueous, and vapour phases can be used to estimate the soil vapour concentration, as follows:

<sup>&</sup>lt;sup>1</sup> A four-phase model for partitioning between the sorbed, aqueous, soil-air and NAPL phases has recently been developed and applied to the vapour intrusion pathway (Park and San Juan, 2000). The four-phase model better accounts for mass and volume conservation between all four phases and may enable more accurate estimation of mole fraction in the NAPL phase, for a multi-component mixture.

$$C_t = C_w \left( K_d + \left( \theta_w + \frac{\theta_a H'}{\rho_b} \right) \right) \text{ where } K_d = K_{oc} f_{oc}$$
[2-3]

where  $C_t$  is the total soil concentration (mg/kg),  $C_w$  is the soil-water concentration (mg/L),  $K_{oc}$  is the organic carbon-water partition coefficient (L/kg),  $f_{oc}$  is the fraction of organic carbon (dimensionless),  $\theta_w$  is the water-filled porosity (dimensionless),  $\theta_a$  is the air-filled porosity (dimensionless), H' is the Henry's Law constant (dimensionless) and  $\rho_b$  is the bulk dry density (kg/L). If, under equilibrium, the three phases become saturated by the chemical, then the remainder of the chemical will be in its pure form (*i.e.*, NAPL). Guidance on calculation of the soil saturation ("Csat") concentration for NAPL is provided in USEPA (1996).

For non-ionizing organic chemicals, a linear equilibrium partitioning model is widely used to predict absorption of organics into native organic carbon. Studies have shown that the sorption of organics by soils is highly correlated with the  $f_{oc}$  (*e.g.*, Chiou *et al.*, 1979; Hassett *et al.*, 1980; Hassett and Banwart, 1989), provided the  $f_{oc}$  is above a critical level. USEPA (1996) suggests that when  $f_{oc}$  is below about 0.001, adsorption to inorganic mineral surfaces becomes important. While soil partitioning models are well established, the accuracy of such models to predict soil vapour concentrations is poor. Therefore, it is generally not good practise to try to estimate soil vapour concentrations from soil concentration data. Instead, they should be predicted from groundwater data using Henry's Law constant (when appropriate) or directly measured.

#### 2.3 Vadose Zone Fate and Transport Processes

Fate and transport processes in the vadose zone that influence the movement of chemicals from a contamination source toward a building include: diffusion; advection; dispersion; partitioning between soil, water and gas phases (sorption, vapourisation, and volatilization); and, biodegradation reactions. Several of the fate and transport processes that influence soil vapour intrusion are conceptually shown in Figure 2-1. In this example, volatilization is occurring just above the top of the capillary fringe to create soil vapours. These vapours are subsequently transported upwards toward the ground surface via diffusion. Closer to the building, if the building is depressurized relative to atmospheric pressure, advective soil gas transport may be the dominant process. The rate of volatilization at the contamination source is controlled by the mass flux rate for chemical migration away from the source. This will vary temporally as a result of fluctuations in various factors such as moisture content, temperature and elevation of the water table.

#### 2.3.1 Diffusion

Diffusion is the movement of molecules from an area of higher concentration to an area of lower concentration, as influenced by their kinetic energy. The rate that a chemical will diffuse is a function of the concentration difference, or gradient, and the compound- and temperature-dependent diffusion coefficient. The mass flux, J (M/L<sup>2</sup>-T), is calculated by Fick's Law, as follows:

$$J = -D \frac{eff \partial Cv}{\partial z}$$
[2-4]

Where  $D^{eff}$  is the effective diffusion coefficient (L<sup>2</sup>/T),  $C_{\nu}$  is the soil vapour concentration (mass/volume of gas) and z is the distance over which the concentration change is measured (L). The diffusive flux is less in soil than in a gas-filled volume as a result of the tortuosity or non-linear migration path for diffusing gas species. Mathematically, this is expressed as the effective diffusion coefficient, typically estimated from the Millington-Quirk relation (Millington and Quirk, 1961):

$$D^{eff} = \frac{D_a \theta_a^{3.33}}{\theta^2} + \frac{D_w}{H} \frac{\theta_w^{3.33}}{\theta^2}$$
[2-5]

Diffusion coefficients in air ( $D_a$ ,  $L^2/T$ ) are about four orders-of-magnitude higher than in water ( $D_w$ ,  $L^2/T$ ); therefore, diffusion is much faster through the air-filled soil pores, than through water-filled soil pores, and the second term in Equation 2-5 tends not be important except under nearly saturated conditions or for compounds with very low Henry's Law constant (*i.e.*, dimensionless *H*' less than 0.001). When contamination is limited to dissolved chemicals in groundwater, diffusion through the capillary fringe is often the rate-limiting process because the moisture content in the capillary fringe is high, and may even be completely saturated. The thickness of the capillary fringe increases with decreasing soil grain size. Diffusion rates may also be highly sensitive to the presence of fine-grained, high moisture content soil layers within the vadose zone. There may also be a "rain-shadow" below a building with locally drier soils beneath the building (although drains and gutters may influence the soil moisture distribution).

#### 2.3.2 Vadose Zone Advection

Soil gas advective transport can occur as a result of fluctuations in atmospheric pressure (*e.g.*, barometric pumping), water movement, water table fluctuations, and density gradients due to composition and temperature variations (soil gas advection due to building depressurization is discussed in Section 2.4). For most geologic environments, diffusion is the dominant vadose zone transport process; however, soil gas advection can be important where there are high permeability, relatively deep unsaturated zone deposits (*i.e.*, tens of metres deep) or where methanogenesis and gas generation is significant. Choi and Smith (2005) through a modeling study found that pressure-driven advective flux increased for deep, drier, permeable deposits; nevertheless, for all combinations of scenarios, the diffusive flux was at least one order-of-magnitude greater than the advective flux. Where there are relatively high soil gas advection rates, dispersion may also be important. Dispersion is a mixing process that is caused by small-scale variations in air velocities in soil. The effects of these velocity variations are similar to the effects of diffusion (Auer *et al.*, 1996).

Soil gas advection also occurs when there is methane generation at sites with petroleum releases or native organic matter and may overwhelm diffusion depending on type of contamination (*e.g.*, petroleum containing ethanol).

#### 2.3.3 Sorption

As soil vapours migrate away from contamination source zones, the transport of soil vapours will be retarded due to sorption to the soil matrix and transfer of chemicals into soil water. Soils with higher native organic carbon will tend to have a greater sorption capacity. While partitioning into soil water will occur rapidly, for some chemicals biodegradation may occur simultaneously to reduce the concentration in soil water. This allows for the continuous partitioning of the chemical into the soil water, thus reducing the concentration in the vapour phase.

# 2.3.4 Biodegradation

Different organic compounds will biodegrade at different rates, and with various oxygen demands. For example, the aerobic biodegradation of volatile petroleum hydrocarbons in the vadose zone (*e.g.*, BTEX) has been demonstrated through several investigations (Ostendorf and Kampbell, 1991; Lahvis and Baehr, 1996; Ririe *et al.*, 1998; Roggemans *et al.*, 2002; Hers *et al.*, 2000; Hers *et al.*, 2002; Sanders and Hers, 2006; Davis *et al.*, 2009; Patterson and Davis, 2009). Several of these studies indicate orders-of-magnitude bioattenuation of hydrocarbon vapour concentrations over relatively small distances within the vadose zone. Since chlorinated solvents such as PCE and TCE degrade primarily under anaerobic conditions through reductive dechlorination (Wiedemeier *et al.*, 1999), biotransformation of these compounds will usually be limited due to the presence of oxygen within the unsaturated zone. There is experience-based evidence of aerobic biodegradation of vinyl chloride in the vadose zone, but little published data.

# 2.4 Near-Building Processes for Soil Vapour Intrusion

The primary process for soil vapour intrusion into buildings is typically soil gas advection, although vapour migration will also occur as a result of diffusion through the building foundation. Model sensitivity analyses suggest that soil gas advection will be the dominant mechanism when the building depressurization (relative to ambient air) is greater than about 1 Pascal (Hers *et al.*, 2003; Johnson, 2005), which will be exceeded at many residential buildings. In addition, several researchers report a positive relationship between cross-foundation pressure gradient and soil gas entry rate indicating that advective flow is an important process (*e.g.*, Nazaroff *et al.*, 1985; Garbesi and Sextro, 1989; Fischer *et al.*, 1996; Robinson and Sextro, 1997).

Soil gas advection can occur through untrapped floor drains, sumps, edge cracks at the building wall and floor slab interface, unsealed entry points for utilities, expansion joints and other cracks, if present. Field research programs that include pressure data for soil adjacent to the building foundation indicate that most of the soil gas flow occurs within 1 to 2 m of the foundation (Garbesi *et al.*, 1993; Hers *et al.*, 2002). Therefore, the properties of the backfill surrounding the foundation are important, as well as any nearby utility corridors. Field measurements and model simulations indicate that for most sites, the permeability of soil near the building will control the rate of soil gas flow, as opposed to the permeability of the building foundation.

Depressurization of the building airspace relative to the ambient (outdoor) air pressure can be caused by a number of factors including temperature differences between indoor and outdoor air (*i.e.*, "stack effect"), wind-loading and operation of the building heating, ventilation and airconditioning (HVAC) systems. The operation of HVAC systems can cause a building to be depressurized through insufficient combustion air for furnaces or unbalanced heating and ventilation systems where the exhaust air flow rate exceeds the intake flow rate. Commercial buildings may be either positively or negatively pressurized depending on HVAC system design, operation and environmental conditions. Diffusion through the building foundation will readily occur through cracks and openings in the foundation. Diffusion rates through intact building

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materials are relatively low, but will depend somewhat on material type (*e.g.*, poured concrete slab, concrete block wall). Plastic moisture vapour barriers placed during the construction of slabs may reduce diffusion to some degree, but will have little effect on reducing advection, since significant soil gas flows can occur through small openings.

# 2.5 Summary

Diffusion is the dominant process for soil vapour transport in many geologic settings, although closer to a building, advective processes may be dominant. Aerobic biodegradation of hydrocarbon vapours is an important mechanism for vapour attenuation at many petroleum sites. Soil vapour intrusion is influenced by building characteristics, geologic setting and anthropogenic features. There can be significant temporal variation in soil vapour intrusion due to environmental and building related conditions. Long-term transient effects may be important if there is depletion of the contamination source through volatilization, leaching and/or biodegradation.

# 2.6 Resources, References and Links

The USEPA has developed a number of on-line assessment tools for groundwater and soil vapour that include, for example, calculators for determining the groundwater hydraulic gradient, retardation factors for solute transport, plume diving, diffusion coefficients, Johnson and Ettinger alpha calculator and unit conversions. (http://www.epa.gov/athens/onsite/)

# **EXHIBIT 2.1:** Conceptual Site Scenarios for Vapour Intrusion

#### Fresh-Water Lens

For chemicals present only in groundwater (*i.e.*, dissolved phase sources), their distribution below the water table will determine their potential to volatilize and migrate to indoor air. If volatile chemicals are present near the surface of the water table, volatilization will readily occur. In contrast, if there is a layer of "clean" groundwater above contaminated water, then the rate of volatilization will decrease since mass transport is controlled by diffusion and dispersion in groundwater. At some sites in wetter areas, the layer of clean water has been observed to increase in thickness with increasing down-gradient distance from a contamination source (*i.e.*, "fresh-water lens formation") (Figure 2.2). Water table fluctuations and upward vertical gradients may prevent the formation of a fresh water lens. The implication for sampling is that wells with short screens at the water table or groundwater profiling methods should be considered (Section 3.9.1).



FIGURE 2.2. Fresh Water Lens

# **Interface Plume Development**

If vapours are diffusing from contamination in the unsaturated zone, they will partition into groundwater (Figure 2.3). This process combined with water table fluctuations can result in an interface zone groundwater plume, which is a shallow plume located within the capillary fringe and groundwater just below the water table (Rivett, 1995). There is both lateral and vertical flow and solute transport within the capillary fringe (Silliman *et al.*, 2002), which contrasts with the common conceptualization of primarily downward vertical fluid flow through the unsaturated zone, with a transition to fully three-dimensional flow only below the water table. Volatilisation from an interface plume may be significant.



FIGURE 2.3. Interface Plume Development

# Falling Water Table

If there is a water table decline of sufficient extent, higher levels of dissolved contamination or NAPL, if present, will become exposed to soil gas (Figure 2.4). This will result in increased volatilization rates. In addition, the beneficial effect of a fresh water lens may be lost if there is a significant drought and the water table drops by a distance larger than the thickness of the fresh-water lens. Long-term water level data should be reviewed where available to assess the potential significance of water table fluctuations on volatilization rates and when to sample soil gas. In laboratory tank experiments conducted by McCarthy and Johnson (1993), for a stable water table, the transfer of TCE from groundwater to soil gas was controlled by vertical diffusion through the capillary fringe. When the water table was allowed to drop, there was a 3 times increase in the mass transfer rate. Other researchers have observed a similar increase in mass transfer rate for water table drop attributed to release of trapped air bubbles with elevated VOCs (Silliman *et al.*, 2002). For soil vapour sampling programs, the implication is that seasonal data should be considered when the water table is dropping.



# Lateral Soil Vapour Diffusion

Organic chemicals released near ground surface may result in a contamination source in the unsaturated zone, which can potentially diffuse laterally toward adjacent buildings (Figure 2.5). For unsaturated zone sources, vapour diffusion in all directions will occur, which tends to result in a rapid decline in soil vapour concentrations with increasing lateral distance from the source, particularly for smaller contamination sources. The presence of anthropogenic features such as paved surfaces, concrete slabs and fine-grained fill materials can reduce soil vapour flux to the atmosphere and may promote lateral diffusion of soil vapour. There will also tend to be greater lateral than vertical diffusion due to depositional history and soil layering, although the effect for most soils is relatively minor.

For the Health Canada vapour intrusion guidance, buildings more than 30 m from contamination were excluded from the screening process partly based on modeling studies that included lateral diffusion and which indicated a significant decline in predicted vapour concentrations over this distance (Mendoza, 1995; Abreu, 2005; Lowell and Eklund, 2004). A semi-logarithmic chart of concentration versus log of distance may help estimate the distance where soil vapour concentrations fall below levels of potential concern.

#### Preferential Pathways

The presence of preferential pathways such as utility conduits with granular backfill, which intersect a contamination source and connect to the building, may result in enhanced soil vapour intrusion. Since most buildings have subsurface utility penetrations, their presence alone is not typically of concern. Of relevance are pathways that facilitate enhanced movement of soil vapour toward and into a building. VOCs will readily partition into air when contaminated groundwater is in contact with sumps or drain tiles, which is a scenario of concern for indoor air quality.



# Transient Soil Vapour Migration

After a spill has occurred, sorption into native organic carbon will initially cause concentrations to be transient as soil vapour migrates from the source. After a period of time, an approximate steady state vapour profile will develop after sorption sites are filled (assuming no biodegradation). There are also transient effects through partitioning into soil moisture, which may be significant for soluble chemicals such as MTBE. The time for a steady state profile to develop will depend on chemical and soil properties and the thickness of the uncontaminated soil layer. The time for steady state conditions can be estimated through an analytical solution for one-dimensional steady-state diffusion and sorption based on linear partitioning into native organic carbon. For example, based on solutions to this equation provided by Johnson *et al.* (1998), for trichloroethylene, the approximate time required for a steady state diffusion profile to develop would be approximately 0.5 years, for a depth to contamination of 3 m, and 5.7 years, for a depth to contamination of 10 m.<sup>2</sup> The time to steady state may have implications for design of soil gas sampling programs (*i.e.*, sampling location and when to sample).

#### Hydrocarbon Vapour Biodegradation

Many petroleum-based hydrocarbons are readily degraded to carbon dioxide  $(CO_2)$  in the presence of oxygen  $(O_2)$  and ubiquitous soil microbes. Oxygen is supplied from the atmosphere through diffusion, barometric and diurnal pumping, and infiltrating water containing dissolved oxygen. Aerobic biodegradation of petroleum hydrocarbons is a rapid process and often occurs over relatively thin layers within the subsurface (Figure 2.6). Aerobic biodegradation is typically primarily controlled by oxygen levels; other potentially important factors include the moisture content, availability of nutrients and pH. Typically, there are indigenous microbes present in the subsurface that degrade petroleum hydrocarbons. Since anaerobic biodegradation of hydrocarbons may also occur in oxygen-depleted zones, methane (CH<sub>4</sub>) may be generated. Methane will also undergo aerobic biodegradation, so its presence represents an additional demand on oxygen within the subsurface environment. Significant bioattenuation of hydrocarbon vapours will occur when the downward flux of oxygen is sufficient to satisfy the requirements for aerobic biodegradation. Where the hydrocarbon flux exceeds the oxygen supply, for example, below a building, an anaerobic zone (sometimes referred to as an "oxygen shadow") may develop.

The key factors affecting biodegradation are source concentrations ("strength") and separation distance between the source and building. The size and depth of the building may also be important depending on whether oxygen can readily penetrate through the foundation or whether most oxygen replenishment is from beside the building. A highly cracked or open foundation may be beneficial for oxygen transport and degradation (but for non-degrading chemicals would be a higher risk condition). Processes such as barometric pumping may also serve to increase oxygen transfer to below the building. Sites with shallow and high levels of contamination with larger buildings or paved surfaces beside buildings conceptually present the greatest potential for an oxygen shadow to develop. Natural soil respiration in soil with high organic carbon content can also result in depletion of oxygen.

 $<sup>^{2}</sup>$  The input parameters for this calculation are water-filled porosity equal to 0.1, total porosity of 0.3 and organic carbon fraction of 0.006.

Chlorinated solvents also can be biodegraded, but the process tends to occur under anaerobic conditions (except for vinyl chloride) and is much slower than the aerobic biodegradation of BTEX.



# FIGURE 2.6. Conceptual Model for Aerobic Biodegradation (API, 2005)

# **Barometric Pumping**

A potentially important mechanism for soil gas advection is "barometric pumping," caused by cyclic changes in atmospheric pressure. These changes create a "piston-like" force on soil gas, causing compression of soil gas when the air pressure increases, and expansion when it decreases. This may result in a cyclic up and down movement of contaminant vapours in the affected interval. Typically, the maximum variation in barometric pressure is about three percent over a 24-hour period (Massman and Farrier, 1992). Assuming gas compression according to the ideal gas law, atmospheric air will be pushed into soil to a depth up to about three percent of the total depth of the unsaturated zone. For a 10 m thick homogeneous unsaturated soil column, this means the top 0.3 m of soil would be affected by the complete barometric flushing of soil gas.

The magnitude of the pumping effect decreases with increasing depth, and also is affected by pressure dampening and time-lag in the pressure response, which can be significant for finergrained deposits. There are unpublished accounts of barometric pumping causing significant movement of soil gas in deep (greater than 100 m), unsaturated, fractured bedrock deposits where a "breathing" phenomena has been observed (*i.e.*, air flowing in and out of wells). "Breathing wells" have been linked to several deaths in Canada (see the Canadian Ground Water Agency website for a link to an associated article on this phenomena:

http://www.cgwa.org/press/breathing\_wells.htm ).

Close to a building, barometric pumping may result in the movement of atmospheric air in and out of foundation subsoils. If there is a low permeability surface seal adjacent to buildings, cross-foundation slab pressure gradients may be generated when the barometric pressure decreases. One study reported measured transient cross-slab differential pressures of up to 500 Pascals (Adomait and Fugler, 1997).

In summary, barometric pumping will not be significant at most sites unless the unsaturated zone is deep, but could be significant at sites with fractured rock and low permeability surface seals.

# Stack and Wind Effect

The heating of a building, either by furnace, radiator, or other sources (*i.e.*, sunlight on the roof) creates a "stack effect" as warm air rises in the building (Figure 2.7). This causes an outward air pressure in upper storeys and inward air pressure near the base of the building. Warm air that escapes is replaced by air infiltrating through doors and windows and soil gas migrating through the foundation. The magnitude of the depressurization at the base of the building is proportional to the height of the building, although tall buildings are designed with features to minimize cross-floor leakage of air and excessive depressurization.

Elevator shafts may represent both a preferential pathway for soil gas intrusion at the base of the building (a drain is often present in the elevator pit) and for upward movement of air within the building. The force of wind on the side of a building will cause a positive pressure on the windward side of the building and a negative pressure on the lee side thus potentially resulting in a depressurised building.

Subslab vapour and indoor air sampling programs should consider stack and wind effects by potentially measuring pressure gradients.



# FIGURE 2.7. Stack and Wind Effect on Depressurisation (NPL = neutral pressure line)

# Foundation Construction

Conceptually, different foundation construction could lead to different processes for soil vapour intrusion. For example, higher soil gas advection rates would be expected for houses with basements, due to higher depressurization and larger subsurface foundation surface area for intrusion. For houses with crawlspace foundations, the degree to which the crawlspace is ventilated by outside air and the influence of cross-floor mixing and leakage between the crawlspace and main floor could affect soil vapour intrusion rates.

In cold climate areas, crawlspaces are more likely to be well sealed to reduce the influx of cold air into the house. Buildings with earthen floors are especially prone to vapour intrusion since there is a large surface area for migration of soil vapour into the overlying structure; however, openings around utilities and a perimeter crack, often observed at the interface between the foundation wall and floor slab, also represent potentially significant entry routes for soil gas migration.

Although working hypotheses have been developed, the influence of foundation type on soil vapour intrusion is still poorly understood. However, there are empirical data indicating that soil vapour intrusion can be significant for several different types of building foundations including basements, crawlspaces and slab-on-grade construction. The importance of the foundation for vapour intrusion may depend on the distance from the contamination source to the building; for larger distances the foundation may have little effect on vapour intrusion rate; for smaller distances or where contamination is close to or in direct contact with the building (*e.g.*, sumps, wet basements), the foundation properties will tend to be significant.

Condominiums or commercial buildings may have one or more levels of below-grade parking. Since ventilation rates are high for parking garages, there will tend to be greater dilution of vapours that may migrate into the garage than for other building types.

#### **Temporal and Seasonal Considerations**

Potential temporal factors influencing soil vapour intrusion are complex. Higher building depressurization and soil gas intrusion rates would be expected during the heating season. Higher soil moisture in near surface soils may limit the surface flux of volatiles to the atmosphere. As a consequence, the migration of soil vapour toward drier soils below the building may be enhanced. In some cases, intensive snowmelt or rain and wetting fronts can induce advective movement of soil gas, which may, in turn, cause non-equilibrium mass transfer of the contaminants between the water and the gas phases (Cho *et al.*, 1993).

Surface soils with high moisture content may also reduce migration of atmospheric oxygen into soil, which may reduce aerobic biodegradation of hydrocarbon vapours (Hers *et al.*, 2002; McAlary *et al.*, 2007). Frost is hypothesized to have a similar effect but there is little data evaluating this factor. An off-setting factor is that during summer, near surface ground temperatures may be higher leading to slightly higher volatilization rates, since the Henry's Law Constant is temperature dependent. The amplitude in seasonal temperature variation decreases with increasing depth below ground surface, and at many sites, temperature effects will be insignificant.

The influence of seasonal factors on building ventilation, which acts to dilute vapours, is difficult to predict. While natural ventilation through open doors or windows may be reduced in winter, there may be increased air exchange through building depressurization and operation of a furnace. There can also be significant short-term variability unrelated to seasonal factors caused by diurnal temperature fluctuations, occupant use (*e.g.*, opening windows and doors), wind, and barometric pressure variations. On balance, the above factors suggest that in Canada, soil vapour intrusion would tend to be greatest during winter months based on climatic conditions.

#### **Buildings and Tanks as Soil Vapour Sources**

While the usual paradigm for soil vapour transport is upward migration from a contamination source located at or near the water table, if there is a surface contamination source, vapours will migrate in all directions, including downwards. Indoor air that is affected by contamination sources within a building may affect subsurface vapour concentrations if the building is positively pressurized (McHugh *et al.*, 2006). In this case, air will move downwards through the foundation. Once below the building, vapours could diffuse away from the building, thus creating a zone of impacted soil vapour. While it would be rare for buildings to have a significant effect on subsurface soil vapour concentrations, a dry cleaner is one possible example of where this could occur. Leaking underground storage tanks also represent potential soil vapour sources.

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# 3.0 SUBSURFACE CHARACTERIZATION FOR EVALUATION OF SOIL VAPOUR INTRUSION

# 3.1 Context, Purpose and Scope

This chapter describes methodologies for characterization of soil vapour through measurements because at many sites soil vapour measurements are an important component of a technically defensible assessment of soil vapour intrusion. A summary of considerations for sampling and analysis of other media (soil and groundwater) is also provided as well as ancillary information that may assist in the interpretation of soil vapour data and evaluation of soil vapour intrusion.

There is significant interest in soil vapour methods and recognition that testing of this media provides for a more direct indication of the contaminant phase that may migrate into indoor air. However, it is critical that an appropriate sampling approach and methods be followed to obtain representative data. The context of this chapter is to provide guidance on characterization of soil vapour intrusion; however, the concepts and techniques described are applicable for any site assessment where soil vapour sampling is proposed.

Since soil vapour characterization programs are highly influenced by site specific conditions and project-specific objectives and potential constraints, it is not possible to provide a standardized template for sampling design and methods. However, the key

#### Soil Vapour Characterisation

This chapter describes the planning, process and methods for soil vapour characterisation. The key elements and their corresponding sections in the chapter are:

- Study objectives (3.2),
- Multiple lines of evidence context (3.3),
- Sampling approach and design (3.4),
- Soil gas probe construction (3.5),
- Soil gas sampling and analysis procedures (3.6 & 3.7),
- QA/QC considerations (3.8),
- Soil and groundwater characterization (3.9),
- and Ancillary data (3.10).

Related tools are Suggested Operating Procedures for Soil Gas Probe Installation (SOP-1), Soil Gas Sampling (SOP-2) and Soil Gas Probe Leak Tracer (SOP-3) provided in Appendix L.

principles and factors that should be considered in developing a sampling strategy are outlined, and a range of methods are described to provide the practitioner with the necessary approaches and tools to investigate this pathway.

# 3.2 Study Objectives

The overall goal of a soil vapour investigation is typically to provide the data needed to evaluate potential risk to occupants of buildings who may be exposed to vapours migrating into indoor air. Specific objectives of the soil vapour investigation may include the following:

• Improve understanding of the conceptual site model (CSM), potential contamination sources and soil vapour migration pathways, and partitioning relationships between concentrations in different media (*e.g.*, through co-located groundwater and soil vapour sampling points);

- Compare measured soil vapour concentrations to generic soil vapour criteria or provide soil vapour data needed for input into models used for site-specific risk assessment;
- Evaluate hydrocarbon vapour biodegradation through collection of soil vapour samples from vertical profiles or lateral transects;
- Evaluate models used to simulate soil vapour transport through collection of soil vapour samples at various points along the migration pathway and comparison to model-predicted soil vapour concentration profiles; and,
- Evaluate the influence of background chemical sources on indoor air samples through concurrent collection of subslab vapour and indoor air samples.

The study objectives should be well defined prior to developing a sampling plan, as there may be substantive differences in sampling plans depending on the type of data required and how these data are intended to be used.

# **EXHIBIT 3.1.** Lessons Learned from Extensively Monitored Sites

Several extensively monitored sites have provided valuable data on spatial and temporal variability in soil vapour concentrations. The lessons learned from these sites highlight the variability in sites ("no two sites are the same") and depending on the site, spatial and temporary variability can be significant.

**Casper, Wyoming** (Hong *et al.*, 2007): High resolution monitoring of hydrocarbon concentrations was conducted at a refinery site with light distillate contamination. Residual NAPL contamination was present at depths between about 1 and 5 ft. below a small warehouse-type building. Monitoring of subslab vapour concentrations indicated variability on a daily basis by a factor of up to seven or eight near cracks in the slab, compared to deeper (4 ft. depth) probes, where the range in concentrations was less than a factor of two. Differential pressure monitoring between the slab and indoor air indicated fluctuating positive to negative pressures inside the building relative to subslab soil gas that tended to follow diurnal (daily) patterns.



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**Endicott, New York** (Wertz (unpublished)): Soil vapour monitoring conducted over 15 months at the Endicott site showed shallow trichloroethylene soil vapour concentrations varied by a factor of four over this time period, while deep soil vapour concentrations varied by a factor of two. The shallow soil vapour concentrations were lowest during the winter months.



# FIGURE 3.2. Temporal Soil Vapour and Groundwater Data for Endicott Site

**Chlorinated Solvent Site** (McAlary, 2008): A site impacted by chlorinated solvents was seasonally monitored for about a decade. The site consisted of sand soils with the water table located at 8 to 16 feet depth. Soil gas samples obtained from 5 ft. depth indicated consistently higher (up to 10X higher) concentrations in fall compared to spring.

**Vandenberg AFB, California** (Hartman *et al.*, 2010): Near-continuous monitoring of trichloroethylene (TCE) concentrations in soil vapour at 3, 8 and 17 ft. depth probes at a site with sandy soils and bare-ground cover indicated less than 10% temporal variability in concentrations over a several month period during dry conditions.

**Cortlandville, New York** (Wertz and Festa, 1997): Groundwater, external soil vapour, subslab soil vapour and indoor air monitoring was conducted in a residential area overlying glacial sands and gravels. The depth to the water table ranged from 7 to 20 feet below ground. The groundwater and subslab soil vapour concentrations were not spatially well correlated at this site. In areas where the TCE concentration in the groundwater ranged from 14 to 20 ppb, the concentration of TCE in the subslab soil vapour ranged from non-detect (below  $0.86 \ \mu g/m^3$ ) to more than 900  $\mu g/m^3$ . In addition to spatial variability observed between neighbouring buildings, there was generally over an order of magnitude variability observed in the concentrations below an individual structure; in contrast, the observed temporal concentration variability was less than an order of magnitude. An example of data obtained below one structure is shown in Figure 3.3.


FIGURE 3.3. Sub-slab Soil Vapour TCE Concentrations at Cortlandville House

**Summary**: The lessons learned indicate spatial and temporal variability in soil vapour is dependent on site conditions and sampling location. Deeper soil vapour sample concentrations near the source tend to be less variable than shallow samples and samples obtained below a building. Greater variability is expected as geologic heterogeneity and climate extremes increase. Monitoring during the heating season may not result in the most conservative results.

## 3.3 Multiple Lines-of-Evidence Context

While the focus of this chapter is soil vapour characterization, for context, it is important to recognize that a multiple lines-of-evidence approach may improve site characterization and decision-making. The multiple lines-of-evidence approach should go beyond media analysis (potentially soil, groundwater, external soil vapour, subslab soil vapour, indoor air and/or outdoor air) and also include consideration of geological, chemical and biological factors that may influence soil vapour intrusion. For example, there tends to be less potential for vapour intrusion when there is relatively deep contamination, fine-grained soil, and/or biodegradable chemicals such as petroleum hydrocarbons. Conversely, there tends to be greater potential for vapour intrusion at sites with shallow contamination, coarse-grained deposits and non-degrading chemicals. The number of lines-of-evidence that will warrant evaluation at a site will depend on site specific conditions. Limitations with each type of data are minimized if decisions are supported by more than one type of data.

An overview of advantages and disadvantages associated with characterization of different media is summarized in Table 3.1. Soil and groundwater data are typically obtained as part of the initial intrusive site investigation phase (and also often to confirm remediation). It is understandable that there would be a desire to use these data for screening purposes; however, the potential limitations should be recognized including the uncertainty in theoretical partitioning relationships used to estimate vapour concentrations, particularly for soil to soil vapour transfer. Characterization of the distribution of the residual NAPL phase is important at petroleum hydrocarbon sites. The main advantage associated with soil vapour is that it provides a direct measurement of the contaminant phase that may migrate into indoor air. The main disadvantages are that the spatial and temporal variability in soil vapour concentrations is often relatively high and that appropriate protocols must be carefully followed to achieve data quality that is acceptable.

Media Investigated	Indoor Air Evaluation Method	Principal Issues
Soil	Partitioning model combined with soil vapour-to-indoor fate and transport model	Partitioning model highly uncertain, significant spatial variability particularly for contaminants with specific gravity greater than water ( <i>e.g.</i> , DNAPLs), negative bias due to losses during sampling – Can be used to identify a potential concern, but not relied upon to screen out for chemicals with a specific gravity greater than one.
Groundwater	Partitioning model combined with soil vapour-to-indoor fate and transport model	Partitioning model uncertain, imprecision of soil vapour transport model requires conservative attenuation factors, moderate to high spatial variability, moderate to low temporal variability, not representative of contamination in vadose zone.
Soil vapour beside building	Soil vapour-to-indoor air fate and transport model	More direct indication of potential exposure, but high spatial variability (generally more so than groundwater), shallow soil vapour may be non representative, moderate to high temporal variability.
Soil vapour below building (at depth below foundation soils)	Soil vapour-to-indoor air fate and transport model	More direct indication of potential exposure but intrusive, lateral spatial and foundation soil variability somewhat mitigated by deeper sampling, moderate to high temporal variability.
Sub-slab vapour <sup>1</sup>	Subslab vapour-to-indoor air model (primarily dilution in indoor air) or empirical attenuation factor approach	Closest representation of potential vapours migrating into building, but intrusive, high spatial and moderate to high temporal variability, exfiltrating air may confound results if building is positively pressurized.
Indoor air	Indoor air concentrations directly measured	Direct measurement, but intrusive, background sources may confound data interpretation; temporal variability likely high.

	<b>TABLE 3.1.</b>	Comparison	of Different	Media for	Vapour	Intrusion	Investigations
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<sup>1</sup> For a building with crawlspace, it is not possible to obtain a subslab vapour sample unless the crawlspace has a concrete floor. A sample from the crawlspace may be obtained but depending on crawlspace ventilation and connection to house, there may be very little attenuation between the crawlspace and house.

## 3.4 Soil Vapour Sampling Approach and Design

## 3.4.1 Overview of Sampling Strategy

The sampling strategy should consider the number of soil gas probes, their location, when to sample and the frequency of sampling. The sampling design will depend on the characteristics, size and distribution of the contamination source, geologic characteristics and heterogeneity, and receptor (building) conditions. Where relevant, anthropogenic features such as utility corridors, particularly where they penetrate confining layers should be taken into account.

A bottom-up soil vapour characterization approach is generally recommended starting with deeper, near contamination source vapour sampling followed by subslab vapour (and potentially indoor) sampling, if required, based on the initial results. The sampling strategy may depend on contamination source location (*e.g.*, vadose zone, dissolved plume) and type of contamination (*e.g.*, chlorinated solvent, petroleum hydrocarbon).

There is often high spatial and temporal variability in soil vapour concentrations (Exhibit 3.1), and sampling designs should take this potential variability into account. Soil vapour concentrations near the contamination source tend to be the most stable and least affected by factors that contribute to variability. For many contamination scenarios, the source consists of NAPL or dissolved constituents at the water table; therefore, deeper samples should typically be a component of a soil vapour sampling program.

Given that the spatial variability in soil vapour concentrations is expected to be higher than for groundwater, soil vapour sampling at a higher resolution than groundwater is often warranted,

## Example Prediction of Capillary Transition Zone Height

Soil gas samples cannot be obtained unless there is a continuous interconnected network of gas-filled pores, which is a function of the capillary transition height above the water table. The height above the water table where the transition to continuous gasfilled pores begins can be approximated using a water retention model (e.g., Van Genuchten US Soil Conservation Service (SCS) soil texture classifications, the predicted height of this transition point is approximately 17 cm for sand and 38 cm for loam. See Health Canada (2010) for additional information on water retention modeling.

although as discussed in Section 3.6.6, large volume soil vapour sampling may be a strategy to reduce concentration variability. Soil vapour testing programs may also need to be repeated to capture seasonal variations. Modeling can be used to provide insight on temporal variability in soil vapour concentrations (*e.g.*, Johnson *et al.*, 1998).

## 3.4.2 Considerations for Sampling Locations

While there is a continuum of possible sampling locations, it is helpful to categorise sampling locations as deep (near source) soil vapour, shallow external soil vapour and subslab (immediately beneath the floor slab), and to identify issues and considerations for these three generic sampling locations, as discussed below and summarized in Table 3.2. Recommendations on sampling locations are provided in Section 3.4.3.

### Deep (Near Source) Soil Vapour

Soil vapour samples obtained from near the vapour contamination source will tend to be stable seasonally and are relatively unaffected by near-surface processes (*i.e.*, building, weather conditions), except in instances where a LNAPL smear zone is present and water levels fluctuate dramatically over time. Near source soil vapour concentrations are also less influenced by biodegradation or biotransformation processes and will reach steady state conditions relatively quickly. The variability in soil vapour concentrations will tend to increase as the distance from the contamination source increases.

Deep soil vapour data are also most representative if the objective is to characterise an undeveloped site and predict vapour intrusion into a future building. This is because changes to surface conditions and development tend to have the greatest effect on shallow vapour concentrations and the least effect on soil vapour concentrations near the contamination source.

#### Shallow Soil Vapour

Shallow soil vapour concentrations are more likely to be affected by geologic heterogeneity, changes in near-surface conditions such as barometric pressure or temperature fluctuations, and surface cover (*e.g.*, paved versus non-paved surface). Near a building, soil gas advection, caused by building depressurization, utilities and variable foundation subsoils can cause variability in soil vapour concentrations. The concentrations of petroleum hydrocarbon compounds such as BTEX in shallow soil vapour are typically low because of rapid aerobic biodegradation, although as indicated below, in some cases there may be oxygen limitations that reduce biodegradation.

There is on-going debate on the use of shallower soil vapour concentrations beside buildings to estimate conditions below buildings. An analysis of data from nine chlorinated solvent sites from the USEPA database (USEPA, 2008) and data recently obtained for a study for Health Canada (Golder, 2010) indicates that when external soil vapour samples are obtained at the same elevation as subslab samples, the external concentrations are generally lower than the subslab concentrations, but that the comparison improves for deeper external samples (Figure 3.4). For chlorinated solvent chemicals, biodegradation is not a factor, but there may be other processes and factors such as differences in moisture content and barometric pumping that contribute to the trends observed.

For petroleum hydrocarbon impacted sites, there are case studies where hydrocarbon and light gas (oxygen and carbon dioxide) concentration profiles were similar beside and below buildings (at the same depth) (*e.g.*, Lundegard *et al.*, 2009) and case studies where hydrocarbon concentrations were lower and oxygen concentrations were higher beside compared to below the building (Laubacher *et al.*, 1997; Paterson and Davis, 2009). The differences may be due to reduced oxygen flux through concrete slabs and drier soils below the building, although it is noted that oxygen diffusion rates vary significantly within concrete depending on it's properties (*e.g.*, Titerelli, 2009; Kobayashi, 1991). Oxygen recharge also occurs when there is high permeability fill below a foundation slab that is connected to atmosphere. The results of a modeling study by Abreu and Johnson (2005) predict higher subslab concentrations of aerobically biodegradable hydrocarbons for a high source strength scenario, but not for a moderate source strength scenario (Figure 3.5). While many factors influence the representativeness of external soil vapour data compared to subslab data, under some conditions, shallow soil vapour samples external to a building could lead to non-conservative predictions of indoor vapour concentrations, leading to the recommendation for minimum depth for external soil vapour sampling provided below.



FIGURE 3.4. Comparison of External and Sub-slab Soil Vapour Concentrations for Chlorinated Solvent Chemicals



FIGURE 3.5. Results of 3-D Oxygen-Limited Soil Vapour Transport Modeling for High Concentration Source ( $C_g = 100 \text{ mg/L}$ ) and Moderate Concentration Source ( $C_g = 20 \text{ mg/L}$ ) (from Abreu and Johnson, 2005)

#### Subslab Soil Vapour

Characterization of subslab soil vapour below a building foundation may be warranted when deeper soil vapour tests indicate a potentially unacceptable health risk or when there is a shallow contamination source. Subslab soil vapour testing may be advantageous when initially screening buildings (*i.e.*, before indoor air quality data are obtained) and in conjunction with indoor air testing to evaluate the potential for a complete pathway and indoor sources of chemicals (see Chapter 5). It is important to recognize that with barometric pressure fluctuations and positively pressurized buildings, it is possible for indoor air to move from the building into the subslab soil gas. If indoor air contains elevated VOC concentrations (*e.g.*, as seen at some dry cleaner sites), this could confound the interpretation of subslab data. The reverse intrusion phenomenon (vapour extrusion) can be evaluated by monitoring the pressure differential across the slab using digital micromanometers.

The following factors should be taken into account when designing a subslab vapour sampling program:

- A coarse-grained soil layer below a building foundation, or small void below the foundation slab due to settlement will tend to promote lateral soil gas flow and will yield gas at appreciable flow rates with minimal vacuum when sampled;
- There may be spatial or temporal variations in subslab soil vapour concentrations as a result of source concentration variability, biodegradation of hydrocarbon vapours, advective pumping of soil gas caused by barometric pressure changes or gas generation, and HVAC operation; and,
- Subslab soil vapour concentrations may be highest near the centre of a building for a uniform contamination source; however, the soil gas advection rates into a building may be greatest at a perimeter crack, which may be present along the interface between the floor slab and foundation wall.

Guidance on subslab soil vapour sampling has been developed by various agencies (ITRC, 2007; EPRI, 2005; USEPA, 2004). Recent data indicates significant spatial variability in subslab soil vapour concentrations even below single family dwelling sized buildings (*e.g.*, USEPA, 2008; Wertz and Festa, 2007) and that multiple samples are typically needed to adequately characterize this variability. Subslab soil vapour nearest to cracks and openings in the building envelope are expected to be most representative of soil vapour intrusion but such openings are usually difficult to find. Given that repeat sampling may also be warranted to address the significant temporal variability typically observed, the scope and cost of subslab soil vapour characterization programs can be significant, especially if monitoring of multiple buildings is required. These findings have called into question the usefulness of subslab soil vapour sampling and suggest deeper soil vapour samples are preferable.

There are practical drawbacks associated with subslab soil vapour sampling. Subslab sampling is intrusive. Drilling or coring equipment must be used inside the building and floor coverings may be damaged, which may be disruptive or undesirable for owners and occupants. The work may require an access agreement from the building owner. It may also be difficult to determine subsurface utility locations below slabs, although geophysical techniques (*e.g.*, ground penetrating radar) may be used for this purpose.

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Type of Soil Vapour Data	Where Obtained	Characteristics	Use of Data and Cautions
Deep Soil Vapour (external)	Close to the building, as near to water table as practical, subject to considerations relating to capillary fringe and depth limitations for drilling.	Concentrations reach near-steady conditions quickly, tend to be stable seasonally and are relatively unaffected by near-surface changes. Least affected by biodegradation. Should represent the highest concentrations of soil vapour.	If deep vapour concentrations are below soil vapour criteria, vapour to indoor pathway likely not significant. For future development scenario, only deep vapour concentrations should be used.
Shallow Soil Vapour (external)	Close to the building, but outside peri- foundational area.	More likely to be affected by changes in near-surface conditions including barometric pumping, temperature changes, moisture content and variability in near building soils May be affected by bioattenuation depending on chemical. Greater potential for non steady state conditions depending on distance from vapour source to measurement point.	If there is significant bioattenuation beside but not below building, use of shallow soil vapour may result in non-conservative predictions of indoor vapour concentrations.
Subslab Soil Vapour	Immediately below foundation slab. Generally, central location away from the foundation footings preferred.	Higher temporal and spatial variability expected as samples are affected by changes in near- surface conditions such as barometric pumping, temperature changes, HVAC systems and variability in foundation subsoils. Greater potential for non steady state conditions depending on distance from vapour source to measurement point.	Logistical issues associated with sample collection. Costly to collect sufficient samples for statistical assessment of spatial and temporal variability using current methods. Depending on where subsurface vapours enter a building, subslab sample location may or may not be representative of the vapour concentrations entering the building. May be affected by subslab utilities ( <i>e.g.</i> , drains, sewers).

# TABLE 3.2: Comparison of Soil Vapour Measurement Locations

### 3.4.3 Recommendations for Sampling Locations

#### Soil Vapour External to Building

The number of probes and lateral spacing of deep soil gas probes needed to characterize soil vapour source zones is highly dependent on site conditions and the number and size of buildings where soil vapour intrusion is of potential concern. For large disperse groundwater plumes, a soil gas probe spacing of several tens of meters may be adequate. For smaller plumes and hydrocarbon sites where steep lateral concentration gradients are expected, more closely spaced probes are warranted (*e.g.*, 5 m to 15 m). Subsurface utility conduits may also be targeted for sampling, with appropriate pre-cautions taken to prevent damage to utilities.

When evaluating potential vapour intrusion into a building, typically soil vapour samples from at least two sides of the building should be obtained, unless trends in soil vapour concentrations can be resolved and contoured on a broader scale. One location should be in the direction of the inferred highest soil vapour concentrations based on soil and groundwater data. The lateral soil vapour sampling locations should be relatively close (within a few meters) of the building (unless property access constraints prevent this), but at least 1 m from the foundation to avoid the zone of disturbance and fill typically located next to a building.

The model-predicted concentration patterns presented by Abreu and Johnson (2005, 2006) support a minimum depth for soil vapour samples equal to half the distance between the building foundation and contamination source, subject to a maximum depth of 10 m based on practical considerations (*e.g.*, drilling cost). The data in

#### **External Soil Vapour Design**

The recommended soil vapour design for risk assessment is:

- 1. When evaluating a specific building, sample on at least two sides, generally within 2-3 m of building.
- 2. For future development scenario, sample at minimum of two locations in each area of potential concern.
- 3. Obtain soil vapour profile data at selected locations.
- 4. Minimum depth equal to half-way between lowest part of building foundation and contamination source, further constrained to be a minimum of 1 m below ground surface (unless pre-cautions are taken – See Section 3.5.3).
- 5. Use maximum near-building concentration.
- 6. Generally repeat sampling on at least two occasions.

Figure 3.4 also suggests external soil vapour samples should be obtained below the depth of the foundation. The minimum depth should generally be further constrained as a minimum of 1 m below the elevation of the foundation slab base and 1 m below ground surface (when no buildings are present) to be beyond the advective zone of influence associated with barometric pumping and building depressurization and of sufficient depth to minimize the potential for atmospheric air to be drawn into the sample. However, representative samples from depths that are less than 1 m can be obtained provided the probe is carefully sealed and the integrity of the seal is confirmed by leak tracer testing. To avoid the zone of excessive moisture, soil gas probes should generally be installed at least 0.5 m above the water table (see previous text box).



FIGURE 3.6. Lateral Transect Concept



FIGURE 3.7. Soil Vapour Sampling Locations and Vertical Profile Concept

#### Lateral Transects and Vertical Profiles

The soil vapour sampling design may employ lateral transects or vertical profiles to characterize spatial variation in concentrations (Figures 3.6 and 3.7). Lateral transects or vertical profiles can provide useful information for more in-depth analysis of the effect of biodegradation or finegrained soil layers on soil vapour transport. Transect or profile data can increase the level of confidence in the CSM for soil vapour transport and data quality.

Lateral transects are generally used when the contamination source is laterally removed from the building. Generally, a minimum of three samples should be used as part of a transect, consisting of soil gas samples from (i) the edge of contamination source nearest to building, (ii) the mid-point between source and building, and (iii) near the edge of building (API, 2005). While three sampling locations are likely sufficient for many sites, consideration could be given to additional intermediate probes if the distance between the contamination source and building is greater than 30 m.

Vertical profiles are generally used when the contamination source is below the building. Three or more samples should be obtained from (i) just above the contamination source, (ii) mid-point between upper and lower sampling point, and (iii) a sampling point located near the building and/or a subslab sample. The contamination source must be at least 1.5 m below the building foundation (and preferably greater than 3 m) for vertical profiles to be effective in resolving vertical concentration trends. Additional probes are recommended where there are changes in lithology.

#### Bioattenuation Assessment

Lateral transects and vertical profiles can provide valuable information on bioattenuation of aerobically biodegradable chemicals. Several case studies indicate a large reduction in soil vapour concentrations over small distances when there is aerobic biodegradation of hydrocarbon vapours or soil layers with high moisture content (*e.g.*, finegrained layer) (Fischer *et al.*, 1996, Hers *et al.*, 2000). There may also be significant lateral concentration gradients over short distances as evidenced by large concentration differences for probes situated on either side of houses (Sanders and Hers, 2006).

Depending on depth, external soil vapour concentrations may not be representative of

### **Factors affecting Aerobic Biodegradation Below Buildings**

When using lateral transects and/or vertical profiles to evaluate bioattenuation, the potential for the building to influence biodegradation should be recognized. The key factors affecting bioattenuation below buildings include source vapour concentration, the depth to the vapour source below the building, the building size, the surface cover and potential capping effect (and conversely the connectivity of foundation subsoils to atmosphere) and lateral uniformity of contamination below the building.

conditions below the building, although the representativeness of external soil vapour samples can be improved through sampling below pavement and in the direction of higher concentrations (*i.e.*, contamination source). Alternatively, the issue may be addressed through soil vapour sample below the building, where practical. At most sites with lower source hydrocarbons concentrations, the above factors will be immaterial as there will be sufficient oxygen to degrade the hydrocarbon vapours to negligible concentrations below the building.

Soil gas samples should be tested for the hydrocarbon vapours of potential concern, and as a minimum, for oxygen, carbon dioxide and methane (laboratory analysis should include nitrogen as a quality control check). These gases provide an indication of microbial activity occurring through aerobic or anaerobic processes. For example, depleted oxygen and elevated carbon dioxide levels are indicators of aerobic biodegradation of hydrocarbons while methane levels are indicative of breakdown of organic matter under anaerobic conditions. Consideration should be given to the analysis of certain hydrocarbon compounds (*e.g.*, cyclohexane, 2,2,4-trimethylpentane) that are more volatile than the BTEX compounds, and potentially less biodegradable, and which serve as useful tracers for hydrocarbon vapour transport (Sanders and Hers, 2006). Continuous or near continuous soil cores, headspace vapour testing (using a photoionization detector) and soil property data (*e.g.*, moisture content and grain size) are useful ancillary data for a bioattenuation assessment. Moisture content testing can be important since high moisture content layers act as diffusive barriers, which give the appearance of bioattenuation.

#### Subslab Soil Vapour

The number and location of subslab soil vapour samples that should be tested will depend on sitespecific conditions. For small to moderate sized houses, a minimum of two to three subslab samples, preferably located in a central location away from the foundation footings, is reasonable for screening purposes. It is recognized that practical considerations (*e.g.*, homeowner access) will often dictate the location of subslab soil vapour samples. For larger buildings, multiple samples are recommended to investigate the variability in subslab soil vapour concentrations and for some buildings, it may be desirable to install sufficient probes to delineate areas with elevated subslab vapour concentrations.

## **Characterisation at Buildings with Shallow Contamination**

A different characterisation approach is typically warranted at sites with contamination below or near a building, such as dry cleaners where releases often occur via building sumps or drains, and where subslab or shallow soil vapour samples below buildings should typically be obtained. Evaluation of preferential pathways may also be important through review of site plans or geophysical techniques. Indoor air testing may also be useful; however, consideration should be given to confounding influence of background sources of chemicals (see Chapter 4).

## 3.4.4 When to Sample and Sampling Frequency

Investigation of the soil vapour intrusion pathway will often require more than one round of soil vapour sampling since there can be significant temporal variability in soil vapour concentrations due to changes in source contamination concentrations, seasonal variations in the water table and conditions for hydrocarbon vapour bioattenuation. For example, if the water table level decreases, soil contamination, which previously was submerged by groundwater, could be exposed to soil gas thus resulting in increased volatilization. For soil vapour samples collected near to the building, there may be weather or building related sources of variability. In general,

the sampling frequency should coincide with seasonal patterns for factors affecting soil vapour such as the water table elevation (*i.e.*, high and low levels) and precipitation (soil moisture) (*i.e.*, wet and dry season).

One sampling event may sometimes be sufficient depending on the results of initial soil vapour testing. For example, if soil vapour concentrations are significantly less (*i.e.*, greater than one order-of-magnitude) than a soil vapour criteria or screening level, and if vapour concentrations are unlikely to increase significantly over time, one monitoring event may be sufficient. Alternately, if soil vapour concentrations are close to the criteria, repeat testing may be warranted.

Soil vapour sampling should be avoided during and after heavy rainfall events or after several days of continuous rain since collection of a representative sample may be difficult. In addition, infiltration of water into soil can result in negative bias in soil vapour concentrations due to partitioning of vapour into soil moisture and, in some cases, induce advective movement of soil gas. The time for moisture to drain from soil pores will depend on the soil type. Coarse-grained soil (sand or gravel) will drain to field capacity within a few hours (from complete saturation) while fine-grained soil will take longer to drain (Hillel, 1980). Field capacity is the soil water content after water drainage by the force of gravity is mostly complete. Based on drainage data, it is recommended that one wait at least one day after a heavy rainfall event (defined here as 1 cm) for coarse-grained soils (sand or gravel), and several days for fine-grained soils.

Barometric pressure effects on deep soil vapour samples will be relatively limited. One conceptual scenario where concentrations are effected by barometric pressure fluctuations are shallower samples obtained at sites with deep water tables (*i.e.*, greater than approximately ten meters) where there is atmospheric pumping of air in and out of soil due to the compression of soil gas. Another scenario is where there is a surface barrier (building slab, clay) that delays propagation of pressure changes and equalization when there are rapid changes in barometric pressure. Adomait and Fugler (1997) reported transient cross-slab pressures of up to 500 Pa during rapid barometric pressure changes. Typically, the scheduling of soil vapour sampling to coincide with decreasing barometric pressure is not warranted. However, it is recommended that barometric pressure (and other weather) data be obtained from a nearby weather station for several days before and after sampling, to enable evaluation of the possible effect of pressure, if desired.

There has been little research on influence of frost cover on soil vapour, although it is hypothesized that depending on the moisture of the ground when it freezes and the properties of the snow cover, there may be reduced fluxes of hydrocarbon vapours and oxygen through this frozen layer. Consideration should be given to repeat sampling for frost and non-frost cover conditions.

### 3.5 Soil Gas Probe Construction and Installation

Soil gas probes can be constructed of a variety of materials and installed using several techniques. Critical aspects to probe construction include: i) the use of materials that are inert and nonsorptive, ii) the design of seals that minimize the potential for short-circuiting of atmospheric air to the probe soil gas collection point, and iii) surface completion including a valve to allow the probe to be sealed between sampling events. The main options for installation of soil gas probes include:

• Permanent probes installed in boreholes constructed using conventional drilling techniques (*e.g.*, hollow stem augers)

#### **Soil Characterization**

Information on soil lithology, preferably from continuous borings, should be used to guide soil vapour probe installation location. Soil property data, including soil gradation, moisture content, density, porosity and organic carbon, is useful for conceptual model development and modeling. Soil samples should also be evaluated for possible contamination, including sources that may be located above the water table (see Section 3.9).

- Permanent probes installed in boreholes advanced using direct push drilling techniques; and,
- Permanent or temporary probes driven directly into the subsurface

Further discussion on the probe materials and installation methods for each of the above probe types is described below. Useful information is also provided in Atlantic PIRI (2006), API (2005), Geoprobe (2006) and EPRI (2005). For all probe types, it is important that subsurface utilities be located prior to installation.

### 3.5.1 Probes Installed in Boreholes

Drilling methods that limit disturbance to surrounding soil such as vibratory core-barrels, augers or rotary sonic are preferred over methods that involve greater disturbance and addition of air or water (*e.g.*, air rotary).

Probes installed in boreholes are constructed in a similar fashion to groundwater monitoring wells; however, there are important differences in design. Generally short screens (0.1 to 0.3 m length) should be used for probes since the objective is typically to characterize local soil gas concentrations (*i.e.*, over a small volume). Longer screens may also be considered for fractured media deposits to intersect a larger number of fractures that may be impacted by contaminants in soil vapour. The probe diameter should be small (generally between 6 mm (1/4 inch) and 19 mm (3/4 inch)) to minimize purge volumes.

Two common probe designs are rigid PVC pipe and "implants" constructed of steel mesh screens connected to flexible tubing. For probes constructed of continuous PVC pipe to ground surface, 19 mm ( $\frac{3}{4}$  inch) diameter pipe is commonly available and suitable for soil gas probes (smaller diameter rigid pipe is more difficult to obtain). While the slot size for groundwater wells is typically No. 10 slot (0.01 inch), a larger slot size (up to No. 40 slot) may be used for PVC soil gas probes since there is less potential for the filter pack to intrude into the probe within the unsaturated zone. Commercially-available implants are typically 0.15 to 0.3 m long, 12.5 mm ( $\frac{1}{2}$  inch) in

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diameter, and connected to ground surface using 6 mm ( $\frac{1}{4}$  inch) tubing. A potential disadvantage of smaller diameter tubing (*i.e.*, 6 mm or smaller) is frictional losses if pneumatic tests are to be performed (see SOP #2). A threaded cap should be placed over top of the riser pipe and riser pipe segments should be flush-threaded with o-ring seal. No glue should be used for construction of probes. Probes should be completed at ground surface with an airtight cap that includes a valve to simplify sample collection and prevent short-circuiting of atmospheric air into the sample probe.

Coarse sand or fine gravel surrounding the screened portion of the probe should extend at least 0.15 m above the screen, and a bentonite seal (minimum 0.3 m thick) should be constructed above the filter pack. Since soil gas probes are installed in the unsaturated zone where soil moisture may be relatively low, careful consideration should be given to the hydration of the bentonite seal. A competent seal can be constructed through use of dry granular bentonite (16 mesh) and addition of distilled water to the bentonite during installation. Granular bentonite has a texture much like the sand used for a filter-pack, and so it will settle effectively within the borehole, but hydrates rapidly (bentonite powder is too fine while chips and pellets are too coarse). Two or three lifts of granular bentonite and water is usually sufficient to form a competent seal. An effective method of sealing the remainder of the borehole annulus is to use a thick slurry of powdered bentonite and water ("Volclay grout") that is tremied to the base of the hole. The seal and filter pack should generally be installed as the rods (or casing) are removed to prevent collapse of the borehole walls, although in cohesive soils, it may be possible to install a probe after the rods are removed providing the hole stays open and a proper filter pack and seal can be installed.

If multiple probes are installed in a single borehole, the borehole above and below each probe should be sealed with granular bentonite. After allowing the seal to set overnight, the integrity of the seal should be checked by drawing a vacuum on each probe, and measuring the vacuum at adjacent probes. For a competent seal, there will be little cross-communication in vacuum between adjacent probes and any vacuum observed will develop slowly.

Soil gas probes should be completed with an air-tight valve or stopcock at surface to prevent atmospheric air from entering the probe, and protected using a well cover or other similar protective casing for security and weatherproofing. If multi-level probes are used, each probe should be tagged with a permanent label, using no glues, or markers. In general, a similar or higher level of care and quality control to that employed for monitoring wells should be followed when installing a soil gas probe.

Potential advantages of permanent probes installed in boreholes are that temporal variability can be assessed through repeat sampling and there is greater installation flexibility (*i.e.*, deep probes, dense soils). In addition, the filter pack that surrounds the screen provides for more open area for drawing a soil gas sample than a driven probe. A potential disadvantage of probes installed in boreholes may be access restrictions for drill rigs.

## 3.5.2 Probes Installed Using Direct Push Technology

Direct-push techniques can be used to install a single soil gas implant in a borehole. Direct push rods are pushed to the desired depth, and implants are installed post-run after the desired depth is reached by lowering the implant down the hollow rods and attaching it to a detachable anchor drive point. A sand pack and bentonite seal should be installed through the push rods as they are removed to minimize the potential for short-circuiting of atmospheric air from ground surface to the sampling point. The position of the filter pack and seal should be confirmed using a tamping rod. Natural collapse of the formation around the probes will not provide a competent seal and should not be relied upon. Direct push equipment can also be used to obtain soil cores prior to probe deployment. Soil data can be useful to target intervals for probe installation.

A potential advantage of using direct push technology to install a probe is that implants can be rapidly installed with minimal disturbance. A potential disadvantage is short-circuiting of atmospheric air from surface to the sampling point, if the borehole above the screen is not well sealed (due to the small diameter of the rods, construction of a seal in some case can be difficult due to bridging). In addition, the presence of gravel, cobbles or dense glacial till may hinder or preclude the use of direct-push technology.

## 3.5.3 Driven Probes

Driven probes are typically used as a temporary sampling device that can be installed using a direct push drilling rig or simple hand tools. One version, called a post-run tubing (PRT) system, involves pushing a conical tip and rods to the desired depth, and then disengaging the tip by pulling up the rods. Tubing is lowered to connect to a sampling point located at the bottom of the rods. Multiple samples from a single push may be obtained using this technology. There are other systems where tubing is permanently connected to a screen that is located within a retractable protective sleeve (located just behind the tip) that is exposed at the desired depth. This technology may only be used to obtain a single sample per location.

Driven probes in their simplest form are hollow steel rods with an internal diameter typically

## Comparison of Different Soil Vapour Probes

DiGuilio et al. (2006) report research Raymark site from the comparing chlorinated solvent soil vapour concentrations from soil gas samples collected using dedicated soil vapour probes, the Geoprobe Post-Run Tubing (PRT) system and AMS Gas Vapour Probe (GVP) kit. Both methods use probes that are pushed or driven in the good comparison ground. А was obtained between the three methods. When concentration ratios for individual probes were evaluated, on average, the PRT concentrations were 1.2 and 2.4 times higher than the concentrations for the dedicated probes and GVP kit, respectively.

ranging between 9 mm and 25 mm (sometimes referred to as ground probes) typically driven by hand. The rods include a loosely-fitting conical tip that is pushed a short distance further into the formation using an inner rod, once the probe is driven to its desired depth. Several holes may also be drilled near the tip of the probe to increase the open area through which soil gas is drawn into the probe.

Driven probes may be advantageous in terms of flexibility of installation, access and cost. Another potential advantage is that when field analytical capabilities are available, multiple soil gas samples may be collected and analyzed from a single driven probe installed to varying depths enabling near real-time evaluation of vertical vapour profiles.

A potential disadvantage of driven probes is that if the rods deflect during installation because of a dense obstruction or if there is cracking of soil, there may be annular leakage along the outside of the probe. If the probe is installed within a low permeability soil zone that is overlain by a higher permeability soil zone, there may be communication along the outside of the rods from this shallower zone during sampling, even though a hydrated bentonite plug is constructed at surface. A larger plastic seal at ground surface (*e.g.*, 1.5 m by 1.5 m), as proposed for shallow (less than 1 m) probes by the British Columbia Contaminated Sites Approved Professional (CSAP) soil vapour task group (BCCSAP, 2009), may reduce potential cross communication and leakage, although this seal may be redundant if leak testing confirms there is no annular leakage. Shallow soil vapour sampling and use of surface seals is evaluated through a modeling study described in Appendix B. A disadvantage of hand-driven probes is that installation depths are limited.

Some practitioners and regulators recommend not using driven probes based on the concern with annular cross communication described above. There are unfortunately few carefully controlled studies where different methods have been evaluated, although one study described in the text box indicated reasonably good comparison between temporary driven probes and dedicated permanent probes. For this guidance, the use of driven probes is considered appropriate provided the following pre-cautions are taken:

- Driven probes should be installed vertically using a hydraulic ram or slide hammer (sledge hammer installed probes may not be used);
- Minimize post-installation disturbance to probes;
- Driven probes should not be used in soils that will crack (*e.g.*, certain types of clay);
- If cobbles or other obstruction causes the rods to deflect, the installation should be abandoned, grouted, and re-tried at a new location;
- The connection between the PRT tubing and sampler should be leak tested after the sampler is retrieved (if Geoprobe system is used); and
- Multiple samples should not be obtained from a single location where there is the potential for contaminant draw-down.

### 3.5.4 Use of Water Table Monitoring Wells as Soil Gas Probes

Soil gas samples can also be obtained from groundwater monitoring wells screened across the water table provided the well screen extends above the capillary fringe, and the annulus above the well screen is sealed with a bentonite slurry or grout. The well should be subjected to a leak tracer test of the seal. Prior to collecting a sample for analysis, an air-tight fitting will need to be attached to the top of the well. The well should then be purged by removing a minimum of three

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casing volumes, although larger purge volumes may be warranted when sampling monitoring wells that are vented, thus allowing dilution of soil vapour. For typical well diameters, a purge rate of several litres per minute may be required, and therefore an appropriate sized pump is required for this approach.

A potential disadvantage of sampling a monitoring well is that it may not provide the desired vertical discretization in soil vapour concentrations and does not characterize the attenuation in soil vapour concentrations above the capillary fringe. The off-gasing of volatiles from groundwater in the well at the water table surface and from within the capillary fringe may also influence the soil vapour concentrations to varying degrees.

## 3.5.5 Subslab Soil Gas Probes

There may be health and safety and/or building integrity issues specifically associated with drilling through building slabs (e.g., post-tensioned reinforcing steel, utilities embedded in slabs). Relevant information should be reviewed and appropriate persons contacted prior to drilling or coring. As warranted and as feasible, geophysical techniques should be used to identify within and below concrete structures. After drilling the hole and prior to installation of the probe, the hole should be temporarily sealed (e.g., using a rubber stopper) to minimize disturbance to subslab vapour concentrations.

Typically, the objective of subslab soil gas sampling is to characterize vapour concentrations in foundation subsoils immediately below the slab. Therefore, permanent probes typically consist of stainless steel or brass inserts installed within a corehole through the slab that is sealed with concrete grout (USEPA, 2004). The concrete grout should consist of Portland cement, aggregate and water, and the MSDS should be reviewed to confirm that the materials do not contain any VOC additives<sup>3</sup>. Hydraulic grout is a fast setting, swelling cement that is commonly used. A subslab probe design by USEPA (2004) is shown in Figure 3.8.

## 3.5.6 Probe Materials

Relatively inert and non-porous materials should be used for soil gas sampling. Implants constructed of stainless steel are preferred but rigid PVC may also be used with sufficient equilibrium and purging to ensure sorption is not biasing results. Hers *et al.* (2004) demonstrated through a laboratory study that sorption of VOCs does occur on PVC pipe. There have only been a few studies evaluating tubing materials, but acceptable materials include Teflon<sup>TM</sup>, Nylon (Nyla-Flow<sup>TM</sup>) and polyetheretherketone (PEEK). Polyethylene tubing is subject to greater sorption than Teflon and Nylaflow and is not recommended. Silicon and Tygon tubing are highly sorptive and are not acceptable. For naphthalene, only Teflon performed satisfactory based on study summarized in text box suggesting Nylaflow should not be used for this compound, or

<sup>&</sup>lt;sup>3</sup> If there is doubt on possible additives, the cement should be tested. Elevated concentrations of tertiary butyl alcohol (TBA) were measured in subslab vapour samples at one site (where oxygenates were not present in source contamination) where QUIKRETE mortar repair was used.



tubing should be "conditioned" by drawing soil gas through tubing. Further research is needed to determine whether this is a viable approach.

Couplings that are compression-fittings or Swage-lok connections are preferred, although tight barbed-fittings (with tubing pushed over at least three barbs) should also provide for a reasonable seal. Glue, tape or other materials that could emit volatiles should not be used as part of probe construction. Relatively small diameter probes and tubing should be used to minimize purge volumes, although if pneumatic tests are performed, tubing diameter should generally be greater or equal to 6 mm to avoid excessive line losses (see SOP #2). Sampling trains should be kept as short as practical to minimize potential sorption.

Only new materials should be used, except when temporary steel probes are re-used. Steel probes should be decontaminated and dried prior to use. Care should be taken when storing and handling probe material to avoid contamination (*e.g.*, flexible tubing should be stored in sealed Zip-loc bags).

## **Tubing Studies**

Caro (2009): The potential for artefacts was evaluated by passing ultra-high purity (UHP) nitrogen through tubing materials then onto a thermal desorption (TD) tube. Of the flexible tubing materials tested, only Nylaflow and Teflon showed VOC concentrations below the laboratory's reported detection limit. Other flexible tubing materials yielded detectable VOC concentrations, which in some cases were considered "appreciable" at concentrations greater than 20% of the referenced regulatory standards. Freshly scratched PVC pipe had higher numbers and concentrations of detected VOCs than unscratched PVC pipe which showed detectable acetaldehyde only.

Hayes *et al.* (2006): Four tubing materials (PEEK, Teflon, Nylon and low density polyethylene (LDPE)) were evaluated for (i) background artefacts generated by a 2-foot length of tubing, and (ii) recovery of known 0.5 ppbV standard after gas flowed through a 2-foot length of tubing. The highest background artefact concentrations were obtained for LDPE; average values for toluene and m&p-xylene, were 12.5  $\mu$ g/m<sup>3</sup> and 4.8  $\mu$ g/m<sup>3</sup>, respectively. The concentrations for other tubing materials were generally much lower, except for 1,1-Difluoroethane for Teflon (average of 13.8  $\mu$ g/m<sup>3</sup>). The recovery test indicated good recoveries (70-130%) for all tubing except LDPE, where recoveries were low for heavier molecular compounds (*e.g.*, 12 % for naphthalene). For Nylon and Teflon, the naphthalene recoveries were 31% and 87%, respectively. This study shows tubing can influence soil vapour and air monitoring results, and are particularly significant given a short length of tubing was used for the study. The study indicates that Teflon and PEEK perform slightly better than Nylon for low-level analysis, but that LDPE performs poorly (note conversion of ppbV to  $\mu$ g/m<sup>3</sup> assumed

### 3.6 Soil Gas Sampling Procedures

Soil gas sampling procedures addressed in this section are soil gas equilibration, probe performance testing, sampling containers, decontamination, methods to detect leaks and short-circuiting, and purging and sampling. The methods used should be documented throughout the sampling process. SOP #2 provides additional details on soil gas sampling procedures. A good overview of sampling procedures is also provided in API (2005), Geoprobe (2006), ITRC (2007) and EPRI (2005).

## 3.6.1 Soil Gas Equilibration

Soil gas probes should be developed by removing air entrained during installation or allowed to re-equilibrate via diffusion prior to sampling. Development followed by equilibration is also acceptable and may be advantageous for PVC probes to enable sorption to occur (studies indicate that sorption on PVC can be significant). A minimum of three probe volumes of air (including the probe pipe or tubing and the pore volume of the sand pack) should be removed during development.

## **Equilibration Time for Sand Pack**

To answer how long does it take for the sand pack to equilibrate with surrounding soil gas, DiGuilio *et al.* (2006) used a model to calculate equilibration times for different distances and soil water contents. For a 50 mm diameter borehole, the equilibration time plot for the sand pack shows a required time of few minutes to a few hours.

Otherwise, the probe should be allowed to re-equilibrate prior to sampling. The time required for

equilibration will depend on the disturbance caused during installation. Suggested minimum equilibration times are: driven probes or where samples are obtained from direct push drive rods that remain in the ground (20 minutes), probes installed in small diameter direct push holes (one day), probes installed in auger holes or rotosonic holes where no air or water is used for drilling (two days). For probes installed using air rotary drilling, development and field screening should be performed after installation until soil vapour concentrations stabilize, and then the probes should be allowed to re-equilibrate for a few weeks prior to sampling.

### 3.6.2 Flow and Vacuum (Probe Performance) Check

The performance testing of selected probes should be conducted prior to soil gas sampling. The objective of the performance test is to verify the flow and vacuum are within acceptable ranges prior to sampling. The test is conducted by withdrawing soil gas from the probe at the desired flow rate using a pump and measuring the vacuum. For high vacuums (greater than about 30 to 40 inches of water), there may be practical issues associated with the ability of pumps or canister flow controllers to obtain samples. A lower flow rate may be desirable to reduce the vacuum. The absence of vacuum that is inconsistent with the known soil conditions (*i.e.*, a higher vacuum would have been expected) can be diagnostic of a leak in the sampling train. Vacuum and flow measurements should be comparable between sampling events.

Vacuum and flow measurements may also be used to estimate the soil-air permeability using mathematical models for soil gas flow to a point probe (Garbesi *et al.*, 1996) or to a well (Johnson *et al.*, 1990) (see SOP #2). Such tests may involve measuring the vacuum for several different flow rates (*i.e.*, step tests). For subslab soil gas samples, a lower vacuum (less than 1 inch of water) would typically be expected since granular materials are commonly present below foundation slabs.

As a minimum, the vacuum generated during performance testing should be allowed to dissipate before collecting a soil gas sample for analysis. If a relatively large volume of soil gas is removed or high pumping rate is employed during the performance test (which may cause a local disequilibrium), the probe should be allowed to re-equilibrate using similar criteria described above in Section 3.6.1.

### 3.6.3 Sampling Container or Device

Sample collection devices can include evacuated steel canisters, sorbent tubes, glass cylinders and gas-bags (*e.g.*, Tedlar<sup>TM</sup> (polyvinylfluoride)), and are compared in Table 3.3. The selection of a collection device is influenced by investigation objectives, analytical requirements and detection limits. Certain sampling devices (*e.g.*, syringes and gas-bags) are not approved methods in the BC Laboratory Manual (2009) for VOC analysis.

For field screening using hand-held detectors, soil gas samples are often collected using Tedlar bags. The use of vacuum chamber ("lung box") to fill Tedlar bags avoids passing soil gas through a pump and possible pump contamination that may result. This is advantageous since pumps may leak and become contaminated over time.

Gas-tight plastic syringes are used for on-site analysis using mobile laboratories, although as indicated by Hayes (2008), there can be large sorptive losses (as much as 80 to 90%) that occur that increase with increasing molecular weight of compound being analyzed.

Soil gas samples collected for analysis by a fixed laboratory for VOCs should generally be obtained using sorbent tubes or stainless steel (*e.g.*, Summa<sup>TM</sup>) or glass-lined steel (*e.g.*, SilcoSteel<sup>TM</sup>) canisters. Tedlar bags may be used for fixed gas analysis (oxygen, carbon dioxide, methane, nitrogen, etc.) provided that holding times are met (Table 3.3). Some laboratories recommend the use of Tedlar bags over canisters for reduced sulphur analysis because studies indicate the recovery of hydrogen sulphide and certain mercaptans is poor for aged glass-lined canisters (Bontempo and Kao, 2008; Rezendes and Lanna, 2004).

Depending on data quality objectives and anticipated soil vapour concentrations, it may also be appropriate to use Tedlar bags for analysis of VOCs. For example, when VOC concentrations are very high (% levels), some laboratories prefer that Tedlar bags be used because canisters are difficult to clean when concentrations are this high. However, Tedlar bags must be cautiously used since they leak over time and produce background artifacts. For example, Coyne *et al.* (2009) report background total VOC concentrations in Tedlar bags that were as high as 2,675  $\mu$ g/m<sup>3</sup>. Some practitioners initially fill a Tedlar bag in a vacuum chamber when sampling soil vapour and then immediately transfer the sample to a canister. This method is acceptable provided that data quality objectives are met, and new dedicated tubing and bags are used to collect the sample.

Due to a shortage of Tedlar, new plastics for air sampling bags are being evaluated. Coyne *et al.* (2009) compared SKC FlexFilm to Tedlar and found that while the concentration of background total VOC concentrations were about three times lower in FlexFilm than Tedlar, greater losses over time were observed for the FlexFilm samples.

TABLE 3.3. Soil	Gas Sample Collection	<b>Containers and Devices</b>
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Tedlar Bags	• Tedlar bags are available in volumes ranging from 10 ml to 10 litre; typically a 0.5 to 1 litre bag is used for soil gas sampling.
	• Tedlar bags can be filled using a: 1) small battery-powered electric pump, 2) peristaltic pump, or 3) vacuum chamber. Electric pumps can become contaminated (resulting in cross-contamination) and may leak over time. The vacuum chamber method involves placing a Tedlar bag in a sealed chamber that is evacuated, which in turn causes the bag to fill with soil gas. The vacuum chamber method avoids potential issues with pump contamination and leakage.
	• Studies indicate significant leakage of Tedlar bags over the first 24 to 48 hours after sampling (Wang <i>et al.</i> , 1996; and Andiro and Butler, 1991). Coyne <i>et al.</i> (2009) indicates recovery for some VOCs tested was less than 80% after three days.
	• Tedlar bag samples should be analyzed as quickly as possible. A maximum holding time of one day is recommended for reduced sulphur compounds and reactive compounds such as 1,3-butadiene while three days is recommended for chlorinated and petroleum hydrocarbon compounds (although two days is preferred).
Gas-Tight Syringes	• Gas-tight syringes are used to collect small volume gas samples (typically 5 to 60 ml). Syringes may be glass/Teflon or plastic, but there are large differences in sorptive properties.
	• Gas-tight syringes are typically used for on-site GC analysis.
	• Samples are analyzed within a short time (30 minutes) of collection.
Sorbent Tubes	• A wide range of sorbent materials are available and are selected based on the types and concentrations of chemicals expected in soil gas.
	• Sorbent tubes are placed in-line between the probe and pump.
	• Sorbent tube sampling rates are typically 100 to 200 ml/min; the flow rate supplied by the sampling pump must be accurately determined.
	• The sampling duration will depend on the expected concentration, flow rate, chemical type, sorbent and desired detection limit.
	• For quality control purposes, sorbent tubes often have a "front" and "back" section, or two tubes may be placed in series to evaluate possible chemical breakthrough.
<b>Stainless Steel or</b>	• Canisters have a relatively inert, passivated interior surface.
Glass-lined Steel	• Available volumes range from 400 ml to 6 litres.
Camsters	• Canisters are supplied under vacuum and should be measured prior to shipping by the laboratory, immediately prior to and after sampling using a gauge, and by the laboratory upon receipt. Significant differences in laboratory and field vacuums (beyond the range of accuracy of the gauge) indicate possible leakage during shipping.
	• There should be a residual vacuum left in the canisters; otherwise, the
	sample will not represent the entire planned sampling interval.
	<ul> <li>The sampling rate is typically controlled by a flow controller (either mass flow controller or critical orifice).</li> </ul>

## 3.6.4 Decontamination of Sampling Equipment

Clean equipment and sample containers should be used for soil gas sampling. This can be through decontamination implemented of equipment or through the use of new, unused equipment. Driven probes should be appropriately cleaned, dried and tested prior to use. Care should also be taken when handling equipment since sampling equipment could be contaminated through dirty containers. permanent marking pens, hands, vehicle exhaust, etc. The level of decontamination may depend on the objectives of the soil gas survey and detection limits for analytical testing.

### Helium Leak Tracer Test

When using helium as a tracer gas, it is important to recognize that the presence of methane in soil gas will result in a positive bias in helium concentrations when measured by common field detectors. A study conducted for this project evaluating the cross-sensitivity of a helium detector to methane found that at 15% methane, the helium detector measured about 4% apparent helium (Appendix D).

If the soil gas survey is limited to testing of soil gas samples using a field photoionization detector (PID) or flame ionization detector (FID) measuring to part-per-million levels, it may be appropriate to re-use the soil gas probes, tubing and sampling containers (*e.g.*, Tedlar bags). However, prior to installing a probe and collecting each sample, a field blank sample comprised of ambient air should be collected through the entire sampling train and tested using the field PID or FID. If concentrations in the field blank are elevated above background ambient levels, the equipment should be cleaned or new equipment should be used.

If the soil gas survey involves collection of soil gas samples for part-per-billion analysis, greater care must be taken with respect to decontamination and verification of clean sampling equipment and containers. It is recommended that the analytical laboratory be required to demonstrate that the containers and flow controllers, if applicable, are clean prior to shipment to the site and that new sample tubing in all cases be used for each soil gas probe. Field blanks should be obtained using certified zero gas as opposed to ambient air.

### 3.6.5 Testing of Probes and Sampling Train for Leaks and Short Circuiting

A leak tracer test may also be conducted by introducing helium beneath a shroud that covers the probe and valve (SOP-3). A soil gas sample is collected from the probe using a gas-bag and analyzed using a hand-held helium detector that provides readings with a range of 0.01% to 100%. Advantages of a helium leak tracer test are that real-time data is obtained, it is a relatively simple test to perform, and helium does not interfere with subsequent laboratory analysis.

A liquid tracer such as iso-propanol may also be deployed by wrapping paper towels soaked with the tracer around the probe and connections in the sampling train. Potential disadvantages with liquid tracers are that they may interfere with laboratory analyses, do not provide for near realtime results (unless analyzed by a field laboratory), and experience suggests the liquid tracer may diffuse or permeate through very small cracks. There are several ways in which the sampling train can be tested for leaks. A similar helium leak tracer procedure may be conducted to that described above when it is possible to place the sampling train within the shroud. A simple method is to apply either a pressure or vacuum to the sampling train and to monitor whether the pressure or vacuum holds over time. When under pressure, a soapy-water solution may also be used to identify any couplings that may be leaking since air bubbles should be observed. A shut-in test method is described in Appendix C.

An alternate method, described by API (2005), involves testing of sampling equipment for potential leaks using a tracer gas (*e.g.*, diluted helium) of known concentration that is drawn through the sampling equipment at the approximate vacuum anticipated during sampling. The API method is described in SOP #3.

Potential short-circuiting of atmospheric air during sampling can also be indirectly evaluated through careful examination of oxygen and carbon dioxide data. For example, oxygen concentrations are generally depleted in the presence of elevated hydrocarbon vapour concentrations near petroleum sources, so if a soil gas sample contains moderate to high concentrations of both hydrocarbons and oxygen, atmospheric air may have leaked into the sample (see Chapter 5 for additional discussion).

## 3.6.6 Sample Probe Purging and Sampling

The purpose of purging is to ensure a representative soil gas sample is collected by removing stagnant air from the probe and filter pack prior to collecting a sample. Typically, the objective is to obtain a soil gas sample from the geologic material immediately surrounding the probe, therefore excessive purging should be avoided.

Cody (2003) evaluated purge volumes on the basis of a differential equation for the sequential and complete mixing of VOCs over each time step within the entire volume under consideration (probe and tubing, but excluding the filter pack). On the basis of this equation, the estimated concentration within the probe volume reaches 90% of the input concentration after purging about three volumes. For narrow diameter tubing, fewer purge volumes are likely

## Purging and Sampling Summary

- 1. Allow probe to equilibrate.
- 2. Check for leaks in sampling equipment.
- 3. Calculate the dead volume based on the inner volume of probe and tubing.
- 4. Purge three volumes from the probe.
- 5. A flow rate between 20 and 200 ml/min should generally be used for purging and sampling.
- 6. Monitor the vacuum during purging; reduce the flow rate if the vacuum exceeds 10 inches water.
- 7. Use direct reading instrument to monitor VOC concentrations during purging, where practical.
- 8. When purging is complete, close the sampling valve and allow the vacuum to dissipate before collecting a sample.

needed to obtain a representative sample due to reduced mixing resulting from more of a "plug flow" phenomena.

Some regulatory agencies and practitioners advocate sequential sampling and field testing of organic vapour and fixed gas concentrations during the purging process to optimize the process (*i.e.*, a sample is collected using a purge volume that corresponds to the maximum concentration obtained for a prior purge study or when the field readings stabilize). For example, California DTSC (CalDTSC, 2010) requires that purge volume testing be initially conducted on a subset of probes where field parameters are measured after removal of 1, 3 and 10 purge volumes. When conducting purge volume tests, samples should be obtained using Tedlar bags (readings should not be obtained by directly connecting the field detector to the probe). The "optimal" purge volume is the volume for which

## Modeling Study of Purging and Sampling

A modeling study was conducted using a finite element numerical model (VapourT) to evaluate the influence of sampling flow rate, probe depth, surface cover, probe annular leakage and contamination source location (Appendix B). The modeling study indicated that for probes installed in homogenous soil with а uniform contamination source, the soil vapour concentration should not change appreciably with sampling flow rate or soil gas volume removed. When heterogeneity is introduced or there is annular leakage, the results are variable.

the highest concentration is measured, with certain exceptions including shallow probes (less than 1.5 m deep) where the purge volume defaults to three probe volumes.

Published studies evaluating the effect of purge volume on soil vapour concentrations have indicated variable results. Hartman (2008) reports test results where the differences in TCE concentrations in soil vapour for samples obtained at increments between one and ten purge volumes were generally less than a factor of two, and a maximum factor of three, and where concentrations at most probes increased over time. DiGuilio *et al.* (2006) report results where chlorinated solvent concentrations were stable with less than 10% difference in concentrations for purge volumes that were 1 litre or greater. A purge volume based on stability analogous to the current practice for groundwater sampling requires further research to determine whether the additional effort is justified and to establish criterion for stability, which currently do not exist.

The removal of three purge volumes, comprised of the internal volume of the probe, tubing and air-filled pore space of the filter pack, prior to collection of sample for analysis is recommended. Purge volume tests as described above may be conducted to refine purge volumes.

#### High Purge Volume (HPV) Sampling

High purge volume (HPV) sampling may be desirable if the intent is to evaluate conditions beyond the immediate proximity of the soil gas probe. If the approximate permeability and soil gas flow regime is known, a volume-integrated concentration may be obtained (McAlary *et al.*, 2010). Transient vacuum response data may also be used to estimate the leakage of a foundation slab, given certain assumptions are fulfilled for boundary conditions and the contrast in permeability between the fill below the slab and underlying native soil. The HPV approach has potential advantages when obtaining subslab samples below larger buildings, where the volume of a conventional discrete soil gas sample is very small compared to the total volume of gas-filled soil pores. For example, for a 5,000 m<sup>2</sup> building, the volume of gas-filled soil pores is 300,000 litres assuming a soil thickness of 0.2 m and gas-filled porosity of 0.3. The concentration trends

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over time as measured by direct reading instruments may also provide qualitative information on spatial variability in source concentrations. For example, slowly increasing concentrations could indicate a higher soil gas concentration zone laterally removed from the probe. Commensurate with HPV sampling is the need for larger pumps, the removal of hundreds or thousands of litres of soil gas and repeat testing over time.

#### Sampling Flow Rate

The soil air permeability has an important influence on sampling flow rate since the vacuum generated increases as the permeability decreases. One study demonstrated that soil vapour concentrations were not sensitive to a flow rate of up to 10 L/min, in samples collected from properly sealed probes screened in moderately permeable materials (McAlary and Creamer, 2006). Conversely, it may not be practical to collect samples at flow rates of 100 ml/min in finegrained soil (e.g., silts and clays) without imposing an excessive vacuum. High vacuums increase the potential for leakage from the probe or sampling train. Some guidance documents also suggest that high vacuums enhance the volatilization or desorption of chemicals (ITRC, 2007; API, 2005). Where possible, the vacuum during sampling should be less than 10 inches water column (by adjusting the flow rate), although in some circumstances sample collection may require vacuums as high as 100 inches. The vacuum and flow can be easily measured using a Tjunction connected to a digital manometer and rotameter to determine an appropriate sampling flow rate for a given geologic material permeability (EPRI, 2005; ITRC, 2007). Practically, the sampling rate is often dictated by the sampling device. For evacuated canisters, use of a flow regulator is good practice, and typically results in sampling rates between about 5 and 100 ml/min. For most sorbent tubes, the analytical protocols indicate that the sampling rate should not exceed 200 ml/min.

#### Sample Collection

Once purging is complete, soil gas samples from conventional soil gas probes should generally be collected using the same sampling flow rate as for purging. For subslab soil gas probes, it may be desirable to collect a subslab gas sample concurrently with an indoor air sample to reduce the influence of short-term variability and enable comparisons to indoor air data over the same time period. Indoor air samples are typically obtained over an 8-hr period for non-residential scenarios and 24-hour period for residential scenarios. The soil gas sampling rate for a 6-litre subslab canister sample collected over 24 hours is about 6 mL/min. Sampling of probes at a site should be completed over a relatively short time period (*e.g.*, within one week) to provide an internally consistent data set (Lahvis, 2002). If any water is drawn in the sample container, re-collect the sample after taking measures to eliminate water.

### Sample Handling and Storage

Soil gas samples obtained using syringes, steel canisters or Tedlar bags should not be placed in a chilled cooler for transport since volatiles may condense out of the vapour phase at lower temperature (Hartman, 2002). Samples should not be subjected to excessive heat.

Tedlar bags and glass cylinders should be placed inside an opaque container immediately after collection to avoid possible photo-oxidation reactions.

For sorbent tubes, cool storage in sealed containers is recommended where during transport the temperature is less than 10°C, and in the laboratory is less than 6°C. Sorbent tubes should be stored in a sealed plastic container containing a bed of activated carbon to minimize the potential for adsorption of ambient VOCs. All soil gas samples should be transported in separate containers from soil and groundwater samples.

## 3.7 Soil Gas Analytical Methods

## 3.7.1 Selection of Method

Analytical testing methods appropriate for analyzing soil gas samples are dependent on risk assessment objectives, sampling method and data quality objectives. Soil gas programs often consist of a combination of field testing of soil gas samples using handheld detectors and laboratory analysis of selected soil samples for specific gas chemicals of potential concern. Since analytical testing is a broad topic, only an overview of the key issues is provided below. Common analytical methods for soil vapour are summarized in Table 3.4, with a detailed list provided in Appendix E. Analytical methods for hydrocarbon fractions are

### **BC Requirements**

In British Columbia, methods for soil vapour analysis must be approved by the Director of the Environment Management Branch of the Ministry of Environment, and are described in the BC Laboratory Manual (2009):

- 1. VOCs in Air by Canister Sampling / GC/MS (reference method EPA TO-15).
- 2. VOCs in Air by Thermal Desorption Tube / GC/MS (reference method EPA TO-17).
- 3. VOCs & Other Volatile Substances in Air by Charcoal Tubes and Miscellaneous Collection Media.
- 4. Volatile Hydrocarbons in Air by GC-FID / GC-MS.

The first three methods are performance based methods, while the fourth method is a prescriptive method with options.

reviewed in Appendix F. The BC Environment Laboratory manual also contains selected methods for air analyses including their adaptations of USEPA Method TO-15 (canisters) and Method TO-17 (sorbent tubes). Laboratory accreditation in BC for air analyses is not required, but may give data users a higher degree of confidence and certainty about the quality of the test results, where available (*e.g.*, under Canadian Association for Laboratory Accreditation (CALA) program).

It is important to understand procedures and potential limitations associated with different testing methods. Since soil vapour and air methods are not as well defined as groundwater methods, adequate consultation with the laboratory is essential. The types of information that should be discussed include optimal sampling flow rate and duration, detection limits, laboratory QA/QC requirements and considerations, and the handling and transport of samples. Communication with the laboratory at the early stages ensures that important analytical considerations are taken into account during the development of the sampling plan.

### 3.7.1 Field Detectors

Field detectors commonly used are photoionization detectors (PID) or flame ionization detectors (FID), combustible gas detectors or explosimeters, and multi-gas detectors for compounds such as oxygen, carbon dioxide and methane, which are important for studies evaluating biodegradation. Photoionization detectors will respond to most organic vapours as well as some inorganic vapours (hydrogen sulphide, ammonia) depending on the ionization lamp energy. The sensitivity of a PID varies depending on the compound, and moisture and flow rate can bias readings; therefore care should be taken when conducting soil gas surveys.

Combustible gas detectors are typically calibrated to methane in air, but also readily respond to heavier hydrocarbon (*e.g.*, gasoline) vapours. Some combustible gas detectors have a methane elimination mode; however, not all methane is eliminated (about 90% for one common combustible gas detector). It is important to document the type of combustible gas detector and mode of operation. Photoionization detectors, which measure hydrocarbon vapour concentrations to ppmV, or even ppbV levels, are generally more sensitive than combustible gas detectors.

While field detectors are valuable for site screening, the limitations associated with these instruments, including non-specificity to compounds of possible interest and the effect of environmental factors and sampling methods, should be clearly understood (Robbins *et al.*, 1990). For example, infrared detectors for methane are subject to significant positive bias when exposed to gasoline vapors or other light hydrocarbon vapours, as described in Appendix G.

Field detectors should generally not be directly connected to sampling probes when taking measurements, unless it can be demonstrated that possible sampling flow rate constrictions and vacuums generated by sampling will not affect the field detector response. Photoionization detectors, in particular, are sensitive to variation in the sampling flow rate. Samples should generally be obtained in gas bags to facilitate readings taken using field detectors. All instruments should be calibrated on a daily or more frequent basis in accordance with manufacturer's instructions. Calibration should be documented.

## 3.7.2 Field Laboratory Analysis

Field laboratory methods are used when a greater degree of precision and/or component-specific information is required to make real-time decisions. The advantages of field laboratory methods are near real-time results, which can be used to modify programs while in progress, and potentially lower costs if the number of samples analyzed is high. The ability to collect repeat samples can also be an advantage for assessing sampling, temporal, and spatial variability. The disadvantage of field laboratory methods are higher detection limits than fixed laboratory methods based on USEPA - protocols (see below). Regulatory acceptance of field laboratory methods should also be reviewed when selecting methods.

	Compound Class	Collection Device	Method	Method No.	Comments
Field Screening	VOCs	Tedlar Bag	PID/FID		• Lower cost, real time results, equipment is simple to use
Methods	Fixed Gases (O <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> )	Tedlar Bag	Infrared (CO <sub>2</sub> , CH <sub>4</sub> ), electrochemic		<ul> <li>PID sensitive to moisture and dust, overhead power lines</li> <li>FID requires H<sub>2</sub> source and</li> </ul>
	Combustible	Tedlar Bag	al (O <sub>2</sub> ) Platinum		<ul> <li>more operator training</li> <li>Generally ppm detection limits (except fixed gases at % level)</li> </ul>
	Uases		cataryst		<ul> <li>Not compound specific, may be cross-sensitivities (e.g., infrared detectors)</li> </ul>
					• Some detectors are designed to sample against vacuum ( <i>e.g.</i> , Landtec); other instruments are sensitive to vacuum and flow rate constrictions
Field Laboratory Methods	VOCs (e.g., BTEX)	Glass and Teflon syringe, Tedlar Bag	GC/PID GC/MS	Modified USEPA 8021B Modified USEPA 8260B	<ul> <li>Near real time results</li> <li>Use of liquid (as opposed to gas) calibration standards may not provide representative data for some compounds</li> <li>May need to analyze sub-set of samples using fixed laboratory methods</li> </ul>

# TABLE 3.4. Summary of Common Soil Vapour Sampling and Analysis Methods

	Compound Class	Collection Device	Method	Method No.	Comments
Fixed Laboratory Analysis	VOCs	sorbent tube, solvent extraction	GC/FID <sup>1</sup>	OSHA 7 / NIOSH methods	<ul> <li>Lower detection limits (except some NMOC &amp; TVOC methods)</li> </ul>
	VOCs and SVOCs	sorbent tube, thermal extraction	GC/MS	USEPA TO-17	<ul><li>More rigorous QA/QC</li><li>Higher cost</li></ul>
	VOCs	Specially– treated) canister	GC/MS	USEPA TO-14A /TO-15	<ul> <li>Depending on chemical, may be issues for sorbent tube analysis (<i>e.g.</i>, recovery, breakthrough)</li> <li>High humidity can cause</li> </ul>
	PAHs	XAD-2 & Polyurethane foam (PUF)	GC/MS	USEPA TO-13A	problems for analysis
	VHv and Hydrocarbon Fractions <sup>2</sup>	Canister or thermal tube	GC/MS or FID	BC Lab Manual	
	TVOC	sorbent tube, solvent extract	GC/FID	NIOSH 1550	
	TVOC	Canister or Tedlar Bag	GC/FID (Cryotrap)	USEPA TO-3	
	NMOC	Canister or on-line	FID	USEPA TO-12	
	Fixed Gases ( <i>e.g.</i> ,O <sub>2</sub> , CO <sub>2</sub> , CH <sub>4</sub> , CO, H <sub>2</sub> )	Canister, Tedlar Bag, Glass syringe	GC/TCD	ASTM D1945-03	

Notes:

- 1. MS is also used by commercial labs but is not part of the reference method.
- 2. Hydrocarbon fractions (*e.g.*, CCME fractions) are not defined in BC Laboratory Manual but are laboratory specific methods.
- 3. GC = gas chromatograph, PID = photoionization detector, FID = flame ionization detector, TCD = thermal conductivity detector, MS = Mass Selective detector
- 4. USEPA = US Environmental Protection Agency
- 5. NIOSH = National Institute for Occupational Safety and Health (USA)
- 6. OSHA = Occupational Safety & Health Administration (USA)
- 7. NMOC = non-methane organic compounds
- 8. CCME = Canadian Council for Ministers of the Environment

Field laboratory methods include the use of portable gas chromatographs (GCs) that are brought to the site to analyze grab samples on an on-going basis. Soil gas air is usually collected using gas-tight syringes and is injected into the GC (or purge-and-trap apparatus) for analysis. The portable GC usually analyses data through photo ionization, flame ionization or electron capture detectors (*e.g.*, modified USEPA Method 8021B). The precision of the results can vary depending on the equipment used. There are now some contractors that provide field testing services using portable mass spectrometers (MS), which provide greater certainty for compound identification (*e.g.*, modified USEPA Method 8260B). Modified water methods (Method 8021B and 8260B) can work well for many compounds, but for polar compounds and heavier molecular weight compounds such as naphthalene, recovery tends to be poor (Hayes *et al.*, 2005). A particularly important aspect is the method used for calibration, which can significantly influence results, and which varies between laboratories (CalDTSC, 2010).

## 3.7.3 Fixed Laboratory Analysis

For risk assessment studies, low detection limits and more rigorous quality control requirements typically require that soil gas samples be collected using either active sorbent tubes (*i.e.*, air is drawn through tube using pump) or steel canisters, and quantified by GC/MS methods. The use of GC/FID analysis is generally not recommended due to non-specificity of detection.

Sampling using a sorbent tube is an indirect method of estimating the soil vapour concentration in that the test measures the mass of chemical trapped on the sorbent. The air concentration is estimated by dividing the mass by the total volume of air drawn through the tube. The canister method involves collection of a "whole air" sample enabling direct analysis of the soil vapour sample. The sorbent tube and canister methods are described below with additional details on analytical methodology provided in Section 4.4.

#### Active Sorbent Tube Method

Sorbent tubes have been used for indoor air quality testing for several decades, but only more recently for soil vapour. There are complicating factors for soil vapour that should be accounted for, including higher humidity (often 100%), and typically much higher concentrations and larger range of analytes that are quantified.

**Analytical Methods**: A key distinguishing factor between methods is whether thermal desorption (*e.g.*, USEPA TO-17) or solvent extraction is used (*e.g.*, modified OSHA 7 or NIOSH 1501 methods). Thermal desorption involves rapidly heating the sorbent to desorb the VOC, while passing an inert carrier gas through the tube. The VOCs are carried by the gas and concentrated on a smaller downstream trap, which usually is cryogenically cooled. For thermal desorption, the whole sample is released from the sorbent during the heated desorption step. While some of the earlier thermal desorption units do not allow for the possibility for replicate analyses, the newest units have the capability of re-collecting a portion of sample during the primary desorption step to allow for re-analysis. Additionally, sample introduction parameters can be modified such that less mass is loaded onto the GC/MS in order to perform sample dilutions. As compared to the application of thermal desorption methods to indoor air, the potentially high contaminant loadings in soil vapor require additional care in determining

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sampling volume and sorbent material to minimize saturation of tubes and analytical instrumentation. The sensitivity of thermal desorption techniques requires a smaller soil gas volume to meet screening levels than solvent extraction techniques.

Solvent extraction involves use of a solvent such as carbon disulphide to extract the sample. In contrast to thermal desorption, replicate analyses can be performed on the extract. While chemical extraction methods are adapted from industrial hygiene practice and are typically not as sensitive as thermal desorption, higher detection limits may not be an issue for soil vapour analysis (but may be problematic for air analyses). To achieve low detection limits, NIOSH or OSHA methods involving chemical extraction are modified and typically utilize a larger mass of sorbent combined with longer sampling durations. As discussed below, longer sampling durations can pose challenges in terms of breakthrough.

**Types of Sorbents:** Sorbents used for VOCs commonly used consist of charcoal, polymeric and/or carbonaceous resins. There are wide variations in sorbent properties. Since soil gas typically has a relative humidity of close to 100 percent, hydrophobic sorbents are required since sorbed water reduces the retention of VOCs, and because water vapour can affect the GC analysis (Harper, 1994). Polar VOC compounds can also partition into the water phase reducing recovery. Elevated ozone levels (150 ppm to 300 ppm) have been reported to result in reduced recovery for certain VOCs such as styrene and aldehydes (McClenny *et al.*, 2002). Other issues for sorbent and adsorbed molecules, and slow breakdown of certain polymeric sorbents and release of aromatic hydrocarbons (Harper, 1994). Special attention should be paid to sorbents selected for analysis of highly volatile chemicals such as vinyl chloride, which are difficult to trap using sorbent media.

For TO-17 soil vapour analysis, the choice of an appropriate sorbent is an area of active research. Combining hydrophobic sorbents of increasing strength allows the collection of a wider volatility range. For example, sorbent tubes containing a combination of Tenax, Carbograph 1TD, and Carbograph 5 TD were shown to successfully retain lighter VOCs such MTBE while allowing for the efficient desorption of naphthalene under sample conditions of high humidity (Hayes *et al.*, 2007). This same study showed that water adsorption on a multi-bed sorbent tube containing Carbosieve S-III resulted in analytical interference resulting in unusable data. These effects were noted under conditions of approximately 75% relative humidity and sample volumes as low as two liters. Marotta (2008) presented results of testing of the PerkinElmer SVI tube (contains three different adsorbants) indicating good recovery obtained over a wide analyte range (dichlorodifluoromethane to phenanthrene), good water management and cleaning properties, and limited carryover of heavier compounds (less than 1.2% for phenanthrene).

For solvent extraction methods, coconut shell charcoal (CSC) is typically used for BTEX analysis (NIOSH 1501). For chlorinated solvent compounds, some laboratories substitute CSC with newer more sorptive materials such as processed synthetic carbon (*e.g.*, Anasorb 747) or molecular sieve materials in place of the CSC.

Sorbents used for semi-volatile (PAH) analyses (naphthalene and heavier molecular weight compounds) often consist of Teflon<sup>TM</sup>-impregnated glass fibres followed by a resin (XAD-2) sorbent (NIOSH 5515 or USEPA Method TO-13A). Since trapping of particulates for soil

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vapour is usually not an objective, typically only the XAD resin sorbent is used for semi-volatile analyses (*i.e.*, polyurethane (PUF) foam is not used).

Sorbent Sampling Volume: The sampling volume carefully should be determined through consideration of the expected VOC concentration and mass, the sorption capacity and required detection limits. When available, the results of field PID analyses of soil vapour should be communicated to the laboratory analyst prior to sorbent sampling to guide selection of a sampling duration and flow rate that would minimize the potential for chemical breakthrough. An option is to collect two samples over different time durations to avoid the possibility of re-sampling.

**Pump Flow Rate:** Since the concentration is sensitive to the flow rate, pumps must be accurately calibrated and provide a constant flow rate throughout the sampling duration. The pump flow

### **Sampling Volume Calculation**

An example sampling volume calculation is provided for sorbent tube analysis for benzene. Assuming a target indoor air concentration of 3  $\mu g/m^3$ , a target detection limit of 30  $\mu g/m^3$  for a soil gas sample is obtained (Eq. 3-1 Section 3.8.2). A typical benzene detection limit is 0.1 µg (MS detector), therefore approximately 3.3 litres of soil gas would need to be through drawn the tube  $(0.1 \mu g/30 \mu g/m^3 \times 1000 L/m^3)$ . At a sampling rate of 100 ml/min, the required sampling duration would be 33 minutes.

rate must be checked prior to and during sampling, since actual pump flow rates may vary considerably depending on the soil air permeability and vacuum. A recent study (Golder Associates, 2007, unpublished) found a significant and roughly linear drop in pump flow rate under vacuum conditions induced by soil (*e.g.*, 11% drop in flow at 3.4 inches  $H_20$ , 40% drop at 9 inches  $H_20$  and 93% drop at 16.5 inches  $H_20$ ).

**Environmental Conditions**: Appropriate measures should be taken to mitigate the effects of high humidity or cold weather when sampling using sorbent tubes, which may not always be practical to avoid. Reducing the air flow rate or sampling with varying volumes of air (using multiple samples) may be a good approach under this circumstance. Further discussion on cold weather considerations is provided in Exhibit 3.2.

### Canister Method

Low detection limits can be achieved utilizing the Summa canister method (USEPA Method TO-15) and, in general, the accuracy and precision of analytical results generated are high. Nevertheless, there are significant issues for this method as described below.

**Analytical Methods:** The analytical protocols for the canister method are USEPA TO-14A (non-polar compounds) (USEPA, 1999a) and USEPA TO-15 (polar and non-polar compounds) (USEPA, 1999b). USEPA Method TO-15 is commonly used for soil vapour analyses since there are a number of significant improvements for Method TO-15 compared to TO-14A, including enhanced measures for quality control, specific canister cleaning procedures, better water management procedures and better recovery of polar compounds. USEPA Method TO-15 utilizes cryotrapping to concentrate analytes, followed by water removal, and then injection in a gas chromatograph (GC) with a mass spectrometer (MS) as the detector. When the MS is run in

full scan mode up to 70 compounds can be readily detected with typical reporting limits between 0.2 to 0.5 parts per billion by volume (ppbV).

Naphthalene is now commonly reported by laboratories that perform TO-15 analysis; however, the analysis of heavier molecular weight compounds such as naphthalene is challenging due to sorption onto sampling materials and reduced recovery. For example, Entech (2007) show sorption onto metal tubing and filters resulted in reduced recovery of trimethylbenzene and heavier compounds. Hayes and Benton (2005) based on a laboratory study of Method TO-15 conclude naphthalene can be quantified to sub-ppbV concentrations in air. They caution that carryover of naphthalene in the TO-15 sampling train appears to be a significant concern relative to other compounds with higher vapour pressures, and that the daily variability in naphthalene recovery was greater for naphthalene compared to other compounds.

**Hardware:** Summa canisters are constructed of passivated electropolished stainless steel<sup>4</sup>, a relatively inert material, and are supplied under vacuum. For soil vapour sampling, a one-litre canister typically provides for sufficient volume.

A uniform flow rate is provided by a flow controller that incorporates a critical orifice. A critical orifice is sometimes used as the sole-restricting device, but it does not provide for a uniform flow because the flow rate is a function of the pressure differential. Flow controllers should deliver a uniform flow rate over most of the sampling interval (*i.e.*, between 30 and 5 inches Hg vacuum). Flow controllers are temperature and altitude dependent; therefore, the sampling location should be communicated to the laboratory so that appropriate adjustments can be made.<sup>5</sup>

While use of a flow controller is preferred to obtain soil vapour samples, it has become fairly common practice to only use a critical orifice for collection of short-duration (less than one hour) soil vapour samples given the much higher cost of a flow controller and challenges associated with cleaning flow controllers. When using critical orifices, the sampling rate is less stable, and there is more often zero vacuum left in the canister at the end of the sampling duration. The use of critical orifices for soil vapour sampling is considered acceptable, but the laboratory should provide the maximum flow rate for the orifice, and this rate should be within project specified sampling requirements.

Particulate filters consisting of sintered steel with 2 to 7 micron pore sizes or deactivated glass frit are placed before the critical orifice. It is essential that all fittings are tight during sampling.

**Equipment Cleaning:** The TO methods and hardware were designed to measure low VOC concentrations in ambient air. At some sites (*e.g.*, dry cleaners, UST sites with free-phase NAPL), canisters may contain soil vapour concentrations as high as 1,000,000  $\text{ug/m}^3$ . Experience has shown that there is a significant potential for contaminant carry-over in the canister, regulator, filter or inlet tube under these conditions. Therefore, laboratories must clean all canisters and

<sup>&</sup>lt;sup>4</sup> Silcosteel canisters are a different type of canister where steel is coated with an inert fused silica layer that is non-reactive with sulphur compounds or compounds that react with metal surfaces

<sup>&</sup>lt;sup>5</sup> Laboratories typically conduct performance studies to verify that flow regulator's provide for an uniform sampling rate over the sampling duration, within an acceptable tolerance. If warranted, flow rates can be verified in the field using an extra canister using an electronic mass flow meter or rotometer, calibrated for vacuum conditions.

flow controllers and test canister blanks. Canisters are typically cleaned by heating the canister and passing humidified high purity air under pressure through the canister.

**Environmental Conditions:** Although a water film on the internal surface of a Summa canister is needed for an inert surface, excessive humidity can create challenges for sample recovery and cryogenic focusing prior to analysis. An alternate method of multiple focusing steps using non-cooled sorbent tubes can reduce problems associated with water vapour.

#### Method Selection

The chemical to be measured, detection limit, ease of use, cost, laboratory certification and quality control are factors that should be considered when selecting the soil gas analysis method. The use of thermal tubes analyzed by Method TO-17 and canisters by Method TO-15 are both considered acceptable methods for a wide range of compounds. Modified OSHA or NIOSH methods may be acceptable for a more limited range of analytes. Analysis by GC/MS is recommended regardless of the collection method, except when hydrocarbon fractions are analyzed (see Appendix F).

The potential advantages with thermal tubes compared to evacuated canisters include that they tend to be easier to clean and provide for better recovery of higher molecular weight compounds. The disadvantages include possible breakthrough, the requirement for a pump, and accurate flow measurements. The potential advantages of evacuated canisters are a more direct measurement through whole air sample collection and easier sample collection. The disadvantages include poorer recovery of higher molecular weight compounds, challenges with hardware (*e.g.*, fittings, controllers, gauges) and greater difficulty in cleaning canisters compared to tubes.

Several studies have compared TO-15 and TO-17 results. Desrosiers *et al.* (2009) report a relatively good comparison between chlorinated solvent concentrations in indoor air measured using co-located samples analyzed by Methods TO-15 and TO-17. For PCE, TCE and 1,1,1-TCA, the percent differences ranged between 0 and 44%, while for 1,1-DCE and cis-1,2-DCE, the differences ranged between 21 and 71%. For lighter molecular weight compounds, on average, the TO-15 concentrations were higher than the TO-17 concentrations, while for tetrachloroethylene, the TO-17 concentrations were higher. Hayes *et al.* (2007) qualitatively compared the total ion chromatographs for TO-15 and TO-17 analysis of gasoline soil vapour samples and found a similar pattern up to n-C11, beyond which there was a reduced response for the TO-15 run, including naphthalene and heavier peaks.

## **EXHIBIT 3.2:** Considerations for Cold Weather Sampling

In many regions of Canada, environmental investigations may be completed during periods of relatively cold weather (*i.e.*, freezing temperatures). Frost and snow cover are hypothesized to potentially influx soil vapour flux and oxygen recharge to subsurface, but there is little empirical data that would either support or refute this hypothesis. There may also be significant temperature gradients between shallow soil beside and below a building, where the temperature may be well above freezing. Obtaining a soil vapour sample within frozen ground, while potentially feasible, is not considered representative and therefore either deeper external vapour samples or samples from below the building should be obtained.

Certain pre-cautions should also be taken when conducting soil vapour programs during cold weather. Field instruments such as photoionization and flame ionization detectors and pumps are not designed to operate when temperatures are below freezing. Field instruments may be kept warm in a heated building or vehicle, with field samples collected and transported in Tedlar bags. Sampling pumps may be kept warm by storing them in insulated coolers or insulated lunch bags with heat packs. While the cold temperature performance of sorbent tubes is not well understood, consideration should be given to heating and insulating of sorbent tubes during sampling and keeping above-ground tubing as short as practical. There may also be condensation through cooling of warmer soil gas during sampling. Condensation can be particularly problematic for sorbent tube sampling and therefore sample tubing and bags should be closely observed for any signs of condensation (*e.g.*, through use of translucent tubing). Further guidance on cold weather sampling is provided in Appendix H.

## 3.8 Quality Assurance / Quality Control Considerations

### 3.8.1 Data Quality Objectives

Data quality objectives should be established as part of the sampling plan in conjunction with the overall study objectives. In broad terms, the objective is to ensure that data quality is acceptable and that data can be relied upon for decision-making purposes. Specific objectives may be developed in terms of precision, accuracy, representativeness, comparability, completeness and detection limits. There may also be specific considerations for cold weather sampling that should be incorporated in the data quality objectives (Exhibit 3.2).

The development of a QA/QC plan will help to ensure that the desired data quality is achieved. Standard operating procedures should be used for sampling and analytical procedures. Systematic data collection and planning helps provide for defensible results and increased credibility.

### 3.8.2 Detection Limits

For risk assessments, the measured soil vapour concentrations are often used to predict indoor air concentrations. Required detection limits may be back-calculated using risk-based target indoor air concentrations combined with a conservative (high) attenuation factor between soil vapour and indoor air (*e.g.*, 0.01 to 0.1). An additional "safety factor" (about 5-10X) should be applied to provide for greater flexibility in data interpretation and since there is increased uncertainty near to the detection limit. The target detection limit is calculated as follows:

$$DL_{target} = C_{air} / (AF * SF)$$
[3-1]

Where DL is the detection limit (assumed to be equal to the reporting limit), AF is the attenuation factor,  $C_{air}$  is the target indoor air concentration, and SF is safety factor (5-10). For thermal desorption tube and canister methods, depending on the compound, it may be possible to obtain lower detection limits. However, when concentrations of selected compounds are very high, there may be raised detection limits due to matrix interference. When concentrations are expected to
be high (*e.g.*, based on PID readings), it is important to discuss strategies for sample collection and analysis with the laboratory.

# 3.8.3 Duplicate Samples

Analysis of duplicate samples is required to assess the precision of the method and variability of the sampling process. The field duplicate samples should be obtained from the same soil gas probe using identical sampling procedures and submitted blind to the laboratory. Duplicate samples can either be obtained simultaneously (*i.e.*, using a splitter) or in sequence. When duplicate samples are collected in sequence, variability due to temporal changes is introduced. For indoor and outdoor air sampling, a duplicate sample may be obtained using a splitter or side-by-side (co-located) samples may be obtained. A review of issues for duplicate analyses is provided in Appendix I.

# 3.8.4 Field Quality Control Tests

The recommended field quality tests for analysis of sorbent tubes are as follows:

- *Cleaning and Proofing*: Thermal tubes should as a minimum be batch proofed and the usage history of each tube should be recorded by the laboratory to enable tracking of suspected contamination (BC Laboratory Manual, 2009).
- *Field duplicates*: Should be obtained by collecting distributed volume pairs submitted blind to the laboratory. The minimum frequency is 10 percent of the samples analyzed. When less than 10 samples are analyzed, it is recommended that one field duplicate per sampling event be analyzed.
- **Tests for Breakthrough**: For tubes that are solvent extracted (*e.g.*, NIOSH methods), the front and back sections of sampling tubes for every sample collected should be analyzed separately to evaluate for chemical breakthrough (see Chapter 5 for thresholds for evaluating breakthrough). For thermal desorption tubes, the laboratory should provide information about safe sampling volumes (SSV) that apply to each test parameter. Two tubes in series may be analyzed to determine whether breakthrough has occurred; however, it is not standard practice to test two tubes and also not required by the TO-17 method. The sorptive capacity of some thermal tubes is relatively high and provided that sampling volumes are not excessive, the potential for breakthrough is low (much of this depends on the experience of the laboratory). It can be helpful to communicate field PID or previous analytical results to the laboratory to evaluate the potential for breakthrough. If there is any uncertainty and in particular at sites with high soil vapour concentrations (*e.g.*, near NAPL zones), it is good practice to analyze two tubes in series.
- *Multiple Tubes with Different Sampling Volumes*: This procedure may be warranted to minimize the potential for breakthrough or when compounds with widely differing sorptive properties are being analyzied. If the laboratory uses a thermal desorption unit with re-

collection feature, collection of multiple tubes may not be warranted because there is greater flexibility for re-analysis.

- *Field transport blank*: For sorbent tubes, a transport blank is typically obtained by removing the caps from tubes and leaving them in the sampling environment for a short time (*e.g.*, 5 minutes), and placing caps back on tubing. The sample should be submitted blind to the laboratory.
- *Equipment blank*: High purity inert gas is drawn through the sampling train and/or probe and analyzed to determine whether the sampling train is clean. Equipment blanks are mandatory if equipment is re-used; optional if new material is used.
- *Field Spikes*: Sample tubes spiked with known concentrations of analytes are used to evaluate the recovery of the spiked compound and accuracy of the extraction and analytical procedure. This test is not typically a field test but may be performed by the laboratory.
- *Sampling Flow Rate and Time*: The flow rate during sampling should be measured and sampling time accurately recorded.

For evacuated canister analysis the following quality control testing is recommended:

- *Cleaning and proofing*: Canisters and flow controllers should as a minimum be batch proofed and the usage history of each canister should be recorded by the laboratory to enable tracking of suspected contamination (BC Laboratory Manual, 2009). For low-level (sub-ppbV) analysis, individual proofing or "certification" of canisters is recommended.
- *Field duplicates*: Should be obtained by collecting two canisters using a splitter. It is recommended that two flow controllers be used (*i.e.*, splitter is upstream of the canister).
- *Field transport blank*: The "blank" canister is filled with ultra high purity air or nitrogen supplied by the laboratory in a separate canister. This is considered an optional test when a higher level of quality assurance is desired, given that other quality control tests are typically performed such as laboratory certification of canisters and testing of the vacuum before and after sampling.
- *Equipment blank*: High purity inert gas is drawn through the sampling train and/or probe and analyzed to determine whether the sampling train is clean. Equipment blanks are mandatory if equipment is re-used; optional if new material is used.
- *Vacuum Measurements*: Measure vacuum in the field prior to and after sampling (see Section 5.2 for criteria). Establish Data Quality Objectives (DQO's) for minimum vacuum required prior to and after sampling (these are not specified in Method TO-15). Do not use canister if the DQO is not met.

All data should be clearly reported, including blanks, and any suspect results should be flagged. The interpretation of quality control data is discussed in Chapter 5.

# 3.9 Soil and Groundwater Characterization

Soil and/or groundwater data are important for developing the CSM that is used to guide the development of the soil vapour characterisation program. Soil data can be used to evaluate contamination source zones, including possible sources that are located above the water table. Shallow groundwater data and predictions of deep soil vapour concentrations along with measured deep vapour concentrations can be used to evaluate the degree to which volatilization from groundwater and migration through the capillary fringe occurs, or the degree to which it may be inhibited through infiltration or geologic barriers. In some cases, it may not be possible to collect a representative soil gas sample due to low permeability deposits; therefore, the use of soil and/or groundwater data alone may be required for evaluation of the soil vapour intrusion pathway (if relevant).

# 3.9.1 Groundwater Data

Groundwater characterisation for evaluation of soil vapour intrusion should provide information on concentrations in groundwater near to the water table. This is because cross-media transfer from groundwater to soil vapour occurs when chemicals in pore-water volatilize into soil gas, which occurs in the capillary transition zone above the water table. Since there can be significant vertical concentration stratification, the use of relatively short monitoring well screens situated across the water table or depth discrete sampling methods such as the Geoprobe<sup>TM</sup>, Waterloo Profiler<sup>TM</sup> or Hydropunch<sup>TM</sup> methods are recommended when evaluating the soil vapour intrusion pathway.<sup>6</sup> Depth discrete samples can also be obtained from existing monitoring wells using Passive Diffusive Bag Samplers (Vroblesky and Hyde, 1997; ITRC, 2002). Diffusive Bag Samplers can also be used to measure VOC concentrations in pore-water within the capillary transition zone.

As well screen lengths increase, there is increased blending of groundwater across the screened interval. This may result in either over-estimation or under-estimation of concentrations at the top of the aquifer, depending on the contamination scenario. At locations down-gradient of LNAPL or where there is an interface plume from fluctuating water table and interaction between soil gas and the water table, longer well screens may under predict concentrations near the top of the aquifer. When LNAPL is present (either residual or free-phase), soil vapour data should be obtained to assess the vapour intrusion pathway. Where there is a fresh-water lens or contamination source below the water table (*e.g.*, DNAPL), longer well screens may over predict concentrations near the top of the aquifer.

Groundwater well installation, well development and purging prior to sampling should be conducted according to current standards of practice. For vapour intrusion assessments, a

 $<sup>^{6}</sup>$  Another potential option may be to install small diameter implants (*e.g.*, 15 cm long) at several depths near the water table, which can be used to sample either soil gas or groundwater depending on water table fluctuations.

saturated screen length of 1 to 2 m is generally recommended. Low flow purging and sampling methods that minimize disturbance, aeration and/or de-gassing of groundwater are recommended (Puls and Barcelona, 1996). Particular attention should be given to groundwater samples collected from submerged screens or wells with long screen intervals. The concentrations from these wells may be of limited value for vapour intrusion assessments.

While the appropriate focus of vapour intrusion studies is shallow groundwater quality, under certain site conditions, data on somewhat deeper groundwater quality may be relevant, including where groundwater concentrations increase rapidly with depth or where the water table declines due to changes in infiltration or groundwater pumping rates (these conditions could reduce the thickness of a fresh-water lens). The vertical concentration variability can be investigated either through the use of nested wells (at different elevations) or vertical profiling using a Geoprobe or similar groundwater sampling technique.

# 3.9.2 Soil Data

There are a number of uncertainties associated with use of soil data for evaluation of soil vapour intrusion as a result of losses of volatile contaminants during soil sampling, handling and chemical analysis. Depending on the contaminant type and geologic conditions, there may be significant spatial variation in soil concentrations, which may be difficult to detect based on conventional sampling programs. Finally, there are uncertainties associated with soil partitioning calculations and predicted soil vapour concentrations are sensitive to the partitioning coefficient between water and organic carbon, and the fraction organic content in soil, a parameter that can be difficult to accurately determine. If soil analyses results are to be used for the vapour pathway, it is recommended that the soil samples be field preserved (*e.g.*, using methanol), where possible (*e.g.*, USEPA SW-846 Method 5035A). A multi-functional sampling device (MFSDs), which act as a coring tool and airtight storage container, can also be used to collect soil samples for volatile analysis (*e.g.*, EnCore<sup>TM</sup> Sampler). The storage chamber is completely soil filled with zero headspace and is then capped to form an airtight seal.

# 3.10 Ancillary Data

In addition to measured soil vapour concentrations, the supplemental data below may assist in understanding the vapour intrusion pathway. Additional information is available in the ITRC (2007) and EPRI (2005) documents.

**Passive Soil Vapour Samplers**: Passive diffusion samplers contain a hydrophobic adsorbent material that collects organic compounds over time. The adsorbed compounds are removed from the adsorbent by thermal desorption or solvent extraction, and typically analyzed using GC/MS methods. The passive soil gas method provides the mass of vapours adsorbed to the media, but currently cannot reliably be used to estimate soil vapour concentrations. Passive soil gas samples are typically deployed for a few days to weeks, and therefore provide a time-integrated sample. The extended sampling duration also provides for high sensitivity. In the context of soil vapour intrusion studies, passive soil gas sampling methods may be useful in mapping the location of subsurface plumes and for identifying pathways (in particular when placed in or along utility

corridors) for determining locations for permanent probe placement when the CSM is not well understood.

Passive diffusive samples can be used to measure VOC concentrations in air and are described in Chapter 5.

*Physical Properties*: The properties of significant soil layers of the vadose zone, including soil moisture, bulk density, air-filled porosity, water-filled porosity and total organic carbon content may be important in evaluating vapour intrusion. Care should be taken to minimize redistribution of soil moisture or drying of soil during drilling, sampling and storage of samples. Water retention tests on samples compacted to approximate *in situ* density can provide useful data on the likely range of water-filled porosity that could be expected in soil. Although not commonly performed, consideration can also be given to *in situ* tests to provide estimates of tortuosity (effective diffusion coefficient) (Johnson *et al.*, 1998; Lahvis *et al.*, 1999) and soil-air permeability (Baehr *et al.*, 1991).

*Hydrogeological Properties*: The groundwater elevation during sampling and during an appropriate period prior to sampling is important when evaluating the possible seasonal influence on volatilization. The hydraulic conductivity and gradient are fundamental parameters required to evaluate groundwater flow systems.

*Meteorological Data*: There are an increasing number of weather stations (government, private) for which meteorological data (temperature, barometric pressure, wind speed and direction, relative humidity and precipitation) can be readily down-loaded. If there is a weather station near the site, this meteorological data should be obtained. Portable weather stations are also relatively inexpensive, and barometric pressure can be readily obtained (*e.g.*, Barologger<sup>TM</sup>). Barometric pressure and precipitation data for a few days prior to sampling should be obtained to enable trends to be evaluated. Frost and snow cover should be noted. Meteorological data may be useful in interpretation of soil vapour intrusion particularly if there were severe weather conditions during sampling (*e.g.*, rapid change in

barometric pressure, strong winds).

**Building Pressure Data**: Highly sensitive manometers (sensitivity less than 1 Pa (1/250 inches of water)) can be used to measure the differential pressure between the building and outdoor air, and building air and subslab soil gas. Information on pressure gradients can be useful in assessing soil gas intrusion potential; for example, soil gas intrusion potential would be low if the pressure in the building is higher than in soil below building. measuring the When pressures, consideration must be given to the potential influence of wind and other environmental variables on the measurements. The building pressure data should be plotted against barometric

## **Commercial Building Evaluation**

Some commercial buildings are designed to be positively pressurized through operation of HVAC system. Vapour intrusion will be significantly curtailed if the building is sufficiently pressurized (*i.e.*, comparable to 6 to 9 Pa recommended in ASTM (2001)). For such scenarios, an evaluation consisting of review of HVAC design, interview with building engineer to review HVAC operation, and series of differential pressure measurements to quantity gradients through building pressure operation, barometric pressure and wind forces may provide valuable information on the potential for a complete vapour intrusion pathway (EPRI, 2005).

pressure and other weather data to assess whether there are any correlations in the data.

**Building Ventilation Tracer Test**: Inert tracers such as carbon dioxide can be used to evaluate building ventilation characteristics and to estimate air change rates (ASTM E741-00). The ventilation test involves release of tracer gas (carbon dioxide) within the enclosed space followed by monitoring of the concentration decay over time. The concentration decay rate is used to estimate the air exchange rate. There are also tracer test methods that use sulphur hexafluoride. For commercial buildings, it may be possible to estimate the ventilation rate from HVAC system design. The air exchange rate should be calculated from the make-up volume, and not the total air handling volume.

**Radon Tracer Test**: Naturally-occurring radon can be used as a tracer to evaluate subslab to indoor air attenuation (McHugh *et al.*, 2008), although results may be somewhat biased by radon emissions from concrete itself or off-gassing from water, if from a groundwater source containing radon. The potential advantages of using radon, compared to analyses for VOCs, are potentially lower analytical costs, there are no common sources of indoor radon (excluding granite countertops), and indoor radon concentrations are in most cases above detectable levels (unlike VOCs where bias may be caused by non-detect values).

*Flux Chamber Test*: The surface emission flux rate of volatile chemicals may be measured by placing an open bottom box on top of bare ground or above a crack on a concrete floor (where the box is appropriately sealed to the concrete) and measuring the increase in volatile chemical concentrations in the chamber over time (static test) or measuring concentrations in air extracted at a steady rate from the chamber (dynamic test) (Hartman and Jacobs, 2005). Flux chamber tests are affected by the methodology used and conditions at the time of sampling and are relatively difficult tests to perform. The use or scaling of data for purposes of a vapour intrusion assessment is also not straightforward, although flux chamber tests may be useful when emissions to outdoor air are estimated.

*Larger-Scale Tracer and Pneumatic Testing*: Several different techniques may be used to estimate soil-air permeability and evaluate soil gas migration pathways. Helium tracers may be released at probes and travel times monitored at a central probe where soil gas is being extracted. Measurements of soil gas flow rates, pressures and vapour concentrations may be used for evaluating contamination source zones and for remediation design.

*Integrating Soil Gas Sampler*: The maximum reliable sampling duration for evacuated canisters is one to two days. To extend the sampling duration (with the objective of reducing temporal concentration variability), an integrating soil gas sampler has been developed where a passive sampling device is placed in a sealed flow-through-cell, through which soil gas is drawn over an extended period (McAlary *et al.*, 2010; Lutes *et al.*, 2010). The technique is still in the research and development phase.

*Tree Coring*: Recent studies have shown tree core concentrations of chlorinated solvent chemicals to be related to soil and groundwater concentrations (Burken *et al.*, 2010; Struckoff *et al.*, 2005). This technique could be a useful screening tool at some sites.

## 3.11 Resources and Weblinks

Useful information is provided in the following references:

Interstate Technology and Regulatory Council (ITRC). The Vapor Intrusion Pathway: A Practical Guide (VI-1)(January 2007, 173 pages) provides a generalized framework for evaluating the vapour intrusion pathway and describes the various tools available for investigation, data evaluation, and mitigation. The Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios (VI-2) (January 2007, 52 pages) is a supplement to Vapor Intrusion Pathway: A Practical Guide. The supplement describes applicable approaches for pathway evaluating the vapor intrusion in six typical scenarios. http://www.itrcweb.org/Documents/VI-1.pdf. http://www.itrcweb.org/Documents/VI-1A.pdf

American Petroleum Institute (API). A Practical Strategy for Assessing the Subsurface Vaporto-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites (November 2005) includes guidance on soil gas sampling approach, methods and analysis (November, 2005). http://www.api.org/ehs/groundwater/Inapl/soilgas.cfm

**New Jersey Department of Environmental Protection**. *Vapour Intrusion Guidance (October, 2005)*. This guidance includes comprehensive methods for site characterization, including soil gas sampling and analysis. <u>http://www.state.nj.us/dep/srp/guidance/vaporintrusion/vig.htm</u>

**California Environmental Protection Agency**. Interim Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air (February 7, 2005). Department of Toxic Substances Control.

http://www.dtsc.ca.gov/AssessingRisk/upload/HERD\_POL\_Eval\_Subsurface\_Vapor\_Intrusion\_i nterim\_final.pdf

**California Environmental Protection Agency**. Advisory – Active Soil Vapor Investigation. (March 2010). Department of Toxic Substances Control.

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# 4.0 INDOOR AIR QUALITY TESTING FOR EVALUATION OF SOIL VAPOUR INTRUSION

## 4.1 Context, Purpose and Scope

This chapter describes methodology for completing indoor air quality (IAQ) testing for evaluation of soil vapour intrusion. The testing of IAQ may be warranted when previous phases of an investigation indicate the potential for unacceptable risks from vapour migration into indoor air (or conducted concurrently with subsurface testing depending on the urgency of IAQ testing). The use of IAQ measurements to evaluate potential health risk associated with vapour intrusion is an option for a current exposure scenario (existing building). While indoor air testing can provide a direct measurement of potential inhalation exposure, there are a number of issues that can complicate indoor

# **Indoor Air Quality (IAQ) Testing**

This chapter describes the planning, process and methods for IAQ studies. The key elements and their corresponding sections in the chapter are:

- Conceptual site model (S 4.2),
- Study objectives (S 4.3),
- Sampling approach (S4.3),
- Sample design (S 4.3), and
- Indoor air analysis (S 4.4)

Since analytical protocols were already described in Chapter 3, the objective of this chapter is to additional information on low level analysis and use of passive diffusive samplers for indoor air quality studies.

air measurements including background sources of the chemicals of interest and often significant variability observed in indoor vapour concentrations due to building or weather related factors. An IAQ testing program is also a relatively intrusive activity that particularly for a residential or institutional setting requires appropriate communication of program objectives and results with the building owners and occupants.

The basic steps for design of an IAQ program are similar to those described for soil vapour characterization and consist of (1) development of a conceptual site model (CSM), with specific consideration of factors that influence IAQ based on site conditions, (2) development of IAQ study objectives, and (3) preparation of a sampling plan. As indicated for soil vapour characterization, a standardized template for IAQ program design is not provided, and instead key principles and factors that should be considered in developing a sampling strategy are discussed below. A detailed flow chart of the framework for an IAQ study is provided in Figure 4.1.

Indoor air sampling should be carried out according to an established plan, considering the study objectives and the data quality objectives. However, the plan should be flexible in that if the circumstances change, the plan could be adapted accordingly. Indoor air quality studies for assessment of soil vapour intrusion typically include some concurrent testing of outdoor air and may also include subslab or near building soil vapour testing. Subslab or near building soil vapour samples may be used to identify the contaminants that have the potential to migrate into indoor air. Similarly, outdoor air samples may provide information with respect to the influence of ambient air quality on IAQ. These types of samples may provide additional lines-of-evidence that are helpful in assessing potential VOC sources.



FIGURE 4.1. Framework for IAQ Sampling and Analysis Program

## 4.2 Conceptual Site Model for Indoor Air

The CSM for soil vapour transport and intrusion into buildings was described in detail in Chapter 2. The purpose of this section is to describe specific aspects of the CSM that could influence indoor air quality (excluding subsurface factors), which are background sources of VOCs in indoor air, building foundation construction, building ventilation, building depressurization and weather conditions, and vapour depletion processes within buildings.

#### 4.2.1 Background Indoor Air Concentrations

When evaluating the impact of subsurface vapour sources on IAQ, it is paramount that background sources of VOCs in indoor air be considered, since many subsurface contaminants of concern are also common "background" VOCs. Common background sources of VOCs include household products, off-gassing from building products (*i.e.*, carpeting, shower curtains, building insulation, pressed wood products, fabrics), home heating (*i.e.*, heating oil storage, combustion emissions), tobacco smoke, attached garages (i.e., vehicle emissions, stored products), volatilization of trihalomethanes from tap water (particularly when heated) as well as through activities occurring in the home or workplace. A list of dominant indoor air sources and associated volatile contaminants is provided in Table 4.1. Due to these and other indoor air sources, contaminant concentrations in indoor air are frequently higher than in outdoor air. Other background sources of contaminants include outdoor sources such as vehicle or industrial air emissions that enter the building through air leakage or ventilation. Compounds present in described various consumer products are in the household products database http://householdproducts.nlm.nih.gov/.

Source	Contaminants					
Paints	Benzene, Toluene, Trimethylbenzenes, Pentane, Tetrachloroethene					
Carpets	Benzene, Toluene, Styrene, Trimethylbenzenes, Chlorobenzenes,					
	Decane					
Wood Burning	Toluene, Xylenes, Styrene, Trimethylbenzenes, Naphthalene					
Polystyrene Board	Styrene, Butadiene					
Paint Removers	Toluene, Acetone, Methylene chloride, Chlorobenzenes, Tetrachloroethene					
Spray Products	Xylenes, Acetone					
Adhesives/Tapes/Glues	Benzene, Toluene, Styrene, Xylene, Tetrachloroethene, Decane					
Room Deodorizers	Ethanol, d-Limonene, Camphor, Phthalates					
Tobacco Smoke	Benzene, Toluene, Ethylbenzene, Xylenes, Styrene					
Gasoline/Driving	Benzene, Toluene, Xylenes, Styrene, Trimethylbenzenes					
Solvents/Degreasers	Toluene, Ethylbenzene, Trichloroethanes, Trichloroethene, Methylene chloride					
Dry Cleaning	Tetrachloroethene, Trichloroethene (spot remover)					
Moth balls	Naphthalene, 1,4-dichlorobenzene					
Pressed wood products	Formaldehyde					

 TABLE 4.1. Dominant Sources of VOCs in Residential Indoor Air

Note: Adapted from Hers et al. (2001)

As a consequence of the large variations in building design, use, and environmental setting, IAQ data is also highly variable. A number of studies have been completed in the United States (*e.g.*, Dawson and McAlary, 2009), but fewer studies have been undertaken in Canada examining background IAQ in residential homes. Table 4.2 provides a summary of VOC data from six key Canadian studies. These studies demonstrate that background concentrations are highly variable, but also show that a large number of compounds can be expected to be found in residential buildings. Although background IAQ can be expected to vary between buildings, regions and time frames, the data from these and other studies can be used to help interpret the results of IAQ investigations (refer to Chapter 5 for further discussion).

Health Canada 1991,1992 <sup>a</sup>			Greater Toronto, Sash 1996 <sup>b</sup> Onte			ewan and 991, 1999°	Hamilton, 1993 <sup>d</sup>				Ottawa, 2002, 2003°				Quebec City, 2005 <sup>f</sup>		
Contaminant	Mean	Max	Mean	Max	Mean	Max	Median	Mean*	95 <sup>th</sup>	Max	Median	Mean*	90 <sup>th</sup>	Max	Median	Geometric	Max
Benzene	54	67.9	3 42	45.8	15	42.3	2.85	3 99	10.67	54 61	2.15	2.85	5 21	20.99	1 18	1 22	22 37
Toluene	40.8	5730	15.2	186	23.9	110.5	15.51	25.04	88.10	156.43	5.53	11 54	25.47	112.93	24.72	26.47	436.33
Ethylbenzene	8.2	540	1.58	20.9	96	32.9	2 38	4 16	15.10	53 21	1.05	4 71	4 76	201.41	24.72	269	19 50
m n Yylene	20.7	1470	1.56	20.7	21.6	74.2	8.22	16.33	41.05	317.10	3.50	7.5	16 35	138.07	0.17	0.85	77.08
	20.7	220	-	-	57	20.2	2.40	4.05	17.29	70.17	1.22	5.09	6.49	205.11	2.02	2.42	26.42
0-Aylene Sturono	0.3	120	-	-	3.7	20.3	1.20	4.95	27.02	176.61	0.46	0.60	0.48	6.52	0.60	0.65	14.02
1 2 5 Trimothylhonzono	0.3	640	0.52	-	4.1	11.5	1.50	2.00	0.22	1/0.01	0.40	2.07	1.49	144.44	0.09	0.05	14.03
1,3,3-11iiiettiyibenzene	2.1	040	0.55	1.4/	5.1	15	5.00	3.99	9.55	146.52	0.39	2.07	4.73	56.60	0.92	1.20	68.00
Naphthalana	-	-	4.81	82.4	7.2	20	3.09	5.00	17.20	72.25	2.21	5.97	0.75	30.00	1.12	1.45	22.02
n havana	124	5.24	4.81	14.5	00.4	30	1.88	7.04	26.00	11/ 86	-	-	-	-	2.17	2 25	28.55
n decene	21.4	5.24	6.85	01.0	77.4		4.00	14 50	53.82	200.85	2.17	5.28	8.00	- 84.60	6.48	6.42	202.25
n-uecalle	51.4	0430	0.85	91.9	-	-	4.90	14.50	57.40	200.83	2.17	5.20	0.09	04.00	0.40	0.42	203.23
n- undecane					147	01.0	0.00	0 00	24.27	170.00	-	-	-	-	-	-	-
n-dodecane Dishlarahanyanas	-	-	-	-	14./	91.9	3.41	0.00	24.27	170.00	-	-	-	-	-	-	-
Dichlorobenzenes	18.9	1390	33.4	1600	12.8	337.3	-	-	-	-	-	-	-	-	-	-	-
1,2,4- Ifichlorobenzene	-	-	-	-	-	-	0.09	0.23	0.00	2.30	-	-	-	-	-	-	-
Tatrachlana ath ana	-	-	-	-	-	- 20	1.18	8.07	39.98	230.47	- 0.47	-	-	-	0.30	0.38	280.37
Tricklassethers	2.7	313	1.39	9.55	8.2	30	1.10	3.00	14.84	2.52	0.47	1.13	3.23	9.23	0.09	0.92	1/9.30
1 richloroethene	0.5	165	-	-	2.3	6.5	0.17	0.30	-	3.53	< 0.02	0.06	0.19	0.87	0.35	0.37	4.68
1,1-Dichloroethene	-	-	-	-	-	-	0.04	0.15	0.77	2.02	< 0.01	0.27	0.83	4.05	-	-	-
Vinyl Chloride	-	-	-	-	-	-	-	-	-	1.00	-	-	-	-	-	-	-
Dichloromethane	-	-	-	-	-	-	9.19	48.99	1/8.80	1209.91	1.87	14.98	43.21	408.37	/.04	/.93	1687.44
1,1,1- Trichloroethane	-	-	-	-	-	-	2.48	9.94	54.07	115.79	-	-	-	-	-	-	-
1,2-Dichloroethane	<0.1	1./	-	-	/.4	25	-	-	-	-	< 0.02	0.03	< 0.02	0.71	-	-	-
Carbon Letrachloride	-	-	-	-	-	-	0.48	0.57	0.90	4.51	-	-	-	-	-	-	-
Bromodichloromethane	-	-	-	-	-	-	0.17	0.28	0.77	1.32	-	-	-	-	-	-	-
1,3- Butadiene	-	-	-	-	-	-	0.15	0.24	0.65	2.40	<0.32	0.5	1.64	3.65	-	-	-
Cyclohexane	-	-	-	-	-	-	0.44	0.80	2.84	11.02	4.51	6.58	15.1	54.12	-	-	-
Isoprene	-	-	-	-	-	-	2.95	5.26	16.76	43.38	-	-	-	-	-	-	-
Acetaldenyde	-	-	-	-	-	-	0.00	40.89	85.26	/92.41	-	-	-	-	-	-	-
Hexanal	-	-	-	-	-	-	9.33	16.79	44.75	57.40	-	-	-	-	-	-	-
Acetone	-	-	-	-	-	-	-	-	-	-	28.48	44.44	/6.4	455.87	-	-	-
Chlorotorm	-	-	-	-	-	-	-	-	-	-	1.19	1.72	4.39	8.23	3.15	3.18	18.59
2-propanol	-	-	-	-	-	-	-	-	-	-	3.32	18.14	68.76	238.17	-	-	-
2-butanol	-	-	-	-	-	-	-	-	-	-	1.48	2.54	6.66	16.45	-	-	-
Phenol	-	-	-	-	-	-	-	-	-	-	0.42	0.70	1.6/	5.16	-	-	-
Carbon disulfide	-	-	-	-	-	-	-	-	-	-	0.13	0.34	0.86	3.29	-	-	-
1-butanol	-	-	-	-	-	-	-	-	-	-	0.4	4.25	5.96	139.66	-	-	-
4-metnyl-2-pentanone	-	-	-	-	-	-	-	-	-	-	0.16	0.26	0.8	1.40	-	-	-
Acrylonitrile	-	-	-	-	-	-	-	-	-	-	0.06	0.27	0.26	8.89	-	-	-
2-butoxyetnanol	-	-	-	-	-	-	-	-	-	-	< 0.28	2.85	/.06	41.44	-	-	-
Nethorly methacrylate	-	-	-	-	-	-	-	-	-	-	< 0.01	0.05	0.06	1.12	-	-	-
Chlanchan	-	-	-	-	-	-	-	-	-	-	< 0.05	0.17	< 0.05	3.32	-	-	-
Chlorobenzene	-	-	-	-	-	-	-	-	-	-	< 0.01	< 0.012	< 0.01	0.04	-	-	-
3,5-dimethylaniline	-	-	-	-	-	-	-	-	-	-	<1.2	<1.2	<1.2	4./1	-	-	-
1,2-dichlorobenze	-	-	-	-	-	-	-	-	-	-	< 0.02	< 0.02	< 0.02	0.11	-	-	-
1,3-dichlorobenze	-	-	-	-	-	-	-	-	-	-	0.15	0.77	1.05	16.19	-	-	-
2-ethoxyethanol	-	-	-	-	-	-	-	-	-	-	< 0.13	0.43	<0.13	27.14	-	-	-
2-metnoxyethanol	-	-	-	-	-	-	-	-	-	-	< 0.23	< 0.23	< 0.23	< 0.23	-	-	-
1,2-dichloropropane	-	-	-	-	-	-	-	-	-	-	< 0.04	< 0.04	< 0.04	< 0.04	-	-	-
Ethylene dibromide	-	-	-	-	-	-	-	-	-	-	< 0.02	< 0.02	< 0.02	< 0.02	-	-	-
1,1,2,2-	-	-	-	-	-	-	-	-	-	-	< 0.02	< 0.02	< 0.02	< 0.02	-	-	-
tetrachioroethane															0.0	0.00	45.40
Cumene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.8	0.88	45.48
α-pinene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.95	9.74	800.68
<i>d</i> -limonene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	28.54	28.06	329.89
p-cymene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.49	1.55	32.90

 TABLE 4.2. Compilation of Indoor Air Quality Data from Canadian Studies

Notes: Concentrations in units of ug/m<sup>3</sup>

\*Arithmetic mean <sup>a</sup>Davis and Otson (1996)

<sup>b</sup>Otson and Zhu (1997) <sup>c</sup>Saskatchewan Research Council (1992). <sup>d</sup>Hamilton 1993 (provided by Camilo Martinez, Ontario MoE)

<sup>f</sup>Héroux et al. (2008)

As a result of these background sources, particular care must be taken in the collection, review and interpretation of IAQ data. For instance, it is important to understand, as well as minimize, the effects of indoor sources through an assessment of building conditions and proper building preparation prior to sampling (Exhibit 4.2), and in certain cases, include sampling to evaluate background air concentrations at the site (see subsequent sections).

# 4.2.2 Building Foundation Construction

The building foundation construction will influence soil vapour intrusion rates into the building. For example, soil vapour can migrate through relatively small cracks or openings in the foundation or through utility penetrations that act as preferential pathways. Soil vapour intrusion rates may vary depending on type of foundation, which include basement, slab-on-grade, crawlspace or earthen floor construction. For houses with concrete slab construction, there is often a perimeter edge crack between the foundation wall and slab. For commercial building slabs, greater attention is usually paid to sealing cracks, which would tend to reduce but not necessarily eliminate soil vapour intrusion. Utilities represent potential entry points for soil vapour intrusion regardless of building type. Building foundation construction can influence air movement to below a building, which may be important for aerobic biodegradation of petroleum hydrocarbon. For example, there will tend to be more aeration of shallow soil below unlined crawlspaces than concrete foundations.

# 4.2.3 Building Ventilation

Through building ventilation and exchange with fresh air, soil vapour concentrations are diluted upon mixing with indoor air. Building ventilation or air exchange rates vary depending on climate, construction and season. Standards in Canada and the U.S. both specify minimum ventilation rates for residential dwellings. In Canada, the minimum required outdoor air ventilation rate under the CSA F326 standard for "Residential Mechanical Ventilation Systems" depends on the number and types of rooms in the house but usually works out to about 0.3 air changes per hour (ACH). In the U.S., the American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. (ASHRAE) 62.2-2007 residential standard for whole building ventilation rate is 7.5 CFM/person (3.5 L/s/person) plus 1 CFM/100 sq. ft. (15 l/s/100 sq. m.) (ASHRAE, 2007a).<sup>1</sup> Mechanical ventilation is required to meet minimum ventilation rates in energy-efficient "tight" houses (e.g., "R-2000" or "Energy Star" in Canada). However. mechanical ventilation systems are often operated at less than the design or installed capacity (Figley, 1997; Hamlin and Gusdorf, 1995). For example, energy-efficient houses that have mechanical ventilation supplied through a heat recovery ventilator may have ventilation rates as low as 0.1 ACH (Fellin and Otson, 1996). For commercial buildings, the ASHRAE 62.1-2007 standard minimum ventilation rates depend on occupancy and use (ASHRAE, 2007b). For office space, the corresponding minimum outdoor air change rate for a single-zone is approximately  $0.57 \text{ ACH.}^2$ 

<sup>&</sup>lt;sup>1</sup> Assumes natural infiltration credit of 2 CFM/100 sq.ft. (if not applicable add 2 CFM/100 sq. ft.). The calculated air change rate is 0.3 ACH for a 1000 sq.ft. single storey house with 4 person occupancy and 8 ft. ceiling.

 $<sup>^{2}</sup>$  Assumes minimum ventilation rate equal to 5 CFM/person plus 0.06 CFM/sq.ft., density of 5 persons per 1,000 sq. ft. and 9 ft. ceiling

A review of approximately 2,800 building ventilation measurements in houses across the U.S. grouped the results according to regions (defined by heating degree-days) and four seasons (Murray and Burmaster, 1995). The average yearly ACH for the four regions ranged from 0.4 to 0.98 hr<sup>-1</sup>. For the north central to eastern part of the US (which most closely approximates most regions in Canada), the average ACH in summer was 0.82 hr<sup>-1</sup>, the average in fall was 0.25 hr<sup>-1</sup>, the average in winter was 0.36 hr<sup>-1</sup> and the average in spring was 0.44 hr<sup>-1</sup>. In an Ontario study, air exchange rates from 70 houses ranged from 0.06 to 0.77 ACH, with the lowest air exchange occurring in summer in R-2000 houses with closed windows (Walkinshaw, 1987). In a study completed in Saskatchewan and Tilsonburg, Ontario, the average measured air exchange rate from 44 houses was 0.34 ACH (SRC, 1992), while in a study completed in the Greater Toronto area, the average air exchange rate from 44 houses was 0.45 ACH (Otson and Zhu, 1997). In a study of houses in Saskatoon of medium air-tightness, the air change rates measured in 18 houses varied from a low of 0.08 ACH to high of 0.43 ACH, with an average air change rate of 0.2 ACH (CMHC, 1995). It was determined that improved mechanical ventilation systems were required to address low ventilation rates and indoor air quality issues. Gilbert et al. (2008) measured ventilation rates in 96 Quebec City houses in Winter 2005 using a tracer. The 20th, 40th, 60th and 80<sup>th</sup> percentiles of the ACHs were 0.11, 0.14, 0.16, 0.23, respectively. Aubin et al. (2010) presents results of another study of 70 homes in Quebec City where the mean ventilation rate for fall/winter of 2008/2009 was 0.26 ACH, while for summer conditions was 0.42 ACH. Additional data on ventilation rates are summarized in Hers et al. (2001).

The USEPA BASE study of one hundred randomly selected commercial buildings, which represented a wide range in construction, found that the  $25^{\text{th}}$ ,  $50^{\text{th}}$  and  $75^{\text{th}}$  percentile air change rates were 0.47 hr<sup>-1</sup>, 0.98 hr<sup>-1</sup> and 2.62 hr<sup>1</sup>, respectively (NIST, 2004). When conducting a site specific assessment, it may be instructive to obtain information on building ventilation from building HVAC engineers since often design and test information providing data on air flow rates for return and supply air will be available.

#### 4.2.4 Building Depressurization and Weather Conditions

Given that building pressures relative to the subsurface soil may have a large influence on vapour intrusion (Section 2.4, Figure 2.7), it is important to understand (and potentially measure) pressures when conducting indoor air quality studies and designing mitigation systems. Buildings may have a net positive or negative pressure, or variable pressure gradients (*e.g.*, on a daily basis). Numerous factors affect pressures including temperature differences between indoor and outdoor air, the number of storeys, degree of air leakage between floors, heating, ventilating and air conditioning (HVAC) system operation, and presence of chimneys, flues, exhaust fans and vents.

Of particular importance is the "stack effect" that occurs during the heating season as a result of hot air rising in a building and leaving near the top of the building (*e.g.*, through a chimney, leaky attic, exhaust vent). This creates a negative pressure in the building (below the neutral pressure line), thus drawing outdoor air and soil gas into the building through openings within the lower regions of the building (*i.e.*, doors, windows, cracks and openings in building foundation). When outdoor temperatures are greater than indoor temperatures, the pressure regime is reversed.

Literature studies indicate that building depressurizations (relative to ambient air) during the heating season for houses with basements typically range from 2 to 10 Pa, but may be as high as 15 Pa (Figley, 1997; Hers *et al.*, 2001). Our experience monitoring houses in Canada during the heating season is that on average basements of houses are depressurized. There is often a diurnal pattern to pressure data, but considerable data scatter may be introduced by the operation of the furnace or environmental variables. During warmer weather, variable positive and negative pressures may be observed during the day, but on average, the pressure will be near neutral.

Commercial buildings typically have HVAC systems that bring outside air into the building through filters, blend it with building return air, and thermally condition the air before distributing it throughout the building. Ventilation systems are often designed to vary the proportion of outside air mixing with return air based on energy considerations. The pressure regime in commercial buildings can be relatively complex and will depend on building code requirements, type of building use (office, restaurant, warehouse, *etc.*), size and height of building, climate, and time of year.

In warmer climates, buildings are designed with a positive pressure to limit the ingress of warm moist air, which is advantageous in reducing mold. Positive pressures may also be desirable to minimize infiltration of outdoor contaminants such as vehicle exhaust and dust. In colder climate areas, excess positive pressures are undesirable since moist indoor air will move across the building envelope and condense when it contacts cold air. Particularly in taller buildings, negative pressures within the lower part of the building and positive pressures in the upper part tend to be unavoidable during the heating season, although buildings are designed to minimize these differences. The pressure regime also typically varies depending on location in the building. Stairwells are typically positively pressurized as a code requirement (fire regulation). Food processing areas tend to be under negative pressure. Commercial buildings that may be under positive pressure when the HVAC system is operating may be under negative pressure during night-time hours.

Wind creates pressure differentials between the upwind and downwind sides of the building, which is another mechanism that causes the building interior to be underpressurized. Changes in barometric pressure as a result of meteorological conditions can also cause pressure differences between the building interior and exterior. These pressure differences may occur at varying temporal scales (hourly to seasonally), but in general, the most significant pressure differences occur under severe winter conditions.

# 4.2.5 Mixing of Vapours Inside Building

Within the building, contaminants will diffuse as a result of chemical gradients and disperse through air movement. Mixing between building floors will depend on the HVAC system and air leakage between floors. Elevator shafts often include a sump with a drain hole at the bottom to allow any water present to drain away, which may allow entry of sub-surface vapours. The movement of the elevator itself can cause pressure differential that may facilitate soil vapour entry. Furthermore, taller buildings with elevators will often have a significant stack effect during Canadian heating season conditions, which may draw in soil gas from elevator pits or

other entry points such as sumps. Elevator shafts can also represent conduits for inter-floor migration of vapours.

# 4.2.6 Vapour Depletion Mechanisms

Chemical or physical mechanisms may result in the removal of vapours from indoor air, in addition to dilution through building ventilation. Since soil vapour intrusion typically occurs over timescales of months to years, the removal of volatiles in air through adsorption onto building materials is unlikely to have a significant long-term effect on indoor vapour concentrations since adsorption sites on building materials will likely be filled over time. Adsorption onto building materials can be reversible (*i.e.*, desorption can occur) and thus should also be considered as a source of volatiles, depending on building conditions. For example, even after soil vapour intrusion is mitigated (*e.g.*, through a subslab venting system), there may be a period of time over which a chemical of concern is detected in indoor air as a result of desorption from building materials. Chemical transformations due to processes such as photo-oxidation are generally relatively slow processes relative to air exchange rates (*i.e.*, half-lives of days) and biodegradation is unlikely to be a relevant process in an indoor environment.

# 4.3 Development of Indoor Air Quality Study Approach and Design

# 4.3.1 Define Study Objectives

The study objectives should be well-defined prior to developing a sampling plan, as the sampling plan could vary substantially depending on the type of data required and how that data is intended to be used. The primary goal of the IAQ study is often to provide data that could be used to evaluate exposure and potential inhalation risk through collection of "exposure point" samples under conditions that generally reflect typical exposure conditions.

**Types of Indoor Samples** 

Two general types of samples are (1) "exposure point" samples obtained to reflect exposure conditions (i.e., breathing height, near middle or room) and (2) pathway samples obtained to evaluate potential entry points for soil gas into a building (i.e., from cracks or utilities).

There may be other specific objectives of the IAQ study that would result in a different sampling strategy, such as evaluation of entry points for soil gas migration through collection of "pathway" samples (see text box) or evaluation of the influence of background on indoor air quality through collection of samples under conditions of positive and negative building pressures (see Section 4.3.10).

The study objectives may also be broadly defined in terms of the phase or level of investigation. An initial preliminary investigation may consist of a limited number of IAQ samples. If the preliminary investigation indicates a potential indoor air quality concern, additional investigation may be appropriate. Finally, if vapour intrusion mitigation systems are installed, follow-up IAQ monitoring may be required for some period of time.

## 4.3.2 Identify Target Compounds

The target compounds for the sampling plan are dependant upon the contaminant source under evaluation. Target compounds would generally include the primary constituents of the contamination source and may also include potential breakdown products of these constituents. In addition to contaminants of potential concern, other compounds that are present as background constituents and that could be useful as tracers should also be considered.

Identification of target compounds is not an easy task given range of contamination sources and chemical volatility. Adding to the complexity is that analytical laboratories offer many different analyte packages, and different regulatory jurisdictions have varying requirements. A key first step is identification of chemicals of concern based on volatility, toxicity and mobility. A simple approach adopted by some jurisdictions (*e.g.*, USEPA, 2002) has been to compare theoretical concentrations from partitioning relationships (*e.g.*, Henry's Law constant) multiplied by a conservative attenuation factor (0.1) to risk-based air concentrations. The outcome of this approach is an extensive analyte list including heavier molecular weight compounds (*e.g.*, three and four-ring polycyclic aromatic hydrocarbons), which presents significant challenges for analysis, and is considered overly conservative and not warranted.

## **BCELQAAC Study**

Important work in defining volatile substances was conducted in 2008 by the BC Environmental Laboratory Quality Assurance Advisory Committee (BCELQAAC). An outcome of their study was a definition of a volatile substance as a compound having both a Henry's Law constant greater than  $1 \times 10^{-5}$  atm-m<sup>3</sup>/mol and vapour pressure greater than 0.05 Torr. Functionally, this threshold results in naphthalene, 1-methylnaphthalene and 2-methylnaphthane identified as volatile substances, but not PAHs with higher molecular weights. With respect to n-alkane compounds, tridecane (n-C13) is the heaviest compound included as a volatile substance. A threshold based on Henry's Law constant alone was considered impractical (*i.e.*, the vapour pressure is needed as a second factor). For example, even heavier molecular weight n-alkanes have Henry's Law constants that exceed  $1 \times 10^{-5}$  atm $m^{3}$ /mol because they have low to moderate vapour pressures, but very low solubility's. The BCELQAAC review of soil vapour data for semi-volatile analyses indicated at sites where PAHs heavier than methyl-naphthalenes were identified (acenaphthylene, acenaphthene and fluorene), they were usually found at concentrations that were below 2.5% of the naphthalene concentrations (if detected). With respect to n-alkane fractions, concentrations in soil vapour drop off significantly for alkanes heavier than n-C13. On average, the review of soil vapour data revealed that the n-c13 to n-C16 fraction was 2 to 4% of the total volatile organic fraction, and never above 25%. A review for CCME completed by Golder (2008) on this same issue also evaluated soil vapour data from coal-tar (MGP) sites and theoretical mobility considerations, and arrived at similar conclusions as BCELQAAC respecting volatilty cut-offs, although further research is considered warranted to refine and confirm volatility cut-offs.

The selection of target compounds for analysis remains a topic of emerging science and policy. The determination of an appropriate target list will depend on project-specific requirements. The predominant vapour-phase chemicals associated with different contamination sources are listed below and the analyte list developed by the British Columbia Contaminated Sites Approved Professional (CSAP) task group (BCCSAP, 2009) is listed in Table 4.3.

**Gasoline**: Analytes include benzene, toluene, ethylbenzene, xylenes, trimethylbenzene isomers, C-4 to C-8 aliphatics (*e.g.*, iso-pentane, hexane, cyclohexane, 2,2,4-trimethylpentane, *etc.*), MTBE, 1,2-dichloroethane, dibromoethane, petroleum fractions and fixed gases O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>. *Comment*: Fuel additives historically included ethylene dibromide and 1,2-dichloroethane in leaded gasoline (Falta *et al.*, 2005). Leaded gasoline in Canada was phased out in the 1990's, although it may have continued to be used for marine and farm purposes for some period of time after that. In Canada, the use of MTBE began in the late 1980's and was mostly phased out by 2000 (Environment Canada, 2003). For some projects, analysis for multiple chemicals according to PIANO (paraffins, isoparaffins, aromatics, naphthenes, olefins) classification may be warranted.

Middle distillate fuels (#2 fuel oil, diesel and kerosene): Analytes include n-nonane, n-decane, n-undecane, n-dodecane, ethylbenzene, xylenes, trimethylbenzene isomers, tetramethylbenzene isomers, naphthalene and fixed gases  $O_2$ ,  $CO_2$ ,  $CH_4$ . *Comment*: Benzene content in diesel is generally low but since it is a risk driver it is prudent to analyze for benzene. Also note in the Canadian north, diesel may be cut with a percentage of gasoline during winter.

**Manufactured gas plant and creosote sites:** Analytes include benzene, toluene, ethylbenzene, xylenes, styrene, trimethylbenzene isomers, tetramethylbenzene isomers, thiophenes, indene, indane, naphthalene and aliphatic hydrocarbons and fixed gases  $O_2$ ,  $CO_2$ ,  $CH_4$ . *Comment*: More research is needed to evaluate potential significance of compounds such as thiophene, indene and indane for vapour intrusion.

**Solvent-using industries** (*e.g.*, **degreasers**): Analytes should include the solvent and its expected degradation products. Daughter products of tetrachloroethylene include trichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, 1,1-dichloroethylene, 1,2-dichloroethane, vinyl chloride, chloroethane, ethylene, ethane, carbon dioxide. Daughter products of 1,1,1-trichloroethane include several of the above compounds and 1,1-dichloroethane. Daughter products of carbon tetrachloride include chloroform, methylene chloride, chloromethane, methane, carbon disulphide, carbonyl sulphide, carbon dioxide. Solvents may also include other halogenated compounds and freons. Analytes should generally include fixed gases O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> *Comment*: Oxygen monitoring is warranted since vinyl chloride and some of the other lesser chlorinated compounds aerobically degrade.

**Dry Cleaner:** As a minimum, analytes include tetrachloroethylene, trichloroethylene, cis-1,2dichloroethylene, trans-1,2-dichloroethylene, 1,1-dichloroethylene, 1,2-dichloroethane, vinyl chloride, chloroethane. Analytes should generally include fixed gases O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> Comment: Tetrachloroethylene is the predominant solvent used in the dry cleaning industry, but historically chemicals such as 1,1,1-trichloroethane, methylene chloride, carbon tetrachloride. chlorofluorocarbons (CFCs) and petroleum-based chemicals have been used (Lohman, 2002; www.drvcleancoalition.org). Spotting agents used include 1,1,1-trichloroethane and

trichloroethylene. Depending on dry cleaner history, analysis of additional compounds may be warranted.

**Landfills:** Although the primary gases produced are methane and carbon dioxide, numerous halogenated solvent and petroleum hydrocarbons may be associated with landfill gas depending on material placed in the landfill. Hydrogen sulphide is a chemical of concern.

Other potential target analytes can include pesticides (e.g., hexachlorobenzene) and vapours associated with volatile metals (e.g., mercury).

Contamination Type	Target Analytes							
Gasoline	Benzene, ethylbenzene, toluene, xylenes, 1,3,5-trimethylbenzene,							
	1,2,4-trimethylbenzene, n-hexane, n-decane, naphthalene, 1,3-							
	butadiene, methylcyclohexane, isopropylbenzene (cumene), Volatile							
	Petroleum Hydrocarbon (VPHv), 1,2-dibromoethane*, 1,2-							
	dichloroethane*, MTBE*							
Diesel	benzene, ethylbenzene, toluene, xylenes, 1,3,5-trimethylbenzene, n-							
	decane, naphthalene, VPHv							
Waste Oil	Concern is not over oil which has low volatility but solvents or other							
	petroleum products introduced in waste oil. Analytes should be determined on site specific basis.							
Dry Cleaner Sites	Tetrachloroethylene, trichloroethylene, cis-1,2-dichloroethylene,							
	trans-1,2-dichloroethylene, vinyl chloride, chloroform, chloroethane,							
	1,1,1-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-							
	dichloroethylene, carbon tetrachloride, methylene chloride							

TABLE 4.3. Analyte List Recommended by CSAP Task Group

Note: Depending on the site, analysis for either the full list, or screening for just the analytes in bold type may be appropriate. \*analytes only required if evaluation indicates gasoline historically containing these substances was potentially used. VPHv = VHv (nC6-nC13) – benzene, toluene, ethylbenzene, xylenes, n-hexane, n-decane.

# 4.3.3 Develop Communications Program

An important part of the IAQ program is communication with the building occupants and owners and other stakeholders, to keep them informed and involved in the process. This can be done throughout the sampling process, but is especially important in the preparatory stage. Issues to address with building occupants include: why the study is being conducted and what the study objectives are; scheduling the pre-sampling building survey; discussing the types of activities to avoid prior to the sampling events and background chemical issues (see 4.3.10); scheduling and discussing the sampling that will be conducted; and communication of the results of the sampling program. Consideration should be given to the development of an access agreement between parties prior to sampling.

# 4.3.4 Conduct Pre-Sampling Building Survey

Buildings should be inspected prior to and during IAQ testing to assess whether there are potential background sources of chemicals and also to describe building conditions that may influence indoor air concentrations. Building occupants may also be interviewed to derive additional information on factors that may affect IAQ and to determine the building occupancy characteristics. A pre-sampling building questionnaire and survey is provided in Appendix J (also see ITRC (2007) and NJDEP (2005)). The pre-sampling building survey may be used as a tool to refine the sampling plan and identify any building preparation activities that should be considered prior to sampling (see Section 4.3.10). Relevant portions of the survey should be reviewed again at the time indoor air sampling is performed. A survey should be completed for each building being investigated.

## 4.3.5 Conduct Preliminary Screening

In conjunction with the pre-sampling building survey, a preliminary screening of the study building using a portable air monitoring instrument such as a photoionization detector (PID) can provide useful information on background VOC sources in indoor air. When sensitive PIDs are used (low ppbV range), they may also be capable of identifying entry points where soil gas intrusion is occurring. It is important to note that most direct-measuring instruments measure multiple organic compounds with varying responses and are not capable of identifying specific compounds. Furthermore, for most conventional PIDs/FIDs, the sensitivity of these instruments is often insufficient to detect compounds at levels that may be of concern for human health. Therefore, while they may be a useful tool for identifying indoor VOC sources or targeting sampling locations at some sites, they may not be used to rule out the presence of background contaminants in indoor air.

The PID measurements in some environments may be biased high. For example, condensation on the PID sensor results in a slowly rising false positive response that may reach several hundred ppm (Western Australia Department of Environment, 2005). Micro particles of dust and wood soot absorb moisture more readily than a clean sensor surface exacerbating the effect of moisture; therefore, relevant conditions during sampling should be noted, and the instrument calibration should be checked frequently.

Another recent development for screening is a field portable GC/MS (HAPSITE). This instrument was successfully used for screening at Hill Air Force Base (AFB) in the U.S. where the concentrations of TCE in soil vapour and air samples were measured with an approximate detection limit of 1  $\mu$ g/m<sup>3</sup>. The data was used to assist in setting sampling volumes for subsequent sorbent tube analysis (McHugh *et al.*, 2010).

#### 4.3.6 Identify Immediate Health or Safety Concerns

If the building survey or preliminary screening identify immediate health or safety concerns associated with chemical odours or where occupants exhibit signs of illness attributable to inhalation of volatiles in indoor air, further actions should be taken to identify the chemical source and mitigate the hazard (increase ventilation, relocate occupants, *etc.*), as warranted. There may also be instances where there are safety concerns associated with the accumulation of potentially explosive levels of methane or oxygen deficient conditions inside or near to buildings.

#### 4.3.7 Define Number and Locations of Indoor and Outdoor Air Samples

The number and locations of indoor air samples will be dictated by several factors. If a preliminary investigation of IAQ is being undertaken, a limited number of samples may be sufficient. If the study objectives require a statistical approach or analysis of results, multiple samples are required. The building characteristics including size, construction and ventilation patterns will also influence the required number of samples. For example, if the building is a small- to moderate-sized house with reasonably good ventilation, the indoor air concentrations within the house may be relatively uniform. For this scenario, one sample may be sufficient. For a larger house, commercial building, or school, where indoor air concentrations may vary in different parts of the building, multiple samples are required to characterize indoor air quality.<sup>3</sup>

For a residence with multiple floors, consideration should be given to collecting at least one sample per floor (per sampling event) to characterize inter-floor variability. Where minimal sampling is conducted for a preliminary assessment, it is generally preferable to target the first level of the building (*e.g.*, basement) since vapour concentrations are expected to be highest in lower regions of the building in instances of soil vapour intrusion. Exposure samples should be collected within the typical breathing zone at a height of approximately 1 to 1.5 m above the floor, preferably near the centre of the room, which is generally representative of overall room conditions. If there is an attached garage, collection of a sample from this location may provide valuable data on potential background sources.

Outdoor air will influence indoor air quality and may also contain chemicals at concentrations that exceed risk-based concentrations. Therefore, it is good practice to obtain outdoor air samples as part of the IAQ program. The number of samples will be site specific, but several samples obtained from multiple locations may be needed. As part of the outdoor air program, it is also important to identify emission sources such as gasoline stations, major highways, paving operations and remediation systems. It is important to protect outdoor air samplers from the elements (rain or snow) and vandalism.

<sup>&</sup>lt;sup>3</sup> Given that the number of indoor air samples is highly influenced by site specific conditions, no standardized guidance for number of samples has been developed for VOC vapour intrusion. In the radon literature, one indoor air sample per 2,000 square feet is found in several guidance documents (e.g., USEPA, 1993).

## 4.3.8 Define Sampling Duration

The duration for sample collection will depend on the study objectives. The selected sample duration should yield an average concentration of chemicals of potential concern over the expected daily exposure duration.

For a residential scenario, it is possible that residents may be present in the home 24 hours per day. Therefore, a 24-hour sample duration is the minimum duration recommended for a residential scenario. To provide perspective on sampling duration it is noted that it is generally recommended that radon samples be collected over a period of one week or longer to account for temporal variability (www.epa.gov/radon). Studies of radon provide valuable insight on potential indoor air concentration variability for vapour intrusion. For example, Groves-Kirkby *et al.* (2006) in a study comparing time-integrated indoor radon sampling for different time scales concluded that natural variability caused many one-week results (compared to three month tests) to be equivocal when compared to action levels, necessitating repetition of the measurement. Continuous radon monitoring indicated roughly diurnal (24-hour) variations that were up to one order-in-magnitude. Font *et al.* (2001) found that soil moisture levels caused by precipitation caused variations in indoor radon concentrations. The feasibility and need for longer duration active air sampling for evaluation of vapour intrusion is an area of current research.

For a commercial scenario, a sample duration equivalent to the standard 8- to 10-hour commercial exposure duration is recommended, unless exposure or site conditions dictate otherwise (*e.g.*, if there are variations in HVAC operation as discussed above).

The potential limitations in the sampling device should be considered when considering sampling durations (*e.g.*, canister flow controllers may not yield stable flow rates beyond 24 hours, chemical breakthrough may occur for long-duration active sorbent tube samples). Passive diffusive samplers are better suited to longer sampling periods than active canister or sorbent tube methods.

#### 4.3.9 Define Sampling Frequency

The sampling frequency will depend on study objectives, the nature of the contamination source and variability expected due to factors such as building characteristics, weather conditions and occupancy characteristics during sampling. Since it is not possible to accurately predict concentration variability due to the site-specific and complex nature of the processes that contribute to soil vapour intrusion, repeat sampling is generally required to establish concentration variability at a given site. In general, a minimum of two sampling events that capture possible seasonal variability (*e.g.*, winter/summer) are recommended; however, additional sampling events may be warranted at some sites. During winter, many buildings in Canada are depressurized, but this may not necessarily lead to higher indoor vapour concentrations because of other factors such as soil moisture, water table level and building ventilation rates. Repeat sampling may also be warranted, for example, if the subsurface source concentrations are changing over time (*e.g.*, mobile groundwater plume, water table fluctuations).

## **EXHIBIT 4.1. Indoor Air Variability at Soil Vapour Intrusion Sites**

One of the concerns with indoor air monitoring at vapour intrusion sites is temporal variability. Radon studies where continuous monitoring has been performed indicate significant temporal variability, but there is little similar information from contaminated sites. While the physical processes for transport of radon and VOCs through a building foundation and mixing inside a building are similar, the conceptual site model for sources and vadose zone transport are different, particularly for dissolved groundwater sources. In such cases, the flux through the capillary fringe may be rate-limiting, which could affect the variability observed. The timescales for variability also could vary from diurnal or daily variations due to temperature to longer timescales due to barometric pressure changes or seasonal changes. Superimposed on this variability, and potentially greater in significance, may be variations due to building processes. All indoor air testing data below is for houses without mitigation systems.

**Lowry AFB** (USEPA, 2008): At the Lowry AFB site, a dissolved chlorinated solvent plume in groundwater has migrated below houses. The soils at the site consist of sandy loam to loamy sand and the depth to the water table was approximately 6 m. Repeat indoor air monitoring was conducted several times at the Site (Figure 4.2). The data shows a seasonal trend with higher indoor air concentrations measured in the winter months.



FIGURE 4.2. Indoor Air Monitoring at Lowry AFB Site

**Wall Township, New Jersey** (USEPA, 2008): At the Wall Township site, a dissolved tetrachloroethylene (*i.e.*, perchloroethylene or PCE) plume in groundwater has migrated below houses. Sandy soils are present at the site and the depth to the water table is approximately 6 m. Repeat indoor air monitoring was conducted several times prior to installation of mitigation systems (Figure 4.3). The difference in the maximum and minimum indoor air concentrations ranged between 1.2 and 3 times.



FIGURE 4.3. Indoor Air Monitoring Wall at Township Site

**Redfield Site** (Unpublished, data provided by Envirogroup): At the Redfield site, a dissolved 1,1dichloroethylene plume in groundwater has migrated below houses. The soils at the site consist of silty clay loess with sand lenses with coarse-grained buried channel areas and the depth to the water table generally ranges from 6 to 9 m. Most houses in impacted areas of the Redfield site have been mitigated so there is only limited temporal data for un-mitigated houses. Given that indoor air data was available for some houses for seven years and that groundwater concentrations may vary over this time period, a groundwater-to-indoor air attenuation factor, as opposed to indoor air data is presented in Figure 4.4. The results show the groundwater-to-indoor attenuation factor varies from ½ to one order-of-magnitude.



## 4.3.10 Preparing the Building for Sampling and Conditions During Sampling

Potential background sources should be eliminated to the extent possible when conducting IAQ programs. For example, consumer products (*e.g.*, paint removers, solvents, fuel containers) may be removed and combustion sources (*e.g.*, candles, wood stoves) temporarily extinguished prior to sampling. Furthermore, consideration should be given to delaying sampling to allow elevated VOCs associated with new construction materials, paint or furnishings, or sealing work, to dissipate. A list of measures that should be considered when performing IAQ sampling programs is provided in Exhibit 4.2. It is important that specific instructions be provided to building occupants in advance of the sampling event.

In some cases, it may be desirable to adjust building HVAC conditions to control conditions for soil gas intrusion. For example, monitoring of IAQ under conditions of positive and negative building pressure may confirm whether volatiles measured in indoor air are from subsurface or background sources. One way to control building conditions is to either extract or blow in air using a blower or fan. This test may be implemented by replacing a door of a building with custom door of the same size fitted with a blower (*i.e.*, referred to as a "blower door test") (Sherman, 1998).

Consideration should be given to obtaining ancillary data (see Section 3.10), such as the differential pressure between the building and outdoor air and meteorological data, to aid in the interpretation of indoor air data. It may also be important to monitor the operation of fans, central vacuum cleaners, or other mechanical devices that could influence ventilation and pressure conditions during indoor air sampling.

# **EXHIBIT 4.2:** Preparation of Building for IAQ Sampling

Summary of measures implemented prior to IAQ sampling:

- Removal of products that are known significant sources of VOCs, such as fuel containers, paint, paint removals or solvents, as practical (preferably three days prior to sampling);
- Ensuring that containers of VOC-containing products are tightly sealed, as practical;
- Combustion sources (*e.g.*, candles, wood stoves) should be extinguished prior to sampling (preferably 24 hours prior to sampling);
- Consideration should be given to delaying sampling to allow elevated VOCs associated with new construction materials, paint, furnishings and sealing work to dissipate;
- After removal or control of known VOC sources (preferably several days before sampling), ventilation may be required to help eliminate residual contaminants. This may be done through operation of the building HVAC system or opening of doors, windows, or operation of exhaust fans. It should be completed at least 24 hours prior to sampling; and,
- HVAC systems (heating and cooling) should generally be operating under normal occupied conditions for at least 24 hours prior to and during the scheduled sampling time (unless the objective is to artificially control building conditions).

Measures to be avoided 24 hours prior to and during sampling are:

- Storage or use of fuel products, solvents, glues or petroleum-based materials within building or attached garages;
- Smoking of cigarettes;
- Operation and storage of automobiles in attached garages; and,
- Operation of fireplaces.

#### 4.4 Indoor Air Analytical Methods

The selection of the indoor air analytical method depends on a number of factors, including data quality objectives, risk assessment objectives, detection limits and the contaminants of potential concern. Typically indoor air samples are obtained using either sorbent materials or canisters (*e.g.*, Summa canisters) and sent to a laboratory for analysis.

Since analytical protocols were addressed in detail for soil vapour, this section is limited to describing differences in analytical considerations for indoor air. Since there are accepted methods for collection of indoor air samples using passive methods (unlike soil vapour), indoor air testing using passive diffusive samplers is also described.

The main differences between soil vapour and indoor air sampling are that lower detection limits, larger sample volumes and longer sampling durations are generally required for indoor air testing. The required analytical reporting limit will depend on the compound, but typically is less than 1  $\mu$ g/m<sup>3</sup>. For some analytes, the target risk-based indoor air concentration may be below a practically achievable detection limit and/or below typical background levels in indoor or ambient air. The low detection limits require that a high level of care be taken to avoid crosscontamination both by the laboratory (e.g., cleaning of sampling device) and by persons performing the sampling (e.g., handling and storage of sampling device). When using canisters, it is important to consider whether they can be cleaned and certified to the levels at which the analysis will be performed.

#### **Canister Cleaning Study**

EPRI (2005) report laboratory QC data where 100 canisters were tested after they were cleaned, with results as follows:

Chemical	Number Detects	Avg. Conc. (µg/m <sup>3</sup> )	Max Conc. (µg/m <sup>3</sup> )
Benzene	100	0.046	0.52
PCE	30	0.063	0.30
TCE	79	0.055	1.42
VC	0	non detect	non detect

Note: PCE = tetrachloroethylene, TCE = trichloroethylene, VC = vinyl chloride

A second study involved testing canisters one and ten days after they had been cleaned. The results indicated higher TCE concentrations for the ten day sample, which was attributed to time dependent desorption from the valve and canister. These studies highlight that the challenges for sub- $\mu$ g/m<sup>3</sup> testing of air samples. For indoor air testing, evacuated canisters (six litre) are frequently used (USEPA TO-15). To provide the sensitivity required to achieve reporting limits at or below risk-based target concentrations, GC/MS analysis may need to be performed in selective ion model (SIM) for some compounds. For active sorbent tube analysis, modified industrial hygiene methods involving solvent extraction (*e.g.*, modified OSHA 7 or NIOSH 5515) usually do not provide sufficiently low detection limits. Instead, thermal desorption methods will usually be required (*e.g.*, USEPA Method TO-17).

# 4.4.1 Air Analysis Using USEPA Method TO-15

USEPA Method TO-15 is a complex analysis that requires a competent laboratory and skilled analyst. The BC Laboratory Manual (2009) identifies minimum requirements, some which go beyond the TO-15 method, including as a minimum batch proofing, tracking of canister use, initial five-point calibration, and requirement to check the certified standard against a second certified standard. When preparing standards, it is important to use NIST-traceable gas-phase standards within the supplier-specified holding time. The specifications for tuning and use of appropriate ions for correct compound identification are also important when using selective ion mode (SIM) for low-level analysis (this also applies to TO-17 analysis).

There is continued research on TO-15 methods, including the use of surrogate standards (Maio and Stearns, 2000) where the standard is added to the canister (this QC test is not normally conducted). Surrogate standards provide a way of determining whether there are losses in the canister and tubing prior to introduction of the sample into the analytical instrumentation, and further research on this is considered warranted. Other developments included heated canisters (to improve semi-volatile compound recovery) and micro-valve helium diffusion samplers, where the helium in a canister is allowed to escape, which creates a vacuum drawing an air sample into the canister.

## 4.4.2 Air Analysis using Passive Diffusive Samplers<sup>4</sup>

Passive diffusive samplers are less commonly used in vapour intrusion assessments than wholegas or active adsorptive sampling, but they are commonly used in Europe, and interest in and use of passive samplers is increasing in North America. The principles of diffusive samplers and a summary of recent developments for new types of samplers are provided below, with additional details and review of research studies provided in Appendix K.

The principle of diffusive sampling is that if the uptake rate is known, the concentration of chemicals can be calculated from the mass adsorbed over a known sampling duration. The uptake rate is a function of the diffusive coefficient, which is compound and sorbent specific, and the geometry of the sampler. The uptake rate may vary over time. Factors that may affect the performance of diffusive samplers include temperature, pressure, humidity, starvation effect (function of face air velocity and uptake rate) and changes in chemical concentrations over the sampling interval. The advantages of passive samplers include that they are easy to use, do not require a sampling pump, and may be less costly than other methods. In addition, passive

<sup>&</sup>lt;sup>4</sup> Not currently an approved method in British Columbia

samplers can be deployed for longer periods of time (some studies indicate one to two weeks) to provide time-averaged concentrations, which is advantageous when the goal is to evaluate longer-term human exposures.

Badge-style samplers have been used for decades for evaluation of workplace exposures to VOCs with reporting limits in the parts per million (ppmV) range for samples collected over an 8-hour period where the sorbent is typically charcoal, which is extracted using solvent (carbon disulphide) and analyzed using GC/FID methods.

In the 1990's, badge-style samplers began to be used for indoor air quality studies, for example, 3M OVM 3500 badges combined with GC/MS analysis were used for one of the largest studies in Canada (757 houses) (Otson *et al.*, 1993). Through longer sampling durations, detection limits on the order of 1 ug/m<sup>3</sup> have been achieved. These badges continue to be used, for example, Bailey *et al.* (2008) report a good comparison between TCE concentrations measured with OVM 3500 badges and active sorbent tubes ( $R^2$  correlation coefficient of 0.99 or higher). Manufacturer-specified limitations with badge type samplers should be recognized. This includes reduced recovery of vinyl chloride, acetone and methyl ethyl ketone when humidity exceeds 50% and the potential need for project specific recovery tests to quantify recovery for contaminant mixtures (3M Bulletin 1028, 2001).

Over the past few years, new types of diffusive samplers have been developed for longer duration, low-level analysis as described below.

- Passive diffusive badges: Recent advances in badge-style samplers include larger samplers, use of different sorbents (Tenax TA, Chromosorb 106, Anasorb GCB1 (Carbopack B) and Carbopack X), thermal desorption and GC/MS analysis (OSHA, 2003). McClenny *et al.* (2005) report on the results of a thermal desorption method involving a larger volume sampler (SKC Ultra-II) filled with Carbotrap C, where compound-specific method detection limits on the order of 0.03 to 0.3 ppbV were reported.
- 2) **Radiello® samplers**: This sampler has a radial symmetry, and is typically filled with a thermally desorbable Carbograph 4 or Carbopack X (Bruno *et al.*, 2004). This sampler has a higher uptake rate than other passive samplers and therefore lower detection limits can be achieved for comparable sampling times.
- 3) Automatic Thermal Desorption (ATD) tube samplers. This sampler is similar to thermal tubes used for active sampling, except that the tube is open at one end (Brown, 2000). A concentration gradient is created within the open air of the tube. Given the geometry of this sampler, the uptake rates are lower than for other diffusive samplers.
- 4) Polydimethylsiloxane (PDMS) membrane samplers (Waterloo membrane sampler): For this sampler, vapour-phase chemicals partition into and diffuse through a PDMS membrane, where there are trapped by a sorbent (typically Anasorb 747) in a small glass vial (Seepathy et al., 2008). PDMS is used as a GC stationary phase on capillary columns used in gas chromatography and the rate of uptake through the membrane is correlated to the gas chromatographic retention indices of the analytes. Therefore, the diffusion rates can be

estimated from the chromatographic retention times of the analytes. ). Groenevelt *et al.* (2010) report a good comparison between PDMS sampler and TO-15 results.

There are significant recent developments for passive sampling technology, which show promise for longer sampling durations and low-level analysis. As described in Appendix K, several studies indicate good comparisons between the results of passive diffusive sampler and active sorbent (TO-17) and/or canister (TO-15) analyses, although there have also been a few studies where concentrations measured with passive samplers were lower than those measured by the TO-15 or TO-17 methods. Research indicates that the uptake rate may decrease for low face velocities and that saturation or back diffusion may result in lower uptake rates for sampling durations longer than one week (for some samplers evaluated). The stability of the uptake rate depends on the sampler geometry and sorbent, and potentially the contaminant mixture. Further research is needed to evaluate these factors.

It is important that passive samplers are validated over the range of face velocities expected in the sampling environment, and that the linear range and uncertainty in uptake rate for each chemical is provided. For example, Radiello publish upper limits to exposure duration and maximum concentration-time values for which the uptake rate is linear to. The implication of the maximum concentration-time values is that as the air concentration increases, the allowable sampling time decreases.

## 4.5 Resources and Weblinks

Selected references with a significant emphasis on indoor air sampling and analysis or background evaluation are listed below:

Interstate Technology and Regulatory Council (ITRC). The Vapor Intrusion Pathway: A Practical Guide (VI-1)(January 2007, 173 pages) provides a generalized framework for evaluating the vapour intrusion pathway and describes the various tools available for investigation, data evaluation, and mitigation. The Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios (VI-2) (January 2007, 52 pages) is a supplement to Vapor Intrusion Pathway: A Practical Guide. The supplement describes applicable approaches for evaluating the vapor intrusion pathway in six typical scenarios. http://www.itrcweb.org/Documents/VI-1.pdf. http://www.itrcweb.org/Documents/VI-1A.pdf

**New Jersey Department of Environmental Protection**. *Vapour Intrusion Guidance (October, 2005)*. This guidance includes comprehensive methods for site characterisation, including soil gas sampling and analysis. <u>http://www.state.nj.us/dep/srp/guidance/vaporintrusion/vig.htm</u>

**Massachusetts Department of Environmental Protection**. Indoor Air Sampling and Evaluation Guide (April, 2002). <u>http://www.state.ma.us/dep/ors/orspubs.htm#air</u>

**Tri-Services Environmental Risk Assessment Working Group** (TSERAWG) 2008. *Tri-Services Handbook for the Assessment of the Vapor Intrusion Pathway*. Rev. 4.0, 15 February (U.S. Air Force, U.S. Navy, U.S. Army). This guidance has a detailed appendix on evaluating background sources of chemicals in indoor air.

https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac\_ww\_pp/navfac\_nfesc\_pp/environ mental/erb/resourceerb/dod%20vi%20guidance%20handbook\_dftfinal.pdf

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# 5.0 DATA INTERPRETATION AND ANALYSIS

The procedures for data interpretation and analysis of soil vapour data are described below.

# 5.1 Data Organization and Reporting

The soil vapour data should be tabulated and plotted to facilitate evaluation and review of data relationships and trends. The following data organization and presentation is recommended:

• Tabulate all data including sample location identifier, sample date, sample depth, sampling methods (including sampling duration and flow rate),

# **Data Interpretation and Analysis**

This chapter describes the data organization and report, data quality analysis based on QA/QC program, and data consistency analysis. The chapter concludes with multiple lines-of-evidence approach describing methods that may be used to evaluate background sources of contamination when conducting indoor air quality studies.

chemical analysis methods, laboratory detection limits and results of chemical analysis;

- Tabulate field screening and laboratory analysis data to enable side-by-side comparisons;
- Prepare plan drawings showing soil vapour concentration data that includes pertinent structures (buildings, utilities, paved areas, vegetated areas);
- Compare soil vapour with nearby groundwater concentration data; consider geologic conditions when evaluating variability;
- Prepare vertical profiles of soil vapour concentration data that includes oxygen, carbon dioxide and methane and boring log data where available; and,
- Identify soil vapour target concentrations and background indoor and outdoor air concentrations, where available.

If indoor air quality data is obtained, the following information should be tabulated:

- Tabulate all data including sample location identifier, sample date, sample height, sample location within room, sampling methods, chemical analysis methods, laboratory detection limits and results of chemical analysis;
- Calculate constituent ratios and evaluate trends with respect to (i) indoor air to soil vapour or subslab vapour samples, (ii) first building level to higher level air samples, and (iii) indoor air to outdoor air samples;
- Note building size, foundation conditions, utility penetrations through floor, sumps and drains, attached garages, and stains on floor;
- Note building HVAC conditions during indoor air sampling and qualitatively describe opening of windows and doors, operation of fireplace, furnace and fans;

- Note potential significant indoor sources of VOCs present during sampling; and
- Identify target risk-based indoor air concentrations and background indoor and outdoor air concentrations, where available.

## 5.2 Data Quality Analysis

Following receipt of the soil vapour and indoor air results, the data should be evaluated to determine whether they meet data quality objectives outlined in the sampling plan (Section 3.8). The data quality checks should include the following:

- Review reported detection limits relative to data quality objectives. In some cases, sample dilution is required, which results in raised detection limits;
- For Summa canister analyses, review canister pressure upon completion of sampling and receipt by the laboratory. Obtain pre-delivery canister testing and certification results from the laboratory. When there are significant differences in the elevation at which the sample was obtained and the laboratory, it may be possible to correct for the effect of ambient pressure on the sample concentration (*i.e.*, using Boyle's Law for an ideal gas), providing that the barometric pressure at the time of sampling and analysis are recorded. Prior to sampling, the vacuum should be close to 29 inches Hg. USEPA Method TO-15 does not provide

criteria for residual vacuum, but if there is no vacuum left in the canister, there is less certainty with respect to sample integrity (due to possible leakage).<sup>5</sup> In addition, a residual vacuum is critical when conducting longer duration sampling where a relatively uniform flow rate is desired. Typically, the target vacuum range is 4 to 6 inches Hg, and as a minimum, there must be a measureable residual vacuum in the canisters;

• For sorbent tube analyses, review results of analyses of front and back sections of the tube (or two tubes in series) to evaluate possible chemical breakthrough. Breakthrough can be caused when the adsorptive capacity is exceeded, the air flow through the tube is too high, and chromatographic effects caused by other compounds. If the laboratory considers the

## **Duplicate Sample DQO's**

Performance criteria under **USEPA** Methods TO-15 and TO-17 require that the relative percent difference (RPD) between laboratory duplicate samples from the same canister be within 25%. The BC Laboratory manual does not specify a requirement for field duplicates. Greater variability would be expected for field compared to laboratory duplicate samples. Experience indicates many field duplicates with RPDs less than 25%, but nonetheless, a significant number of samples with RPDs that are 25-100% or higher. Analysis of consistency in RPDs between compounds may assist in identifying possible reasons for the Research variability. is needed on establishing appropriate DQO's for field duplicates, but 50% as a provisional target RPD is recommended.

<sup>&</sup>lt;sup>5</sup> Oil-filled gauges supplied by the laboratory for field measurements have an accuracy of plus or minus 1 or 2 inches Hg, so only approximate readings can be obtained in the field using oil-filled gauges. Pressures may also be measured using digital manometers. Laboratories typically use a much more accurate pressure gauge to measure pressure in the canister.

first tube saturated, then results are potentially biased and re-sampling should occur. The criterion for evaluating breakthrough is method and chemical dependent but typically is a concentration in the second tube that is greater than 10 to 25 percent of the concentration in the first tube<sup>6</sup>. If the sample media is not saturated, the front and back concentrations should be added together for numerical evaluation;

- Compare precision for laboratory and field duplicate or co-located samples, as quantified by the relative percent difference (RPD);
- Review analytical results for blank samples (*e.g.*, field blanks, laboratory blanks and trip blanks) to identify possible issues with the laboratory or field procedures that may have affected the results; and
- Recognize that reported concentrations within five times of the quantification limit are typically more uncertain than higher concentration values.

# 5.3 Data Consistency Analysis

The results of the soil vapour and indoor air sampling programs should be reviewed in terms of the expected results, based on consistency with the conceptual site model and internal consistency between sampling points. These consistency checks should include the following:

- The soil vapour concentrations should be spatially consistent with the soil and groundwater concentrations, for example, the highest soil vapour concentration should be measured in source contamination areas where soil and groundwater concentrations are also highest;
- The soil vapour concentrations should decrease with increasing distance from a source, and, in general, oxygen concentrations should decrease and carbon dioxide concentrations should increase close to petroleum hydrocarbon sources. If this pattern is not observed, there may be additional contamination sources present (and possibly lateral soil vapour migration), or there may be data quality issues (*e.g.*, short circuiting);
- The vertical gradients of petroleum hydrocarbon vapours, oxygen, carbon dioxide and methane should be internally consistent. A decrease in hydrocarbon vapour concentrations should be associated with a decrease in oxygen and increase in carbon dioxide concentrations. As described in API (2005), stoichiometric relationships for aerobic biodegradation can be used to quantify the fluxes and concentration profiles expected;
- Significant depletion in oxygen concentrations are observed close to petroleum hydrocarbon source zones and below confining layers. Elevated oxygen concentrations that coincide with elevated hydrocarbons concentrations close to hydrocarbon sources suggest that the soil gas sample was compromised through short-circuiting or leakage; and

<sup>&</sup>lt;sup>6</sup> BC Laboratory Manual (2009) criteria for breakthrough is 25% in second tube. When the concentration in the second tube is less than 25% of the first tube, then the concentrations in the two tubes are summed.

• Soil vapour concentrations should be consistent with expected temporal trends. A priori it may be difficult to predict the effect of temporal factors on soil vapour data; therefore, a database that already includes some temporal data may be required to make this evaluation.

# 5.4 Methods for Discerning Contributions of Background from Indoor Sources

When conducting indoor air quality testing program, consideration of potential background sources is an important part of the data interpretation, and for this reason a number of different methods for evaluating the contribution of background sources are described below. To the extent possible, multiple lines-of-evidence should be considered when evaluating IAQ data. By relying on several lines-of-evidence rather than a single line-of-evidence, the overall level of uncertainty of the study can be reduced. The relative importance of various lines-of-evidence should be based on professional judgment and should consider site conditions, data quality, as well as an understanding of background sources of contamination, factors affecting IAQ as well as contaminant fate and transport mechanisms.

## Building Survey and Occupant Use

A common sense evaluation of potential background sources should include a building survey where visual inspection of possible indoor sources (*e.g.*, consumer products, chemical storage, connection of house to garage) together with information on occupant use (*e.g.*, cigarette use, hobbies, *etc.*) is gathered. Available databases should be consulted to link consumer products with their chemical composition, to the extent possible.

## Comparison of Subslab Vapour and Indoor Air Concentrations

Subslab vapour concentrations may be compared to indoor air concentrations to evaluate whether there is a significant potential for vapour intrusion. Evaluation of empirical data indicates a high percentage (about 95%) of subslab vapour to indoor air attenuation factors are less than 0.02 (this is equal to dilution factor of 50) (USEPA, 2008). A compilation of subslab vapour to indoor air attenuation factors for trichloroethylene for data compiled by USEPA and Health Canada is shown in Figure 5.1.

If the ratio of subslab vapour to indoor air concentrations are less than approximately 10 (the above dilution factor is adjusted downward to reflect data uncertainty), then this is a line-of-evidence for indoor contaminants not being due to vapour intrusion and for background sources. The strength of this line-of-evidence increases with the confidence in the subslab vapour data representativeness (*e.g.*, there would be greater confidence in a larger than smaller dataset).

Factor	Suggests Potential for Vapour Intrusion	Suggests Potential for Background Source	
Results of Building Survey		Chemical with elevated air concentration linked to product in building	
Comparison of Subslab and Indoor Air Concentrations	Ratio subslab vapour to indoor air $> \sim 10$	Ratio subslab vapour to indoor air $< \sim 10$	
Ratio of Indoor to Outdoor Air Concentrations		Close to One	
Comparison of Indoor Air Concentrations to Literature Background	Significantly higher than background	Similar to background	
Comparison between Constituent Ratios Between Subsurface and Indoor Air	Similar ratios for chemicals with similar properties repeated in multiple buildings	Large differences in ratios for chemicals with similar properties	
Marker chemicals	Detected in indoor air when no background sources		
Building Pressure Manipulation	Significant difference in indoor air concentrations under positive and negative pressure	Similar indoor air concentrations under positive and negative pressure	
Tracer Tests	Similar attenuation factor for VOC and tracer	Significantly higher attenuation factor for VOC than tracer	

# TABLE 5.1. Lines-of-Evidence for Evaluating Contribution of Background Indoor Air Sources

As the ratio of the subslab vapour to indoor air concentrations increases, this is a weak line-ofevidence for vapour intrusion; however, there may be elevated subslab vapour concentrations but only negligible vapour intrusion depending on building conditions (*e.g.*, pressure gradients). The strength of this line-of-evidence could improve with information on building conditions.

While often this line-of-evidence focuses on subslab vapour data, deeper soil vapour data may also be used in this evaluation, if it is representative of the vapour pathway from contamination source to indoor air.



# FIGURE 5.1. Subslab Vapour to Indoor Air Attenuation Factors for Trichloroethylene – USEPA and Health Canada Database.

## Comparison of Indoor and Outdoor Air Concentrations

Due to exchange of building air with outdoor air, the chemical concentrations measured indoors will, in part, reflect the outdoor air quality. For some chemicals such as benzene, the ratio of indoor to outdoor concentrations is often close to one (Hers *et al.*, 2001) in urban environments where there is no significant indoor source of benzene (*e.g.*, gasoline storage, cigarette smoke). For other chemicals, the ratio of indoor to outdoor concentrations may be much higher than one due to indoor chemical sources.

If the ratio of indoor to outdoor concentrations is approximately equal to one (e.g., within a factor of two), then this is a moderate strength line-of-evidence that indoor air contaminants are not due to soil vapour intrusion.

If the indoor air concentration is significantly higher than the outdoor concentration, caution should be exercised in interpreting this as a line-of-evidence for vapour intrusion because there may indoor sources of chemicals, and at best this may be a weak line-of-evidence for vapour intrusion.

## Constituent Ratios

An evaluation of the ratios between contaminant concentrations in groundwater, soil vapour, indoor air and outdoor air for concurrent data and chemicals with similar fate and transport properties can assist in discerning background sources of contaminants. Chemical ratios in indoor air and soil vapour should be similar if vapour intrusion is the cause for the elevated indoor air concentrations for chemicals with similar fate and transport properties. If the ratios are significantly different (*e.g.*, by more than one order-of-magnitude), there are likely background contributions of VOCs for some or all the chemicals under consideration. The chemical with the higher vapour attenuation factor (ratio of indoor air to soil vapour concentration) is more likely to be affected by background sources than the chemical with the lower attenuation factor.

Ratios of more than two compounds can be inspected using multi-linear diagrams (*e.g.*, trilinear), where the concentrations of each chemical are plotted on an axis and where lines are drawn to connect the plotted points (Figure 5.2). Depending on the source, the outline may have a characteristic shape. If groundwater data are used, adjustments should be made to take into account different relative volatilities between contaminants (*i.e.*, corrected for varying Henry's Law constants). For example, a "Super Ratio" may be calculated, as follows:

Super Ratio = 
$$(C1/C2)_{air} / [(C1/C2)_{gdw} * (H2/H1)]$$
 [5-1]

where  $(C1/C2)_{air}$  is the ratio of the indoor air concentration for chemicals 1 and 2,  $(C1/C2)_{gdw}$  is the ratio of the groundwater concentration, and (H2/H1) is the ratio of the dimensionless Henry's Law Constant. The Super Ratio was calculated for the Redfield, Colorado site where a large groundwater plume consisting primarily of 1,1-DCE and TCE migrated below a residential area (Figure 5.3). Outliers in the data suggest indoor TCE sources for some buildings.



## FIGURE 5.2. Tri-Linear Plot Comparing Soil Vapour and Indoor Air from Petroleum Contaminated Site.

The constituent ratio analysis works best for chemical groups with similar physical-chemical and fate properties, such as tetrachloroethylene and trichloroethylene. Where there are potential significant differences in fate and transport processes (e.g., sorption, biodegradation rates) this technique is not effective.



# FIGURE 5.3. Evaluation of possible background influence using concentration ratios for Redfield site(N=344, data provided by Jeff Kurtz, Envirogroup).

#### Marker Chemicals

Marker chemicals are compounds that are associated with the subsurface contamination, but not background air sources. An example of a marker chemical is 1,1-dichloroethylene (DCE), which is a degradation product of 1,1,1-trichloroethane and trichloroethylene, and which is generally considered not to be present as a background chemical in indoor air. Therefore, detectable levels of 1,1-DCE in indoor air would suggest soil vapour intrusion is occurring (unless from an ambient air source). Marker chemicals, if present, are also useful compounds when evaluating constituent ratios using the method described above.

## Spatial Trends

An evaluation of spatial trends may provide insight on differentiating background sources from the contaminants of interest. For instance, VOC concentrations in a basement may be higher than in upper floors. This provides support for a subsurface vapour source, but care must be taken to ensure that the results were not biased by products stored in the basement. Also, testing of "pathway" samples collected near foundation cracks, unsealed utility entry points or other possible preferential transport zones could be compared to samples collected at other parts of the building. Concentrations in pathway samples that are elevated relative to concentrations in samples from other parts of the building may indicate soil vapour intrusion is occurring. Conversely, elevated concentrations in proximity to chemical storage inside the building may indicate background sources are significant. However, spatial differences may be minimal in buildings with efficient ventilation systems. For sites with larger scale impacts with where multiple buildings are tested, it may be possible to compare the spatial trends in subsurface data, if well characterized (*e.g.*, contoured groundwater or soil vapour plume, location of hot spots) and compare this to indoor air concentrations measured in multiple buildings. Caution should be exercised when following this approach depending on the confidence in the subsurface data.

## Comparison of Indoor Air Data to Literature Background Concentrations

Indoor air quality data may be compared to published data on indoor air quality from sites that are not impacted by vapour intrusion. Typical background sources and concentrations of VOCs in indoor air were discussed in Section 4.3. A recent study compiling indoor air data from multiple sites that provides statistical summary of indoor air concentrations is provided by Dawson and McAlary (2009). The site data should be compared to data for buildings of similar type (*e.g.*, single family residence, apartment, commercial).

## Comparison of Indoor Air Data to Control Building Survey

IAQ data from buildings above the contaminated area may be compared to IAQ data from nearby "reference" buildings outside the contaminated area. This method requires a sufficient number of buildings to be tested such that statistical comparisons between data sets can be made. There are a number of confounding factors that could contribute to differences in air quality unrelated to soil vapour intrusion. To the extent possible, building construction and occupant usage of the reference buildings should be similar to the buildings of interest. This approach is infrequently used since it is not practical.

## Modification of Building Pressurization

Indoor air quality testing under positive and negative building pressurization can be used to determine whether soil vapour intrusion is occurring and to evaluate the possible influence of background sources on indoor air quality. Indoor air concentrations that are significantly different under positive and negative pressures suggest vapour intrusion is occurring, since typically, soil gas advection caused by building depressurization is the main cause for soil vapour intrusion. Building pressures can be modified through control of the building HVAC system and use of temporary fans or blowers. While modification of building pressurization goes beyond the typical scope of testing for IAQ studies, it could be considered when it is important to distinguish background from possible subsurface vapour sources.

## Emerging Methods

Carbon stable isotope analysis (CSIA) is an emerging method for identifying potential vapour sources. Isotopes have a different atomic mass (number of neutrons); one example is carbon 12 and 13. Fractionation may occur when biodegradation or other transformation processes preferentially break down lighter isotopes. McHugh *et al.* (2010) present preliminary analysis where isotope ratios of TCE were determined by a modified PT-GC-IRMS (purge-and-trap-gas chromatography–isotope ratio mass spectrometry). The results indicated a difference in the carbon isotope ratios for a subsurface and indoor source.

Naturally-occurring radon can be used as a tracer to evaluate sub-slab to indoor air attenuation for VOCs (assuming similar transport properties across the building envelope) through simultaneous measurement of VOCs and radon in indoor air, outdoor air and subslab soil gas. Potential advantages of radon are that there are limited sources of indoor radon (excluding granite counter tops and other decorative stone) and indoor radon concentrations are in most cases above detectable levels (unlike VOCs where bias may be caused by non-detect values).

## Comparison of Measurements to Empirical Data and/or Modeling Results

Where there is relatively high confidence in the data and where representative spatially- and temporally-averaged attenuation ratios can be calculated for a building, the internal consistency between measurements and empirical and/or modeling data can be evaluated. For non-degrading chemicals, the upper range in empirical attenuation factors are approximately  $10^{-3}$  for groundwater-to-indoor air,  $10^{-2}$  for soil vapour-to-indoor air and  $10^{-1}$  for subslab vapour-to-indoor air (USEPA, 2008). A measured ratio that exceeds these empirical ratios by a significant degree may suggest a background component. Site-specific modeling may also be performed, for example using the Johnson and Ettinger (1991) model. When there is good quality input data, the modeled and measured values can be expected to agree within about an order-of-magnitude (Hers *et al.*, 2003; Abreu and Johnson *et al.*, 2005; EPRI, 2005). When using this approach, caution must be taken in that the conceptual site model must be well understood and data adequacy and quality must be high. Comparisons using the Johnson and Ettinger model may not be meaningful if there are conditions that fall outside of the processes included in the Johnson and Ettinger model such as preferential pathways, barometric pumping or biodegradation.

## 5.4.1 Further Evaluation

The data quality and consistency should be evaluated to determine whether there are data gaps or quality issues that warrant additional soil vapour testing. The soil vapour concentrations will also typically be compared to risk-based generic (if available) or site-specific soil vapour criteria for the vapour intrusion pathway. Depending on the results of this comparison, additional soil vapour characterisation and/or indoor air testing may be warranted.

## 5.5 References

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# 6.0 ACRONYMS

ACH	air change per hour
AEC	area of environmental concern
API	American Petroleum Institute
APHA	American Public Health Association
APEC	Area of Potential Environmental Concern
ASTM	American Society Testing Materials
AAS	atomic adsorption spectrometry
ATSDR	US Agency for Toxic Substances and Disease Registry
høs	below ground surface
BTEX	benzene toluene ethylbenzene and xylenes
CALA	Canadian Association for Laboratory Accreditation Inc
CCV	Continuing Calibration Verification
CPPI	Canadian Petroleum Producers Institute
carcinogenic	cancer-causing chemical
CCME	Canadian Council of Ministers of the Environment
CEOG	Canadian Environmental Quality Guidelines
CEAA	Canadian Environmental Assessment Act
CEAA	concentual exposure model
	Methane
$C\Omega_{2}$	Carbon Dioxide
COPC	contaminant of potential concern
CSM	concentual site model
CSA	Canadian Standards Association
CV	coefficient of variation (standard deviation divided by mean) same as
C V	relative standard deviation)
CWS_PHC	Canadian Wide Standards - Petroleum Hydrocarbon Compounds (CCMF
CWS-IIIC	guidance)
DOI	data quality indicators
DNAPI	dense non-aqueous phase liquid (more dense than water)
DRA	detailed risk assessment
FCD	electron canture detector
ECD F2 F3 F4	Petroleum Hydrocarbons in the carbon range of $nc10$ - $nc16$ $nC16$ - $nC34$
12,13,14	and n34-nc50 respectively as defined by the CCME method
FID	flame ionization detector
GC/FID	gas chromatography/flame ionization detection
GC/MS	gas chromatography/mass spectrometry
HVAC	building heating ventilation and air-conditioning systems
HI	hazard index (sum of HOs)
НО	hazard motiont
HVAC	heating ventilation and air conditioning
IAO	indoor air quality
ID	inside diameter
IRIS	Integrated Risk Information System
J&E	Johnson and Ettinger
LCS	laboratory control sample
LRL	laboratory reporting limit
LNAPL	light non-aqueous phase liquid (less dense than water)
MDL	Method Detection Limit

### **Golder Associates**

mg/LMilligrams per LitreMTBEMethyl tert-butyl etherNAPLnon-aqueous phase liquidPAHPolycyclic Aromatic HydrocarbonsPCEperchloroethylene							
MTBEMethyl tert-butyl etherNAPLnon-aqueous phase liquidPAHPolycyclic Aromatic HydrocarbonsPCEperchloroethylene							
NAPLnon-aqueous phase liquidPAHPolycyclic Aromatic HydrocarbonsPCEperchloroethylene							
PAHPolycyclic Aromatic HydrocarbonsPCEperchloroethylene							
PCE perchloroethylene							
1 2							
ppm Parts per Million (Equivalent to mg/Kg or mg/L)							
ppb Parts per Billion (Equivalent to ug/Kg or ug/L)							
PQL practical quantification limit							
OSHA Occupational Safety and Health Administration	Occupational Safety and Health Administration						
O <sub>2</sub> Oxygen							
PARCC Five principal DQIs consisting of Precision, Accurac	y,						
Representativeness, Comparability, and Completeness	5,						
PID photo ionization detector							
PVC polyvinyl chloride							
OAPP quality assurance project plan							
OA/OC quality assurance/quality control							
O <sub>soil</sub> advective soil gas flow rate into building							
O <sub>build</sub> building ventilation rate							
RA risk assessment							
RL reporting limit							
RPD relative percent difference							
RSD relative standard deviation (standard deviation divided by mean), same	as						
coefficient of variation)							
SABCS Science Advisory Board for Contaminated Sites (British Columbia)							
SCC Science Council of Canada							
SFR single family residence							
SLRA screening-level risk assessment							
SOP Suggested Operating Procedure	Suggested Operating Procedure						
SSD subslab depressurization (vapour intrusion mitigation system)	subslab depressurization (vapour intrusion mitigation system)						
TCE trichloroethene (trichloroethylene)							
TIC tentatively identified compound	tentatively identified compound						
TRV toxicity reference value	toxicity reference value						
Type 1 error Null hypothesis (baseline condition) is rejected when it is actually true.	Null hypothesis (baseline condition) is rejected when it is actually true						
Probability of this error occurring is called alpha ( $\alpha$ ) or level of							
significance.							
Type 2 error Null hypothesis is not rejected when it is actually false. Probability that							
this error will occur is called beta ( $\beta$ ) or statistical power.							
USEPA US Environmental Protection Agency	US Environmental Protection Agency						
USSCS US Soil Conservation Service (for soil texture classification)	US Soil Conservation Service (for soil texture classification)						
ug/g Micrograms per Gram (Soil)	Micrograms per Gram (Soil)						
ug/L Micrograms per Litre (Water)	Micrograms per Litre (Water)						
UV ultraviolet	ultraviolet						
VOC volatile organic compound	volatile organic compound						
WHO World Health Organization	World Health Organization						

# 7.0 CLOSURE

Golder Associates has appreciated the opportunity to be able to prepare this important guidance for the Science Advisory Board for Contaminated Sites in British Columbia.

## GOLDER ASSOCIATES LTD.

# **ORIGINAL SIGNED**

Jeanette Southwood, M.A.Sc., P.Eng. Principal/Senior Risk Assessment and Risk Management Specialist

# **ORIGINAL SIGNED**

Eric Hood, Ph.D. Senior Scientist

# **ORIGINAL SIGNED**

Ian Hers, Ph.D. P.Eng. Principal/Senior Environmental Engineer, Vapour Intrusion Practice Leader

 $\label{eq:linear} $$ Wapour Charact - FINAL 009-1436-0057 REP 0512_11 SABCS Soil Vapour Charact - FINAL 0512_11$ 

# **APPENDIX A**

CHECKLIST FOR VAPOUR INTRUSION CONCEPTUAL SITE MODEL



# CHECKLIST FOR VAPOUR INTRUSION CONCEPTUAL SITE MODEL

This checklist is intended to address conceptual model development for soil vapour intrusion studies, but does not include considerations relating to characterization of indoor air quality. It is recognized that some of the information on buildings may not be available in the absence of indoor air sampling.

#### Information Sources and Status

- □ Summarize the information sources that have been used to develop the conceptual site model
- □ Summarize the status of investigations completed at the site
- □ Summarize the status of remediation completed at the site including contamination source zone, groundwater or vapour remediation

#### **Contamination Source Characteristics**

- Describe the type, source and history of the contamination release
- Describe the presence, distribution and composition of LNAPL and/or DNAPL, if present at the site, describe whether LNAPL and/or DNAPL is potentially mobile
- Describe the distribution and extent of dissolved organic chemicals in groundwater
- Describe whether there could be transformations to daughter products of potential concern (*e.g.*, chlorinated solvents)
- Describe the migration characteristics of the dissolved plume, and whether the plume is expanding, stable or shrinking,
- Describe possible evidence for natural attenuation and bioattenuation in both saturated and unsaturated zones

#### Geology/Hydrogeology

- Describe the physical properties of soil in the unsaturated zone and shallow saturated zone (grain size, moisture content, porosity, density, permeability)
- Describe the natural organic carbon (or organic matter) content in soil
- Describe the soil lithology (*i.e.*, type of soil) with particular attenuation to soil layering
- Describe the bedrock with particular attenuation to fracture occurrence and orientation, if bedrock is present
- Describe the depth to groundwater and fluctuations in the water table (*e.g.,* seasonal, tidal, long-term due to pumping)
- Describe the hydrostratigraphic units and shallow groundwater flow system, and perched water table, if present
- Describe hydrogeological parameters (*e.g.,* hydraulic conductivity, hydraulic gradient)
- Describe foundation subsoils



## Utilities

- □ Identify the location of subsurface utilities; indicate the type of utility, the plan location, depth, and backfill properties, as available
- □ Identify the location of any utilities that intersect the vapour contamination zone and directly connect to buildings

## **Site Characteristics and Anthropogenic Features**

- Describe the surface cover in the area of the vapour contamination source(s) and nearby buildings
- □ Estimate the vertical and lateral distances from the vapour contamination source(s) to nearby buildings. Estimate distances for soil, groundwater (dissolved) and NAPL contamination sources.
- Describe potential future changes to land use and implications for surface cover

#### **Buildings**

- □ Identify location of existing buildings
- □ Identify potential future buildings
- Describe the occupancy and use of the buildings (residential, institutional, recreational, commercial, industrial)
- □ Approximate age of building
- Describe characteristics of the building
  - Size of building
  - Number of storeys
  - Height of storeys
  - Foundation type (*e.g.*, basement, crawlspace, slab-at-grade); if combination of foundations, indicate percentage for each type
  - Depth below grade to base of foundation
  - Foundation construction for both floor and subsurface walls (*e.g.*, poured concrete, concrete block, brick, wood)
  - General condition of foundation (cracks, openings)
  - Building construction (*e.g.*, wood frame, concrete, brick)
  - Elevator shafts
  - Moisture vapour barrier below building
  - Sumps
  - Attached garage (*i.e.*, single family residential)
  - Below building parking (*i.e.*, apartment, commercial building)
  - Chemical use and storage.





- Describe the HVAC system in the building including:
  - Type of heating system (natural gas, oil, radiant, steam, electrical)
  - Type of air conditioning system
  - Location of heating and air conditioning units
  - For commercial buildings, air intake and exhaust units
  - For residential buildings with forced air furnace systems, return air ducting, does furnace have source of combustion air
  - Describe sub-slab ventilation systems or moisture barriers present on existing buildings, or identify building- and fire-code requirements for sub-slab ventilation systems (*e.g.*, for methane) or moisture barriers below foundations.



**APPENDIX B** 

MODELING STUDY OF SOIL VAPOUR SAMPLING



# **Scope and Purpose**

The VapourT numerical computer model was used to evaluate the chemical concentrations in soil vapour that would be predicted during sampling from a soil vapour probe for different probe construction and site condition scenarios. The modeling scenarios were designed to evaluate the effect of varying probe depths, sampling flow rates, proximity of the probe to the contaminant source zone, and probe construction and surface sealing methods (*i.e.*, annular leakage and surface seal).

The purpose of the modeling study is to help improve soil vapour probe design and sampling methodology through an understanding of probe construction and site conditions on soil vapour concentrations. The rationale for this study is that there remain questions on appropriate protocols for soil vapour sampling, including the purge volumes, effect of annular leakage and representativeness of shallow soil vapour data.

# **Model Description**

The VapourT (version 2.16), developed by Dr. Carl Mendoza, is a finite-element model designed to simulate the flow of gas and/or the transport of vapours in the unsaturated zone. The VapourT model is an enhanced version of the model presented by Mendoza and Frind [1990] and Mendoza and McAlary [1990]. Flow and transport may be for situations involving either passive vapour migration or forced air venting (vacuum extraction). It must be noted, however, that equilibrium phase partitioning is assumed for all transport processes and the soil gas phase is assumed to be incompressible. These assumptions may not be appropriate for some vacuum extraction scenarios. Gas flow may be due to applied pressure gradients, density gradients or the vapourization process. Gaseous transport due to advection, mechanical dispersion, diffusion and sorption is included; aqueous transport due to vertical, steady-state infiltration, mechanical dispersion and diffusion are also included. Transport is limited to a single compound.

The model is formulated using the Galerkin finite-element method. Triangular elements and linear basis functions are used. The simulation domain may be either a two-dimensional vertical cross-section of constant thickness or an axisymmetric cross-section rotated about a vertical axis. The latter description in axisymmetric coordinates is used in the following model scenarios.

# **Model Assumptions, Inputs and Scenarios**

The VapourT model is used to predict two-dimensional transport of benzene vapours within the vadose zone. Benzene is selected as a surrogate chemical since its behaviour, excluding aerobic biodegradation, is representative of other hydrocarbons (*e.g.*, BTEX) and common chlorinated solvents such as trichloroethene. Biodegradation was not simulated since the purpose of the study was to model the soil vapour sampling process.

The modeling assumes a uniform, homogenous soil except otherwise specified (see scenarios described below). The soil properties are summarized in Table 1.





Parameter	Value				
Soil total porosity	0.35				
Water-filled porosity	0.10				
Fraction organic carbon	0.005				
Bulk density	1.65 g/cm <sup>3</sup>				
Soil-air permeability	$1.0 \times 10^{-12} \text{ m}^2$				
Dispersivities (x and z)	0.50 m				
Free-air diffusion coefficient benzene	8.0 x 10 <sup>-6</sup> m <sup>2</sup> /s				
Free-water diffusion coefficient benzene	5.0 x 10 <sup>-11</sup> m <sup>2</sup> /s				
Gram molecular weight of benzene	78.1 g/mol				
System temperature	293.0 K				
System pressure	101.3 x 10 <sup>3</sup> Pa				
Henry's law constant benzene	0.23 (dimensionless)				
Organic carbon partitioning coefficient benzene	91 ml/g				
Soil-air viscosity	1.80 x 10 <sup>-5</sup> Pa*s				
Reference fresh air density	1.20 kg/m <sup>3</sup>				
System molar concentration (P/RT)	41.58 mol/m <sup>3</sup>				
Fluid compressibility	0.0 Pa <sup>-1</sup>				
Gas viscosity of pure organic carbon	9.00 x10 <sup>-6</sup> Pa*s				
Gram molecular weight of soil-air	28.8 g/mol				
Effective properties:					
Gaseous diffusion coefficient	2.57x10 <sup>-6</sup> m <sup>2</sup> /s				
Aqueous diffusion coefficient	1.89 x10 <sup>-12</sup>				
Water/soil retardation	1.739 / 13.06				
Total retardation	15.80				

## Table 1. Soil Properties for Modeling

# **Model Scenarios**

The modeling scenarios assume steady state vapour concentrations at the contamination source and two different contamination distributions: (i) a laterally continuous vapour contamination source located below the probe (Scenarios 1 to 4) or (ii) a discrete contamination source laterally adjacent to the probe (Scenarios 5-8).

For the baseline scenarios (1, 5, and 7), only diffusive transport is simulated. For the non-baseline scenarios, diffusive and advective transport due to extraction of soil vapour from the probe is simulated. The boundary conditions are a constant concentration at the contamination source, no flow (vertical) boundaries at the left and right edges of the domain, and zero concentration at ground surface excluding scenarios where soil is covered with a plastic barrier, for which no flow or transport is assumed. The water table is assumed impermeable to the gas phase.

The initial conditions for the baseline scenarios are a constant soil vapour concentration at the contamination source and zero concentrations at all other locations within the domain. The initial conditions for the non-baseline scenarios are the steady state concentrations predicted for the baseline scenarios.

Table 2 summarizes the parameters used in each scenario. Each scenario is summarized below.





# Scenario 1 (Baseline for Uniform Source Below Probe)

This scenario is the baseline scenario for the laterally continuous vapour contamination source. The purpose of this scenario is to predict soil vapour concentrations prior to simulated probe installation and sampling for Scenarios 2 to 4.

# Scenario 2 (Regular Probe with Source Below Probe)

This scenario simulates soil vapour sampling of a probe with a uniform contamination source located below the probe. The depth to the contamination source from ground surface is 1.45 m. The simulated probe dimensions, which are constrained by reasonable model grid spacings, are 0.05 m wide by 0.15 m long. Soil gas is extracted from the probe at a rate of 200 ml/min. Two different cases are simulated with respect to the probe depth:

- Probe depth of 1 to 1.15 m, and
- Probe depth of 0.75 to 0.9 m.

# Scenario 3 (Leaking Probe with Source Below Probe)

This scenario is identical to Scenario 2 except that a leaking probe (*i.e.*, caused by a poor annular seal) is simulated by specifying a highly conductive conduit that extends from the probe to ground surface. The soil-air permeability of the conductive zone is 1,000 times the soil-air permeability of the surrounding soil, which is  $1 \times 10^{-12} \text{ m}^2$ . The probe is assumed to have the same soil-air permeability as the leaky conduit. The width of the conductive zone is much larger than possible fracturing of soil or opening around a disturbed probe, but this is countered by a soil-air permeability that is representative of gravel, and not air.

## Scenario 4 (Leaking Probe with Source Below and Surface Seal)

This scenario is identical to Scenario 3 except that an impermeable surface cover (no flow boundary) is placed at ground surface surrounding the probe. The cover has a radius of 0.75 m centered above the sampling probe. The intent is to simulate a plastic barrier that is often now used in British Columbia to reduce possible leakage for shallow probes. While plastic will have a finite permeability, when compared to the soil-air permeability it is very small and thus a no flow boundary can be assumed.

## Scenario 5 (Baseline for Laterally Located Contamination Source)

This scenario is the baseline scenario for the laterally adjacent vapour contamination source. The purpose of this scenario is to predict soil vapour concentrations prior to simulated probe installation and sampling for this scenario. The model setup is identical to Scenario 1 except for the location of the source and domain length of 2.5 m (compared to 2.0 m in Scenario 1).

## Scenario 6 (Laterally Adjacent Source)

This scenario simulates soil vapour sampling for the laterally adjacent vapour contamination source. Aside from the difference in the source location and domain length of 2.5 m, all other assumptions are the same as Scenario 2A.





# Scenario 7 (Baseline for Laterally Located Contamination Source, High Permeability Layer)

This scenario is the baseline scenario for the laterally adjacent vapour contamination source, but with a high permeability layer at the elevation of the probe. The purpose of this scenario is to predict soil vapour concentrations prior to simulated probe installation and sampling for this scenario.

# Scenario 8 (Laterally Adjacent Source, High Permeability Layer)

This scenario simulates soil vapour sampling for the laterally adjacent vapour contamination source with high permeability layer. Aside from the difference in the soil permeability, all other assumptions are the same as Scenario 6.

		Model Inputs				Model Outputs			
Scenario		Probe depth (m)	Pressure (Pa)	Flow rate (L/min)	Conduit (Darcies)	Conductive Zone (Darcies)	Cover	Concentration at one hour sampling (normalized)	Baseline Concentration (normalized)
2	А	1.0	-80	0.2	N/A	N/A	No	0.77	0.76
	В	0.75	-78	0.2	N/A	N/A	No	0.61	0.59
3	А	0.75	-3.7	0.2	1,000	N/A	No	0.42	0.59
	В	0.75	-40	2.0	1,000	N/A	No	0.19	0.59
	С	0.75	-0.1	0.02	1,000	N/A	No	0.56	0.59
4		0.75	-27	0.2	1,000	N/A	Yes	0.50	0.59
6		1.0	-79	0.2	N/A	N/A	No	0.76	0.75
8		1.0	-2.0	0.2	N/A	1000	No	0.78	0.77

## Table 2. Summary of Model Input and Output for Scenarios

## **Model Domain**

Scenarios 1-4 are represented by domain length of 2.0 m and depth of 1.5 m. The grid spacing is uniform in the radial and vertical directions, measuring 1 cm and 5 cm, respectively. Scenarios 5-8 are represented in the same way as Scenarios 1-4 except for a wider domain of 2.5 m.

The probes are positioned on the vertical axis at depths of 1.0-1.15 m for scenarios 2A, 5-8, and at 0.75-0.90 m for Scenarios 2B, 3A, 3B, 3C, and 4. The probe width is assumed to be 5 cm.

Slightly larger radial spacings (2 cm and 5 cm) were also evaluated with little difference observed between the grid spacing selected (1 cm) and larger grid spacings.





# **Model Verification**

Model verification of the pressure at the soil vapour probe predicted by VapourT was compared to that predicted using an analytical model for (i) spherical flow to a point (Garbesi *et al.*, 1996) and ii) 2-D radial flow to a well (Jonhson *et al.*, 1990) for Scenario 2A using the model inputs described above. For the 2-D radial flow model, the analytical solution includes the radius of influence for gas flow which must be assumed and can not be calculated. The solution is somewhat sensitive to the radius of influence.

The results indicate the spherical flow model predicted a pressure of -98 Pa while the radial flow model predicted a pressure of -226 Pa for 1 m radius of influence and -184 Pa for 0.5 m radius of influence. The spherical model compares reasonably well to the VapourT prediction of -80 Pa for Scenario 2A. The reason for the larger difference for the radial flow model is not known.

# **Model Results**

For each modeling scenario, a benzene vapour concentration versus time plot is shown. The model does not provide a volume integrated prediction of the concentrations in the extracted soil gas. For this reason, the soil vapour concentration was obtained at the approximate mid-point of probe. Comparison of the concentrations predicted at nodes within the probe area indicates that this is reasonable approach. For selected scenarios, a cross-section of the normalized concentration and flow vectors are presented.

# Scenario 1 (Baseline Uniform Source)

As expected for a diffusion transport scenario, a linear concentration profile with depth is predicted for Scenario 1. The normalized concentration at the future soil vapour probe location is 0.76 (1.0-1.15 m depth) and 0.59 (0.75-0.9 m probe). The concentration contours are shown in Figure 1.

# Scenario 2 (Regular Probe with Source Below)

The results of this scenario for a 1-1.15 m deep probe indicate a normalized concentration of 0.77 after one hour of sampling (corresponds to 12 L of soil gas removed from the probe), indicating only a slight increase relative to the baseline condition (Table 2).

The results of this scenario for a 0.75 to 0.9 m deep probe indicate a normalized concentration of 0.61 after one hour of sampling, again with only a slight increase relative to the baseline condition (Table 2). At short times, the soil vapour concentrations at the probe may be more influenced by deeper higher vapour concentrations while at longer times there is a slight decrease that may reflect shallower soil vapour that is being drawn to the probe.







## Scenario 1











Figure 2: Concentration at the probe versus sampling time for Scenarios 2A and 2B. Dashed lines are steady state concentrations before sampling of the baseline Scenario 1.







Scenario 2A

Figure 3: Concentration contours normalized to source concentration and velocity vectors after 36 hours sampling time. 12 contours are drawn that represent constant concentrations of 0.001, 0.01, and 0.1 – 1.0 at 0.1 intervals. Velocity reference vector is shown in units of m/s corresponding to the maximum value on the plot. Vectors smaller than 5% of this value are omitted.





#### Scenario 3 (Leaking Probe with Source Below)

The results of this scenario indicate the following (Figure 4 and Table 2):

- The normalized concentrations decrease with time, with the decrease in concentration being proportional to the flow rate (*i.e.*, higher decrease observed for higher flow rate).
- After one hour of sampling, the normalized concentrations were as follows (for comparison purposes the baseline scenario normalized concentration is 0.59):
  - Scenario 3A 0.2 L/min: 0.42;
  - Scenario 3B 2 L/min: 0.19; and
  - Scenario 3C 0.02 L/min: 0.57.
- Between 1 hour and 36 hours, the predicted concentrations continue to decrease, but appear to reach a quasi-steady state condition by 36 hours.

The length of time needed to reach quasi-steady state is due to the relatively low sampling flow rate combined with sorptive processes that retard the rate at which changes occur in soil vapour concentrations. At a flow rate of 0.2 L/min, 432 litres of soil gas is removed after 36 hours. For comparison purposes, there is 250 litres of soil gas in a 1  $m^3$  volume of soil.

## Scenario 4 (Leaking Probe with Source Below and Surface Seal)

The results of this scenario indicate the following (Figure 4):

- There is a significant difference between Scenario 3A (no cover) and 4 (cover) in that lower concentrations are predicted for the no cover scenario,
- After one hour of sampling, the normalized concentrations were as follows (for comparison purposes the baseline scenario normalized concentration is 0.59):
  - Scenario 3A (no cover): 0.42; and
  - Scenario 4 (cover): 0.50.
- Between 1 hour and 36 hours, the predicted concentrations continue to decrease, but appear to reach a quasi-steady state condition by 36 hours, where the normalized concentration for the cover scenario is 0.46.





Figure 4: Concentration at the probe versus sampling time for Scenarios 3-4 with leaking conduit/probe. Scenario 2B with shallow probe is shown for comparison. The dashed lines are the steady state concentrations before sampling of the baseline Scenario 1.







Scenario 3A

Figure 5: Concentration contours normalized to source concentration and velocity vectors after 36 hours sampling time. 12 contours are drawn that represent constant concentrations of 0.001, 0.01, and 0.1 – 1.0 at 0.1 intervals. Velocity reference vector is shown in units of m/s corresponding to the maximum value on the plot. Vectors smaller than 5% of this value are omitted.





# Scenario 5 (Baseline for Laterally Located Contamination Source)

The results of this scenario are for a scenario with lateral contamination source and uniform soil. The normalized concentration at the future soil vapour probe location is 0.75 (Figures 6 and 7).

## Scenario 6 (Laterally Adjacent Source)

The results of this scenario indicate only a very slight change in normalized concentration (0.76 versus baseline of 0.75) due to soil vapour sampling (Figure 7). The normalized concentrations and velocity vectors for this scenario are shown in Figure 8.

# Scenario 7 (Baseline for Laterally Located Contamination Source, High Permeability Source)

The results of this scenario are for a scenario with lateral contamination source and high permeability conduit (1000 Darcies) between the contamination sources. The normalized concentration at the future soil vapour probe location is 0.77 (Figures 7 and 9).

# Scenario 8 (Laterally Located Contamination Source, High Permeability Source)

The results of this scenario indicate when a high permeability conduit is modeled there is a slow rise in concentrations over the 36 hour period, for which the change relative to the baseline becomes significant over time (Figure 7). After 36 hours, the normalized concentration is 0.82. The normalized concentrations and velocity vectors for this scenario show that the high permeability layer causes soil gas transport toward the soil gas probe, as shown on Figure 10.





Scenario 5 steady state



Figure 6: Concentration contours normalized to source concentration. 12 contours are drawn that represent constant concentrations of 0.001, 0.01, and 0.1 - 1.0 at 0.1 intervals.







Figure 7: Concentration at the probe versus sampling time for scenarios 6 and 8. The dashed lines are steady state concentrations before sampling of the baseline Scenarios 5 and 7, respectively.







Scenario 6

Figure 8: Concentration contours normalized to source concentration and velocity vectors after 36 hours sampling time for Scenario 6. 12 contours are drawn that represent constant concentrations of 0.001, 0.01, and 0.1 – 1.0 at 0.1 intervals.
Velocity reference vector is shown in units of m/s corresponding to the maximum value on the plot. Vectors smaller than 5% of this value are omitted.






Figure 9: Concentration contours normalized to source concentration for Scenario 7. 12 contours are drawn that represent constant concentrations of 0.001, 0.01, and 0.1 - 1.0 at 0.1 intervals.







#### Scenario 8

Figure 10: Concentration contours normalized to source concentration and velocity vectors after 36 hours sampling time for Scenario 8. 12 contours are drawn that represent constant concentrations of 0.001, 0.01, and 0.1 - 1.0 at 0.1 intervals. Velocity reference vector is shown in units of m/s corresponding to the maximum value on the plot. Vectors smaller than 5% of this value are omitted.





### **Discussion and Conclusions**

There is a negligible change in concentrations for the soil vapour probe without leakage over time for the scenario with a laterally continuous contamination source below the probe (Scenario 2).

For probe with leakage, there is a significant change in concentration (difference of up to 0.51 in normalized concentrations) for the conditions modeled (Scenario 3). For the leakage scenario, the decrease in concentration (downward bias) increases with increasing sampling flow rate.

An impermeable cover of 0.75 m radius at surface results in significantly lower leakage than the comparable case without a cover. A decrease in the leakage would be observed for a larger cover.

If there is a lateral contamination source and uniform soil layer, there is a small change in normalized concentration (0.01) over time, but if there is a high permeability soil layer, there is a larger increase in the normalized concentration (0.05). For this scenario, the concentration changes slowly because the sampling flow rate is slow.

The implications of the modeling for soil vapour sampling are that probes should be sealed, which is particularly important for shallow probes. If there is leakage (which should be avoided to the extent possible through appropriate measures and checked using leak testing), the model results indicate the use of a surface cover and lower sampling flow rate will reduce the effect of leakage. The model results suggest that it is feasible to sample soil vapour probes that are less than a metre deep. It also appears that representative soil vapour concentrations may be obtained using driven probes (which may have some annular leakage that can not be sealed) provided that measures are taken to seal around the probe and that low purge rate and low flow sampling procedures are used.

When there is a laterally uniform contamination source and uniform soil properties, the model results suggest that the purge volume should not impact the concentrations measured. If sequential samples are collected, similar concentrations should be obtained. If there are heterogeneous conditions with respect to sources and soil properties, then concentrations may vary with time. The concentration trends observed may reflect the proximity of the contamination source to the probe as shown by the model scenario considered where a slow rise in concentration was observed for a contamination source laterally removed (1 m) from the probe. However, much larger sampling volumes are required to observe such changes compared to conventional sampling where often approximately three purge volumes are removed prior to sample collection.

The model simulations also demonstrate how a numerical model can be used to evaluate different scenarios for sampling probes with different probe installation details and contamination sources. There are additional scenarios that could be evaluated to better understand variability with respect to parameters considered for this study, such as probe depth, sampling flow rate, sample volume, surface cover and leakage. The model also could potentially be of great benefit in evaluating other scenarios such as the influence of changes in site conditions (*e.g.*, water table fluctuations, construction of new slabs or buildings) on transient soil vapour migration.

### Limitations

The model simulations presented for the study were limited to a small number of possible scenarios. Given the resources available for this study, only a few different parameters could be adjusted and evaluated as to their effect on model results. Therefore, the modeling study is representative of only a limited number of possible model outcomes and care should be taken in extrapolating the results to conditions not modeled. There is also significant uncertainty in certain model parameters and assumptions, such the width and soil-air permeability of leaking conduit.





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APPENDIX C

CONSIDERATIONS FOR SHUT-IN VACUUM TESTING



## Purpose

Shut-in vacuum testing is performed to demonstrate that the soil vapour sampling train (*i.e.*, from the connection to the sample probe to the sample container) is sufficiently air-tight that the leakage of ambient atmospheric air into the sample stream during sample collection is unlikely to result in a significant measurement errors. There are several different sources of errors and resultant potential for sample concentration bias as described below.

### **Sources of Errors**

Significant sample train leakage may result in the following errors:

- Error in the vacuum measurements obtained during purging at a constant flow rate. Leakage will systematically and positively bias (*i.e.*, higher in terms of the absolute pressure) this measurement. The magnitude of the associated error will be greatest for sample probes screened in low-permeability geologic materials (*e.g.*, clays).
- Errors in the results of field or laboratory analyses (e.g., concentrations of oxygen, organic vapours, etc.). This can result in either a positive or negative concentration bias, depending on the difference between the analyte concentration in the ambient atmosphere and the concentration at the sample probe. For example, assuming a subsurface environment where oxygen is depleted and carbon dioxide is elevated, the leakage of atmospheric air into the sample train would cause a positive error in the measured oxygen concentration and a negative error in the measured carbon dioxide concentration.

If ambient atmospheric air does not contain a measureable concentration of any of the target field or laboratory analytes, ambient air leakage will cause a negative concentration bias in the sample due to dilution that is proportional to the ratio between the leakage rate and the sampling rate ( $Q_{leak}/Q_{purge}$ ). If ambient atmospheric air contains a "background" concentration of a target analyte, ambient air leakage can potentially cause a positive concentration bias (*i.e.*, a false-positive) in a soil gas sample. The significance of the concentration bias would depend on the background analyte concentration relative to the indoor air criteria and the likely concentration attenuation factor between the soil gas probe and indoor air (see discussion below).

The simplest case for evaluating the impact of the leakage rate is where fixed gas concentrations are biased through leakage of atmospheric oxygen concentrations. For example, at petroleum hydrocarbon-contaminated sites, the oxygen concentrations within hydrocarbon source zones are often at negligible levels where aerobic biodegradation is occurring. For such scenarios, a leakage ratio of 0.01 is sufficiently protective since such leakage will only result in a negligible upward bias in measured oxygen concentrations. In a fully oxygen deficient subsurface environment, a leakage ratio of 0.01 would result in a measured oxygen concentration of 0.2% (assuming approximate atmospheric oxygen concentrations).

A more complex scenario that could result in a false positive bias is where soil vapour samples are obtained within an indoor environment with highly elevated background concentrations. In such a setting, leakage during sampling could cause soil vapour sample concentrations to be biased high (*i.e.*, by the "dirty" background air), where in fact the soil vapour is not impacted. Where the background concentration significantly exceeds a risk-based criteria, there is the potential for the upwardly biased soil vapour concentration to exceed a back-calculated soil vapour criteria, or if a forward calculation of predicted indoor air concentration is completed, the predicted air concentration may exceed the risk-based air concentration. While this scenario is relatively uncommon, an acceptable leakage ratio criterion is developed below to account for possible upward bias in soil vapour through leakage with the goal of setting the leakage ratio sufficiently low to avoid an apparent exceedance of an indoor air criteria.



#### APPENDIX C CONSIDERATIONS FOR SHUT-IN VACUUM TESTING

There is only limited data with which to establish such a criterion. In the case of residential indoor air, background benzene concentrations can exceed risk-based criteria (based on a target incremental lifetime cancer risk of  $1 \times 10^{-6}$ <sup>1</sup>) by up to approximately 100 times (Dawson and McAlary, 2009). In industrial/commercial settings, significantly higher background concentrations of specific target compounds may be present in indoor air, with a corresponding increase in the potential for a false positive measurement (*e.g.,* elevated perchloroethylene concentrations in dry cleaning facility where this chemical is actively used).

Accounting for both dilution of the leakage flow and subsurface attenuation, the necessary condition for avoiding a false-positive exceedence of an indoor air criterion is given by,

$$C_{background} \times \frac{Q_{leak}}{Q_{purge}} \times \alpha < C_{criteria}$$

which may be re-written as,

$$\frac{Q_{leak}}{Q_{purge}} < \frac{C_{criteria}}{\alpha \times C_{background}}$$

where  $Q_{leak}/Q_{purge}$  is the leakage ratio,  $C_{criteria}$  is the indoor air criteria,  $C_{background}$  is the background concentration of the target analyte in indoor air, and  $\alpha$  is the vapour attenuation factor reflecting the decrease in soil vapour concentration occurring during migration from the sample probe depth into indoor air.

A highly conservative vapour attenuation factor accounting for the decrease in the soil vapour concentration occurring during transport from the subsurface to indoor air is 10<sup>-1</sup> although much lower attenuation factors are not uncommon. For an indoor air exposure scenario with a moderately elevated indoor benzene concentration (which would not be uncommon with indoor storage of a fuel container):

- Benzene risk-based indoor air criteria (target incremental cancer risk of 1x10<sup>-6</sup>) = 0.3 ug/m<sup>3</sup>
- Background indoor air concentration =  $30 \mu g/m^3$
- Vapour attenuation factor = 0.1

the corresponding acceptable leakage ratio would be  $Q_{leak}/Q_{purge} < 0.1$  (*i.e.*, 10% of the purged air would actually be indoor air rather than soil vapour). While there may be instances with a higher indoor air concentration and thus a lower acceptable leakage rate (for the same risk-based air concentration and attenuation factor), in most cases the acceptable leakage ratio would be greater than 0.1.

For this reason, in most instances, constraining  $Q_{leak}/Q_{purge} < 0.01$ , which is an easily achievable target leakage ratio, will be sufficient to avoid measurement errors, including false-positive exceedences of applicable indoor air criteria. Based on a leakage ratio of <0.01, at a typical purging rate of 200 millilitres per minute (mL/min), the acceptable sample train leakage rate would be <2 mL/min.

<sup>&</sup>lt;sup>1</sup> Under the British Columbia regulatory regime as reflected by the Schedule 11 Vapour Standards, the potential difference between typical background concentrations and Schdule 11 Vapour Standards, for instances where background is less than the Vapour Standard, would be less in magnitude since the Vapour Standards are based on a target incremental lifetime cancer risk of 10<sup>5</sup> and hazard quotient of 1.0



#### APPENDIX C CONSIDERATIONS FOR SHUT-IN VACUUM TESTING

## **Determining Leakage Rates**

Sample train leakage rate may be determined through a shut-in vacuum test completed at the start of every sampling event. This test may be completed using the following protocol:

- Close the valve on the sample train located closest to the sample probe and apply a vacuum to the sample train. The applied vacuum should be comparable to or greater than the vacuum generated during sampling. In highly impermeable materials such as clays, vacuums as high as 100 inches H<sub>2</sub>O are possible.
- 2) Close the valve on the sample train located furthest from the sample probe to close the sample train and shut-in the applied vacuum.
- 3) Monitor the change in the applied vacuum in the sample train over at least five minutes. Calculate the leakage rate using,

$$n_2 - n_1 = \frac{P_2 V_{train}}{RT} - \frac{P_1 V_{train}}{RT}$$
$$\Delta n = \frac{V_{train}}{RT} (P_2 - P_1)$$
$$\Delta n = \frac{V_{train}}{RT} (P_2 - P_1)$$

where  $n_1$  and  $n_2$  are the initial and final molar masses of air in the sample train (moles),  $P_1$  and  $P_2$  are the initial and final absolute pressures observed during shut-in testing (atm),  $V_{train}$  is the sample train internal volume (L), R is the ideal gas constant (0.082 L atm M<sup>-1</sup> K<sup>-1</sup>), T is temperature (K). Absolute pressures can be determined using,

$$P_{absolute} = P_{barometric} - P_{gauge}$$
$$P_{absolute} = (406 - VH_{gauge})/406$$

where  $P_{absolute}$  is the absolute pressure (atm) and  $VH_{gauge}$  is the observed vacuum head (inches H<sub>2</sub>O).

The difference in the molar mass of air (*i.e.*, the leakage into the sample train during the shut-in test) can be converted to an equivalent volume of air at standard conditions using,

$$\Delta V = \frac{\Delta n R T}{P_{barometric}}$$

and the leakage rate is then given by,

$$Q_{leak} = \frac{\Delta V}{\Delta t}$$

where  $\Delta t$  is the duration of the shut-in test. By substitution, the leakage ratio may be determined using:

$$Q_{leak}/Q_{purge} = \frac{V_{train}}{406 \times Q_{purge} \times P_{barometric} \times \Delta t} (VH_1 - VH_2) < 0.01$$

For example, for a sample train with an internal volume of 25 millilitres, a sample purge rate of 200 mL/minutes, a shut-in test where the initial gauge vacuum of 100 inches H<sub>2</sub>O decreased to 95 inches H<sub>2</sub>O over five minutes, the corresponding leakage ratio is 0.0003 ( $Q_{leak}$ =0.06 mL/min), indicating that the small amount of sample train leakage occurring during the shut-in test is acceptable.





### References

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### APPENDIX D

# MGD-2002 HELIUM DETECTOR METHANE INTERFERENCE TESTING



# **INTRODUCTION**

To test the integrity of the soil vapour probe surface seal and assess if there is introduction of atmospheric air into the soil vapour probe, leak testing is often conducted. One common procedure for completing a soil vapour probe leak test involves enclosing the probe in a shroud filled with a tracer gas (e.g., helium). The concentration of helium is measured in the shroud and in a soil vapour sample collected in a Tedlar bag. The concentrations of helium infer the percentage of atmospheric air introduced into the soil vapour sample. In general, a helium concentration in soil gas that is less than 1% to 2% of the helium concentration within the shroud is considered acceptable.

Although laboratory analysis of helium concentration is an option, a more common approach is to measure the helium concentration in the field using a hand-held leak detector containing a thermal conductivity sensor (e.g., Radiodetection Dieletric Technologies MGD-2002 Multi-Gas leak detector, Figure D1) with a typical sensitivity range of 25 parts per million by volume (ppmv) to 100% v/v helium. The sensor is not specific to helium, but takes advantage of the high thermal conductivity of helium in comparison to most other gases. The thermal conductivity of hydrogen gas is comparable to that of helium; however, hydrogen concentrations high enough to interfere with helium measurements are unlikely to occur in soil gas.

Thermal conductivity sensors are calibrated relative to clean dry air. Any gases (including water vapour) with a different thermal conductivity from air can potentially bias helium measurement. The MGD-2002 includes separate pre-filters to removal water vapour and chlorofluorocarbon gases; however, some common soil gas constituents cannot be readily removed using this approach, with varying effects on helium measurement. Nitrogen and oxygen have the same thermal conductivity as air and will not interfere with helium measurement. Carbon dioxide and many light hydrocarbon gases (*e.g.*, propane, butane, ethane) have a lower thermal conductivity than air and tend to negatively bias helium measurements if present at sufficiently high concentrations. In contrast, the thermal conductivity of methane is higher than that of air and this gas will tend positively bias helium measurement. The following provides data characterizing the magnitude of the potential positive bias.



Figure D1: The Radiotection Dieletric Technologies MGD-2002 Multi-Gas leak detector (MGD-2002). Source: http://www.radiodetection.com/products\_det.asp?sec\_id=2859&art\_id=5642





### **METHODOLOGY**

Methane gas standards (100 ppm, 1000 ppm, 10,000 ppm, and 15% methane) were prepared in separate I Litre Tedlar® bags by speciality gas supply company. Each standard was analyzed with the MGD-2002 to determine the apparent helium concentration. A minimum of four replicate measurements were made for each methane standard.

### RESULTS

The average apparent helium concentrations measured by the MGD-2002 are shown in Figure D2. In general, the apparent helium concentration reported by the MGD-2002 increases with increasing methane concentration. At 15% methane, the MGD-2002 measured about 4% apparent helium. The MGD-2002 appears to be sensitive to concentrations of methane as low as 100 ppm (apparent He measurement of 3,675 ppm).





If the range of helium concentrations beneath the shroud ranges from 20% to 50% and a helium concentration of 1% of the helium concentration within the shroud is considered acceptable (Health Canada, 2009), the acceptable helium concentration in a soil vapour sample ranges from 0.02% (200 ppm) to 0.5% (5,000 ppm). Given that a low concentration of methane (100 ppm) can be interpreted by the MGD-2002 as helium (3,675 ppm), even low concentrations of methane in the soil vapour have the potential to falsely indicate a soil vapour probe is leaking. Higher concentrations of methane (*e.g.*, 15%) in the soil vapour would falsely indicate (4% apparent helium) that the soil vapour probe is leaking high volumes of atmospheric air.





# CONCLUSIONS

The thermal conductivity leak detectors such as the MGD-2002 are often used to measure helium concentrations as part of soil vapour leak tests. However, the presence of methane in the soil vapour at a site has the potential to falsely indicate that a soil vapour probe is leaking. In the event that a sample location fails helium tracer testing, a reasonable first step is to attempt to identify any potential cause of a leak (e.g., loose connections) in the field prior to sample collection. The collection of a screening sample prior to helium tracer testing for field analysis of both combustible gas concentration and apparent helium concentration may be used to indicate the potential for such a false positive indication of a leak. If a leak cannot be identified or the absence of a helium interference cannot be confirmed, the soil vapour sample may still be collected but helium should be included in the list of laboratory analytes to confirm the occurrence of a leak.

### REFERENCES

British Columbia Science Advisory Board (BC SAB), 2006. *Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion into Buildings, Final Draft Report*, February 2006.

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APPENDIX E

# SELECTED LABORATORY ANALYTICAL METHODS



### SELECTED LABORATORY ANALYTICAL METHODS

Method No.	Type of Compounds	Collection Device	Method	Stability	Detection Limit <sup>2</sup>	Reference
TO-1	VOC	Tenax® solid sorbent	GC/MS or GC/FID		0.02 - 200 ug/m <sup>3</sup> (0.01-100 ppbv)	USEPA 1999 <sup>6</sup>
TO-2	VOC	Molecular sieve sorbent	GC/MS		0.2 - 400 ug/m <sup>3</sup> (0.1-200 ppbv)	USEPA 1999
TO-3	VOC	Canister, Tedlar Bag (Cryotrap)	GC/FID		0.2 - 400 ug/m <sup>3</sup> (0.1-200 ppbv)	USEPA 1999
TO-9A, 10A	SVOC	Polyurethane foam (PUF)	GC/MS		1 - 20 ug/m <sup>3 5</sup> (0.4-2.5 ppbv)	USEPA 1999
TO-12	NMOC	Canister or on-line	FID		200 - 400,000 ug/m <sup>3</sup> (100-200,000 ppbvC)	USEPA 1999
TO-13A <sup>3</sup>	РАН	XAD-2 Resin + Polyurethane foam (PUF)	GC/MS		0.5-500 ug/m <sup>3</sup> (0.6 - 600 ppbv)	USEPA 1999
TO-14A	VOC (nonpolar)	Specially-treated canister	GC/MS		0.4 - 20 ug/m <sup>3</sup> (0.2-2.5 ppbv)	USEPA 1999
TO-15	VOC (polar/nonpolar)	Specially-treated canister	GC/MS	30 days	0.4 - 20 ug/m <sup>3</sup> (0.2-2.5 ppbv)	USEPA 1999
TO-17	VOC	Single/multi-bed adsorbent	GC/MS, FID	30 days	0.4 - 20 ug/m <sup>3</sup> (0.2-2.5 ppbv)	USEPA 1999
Modified OSHA 7	VOC	sorbent, solvent extraction	GC/MS, FID	14 days	1 - 20 ug/m <sup>3 5</sup> (0.4-2.5 ppbv)	OSHA 2000
Modified NIOSH 1550	Hydrocarbon fractions	sorbent, solvent extraction	GC/FID	30 days⁴	100 - 400 ug/m <sup>3 5</sup>	NIOSH 1984
Method 3C	$N_2$ , $O_2$ , $CO_2$ , and $CH_4$	Canister	GC/TCD		20,000 - 150,000 ug/m <sup>3</sup> (10,000 ppbv)	USEPA 2002a
Method 16	H <sub>2</sub> S	Tedlar Bag, Canister, Glass vials	GC/FPD		100 - 700 ug/m <sup>3</sup> (50 ppbv)	USEPA 2002a
VHv BC Laboratory Method	VH (C6-13)	Canister, Sorbent Tube	GC/MS or FID			BC Laboratory Manual (2009)





Method No.	Type of Compounds	Collection Device	Method	Stability	Detection Limit <sup>2</sup>	Reference
Modified 8021B	VOC	Tedlar Bag, Canister, Glass vials	GC/PID		4.0 - 60.0 ug/m <sup>3</sup> (0.3 ppbv to 30 ppbv)	USEPA 1996
Modified 8260B	VOC	Tedlar Bag, Canister, Glass vials	GC/MS		10.0 - 50.0 ug/m <sup>3</sup> (0.6 ppbv to 25 ppbv)	USEPA 1996
D1945- 03(2010)	natural gases and mixtures	Tedlar Bag, Canister, Glass vials	GC/TCD		800 - 29,000 ug/m <sup>3</sup> (10,000 ppbv)	ASTM 2010
D1946- 90(2006)	$H_2, O_2, CO_2, CO, CH_4, C2H6, and C_2H_4$	Tedlar Bag, Canister, Glass vials	GC/TCD		800 - 18,000 ug/m <sup>3</sup> (10,000 ppbv)	ASTM 2006

Notes:

Adapted from API (2005).

<sup>1</sup>This is not an exhaustive list. Some methods may be more applicable in certain instances. Other proprietary or unpublished methods may also apply.

<sup>2</sup>Detection limits are compound specific and can depend upon the sample collection and the nature of the sample. Detection limits shown are for the range of compounds reported by the analytical methods.

<sup>3</sup>To achieve high sensitivity, the indicated methods utilize a trapping-type sampling method and relation of results to air-borne concentrations may not be possible.

<sup>4</sup>Taken from NIOSH 1500 "Hydrocarbons, BP 36°-216 °C" and NIOSH 1501 "Hydrocarbons, Aromatic".

<sup>5</sup>Based on a sample volume of 50L. Larger volumes can be collected to improve sensitivity.

<sup>6</sup>TO-methods posted 1999 at <u>http://www.epa.gov/ttnamti1/airtox.html</u>, some methods older than 1999.

GC/MS = Gas chromatography/mass spectrometry

GC/FID = Gas chromatography/flame ionization detector

GC/FPD = Gas chromatography/flame photometric detector

GC/TCD = Gas chromatography/thermal conductivity detector

VOC = Volatile organic compounds

PAH = Polycyclic aromatic hydrocarbons

NMOC = Non-methane organic compounds

SVOC = Semi-volatile organic compounds

Hydrocarbon Fractions include TVOC C6-10, TVOC C10-19, CCME CWS-PHC fractions for F1 and F2



# APPENDIX F

# OVERVIEW OF ANALYTICAL APPROACHES FOR HYDROCARBON FRACTIONS FOR SOIL VAPOUR AND INDOOR AIR



# Introduction

Consideration of total petroleum hydrocarbons (TPH) and hydrocarbon fractions are part of many jurisdictions' regulatory frameworks for soil and groundwater at sites impacted by petroleum releases, but few jurisdictions have well-defined approaches for soil vapour and indoor air. There are a number of challenges for developing regulatory frameworks to address petroleum hydrocarbons. Of significant importance is that TPH comprises a broad range of hydrocarbon compounds with varying toxicological, physical-chemical and fate and transport properties. While petroleum products are comprised of several hundred compounds, there is only toxicological data for a relatively small subset of compounds. There are also a range of possible analytical methods that have been developed to quantify TPH and sub-fractions based on aliphatic and aromatic components. Given the importance of vapour intrusion, a closer examination of methodology for TPH focusing on soil vapour and indoor air is warranted.

# **Background and Review of Different Regulatory Approaches**

The genesis for TPH approaches were conservative non-risk based regulatory criteria for TPH in place in early 1990. Recognizing that an approach based on a small sub-set of compounds (*e.g.*, BTEX) was not sufficiently broad and that a single non-risk-based TPH was counterproductive, new approaches based on hydrocarbon fractions were developed. The initial work in this area considered a whole mixture approach, but limited toxicity data on whole products and changes in composition and toxicological properties due to weathering made this approach impractical. The approach that emerged for petroleum mixtures, most notably based on efforts of the Massachusetts Department of Environmental Protection (MADEP) and the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), was a fraction-based approach that defines petroleum hydrocarbon fractions on the basis of expected transport in the environment and analytical methods that may be applied to quantify individual components or fractions. Within this framework, the health risk associated with exposure to different fractions is quantified as follows:

- 1) Surrogate Method: The toxicological properties for a surrogate aromatic or aliphatic hydrocarbon or mixture is taken to represent the entire mass of the fraction;
- 2) Component Method: The toxicity values for individual compounds that represent a large portion of the fraction are used together with estimate of exposure under an assumption of dose- or response-addition.

For approaches developed by TPHCWG and MADEP, a hybrid approach is used in that depending on the fraction or range, either components or surrogates are used.

While the framework is similar, MADEP and TPHCWG developed slightly different approaches. MADEP divides petroleum hydrocarbon into two main fractions based on volatility and analytical considerations, consisting of volatile petroleum hydrocarbon (VPH) and extractable petroleum hydrocarbon (EPH), with some overlap in fractions. The MADEP fractions and components are summarized in Table 1. The division between fractions is based on the retention time of marker compounds.

VF	ч	EPH		
Aromatic	Aliphatic	Aromatic	Aliphatic	
BTEX	C5-C8	C11-C22	C9-C18	
C9-C10	C9-C12	PAHs	C19-C36	

#### Table 1. MADEP Fractions



The TPHCWG developed an approach with a larger number of fractions (12) defined on equivalent carbon number and reasonably similar fate and transport properties for compounds within each fraction.

#### **Table 2. TPHCWG Fractions**

Aromatics	Aliphatics
EC5-EC6	Benzene, Toluene
>EC6-EC8	>EC8-EC10
>EC8-EC10	>EC10-EC12
>EC10-EC12	>EC12-EC16
>EC12-EC16	>EC16-EC21
>EC16-EC35	>EC21-EC35

Note: EC in this table refers to equivalent carbon ranges.

Other jurisdictions implementing a fraction-based TPH approach have either adopted the MADEP or TPHCWG approaches, some with slight modifications.

In Canada, the Canadian Council Ministers of the Environment (CCME) adopted the TPHCWG approach with modifications in the development of Canada Wide Standards (CWS) for Petroleum Hydrocarbon Compounds (CCME, 2001, updated 2008). The CWS framework consists of four fractions, F1 (C6-C10), F2 (C10-C16), F3 (C16-C34) and F4 (C34-C50), and aliphatic and aromatic sub-fractions for each fraction above. The sub-fractions consist of aliphatics between C6-C8, C>8-C10, C>10-C12, C>12-C16, C>16-C21, C>21-C34 and C>34, while aromatic fractions are C>7-C8, C>8-C10, C>10-C12, C>12-C16, C>16-C21, C>21-C34 and C>34. A notable difference relative to other jurisdictions is that the CCME CWS include consideration of ecological risk in their derivation.

California DTSC (2009) modified the MADEP approach and designated the following six fractions, as follows: C5-C8 aliphatics, C9-C18 aliphatics, C6-C8 aromatics, C9-C16 aromatics, C19+ aliphatics and C17+ aromatics. The DTSC also revised some of the toxicity factors for surrogates.

USEPA (2009) conducted a review of toxicity values for complex aromatic and aliphatic mixtures for six fractions based on slight modification of MADEP approach. The sub-fractions considered were aliphatics consisting of C5-C8 (EC5-EC8), C9-C18 (EC>9-EC16), C19-C32 (EC>16-EC35) and aromatics consisting of C6-C8 (EC6-EC<9), C9-C16 (EC9-EC<22) and C17-C32 (EC22-EC35). Depending on data availability, both chronic and subchronic toxicity factors were recommended for each fraction. For the aliphatic C5-C8 fraction, toxicity data for either commercial or n-hexane is used to represent the fraction depending on the proportion of n-hexane present in the fraction.

In British Columbia, a single regulatory hydrocarbon fraction VHv (C6-13) has been defined, which includes the sum of those compounds that elute on a 100% polydimethylsiloxane gas chromatographic column between the retention times for n-hexane (nC6) and n-tridecane (nC13) (BC Laboratory Manual, 2009). VHv6-13 encompasses a vapour pressure range of approximately 0.05 - 150 Torr (at  $25^{\circ}$ C), or a boiling point range of approximately  $69^{\circ}$ C to  $234^{\circ}$ C. Volatile Petroleum Hydrocarbons (VPHv), a calculated parameter, is equal to VHv minus the sum of: benzene, ethylbenzene, n-decane, n-hexane, toluene and xylenes. Ambient air or soil gas samples for VHv6-13 are collected using stainless steel canisters, or with appropriate sorbent tubes. VHv(C6-13) is analyzed by GC/FID or by GC/MS in scan mode, and is quantified in two ranges; the nC6 – nC10 range is quantitated against toluene, and the nC10 – nC13 range is quantitated against n-dodecane (nC12), using 3 point (minimum) linear calibrations.



# **Rationale for Petroleum Hydrocarbon Fraction Approach**

The rationale for petroleum hydrocarbon fraction approach for soil vapour is that there are numerous compounds present in soil vapour at petroleum release sites that go beyond the small number of compounds typically analyzed (*e.g.*, BTEX, naphthalene). Given the large number (hundreds) of compounds in petroleum fuels, a component approach is not practical, and therefore an approach based on hydrocarbon fractions is warranted. A single hydrocarbon parameter approach (*e.g.*, VPH or TPH) can be useful for site screening purposes, but may lack specificity needed to accurately quantify risk. It is also important to recognize that VPHv or TPH results potentially include non-petroleum compounds. This is a challenging issue because it is not straightforward to remove non-petroleum compounds. It is noted that in British Columbia, the Ministry of Environment now allows the subtraction of siloxane concentrations from the VHv results.

A recent development in analytical testing capabilities is the characterization of PIANO compounds (paraffins, iso-paraffins, aromatics, naphthenes and olefins). The results of PIANO analysis for 163 compounds (TestAmerica) for soil vapour samples obtained near a gasoline NAPL and coal-tar NAPL source are presented in Table 1 along with Vapour Standards<sup>1</sup> for Residential Land Use in the British Columbia Contaminated Sites Regulation. As shown, there are only standards for a handful of compounds detected (most of the BC Soil Vapour Standards are based on available toxicity factors in the USEPA IRIS database).

For the soil vapour sample near the gasoline NAPL, the proportion of BTEX relative to the sum of all detected VOCs in the sample was 2%. The most prevalent hydrocarbon compound was 224-trimethylpentane at 17%. The ratio of the measured soil vapour concentration to the Vapour Standards ranged from 240 (124-trimethylbenzene) to 0.045 (n-decane).

For the soil vapour sample near the coal tar NAPL, the proportion of BTEX relative to sum of all detected VOCS in the sample was 63%. The most prevalent hydrocarbon compound was benzene at 36%. The ratio of the measured soil vapour concentration to the Vapour Standard ranged from 55,000 (benzene) to 0.068 (n-decane).

The gasoline results suggest the need for a hydrocarbon fraction approach to characterize the significant proportion of hydrocarbon for which there is no Vapour Standard, although it is noted that the toxicity of many compounds without Vapour Standards is likely low.

### **Analytical Methods**

For hydrocarbon fractions, there are few prescriptive published analytical protocols (*e.g.*, Massachusetts Air Phase Method, described below) and significant differences that will result depending on the methodology that is followed. While GC/MS analysis is typically conducted, which is a requirement when canisters (USEPA TO-15) or thermal tubes (USEPA TO-17) are used to obtain samples, GC/FID analysis is performed by some laboratories when solvent extracted sorption tubes are used (although typically GC/MS analysis is now conducted). When GC/MS is used for analysis of hydrocarbon fractions, differences in the way each fraction is defined (*i.e.*, the marker compound or retention time used to bracket the fraction), the number of and specific ions selected for quantification and calibration, and the way in which non-petroleum hydrocarbons are addressed (*e.g.*, subtracted from the total concentrations) will influence the analytical results to varying degrees. The lack of defined methods and standardization means that results may not be comparable between laboratories and also potentially non representative when non-petroleum hydrocarbons are included in the analysis.



<sup>&</sup>lt;sup>1</sup> The BC Vapour Standards apply to air in the breathing zone



#### **CCME Hydrocarbon Fractions**

For soil vapour and air, the CCME fractions of interest are F1 (C6-C10) and F2 (C10-C16) fractions. The aliphatic fractions of interest are C6-C8, C>8-C10, C>10-C12 and C>12-C16<sup>2</sup>, while the aromatic fractions of interest are C>7-C8<sup>3</sup>, C>8-C10, C>10-C12 and C>12-C16. Unfortunately, CCME (2008) does not prescribe methods for how the analysis should be performed for soil vapour or air since it is a soil method involving fractionation and GC/FID analysis. As a result, individual laboratories have developed their own protocols following the soil method as a guide. The development of different methods based on CCME approach is described below.

#### Thermal Tube (TO-17) and Canister (TO-15) Analysis (GC/MS)

CCME (2008) for soil analysis defines F1 as the total area summation between the apex of the hexane and decane peaks, and F2 as between the apex of the decane and hexadecane peaks. The BTEX and naphthalene peak areas (and other non-target compounds such as siloxane derivatives, nitrogen and sulphur-containing compounds) are removed from the total area summations for each fraction. The F1 is calibrated against the toluene response generally obtained as a full scan GC/MS peak. The F2 is typically calculated against decane response as a full scan GC/MS peak. This is a slight deviation from CCME (2008), which indicates the average of the decane and hexadecane response should be used; however, laboratories find it is difficult to generate and maintain a known vapour concentration of hexadecane. Therefore, the response of decane alone is often used to calibrate for the F2 fraction.

While CCME (2008) defines the method F1 and F2 fractions in soil, no such guidelines exist for sub-fractions. This has led to variable and uncertain definitions. For example, the C6-C8 aliphatic fraction is referenced as either C6-C8 or >C6-C8. The first implies including the n-hexane peak in the area summation. The second implies excluding n-hexane. The n-hexane peak should be included in the analysis considering it has a relatively high toxicity. The methodology for quantifying the aromatic and aliphatic fractions is not well defined, although some laboratories quantify the total hydrocarbon concentration, and subtract the sum of individually quantified aromatics to obtain the aliphatic fraction. Aliphatic sub-fractions are often quantified against the full mass spectra response of n-hexane; aromatics against toluene. Some laboratories will also subtract non-petroleum hydrocarbon compounds such as siloxanes from the total "hydrocarbon" concentration, if requested.

The F1 and F2 methods for air are loosely based on the methodology described above. However, the procedures used are laboratory specific. Greater consistency is required for the definition of these test methods.

#### Massachusetts Air-Phase Hydrocarbon (APH) Method

The Massachusetts (MA) APH Method was designed to measure the gaseous phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons that are collectively quantified in the air and soil gas in the ranges:

- C5 through C8 aliphatics;
- C9 through C12 aliphatics, and
- C9 through C10 aromatics.

The aliphatic and aromatic ranges correspond to a boiling point range between approximately 28°C (isopentane) and 218°C (naphthalene). The APH method also identifies and quantifies the individual concentrations of 10 target analytes, including BTEX, MtBE, 1,3-butadiene and certain naphthalenes. The MA APH Method is relatively prescriptive with respect to quantification and calibration requirements.



<sup>&</sup>lt;sup>2</sup> Some laboratories also quantify C>16-C21, although the vapour-phase concentrations within this carbon range tend to be negligible.

<sup>&</sup>lt;sup>3</sup> This fraction is comprised mostly of toluene, ethylbenzene and xylenes (TEX) and therefore is sometimes not quantified

APPENDIX F Overview of Analytical Approaches for Hydrocarbon Fractions for Soil Vapour and Air

The MA method is based on collection of whole air samples in passivated stainless steel canisters and modification of USEPA Method TO-15. The total concentration is initially calculated through total ion integration for each range and the response factors for calibration compounds. The C5-C8 aliphatics are obtained by subtracting BTEX from the total concentration within this range. The C9-10 aromatic hydrocarbons are based on sum of all peaks in extracted ions 120 and 134. The C9-12 aliphatics are obtained by subtracting C9-10 aromatics (and possibly naphthalene) from the total concentration within this range.

The MA method indicates that at the discretion of the data user, the contribution of non-APH compounds (*e.g.*, chlorinated solvents, siloxanes, terpenes, aldehydes) that elute within the method-defined retention time windows for the aliphatic and aromatic ranges may be excluded from collective range concentration calculations. Specifically, the total ion area counts for these non-APH compounds may be excluded providing the compound is positively identified by GC/MS. However, if the non-APH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count cannot be subtracted from the range. In addition, the MA method indicates that this type of data adjustment may not be feasible in complex sample matrices where there are many co-eluting peaks or complex petroleum patterns.

#### **Emerging Methods**

Although no published method exists, several laboratories in Canada have developed analytical methods to support the CCME aliphatic and aromatic sub-fraction approach. The methodology is similar in concept to the Massachusetts approach but is more rigorous in that a larger number of aromatic compounds are directly quantified (for example, Caro Laboratories quantify 14 aromatics for nC8-nC10, and 23 aromatics for nC10-nC12). The aliphatic fraction, or more correctly stated, the non-aromatic fraction, is obtained by subtracting the sum of the aromatics from the total concentration.

#### **Summary of Possible Options**

A single hydrocarbon fraction approach (*i.e.*, VPHv C6-13) such as that adopted by BC offers advantages in terms of simplicity and cost, but lacks the analytical and toxicological specificity of the CCME sub-fraction approach. The CCME toxicological fractions were adapted from the extensive review conducted by the TPHCWG, but consideration should be given to the updated toxicological fractions published by USEPA (2009). Further research should be conducted to determine whether the C12-14 fraction is relevant for soil vapour intrusion. This could be conducted through review of laboratory test results for different types of contamination (some of this analysis has already been performed, see main text). With respect to analytical methods, the emerging more rigorous methods described above are proposed. Consideration should also be given to methods by which non-hydrocarbon compounds may be subtracted from the analysis, such that the results are more representative of the hydrocarbons of interest.

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#### Table 1. Comparison of Measured Soil Vapour Concentrations to BC CSR Schedule 11 Vapour Standards

Soil Gas Probe Near Small Release Gasoline NAPL			Soil Gas Probe Above MGP Coal Tar NAPL						
	Soil Vapour	Ratio Conc/	Sch. 11 Vapour	Ratio Conc./Sch.		Soil Vapour	Ratio Conc/ Sum	Sch. 11 Vapour	Ratio Conc./Sch.
Chemical	Conc.	Sum Conc	Standard	11 Std.	Chemical	Conc.	Conc	Standard	11 Std.
2.2.4 Trimothylpoptopo	(ug/m <sup>°</sup> )	<u>(%)</u>	(ug/m˘)	(unitless)	(ug/m <sup>°</sup> )	(ug/m <sup>°</sup> )	<u>(%)</u>	(ug/m°)	(unitless)
2.3-Dimethylpentane	87500	10.3			Ethylbenzene	56400	24.3	1000	5.5E+04
Isohexane	73200	8.59			Methylcyclohexane	10400	4.49	3000	3.5E+00
Isopentane	71000	8.33			n-Pentane	7970	3.44		
2,4-Dimethylpentane	56700	6.65			2-Methylbutane	6200	2.68		
3-Methylpentane	40800	4.79			2-Methylpentane	5640	2.43		
Methylcyclopentane	38400	4.50	700		Methylcyclopentane	5160	2.23	400	
Hexane	29000	3.40	700	4.1E+01	Isopropylbenzene (cumene)	4920	2.12	400	1.2E+01
2,3,4-Thinethylpentane	26200	3.31			Total Xylenes	4170	1.95	100	4 2E+01
3-Methylhexane	25400	2.98			3-Methylpentane	3880	1.67	100	4.22101
Isoheptane	23300	2.73			Indane	3240	1.40		
2,3-Dimethylbutane	22000	2.58			o-Xylene	2820	1.22		
Methanol	15700	1.84			2-Ethyltoluene	2700	1.17		
Methylcyclohexane	11700	1.37	3000	3.9E+00	n-Hexane	2430	1.05	700	3.5E+00
Heptane	11100	1.30				2410	1.04	5000	4.8E-01
2,2,3- I rimethylpentane	10400	1.22			2-Methyl-1-butene	2300	0.99	6	3 4 5 + 02
Xylenes total	8780	1.10	100	8 8E+01	Cyclopentane	1780	0.03	0	J.4L+02
m-Xylene & p-Xylene	6870	0.81		0.02.001	2,3-Dimethylpentane	1760	0.76		
2-Methyl-2-pentene	6830	0.80			2-Methylhexane	1560	0.67		
Cyclohexane	6260	0.73			n-Propylbenzene	1520	0.66		
cis-3-Heptene	6030	0.71			m-Xylene & p-Xylene	1350	0.58		
2,2,5-1 rimethylhexane	5850	0.69			2,3-Dimethylbutane	1200	0.52		
2-Methylheptane	5850	0.69			2,4-Dimetnyinexane	1070	0.46		
trans-2-Hexene	4480	0.53			1 2 3-Trimethylbenzene	983	0.40		
cis-3-Hexene	4040	0.47			n-Heptane	943	0.41		
2-Methyl-2-butene	3930	0.46			n-Octane	934	0.40		
cis-3-Methyl-2-pentene	3790	0.44			2-Methylheptane	841	0.36		
1-Methylcyclopentene	3750	0.44			n-Nonane	839	0.36		
Toluene	3700	0.43	5000	7.4E-01	2,4-Dimethylpentane	820	0.35		
Lyciopentane	3560	0.42			2,5-Dimethylnexane	794	0.34		
Butane	3300	0.39			3-Ethylbexane	654	0.28		
2-Methyl-1-pentene	3280	0.38			4-Ethyltoluene	639	0.28		
trans-2-Pentene	2830	0.33			trans-2-Pentene	402	0.17		
cis-2-Hexene	2560	0.30			2,2-Dimethylpentane	369	0.16		
n-Octane	2550	0.30			1-Pentene	316	0.14	0500	
cis/trans-4-Methyl-2-pentene	2470	0.29	1000	2 45.00	n-Decane	169	0.073	2500	6.8E-02
1-Octene	2420	0.26	1000	2.4E+00	cis-2-Pentene	120	0.055		
2.2-Dimethylbutane	2030	0.24			sec-Butylbenzene	87.8	0.038		
o-Xylene	1900	0.22			Ethanol	71.6	0.031		
trans-3-Heptene	1900	0.22			1-Methyl-3-propylbenzene	60.4	0.026		
1-Hexene	1740	0.20			1-Methyl-4-propylbenzene	60.4	0.026		
trans-2-Heptene	1430	0.17	_		2,2,3-Trimethylpentane	40.7	0.018	_	
1,2,4-Trimethylbenzene	1420	0.17	6	2.4E+02	naphthalene	<	N/A	3	
cis-2-Pentene	1320	0.15			Sum Detectable VOC	231677			
1-Methylcvclohexene	939	0.13			Sum BTEX	146080			
1,3,5-Trimethylbenzene	928	0.11	6	1.5E+02	% BTEX/Total VOC	63			
Cyclohexene	768	0.090							
1-Pentene	752	0.088							
4-Methyl-1-pentene	703	0.082							
4-Ethyltoluene	578	0.068							
2-Ethyltoluene	536	0.063							
n-Nonane	441	0.052							
n-Propylbenzene	414	0.049							
Isopropylbenzene (cumene)	270	0.032	400	6.8E-01					
Chloroform	242	0.028							
Isobutane	223	0.026							
3-Methyl-1-butene	206	0.024							
Renzene	102	0.021	15	1 2E+02					
1.4-Diethylbenzene	127	0.021	1.0	1.20702					
Tetrachloroethene	115	0.013							
n-Decane	112	0.013	2500	4.5E-02	1				
Neopentane	92.7	0.011							
Indan	75	0.009							
Chlorobenzene	47.2	0.006							
1-Butene/Isobutene	42.2	0.005	0.4						
i,∠-dichloroethane*	<	N/A	0.4						
naphthalene	<	N/A	3						
1.3-butadiene	~	N/A	2						
MTBE	<	N/A	3000						
Sum Detectable VOC Sum BTEX % BTEX/Total VOC	852427.1 17173.8 2.0								



APPENDIX G

# FIELD INSTRUMENTS AND POSSIBLE INTERFERENCES



### **INTRODUCTION**

Field instruments provide valuable data that can be used to assess analytical data quality and assess subsurface soil vapour conditions. Field detectors commonly used for soil vapour screening include photoionization detectors (PID), combustible gas detectors, multi-gas detectors (for oxygen, carbon dioxide, and methane), and helium detectors (for leak tests). Prior to their use in the field, the limitations associated with a given instrument, including non-specificity to compounds of possible interest and other possible interferences, should be understood.

### **METHODOLOGY**

Field screening of soil vapour probes is typically undertaken prior to the collection of samples for laboratory analysis. The results of the field screening program may be used to direct the sampling program (*e.g.*, selective sampling) or to interpret the analytical results (*e.g.*, biodegradation assessment). Field detectors should generally not be directly connected to soil gas probes when taking measurements, unless it can be demonstrated that sampling flow rate constrictions and/or the vacuum generated by sampling will not affect the response of the field instrument. Field screening samples should generally be collected in Tedlar bags to facilitate readings with field instruments.

Interferences for some specific field instruments commonly used for field screening of soil vapour samples are provided in Table G1. An overview of important factors that should be considered when using field instruments are:

- All instruments have different operating characteristics, which must be understood and matched to project requirements. Refer to the manufacturer for instrument-specific information;
- Photo-ionization detectors (PIDs) and combustible gas detectors measure the response to the total organic vapour concentration rather than the concentration of individual organic compounds. The instrument response can vary depending on the chemicals present. For example, a PID is relatively sensitive to monocyclic aromatic hydrocarbon compounds (e.g., benzene, toluene, xylene) but less sensitive to straight-chain aliphatic hydrocarbon compounds (e.g., pentane, hexane, octane). In samples where only a single organic compound is present, compound-specific response factors may be used to estimate concentration;
- Instruments must be calibrated in accordance with manufacturer's instructions. In some cases, the calibration gas that should be used will depend on the types of gases or vapours at the site. For example, when using a combustible gas detector at a gasoline-contaminated site, instruments providing %LEL readings should be calibrated to hexane; when used at a site where biogenic gases are being generated through degradation of organic matter, instruments should generally be calibrated to methane;
- Instruments that measure specific gases such as methane or carbon dioxide are subject to interferences. An infrared methane sensor will be affected by other hydrocarbon gases with similar infrared spectrum to methane. For example, the Landtec GEM-2000 methane reading is filtered to an absorption frequency of 3.41 micrometers, which is equal to a wavenumber of 2930 cm<sup>-1</sup>. Ethane, propane, n-pentane and isopentane have similar infrared spectra compared to the GEM-2000. While the interference will depend on the instrument, there is the potential for significant upward bias in measured methane concentrations when infrared detectors are used at sites with higher concentrations of alkane hydrocarbons. The absorption frequency for methane is compared to the wavenumber distribution for selected compounds in Figure G1; and





Some combustible gas detectors have a methane elimination mode. It should be noted that not all the methane is eliminated (about 90% for RKI Eagle) and that the response of other hydrocarbons could also be reduced (about 15% for hexane for RKI Eagle).

The most common type of combustible gas detector works on catalytic oxidation mode. Experience gained on projects indicates that when combustible gas concentrations are high (close to or above explosive limits) readings from this type of instrument can be erroneous. It is noted that guidance from United Kingdom CIRIA 665 does not recommend a catalytic oxidation type instrument for methane monitoring. While further evaluation is required, the provisional recommendation is to use this instrument for ppm measurements of vapours (*e.g.*, screening at petroleum sites) and not for methane surveys when concentrations are at explosive levels.

### **CONCLUSIONS AND RECOMMENDATIONS**

Field instruments provide valuable information for site screening; however, prior to their use in the field, the limitations associated with a given instrument, including non-specificity to compounds of possible interest and other possible interferences, should be understood.

### REFERENCES

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#### APPENDIX G Field Instruments and Possible Interferences

Instrument	Gases Detected	Detection Principle	Possible Interferences	Possible Solutions
Landtec GEM2000 Plus (Landfill gas meter)	CO <sub>2</sub> , CH <sub>4</sub> , O <sub>2</sub> , CO, H <sub>2</sub> S	$CO_2$ , $CH_4$ – dual wavelength infrared cell with reference channel $O_2$ , CO, $H_2S$ – internal electrochemical cell	Cell phones and other sources of RF interference can affect the gas sensor readings (especially methane). The presence of hydrocarbon gases (e.g. ethane, propane, butane, etc.) will give artificially high readings of CH <sub>4</sub> . The extent of the bias will depend both on the methane and hydrocarbon concentrations. The presence of carbon disulfide may create high readings of CO <sub>2</sub> due to the similar absorption frequency. The CO sensor is compensated for H <sub>2</sub> ; however, concentrations of H <sub>2</sub> above the compensation limit will give artificially high readings of CO. If the internal H <sub>2</sub> S filter's capacity is exceeded, the CO sensor will give artificially high readings.	Refrain from cell phone use while taking readings. None at this time. None at this time. Note the rough indication of H <sub>2</sub> concentrations (LO, MED or HI) provided by the meter. HI levels of H <sub>2</sub> may require lengthy purge times to ensure subsequent CO readings are accurate. To check if the filter capacity has been exceeded, purge the sample gas from the instrument and after the CO reading is zero, check the CO readings of a calibration gas which contains H <sub>2</sub> S but not CO.
miniRAE 2000	organic vapours	Photo-ionization of compounds with ionization potentials lower than that of the lamp (standard 10.6 eV lamp excludes helium, methane, some single-bond chlorinated hydrocarbons)	Moisture or condensation can increase PID readings. PID detectors are also highly sensitive to flow rate and will result in low bias when flow rate is restricted. PID will detect wide range of organic chemicals but also some inorganics (ammonia, hydrogen sulphide)	Keep sensor dry using water trap filter Never use PID for direct reading from soil gas probe, but instead use Tedlar <sup>TM</sup> bag. Check ionization potential of compounds of interest and confirm correct lamp energy

#### Table G1: Possible field interferences with common field instruments used for soil vapour sample screening







#### **APPENDIX G** Field Instruments and Possible Interferences

Instrument	Gases Detected	Detection Principle	Possible Interferences	Possible Solutions
Gastech Model 1238ME) Combustible gas meter	combustible gases (hydrocarbons)	Increase in electrical resistance when gas oxidizes when in contact with heated platinum filament	If the instrument encounters silicone, silicane, halogenated hydrocarbons, antiknock compounds in gasoline, or high levels of combustible gases, it can affect the sensor's ability to measure combustible gases. The instrument is sensitive to humidity. Oxygen deficient mixtures (<10% O <sub>2</sub> ) may read lower concentrations of combustible gases as there is insufficient oxygen to react with the combustible gases.	Recalibrate instrument if it encounters one of the compounds listed in the previous column. Severe exposure to chlorinated compounds may permanently damage the sensor. Zero the instrument in an atmosphere with a humidity level similar to the atmosphere in which it will be operating.
RKI Eagle	combustible gases, O <sub>2</sub> , CO, H <sub>2</sub> S (standard) Some models include CH <sub>4</sub> and other gases	combustible gases – increase in electrical resistance when gas oxidizes when in contact with catalytic platinum element $O_2$ – electrochemical cell which reacts to the $O_2$ in the atmosphere and produces a proportional voltage change CO, H <sub>2</sub> S – electrochemical cells, which react to the target gas in the atmosphere and produces a proportional current change. CH <sub>4</sub> – infrared sensor	Selected combustible gases (ethane, hexane, isopropanol, isobutane, methyl ethyl ketone, propane, and toluene) are known to respond to the CH <sub>4</sub> sensor.	None reported
MGD-2002	Hydrogen and Helium	He – thermal conductivity	The presence of CH₄ gives artificially high readings of He.	Measure CH <sub>4</sub> concentrations and apparent He concentrations in soil vapour sample prior to He leak testing. See Appendix B for further details.

Note: Inclusion of brand names in this summary table is not an endorsement of the instrument. Brand names are included for illustration purposes.





APPENDIX G Field Instruments and Possible Interferences







APPENDIX H

# CONSIDERATIONS FOR COLD-WEATHER SAMPLING



# Purpose

In British Columbia, soil vapour sampling may occur during cold weather, particularly in northern areas of the Province. There are unique issues associated with cold weather conditions that should be taken into consideration when installing soil vapour probes, collecting and analyzing soil vapour samples, and interpreting soil vapour data.

### **Potential Issues**

Precautions that should be taken when installing probes and collecting and analyzing soil vapour samples during cold weather include:

- Pre-cautions should be taken during installation of soil vapour probe seals in cold weather to avoid cracking due to freezing.
- To avoid the potential for frost heave, permanent vapour probes should be installed to a depth that is below the local frost line (when monitoring is to be conducted in winter). In areas of northern British Columbia, discontinuous permafrost may be present, particularly at high altitudes. Vapour probes should not be installed into permafrost although installing probes in the active layer above the permafrost is possible.
- Electronic field instruments, such as handheld photoionization detectors, are not designed to operate in cold temperatures and should not be exposed to temperatures below freezing (refer to the specific manufacturer's recommended temperature range to ensure that equipment is protected from damage). Field instruments should be kept in a heated space (*e.g.*, a building or vehicle) with field samples analyzed at that location. Sampling pumps used at outdoor sampling locations may be kept warm by storing them in insulated bags (*e.g.*, an insulated lunch bag) with heat packs.
- Condensation can occur when humid soil vapour rapidly cools during sample collection and has the potential to adversely affect sample representativeness. Sample tubing and bags should be closely observed for any signs of condensation (e.g., through use of translucent tubing). To avoid condensation, tubing should be kept as short as possible. Condensation is particularly problematic for sorbent tube sampling. If possible, sorbent tubes and tubing should be kept warm to minimize condensation; however, excessive heating of sorbent tubes should be avoided since their sorption efficiency decreases with increasing temperature.
- Where possible, avoid storing Summa<sup>TM</sup> canisters in conditions where the temperature is substantially lower than the ambient soil gas temperature. As during sampling, there is the potential for condensation to form within the canister that will adversely affect sample representativeness.

When interpreting soil vapour data, the influence of frozen soil and snow cover on the soil vapour transport should be considered. Frozen soil and snow cover reduce soil permeability above the frost line, which may limit the flux of contaminant vapours to atmosphere and/or oxygen recharge to subsurface. Typically, soil below a building will remain unfrozen. The capping effect of frozen ground may result in higher soil vapour concentrations. Frozen ground may behave like fractured bedrock with respect to soil gas advection and a depressurized building may draw soil gas from a larger zone of influence.

### **Recommendations**

Collecting vapour probes during winter conditions is challenging, even if the temperature is only slightly below freezing. Collecting vapour samples from vapour probes located outdoors during extremely cold conditions is not recommended to avoid damage to measurement instruments.



**APPENDIX I** 

DUPLICATE SOIL VAPOUR SAMPLING METHODOLOGY



### **INTRODUCTION**

Duplicate soil vapour samples are collected and analyzed to assess the precision of the analytical method and the variability of the sampling process. Elevated variability between duplicate soil vapour sample concentrations may be an indication of a sampling and/or analytical protocol that could be improved.

Duplicate soil vapour samples are commonly recommended by regulatory agencies but there is no widely accepted methodology for collecting the duplicate samples. A good duplicate soil vapour sample would be collected under conditions as similar as possible to those of the primary sample (i.e. similar flow rates, sample volume, *etc.*). This Appendix describes methods of collecting duplicate soil vapour samples, summarizes the available guidance on methodology in existing guidance documents, and discusses some of the published literature regarding the variability between duplicate samples.

The precision of laboratory analytical results is often quantified by the relative percent difference (RPD). The RPD can be calculated by dividing the difference between two measurements by the average of the two measurements,

$$RPD(\%) = \frac{abs|x_1 - x_2|}{(x_1 + x_2)/2} (100\%)$$

where  $x_1$  and  $x_2$  are the parameter concentrations for the primary and duplicate samples, respectively. USEPA Method TO-15 for canister sampling and USEPA Method TO-17 for active sampling using sorbent tubes requires a laboratory analytical precision of 25% for duplicate analyses (USEPA, 1999a; USEPA, 1999b). For field duplicates, the acceptable RPD is often higher since there is sampling variability as well as laboratory variability.

# **METHODOLOGY**

Existing guidance documents vary on the methodology of duplicate soil vapour sample collection. Many guidance documents recommend the collection of field duplicates but do not provide guidance on collection methodology (*e.g.*, API, 2005; NY DOH, 2006; ITRC, 2007; DOD, 2008). Recommendations for soil vapour duplicate sample collection frequency and methodology are summarized in Table I1.

In general, duplicate soil vapour samples can be collected using two methods: simultaneous or sequential collection (Figure 11). Simultaneous duplicates are collected simultaneously using a sampling tee and two separate sample containers (e.g., Summa canister, Tedlar bag, sorbent tube). For Summa canisters, the sample containers can either use a single shared or two individual flow controllers. When using a shared flow controller the variability may be reduced slightly because possible differences in the flow rate are no longer a concern. For sorbent tubes, generally one pump drawing on two flow controllers is sufficient to provide good variability. Sequential duplicates are collected using an identical sample container immediately following the collection of the primary sample.



#### APPENDIX I DUPLICATE SOIL VAPOUR SAMPLING METHODOLOGY



Figure 11: Sequential and simultaneous duplicate sample collection using Summa canisters with either dedicated or shared flow controllers. Similar configurations are possible with sorbent tubes using one or two flow controllers and a sampling pump.

Similar configurations are possible for samples collected using sorbent tubes although the use of one pump and one flow controller to simultaneously draw on two sorbent tubes is not a recommended practice and instead use of one pump and two flow controllers is recommended. By setting the pumps at a high flow rate (*i.e.*, 1000 mL/min) and the flow controllers at lower rates (i.e. 100 ml/min) issues with impedance affecting flow rates can be minimized. It should also not noted that for tubes that are thermally desorbed, the analysis is destructive; any re-analysis that may be required can only be done if a second tube is available (unless the laboratory has a thermal desorption unit with re-collection feature). While not a duplicate analysis, for sorbent tube analysis, both the front and back sections of sampling tubes (or two tubes in series) should be analyzed separately to evaluate for chemical breakthrough. Ideally, a duplicate sample should be collected simultaneously at the same flow rate and vacuum as the primary sample to avoid sample bias associated with any changes in analyte concentration occurring over the duration of sample collection and/or resulting from changes in subsurface soil gas flow at the sample probe.

# **DUPLICATE SOIL VAPOUR SAMPLING IN PRACTICE**

#### Simultaneous collection

McAlary *et al.* (2009) collected eight simultaneous duplicates in Summa canisters connected via new Nylaflow tubing and compression fittings from a single soil vapour probe. Two canisters were sent to four laboratories as blind duplicates. The laboratory analytical results indicate the mean RPD values for duplicates within the same laboratory was 11% (standard deviation 10%) for benzene, toluene, ethylbenzene, xylenes, and 2,2,4-TMP, a result that is well within the required control limit of 25%. Greater variability was observed for samples analyzed by different laboratories (mean RPD 39%; standard deviation 37%).

DiGuilio (2006) collected simultaneous duplicate samples in Tedlar bags using a peristaltic pump and a sampling tee. The mean RPD of duplicate samples collected from five locations with detectable VOCs concentrations was 1.8% (range 0% to 9.1%).





#### **Sequential Collection**

DiGiulio (2007) assessed the effect of extraction volumes at a site in Stratford, Connecticut. Five sequential 1L sub-slab soil vapour samples were collected at three locations. Similar concentrations were obtained between the sequential samples indicating significant recharge of atmospheric air did not occur during sample collection (Figure I2). Two replicate canister samples were also collected from a sub-slab vapour probe (extraction volumes of 9L and 14 L, respectively). DiGiulio (2007) reports little change in sample concentrations over purge volumes as large as 103 Litres. Hartman (2008) reported the results of a similar study where sequential samples were analyzed but indicated greater variability with respect to purge volumes (Figure I3). At some locations, the TCE vapour concentrations continued to increase with increasing system volumes suggesting non-equilibrium conditions possibly within the sand pack or non-uniform contaminant distribution.

Following on the idea that increased purge volumes can produce samples with variable concentrations, Wong (2009) provides a design of a soil vapour probe with extra volume which enables the collection of a duplicate sample without the need to collect soil vapour from the adjacent native soils.



Figure I2: Comparison of VOC concentrations in sequential 1 L sub-slab soil vapour samples. The total sample volume (5 L) was equal to at least 500 internal soil vapour probe volumes (DiGiulio, 2007).



#### APPENDIX I DUPLICATE SOIL VAPOUR SAMPLING METHODOLOGY



Figure I3: Comparison of TCE concentrations in sequential external soil vapour samples (Hartman, 2008).

# **CONCLUSIONS AND RECOMMENDATIONS**

Duplicate soil vapour samples are collected to assess the precision of the analytical method and the variability of the sampling process. Although the collection of duplicate samples is widely recommended by guidance documents, there are no definitively recommended methods for duplicate soil vapour sample collection and the method of collection is subject to the best judgement of the practitioner. In general, duplicate soil vapour samples can be collected either simultaneously or sequentially. As a general practice, duplicate samples should be collected from sampling locations where the highest concentrations of the target analytes are likely to occur to ensure that detectable analyte concentrations are present in the samples.

Limited research on duplicate sample methodology has been published. There is some evidence to suggest that soil vapour concentrations do not appreciably change over relatively large purge volumes (e.g., 100L) and, accordingly, that the sequential duplicate collection may be an acceptable strategy; however, further evaluations of duplicate sample collection methods are essential to further assess the performance of these approaches.

Alternatively, the collection of a simultaneous duplicate under the exact sampling conditions as a primary sample is achievable and should be considered as the preferable duplicate sampling method. By setting the flow controllers for the duplicate sample containers to one-half the sampling flow rate (for example, collecting duplicates using two containers with 1 hour flow controllers rather than a 30 minute flow controller), simultaneous samples may be collected under the same flow and vacuum conditions as comparable primary samples. If site conditions indicate that the prolonged sampling duration may adversely impact sample representativeness due to low permeability soils, the collection of a half-full sample container (i.e., the identical sample volume as a typical primary sample, but split equally between two sample containers) is feasible with only a minor change in the detection limits (i.e., an increase of about a factor of two).




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## Table I1: Recommendations for duplicate sample collection frequency and methodology from selected guidance documents.

Guidance Document	Year	Recommended Duplicate Frequency	Recommended Duplicate Methodology
U.S. Environmental Protection Agency (USEPA)	1996	A minimum of 5% of all soil vapour samples should be collected in duplicate. Soil vapour samples collected with sorbent tubes should be taken in duplicate, when possible.	Duplicate soil vapour samples should only be collected at probes where, after collecting the first sample and purging the well for 15 seconds, the second field screening measurement is within 50% of the first field screening measurement (sequential duplicate sample collection).
California Environmental Protection Agency (CalEPA), California Regional Water Quality Control Board – Los Angeles Region (CRWQCB)	1997	No guidance provided.	No guidance provided.
Massachusetts Department of Environmental Protection (Ma DEP)	2002	Indoor air samples – collect at least one set of duplicate samples per sampling event.	Indoor air samples – collect duplicate samples simultaneously.
San Diego County	2002	No guidance provided.	No guidance provided.
California Environmental Protection Agency, Department of Toxic Substances Control (DTSC) and California Regional Water Quality Control Board – Los Angeles Region (CRWQCB)	2003	At least one duplicate sample per laboratory per day should be field duplicate(s).	For active soil vapour samples, duplicate samples should be collected immediately after the original sample and collected in separate sample containers, at the same location and depth.
U.S. Environmental Protection Agency (USEPA)	2004	Collect at least one duplicate sub-slab sample per building	Collect duplicate samples using dedicated stainless steel tubing and a sampling tee.
American Petroleum Institute (API)	2005	Collect duplicate samples from 10% of the sampling intervals.	No guidance provided.
Missouri Department of Natural Resources (Mi DNR)	2005	Collect one field duplicate per soil vapour sampling event or one per twenty samples, whichever is greater.	Preferably, duplicate samples should be collected simultaneously to collection of the primary sample using a sampling tee. Alternatively, the duplicate may be collected immediately after the collection of the primary sample. Duplicate samples shall be collected in separate sample containers, using the same procedures and at the same location and depth as the original sample.
New Jersey Department of Environmental Protection (NJ DEP)	2005	NJDEP does not require the collection of field duplicates for Method TO-15 (laboratory control samples instituted instead)	Not applicable. Two laboratory control samples to be analyzed each time a method blank is analyzed.



# APPENDIX I DUPLICATE SOIL VAPOUR SAMPLING METHODOLOGY

Guidance Document	Year	Recommended Duplicate Frequency	Recommended Duplicate Methodology
Atlantic Partners in RBCA (Risk Based Corrective Action) Implementation (PIRI)	2006	Soil vapour samples collected in sorbent tubes should be collected in duplicate.	Duplicate samples may be collected using two pumps, each fitted with sorbent tubes, or using one pump connected to a splitter.
New York Department of Health (NY DOH)	2006	No guidance provided.	No guidance provided.
British Columbia Science Advisory Board (BC SAB)	2006	The frequency of field and laboratory duplicate sample analyses, while often each set at 10 percent of the samples analyzed, may depend on the total number of samples analyzed and analytical method.	Field duplicate samples should be obtained from the same soil vapour probe using identical sampling procedures and submitted blind to the laboratory. Duplicate samples can either be obtained simultaneously (i.e., using a splitter) or in sequence. When duplicate samples are collected in sequence, variability due to temporal changes is introduced.
Interstate Technology Regulatory Council (ITRC)	2007	No guidance provided.	No guidance provided.
Department of Defence (DOD) - U.S. Air Force, U. S. Navy, U. S. Army	2008	Sub-slab samples – collect at least one duplicate sample per building Active air samples –evacuated canisters – collect at least one duplicate per building Active soil vapour samples – evacuated canisters – collect duplicate samples Passive soil vapour samples – adsorbents – collect duplicate samples	Sub-slab samples – collect samples using dedicated stainless steel or Teflon® tubing. No other guidance provided.
SPAWAR Systems Center Pacific (SSC Pacific)	2009	No guidance provided.	No guidance provided.



# **APPENDIX J**

# EXAMPLES INDOOR AIR QUALITY TESTING PROGRAM BUILDING SURVEYS

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May-11

# SCIENCE ADVISORY BOARD FOR CONTAMINATED SITES (SABCS)

# in BRITISH COLUMBIA

Indoor Air Quality Questionnaire and Building Survey<sup>1</sup>

Prepared by Golder Associates Ltd. , Burnaby, BC, Canada

Preparer's Name:	·····	Date/Time	Prepared:	
Preparer's Affiliation:		Phone No:		
Purpose of Investigation:				
<b>1. SITE INFORMATION</b>				
Site Name and Building ID:				
Address:				
2. OCCUPANTS (residential) or	TENANTS (commercial or	r industrial)		
Interviewed: Y / N				
Last Name:		First Name	:	
Address:				
Home Phone:		Cell Phone	:	
Work Phone:				
Age Range of Occupants:		Number Occupants at Location:		
3. OWNER. BUILDING OR PROP	PERTY MANAGER (Check i	if same as o	ccupant )	
Interviewed: Y / N			,	
Last Name:		First Name	:	
Address:				
Work Phone:				
Home Phone:		Cell Phone	·	
4. BUILDING INFORMATION				
Building Type: Circle applicable	resnonses			
Residential Single Family	Residential Townhous	e	Residential Apartment/Condominium	
School	Place of Worship		Commercial	
Commercial with Residential Ab	oove		Industrial	
Other:				
If Commercial, describe use:				
If Industrial, describe use:				
Age of Building:		Footprint A	Area of Building:	
Number of Floors:		Parking Ga	rage:	
Describe frequency of occupant	cy for different parts of the	e building (e	.g., basement, mechanical room)	
and, if applicable, hours of occu	pancy per day:			
Additional Information:				

### 5. BUILDING CONSTRUCTION CHARACTERISTICS

### Circle applicable responses

a. Above-grade construction:	Wood frame	Concrete	Stone	Brick		
b. Foundation type:	Basement	Crawlspace <sup>2</sup>	Slab-at-grade	Wood <sup>2</sup>		
c. Basement floor:	Concrete	Stone	Dirt			
d. Basement floor seal:	Unsealed	Sealed	Sealed with:			
e. Basement floor cover:	Uncovered	Covered	Covered with:			
f. Basement finish:	Unfinished	Finished	Partly Finished			
g. Basement moisture:	Dry	Damp	Wet	Moldy		
h. Below-grade walls:	Concrete poured	Concrete block	Other:			
i. Crawlspace:	Unlined	Concrete	Plastic			
j. Sump present: Y / N V	Vater in Sump? Y / N / I	N/A				
Basement floor/lowest floor depth below grade: Identify potential soil vapour entry points and approximate size (e.g., cracks, utility ports, drains):						

Additional Information: \_\_\_\_\_

## 6. HEATING, VENTILATION AND AIR CONDITIONING (HVAC) SYSTEM

### Type of heating system(s): Circle applicable responses and underline primary system

Hot air circulation	Electric baseboard	Heat pump	Wood stove				
Radiant floor	Steam	Hot-water baseboard					
Other (describe):							
Type of fuel(s) used: Circle applicable responses and underline primary fuel							
Natural gas	Fuel oil	Kerosene	Wood				
Coal	Electric	Propane	Solar				
Additional Information							
Furnace/boiler located where:							
Hot-water tank fueled by:							
For residential buildings (if applicable), describe the forced air duct systems, supply and return air							
ductwork where visible, and whether there is fresh air supply to furnace:							

For commercial or industrial building (if applicable), describe the HVAC system. Obtain information from HVAC engineer or building operations person on technical specifications, air exchange rates and building pressures, where available: \_\_\_\_\_\_

Is there any diagnostic type testing of pressure and/or air flow (e.g., smoke pencil, differential pressure testing. If so, please describe: \_\_\_\_\_\_

## 7. FACTORS THAT MAY INFLUENCE INDOOR AIR QUALITY

a. Is there an attached garage? Y / N
b. Are petroleum-powered vehicles or equipment Y / N / NA
stored in the garage (e.g. lawn mower,atv,car) Please specify
c. Has the building ever had a fire? Y / N When?
d. Is a kerosene or unvented gas space heater present? Y / N Where & Type?
e. Is there smoking in the building? Y / N How Frequently?
f. Have cleaning products been used recently? Y / N When & Type?
g. Have cosmetic products been used recently? Y / N When & Type?
h. Has painting/staining been done in the last 6 months? Y / N Where & When?
i. Is there new carpet, drapes or other textiles? Y / N Where & When?
j. Have air fresheners been used recently? Y / N When & Type?
k. Is there a kitchen exhaust fan? Y / N If yes, where vented?
I. Is there a bathroom exhaust fan? Y / N If yes where vented?
m. Is there a clothes dryer? Y / N If yes, is it vented outside? Y / N
n. Has there been a pesticide application? Y / N When & Type?
o. Are there odours in the building? Y / N
If yes, please describe:
p. Do any of the building occupants use solvents at work? Y / N
(e.g. chemical manufacturing or laboratory, mechanic or auto body shop, painting, fuel oil delivery
pesticide application, cosmetologist, dry cleaner)
If yes, what is occupation and solvents used?
If yes, are their clothes washed at work? Y / N
q. Do any of the building occupants regularly use dry-cleaner service? (Circle appropriate response)
Yes, use dry-cleaning regularly (weekly) Yes, use dry-cleaning infrequently (monthly or less) No
r. Is there a radon mitigation system for the building/structure? Y / N Date of Installation:
Is the system active or passive? Active / Passive
8. WATER AND SEWAGE
Water supply: Public Water Drilled Well Dug Well Other:
Sewage Disposal: Public Sewer Sentic Tank Leach Field Other:

# 9. PRODUCT INVENTORY FORM

Make and model of field instrument used:

List specific products found in the building that have the potential to affect indoor air quality.

Location	Product Description	Size	Condition	Chemical Ingredients	Field Instrument	Photo
				(optional if known)	Reading (unit =)	(Y/N)

1. Describe the condition of the product containers as Unopened (UO), Used (U), or Deteriorated (D)

2. Take photographs of containers including label

## **10. FLOOR PLANS**

Draw a plan view sketch of the building. Indicate air sampling locations, possible indoor air sources of background contamination, location of photographs, PID readings, other pertinent information. Indicate Floor: \_\_\_\_\_



## 11. OUTDOOR PLOT

Draw a sketch of the area surrounding the building being sampled. If applicable, provide information on potential background contamination sources such as gasoline stations, major highways, remediation systems, manufacturing plants, etc. Note the weather conditions including approximate wind speed and direction at the time of sampling. Include north arrow and approximate scale.

8		-		-	-	-

Note: 1. Adapted from New York Vapor Intrusion Guidance questionnaire

# APPENDIX K

# REVIEW OF PASSIVE DIFFUSIVE SAMPLER METHOD OF ANALYSIS



# **Overview of Method**

This appendix provides an overview of passive diffusive sampler principles followed by research on key factors affecting the results for this method.

The principle of diffusive sampling is that if the uptake rate is known, the concentration of chemicals can be calculated from the mass adsorbed over a known sampling duration. The uptake rate is a function of the diffusive coefficient, which is compound and sorbent specific, and the geometry of the sampler. The uptake rate may vary over time. Factors that may affect the performance of diffusive samplers include temperature, pressure, humidity, starvation effect (function of face air velocity and uptake rate) and changes in chemical concentrations over the sampling interval. The advantages of passive samplers include that they are easy to use, do not require a sampling pump, and may be less costly than other methods. In addition, passive samplers can be deployed for longer periods of time (some studies indicate one to two weeks) to provide time-averaged concentrations, which is advantageous when the goal is to evaluate longer-term human exposures.

The concentration is estimated using the following equation:

C = M / (k \* t)

Where M is the mass absorbed onto the sorbent, k is the uptake rate (volume/time) and t is time.

# Background

Badge-style samplers have been used for decades for evaluation of workplace exposures to VOCs with reporting limits in the parts per million (ppmV) range for samples collected over an 8-hour period where the sorbent is typically charcoal, which is extracted using solvent (carbon disulphide) and analyzed using GC/FID methods.

In the 1990's, badge-style samplers began to be used for indoor air quality studies, for example, 3M OVM 3500 badges combined with GC/MS analysis were used for one of the largest studies in Canada (757 houses) (Otson et al., 1993). Through longer sampling durations, detection limits on the order of 1 g/m3 have been achieved. These badges continue to be used, for example, Bailey et al. (2008) report a good comparison between TCE concentrations measured with OVM 3500 badges and active sorbent tubes (R2 correlation coefficient of 0.99 or higher). Manufacturer-specified limitations with badge type samplers should be recognized. This includes reduced recovery of vinyl chloride, acetone and methyl ethyl ketone when humidity exceeds 50% and the potential need for project specific recovery tests to quantify recovery for contaminant mixtures (3M Bulletin 1028, 2001).

# **New Diffusive Samplers**

Over the past few years, new types of diffusive samplers have been developed for longer duration, low-level analysis as described below.





- Passive diffusive badges: Recent advances in badge-style samplers include larger samplers, use of different sorbents (Tenax TA, Chromosorb 106, Anasorb GCB1 (Carbopack B) and Carbopack X), thermal desorption and GC/MS analysis (OSHA, 2003). McClenny *et al.* (2005) report on the results of a thermal desorption method involving a larger volume sampler (SKC Ultra-II) filled with Carbotrap C, where compound-specific method detection limits on the order of 0.03 to 0.3 ppbV were reported.
- 2) **Radiello® samplers**: This sampler has a radial symmetry, and is typically filled with a thermally desorbable Carbograph 4 or Carbopack X (Bruno *et al.*, 2004). This sampler has a higher uptake rate than other passive samplers and therefore lower detection limits can be achieved for comparable sampling times.
- 3) Automatic Thermal Desorption (ATD) tube samplers. This sampler is similar to thermal tubes used for active sampling, except that the tube is open at one end (Brown, 2000). Given the geometry of this sampler, the uptake rates are lower than for other diffusive samplers.
- 4) Polydimethylsiloxane (PDMS) membrane samplers (Waterloo membrane sampler): Vapours partition into and diffuse through a PDMS membrane, where there are trapped by a sorbent (typically Anasorb 747) in a small glass vial (Seepathy *et al.*, 2008). The diffusion rate can be estimated from GC retention indices (PDMS is used as a GC stationary phase). Groenevelt *et al.* (2010) report a good comparison between PDMS sampler and TO-15 results.

McAlary *et al.* (2010) report the initial results of detailed study where passive automated thermal desorption (ATD) tubes (*i.e.*, Perkin Elmer tubes), Radiello samplers, SKC Ultra II badge samplers and Waterloo Membrane Samplers (WMS) are being compared to active sampling methods. Low and high concentration laboratory experiments are being run, with low concentration (1 to 100 ppbV) experiments including one to seven day tests to assess the effects of temperature, relative humidity, concentration, exposure time and face velocity. Compounds being tested are 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, carbon tetrachloride,1,2-dichloroethane, 1,2,4-trimethylbenzene (TMB), hexane, methyl ethyl ketone (MEK) and naphthalene. The linitial low concentration results indicate the ATD Tenax sampler, Radiello sampler and the WMS performed well. For these samplers, the passive sampler concentrations were within 50% of the Summa canister results, except for MEK (Radiello, WMS and ATD Tenax), naphthalene (Radiello and WMS) and 124-TMB (WMS). For high concentration test results, negative bias was observed for some passive samplers (*e.g.*, Radiello sampler), which was expected based on the increased uptake rate.

# **Factors Affecting Passive Sampler Use**

Given that passive diffusive sampling methods have only recently begun to be used for low-level indoor air analysis, considerations relating to their use and results of selected research studies are summarized below:

**Uptake Rate:** There are up to four levels of validation studies. The highest level is statistically-based laboratory testing programs designed to evaluate the stability of the uptake rate under varying conditions and contaminant mixtures. The lowest level is estimates from the diffusion coefficient of the chemical. The uptake rate typically is relatively stable over a certain time interval, but decreases once saturation of the media is approached; this effect is more pronounced for more volatile VOCs and weaker adsorbants. Published uptake rates are often for a 24-hour sampling duration. Validation studies often include the uncertainty in the uptake rate.

**Face velocity**: In stagnant air, the uptake rate may decrease due to a starvation effect. Selected studies are summarized below:





- A review of 28 studies between 1973 and 2003 where the effect of face velocity on sampling rate was evaluated indicated, except for one study, significant underestimation in the uptake rate (about 20 to 60%) in the wind velocity range encountered in the indoor environment (Lee and Yun, 2004).
- A study by OHSA (1998) indicated a significant decline in uptake rate for face air velocities that were less than 50 cm/s, while SKC (2006) reported their badges performed satisfactorily down to face velocities as little as 5 cm/sec, but reported that face velocities inside houses are typically less than 2.5 cm/sec indicating the potential for a starvation effect (SKC, 2006).
- Matthews et al. (1989) measured face velocity in different rooms in seven houses. The median face velocities for different room types ranged from 4.2 to 12.4 cm/s with the HVAC system off, and from 5.7 to 15.5 cm/s with HVAC systems on.
- Coyne (2009) present results indicating a good comparison between canisters analyzed by TO-15 and Ultra II badges (Anasorb GCB1 and Tenax TA), but only when uptake rates experimentally derived at zero face velocity were used. The sampling rates for zero face velocity were approximately 40% less than sampling rates obtained for the original validation study. Measured air velocities in houses were less than 1 cm/sec. A closer match was obtained between Anasorb GCB1 and TO-15 results compared to Tenax TA and TO-15 results.

**Longer-term sampling**: A potential concern with longer-term sampling is potential saturation of sorption sites and competion for sorption sites where chemicals with stronger affinity to the sorbent may displace chemicals with weaker affinity. If there are changing concentrations over time, back diffusion may be a potential issue. Selected studies are summarized below:

- Hayes (2009) compared 7-day concentrations for different passive samplers to average concentrations from multiple canister samples and TO-15 analysis. A good comparison was obtained between Radiello samplers with Carbograph 4 sorbent and TO-15 analysis. For passive badges with Tenax TA, the benzene concentrations were 20% of the TO-15 concentrations, which was attributed to back diffusion because Tenax TA is a weak sorbent. Tube style samplers with Chromosorb 106 were found to have higher detection limits (due to lower uptake rates) than other sorbents and also exhibited benzene artifacts.
- Pennequin-Cardinal (2005) present data comparing Radiello uptake rates between different time periods indicating a decrease of 30% between 1 day and 2 week results for benzene (test concentration was 10 ug/m3) and 14% for toluene (30 ug/m3).
- Plaisance et al. (2008) found that the uncertainty in the uptake rate for Radiello samplers increased as the sampling duration was increased from one to two weeks.
- Jia et al. (2007) report passive sampler concentrations that were 12% lower than those measured using active sorbent tubes, a difference attributed to declining uptake rates at higher concentrations over the three to four day sampling period.
- Strandberg et al. (2005) evaluated both Radiello and SKC Ultra samplers and found a decrease in the uptake week between 24 hours and one-week for 1,3-butadiene (decrease not quantified), but concluded the diffusive samplers were acceptable for sampling durations tested.
- Odencrantz et al. (2008) compared canisters (TO-15), active sorbent tubes (TO-17) and ATD passive diffusive samplers (PDS) for two week sampling of trichloroethylene. The PDS results were consistently lower (on the average) than both the TO-15 and TO-17 concentrations and the effects of time-weighting of the samplers were more evident at increasing concentrations. On average, the PDS concentrations were about 2X lower than the TO-15 concentrations.





Lutes et al. (2010) compared indoor TCE concentrations for Radiello passive samplers obtained over two weeks to three 24-hour Summa canister samples (TO-15) obtained over the two-week period for a study conducted at the Moffatt air force base. The Radiello samplers with solvent extracted sorbents were on average approximately 20% lower than the Summa TO-15 results, while Radiello samplers with thermal extracted sorbents were on average approximately 50% lower. The authors concluded that a two-week sampling duration was too long for Radiello samplers.

# Summary

There are significant recent developments for passive sampling technology, which show promise for longer sampling durations and low-level analysis. Several studies indicate good comparisons between the results of passive diffusive sampler and active sorbent (TO-17) and/or canister (TO-15) analyses, although there have also been a few studies where concentrations measured with passive samplers were lower than those measured by the reference methods. As discussed above, research indicates that the uptake rate may decrease for low face velocities and that back diffusion may result in lower uptake rates for sampling durations longer than one week (for samplers evaluated). The stability of the uptake rate also depends on the sorbent used (Tenax TA is not recommended), and may also depend on the contaminant mixture. Further research is needed to evaluate these factors.

It is important that passive samplers are validated over the range of face velocities expected in the sampling environment, and that the linear range and uncertainty in uptake rate for each chemical is provided. For example, Radiella publish upper limits to exposure duration and concentration-time values for which the uptake rate is linear to. The implication of the maximum concentration-time values is that as the concentration increases, the allowable sampling time decreases.

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APPENDIX L

SUGGESTED OPERATING PROCEDURES

### SUGGESTED OPERATING PROCEDURE NO. 1: SOIL GAS PROBE INSTALLATION

- **SCOPE** The purpose of this suggested operating procedure (SOP) is to provide guidance on the installation of soil gas probes. Since there are different ways of constructing and installing probes that provide for acceptable results, a range of options are provided. This SOP is based on and updates the SOP in Volume I of Health Canada *Guidance Manual* for Environmental Site Characterisation in Support of Human Health Risk Assessment, prepared by Golder Associates (referred to as "Guidance Manual"). Note that reference to product brand names does not constitute endorsement of these products.
- **WHEN?** Soil gas probes are typically installed for one of three purposes: (i) to collect data in support of a risk assessment, (ii) for screening of volatile contamination in soil and groundwater and to optimize subsequent intrusive investigations and (iii) to monitor biodegradation processes (*e.g.*, oxygen, carbon dioxide and methane measurements).
- **HOW?** Soil gas probes can be constructed of a variety of materials and installed using several techniques. Critical aspects to probe construction include: i) the use of materials that are inert and non-sorptive, ii) the design of seals that minimize the potential for short-circuiting of atmospheric air to the probe soil gas collection point, and iii) surface completion including a valve to allow the probe to be sealed between sampling events.

Subslab soil vapour samples may also be collected through probes installed holes drilled directly through concrete foundations. Existing groundwater monitoring wells with screens that extend above the capillary fringe may also be used to collect soil vapour samples, but there are potential limitations related to the size of the well, purge volume, and screen length that should be recognized.

A soil gas probe installation program typically should consist of the following components:

- 1. Preparation of Health and Safety Plan (essential step but not part of this SOP).
- 2. Soil gas sampling design.
- 3. Planning and preparation.
- 4. Material handling, storage, decontamination and field blanks (see SOP #2 for additional details).
- 5. Installation of soil gas probes.
- 6. Decommissioning of boreholes and probes.
- 7. Documentation.

Leak testing of probes is described in SOPs #2 and #3.

## PROCEDURE

### Soil Gas Sampling Design:

An overview of selected considerations for soil gas sampling design is provided below. Refer to the main text of the *SABCS Guidance* for additional details.

- □ Identify the objectives of the soil gas sampling program.
- □ Integrate the conceptual site model into the soil gas sampling design.
- □ Identify areas and/or buildings of potential concern.
- Identify targeted areas for investigation. Typically, start with soil gas characterisation near the source of the vapour contamination. Consider using grid patterns or transects, and vertical profiles between the contamination source and the receptor (*e.g.*, building) of potential concern to evaluate the vapour transport pathway.
- □ Where possible probes should be installed at a depth of 1 m or deeper to reduce the likelihood of ambient air being drawn through surficial soils (referred to as "short-circuiting").
- □ Shallow soil gas probes may be installed at less than 1 m depth (*e.g.*, when the water table is shallow); however, consider installing a plastic sheet at ground surface to reduce potential short-circuiting. Plastic should be non-VOC emitting. The size of the sheet will depend on anticipated soil gas flow paths, but a 1.5 m of 1.5 m sheet may be sufficient. The rationale for surface sealing is described in the main text and Appendix B of SABCS Guidance.
- The probe should be situated above the capillary fringe to enable soil gas samples to be obtained and prevent potential damage to pumps. The thickness of the capillary fringe increases as soil becomes finer-grained.
- □ When soil vapour data is being used to predict concentrations for either an existing or future building scenario, it is essential that representative data be obtained. For external (*i.e.*, beside building) probes that are used for such purposes, the probes should be installed to a minimum depth half-way between the source of vapour contamination and the lowest point of the building of concern.
- When external soil vapour concentrations are being used to assess an existing building, generally soil vapour probes should be installed within 2 to 3 m of the building, but outside the zone of disturbance along the foundation wall. Probes on at least two sides of the building should typically be installed.
- □ Consider the need for sub-slab soil gas probes (*i.e.*, probes installed through a building foundation). Multiple sub-slab soil gas probes are often needed to obtain representative data.
- □ Consider the influence of utilities and possible preferential pathways on soil gas sampling design.

### **Planning and Preparation**

- □ Health and Safety Plan, Permits, Approvals and Utility Clearances: Develop a separate project Health and Safety Plan (this is beyond scope of this SOP) and obtain all necessary permits and/or approvals in advance of drilling activities. Review and locate underground and aboveground utility locations.
- Evaluate Potential Safety Issues: Evaluate safety issues and whether integrity of building envelope, structure, and underground utilities could be affected. As necessary, review available building plans and contact knowledgeable persons (*e.g.*, structural engineer if subslab probes are installed) and perform geophysical testing. Subslab probes should not be installed through slabs where there is post-tensioned steel unless all necessary pre-cautions have been taken.
- Select Probe Installation Method. The main options include:
  - 1. Permanent probes installed in boreholes constructed using conventional drilling techniques.
  - 2. Permanent probes installed using direct push drilling techniques.
  - 3. Probes driven into the subsurface (typically temporary probes) either by hand, electric rotary hammer or direct push rig.

The advantages and disadvantages of each option are described in the main text of the *SABCS Guidance*. Advantages of installing probes in drilled boreholes include that the soil stratigraphy can be inspected during installation and it is possible to construct a filter pack and seal. For direct push technology, soil cores may be obtained, so consideration should be given to first obtaining a soil core to evaluate soil conditions, prior to either installing an implant in the open borehole (providing it does not collapse) or installing the implant "post-run" through the Geoprobe drill rods at a second location a short distance away from the first hole. When installing an implant post-run, a filter pack and seal may also be installed, but depending on the size of the rods used, sometimes bridging occurs. An advantage of driven probes is that shallow probes can be efficiently installed. Disadvantages include that driven probes depending on design and installation may be more susceptible to air leakage. Driven probes should not be used in soils that will fracture when the probe is driven temporary probes are used.

□ Select Drilling Method for Permanent Probes: Drilling methods will vary depending on geologic materials, target depth and access constraints. Methods that create smaller boreholes with the least amount of disturbance are highly preferred (Geoprobe, auger). Rotary sonic methods are acceptable but the use of air or water should be avoided to the extent possible. Air rotary methods should not be used unless there are no other alternatives. Installing soil gas probes in a Hydro-vac hole should also not be used unless there are no other alternatives. Mud rotary is not an acceptable method. The drilling method may also depend whether multiple probes are to be installed in a single borehole. Since typical hollow stem augers have an inside diameter of 107 mm (4 ¼ inches), it is possible to install three 19 mm (¾ inch) probes inside the augers, although care must be taken to avoid bridging when placing filter and seal materials. If a proper installation cannot be achieved for multiple probes, install probes in separate boreholes. Soil gas probes may also be installed in an open borehole, but only if the hole does not collapse. Care must be taken to install a proper filter pack and seal.

**Select Installation Method for Driven Probes**: Options include include AMS Retract-a-Tip, Geoprobe PRT or Solinst systems. For AMS system, probes can be installed by hand using a slide hammer (do not use sledge hammer) or using an electric rotary hammer.<sup>1</sup> In sandy or silty soils, it is often possible to install probes to about 3 m depth. Dense or coarse-grained soils may preclude the use of AMS probes. The Geoprobe PRT probe is deployed using a direct push drill rig and therefore can be installed to greater depths and in a variety of different types of soils.

- Select Probe Materials. The probe should be constructed of relatively inert and non-porous materials (e.g., stainless steel, Teflon®, PVC or nylon (Nylaflow®). If naphthalene is an analyte of concern, only Teflon tubing is recommended (see SOP #2). The probe should not be constructed using any glues, tape, or other materials that could emit volatiles. Only new materials should be used for probes, except when using temporary steel probes.
- □ Select Soil Gas Probe Construction. The material type, diameter, screen length, and connections should be determined:
  - □ Common probe material types are: continuous rigid PVC to ground surface; steel mesh screens ("implants") attached to flexible tubing to ground surface; and stainless steel probes with drive points. Rigid PVC probes are typically installed in boreholes, implants may be installed in boreholes or "post-run" using direct push methods, and hollow steel probes with points are driven to the desired depth.
  - □ A probe diameter of 19 mm (1 inch) or smaller should generally be used to minimize the purge volumes. Short screens (0.1 to 0.3 m length) should be used for probes, unless there are thick vadose zones (*i.e.*, greater than about 10 m) where longer soil gas probe screens may be appropriate or where the objective is high volume large-scale soil gas sampling.
  - □ For probes constructed of **rigid PVC pipe**, generally 19 mm (¾ inch) diameter pipe is recommended. Screens may consist of No. 10 to No. 40 slot pipe. An airtight cap with a sampling port should be placed over top of the riser pipe and riser pipe segments should be flush-threaded. No glue should be used for construction of probes.
  - □ For probes constructed of **implants**, options include Geoprobe AT-86 and AMW Vapor Implants. The typical implant length is 0.15 m to 0.3 m, while the diameter is commonly 12.5 mm (½ inch). Flexible tubing (typically 6 mm (¼ inch) diameter) is used to connect the implant to ground surface. It is critical that there is a strong, air-tight connection between the tubing and the implant.
  - □ For probes constructed of **driven probes**, options include AMS Retract-a-Tip, Geoprobe PRT or Solinst systems. The AMS Retract-a-Tip system consists of 22 mm (7/8 inch) outer diameter rods. Soil gas samples are collected using plastic tubing that is connected to a 50-mm long screened tip that is exposed when the rods are retracted at the desired depth. The Geoprobe Post Run Tubing System (PRT) is similar to AMS but larger diameter (31.5 mm or 1.25 inches) (Geoprobe,

<sup>&</sup>lt;sup>1</sup> See video at <u>http://www.ams-samplers.com/category.cfm?CNum=3</u>

2006). In addition, new tubing is threaded down the rods for collection of each new sample as the rods are pushed deeper. The driven probe should not have rods with smaller diameter than the tip because an open annulus for air movement will be created behind the tip. It is also critical that the tubing connected to probes be air tight.

- □ Probes should be completed with an air-tight valve or stopcock at surface to prevent atmospheric air from entering the probe.
- □ Probes should be labelled without using VOC-emitting markers.
- □ Permanent probes should be protected using a well cover or other similar protective casing for security and weatherproofing.
- Select Subslab Soil Gas Probe Construction: The recommended design for permanent subslab probes consists of a stainless steel or brass insert installed within a corehole that is sealed with concrete grout (USEPA, 2004). The concrete grout should consist of Portland cement, aggregate and water, and should not contain any additives that could contain VOCs. Since regular concrete may develop shrinkage cracks over time, an expanding or swelling concrete designed to seal wet cracks in concrete floors may provide for better performance. Other sealants such as polyethylene glue or bees-wax have also been used for subslab probes. The subslab probe design by USEPA (2004) consists of brass or stainless steel tubing that is connected to a threaded fitting (Figure 1). When not in use, the probe is sealed with a recessed threaded cap. For sampling, the threaded cap is replaced with a fitting with threads on one end and ¼-inch compression or barbed fitting on the other end.

### **Schedule the Work**.

#### Material Handling, Storage, Decontamination and Field Blanks:

- □ **Handling and Storage**: Probe materials (*e.g.*, PVC pipe, tubing and implants) should be delivered to the site wrapped in plastic. Use care when storing materials on-site and when installing probes to avoid contamination. Do not expose probe materials to vehicle exhaust or other point sources of contamination.
- Decontamination of Temporary Steel Probes: Steel probes should be thoroughly washed with a hot-water soap solution followed by a distilled-deionized water rinse. Probes should be completely dry prior to reuse, as water droplets on the inside of the probe could affect soil gas concentrations. See SOP #2 for testing of blanks.

#### Installation of Probes in Boreholes

- 1. This procedure applies to probes installed in open boreholes or within drill rods of borehole.
- 2. Log the borehole as drilling proceeds. Adjust the depth of the soil gas probe, if warranted based on the soil stratigraphy observed and field screening results.
- 3. Place a thin sand layer (2.5 to 5 centimeters) at the base of borehole when installing probe so that it is not in direct contact with native soil to avoid clogging.

- 4. Insert the probe through the drill rods or in open hole. Install filter pack and seal while removing the rods as described below.
- 5. Place a filter pack comprised of coarse sand or fine gravel around the screen. Extend the filter pack 0.15 m above the top of the screen. If gravel is used, a thin sand layer between the gravel and bentonite should be used.
- 6. Install a bentonite seal above the filter pack consisting of dry granular bentonite (16 mesh). The bentonite seal should be a minimum 0.3 m thick. Place seal in two to three lifts that are a few centimeters thick and hydrate with distilled-deionized water.
- 7. Seal the remainder of the borehole annulus to near to ground surface using a thick slurry of powdered bentonite and water ("Volclay Grout") installed using a tremie pipe.
- 8. Use a tamping rod and weighted tape to verify position of filter pack and seal.
- 9. Where more than one probe is installed within a single borehole, install a minimum 0.15-m thick granular bentonite seal between probes. The seals between multi-level probes can be tested by pumping from one probe with a minimum vacuum of 10 inches H<sub>2</sub>0 column and monitoring adjacent probes for vacuum. A faulty seal will result in a rapid increase in vacuum in adjacent probes to significant levels.

### Installation of Probes using Direct Push Technology

- 1. Larger size rods<sup>2</sup> should be used to facilitate the installation of a proper filter pack and seal. Never allow the borehole to collapse around the probe when using direct push technology to install probes.
- 2. Push probes to desired depth.
- 3. Lower implant and connect to expendable drive tip with threaded connection.
- 4. Use same procedure for installing filter pack and seal as for probes installed in boreholes.

#### Installation of Driven Probes

- 1. Drill small pilot hole where there are asphalt or concrete surfaces, as required.
- 2. Install probes vertically using a hydraulic ram or slide hammer (do not use a sledge hammer).
- 3. Minimize post-installation disturbance to probes.
- 4. Driven probes should not be used in soils that will fracture (*e.g.*, certain types of clay).

<sup>&</sup>lt;sup>2</sup> For Geoprobe systems use DT-21 dual-tube system with 2.125 inch OD and 1.5 inch ID rods. See <u>www.geoprobe.com</u> Direct Push Installation of Devices for Soil Gas Sampling and Monitoring [Tech.Bulletin No. MK3098]

- 5. If cobbles or other obstructions cause the rods to deflect, the installation should be abandoned, grouted, and re-tried at new location.
- 6. Place a bentonite seal around the probe at ground surface.
- 7. Retract sleeve and start sampling process (SOP #2 and #3).

#### Installation of Sub-Slab Probes

- 1. Probes that are installed directly below the slab are described below. For deeper probes, use the applicable procedure described above.
- 2. Drill hole in concrete using a heavy duty electric rotary hammer drill. Avoid the use of gasoline powered drills. Collect concrete dust during drilling using a dry/wet vacuum cleaner.
- 3. After drilling the hole and prior to installation of the probe, the hole should be temporarily sealed (*e.g.*, using a rubber stopper) to minimize disturbance to subslab vapour concentrations.
- 4. Install stainless steel or brass insert (Figure 1) and connect fitting on insert to valve. Use non-VOC emitting concrete grout.
- 5. After installing the probe, close the valve to the probe and allow time for the concrete seal to set before collecting a sample. For fast-setting concrete, about one hour may be sufficient. If the hole has stayed open for any appreciable time and there are pressure gradients between the building and subsoils, a longer waiting period between installation and sampling may be warranted to allow soil vapour concentrations to return to equilibrium.

#### **Decommissioning of Boreholes and Probes**

All open boreholes or holes created by driven probes should be sealed with bentonite grout if they are not used for installing permanent soil vapour probes. The grout should be placed using a tremie pipe if the hole is of sufficient diameter, otherwise, bentonite should be poured down the hole.

When sub-slab probes are decommissioned, the probe holes should be sealed by filling them with non-shrinking cement grout or other appropriate material in order to prevent soil vapour from entering the building.

### Documentation

Each soil gas probe installation should be documented on a separate borehole log form. The volume of air removed during development should be noted, where applicable.



FIGURE 1. USEPA (2004) Recommended Design for Subslab Probes

## REFERENCES

- United States Environmental Protection Agency (US EPA), 2004. Standard Operating Procedure (SOP) for Installation of Sub-Slab Vapor Probes and Sampling Using US EPA Method to Support Vapor Intrusion Investigations. ORD, Ada, OK, Draft February 12, 2004.
- Geoprobe, 2006. *Direct Push Installation of Devices for Active Soil Gas Sampling and Monitoring.* Technical Bulletin MK-3098. May.

## SUGGESTED OPERATING PROCEDURE NO. 2: SOIL GAS SAMPLING

- **SCOPE** The purpose of this Suggested Operating Procedure (SOP) is to provide guidance on the collection of soil gas and subslab gas samples for chemical analysis. The scope of this procedure includes soil gas sampling methods and sampling containers or devices used to obtain samples. Limited information is provided on laboratory chemical analysis. Since there are different ways of soil gas sampling that provide for acceptable results, a range of options are provided. This SOP is based on and updates the SOP in Volume I of Health Canada *Guidance Manual for Environmental Site Characterisation in Support of Human Health Risk Assessment,* prepared by Golder Associates (referred to as "Guidance Manual"). Note that reference to product brand names does not constitute endorsement of these products.
- **WHY?** The term soil gas refers to the gas present in soil pore spaces. Soil gases may be generated through two different types of processes: (i) partitioning that occurs when chemicals volatilize into soil gas from non-aqueous phase liquids (NAPLs), dissolved chemicals in groundwater, and chemicals sorbed onto soil particles, and (ii) anaerobic decomposition of organic chemicals, waste material (*e.g.*, refuse) or native organic matter (*e.g.*, peat) and generation of methane, carbon dioxide and, in some cases, hydrogen sulphide, or aerobic biodegradation of hydrocarbons and generation of carbon dioxide and consumption of oxygen.
- **HOW?** The soil gas sampling process is summarized in Figure 1. Soil gas samples may be analyzed in the field for organic vapour concentrations (non-compound specific) using hand-held instruments such as a photoionization detector (PID), flame ionization detector (FID), combustible gas detector or landfill gas monitor (*e.g.*, oxygen, carbon dioxide, methane, hydrogen sulphide). Soil gas samples may also be analyzed for specific compounds of interest using more advanced analysis methods, typically at an off-site analytical laboratory. When soil gas data is used in support of a human health risk assessment, chemical analysis of soil gas for specific compounds of interest to low detection limits (*i.e.*, low ppbV levels) is typically required. However, field instruments can be effectively used as a screening tool to locate worst-case areas of contamination and to minimize overall analytical costs.

There are several different methods available for the collection and analysis of soil gas samples for laboratory analysis. The two main options are sampling using sorbent tubes and canisters. The choice of analytical method will depend on project objectives, sampling methods, detection limits required, and data quality objectives. In the case of field analytical methods, soil gas samples are typically collected in gas-bags or syringes.



FIGURE 1. Soil Gas Sampling Process

## PROCEDURE

Planning and preparation:

- □ **Prepare project Health and Safety Plan** (beyond the scope of this SOP).
- □ **Review soil gas probe installation details:** Determine if existing probes are adequate to achieve current project objectives and are in good condition. If groundwater monitoring wells are to be sampled, review well logs for screen completion depths relative to water table and construction methods (*e.g.*, filter pack and seal), and determine whether well is vented at surface (modifications to well and additional purging may be required).
- □ Select Analytical Method and Sampling Device: Identify the chemicals of potential concern (COPCs), and select the sampling method, analytical method, detection limits required, and data quality objectives. Based on the analytical method selected, determine the type of sample collection device. The typical options are described in Table 1. Some laboratories prefer or require gas-bags (*e.g.*, SKC Tedlar® bags) to be used instead of canisters for USEPA Method TO-15 analysis when concentrations are above a certain threshold. Note that Tedlar® is being phased out by SKC and replaced by Flexfilm, which is considered an acceptable alternative. The use of gas-bags for TO-15 analysis may be acceptable on a case-by-case basis with certain precautions. USEPA Method TO-17 may be an acceptable alternative when canisters can not be used.

Method	Sampling Device	Compounds Analyzed	Sample Holding Time
USEPA Method TO-15 <sup>9</sup> (BC Lab Manual: VOCs by Canister)	Summa polished or fused silica lined (FSL) evacuated canisters (typically 1-6 L volume)	Broad range of VOCs from propane to naphthalene <sup>2</sup>	30 days from sample collection <sup>1</sup>
USEPA Method TO-17 (BC Lab Manual: VOCs by Thermal Desorption Tube)	Thermally desorbable sorbent tubes collected using low flow pumps	Wide volatility range from light molecular weight VOCs such as 1,3-butadiene to 4-ring PAHs if multi-bed sorbent tubes are used <sup>5</sup>	30 days, if stored at 4°C
Modified NIOSH 1501 or OSHA 7 (BC Lab Manual: VOCs/Other Volatiles by Charcoal Tubes)	Solvent extracted charcoal tube	Typically BTEX & other petroleum hydrocarbons <sup>6</sup> -higher DLs than TO-17	Contact laboratory
ASTM D1946-90 (2006) <sup>3</sup> or D1945- 03(2010) <sup>4</sup>	Gas <sup>8</sup> Bags or Canister	Fixed gases, light hydrocarbons	1 to 3 days for Gas Bags; 30 days for canisters
ASTM D5504	Gas <sup>7</sup> Bags or FSLCanister <sup>8</sup>	Reduced sulphur compounds	Generally 24 hours

TABLE 1.	Summary of Co	mmon Analytical	Methods for	Soil Gas
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Notes:

- 1. BC Laboratory Manual (2009). Some jurisdictions (California DTSC, NJDEP) require samples be analyzed within 14 days of collection. Recommend that canisters be used for sampling within 15 days of preparation by the laboratory.
- 2. Naphthalene performance by TO-15 may be relatively poor. USEPA TO-17 is generally a better option if naphthalene is an analyte (project manager decision).
- 3. Hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene.
- 4. Hydrogen, oxygen/argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen sulphide, helium, C1-C5 specification, C6+.
- 5. Research indicates that method performance highly dependent on sorbent tube. Recommend PerkinElmer SVI tube for TO-17 analysis (see CARO studies). With this tube, good recovery and minimal breakthrough has been demonstrated for all but very light molecular compounds (*e.g.*, chloromethane). Use TO-15 if analysis of very light compounds is required.
- 6. May also be used for selected chlorinated solvents.
- 7. Tedlar® film is currently being phased out by the manufacturer; alternatives from SKC include FlexFilm, Kynar, and FlexFoil.
- 8. Researchers have reported inconsistent recoveries of reactive sulfur compounds from aging FSL canisters.
- □ **Gas Bag Collection:** For gas-bags, use a vacuum chamber (or "lung box") to collect samples. This avoids passing soil gas through a pump and possible bias due to cross-contamination from pump and/or pump leakage.

- □ **Determine Sample Volume, Flow Rate and Time**: Based on the expected concentrations and required detection limits, determine the sample volume, flow rate and time (duration) requirements. Note that the sample flow rate should be checked in the field (see flow and vacuum (performance) check below).
- □ **Determine Pump Requirements**: From flow and vacuum date, determine pump requirements for collection of gas-bag and sorbent tube samples. For sorbent tubes, use air sampling pump with low-flow adapter calibrated to required flow rate (generally 100-200 ml/min). For high vacuum sampling, specialty pumps may be required. No pump is required for canister collection.
- □ Identify Field Quality Control Procedures and Samples: Identify and plan the quality control testing procedures for the project including probe performance (flow and vacuum) check and leak testing. Determine sampling container certification and the field quality control samples that will be obtained including duplicate samples, equipment blanks and trip blanks. If practical, test quality control samples early on in the field program so that adjustments can be made, when warranted. Make arrangements for the laboratory to supply ultra high purity nitrogen to field, if needed. Experience indicates canisters occasionally leak (evidenced by vacuum lower than about 27 inches Hg when canisters arrive on site) or connections are not tight (*e.g.*, due to stripped threads) and gas-bags leak (evidenced by deflation after sampling). Therefore, consider ordering extra canisters and bags.
- Select Sampling Train Materials. Fluorinated ethylene propylene (Teflon®), nylon (Nylaflow®) and stainless steel are acceptable sampling train materials for most analytes. When naphthalene is an analyte, use Teflon® or stainless steel because studies that indicate significant sorptive losses for Nylaflow®. The recommended tubing size is ¼ inch diameter OD. Flexible tubing materials such as silicone, rubber or Tygon® are not acceptable. Couplings should be Swagelok® compression-fittings, barbed-fittings, or threaded fittings wrapped with Teflon® tape (slip fittings should not be used). When barb-fittings are used, push tubing over a minimum of three barbs. Do not use any glue, tape, or other materials that could emit volatiles.<sup>1</sup>
- □ **Determine Purge Volumes**: The purge volume should take into account filter pack and may be calculated from:

Probe Volume (cm<sup>3</sup>) = 
$$\pi^{*}1/4^{*}[\theta_{a}^{*}(D_{B}^{2}-D_{P}^{2})^{*}L_{S} + D_{B}^{2*}L_{P} + D_{T}^{2*}L_{T}]$$

where  $\theta_a$  is the air-filled porosity (0.25 is a reasonable assumption),  $D_B$  is diameter borehole (cm),  $D_P$  is the diameter of the probe (cm),  $L_S$  is the length of the sand pack (cm),  $D_B$  is the diameter of the probe (cm),  $L_P$  is the length of the probe (cm),  $D_T$  is the diameter of the tubing (cm).

□ **Temporal and Seasonal Considerations**: Consider possible temporal and seasonal variations when determining when to sample. Do not conduct sampling during and after moderate to heavy rain (*i.e.*, greater than 1 cm). Generally wait at least one day or longer depending on soil type (project-specific decision).

<sup>&</sup>lt;sup>1</sup> Vacuum grease is sometimes applied by the manufacturer to Tedlar bag valves, but should not be used for low-level analysis.

- □ Cold Weather Considerations: Most field instruments and pumps are not designed to operate when temperatures are below freezing. Keep field detectors in an environment where temperature > 0°C. Keep pumps warm in insulated coolers or insulated lunch bags with heat packs. If warm soil gas cools in tubing, condensation may occur and adversely affect the sampling and analysis process (*e.g.*, reduced retention for sorbent tubes). Watch for signs of condensation. Sorbents and tubing may also be kept warm in insulated lunch bags (or possibly other ways) to reduce condensation. Do not collect soil gas samples from frozen ground. Such samples are not expected to be representative due to reduced volatilization.
- □ Schedule the Work: Conduct probe performance testing, leak tests and field screening prior to collecting samples for laboratory analysis. It may be advantageous to screen all probes then return to select probes to collect samples for laboratory analysis. For holding time sensitive analyses, coordinate shipping and receipt by laboratory (consider impact of weekends). Follow-up appropriate shipping and placarding requirements for compressed gases such as helium.

### Material Handling, Storage, Decontamination and Field Blanks:

- Handling and Storage: Sampling train materials (*e.g.*, tubing, valves and fittings) should be wrapped in plastic or in food-grade plastic bags during delivery to site and storage on site. Use care when storing and handling materials and sampling devices to avoid contamination. Consider clean, medical grade nitrile gloves for sampling. Do not expose sampling materials to vehicle exhaust or other point sources of contamination.
- Decontamination: For *laboratory analysis* (*i.e.*, ppbV levels), it is recommended that dedicated new materials be used for each new probe (there is generally no need to decontaminate new materials properly handled<sup>2</sup>). Sampling materials to be reused for laboratory analysis should be thoroughly washed with a hot-water soap solution followed by tap-water and distilled-deionized water rinses. The valves and fittings should be completely dry prior to reuse, as water droplets on the inside of the valves and fittings could affect soil gas concentrations. A low-temperature bake (*e.g.*, 70°C) may be used to dry stainless steel and brass. Cleaning procedures should be verified through testing of equipment blanks (see below). When sampling train materials are to be re-used for *field screening analysis* (*i.e.*, ppmV levels), decontamination of relatively inert materials such as stainless steel, brass and Teflon® may not be required; however, blank samples should be tested.
- □ **Cleaning of Retractable Tip Probes**: Soil typically clogs in retractable screen type probes requiring cleaning with brushes, followed by soapy water, tap water and distilled water rinse.
- □ Field Blanks for Field Screening (ppmV levels): Where field screening and ppmV analyses are performed, collect and test a field blank to verify that sampling materials are clean. Draw ambient air through the probe (prior to installation)<sup>3</sup> and sampling train into a gas bag and measure the concentration in the bag using a PID. If there is any detectable concentration, the probe and sampling train should be cleaned or replaced. The background PID levels in ambient air must be non-detect for this procedure to apply.

 $<sup>\</sup>frac{2}{3}$  Sampling tips or implants in contact with cutting oils should be soaked in isopropyl alcohol and then rinsed as described above.

<sup>&</sup>lt;sup>3</sup> This procedure is generally only applicable to temporary probes

□ Field Blanks for Laboratory Analysis (ppbV levels): When re-using soil gas probes and/or sampling trains where laboratory analyses (*i.e.*, ppbV levels) are to be performed, the following procedure should be followed: (i) connect a Summa or FSL canister containing zero ultra pure air or nitrogen to one end of the sampling train (ii) connect the other end of the sampling train to an evacuated canister, (iii) simultaneously open both canister valves and then fill the canister at the planned flow rate. Submit the canister sample for laboratory analysis. A sorbent tube may also be used to obtain a field blank sample; however, the regulator and valve on the gas canister must be capable of delivering a constant flow rate between 100 and 200 ml/min, and a flow gauge must be used to measure the flow rate. It is recommended that a minimum of 10 percent of the probes and sampling trains that are re-used should be tested using the above procedure.

When using new materials that are properly stored and handled, there is less potential for cross-contamination during sampling. The testing of equipment blanks of new materials should be considered depending on quality control requirements. Note that there are some agencies (*e.g.*, California Department of Toxic Substances Control (DTSC)) and practitioners that require or advocate this. There may be practical challenges to testing blanks, for example, for probes constructed of pieces of solid PVC pipe.

### Probe Equilibration and/or Probe Development

- □ Soil gas probes should be developed by removing air entrained during installation and/or allowed to re-equilibrate via diffusion prior to sampling. Development also provides for "conditioning" of PVC probes (studies have shown some sorption on to PVC occurs).
- □ A minimum of three probe volumes of air (consisting of the probe volume, tubing volume and air-filled pore volume of the sand pack) should be removed during development. Otherwise, the probe should be allowed to re-equilibrate prior to sampling.
- □ The time required for equilibration will depend on the disturbance caused during installation. Recommended minimum equilibration times are provided in Table 2.

Probe Type	Equilibration Time	
Driven probes (AMS, Geoprobe PRT)	20 minutes	
Probes installed in small diameter borehole (<50 mm), no fluids (air or water) used for drilling	1 day	
Probes installed in larger diameter borehole (>50 mm), no fluids (air or water) used for drilling	2 days	
Probes installed in hydro-vac hole (not recommended, but may be health and safety or client requirement)	1 week	
Probes installed in borehole where fluids (air or water) used for drilling (not recommended)	Conduct field screening over several weeks until concentrations stabilize	

Table 2. Recommended Minimum Equilibration Times

### Flow and Vacuum (Probe Performance) Check:

- □ The purpose of the probe performance test is to verify that an acceptable soil gas flow rate and vacuum can be achieved and that the calculated soil-air permeability is consistent with geologic materials in which the probe is screened. If the vacuum is much higher than expected, the probe may be plugged or within the saturated zone.<sup>4</sup> If the vacuum is much lower than expected, there may be short circuiting. When interpreting results, recognize that soil moisture (and hence precipitation events) affects soil-air permeability.
- □ The flow and vacuum measurements may be used to estimate the soil-air permeability using mathematical models for soil gas flow (Appendix I).
- □ The flow and vacuum check is conducted by measuring the vacuum at the desired flow rate. If the vacuum exceeds 10 inches of water, a lower flow rate should be used to reduce the vacuum, where practical. A vacuum of greater than 10-20 inches water column may also require a specialized pump.
- □ As a minimum, allow the vacuum generated during performance testing to dissipate before collecting a soil gas sample for analysis. If a relatively large volume of soil gas is removed or high pumping rate is employed during the performance test (which may cause a local disequilibrium), the probe should be allowed to re-equilibrate using similar criteria described above.<sup>5</sup>

### Leak Tracer Test and Shut-in Vacuum Test

- □ The purpose of the leak tracer test and shut-in vacuum test is to verify that leakage of the sampling train is within acceptable limits.
- □ Conduct leak tracer test using helium (from reputable supplier (*e.g.*, Praxair, Air Liquide) with less than 0.5 ppmV total hydrocarbons) at each new probe being sampled, and at 10% of probes for each subsequent monitoring round.
- Place plastic shroud over the sample probe and valve and slowly fill the shroud until the helium concentration measured using a Dielectric MGD-2000 (or equivalent) is between 30% and 100% ("top up" helium during test as necessary). Purge probe (see procedure below) and then obtain soil gas sample in gas bag and measure helium concentration. Quantify leakage as follows:

Leakage (%) = (He Conc. Soil Gas/ He Conc. Shroud) \* 100

- □ If Leakage is greater than 2%, it is recommended that the a sample not be collected until the probe is repaired or a new probe is installed.
- □ Conduct shut-in vacuum tests twice daily by creating 10 inches water column vacuum in sampling train. Close valve at probe and furthest down-stream end of sampling train and monitor the change in vacuum over time. While criteria for vacuum loss from shut-in tests are still be developed it is suggested that there should be no more than 5% loss in vacuum over 5 minutes.

<sup>&</sup>lt;sup>4</sup> Criteria for typical vacuums for different geologic media are being developed.

<sup>&</sup>lt;sup>5</sup> The sampling radius may be calculated assuming the soil gas sampling zone is a sphere and equation for volume of sphere (4/3 \*PI \*R<sup>3</sup>). The radius (cm) is calculated as follows R = [ 3 \* V / (4\*PI\* $\theta_a$ ) ]^0.33 where V is sample volume (cm<sup>3</sup>) and  $\theta_a$  is the air-filled porosity. Assuming sample volume of 10L and air-filled porosity of 0.1, a sampling radius of 28 cm is calculated.

### Purging and Sampling:

Purging and sampling procedures are summarized below. Specific considerations for canisters and sorbent tubes are described in subsequent sections. Schematics showing different sampling configurations are shown in Figures 2 and 3. The use of smaller diameter probes (generally equal or less than 19 mm diameter) is recommended to reduce purge volumes and sampling times.

- 1. The valve on the probe should be closed at all times unless the probe is being purged or sampled.
- 2. Measure the static pressure between the probe and ambient air using a manometer with resolution of 0.01 inches H<sub>2</sub>O. The static pressure may provide useful information on possible pressure gradients and advective soil gas transport (optional).
- 3. Assemble the sampling train and check that fittings and connections are tight. Use the minimum length of tubing practical, to minimize the sorption of chemicals to the tubing.
- 4. Start leak tracer test as described above.
- 5. Connect the sampling apparatus (train, vacuum chamber, pump, *etc.*), open valves and purge at a nominal rate of 20 to 200 ml/min. If a larger diameter probe is sampled (*e.g.*, monitoring well screened across the water table), a purge rate of up to 5 L/min may be used. Record the vacuum during purging and reduce the flow rate, as practical, if the vacuum is greater than 10 inches water column.
- 6. Purge volume criteria options are as follows (project specific decision):
  - i. **Basic Method**: Purge three probe volumes including the filter pack pore-space and then collect sample.
  - ii. **Purge Stabilization Test**: Collect sample after soil gas concentrations (PID, oxygen, carbon dioxide) stabilize (consecutive readings are within 10 percent of each other). Obtain samples at approximately one purge volume increments. If the purge volume is less than one litre, collect successive 1-litre samples. This method is recommended where soil gas samples are collected from monitoring wells or from probes installed in hydro-vac holes.
  - iii. Initial Purge Volume Test: Initially conduct purge volume test on subset of probes and obtain PID readings after one, three and ten purge volumes. Desired purge volume corresponds to the purge volume for which maximum PID concentrations are obtained. Use this purge volume for subsequent probes (California DTSC method).
- 7. Once purging is complete, stop the flow of the pump and close the valve immediately upstream of the pump.
- 8. Allow the vacuum inside the probe to dissipate to atmospheric conditions (record the time for the vacuum to dissipate).

- 9. Once atmospheric conditions have been reached, connect the sampling device to the sampling train, open the valve and collect the sample at a flow rate between 20 and 200 ml/min unless high volume purge (HPV) sampling is being conducted (see main text of *SABCS Guidance*). The procedure will depend on the sample collection method: (i) *Gas bags*: collect sample using vacuum chamber using same sample train used for purging; (ii) *Evacuated canister*: close valve at probe, disconnect tubing from pump, and connect to canister (minimize tubing length)<sup>6</sup>; (iii) *Sorbent tube*: close valve at probe, disconnect tubing from pump, place sorbent in-line (minimize tubing length upstream of sorbent tube).
- 10. If multiple samples are required, allow vacuum to dissipate between collection of samples. Collect samples for different analyses in the same order using the same procedure.

### Screening Using Field Instruments:

- 1. Be aware of the capabilities and limitations of detectors when selecting field instruments and sample volume requirements (Table 3). Key points are:
  - a) Use appropriate detector for contaminant type. For chlorinated solvents, use photoionization detector (PID); for petroleum hydrocarbon generally use combustible gas detector (catalytic type) or flame ionization detector (FID).
  - b) Be aware of potential cross-sensitivity and bias. For example, infrared methane detector response is biased upward by other light hydrocarbons and solvents, and helium detector response is biased upward by methane. For infrared detectors, take readings with and without charcoal filter.
  - c) Calibrate and bump-test instruments in accordance with manufacturer's specifications. Keep calibration records in project files. Combustible gas detectors when used for petroleum hydrocarbon sites should generally be calibrated to hexane, and when used for landfill or similar sites should generally be calibrated to methane.
  - d) Combustible gas detectors (catalytic) are inaccurate at high hydrocarbon concentrations when concentrations approach and exceed the lower explosive limit of methane.
- 2. Use a new gas bag for each location or clean bag prior to re-use by filling the bag with ambient air and then emptying the contents of the bag three times. At the end of cleaning process, measure the air concentrations in the bag using the field detector. If the concentrations are not representative of ambient air, fill and empty the bag another three times. If the bag is still not clean after five cleaning cycles, discard the bag.
- 3. Collect soil gas samples in a 1-litre gas bag using a vacuum chamber to eliminate the potential for cross-contamination from the sampling pump.
- 4. Field readings from gas bags should be measured as soon as practical after collection (suggest within one hour) due to potential leakage and permeation (longer hold times are acceptable when submitting samples to the laboratory).

<sup>&</sup>lt;sup>6</sup> Collection of sample in gas-bag and in-field transfer to canister is acceptable provided that new un-used gas-bags and sample tubing are used and blanks are tested
Instrument	Compounds Detected	Potential Advantages	Potential Disadvantages
Detector Tubes	Aliphatics, aromatics, alcohols, inorganics ( <i>e.g.</i> , HCN, H <sub>2</sub> S)	Inexpensive Easy to use Immediate results Specific compounds can be detected (although may be cross- sensitivities)	Low sensitivity Cross-sensitivity to other compounds Affected by humidity, sample flow rate, temperature extremes Limited shelf life
Portable Photo- ionization Detector (PID)	Organic vapours, most sensitive to aromatics, somewhat less sensitive to aliphatics, does not detect methane, detects some inorganics (H <sub>2</sub> S, ammonia), response dependent on lamp energy	Relatively inexpensive Easy to use Rapid detector response Immediate results Can obtain intrinsically safe instruments	Low sensitivity (ppmV level), unless ppbV instrument used Non chemical specific Instrument response affected by humidity, cold temperatures (<0°C), dust and electrical currents (power lines) Biased low when CH <sub>4</sub> levels > about 1%
Portable Flame Ionization Detector (FID)	Organic vapours, most sensitive to aliphatics, somewhat less sensitive to aromatics, detects methane	Rapid detector response Measures a wide range of organic vapours including methane Less affected by humidity and dust than PIDs Some FIDs have lower detection limits than PIDs	Low sensitivity (ppmV level) Non chemical specific More operator training needed than PID, requires H <sub>2</sub> gas (may be shipping issues) Instrument response may be affected by wind and cold temperatures (<0°C) Inconsistent readings when low O <sub>2</sub> (< 15%) and high CO <sub>2</sub>
Explosi- meter	Platinum catalytic detector - Any flammable gas ( <i>e.g.</i> , methane) or vapour ( <i>e.g.</i> , gasoline)	Relatively inexpensive Rapid detector response Easy to use Responds to any flammable gas, less sensitive to environmental effects than PIDs and FIDs Generally range is 0.1 % to 100 % of LEL of methane or hexane, although ppmV instruments also available	Not intended for very low level analysis Non chemical specific Inaccurate readings when O <sub>2</sub> less than about 12% v/v (depending on instrument) Detector prone to aging, poisoning, moisture Inaccurate readings when combustible gas concentrations are high (approach or exceed the LEL of methane or hexane)
Multi-gas Detector for mixed gases	Infrared, electrochemical, galvanic detectors - Landfill gases such as CH <sub>4</sub> , H <sub>2</sub> S, CO <sub>2</sub> , O <sub>2</sub> Wide variety of options available	Easy to use, some instruments designed to sample against vacuum Rapid detector response Specific gases can be detected Infrared CH <sub>4</sub> detectors less prone to interference than catalytic type detectors, and cannot be poisoned	Low sensitivity (generally % level) May be cross sensitivities, for example, can be very significant positive bias in infrared methane concentrations when other light hydrocarbon or solvents are present Performance dependent on type of detector
Mercury meters	Mercury	Direct measurement device	Low sensitivity, <i>e.g.</i> , Ohio Lumex RA-915+ vapor Analyzer can detect Hg to 0.002 µg/m <sup>3</sup> , Jerome 431-X can detect to 3 µg/m <sup>3</sup>

# TABLE 3: Common Field Detectors for Soil Gas

Note: A field screening instrument recently introduced to the market is called a z-Nose<sup>TM</sup>, an "electronic nose" that utilizes a GC and surface acoustic wave (SAW) quartz microbalance to quantify individual chemicals to ppbV sensitivity.

### Sampling Using Sorbent Tubes:

 Determine the type of sorbent required, detection limits, pumps and quality control procedures and samples. The sample volume is a key parameter that is dependent on analyte and anticipated concentrations. It is often helpful to provide PID data to the laboratory and to then determine required sample volume in consultation with the laboratory. The sample volume should be sufficiently large to provide required detection limit but less than the safe sampling volume (SSV) for the sorbent to avoid breakthrough. The minimum sampling time to achieve a desired detection limit may be calculated as follows:

 $t_{sample} = 1000 * (DL_{lab}) / (DL_{desired} * Q)$ 

Where:

t<sub>sample</sub> = duration of sample in minutes

 $DL_{lab}$  = detection limit that can be achieved by laboratory in  $\mu g$ 

 $DL_{desired}$  = desired detection limit in  $\mu g/m^3$ 

Q = sampling flow rate in L/minute

- Calibrate pumps to desired flow rate using the type of sorbent tube that will be used. If two sorbent media are being used, samples are collected in parallel using Yconnections. Each side of the Y-connector must be calibrated separately for the specific sorbent tube used (see Figure 4).
- 3. Recharge the pumps fully prior to use and be aware of battery limitations as pumps used for sorbent sampling typically operate for a maximum of 8 hours on battery. If longer sampling durations are required, pumps may need to be plugged into an A/C power source<sup>7</sup>.
- 4. When samples are ready to be collected, for thermal tubes used for Method TO-17, remove caps from metal tube. For tubes used for NIOSH or OSHA methods, cut off the ends of the sorbent tube using a clean glass cutter. Cut the glass such that a 2 to 3 mm opening is created. Follow proper health and safety protocols while cutting the glass.
- 5. Connect the sorbent tube in-line between the probe and pump. Tubes used for Method TO-17 use Swage-lok connections. Tubes used for NIOSH and OSHA methods must be connected using flexible silicon tubing to create an air-tight seal. Butt sorbent tube to sample tubing such that there is minimal contact between soil gas and the silicon tubing. Since sorbent tubes typically have a front and back section, they must be connected in the correct direction (often the tubes have an arrow indicating the direction of flow). If using more than one type of sorbent tube in parallel, be sure that the sampling tubes are in the correct location, as each side of the splitter is calibrated separately to the tube being used.

<sup>&</sup>lt;sup>7</sup> Generators are not recommended as an AC Power Source due to potential air emissions.

- 6. Once the sorbent tubes have been connected to the probe, open the valves of the sampling train and turn on the pump. Record the exact start time and stop time of the sample collection, and record the pump identification number for each sorbent tube.
- 7. The pump flow rate must be checked in the field during sampling since flow rates vary depending on permeability of the soil. Use a mass flow meter or alternate instrument with accuracy within +/- 5 percent. The actual field flow rate should be used for calculation of concentrations.
- 8. After sampling is complete, stop the pump and close the valves. Disconnect the sorbent tubes and snuggly place an air-tight cap on each end of the sampling tube. Fill out label with pen (no Sharpies) and place label on tube<sup>8</sup>. As required, place tubes in a protective case to prevent breakage during shipping.
- 9. Field quality control samples should at a minimum consist of field duplicate samples and trip blanks. Sorbent tubes in series, distributed volume pair samples and equipment blanks may be required depending on project requirements.
  - i. **Field duplicates**: Samples are obtained using a splitter or Y-connector provided by the laboratory and certified as clean (tubes in parallel). The flow rate for each tube should be calibrated separately and should be approximately equal for each tube. Samples may also be collected successively; however, additional variability to the sampling process may be introduced.
  - ii. **Trip blanks:** Are obtained by opening the ends of sorbent tube for a short period of time (e.g., approximately 5 minutes), leaving the tube open to atmosphere, sealing the tube and transporting the trip blank with other samples being analyzed.
  - iii. Sorbent tubes in series: Chemical breakthrough of the sorbent is a significant potential problem for soil vapour due to humidity and often elevated concentrations. For NIOSH and OSHA methods, collection and analysis of the "front" and "back" of the sorbent tube is mandatory. If the concentration in the back tube exceeds 10% of the concentration in the front, breakthrough is considered to have occurred and generally results are not considered valid. For Method TO-17, there is no front and back of the tube, but two tubes may be collected in series. With Perkin Elmer SVI tubes, laboratories do not routinely recommend analysis of tubes in series and such testing is not required by the TO-17 method. Decision to test tubes in series is project specific decision, but should be conducted when higher level of quality control is warranted.
  - iv. **Distributed volume pairs:** The sample set-up is identical to duplicate analysis, except that samples are collected at different flow rates, intended to determine if breakthrough occurred (project specific decision).
  - v. **Equipment blanks:** Are mandatory if non-dedicated probes or sampling train are used and good practice if new materials are used (see above).

<sup>&</sup>lt;sup>8</sup> While not ideal, laboratories indicate that this does not affect analysis.

- vi. **Frequency**: Field duplicate and trip blanks are recommended at a frequency of one in ten samples. If the batch size is less than 10 samples, a field duplicate and trip blank should generally still be collected.
- 10. Submit samples under signed chain-of-custody.

### Sampling Using Summa (or Silco) Canisters:

- 1. Determine the type and volume of canister required, detection limits, flow controllers, quality control procedures and quality control samples. Several laboratories have developed helpful protocols for canister sampling.
- 2. The sampling rate is regulated by either mass flow controller or critical orifice. Mass flow controllers provide for a more uniform flow rate and should be used for sampling durations longer than two hours. Critical orifices provide for a less uniform rate and may be used for durations less than two hours (mass flow controllers are also acceptable for shorter durations). Communicate to laboratory the altitude and temperature under which sampling will occur because mass flow controllers are affected by pressure and temperature and may need to be adjusted as part of controller preparation. Some controllers or orifices come with a dedicated vacuum gauge; this is useful for monitoring the flow rate during sampling, which is proportional to the rate at which the vacuum drops.
- 3. Prior to sampling, check the canister vacuum by attaching a vacuum gauge to the top of the canister. An oil-filled vacuum gauge is typically provided by the laboratory but often accuracy of such gauges is poor. As required, bring more accurate hand-held digital manometer to field. Prior to connecting the gauge, double check that the control knob on the side of the canister is fully closed. Using a wrench, remove the valve cap on the top of the canister, and attach the gauge. When attached correctly, it should not be possible to turn the gauge assembly (follow the laboratory instructions for tightening). After taking the reading, close the control knob tightly, and disconnect the gauge.
- 4. Some laboratories provide a gauge that is attached to the flow controller. In this case, the sample collection begins at the same time as the vacuum is checked. Attach the canister to the soil gas probe prior to checking the vacuum. To check the vacuum, open the control knob and record the vacuum.
- 5. The canister vacuum should be between 27 and 30 inches mercury. As altitude increases, the vacuums measured will decrease. Typically, canisters with less than 27 inches mercury should not be used.
- 6. After checking the vacuum, attach the particulate filter and flow controller (unless it is attached to the vacuum gauge), also using a wrench. When attached correctly, it should not be possible to turn the flow controller assembly.
- 7. When ready to sample, connect the canister to the probe using air-tight fittings. Open the control knob on the side of the canister to begin sample collection, and record the start time of the sample collection.

- 8. After sampling is complete, check the vacuum again. There should be a residual vacuum left in the canister (ideally between 4 and 6 inches mercury). If there is no vacuum left in the canister at the end of the sampling process, the data is still considered valid (there is no mandatory minimum vacuum requirement in method TO-15); however, results should be flagged.
- 9. Fill out label with pen (no Sharpies) and attach label to canister.
- 10. The vacuum should be measured upon receipt by the laboratory. This data should be obtained and reported.
- 10. Field quality control samples should at a minimum consist of field duplicate samples. Field blanks and equipment blanks may be required depending on project requirements.
  - i. **Field duplicates**: Samples are obtained using a splitter or Y-connector provided by the laboratory and certified as clean. The splitter should be situated upstream of the canister (each canister should have a flow controller). Samples may also be collected successively; however, some additional variability to the sampling process may be introduced.
  - ii. **Field blanks:** A trip blank is not meaningful since canisters are supplied under vacuum. A field blank may be collected by filling a canister with ultra pure nitrogen from a second canister supplied by the laboratory using a short piece of clean Teflon® tubing. A field blank obtained in this way is another test of laboratory canister cleaning procedures and may be warranted depending on whether the laboratory is batch or individually certifying canisters as clean and level of quality assurance required for the project (project specific decision).
  - iii. **Equipment blanks:** Are required if non-dedicated probes or sampling train are used (see above).
  - iv. **Frequency**: Field duplicates are recommended at a frequency of one in ten samples. If the batch size is less than 10 samples, a field duplicate should generally still be collected.
- 11. Submit samples under signed chain-of-custody.

#### Storage and Handling of Soil Gas Samples:

- 1. Soil gas samples obtained using steel canisters, gas bags, glass cylinders or syringes should not be placed in a chilled cooler for transport since volatiles may condense out the vapour phase at lower temperatures. Samples should not be subjected to excessive heat.
- 2. Gas bags, glass cylinders and syringes should be placed inside a container immediately after collection to avoid possible photo-oxidation reactions.
- For sorbent tubes, cool storage (approximately 4°C) in sealed containers is required. Sorbent tubes should be stored in a sealed plastic container containing a bed of activated carbon to minimize the potential for adsorption of ambient VOCs and keep moisture away from tubes.

- 4. All soil gas samples should be transported in separate containers from soil and groundwater samples, and separate from pumps.
- 5. All soil gas samples should be submitted to the analytical laboratory under signed chain-of-custody. Additional requirements apply to "legal" samples.
- 6. Gas bag samples may be shipped by air but should only be filled approximately halffull to avoid problems with pressure changes. Confirm requirements with laboratory. Ground transport is preferable if holding times can be met.

### Ancillary Data:

- 1. Record qualitative weather conditions during sampling. This should include approximate temperature, sunshine, cloud cover, precipitation, wind (strong, moderate, slight), frost and snow cover. For subslab sampling, note the indoor temperature.
- 2. For cold weather or northern sampling, if possible, determine the depth of frost (or permafrost). It may be possible to estimate the depth to the frost line through test pits or installation of thermistors in soil gas probes. Sampling of soil gas from frozen ground will likely be non-representative.
- 3. Obtain weather data from a nearby meteorological station. Where feasible, obtain temperature, barometric pressure, wind speed and direction, and precipitation data from three days prior to sampling to one day after sampling (to determine trends in barometric pressure).
- 4. Note other site conditions that could influence soil gas data including ground surface cover near probe (*e.g.*, asphaltic pavement, concrete, condition of concrete, dirt, grass, etc.) and site remediation activities (*e.g.*, operation of soil venting, air sparging, oxidation, or groundwater pumping systems) or other possible emission sources.

### Documentation:

The soil gas sampling and analysis program should be documented on the Soil Gas Sampling Form (attached) and field note book. The information that should be recorded includes the sampler's name, date and time, type of probe sampled, leak tracer test results, flow rate and pressure data, purge volumes and sampling rate, field screening instruments used, pumps used, calibration data and ancillary described above. For canister sampling, the canister and flow controller identification number should be noted. Take photographs.

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- Hayes, H.C., D.J. Benton and N. Khan. 2006. Impact of Sampling Media on Soil Gas Measurements. AWMA "Vapor Intrusion – The Next Great Environmental Challenge", Philadelphia, PN, January 25-27.







FIGURE 4. Flow Rate Calibration of Sorbent Tubes (courtesy ALS, Vancouver, BC)



FIGURE 5. Soil Gas Sampling Kit (photo courtesy Golder Associates)

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FINAL DRAFT

#### Appendix I: Soil-Air Permeability Testing

Flow and vacuum measurements may be used to estimate the soil-air permeability using mathematical models for soil gas flow. Typically, the vacuum is measured for several different flow rates (*i.e.*, step test). For a small diameter, short probe (*e.g.*,  $\frac{1}{2}$  inch diameter, 6 inch long implant), a model for flow to a point (Garbesi *et al.*, 1996) may be used:

$$k = \mu Q / (S \Delta P_f)$$
[1]

For a larger, longer probe, a model for 1-D radial flow to a well (Johnson *et al.*, 1990) may be used:

$$Q = H^* \pi^* (k/\mu)^* P_p^* (1 - (P_{atm}/P_p)^2) / \ln(R_p/R_i))$$
[2]

Re-arranging Equation 2 for the soil-air permeability yields:

$$k = Q * \mu * ln(R_p/R_i) / [H * \pi * Pp * (1-(P_{atm}/P_p)^2)]$$
[3]

There are two unknowns in the above equation; the soil-air permeability and radius of influence for soil gas flow. Fortunately, equation 3 is not sensitive to the radius of influence. As a rough rule-of-thumb, the radius-of-influence can be set equal to the depth of the probe.

When there are higher pressures, soil gas flow is influenced by frictional losses at the pore walls, referred to as slip flow. There is an empirical correction, the Klinkenberg correction, which may be applied to correct for slip flow:

$$k = k_{cor} (1 + b / P)$$
 [4]

For small diameter tubes, frictional losses may be significant and should be factored in the above calculations. For example, for <sup>1</sup>/<sub>4</sub> inch tubing, frictional losses may become significant for flows greater than about 1 L/min. For 1 inch pipe, frictional losses will tend not to be significant at the flow rates commonly used for pneumatic testing of soil gas probes. Methods for estimating frictional losses can be found in textbooks or on-line tools (*e.g.*, <u>http://www.engineeringtoolbox.com/darcy-weisbach-equation-d 646.html</u>)

## Parameters

 $\begin{array}{l} \Delta P_{f} = \mbox{pressure difference between surface & probe tip (g/cm-sec^{2}) \\ S = \mbox{shape factor, for spherical pressure source, S = 4 $\pi$ r; $r$ = \mbox{probe radius (cm)} \\ k = \mbox{permeability (cm^{2})} \\ k_{cor} = \mbox{permeability corrected for Klinkenberg effect (cm^{2})} \\ \mu = \mbox{viscosity (g-cm/sec)} \\ R_{p} = \mbox{radius probe (cm)} \\ R_{i} = \mbox{radius influence (cm)} \\ P_{p} = \mbox{pressure probe (g/cm-sec^{2})} \\ Q = \mbox{flow (cm^{3}/sec)} \\ H = \mbox{height well screen (cm)} \\ P = \mbox{pressure (atm)} \\ b = \mbox{empirical correction factor (0.05)} \\ 1.013E6 \mbox{g/cm-sec}^{2} = 1 \mbox{atm} \end{array}$ 

## REFERENCES

- Garbesi, K., R. Sextro, A. Robinson, J. Wooley, J. Owens and W. Nazaroff. 1996. *Scale dependence of soil permeability to air: Measurement method and Field Investigation*. Water Resources Research, Vol. 32, No. 3, March, 1996.
- Johnson, P.C., C.C. Stanley, M.W. Kemblowski, D.L. Byers, and J.D. Colthart. 1990. *A practical approach to the design, operation, and monitoring of in-situ soil venting systems*, Ground Water Monit. Rev., 10(2), 159-178, 1990.

### Appendix II. Unit Conversions

Soil vapour analytical results are typically reported in units of either volume per volume (*e.g.*, parts per billion volume [ppbv]) and mass per volume (*e.g.*, micrograms per cubic meter [ug/m<sup>3</sup>]). The conversion of a gas concentration in ppbV units to ug/m<sup>3</sup> units is made assuming an ideal gas:

$$PV = nRT$$

where:

*P* [atm] = atmospheric pressure (1 atm)

V[L] = volume

n = moles of air

R [L-atm/mol-K] = universal gas constant = 0.0821

T [K] = standard temperature (273 K)

At standard temperature and pressure (*i.e.*, 273 K and 1 atm), one mole of air will occupy a volume equal to 22.4 litres. For a ppbV concentration, there will be one mole of chemical per 109 moles of air. The conversion for ppbV to  $ug/m^3$  is:

$$\left(C\frac{\mu g}{m^3}\right) = (C \ ppbv) \times \frac{1 \ mol \ COC}{10^9 \ mol \ air - ppbv} \times \frac{1 \ mol \ air}{22.4 L} \times \frac{273 \ K}{298 \ K} \times \frac{10^3 \ L}{1m^3} \times MW \ \frac{g}{mol \ COC} \times \frac{10^6 \ \mu g}{g}$$
$$\left(C\frac{\mu g}{m^3}\right) = (C \ ppbv) \times \frac{1}{22.4} \times \frac{273}{298} \times MW$$

The temperature commonly used for the above conversion is 20°C (293K) since this is the temperature at which laboratory testing is conducted. Therefore, substitute 293 (or relevant temperature) in place of 298 for above equation.

#### SUGGESTED OPERATING PROCEDURE NO. 3: SOIL GAS PROBE LEAK TESTS

- **SCOPE** The purpose of this suggesting operating procedure (SOP) is to provide a procedure for conducting leak testing of soil gas probes and sampling trains. Since there are different ways of soil gas sampling that provide for acceptable results, a range of options are provided. This SOP is based on and updates the SOP in Volume I of Health Canada *Guidance Manual for Environmental Site Characterisation in Support of Human Health Risk Assessment,* prepared by Golder Associates *(referred to as "Guidance Manual").* Note that reference to product brand names does not constitute endorsement of these products.
- **WHEN?** Leak testing should be conducted to test the seal of the soil gas probe to assess whether there is an introduction of atmospheric air into soil gas probes (referred to as "short-circuiting") and to test the connections of the sampling train.

A leak test of each new probe that is installed should be conducted. For each subsequent monitoring round, it is recommended that leak testing be conducted on a subset (*e.g.*, 10 to 20%) or all of probes to check that conditions have not changed. Leak tests should also be conducted when assessing the suitability of previously installed soil gas probes that may have been damaged over time.

A leak test of each sampling train should also be conducted on a regular basis by conducting a vacuum shut-in test.

- **WHY?** Depending on the depth and construction of the probe there may be the potential for short-circuiting of atmospheric air into soil gas probes, which can lead to dilution or contamination of the soil vapour sample. If probes are disturbed, the potential for short-circuiting may be increased. Although the leakage rate does not necessarily change with vacuum, if there are very high vacuums, leakage is potentially induced through openings created in the sampling train. For the above reasons, leak testing is an important part of the quality assurance and quality control (QA/QC) program for soil gas.
- **HOW?** Soil Gas Probe Seal: A leak test of a soil gas probe seal is performed by applying a tracer compound at the base of the probe (typically within a shroud) at ground surface and then analyzing a soil gas sample from the probe for the tracer compound. The leakage is defined as follows:

Leakage (%) = (Tracer conc. in soil gas / Tracer conc. in shroud) \* 100

When leakage is greater than an acceptable threshold (2% is recommended), the probe and/or sampling train should be repaired prior to sampling. For gaseous tracers (*e.g.*, helium), the starting concentration is the measured concentration under a shroud that is used to encapsulate the tracer gas (described below). For liquid tracers, the initial leak compound concentration is a theoretical estimate based on the vapour pressure of the compound at ambient temperature.

The two common types of tracers (gaseous and liquid) and basic test procedures are as follows:

- Enclosing the probe in a shroud filled with tracer gases (*e.g.*, propane, butane, helium or sulphur hexafluoride (SF<sub>6</sub>)); and
- Wrapping a towel soaked with a volatile liquid compound to the potential leaking areas (*e.g.*, 2-propanol (rubbing alcohol), pentane and freons).

The potential advantages of using a tracer gas such as helium and  $SF_6$  are that sensitive field instruments are available to enable real-time measurements in the field and direct quantification of potential leaks. There currently are advantages with using helium compared to  $SF_6$  since detectors are more readily available at lower cost. By using a shroud, the connection between the probe and sampling train can also be tested. The potential disadvantages are that the test is somewhat cumbersome to perform and may require certifications and/or training for transportation and use of gases. There may be trace VOCs associated with party-grade helium; however, ultra pure helium can be easily obtained, and the helium itself should not affect analysis for VOCs (*e.g.*, using USEPA Method TO-15), although the laboratory must be notified ahead of time if helium tracer tests are to be conducted at the same time as sample collection for laboratory analysis. The presence of chlorinated solvents in the soil gas sample may interfere with  $SF_6$  measurements.

The advantages of liquid tracers are that they are easy to apply and may be quantified to low levels using laboratory analysis (*e.g.*, USEPA Method TO-15). The potential disadvantages include: 1) this method is generally not amenable to obtaining real-time data (unless there is field laboratory with this capability); 2) there may be liquid permeation through very small cracks in the sampling train (a process that is different than gas migration); 3) care must be taken with handling with liquid tracers since small spills can cause cross-contamination, and 4) higher concentrations of the leak compound may interfere with analyses for other VOCs and result in raised detection limits. As a result of these disadvantages the use of liquid tracers is not recommended. Additional information on leak testing is provided in ITRC (2007), CRWQCB (2003) and Hartman (2007, 2002).

Since helium has a number of positive features for use as a tracer compound, a more detailed procedure for leak tracer testing using helium is provided in procedure section below.

**Sample Train Leak Test**: There are at least three ways in which the sampling train can be tested for leaks: (i) "shut-in" vacuum test, (ii) leak tracer line test, and (iii) application of a tracer compound to connections.

A shut-in test involves creating a vacuum in the sampling train and monitoring vacuum over time to confirm that the vacuum does not dissipate. The applied vacuum should be a minimum of 10 inch  $H_{20}$  water column. The decline in vacuum should generally be less than 5% over 5 minutes. If a pressure test is conducted, a soapy-water solution can be used to identify any couplings that may be leaking.

The leak tracer line test, described by API (2005), involves testing of sampling equipment for potential leaks using a tracer gas (*e.g.*, diluted helium) of known concentration that is drawn through the sampling equipment at the approximate vacuum anticipated during sampling.

Liquid tracers can be applied by wrapping a towel soaked in the tracer around the fitting or an aerosol product such as difluoroethane (*i.e.*, "Dust-off") can be sprayed over the fittings. The potential disadvantages of this method of testing the sampling train are the same as those described above with respect to testing the probe seal leak using liquid tracers.

## PROCEDURE

#### Leak Detection Test of a Soil Vapour Probe using Helium:

- 1. Construct a shroud for conducting the leak detection test. The shroud should consist of a rigid enclosure made of an inert material such as stainless steel or rigid plastic (*e.g.*, 10- to 20-litre pail) and should be large enough to sufficiently encapsulate and enclose the element being tested (*i.e.*, the probe and annulus, or the probe and sampling train fittings). There should be three small openings in the shroud: two at the top, one to place the sampling train through, and the other to use as a sampling port for measuring the helium concentration inside the shroud; and one near the bottom to be used for filling the shroud with the helium gas. As needed, a soft gasket may be placed around the bottom of the shroud to create a seal against the ground surface.
- 2. Obtain a pressurized canister of helium gas from reputable supplier (*e.g.*, Praxair, Air Liquide) with less than 0.5 ppmV total hydrocarbons. Obtain regulator for controlling the flow of the helium. Follow appropriate health and safety procedures when transporting and working with helium gas. Note that the transportation of pressurized canisters of helium falls under the Canadian Transportation of Dangerous Goods Regulation. Obtain a helium detector capable of measuring concentrations ranging from 0.01% (or less) to 100% (*e.g.*, Dielectric Technologies Model MGD-2002).
- 3. Place the shroud around the element to be tested and seal any significant openings in the test apparatus using inert sealing materials (*e.g.*, bentonite or Silly Putty®).
- 4. Slowly fill the shroud will helium gas until the concentration of helium within the shroud reaches 30 to 100% helium. Take caution to fill the shroud slowly and to not over-pressurize the enclosure. Stop the flow of helium once the concentration of helium in the shroud reaches the desired concentration. "Top up" helium as required during the test.
- 5. Purge the soil vapour probe being tested, and collect a soil vapour sample in a gas bag (e.g., Tedlar<sup>™</sup>). Measure the concentration of helium in the sample and calculate the Leakage as defined above. As a general rule, a Leakage less than 2% is considered to be acceptable. If the Leakage is greater than 2% repair or replace the probe.

#### Sample Train Leak Test Using API (2005) Method

The leak tracer line test, described by API (2005), involves testing of sampling equipment for potential leaks using a tracer gas (*e.g.*, diluted helium) of known concentration that is drawn through the sampling equipment at the approximate vacuum anticipated during sampling. The gas removed under vacuum at the end of the sampling train is tested for the tracer gas. If the measured gas concentration is less than the input concentration, leakage has occurred. The test requires the following equipment:

- Large bag (*i.e.*, 10 litre Tedlar<sup>™</sup>) filled with known concentration of helium;
- Small bags (*i.e.*, 1 litre Tedlar<sup>™</sup>) to take samples;
- Helium cylinder, pressure and flow regulator;

- Helium gas detector;
- Vacuum gauge, and
- Tubing and fittings.

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