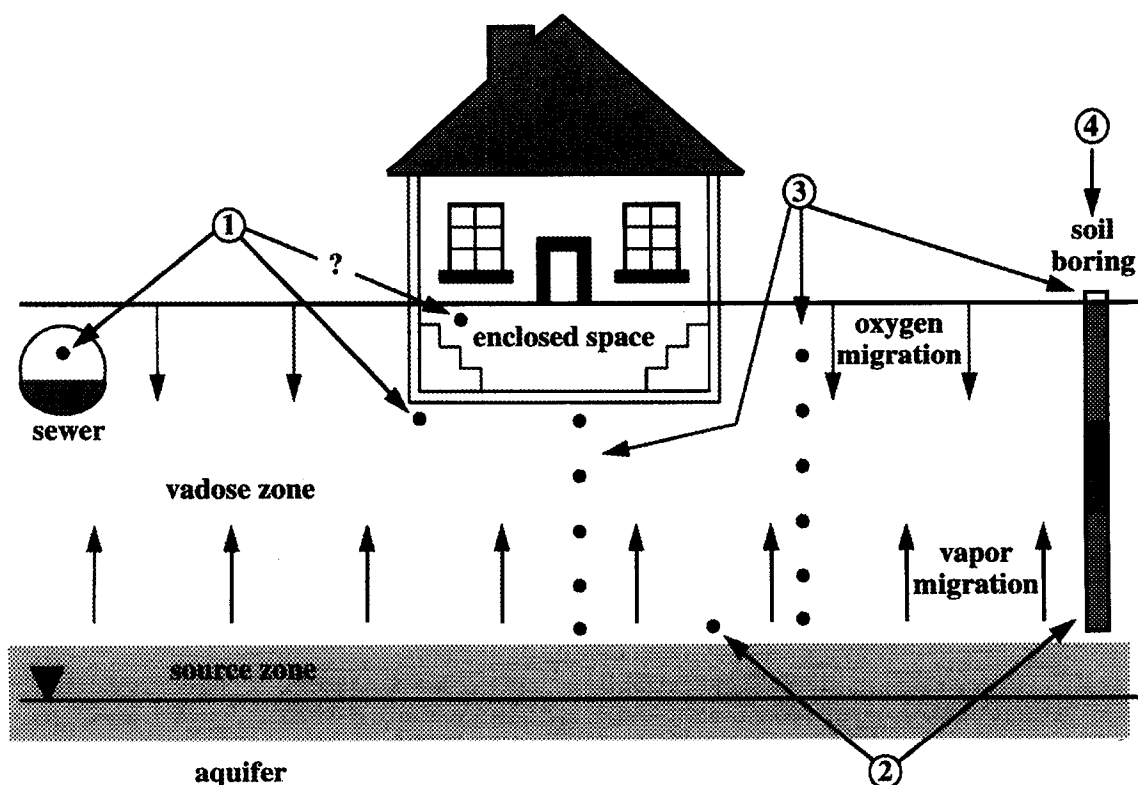
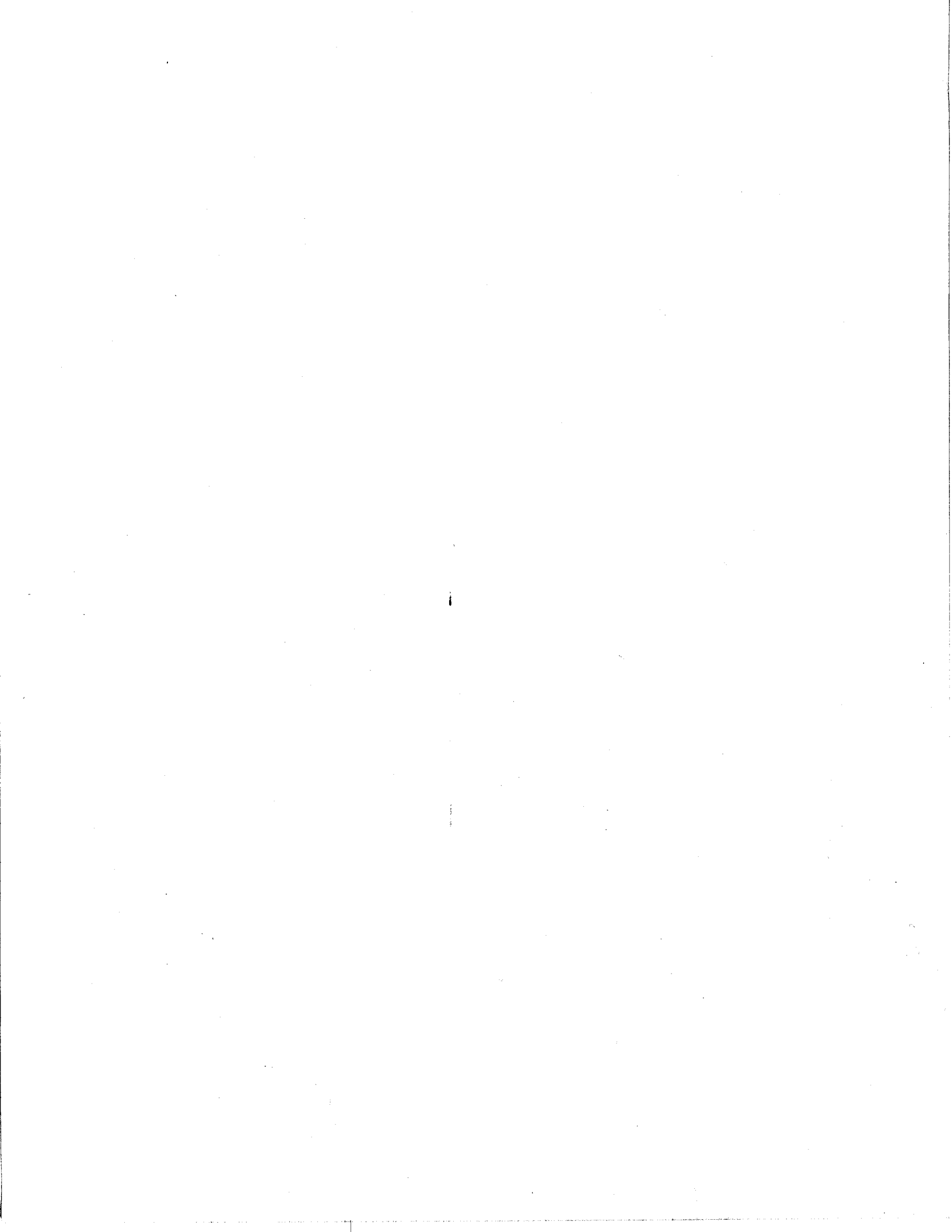


# ASSESSING THE SIGNIFICANCE OF SUBSURFACE CONTAMINANT VAPOR MIGRATION TO ENCLOSED SPACES

## SITE-SPECIFIC ALTERNATIVES TO GENERIC ESTIMATES

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT  
PUBLICATION NUMBER 4674  
DECEMBER 1998





# **Assessing the Significance of Subsurface Contaminant Vapor Migration to Enclosed Spaces**

## **Site-Specific Alternative to Generic Estimates**

**Health and Environmental Sciences Department**

API PUBLICATION NUMBER 4674

PREPARED UNDER CONTRACT BY:

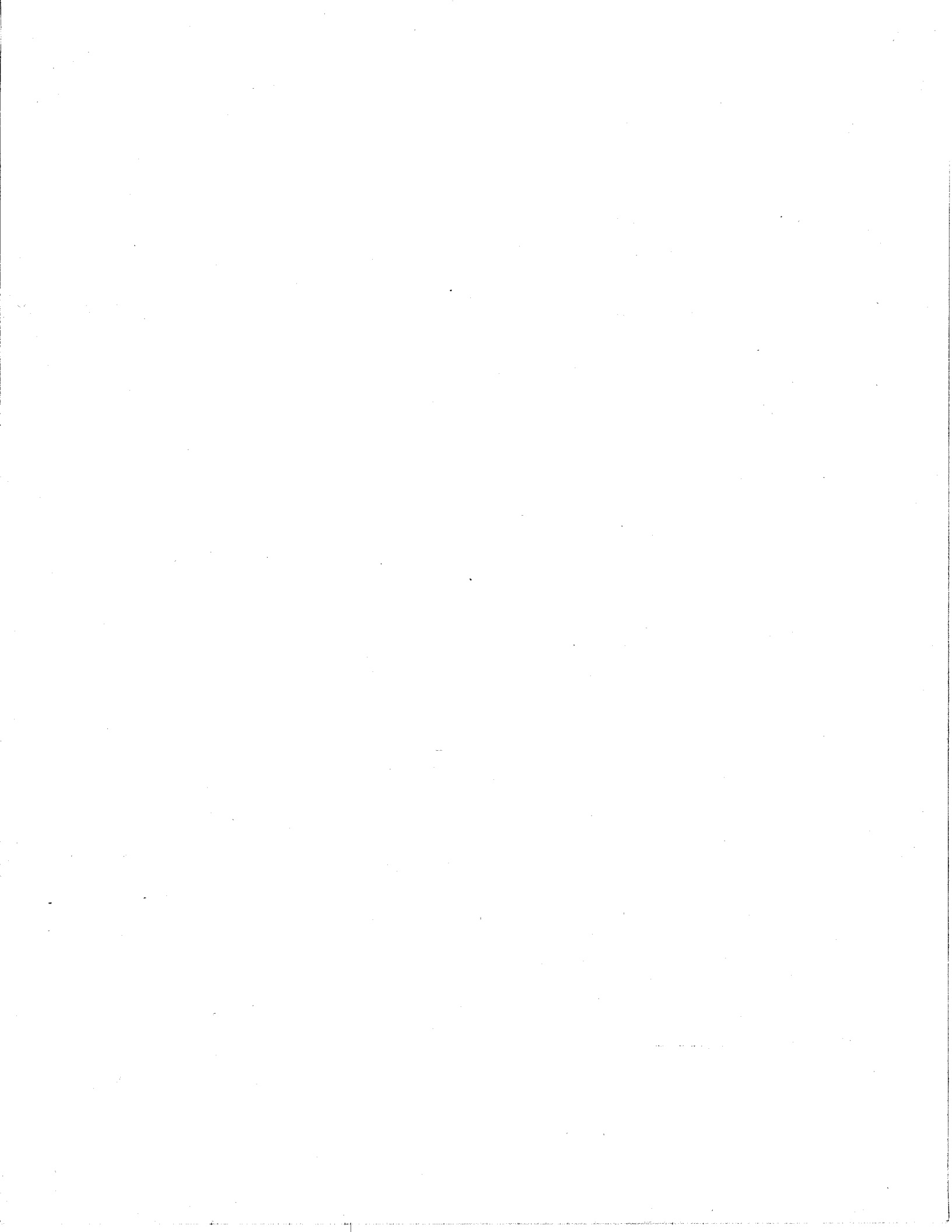
PAUL C. JOHNSON, PH.D.  
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING  
ARIZONA STATE UNIVERSITY

MARIUSH W. KEMBLOWSKI, PH.D.  
UTAH WATER RESEARCH LABORATORY  
UTAH STATE UNIVERSITY

RICHARD L. JOHNSON, PH.D.  
DEPARTMENT OF ENVIRONMENTAL SCIENCE AND ENGINEERING  
OREGON GRADUATE INSTITUTE

DECEMBER 1998





## FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

*All rights reserved. No part of this work may be reproduced, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the publisher, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005.*

Copyright © 1998 American Petroleum Institute



## **ACKNOWLEDGMENTS**

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

### API STAFF CONTACTS

Roger Claff, Health and Environmental Sciences Department  
Harley Hopkins, Health and Environmental Sciences Department

### MEMBERS OF THE VAPOR MIGRATION WORKGROUP

Phil Bartholomae, BP Oil Company  
Tim E. Buscheck, Chevron Research & Technology Company  
Chen Chiang, Shell Development Company  
George Duvall, Shell - Westhollow  
Lesley Hay Wilson, BP Oil Company  
Urmias Kelmser, Chevron Research & Technology Company  
Victor Kremesec, Amoco Corporation  
Tom Moldanato, Exxon Biomedical Sciences, Inc.  
Norm Novick, Mobil Business Resource Corporation  
R.E. Payne, Mobil Oil Corporation  
Tom Peargin, Chevron Research & Technology Company  
Joseph P. Salanitro, Shell Development Company  
Adolfo E. Silva, Petro-Canada, Inc.  
Curtis Stanley, Shell Development Company  
Tim Strawn, Exxon Biomedical Sciences, Inc.  
Terry Walden, BP Oil Company  
Andy Woerner, Exxon Research & Engineering  
Xiaoping Yang, Amoco Research Center





# Table of Contents

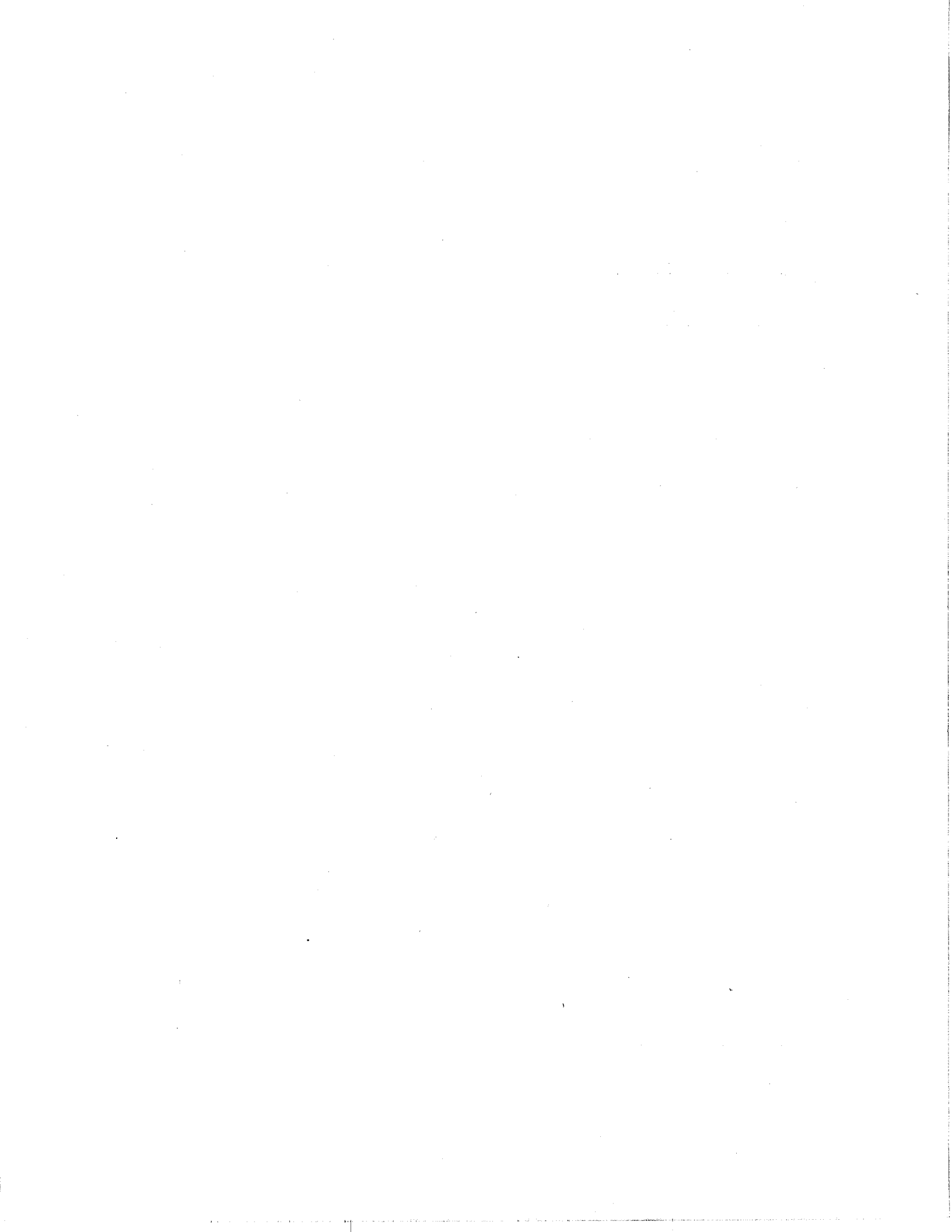
| <u>Section</u>   | <u>Page</u> |
|--|-------------|
| Executive Summary .....  | ES-1        |
| 1.0 Introduction.....  | 1           |
| 2.0 Current Approaches for the Development of Generic RBSLs.....                               | 3           |
| 3.0 Key Technical Considerations .....   | 7           |
| 4.0 Site-Specific Assessment of the Significance of Vapor Migration to<br>Enclosed Spaces..... | 9           |
| 4.1 Direct Measurement of Enclosed-Space Vapor Concentrations .....                            | 10          |
| 4.2 Use of Soil Gas Samples Collected Near-Surface or Near Foundation .....                    | 11          |
| 4.3 Use of Site-Specific Diffusion Coefficients in Generic RBSL Algorithms ....                | 12          |
| 4.4 Use and Interpretation of Soil Gas Data with Depth.....                                    | 14          |
| 4.5 Accounting for Attenuation Due to Biodegradation .....                                     | 16          |
| 4.6 Other Refinements.....   | 23          |
| 5.0 An Opportunity for the Future .....  | 23          |
| 6.0 References.....  | 27          |

## List of Figures

| <u>Figure</u> |   | <u>Page</u> |
|---------------|---|-------------|
| Figure 1      | Schematic of vapor migration scenario and sampling options .....  | 34          |
| Figure 2      | Johnson and Ettinger (1991) site-specific vapor attenuation coefficient $\alpha=(C_{\text{indoor}}/C_{\text{source}})$ estimate as a function of the overall effective vapor-phase porous media diffusion coefficient $D_T^{\text{eff}}$ and distance between the source and foundation $L_T$ ..... | 35          |
| Figure 3      | Estimated time for non-retarded chemicals to reach near steady vapor concentrations ( $\tau_{ss}/R_v$ ) at the distance $L$ from a source. For retarded compounds multiply the ( $\tau_{ss}/R_v$ ) value by the retardation factor $R_v$ defined in Equation (4).....                               | 36          |
| Figure 4      | Sample presentation using data from a) BP (1997) and b) Fischer <i>et al.</i> (1996).....   | 37          |
| Figure 5      | Vapor concentration data compared with predictions for one-dimensional transport through a layered system without degradation, using data from a) BP (1997) and b) Fischer <i>et al.</i> (1996).....  | 38          |
| Figure 6      | Normalized hydrocarbon and oxygen soil gas concentrations in a shallow near-homogeneous setting; data from Ostendorf and Kampbell (1991). Lines show expected concentration profiles in homogeneous settings at near steady conditions for no degradation, and first-order degradation.....         | 39          |
| Figure 7      | Predicted vapor concentration profiles for a homogeneous system at steady-state with a first-order reaction using Equation (8).....   | 40          |
| Figure 8      | Attenuation coefficient predicted by Equation (10) for the case of a homogeneous medium at steady-state with a first-order degradation reaction.....  | 41          |
| Figure 9      | Schematic of dominant layer model bio-attenuation scenario .....  | 42          |
| Figure 10     | Comparison of dominant layer model with data from Fischer <i>et al.</i> (1996).....   | 43          |
| Figure 11.    | Hypothetical plot showing conditions necessary for significant bio-attenuation .....  | 44          |

## List of Tables

| <u>Table</u> |   | <u>Page</u> |
|--------------|---|-------------|
| Table 1      | Refinement options and associated data collection and analysis needs.....   | 32          |
| Table 2      | Sample use of field data (data from BP 1997) to determine site-specific effective vapor-phase diffusion coefficients..... | 33          |
| Table 3      | Inputs used in generating Figure 10 using the dominant layer model.....   | 33          |



## **Executive Summary**

The move toward more structured risk-based corrective action (RBCA) approaches has led to an interest in better understanding vapor migration to enclosed spaces. The significance of this pathway is currently the subject of intense debate, with many believing that existing non-site-specific risk-based (“generic” or “Tier 1”) screening levels are too conservative. As little data are available to justify generic approaches, this pathway must be addressed on a more site-specific basis. This document provides options for addressing the vapor migration pathway on a more site-specific basis.

Vapors in enclosed spaces pose two levels of concern. First, enclosed-space vapors may be found at concentrations near those that pose immediate flammability and/or health risks. These sites warrant immediate attention and response as required by most state and federal regulatory guidance. In the second class of sites, concentrations are lower and the concern is for longer term health risks. This report focuses exclusively on this second class of sites, where advection and diffusion occur through a soil layer and into an enclosed space and time is available to adequately address the problem on a site-specific basis.

The options considered in this document for refining generic vapor migration calculations and assessing the significance of this pathway on a more site-specific basis include:

- a) direct measurement through sampling of enclosed-space vapors,
- b) use of near-foundation or near-surface soil gas sampling results,
- c) use of site-specific homogeneous and layered soil diffusion coefficient estimates in generic algorithms, and
- d) assessment of bio-attenuation potential.

Data requirements, data presentation, and data interpretation are discussed and illustrated for each option. As discussed in the document, it is envisioned that options (c) and (d) will be used much more often than options (a) and (b) for the assessment of longer term impacts, due to a variety of technical and practical considerations.

Also, a vision for a simpler site-specific assessment approach is presented and accompanied by a discussion of the steps necessary to progress toward that goal. This improved approach considers bio-attenuation, but requires only soil moisture content measurements, or alternatively, in-situ diffusion coefficient measurements, to screen sites.

## 1.0 INTRODUCTION

When soils are impacted by leaks or spills, or wastes are placed in impoundments, the potential exists for contaminant vapor migration to enclosed spaces (buildings, conduits, etc.) and leachate migration to groundwater. Regulations have historically considered the leachate impacts on groundwater; however, the issue of vapor migration has only recently been formally and quantitatively considered. This focus has been brought about in large part by the move toward more structured risk-based corrective action (RBCA) approaches (e.g., ASTM 1995), coupled with an increased awareness of this pathway.

The significance of the vapor intrusion pathway and natural attenuation of vapors in the vadose zone is currently the subject of intense debate. When common screening-level algorithms (e.g., Johnson and Ettinger 1991, Little *et al.* 1992) are combined with conservative soil properties, geometries, and exposure assumptions, the resulting risk-based screening levels (RBSLs) are very low. In fact they are often one-tenth to one-thousandth the existing cleanup guidelines in many states. For example, the sample calculation in the ASTM RBCA Standard (ASTM, 1995) suggests that benzene concentrations in excess of 5  $\mu\text{g}/\text{kg}$ -soil could be of concern if one wishes to be protective to a  $10^{-6}$  excess cancer risk level.

Many intuitively feel that the current generation of screening-level predictive models is too conservative and leads to unnecessarily low cleanup levels. Some point to the fact that the algorithms generally do not account for biodegradation and other possible vadose zone attenuation mechanisms. It is reasonable to expect that some chemicals of interest degrade as they migrate, especially those originating from petroleum spills (e.g., benzene). If this is true, then these chemicals should be found at concentrations much less than those predicted by the current generation of screening level algorithms. This hypothesis is supported to some degree by the Fitzpatrick and Fitzgerald (1997) Massachusetts indoor air survey, the data of Fischer *et al.* (1996), and others who have observed and reported on petroleum hydrocarbon biodegradation in the vadose zone under natural conditions (e.g., Ostendorf and Kampbell 1991).

Unfortunately, little data exist to refute or support existing algorithms, or to quantify the degree of over-conservatism. This lack of data is a result of many factors, including the fact that interest in this pathway is relatively new. From a comparison of model predictions with published radon intrusion data, Johnson *et al.* (1991) and Little *et al.*

(1992) conclude that the screening algorithms should predict reasonable results when contaminants are present in soil gas immediately adjacent to a basement (e.g., Nazaroff *et al.* 1987). Yet to be reported are rigorous comparisons of model predictions and measurements for well-characterized sites where the contaminant sources are located at a distance from the buildings. Recently, Fitzpatrick and Fitzgerald (1997) presented their conclusions from a study of Massachusetts sites where indoor air samples were collected. Their goal was to review site characteristics and then identify specific trends and field conditions that most influence vapor migration and vapor intrusion into buildings. They also were interested in assessing the validity of generic state guidance derived from use of the Johnson and Ettinger (1991) algorithm. In summary, they noted that the generic Massachusetts guidelines overestimated vapor intrusion impacts for petroleum fuel hydrocarbon sites; however, they also found that the generic screening guidelines sometimes under-predicted indoor concentrations at sites where chlorinated organic vapors were present. Contrary to the popular belief that the models are overly conservative, the authors concluded that the generic Massachusetts guidelines were not conservative enough for site screening purposes, at least for chlorinated compound sites.

Given limited data and limited understanding, the potential for high sensitivity to site-specific conditions, and the tendency to lean toward conservativeness when developing regulations, it seems unlikely that technically defensible alternatives for developing generic screening levels will surface in the near-term. The inevitable consequence is that many sites containing volatile carcinogens are unlikely to satisfy generic RBSLs for this pathway. Thus, this pathway will need to be addressed on a more site-specific basis, and options are needed to ensure that this is done in a technically defensible manner. Some state-level regulatory agencies are already struggling with developing site-specific guidance for assessing this pathway.

In answer to this need, options for addressing the vapor migration pathway on a more site-specific basis are proposed here. These include more refined use of existing screening algorithms for layered geologic settings, as well as use of updated algorithms that consider biodegradation. These options stem from consideration of available data, existing algorithms, theoretical considerations, and empirical experience (Jury *et al.* 1983, Kampbell *et al.* 1987, Nazaroff *et al.* 1987, Garbesi and Sextro 1989, Jury *et al.* 1990, Johnson *et al.* 1990, Loueiro *et al.* 1990, Ostendorf and Kampbell 1990, Johnson and Ettinger 1991, Johnson and Perrot 1991, Hodgson *et al.* 1992, Little *et al.* 1992, Unlu *et al.* 1992, Ostendorf 1993, Jin 1994, Acomb *et al.* 1996, Auer *et al.* 1996, Fischer *et al.*



1996, Jeng et al .1996, Lahvis and Baehr 1996, Smith *et al.* 1996, Uchrin 1996, BP 1997, DeVauil *et al.* 1997, Li 1997, Sextro 1997, Stout 1997). The data collection and data reduction activities can easily be arranged in a sequence of increasing complexity, increasing data requirements, and likely increasing cost. Whether or not this approach is reasonable and defensible can only be determined by application to actual field sites followed by review of the results and experiences. It is recognized that with application, knowledge will continue to grow, and opinions and recommended practices are likely to evolve and become refined over the next few years.

In order to provide insight to the technical challenges, the reader is first provided an introduction to current approaches for developing generic risk-based screening levels, and a discussion of other technical considerations important to the development of the options described here. This is followed by the proposed array of options for assessing the significance of the vapor intrusion pathway on a more site-specific basis. At the end of this report, a vision for a much simpler site-specific assessment is presented and accompanied by a discussion of the developments necessary to progress toward that goal.

## 2.0 CURRENT APPROACHES FOR DEVELOPMENT OF GENERIC RBSLs

For reference, Figure 1 presents a conceptual model of the situation of interest. The concern here is the potential for adverse impacts due to contaminant vapors emanating from vadose zone soils, impacted capillary fringe soils, or dissolved chemicals in groundwater.

Incidence of vapors in enclosed spaces fall into two major classes. In one class, enclosed-space vapors are found at concentrations near those that could cause immediate impacts (e.g., fire, explosion, acute health risks, etc.). This is most often due to a direct or highly permeable connection (e.g., electrical conduit, gasoline entering a sewer, etc.) between a flammable liquid/vapor and the enclosed space. This class of sites deserves immediate attention and response as required by most state and federal regulatory guidance. In the second class of sites, the concern is with diffusion and advection from the vapor source through a soil layer and into an enclosed space. This report focuses exclusively on this second class of sites, where the concern is for longer term health effects and time is available to adequately address the problem on a more site-specific basis.

Screening level algorithms for the vapor intrusion pathway (Johnson and Ettinger 1991, Little *et al.* 1992, Johnson and Kemplowski 1998) couple source zone partitioning, vadose zone transport, building foundation transport, and enclosed-space mixing algorithms. The resulting algorithms then depend on parameters related to soil, chemical, and building characteristics. ASTM (1995), USEPA (1996), and some state regulatory agencies have used the Johnson and Ettinger (1991) algorithm to relate the estimated indoor vapor concentration  $C_{\text{indoor}}$  [ $\text{mg}/\text{m}^3$ ] to the source zone vapor concentration  $C_{\text{source}}$  [ $\text{mg}/\text{m}^3$ ]:

$$\alpha = \frac{C_{\text{indoor}}}{C_{\text{source}}} = \frac{\left[ \frac{D_T^{\text{eff}} A_B}{Q_B L_T} \right] \exp\left( \frac{Q_{\text{soil}} L_{\text{crack}}}{D_{\text{crack}}^{\text{eff}} \eta A_B} \right)}{\exp\left( \frac{Q_{\text{soil}} L_{\text{crack}}}{D_{\text{crack}}^{\text{eff}} \eta A_B} \right) + \left[ \frac{D_T^{\text{eff}} A_B}{Q_B L_T} \right] + \left[ \frac{D_T^{\text{eff}} A_B}{Q_{\text{soil}} L_T} \right] \left( \exp\left( \frac{Q_{\text{soil}} L_{\text{crack}}}{D_{\text{crack}}^{\text{eff}} \eta A_B} \right) - 1 \right)} \quad (1)$$

Here  $\alpha$  is the vapor attenuation coefficient, and:

- $A_B$  = surface area of enclosed space in contact with soil [ $\text{m}^2$ ]
- $D_{\text{crack}}^{\text{eff}}$  = effective overall vapor-phase diffusion coefficient through the walls and foundation cracks [ $\text{m}^2/\text{d}$ ]
- $D_T^{\text{eff}}$  = effective overall vapor-phase diffusion coefficient between the source and foundation [ $\text{m}^2/\text{d}$ ]
- $L_{\text{crack}}$  = thickness of enclosed space walls and foundation [ $\text{m}$ ]
- $L_T$  = source - foundation separation [ $\text{m}$ ]
- $Q_B$  = enclosed space air exchange rate [ $\text{m}^3/\text{d}$ ]
- $Q_{\text{soil}}$  = soil gas flow rate into enclosed space due to under-pressurization [ $\text{m}^3/\text{d}$ ]
- $\eta$  = fraction of enclosed space surface area open for vapor intrusion [ $\text{m}^2/\text{m}^2$ ]

Johnson and Ettinger (1991) discuss in detail the development of this equation, the significance of each parameter grouping, and the results for certain limiting cases. In brief, diffusion through the soil and foundation is characterized by the parameters  $D_T^{\text{eff}}$ ,  $L_T$ ,  $D_{\text{crack}}^{\text{eff}}$ ,  $L_{\text{crack}}$ ,  $A_B$ , and  $\eta$ . Advective flow of vapors from the soil, through the

foundation, and into the building is characterized by  $Q_{\text{soil}}$ ,  $A_B$ , and  $\eta$ , and mixing within the enclosed space is characterized by  $Q_B$  and  $A_B$ .

The effective porous media overall vapor-phase diffusion coefficients are generally determined from the Millington-Quirk formulation (Millington 1959, Millington and Quirk 1961, Millington and Shearer 1971):

$$D^{\text{eff}} = D^{\text{air}} \frac{\theta_v^{3.33}}{\theta_T^2} + \left( \frac{D^{\text{H}_2\text{O}}}{H_i} \right) \frac{\theta_m^{3.33}}{\theta_T^2} \quad (2)$$

where:

- $H_i$  = Henry's Law constant [(mg/m<sup>3</sup>-vapor)/(mg/m<sup>3</sup>-H<sub>2</sub>O)]
- $\theta_m$  = volumetric moisture content [m<sup>3</sup>-H<sub>2</sub>O/m<sup>3</sup>-soil]
- $\theta_T$  = total porosity [m<sup>3</sup>-voids/m<sup>3</sup>-soil]
- $\theta_v$  = volumetric vapor content [m<sup>3</sup>-vapor/m<sup>3</sup>-soil]
- $D^{\text{air}}$  = molecular diffusion coefficient in air [m<sup>2</sup>/d]
- $D^{\text{H}_2\text{O}}$  = molecular diffusion coefficient in water [m<sup>2</sup>/d]

For reference, molecular diffusion coefficients in air for most petroleum fuel compounds range from 0.05 - 0.10 cm<sup>2</sup>/s (0.4 - 0.9 m<sup>2</sup>/d); molecular diffusion coefficients in water are roughly 1/10000 of molecular diffusion coefficients in air. USEPA (1996) tabulates relevant chemical properties such as  $D^{\text{air}}$  and  $D^{\text{water}}$  for many chemicals of interest. Total porosity varies roughly between 0.35 and 0.45 for most soil types; in many well-drained sandy soils,  $\theta_m < \theta_T / 5$ ,  $\theta_m$  can approach  $\theta_T / 2$  in clayey soils, and  $\theta_m$  approaches  $\theta_T$  as depth increases through the capillary fringe to groundwater. More information on the parameterization of moisture levels through unsaturated soils and the capillary fringe in various soil types is presented in Guymon (1994).

In typical RBSL calculations, the source zone vapor concentration  $C_{\text{source}}$  [mg/m<sup>3</sup>] is often assumed to be related to the source zone total soil concentration  $C_T$  [mg/kg-soil], assuming a single-component, linear-partitioning relationships, and three-phase equilibrium (vapor, sorbed, dissolved phases):

$$C_T = \frac{C_{\text{source}} \theta_v}{\rho_b} \left[ 1 + \frac{\theta_m}{\theta_v H_i} + \frac{\rho_b K_s}{\theta_v H_i} \right] = \frac{C_{\text{source}} \theta_v}{\rho_b} R_v \quad (3)$$

where:

$K_s$  = soil sorption coefficient [(mg/kg-soil)/(mg/m<sup>3</sup>-H<sub>2</sub>O)]

$R_v$  = soil vapor retardation factor [unitless]

$\rho_b$  = soil bulk density [kg-soil/m<sup>3</sup>-soil]

While this expression is used frequently, it is not appropriate for cases where an immiscible phase is present (e.g., residual hydrocarbon source zones). In those cases the partitioning calculations are much more complex and generally nonlinear (Johnson *et al.* 1990). At high residual soil concentration levels (typically >500 mg/kg total hydrocarbons for gasoline; see Johnson *et al.* 1990), the partitioning is better approximated by Raoult's Law. Equation (3) may over- or under-predict the vapor concentration calculated using Raoult's Law.

As an example of the use of Equation (1), Figure 2 presents  $\alpha$  vs.  $D_T^{\text{eff}}/L_T$  for the following reasonable parameter values:

$A_B$  = 50 m<sup>2</sup>

$Q_B$  = 1200 m<sup>3</sup>/d (12 air changes per day in 100 m<sup>3</sup> enclosed space)

$Q_{\text{soil}}$  = 1.5 m<sup>3</sup>/d (=1 L/min)

$L_{\text{crack}}$  = 0.15 m

$D_{\text{crack}}$  = 0.1 m<sup>2</sup>/d (cracks filled with well-drained sandy soil; note - the results are not sensitive to reasonable changes in this parameter for these conditions)

$\eta$  = 0.001 m<sup>2</sup>/m<sup>2</sup> (note - the results are not sensitive to reasonable changes in this parameter for these conditions)

This graph allows examination of changes in attenuation with changes in distance from source ( $L_T$ ) and effective diffusion coefficient ( $D_T^{\text{eff}}$ ). For reference, moving along the x-axis in the direction of increasing  $D_T^{\text{eff}}/L_T$  corresponds to moving a source closer to the enclosed space, or alternatively, to increasing the effective diffusion coefficient (e.g., when decreasing the moisture content). As can be seen, no matter where the source is placed, or what the soil properties are,  $\alpha < 10^{-3}$ . The upper asymptote of  $\alpha = 10^{-3}$  corresponds to the case where sources are very close to buildings, transport is controlled by advection through the foundation, and attenuation is due solely to dilution by mixing

within the enclosed space (e.g., radon intrusion). Below  $D_T^{\text{eff}}/L_T=0.1$  m/d,  $\alpha$  is sensitive to changes in moisture content and distance from the source to the enclosed space. For  $Q_{\text{soil}}$  values in this range, it can be shown that the results in Figure 2 are not sensitive to changes in  $\eta$  or  $D_{\text{crack}}^{\text{eff}}$ , within a reasonable range of  $\eta$  and  $D_{\text{crack}}^{\text{eff}}$  values.

Due to this sensitivity to soil moisture content and distance from the source, and the potential for a wide range of conditions to be encountered in practice, generic calculations are often biased toward relatively close sources and well-drained sandy soils. Thus,  $\alpha$  ranges from  $10^{-4}$  to  $10^{-3}$  in most generic RBSL developments.

These results also point toward a practical opportunity for improving the generic RBSL screening process. Rather than entailing the calculation of a single attenuation factor for the most conservative geometry and soil type, the RBSL process might employ a table of values or a contour plot for a range of possible source distances and soil types.

Johnson and Ettinger (1991) also show how to account for depleting sources; although, this option has not often been used by those developing generic RBSLs. This may be attributed to the fact that users must also define a generic source zone thickness. The impact of considering depleting sources is more significant for carcinogenic compounds, as exposure to these compounds is averaged over a longer period of time (often 30 y) than for noncarcinogens (often 7 years or less).

### 3.0 KEY TECHNICAL CONSIDERATIONS

Factors not typically considered in generic RBSL development include: a range of soil types, layered stratigraphies, biodegradation of contaminants, and depleting sources. Any, or all of these can be considered when assessing the significance of the vapor intrusion pathway on a site-specific basis. Also, as shown in Figure 1, there are a myriad of site-specific sampling options. The following technical considerations play an important role in the selection of site-specific data collection and analysis options presented below:

- the options should rely upon measurements that are easily integrated into typical site assessments; placing an emphasis on using soil cores, soil moisture, and soil gas measurements.

- for reasons discussed above (see discussion associated with Equation (3)), methods that do not rely on soil vapor - soil contamination partitioning calculations are preferred; thus, emphasis is placed on use of soil gas measurements.
- given current site assessment practices and tools, it is difficult to define source zone masses with any reasonable accuracy. Considering depleting sources on a site-specific basis is not typically a practicable option, although it could be considered in developing generic RBSLs as discussed above.
- the time required for vapors to reach near-steady concentrations at any point increases with the square of the distance from the source and also is affected by the chemical properties of the compound of interest. In addition, the presence or absence of surface barriers (pavement, buildings, etc.) can affect near surface vapor concentrations. In making decisions involving potential future impacts, some emphasis is placed on soil gas measurements near the source rather than measurements near the surface or enclosed-space.

An estimate of the time  $\tau_{ss}$  [d] required to reach near-steady vapor concentrations and fluxes at any distance  $L$  [m] from a source is:

$$\tau_{ss} \approx > \frac{R_v \theta_v L^2}{D_v^{eff}} \quad (4)$$

where all quantities are as defined above with  $R_v$ , the vapor-phase retardation factor, given by Equation (3). Equation (4) is derived from solutions to transient diffusion problems (Crank 1956) with step-change boundary conditions imposed at zero time. Figure 3 presents calculated  $\tau_{ss}/R_v$  values for a range of soil moisture contents and:

$$\begin{aligned} D^{air} &= 0.09 \text{ cm}^2/\text{s} (= 0.78 \text{ m}^2/\text{d}) \\ D^{H_2O} &= 1 \times 10^{-5} \text{ cm}^2/\text{s} (= 8.6 \times 10^{-5} \text{ m}^2/\text{d}) \\ \theta_T &= 0.35 \text{ m}^3\text{-voids}/\text{m}^3\text{-soil} \\ H_i &= 0.2 \text{ (mg}/\text{m}^3\text{-vapor)}/(\text{mg}/\text{m}^3\text{-H}_2\text{O}) \end{aligned}$$

For reference, the chemicals most likely to cause exceedences of flammable levels ( $C_{\text{indoor}} > 1\% \text{ v/v}$ ) at fuel release sites will have retardation factors close to unity (e.g., propanes, butanes, pentanes). Oxygen will move relatively unretarded (high Henry's Law constant, and low sorption), and chemicals most often of concern from health considerations (e.g., benzene) will have vapor-phase retardation factors on the order of  $10 < R < 100$ . Thus, different chemicals will approach near-steady concentrations at different times.

Figure 3 again emphasizes that soil gas hydrocarbon concentrations closer to the source zone reach near-steady values relatively quickly (hours - days); those several meters away may require years or decades to reach near-steady conditions as  $\tau_{\text{ss}}$  increases with the square of the distance from the source. Analyses that consider chemical reactions show that near-steady conditions can be reached faster than shown in Figure 3, when significant degradation rates occur and steady state conditions at a given distance from the source are reached at much lower concentrations. Significant advection will also decrease the time to reach near steady conditions, as might be the case if pressure-driven vapor flow occurs along or within a permeable conduit.

The major conclusions here are that soil gas concentrations measured near a source will, in most cases, be representative of near-steady conditions; meanwhile, near-surface concentrations or soil gas concentrations measured several meters from a source may or may not be representative of near-steady conditions. Thus, the reader is cautioned that site-specific assessment relying on indoor (§4.1), near-surface and near-foundation (§4.2) soil gas concentrations, or soil gas concentrations measured several meters from a source (§4.5) should only be used when one is confident that the time since the release exceeds the Equation 4 estimate of the time to reach near-steady conditions. Site-specific assessment using soil gas concentrations measured near the source is always an option, provided that the user has an understanding of the subsurface geology between the source and enclosed space (§4.3).

#### 4.0 SITE-SPECIFIC ASSESSMENT OF THE SIGNIFICANCE OF VAPOR MIGRATION TO ENCLOSED SPACES

It is assumed that situations requiring emergency response have been addressed, site conditions have already been compared against generic risk-based screening levels, and exceedences have been noted. Therefore, a more site-specific assessment of future and long-term impacts is desired.

As discussed above, generic RBSLs often assume a vadose zone that is homogenous, sandy, and relatively dry. Furthermore, biodegradation is neglected and the vapor source is assumed constant with time. Thus, on a site-specific basis, one might assess the potential for increased attenuation (relative to the generic RBSL case) due to: a) layered strata, b) higher moisture contents, c) biodegradation in the vadose zone, and d) source depletion with time. One might also elect to pursue direct measurement of enclosed-space concentrations or near-foundation soil gas measurements.

In the following, this range of options is discussed. Direct enclosed-space measurement is discussed in §4.1 and near-foundation measurements are discussed in §4.2. Factors that decrease the potential for vapor migration impacts, relative to typical regulatory generic base cases, are considered in §4.3 - §4.5. Increased diffusion resistance is discussed in §4.3, the use of soil gas concentrations with depth to guide refined analyses are discussed in §4.4, and the incorporation of vadose zone biodegradation in the analysis is addressed in §4.5. Source depletion is discussed briefly in §4.6.

Table 1 summarizes the options and data collection requirements for each.

#### 4.1 Direct Measurement of Enclosed-Space Vapor Concentrations

Whenever it is suspected that explosions, fires, or acute health impacts might occur, vapor samples are quickly collected from the enclosed space or building. Use of this same direct measurement approach for the more refined site-specific assessments of future and long-term impacts, however, is envisioned to be more limited. Obtaining vapor samples from enclosed spaces and interpreting the results involve a host of complex issues and sensitivities. For example, there may be alternate indoor vapor sources already within the enclosed space. Also sampling occupied buildings or residences often causes unnecessary emotional stress to the occupants. For these considerations alone, unless other data (odors, flammable sub-foundation vapor concentrations, etc.) suggest a short-term threat, direct collection of indoor vapor samples is generally not preferred. Guidance on considerations for indoor air sampling is given in USEPA (1992). Some of the complications and interferences of indoor air sampling are covered in a series of Total Exposure Assessment Methodology (TEAM) studies undertaken by USEPA (1987).



There is also the issue discussed in the previous section concerning whether or not the current vapor concentrations are representative of long-term conditions. Enough time may not have passed to ensure near-steady conditions; moreover, the concentrations may be affected by other dynamic processes (e.g., seasonal changes in soil conditions).

In addition, many site-specific assessments will involve sites where a building or enclosed space does not currently exist, and the concern is for impacts under reasonable potential future scenarios.

Therefore, as stated above, this option is envisioned to be of limited use when making more refined site-specific assessments of potential impacts from vapor migration to enclosed spaces.

#### 4.2 Use of Soil Gas Samples Collected Near Surface, or Near the Foundation of the Enclosed Space

Near surface and sub-foundation sampling is an option that is attractive for two primary reasons. First, obtaining samples is relatively straightforward and vapor sampling probes can often be driven to depth by hand, or with hand-operated power tools. Second, data analysis generally does not require additional characterization of the subsurface, nor does it rely on prediction of vapor transport through the subsurface between the source and enclosed-space foundation. For example, using Figure 2, one can estimate near-term indoor concentrations from sub-foundation measurements:

$$C_{\text{indoor}} \approx \frac{C_{\text{soil gas}}}{1000} \quad (5)$$

where  $C_{\text{soil gas}}$  [ $\text{mg}/\text{m}^3$ ] is the chemical concentration in soil gas immediately adjacent to the basement wall or foundation. This estimate is specific to the inputs defined previously above, but it is consistent with published data from field studies focused on the relationships between concentrations of radon in soil gas and indoor radon concentrations (Nazaroff 1987). For enclosed spaces with less air circulation, the resulting indoor concentrations could be greater.

As in the case of direct indoor measurement, it should be noted that there are also serious limitations to this approach, mainly:

- Near-surface soil gas measurements are more prone to sampling errors (short-circuiting along the sampling probes).
- Surface barriers (pavement, buildings, or lack thereof) can affect near-surface vapor concentrations. For example, near-surface measurements made at open surface sites are unlikely to be representative of near-surface soil gas concentrations under buildings (e.g., see BP 1997). In contrast, vapor concentrations at depths near the source are not affected significantly by the surface conditions.
- It is possible that not enough time has passed since the release for near-steady soil gas concentrations to be achieved near the surface as discussed above.

#### 4.3 Use of Site-Specific Diffusion Coefficients in the Generic RBSL Algorithms

In this simple refinement option, algorithms employed in generating generic RBSLs are used; however, generic effective diffusion coefficients, soil types, moisture contents, and source-receptor distances are replaced with values more representative of the site under consideration. In this case the data required for generating a conservative site-specific indoor air concentration estimate include:

- the source zone vapor concentration, and
- the location, thickness, and moisture content of all subsurface strata located between the source and enclosed space.

Once the required inputs are measured or estimated from available data, the following analyses are performed:

- 1) a subsurface conceptual model is created in which the subsurface is divided into distinct strata, each having a thickness  $L_i$  [m].

- 2) effective vapor-phase porous media diffusion coefficients ( $D_i^{\text{eff}}$ ) are calculated for each layer using Equation (2); alternatively, site-specific values can be measured using the method described by Johnson *et al.* (1998).
- 3) the overall effective diffusion coefficient for the region between the source and enclosed space  $D_T^{\text{eff}}$  [ $\text{m}^2/\text{d}$ ] is calculated using:

$$\frac{D_T^{\text{eff}}}{L_T} = \frac{1}{\sum_{i=1}^n \left( \frac{L_i}{D_i^{\text{eff}}} \right)} \quad (6)$$

where  $L_T (= \sum L_i)$  is the distance between the source and building. Resistances ( $L_i/D_T^{\text{eff}}$ ) to diffusion are in series and additive.

- 4) use the ( $D_T^{\text{eff}}/L_T$ ) value calculated with Equation (6) and Equation (1) to calculate  $\alpha$ , or read the attenuation factor value from Figure 2, if the Figure 2 inputs are reasonable for that site.
- 5) use  $\alpha$  and the measured source zone vapor concentration  $C_{\text{source}}$  to determine if expected indoor concentrations exceed target levels.

For example, consider the data shown in Table 2 for a site that has been conceptualized as having five depth intervals as shown in Figure 4a (BP 1997). There the moisture content decreases with depth, thereby causing the effective diffusion coefficient to increase with depth. From this table we see that  $(D_T^{\text{eff}}/L_T) = 0.0042 \text{ m/d}$ . Using Figure 2, this yields  $\alpha = 1.5 \times 10^{-4}$ . For reference, using standard generic assumptions for sandy soil at 1 m depth (ASTM, 1995), the corresponding values would be  $(D_T^{\text{eff}}/L_T) = 0.061 \text{ m/d}$  and  $\alpha = 8.4 \times 10^{-4}$ . Thus, by considering the site-specific soil moisture distribution, the generic enclosed-space concentration estimate was reduced to a factor of about one-sixth.

At this site, the source zone vapor concentrations are  $94,000 \text{ mg/m}^3$  (approx. 0.02% v/v) for total hydrocarbons and  $120 \text{ ppm}_v$  for benzene. Using the site-specific estimate for  $\alpha$  yields indoor concentration estimates of  $14 \text{ mg/m}^3$  (approx. 3  $\text{ppm}_v$ ) for total hydrocarbons and  $20 \text{ ppb}_v$  ( $80 \text{ }\mu\text{g/m}^3$ ) for benzene.

The results of this analysis indicate that concentrations within the enclosed space should remain well below flammable levels. This low benzene level would not likely be detected on a portable field instrument, and the benzene concentration is at most an order of magnitude greater than typical urban background levels (Shaw and Singh 1988). Consistent with this analysis, petroleum hydrocarbons and benzene were not detected above background levels in the building at this site.

Fischer *et al.* (1996) also present soil gas and indoor air concentrations at a petroleum spill site. From their SF<sub>6</sub> tracer gas study data,  $\alpha \approx 10^{-4}$  for nondegrading compounds located close to the building that they studied. This is in good agreement with the generic  $\alpha$  plot given in Figure 2; using Figure 2 with the soil moisture and porosity data for that site produces  $(D_T^{\text{eff}}/L_T) \approx 0.035$  m/d and  $\alpha \approx 7 \times 10^{-4}$ . On the other hand, using the measured soil gas and indoor air isopentane concentrations yields  $\alpha \approx 7 \times 10^{-7}$ . Thus, due to degradation, indoor concentrations are about one-thousandth of those predicted using Figure 2. The agreement between the field observation and the screening-level model estimate is actually within a factor of about 100, when using the site-specific building characteristics and exchange rates reported by the authors, rather than the values used to create Figure 2.

#### 4.4 Use and Interpretation of Soil Gas Data with Depth

While soil gas samples with depth are not required in the analysis above, such data can be used to corroborate assumptions built into the site conceptual model (e.g., soil moisture and geology assumptions). They are also useful for assessing if additional model refinements are warranted.

Soil gas data can be relied upon to fully characterize the site only if enough time has passed for near steady conditions to have been reached at that sampling depth. The distance from the source, knowledge of the spill history, and Figure 3 can be used in making this decision.

Soil gas concentrations should be plotted vs. depth and then compared with the expected soil gas concentration profile for the soil moisture content and soil type, or with the soil concentration profile for the measured site-specific effective diffusion coefficients (Johnson *et al.* 1998).

Figures 4a and 4b show sample data presentations for data from BP (1997) and Fischer *et al.* (1996). The BP data represent soil gas samples obtained with depth adjacent to a building, while the Fischer *et al.* data represent soil gas samples collected from beneath a building. When plotting data, it is preferable to overlay soil gas concentrations on, or to plot soil gas concentrations next to, a conceptual model of the subsurface. Available moisture content data should be presented as well. Once the data are plotted, regions across which concentrations decrease or increase sharply should be identified.

To check data consistency with the initial refinement discussed above in §4.1, the measured vapor concentrations should be compared with the expected concentration profile for the conservative case where soil properties vary with depth, but there is no degradation. For a system composed of  $n$  layers, the concentration  $C_j(z)$  in any layer  $j$  is expected to be:

$$C_j(z) = C(z=0) + [C(L_T) - C(z=0)] \frac{\sum_{i=1}^{j-1} \left( \frac{L_i}{D_i^{\text{eff}}} \right) + \frac{z}{D_j^{\text{eff}}}}{\sum_{i=1}^n \left( \frac{L_i}{D_i^{\text{eff}}} \right)} \quad (7)$$

where  $z$  [m] is measured up from the bottom of layer  $j$ ,  $C(L_T)$  is the concentration at the upper boundary, and  $L_i$  [m] is the thickness of layer  $i$  having the effective diffusion coefficient  $D_i^{\text{eff}}$  [ $\text{m}^2/\text{d}$ ]. In layered settings, larger concentration gradients are expected across regions with finer grained soils and larger moisture contents. For example, Figures 5a and 5b present the predicted concentration profiles for the data presented in Figures 4a and 4b, respectively. For open surfaces,  $C(L_T)$  is generally much less than  $C(z=0)$  and can be neglected; however, this may not hold true for covered sites, or below a building (Fischer *et al.* 1996, BP 1997).

At this point, the predicted concentration distributions should be compared with the field data. If there is good agreement, then diffusion is likely the dominant transport attenuation mechanism, biodegradation is not playing a significant role, and the initial site-specific estimate of attenuation (§4.3) likely describes behavior adequately at the site. For example, consider Figures 4a and 4b. Here the concentration profiles are not well predicted; although the qualitative features are better predicted in Figure 4b than in 4a. Agreement would be better in Figure 4b, if it happened that the moisture content in

the 0.48 to 0.58 m region below ground surface (BGS) was closer to 0.15 g-H<sub>2</sub>O/g-soil than to 0.10 g-H<sub>2</sub>O/g-soil. The effect of this change on the predictions is shown in Figure 5b.

As in Figure 5a, the sharp transitions observed in actual concentration profiles may not appear in the predicted concentration profiles, and deviations might not be easily attributable to reasonable errors in soil property measurements. One possibility is that these sharp transitions could be the result of thin finer grained soil layers not detected in the initial geologic assessment. To test this hypothesis at a site, the user can either collect additional continuous soil cores, or conduct in situ diffusion coefficient measurements in the region of the sharp transition. For example, given the data in Figure 4a, in situ diffusion coefficient measurements would be made in the 4 - 8 ft BGS, 8 - 12 ft BGS, and 12 - 16 ft BGS intervals. It should be noted that there may be more than one plausible hypothesis for a given data set. For example, Fischer *et al.* proposed that their observed sharp transition was the result of more highly transmissive near-surface soils and subsurface advective flow resulting from wind-induced pressure gradients.

Ideally, soil gas samples should be collected from each distinct soil stratum identified by the geologic assessment at a site. Vadose zone sampling implants connected to ground surface with small diameter (1/8" OD) non-adsorbing tubing are the preferred method of data collection. It is recommended that the implants be left in place for future sampling, as more than one sampling event is often necessary. The implants can then also be used for performing in situ diffusion coefficient measurements. The intent here is not to provide detailed guidance for soil gas sampling; however, the two main concerns in soil gas sampling are the ability to collect discrete depth samples and to prevent atmospheric dilution. For this reason, readers should note that: a) sample line and vapor sampler volumes should be minimized so that the purge volume is small, b) the potential for atmospheric short-circuiting along the annulus between the soil and sampler should be minimized, and c) sampling flow rates in the range of about 1 L/min or less are preferred.

#### 4.5 Accounting for Attenuation Due to Biodegradation

Incorporation of aerobic biodegradation into the site-specific assessment of potential vapor migration impacts is discussed here. As in §4.1, §4.2, and §4.4, much of the following analysis is appropriate only for sites that have reached near-steady conditions.

In the case that near-steady conditions are not likely to have been achieved, the user should review the discussion below in §5.0 concerning site conditions that are likely more conducive for degradation, and identify if such conditions exist at the site.

To assess if significant vapor migration attenuation due to biodegradation is occurring, it is necessary to characterize the vertical soil gas distribution and vapor transport properties of the unsaturated zone. Needed information includes:

- total hydrocarbon soil gas concentration vs. depth,
- specific chemical (e.g., benzene) soil gas concentration vs. depth,
- oxygen soil gas concentration vs. depth,
- subsurface conceptual model (layers, soil types, depth to source, etc.).

When selecting specific analytes, it is useful to include at least one compound that is known to be recalcitrant to degradation and is relatively unretarded, even though it may not be of concern from a health risk perspective.

In some cases, there will be large discrepancies between the measured concentrations and those predicted with Equation (7), as is the case in Figure 4a and Figure 6 (Ostendorf and Kampbell 1991). This may be an indication of significant biodegradation, but may also be due to either poor site characterization data, or non near-steady conditions. Thus, if it is hypothesized that biodegradation is playing an important role, then it is important to look for multiple lines of supporting evidence, including:

- decreasing oxygen concentrations with depth, consistent with the contaminant vapor concentration profile (e.g., sharp transitions in same region),
- carbon dioxide concentration profile consistent with oxygen profile,
- relatively stable soil gas concentrations with time

These are traditional indicators of aerobic biodegradation. If one simply desires only to demonstrate that natural attenuation is occurring in the vadose zone, then the data needs listed above are sufficient for this purpose at most sites. If, however, one wishes to be more quantitative and to incorporate bio-attenuation into the development of site-specific vapor intrusion pathway screening levels, additional analysis is necessary.

At this point in time it is not clear how to best accomplish this in general, as available data are limited and models are still being developed, tested, and refined. Two possible screening-level model refinements (Johnson and Kemblowski 1998) are presented. These are inspired by available field and laboratory soil column data. Neither model has undergone rigorous comparison with extensive field data. Both are capable of mimicking characteristics of the available data as shown below, and hence are adequate for fitting and extrapolation purposes. Both decouple oxygen and hydrocarbon vapor transport so that complete speciation of the hydrocarbon vapors is not required.

The first algorithm mimics data from shallow (<4 m BGS) and relatively homogeneous settings, such as those studied by Ostendorf and Kampbell (1991) in the field and DeVaul (1997) in the laboratory. Figure 6 presents a subset of the data from Ostendorf and Kampbell (1991) as an illustration. Generally in these settings the oxygen concentration in the soil gas remains high (>5% v/v), except perhaps in the vicinity of the source zone. The contaminant vapor concentrations appear to decrease exponentially with distance away from the source, and at any point are less than those that would be predicted by the one-dimensional steady-state model discussed in §4.4, assuming uniform properties and no degradation.

Here a screening model that assumes a first-order reaction in a homogeneous medium is used. In this case the equation describing the steady-state vapor concentration profile  $C(Z)$  [ $\text{mg}/\text{m}^3$ ] is:

$$C(Z) = \frac{C(Z=1)[e^{-\eta Z} - e^{\eta Z}] + C(Z=0)[e^{-\eta(1-Z)} - e^{\eta(1-Z)}]}{[e^{-\eta} - e^{\eta}]} \quad (8)$$

where  $L$  [m] is the depth interval of interest,  $Z=z/L$  is the normalized height above the source zone, and  $\eta$  is given by:

$$\eta = \sqrt{\frac{\lambda_i \theta_m L^2}{H_i D^{\text{eff}}}} \quad (9)$$

where  $\lambda$  [ $\text{d}^{-1}$ ] is a first-order decay coefficient for degradation that is assumed to occur in the soil moisture. The parameter  $\eta$  represents a ratio of degradation rate to diffusion rate; therefore, it is expected that attenuation will increase with increasing  $\eta$ .



For reference, Figure 7 presents a family of type curves predicted by Equation (8) for a range of  $\eta$  values, assuming that  $C(Z=1) \ll C(Z=0)$ . Note that the curves in Figure 7 suggest that degradation does not significantly impact the shape of the vapor concentration distribution unless  $\eta > 1$ .

Incorporating Equation (8) into the development of Johnson and Ettinger (1991) yields the following refined equation for the attenuation factor (Johnson and Kemblowski 1998):

$$\alpha = \frac{C_{\text{indoor}}}{C_{\text{outdoor}}} = \left\{ \frac{1 - \beta}{(1 - \beta) \left( \frac{Q_B L}{D^{\text{eff}} A_B} \right) \left( \frac{e^\eta - e^{-\eta}}{2\eta} \right) + \beta \left( \frac{Q_B}{Q_{\text{soil}}} \right) \left( \frac{e^\eta - e^{-\eta}}{2} \right) + \left( \frac{e^\eta - e^{-\eta}}{2} \right)} \right\} \quad (10)$$

where:

$$\beta = 1 - \exp\left(-\frac{Q_{\text{soil}} L_{\text{crack}}}{D_{\text{crack}} A_{\text{crack}}}\right) \quad (11)$$

and all other parameters are as defined for Equation (1).

Figure 8 plots the attenuation factor  $\alpha$  as a function of  $(D^{\text{eff}}/L)$  for a range of  $\eta$ . All parameter values are the same as those used in Figure 2. Note that unless  $\eta > 1$ , the effect of including degradation is negligible. In addition,  $\alpha$  is very sensitive to small variations in  $\eta$  when  $\eta > 1$ .

The procedure for using this refined model is as follows:

- 1) compare field data with predictions given by Equation (8) for a range of  $\eta$  values (one simple approach would be to plot normalized data on top of Figure 7),
- 2) assess whether or not Equation (8) adequately describes the data, and if so, find the value of  $\eta$  that best fits the field data,

- 3) then use this value of  $\eta$  to obtain a value of  $\alpha$  from Equations (10) and (11), or Figure 8, and
- 4) use  $\alpha$  and the measured source zone vapor concentration  $C_{\text{source}}$  to determine if expected indoor concentrations exceed target levels.

For example, as shown in Figure 6, the Ostendorf and Kampbell data can be reasonably fit with Equation (8) using  $\eta=4$ .

Given the sensitivity to small changes in  $\eta$  when  $\eta>1$ , it is recommended that  $\eta$  be regarded simply as a site-specific fitting parameter. It is also recommended at this time that  $\eta$  values derived for one site not be used at other sites. In addition,  $\eta$  values may be specific only to the setting for which they are measured; for example, the data in Figures 4a and 6 are specific to two sites without ground cover. It is not yet known if it is appropriate to extrapolate that data to covered areas at those two sites.

If one is interested in developing a database of first-order degradation rate values ( $\lambda_i$ ) with an aim toward justifying conservative base-level generic degradation rates, then great care should be taken to also characterize the diffusive properties of the system at each site contributing to the database.

Data of the type shown previously in Figure 4a are not well fit by the simple first-order degradation model discussed above. These data sets are characterized by substantial changes in contaminant and oxygen concentrations across relatively thin vadose zone sections. Generally these sections also correspond to regions of higher moisture content, or decreased air-filled porosity. Thus, the processes occurring in these sections dominate the overall observed behavior for a number of reasons, including higher diffusion resistances and increased residence times for reaction.

Data of this type might be reasonably fit by a “dominant layer” model (Johnson and Kemblowski 1998). In this approach the vadose zone is conceptualized as having three zones as shown in Figure 9. A central zone in which the reaction takes place is bordered by two zones through which transport occurs without reaction. At near steady state conditions the concentration profile for this scenario is given by (Johnson and Kemblowski 1998):

$$C(z) = C_{\text{source}} - (C_{\text{source}} - C_2) \left( \frac{z}{L_1} \right) \quad \text{Region 1 } (0 < z < L_1) \quad (12)$$

$$C(z) = \frac{[C_3 e^{\eta \frac{(L_1 - z)}{(L_2 - L_1)}} - C_2 e^{\eta \frac{(L_2 - z)}{(L_2 - L_1)}}]}{[e^{-\eta} - e^{\eta}]} + \frac{[C_2 e^{-\eta \frac{(L_2 - z)}{(L_2 - L_1)}} - C_3 e^{-\eta \frac{(L_1 - z)}{(L_2 - L_1)}}]}{[e^{-\eta} - e^{\eta}]} \quad \text{Region 2 } (L_1 < z < L_2) \quad (13)$$

$$C(z) = C_3 - (C_3 - C_4) \left( \frac{z - L_2}{L_3 - L_2} \right) \quad \text{Region 3 } (L_2 < z < L_3) \quad (14)$$

where:

$$\eta = \sqrt{\frac{\lambda_i \theta_m (L_2 - L_1)^2}{H_i D^{\text{eff}}}} \quad (15)$$

Using the general development of Johnson and Ettinger (1991), the attenuation coefficient  $\alpha$  for this approach becomes (Johnson and Kemblowski 1998):

$$\alpha = \frac{C_{\text{indoor}}}{C_{\text{source}}} \left\{ \frac{1 - \beta}{\left[ (1 - \beta) \left( \frac{Q_B}{2\phi\gamma\psi} \right) + \left( \beta \left( \frac{Q_B}{Q_{\text{soil}}} \right) - 1 \right) \left( \frac{1 + \gamma\psi - 4\psi^2}{2\gamma\psi^2} \right) \right]} \right\} \quad (16)$$

where:

$$\beta = 1 - \exp\left(-\frac{Q_{\text{soil}} L_{\text{crack}}}{D_{\text{crack}} A_{\text{crack}}}\right) \quad (17)$$

$$\gamma = \left( \frac{D_3^{\text{eff}}}{D_2^{\text{eff}}} \right) \frac{[e^{-\eta} - e^{\eta}]}{\eta} \frac{(L_2 - L_1)}{L_1} \quad (18)$$

$$\sigma = \left( \frac{D_3^{\text{eff}}}{D_2^{\text{eff}}} \right) \frac{[e^{-\eta} - e^{\eta}]}{\eta} \frac{(L_2 - L_1)}{(L_3 - L_2)} \quad (19)$$

$$\psi = \frac{1}{e^{-\eta} + e^{\eta} - \gamma} \quad (20)$$

$$\phi = \left( \frac{A_B D_3^{\text{eff}}}{L_3 - L_2} \right) \frac{1}{[\sigma - (1/\psi) - \gamma + 4\psi]} \quad (21)$$

To solve for the concentration profile, Equation (16) is first solved to get  $\alpha$ . Then each of the following relations is solved sequentially for  $C_4$ ,  $C_3$ , and  $C_2$  in terms of  $C_1$ .

$$\frac{C_4}{C_1} = \frac{2\beta\gamma\psi\phi - \alpha Q_{\text{soil}}}{(\beta - 1)Q_{\text{soil}} - \frac{\beta\phi}{\psi} - \beta\gamma\phi + 4\beta\psi\phi} \quad (22)$$

$$\frac{C_3}{C_1} = \frac{2\gamma\psi + \sigma(C_4/C_1)}{\sigma - \frac{1}{\psi} - \gamma + 4\psi} \quad (23)$$

$$\frac{C_2}{C_1} = 2\psi(C_3/C_1) - \gamma\psi \quad (24)$$

These equations are easily set-up and solved within any standard spreadsheet. Figure 10 illustrates model predictions compared with the data from Fischer *et al.* (1996) for the case of the parameters defined in Table 3. No attempt has been made to find a best fit here, and it is clear that results are sensitive to small changes in  $\eta$ . With  $\eta=6$  in Equation (16), then  $\alpha=10^{-6}$ , which is of the same order of magnitude as the empirical value based on measured soil gas and indoor isopentane concentrations. It is also roughly one-thousandth the estimate generated in §4.1 for the case of a layered system without degradation. Even though good agreement is achieved here, it should be cautioned that there may be other reasonable hypotheses consistent with this data set, as discussed above. This is especially true for this data set, since the first-order decay constant consistent with Equation (15),  $\eta=6$  and the other site-specific data are about  $10^5$  times the typically reported first-order biodegradation rates (roughly  $\lambda=22 \text{ d}^{-1}$  vs. 0.01 to 0.001  $\text{d}^{-1}$  based on dissolved groundwater plume data fitting). Here the data are used simply to demonstrate use of the equations as fitting and extrapolation tools, and it is recognized that there may be alternate mechanistic explanations for the behavior observed at this site.

To provide strong proof that the site characterization data and conceptual model adequately describe the site, and that reasonable estimates for effective diffusive properties are being used, one can also check for good agreement between predictions and field data for the vapor concentration profiles of known recalcitrant compounds.

#### 4.6 Other Refinements

One can also consider source zone depletion when refining the assessment of potential vapor migration impacts. This requires knowledge of contaminant distributions in soil and knowledge of contaminant partitioning properties and behavior. Johnson and Ettinger (1991) describe how to account for depleting sources using this information. It is not discussed further here, as it is unlikely that the necessary data will be known with any degree of accuracy greater than what would be assumed when generating generic RBSL estimates. It is also felt that the majority of sites can be adequately assessed on a site-specific basis using the guidance provided in §4.3 through §4.5. In addition, the issue of source longevity is one that has received little attention to date, and is not well understood.

### 5.0 AN OPPORTUNITY FOR THE FUTURE

Figures 7 and 8 and the data from Fischer *et al.* (1996) and BP (1997) suggest that there is potential for a much simpler site-specific screening methodology to be developed. Collectively, this information suggests that there might exist conditions for which bio-attenuation is so significant that there would be no potential for adverse impacts at any possible source vapor concentration. If these critical conditions could be defined, then vertical soil gas profiling and determination of biological rate constants at each site would not be necessary. Instead, one would focus site assessment activities on identifying whether the critical conditions were satisfied. As an added benefit, it would not be as important to determine if vapor concentrations had reached near-steady conditions before reaching a conclusion regarding the significance of vapor migration.

One hypothesis is that these critical conditions include the following:

- no significant advective vapor flow ( $uL/D_T^{\text{eff}} < 1$ ;  $u$ =velocity);

- sufficient oxygen for aerobic biodegradation (>5% v/v);
- non-recalcitrant, aerobically biodegradable compounds; and
- slow enough diffusion rates and long enough distances for degradation to be significant.

The second can be reasonably quantified based on existing literature; for example, both the bioventing and groundwater biodegradation literature suggest that aerobic degradation slows significantly when oxygen concentrations are less than about 25% of air-saturated conditions (5% v/v or 2 mg/L-H<sub>2</sub>O).

The last condition is the one for which future study is needed. To help show how it might be quantified, Figure 11 has been prepared. It presents the distance  $L_{crit}$  [m] over which the vapor concentration would be reduced by 99.9% as a function of soil moisture content, for the range of first-order decay rates displayed. Figure 11 is derived from Equation (8), which yields the condition for this case that:

$$\frac{L_{crit}^2 \lambda_i \theta_m}{H_i D^{eff}} = 6.9 \quad (25)$$

Figure 11 is presented for illustrative purposes only. It should be noted that at this time a range of reasonable first-order degradation rates has yet to be identified, and first-order expressions may not adequately describe the kinetics. The reader is referred to DeVaul *et al.* (1997) for more discussion on this issue.

However, for the sake of illustration, suppose that  $10^{-6} < \lambda \theta_m / H_i < 10^{-5} \text{ s}^{-1}$  is a reasonable range and that a concentration reduction of 99.9% is sufficient to alleviate vapor migration concerns at service station spill sites. A graph of this type would define all possible combinations of acceptable vadose zone thicknesses and moisture contents. In the initial assessment, a user would simply collect and compare the site-specific moisture content distribution and source - receptor distance with the graph to verify bio-attenuation. For example, soils with moisture contents  $\approx 0.1 \text{ g-H}_2\text{O/g-soil}$  require soil thicknesses of  $\approx 0.2 - 4.0 \text{ m}$  to assure a 99.9% reduction. Figure 11 shows that much thinner strata of higher moisture content would also achieve the same effect.

More well-documented data and fundamental research studies are needed to identify reasonable kinetic expressions and kinetic parameters, and to verify the hypotheses presented above.





## 7.0 REFERENCES

Acomb, L., C. Rea, T. Simpkin, R. Hoffman, and B. Elder. 1996. Intrinsic Remediation of Shallow Vadose Zone Petroleum Hydrocarbons. The Proceedings of the API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation. Houston, TX. November 13 - 15. 367 - 382.

ASTM. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites. E1739-95; American Society for the Testing of Materials, 100 Barr Harbor Dr., West Conshohocken, PA 19428. 1995.

Auer, L.H., N.D. Rosenberg, K.H. Birdsell, and E.M. Whitney. 1996. The Effects of Barometric Pumping on Contaminant Transport. Journal of Contaminant Hydrogeology. 24. 145 - 166.

British Petroleum. 1997. Summary of Field Activities Hydrocarbon Vapor Migration Research Project BP Oil Test Site Paulsboro, New Jersey. Prepared by Integrated Science and Technology, Inc. Cleveland, OH. February.

Crank, J. 1956. The Mathematics of Diffusion. Oxford at the Clarendon Press.

DeVaul, G. E. 1997. Biological and Other Loss Mechanisms Associated with Gasoline Volatilization from Soils. Presented at the Petroleum Environmental Research Forum (PERF) Workshop. Brea, CA. February 6 - 7.

DeVaul, G. E., R. A. Ettinger, J. P. Salanitro, and J. B. Gustafson. 1997. Benzene, Toluene, Ethylbenzene and Xylenes [BTEX] Degradation in Vadose Zone Soils During Vapor Transport: First-Order Rate Constants. The Proceedings of the API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation. Houston, TX. November.

Fischer, D. and C.G. Uchrin. 1996. Laboratory Simulation of VOC Entry into Residence Basements from Soil Gas. Environmental Science and Technology. 30 (8). 2598 - 2603.

Fischer, M.L., A.J. Bentley, K.A. Dunkin, A.T. Hodgson, W.W. Nazaroff, R.G. Sextro, and J.M. Daisey. 1996. Factors Affecting Indoor Air Concentrations of Volatile Organic

Compounds at a Site of Subsurface Gasoline Contamination. *Environmental Science and Technology*. 30 (10). 2948 - 2957.

Fitzpatrick, N.A. and J.J. Fitzgerald. 1997. An Evaluation of Vapor Intrusion into Buildings through a Study of Field Data. Massachusetts Department of Environmental Protection.

Garbesi, K. and R.G. Sextro. 1989. Modeling and Field Evidence of Pressure-Driven Entry of Soil Gas into a House through Permeable Below-Grade Walls. *Environmental Science and Technology*. 23(12):1481-1487.

Guymon, G.L. 1994. *Unsaturated Zone Hydrogeology*. Prentice Hall. New York.

Hodgson, A.T., K. Garbesi, R.G. Sextro, and J.M. Daisy. 1992. Soil-Gas Contamination and Entry of Volatile Organic Compounds into a House Near a Landfill. *J. Air & Waste Management Association*. 42: 277-283.

Jeng, C.Y., V.J. Kremesec Jr., and H.S. Primack. 1996. Models of Hydrocarbon Vapor Diffusion Through Soil and Transport into Buildings. *The Proceedings of the API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation*. Houston, TX. November 13 - 15. 319 - 338.

Jin, Y.. 1994. Transport and Biodegradation of Toluene in Unsaturated Soil. *Journal of Contaminant Hydrology*. 17. 111 - 127.

Johnson, P.C., C. Bruce, R.L. Johnson, and M.W. Kemblowski. 1998. In Situ Measurement of Effective Vapor-Phase Porous Media Diffusion Coefficients. Submitted to *Environmental Science and Technology*.

Johnson, P.C. and R.A. Ettinger. 1991. Heuristic Model for Predicting the Intrusion of Contaminant Vapors into Buildings. *Environmental Science and Technology*. 25(8): 1445-1452.

Johnson, P.C., Hertz, M.B. and D.L. Byers. 1990. Estimates for Hydrocarbon Vapor Emissions Resulting from Service Station Remediations and Buried Gasoline-

Contaminated Soils. In Petroleum Contaminated Soils Volume 3 (P.T. Kostecki and E.J. Calabrese Eds.). Lewis Publishers. 295-326.

Johnson, P.C. and M. W. Kemblowski. 1998. Refinements to the Heuristic Model for Assessing Impacts of Vapor Migration to Enclosed Spaces: Bio-Attenuation. In Preparation.

Johnson, R.L. and M. Perrott. 1991. Gasoline Vapor Transport through a High Water Content Soil. *Journal of Contaminant Hydrology*. 8. 317 - 334.

Jury, W.A., Spencer, W.F., and Farmer, W.J.. 1983. Behavior Assessment Model for Trace Organics in Soil - I: Model Description. *Journal of Environmental Quality*. 12. 558-564.

Jury, W.A., D. Russo, G. Streile, and H. El Abd. 1990. Evaluation of Volatilization of Organic Chemicals Residing Below the Soil Surface. *Water Resources Research*. 26 (1). 13- 20.

Kampbell, D.H., J.T. Wilson, H.W. Read, and T.T. Stocksdale. 1987. Removal of Volatile Aliphatic Hydrocarbons in a Soil Bioreactor. *Journal of the Air Pollution Control Association*. 37. 1236 - 1240.

Lahvis, M.A, and A.L. Baehr. 1996. Estimation of Rates of Aerobic Hydrocarbon Biodegradation by Simulation of Gas Transport in the Unsaturated Zone. *Water Resources Research*. 32 (7). 2231 - 2249.

Li, D.X. 1997. Diurnal Changes in Subsurface Vapor Transport. Presented at the Petroleum Environmental Research Forum (PERF) Workshop. Brea, CA. February 6 - 7.

Little, J.C., J.M. Daisey, and W.W. Nazaroff. 1992. Transport of Subsurface Contaminants into Buildings. *Environmental Science and Technology*. 26(11): 2058-2066.

Loureiro, C.O., L.M. Abriola, J.E. Martin, and R.G. Sextro. 1990. Three-Dimensional Simulation of Radon Transport into Houses with Basements under Constant Negative Pressure. *Environmental Science and Technology*. 24(9): 1338-1348.

Millington, R. J., *Gas Diffusion in Porous Media*, Science, 1959, 130, 100-102.

Millington, R. J.; Quirk, J. P., *Permeability of Porous Solids*, Trans. Faraday Soc., 1961, 57, 1200-1207.

Millington, R. J.; Shearer, R. C., *Diffusion in Aggregated Porous Media*, Soil Sci., 1971, 111, 372-378.

Moore, A., S. Revell, and B. Norland. 1997. Calibration of Models of Vapor Transport into Buildings. *The Proceedings of the API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation*. Houston, TX. November 13 - 15.

Moyer, E.E., D.W. Ostendorf, R.J. Richards, and S. Goodwin. 1994. Determination of Petroleum Hydrocarbon Bioventing Kinetics in an Intact Unsaturated Zone Soil Core. Submitted to *Water Resources Research*.

Nazaroff, W.W., S.R. Lewis, S.M. Doyle, B.A. Moed, and A.V. Nero. 1987. Experiments on Pollutant Transport from Soil into Residential Basements by Pressure-Driven Airflow. *Environmental Science and Technology*. 21(5): 459-466.

Ostendorf, D. 1993. Hydrocarbon Vapor Diffusion in Intact Core Sleeves. *Ground Water Monitoring and Remediation*. Winter. 139 -150.

Ostendorf, D.W. and D.H. Kampbell. 1990. Bioremediated Soil Venting of Light Hydrocarbons. *Hazardous Waste and Hazardous Materials*. 7 (4). 319 - 334.

Ostendorf, D.W. and D.H. Kampbell. 1991. Biodegradation of Hydrocarbon Vapors in the Unsaturated Zone. *Water Resources Research*. 27. 453 - 462.

Sextro, R.. 1997. Factors Controlling Entry of Soil Gas Contaminants into Buildings. Presented at the Petroleum Environmental Research Forum (PERF) Workshop. Brea, CA. February 6 - 7.

Shah, J.T. and H.B. Singh. 1988. Distribution of Volatile Organic Chemicals in Outdoor and Indoor Air. *Environmental Science and Technology*. 22(12): 1381-1386.

Smith, J.A., A.K. Tisdale, and J.H. Cho. 1996. Quantification of Natural Vapor Fluxes of Trichloroethylene in the Unsaturated Zone at the Picatinny Arsenal, New Jersey. *Environmental Science and Technology*. 30. 2243 - 2250.

Stout, S. 1997. Field Case Studies Chlorinated Hydrocarbon Vapors. Presented at the Petroleum Environmental Research Forum (PERF) Workshop. Brea, CA. February 6 - 7.

Unlu, K., M. W. Kemblowski, J. C. Parker, D. K. Stevens, P. K. Chong, and I. Kamil, 1992, A screening model for effects of land-disposed wastes on groundwater quality, *Journal of Contaminant Hydrology*, (11), pp. 27-49.

United States Environmental Protection Agency. 1987. Total Exposure Assessment Methodology TEAM Study, Vols. 1 - 4. Office of Acid Deposition.

United States Environmental Protection Agency. 1992. Assessing Potential Indoor Air Impacts for Superfund Sites. Office of Solid Waste and Emergency Response. EPA/540/R-95/128. PB96-963502. May.

United States Environmental Protection Agency. 1996. Soil Screening Guidance: Technical Background Document. Office of Solid Waste and Emergency Response. EPA/540/R-95/128. PB96-963502. May.

Table 1. Refinement options and associated data collection and analysis needs.

| Analysis Step                             | Refinement Relative to Previous Analysis  | Description   | Data Needs Relative to Base List of Needs (1)   |
|---|---|---|---|
| Generic RBSL                              | none  | calculation of base case RBSLs using generic properties; user should ensure that generic inputs are conservative relative to actual site conditions, soil type and depth to contamination should be known | <ul style="list-style-type: none"> <li>• none</li> </ul>  |
| Indoor Sampling                           | direct measure - no prediction  | vapor sample collected in enclosed space and compared with regulatory limits  | <ul style="list-style-type: none"> <li>• indoor vapor samples at different times of the year</li> <li>• surety of no other sources</li> <li>• time since release</li> </ul>   |
| Near-Foundation and Near-Surface Sampling | direct measure of current conditions in soil near enclosed-space and estimate of impact to enclosed space | near-foundation measurement coupled with simple advective-driven vapor intrusion equation   | <ul style="list-style-type: none"> <li>• near-foundation soil gas sample</li> <li>• estimate of enclosed-space air exchange rate</li> <li>• time since release</li> </ul>   |
| Site-Specific: Simple Refined Calculation | site-specific estimates of effective porous media diffusion coefficients                                  | use of algorithms employed in Generic RBSL calculation, but input of site-specific effective diffusion coefficient estimate (or value measured in situ), and source zone vapor concentration              | <ul style="list-style-type: none"> <li>• source zone soil vapor concentration</li> <li>• moisture content vs. depth</li> <li>• effective diffusion coefficients measured in situ (optional)</li> </ul>  |
| Site-Specific: Refined 1                  | site-specific assessment of attenuation due to biodegradation   | use of modified screening-level algorithms, degradation fitting parameter determined from vertical soil gas profile and soil properties, and possibly effective diffusion coefficient measured in situ    | <ul style="list-style-type: none"> <li>• source zone soil vapor concentration</li> <li>• moisture content vs. depth</li> <li>• estimate of time since release</li> <li>• soil vapor concentrations with depth, including O<sub>2</sub></li> <li>• effective diffusion coefficients measured in situ (optional)</li> </ul> |
| Site-Specific: Refined 2                  | source zone depletion   | same as above, except model refinements account for source depletion  | <ul style="list-style-type: none"> <li>• same as above, plus source zone dimensions and source mass</li> </ul>  |

(1) Base case data needs include: subsurface lithology and depth to contamination.

Table 2. Sample use of field data (data from BP 1997) to determine site-specific effective vapor-phase diffusion coefficients.

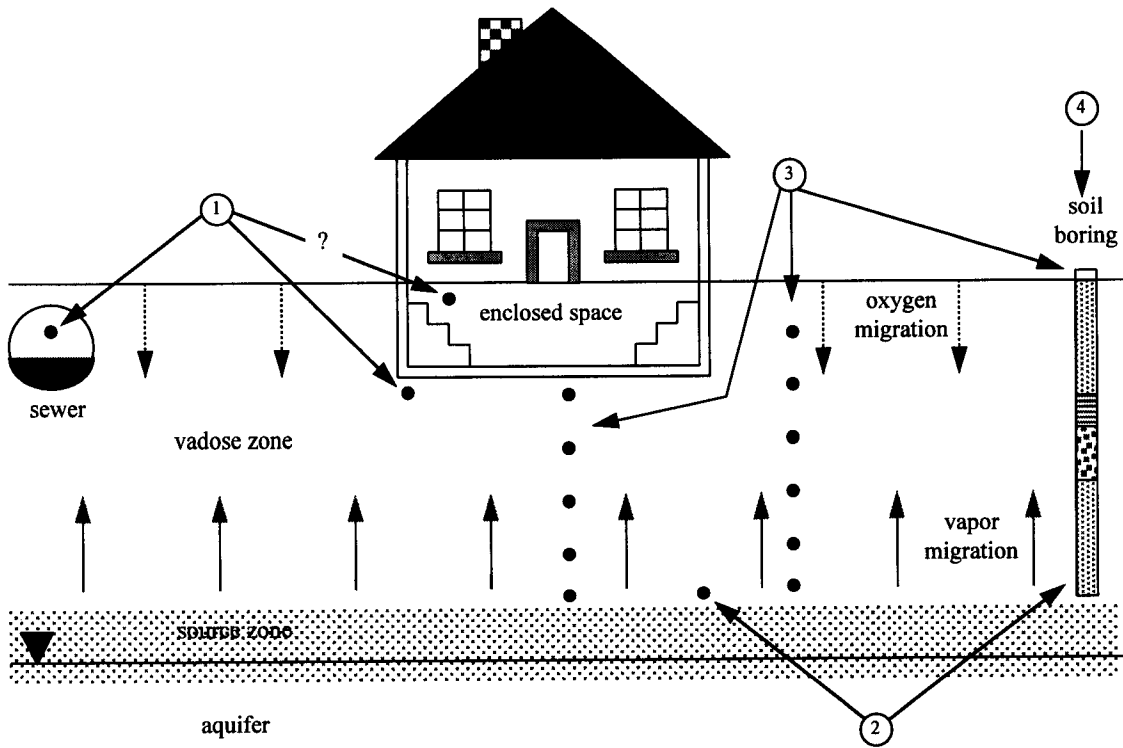
| Depth [ft BGS] | Type       | $\theta_m$ [g-H <sub>2</sub> O/g-soil] | $\theta_m$ [m <sup>3</sup> -H <sub>2</sub> O/m <sup>3</sup> -soil]* | $D_i^{eff}$ [m <sup>2</sup> /d]** | $D_i^{eff}/L$ [m <sup>2</sup> /d] |
|----------------|------------|--|---|-----------------------------------|-----------------------------------|
| 0-4            | silty sand | 0.11                                   | 0.19  | 0.016                             | 0.013                             |
| 4-7            | silty sand | 0.12                                   | 0.20  | 0.010                             | 0.011                             |
| 7-10           | silty sand | 0.10                                   | 0.16  | 0.023                             | 0.025                             |
| 10-13          | sand       | 0.056                                  | 0.10  | 0.067                             | 0.073                             |
| 13-16          | sand       | 0.059                                  | 0.10  | 0.062                             | 0.068                             |
|                |            |  |   | $D_T^{eff}/L_T =$                 | 0.0042                            |

\* assuming a bulk soil density of 1.7 g-soil/cm<sup>3</sup>-soil

\*\* for  $D^{air} = 0.09 \text{ cm}^2/\text{s} = 0.78 \text{ m}^2/\text{d}$

Table 3. Inputs used in generating Figure 10 using the dominant layer model.

| Property                      | Layer |      |      |
|-------------------------------|-------|------|------|
|                               | 1     | 2    | 3    |
| Thickness [m]                 | 0.3   | 0.2  | 0.4  |
| $\eta$                        | 0     | 6    | 0    |
| $D^{eff}$ [m <sup>2</sup> /d] | 0.07  | 0.02 | 0.05 |



- 1 - data used when assessing near-term impacts
- 2 - data used when making initial site-specific estimate of longer-term impacts
- 3 - data used when making estimates accounting for attenuation due to biodegradation
- 4 - data required for possible future screening approach

Figure 1. Schematic of vapor migration scenario and sampling options.



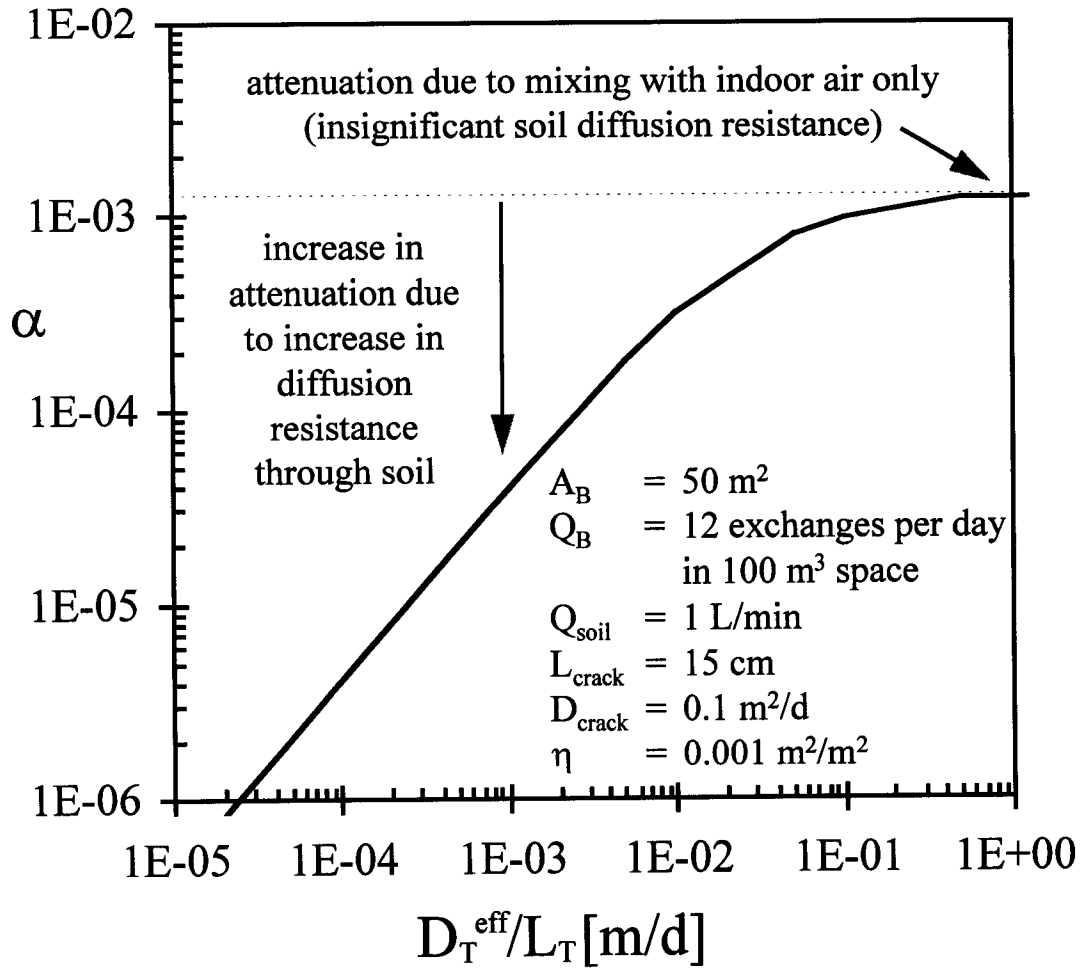


Figure 2. Johnson and Ettinger (1991) site-specific vapor attenuation coefficient  $\alpha=(C_{\text{indoor}}/C_{\text{source}})$  estimate as a function of the overall effective vapor-phase porous media diffusion coefficient  $D_T^{\text{eff}}$  and distance between the source and foundation  $L_T$ .

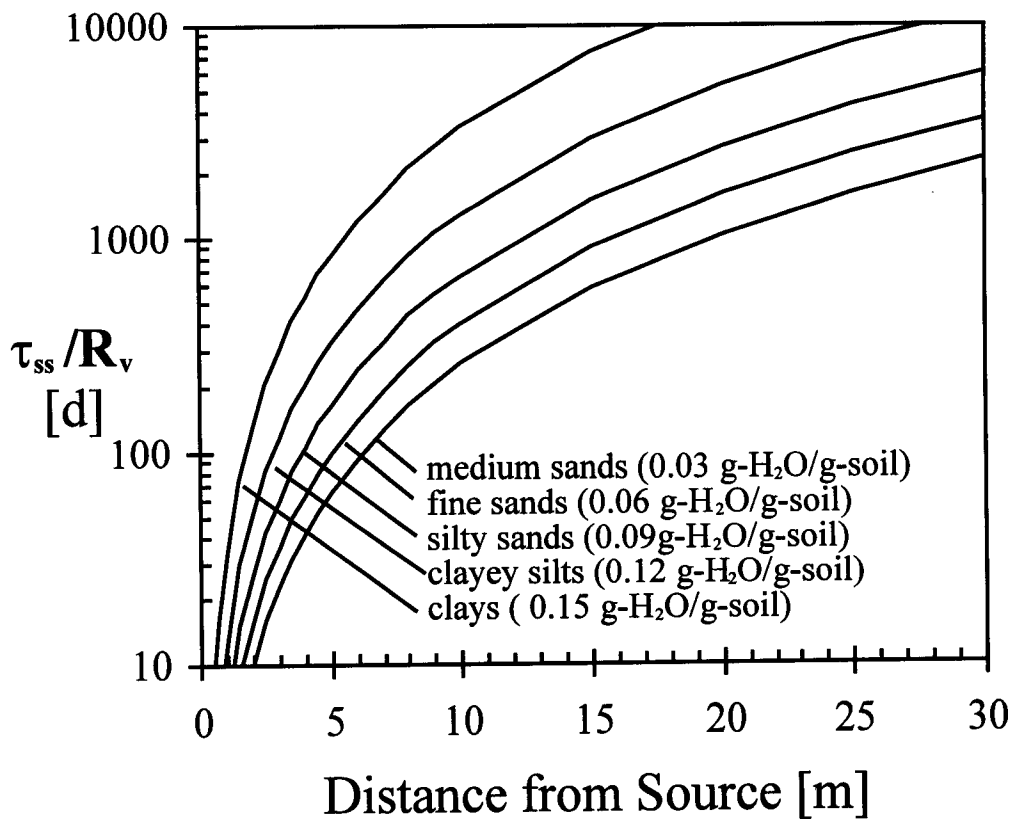
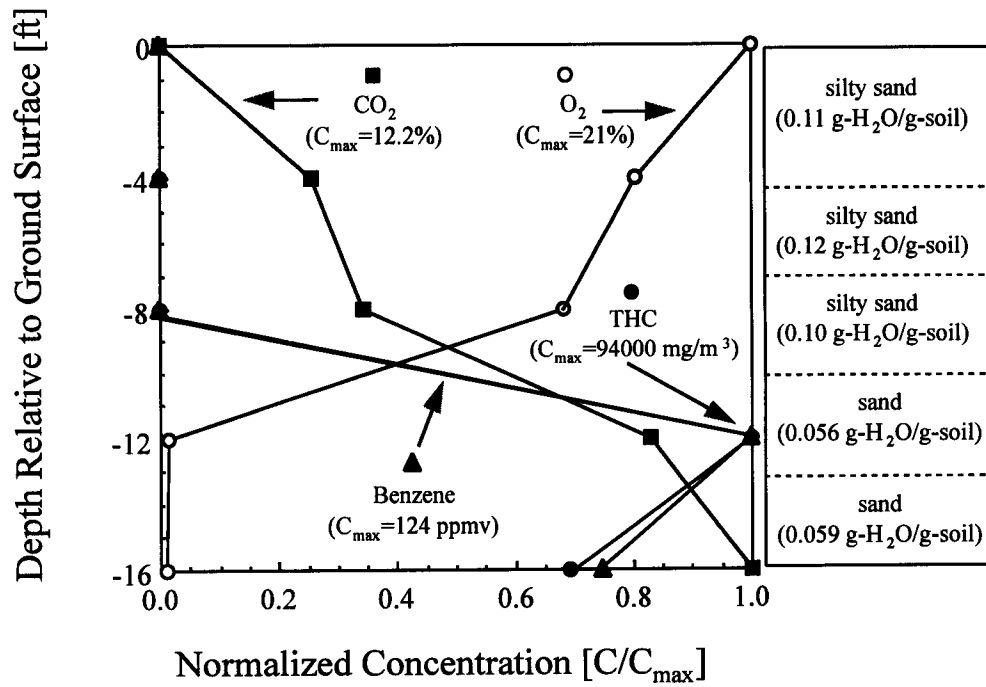


Figure 3. Estimated time for non-retarded chemicals to reach near steady vapor concentrations ( $\tau_{ss}/R_v$ ) at the distance L from a source. For retarded compounds multiply the ( $\tau_{ss}/R_v$ ) value by the retardation factor  $R_v$  defined in Equation (4).

a)



b)

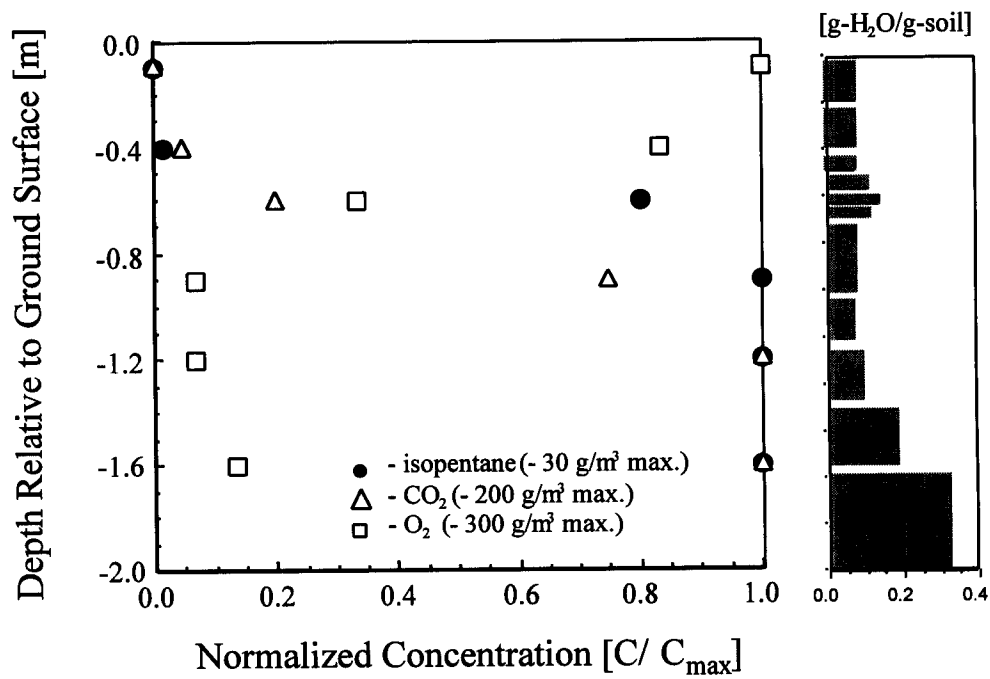


Figure 4. Sample presentation using data from a) BP (1997) and b) Fischer *et al.* (1996).

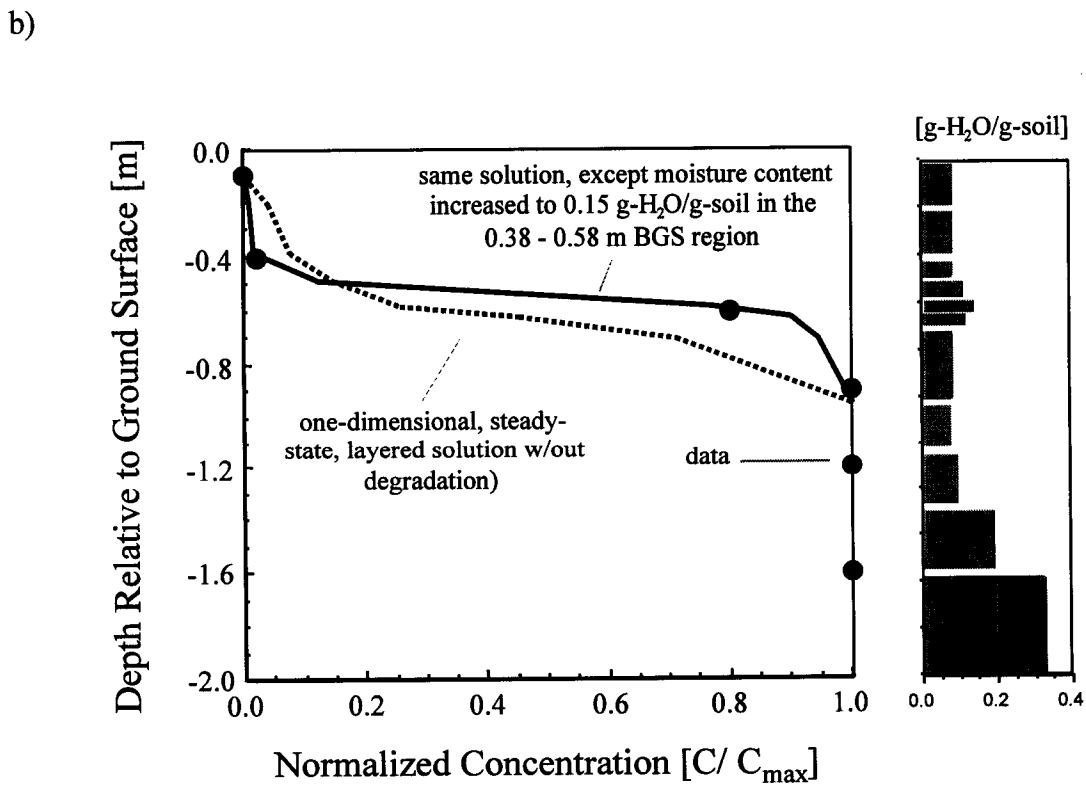
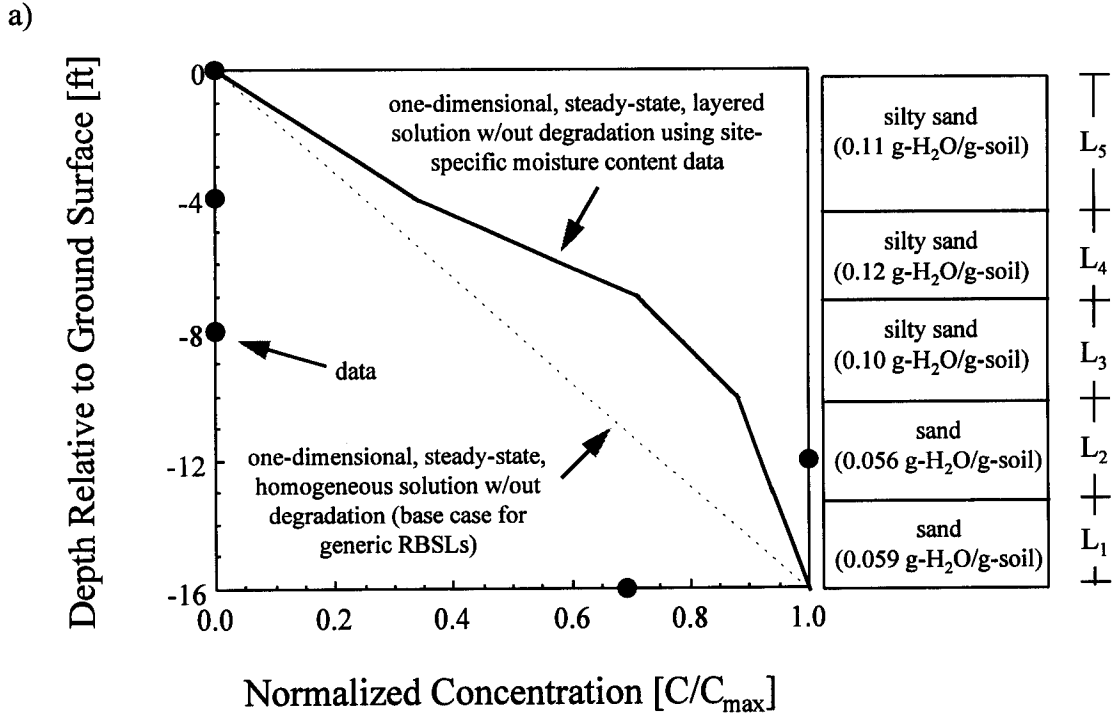


Figure 5. Vapor concentration data compared with predictions for one-dimensional transport through a layered system without degradation, using data from a) BP (1997) and b) Fischer *et al.* (1996).

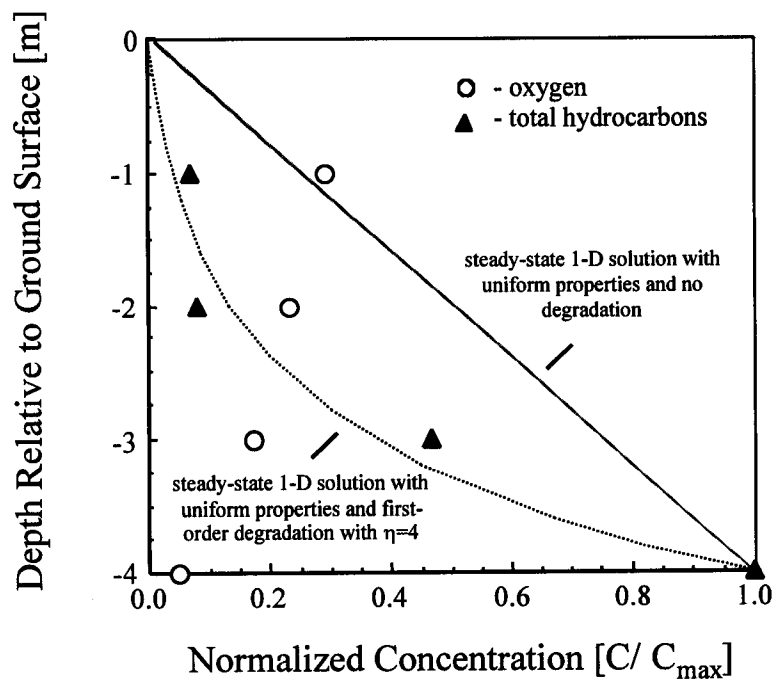


Figure 6. Normalized hydrocarbon and oxygen soil gas concentrations in a shallow near-homogeneous setting; data from Ostendorf and Kampbell (1991). Lines show expected concentration profiles in homogeneous settings at near-steady conditions for no degradation, and first-order degradation.

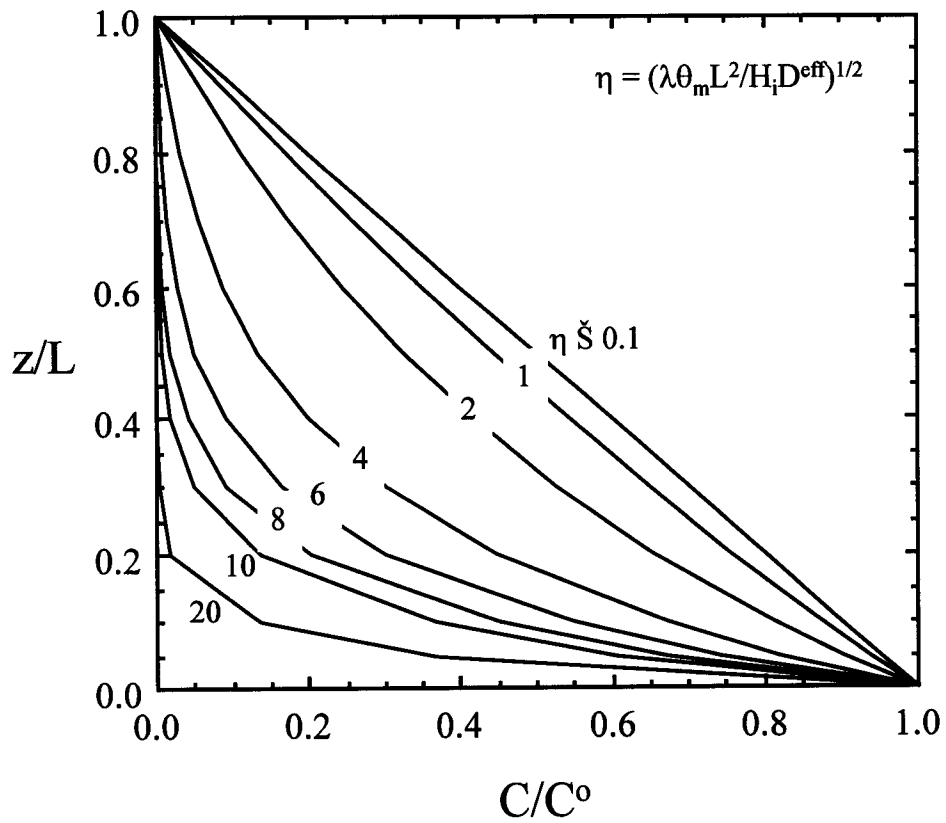


Figure 7. Predicted vapor concentration profiles for a homogeneous system at steady-state with a first-order reaction using Equation (8).

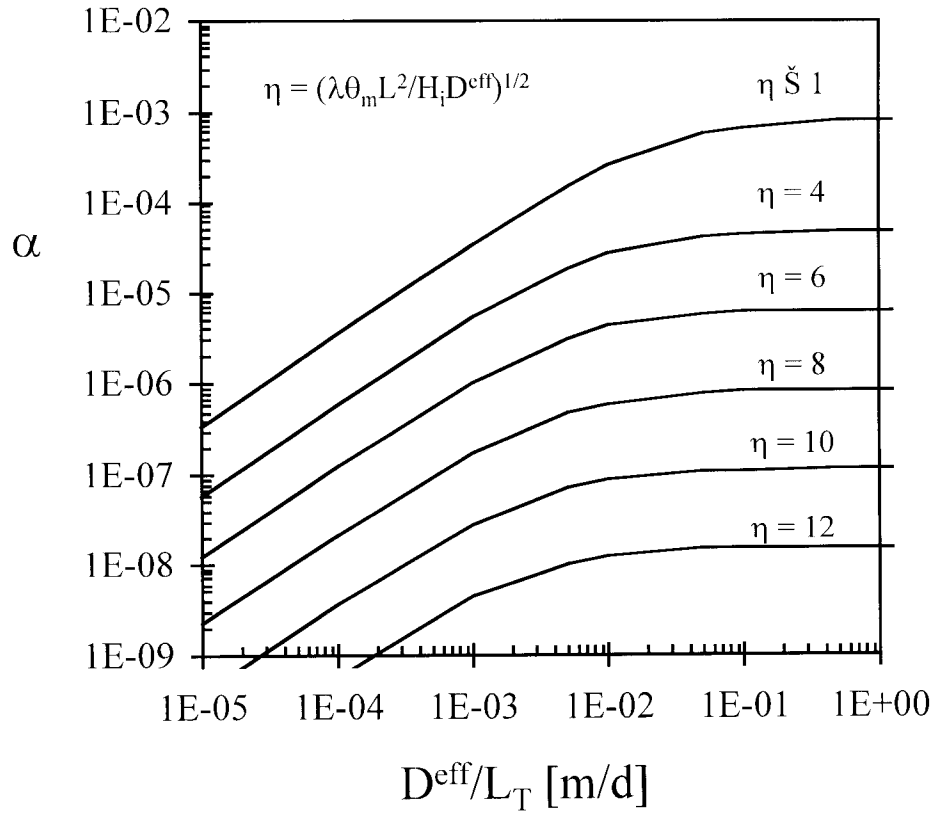


Figure 8. Attenuation coefficient predicted by Equation (10) for the case of a homogeneous medium at steady-state with a first-order degradation reaction.

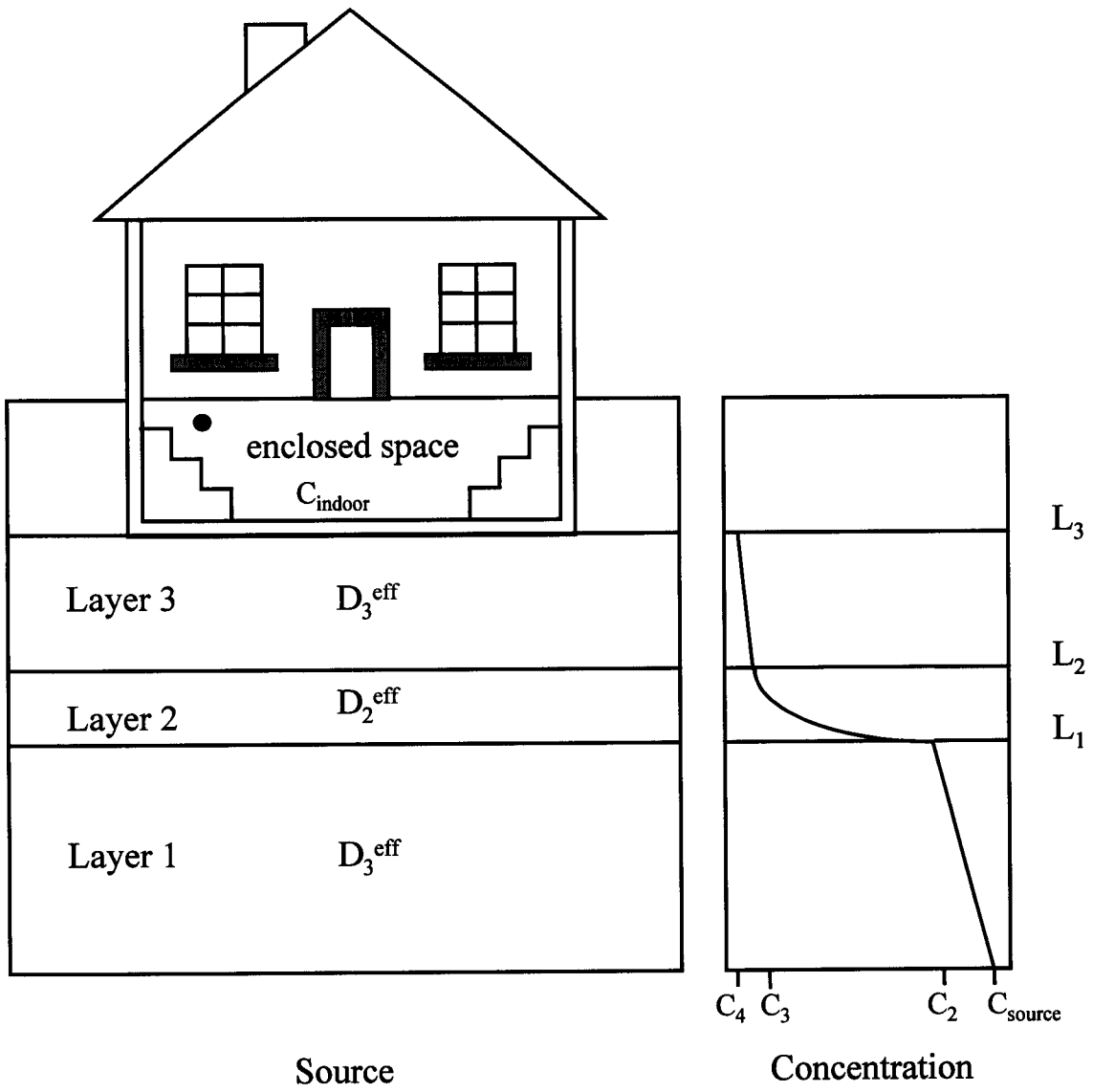


Figure 9. Schematic of dominant layer model bio-attenuation scenario.



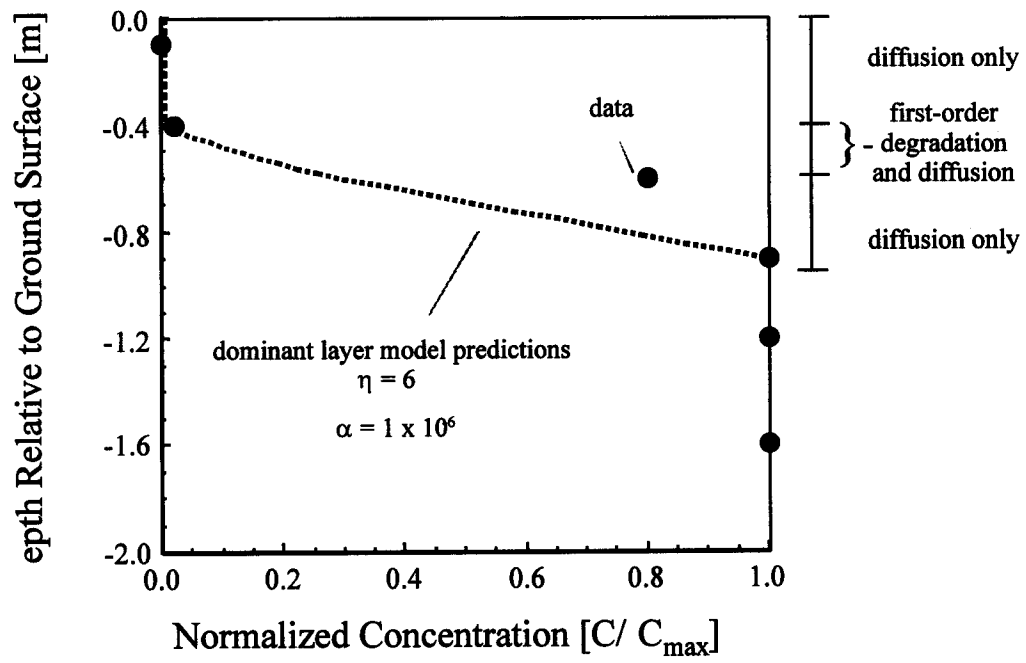


Figure 10. Comparison of dominant layer model with data from Fischer *et al.* (1996).

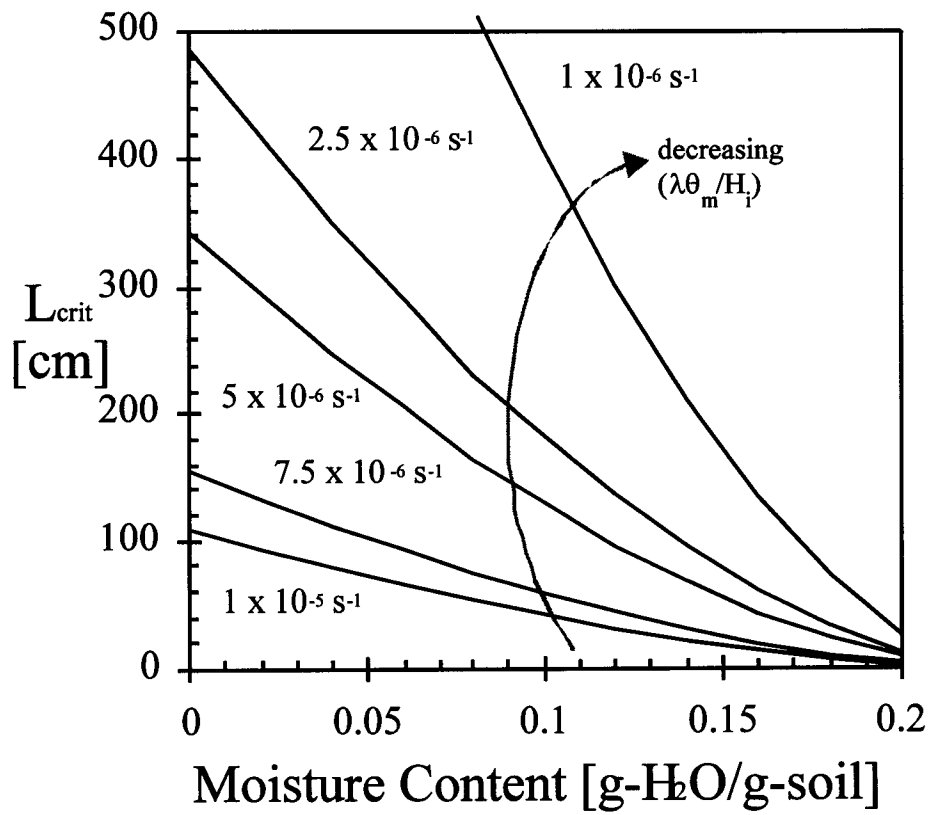


Figure 11. Hypothetical plot showing conditions necessary for significant bio-attenuation.



Additional copies are available through Global Engineering Documents at (800) 854-7179 or (303) 397-7956

Information about API Publications, Programs and Services is available on the World Wide Web at: <http://www.api.org>



**American  
Petroleum  
Institute**

1220 L Street, Northwest  
Washington, D.C. 20005-4070  
202-682-8000

Product No. I46740