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EVALUATION OF SOIL-GAS TRANSPORT OF ORGANIC CHEMICALS INTO RESIDENTIAL BUILDINGS

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Alfred T. Hodgson, Karina Garbesi
Richard G. Sextro, Joan M. Daisey

Indoor Environment Program
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Larry E. Williams
Authorizing Official
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ABSTRACT: This investigation consisted of theoretical, laboratory and field study phases with the overall objective of determining the importance of pressure-driven flow of soil gas in the transport of volatile organic compounds (VOC) from soil into a house. In the first phase, the mechanisms of advection, diffusion, and retardation of VOC in soil were evaluated. Using the theory of fluid mechanics and empirical relations for equilibrium partitioning of VOC among gas, aqueous, and solid phase of soil, a one-dimensional advection-diffusion equation for the transport of gas-phase VOC through soil was developed.

An experimental apparatus and method were developed for the direct observation of pressure-driven transport of VOC through soil under controlled laboratory conditions. The retardation of sulfur hexafluoride (SF_6) and hexafluorobenzene with respect to the flow of the bulk gas was measured in soil-column experiments using different soils and soil-moisture conditions. The results were in good agreement with theoretical predictions. Since SF_6 was not lost by sorption to soil, it was selected for use as a tracer gas in the field study to study the advective flow of soil gas.

The overall objective of the investigation was directly addressed by the field study. This study was conducted at a house which had a basement and which was located adjacent to a covered municipal landfill. The soil at the site was characterized, pressure coupling between the basement and the surrounding soil was measured, the entry rate of soil gas as a function of basement depressurization was mesured, and VOC in soil gas, indoor air and outdoor air were quantified.

The average permeability of the soil at the field site was approximately 2×10^{-12} m^2. The VOC identified in soil gas around the house were predominately halogenated and oxygenated compounds. The concentrations of many of these VOC were much higher in soil gas than in indoor and outdoor air. An extensive pressure field was developed in the soil around the house when the basement was depressurized, demonstrating that soil gas could potentially be drawn from a relatively large area that extended out toward the landfill. However, the flow of tracer gas from the soil into the basement with depressurization was low. The entry rate of soil gas due to pressure-driven flow was estimated to be less than 1 m^3 h^{-1} at a basement depressurization of a few Pascals, a pressure that would result from typical wind and indoor-outdoor temperature differentials. This flow, which was probably limited by the low below-grade leakage area of the basement, would be less than one percent of the estimated inflow of air into the house due to infiltration under similar conditions. It was concluded that pressure-driven flow of soil gas into the basement of this house would not result in high indoor concentrations of VOC. However, for houses with higher below-grade leakage areas, soils of equal or greater permeability and low infiltration rates, pressure-driven inflow could be more important relative to the total inflow of air into the house and could be an important entry mechanism for VOC.

Two shower experiments were conducted in the study house to measure the transfer of VOC from water to air and to estimate inhalation exposures due to the household use of contaminated water. Transfer efficiencies for five VOC for a ten-minute shower were all about 84 percent based on the water data. Exposures were estimated from the experimental data for a ten-minute shower combined with a ten-minute post-shower period. These exposures were equivalent to exposures estimated to be due to the entry of VOC into the house from the soil. Therefore, even though the entry of VOC from soil gas was low, soil gas was a relatively important source of exposure to VOC compared to the household use of water.

CHAPTER 1

STUDY OBJECTIVES AND ORGANIZATION

INTRODUCTION

The emphasis in assessments of population exposures to toxic volatile organic compounds (VOC) has generally shifted away from the almost exclusive analysis of outdoor air and now often includes analyses of indoor air and potable water which also contribute to exposures (*e.g.* Wallace *et al.*, 1986). Indoor air has been included because it is recognized that most people spend a majority of their time indoors and that the airborne concentrations of many compounds are higher indoors than outdoors. Ingestion of water is of particular concern in areas where well water has become contaminated.

Landfills are potentially important sources of exposure to VOC by all of these routes for residents of nearby houses. Even municipal landfills accepting only nonhazardous material have been found to contain toxic VOC at concentrations high enough to cause concern. In a study by Wood and Porter (1987), vinyl chloride and benzene were detected in gas drawn from the refuse zone in 85 percent of 20 municipal landfills investigated, often at concentrations exceeding 1 ppm. Several landfills closed for many years were among those with relatively high concentrations of these compounds. Release of VOC directly to the atmosphere can result in inhalation exposures to nearby populations. Contaminants can also be transported away from a site through the subsurface environment. Most research on the subsurface migration of VOC has focused on aqueous transport (Bennett, 1986; Roy and Griffin, 1987). Direct exposures due to contaminated ground water occur when the water is ingested. In addition, inhalation exposures occur when the contaminants are released from water to indoor air by household activities such as showering (Andleman, 1985a,b). Subsurface gas migration can also play a role in the transport of VOC away from landfills and in the entry of VOC into houses. In cases where gas-phase migration has been studied, transport by diffusion has been emphasized. But, if an adequate pressure gradient is present, gas-phase advective flow may also be an important mechanism for movement of contaminants through soil (*e.g.* Nazaroff *et al.*, 1987; Sextro *et al.*, 1987).

The State of California has recently passed legislation which acknowledges the potential problem of gas-phase migration of contaminants from landfills (California HSC, 1986 and 1988). The purpose of this legislation is to screen landfills to determine which sites may pose a public health risk. The legislation mandates sampling and analysis for selected toxic VOC at all landfills. At each site, gas from within and from outside the perimeter of the refuse zone is to be characterized. When these surveys are completed and they are summarized and analyzed, it is anticipated that a much more clear picture of the potential for exposure to toxic VOC by subsurface gas-phase migration from landfills will emerge.

Estimation of subsurface gas-phase migration of VOC from landfills requires an understanding of both the potential for flow of gas through soil and the physical and chemical parameters which affect partitioning of VOC among the gas, aqueous and solid phases of the system soil. Many of the soil parameters which are relevant to soil-gas flow and partitioning can be determined by standard laboratory methods. Soil permeability, the parameter which determines the flow rate of soil gas due to a pressure gradient, can be measured in-situ as described in Chapter 4.

Estimates of the parameters which affect the transport and partitioning of individual compounds, such as the Henry's Law constant and the soil-sorption coefficient, are more difficult to obtain. Although there are some compilations of Henry's Law constants (*e.g.*, Mackay and Shiu, 1981), few data exist of soil-sorption coefficients. Equations do exist for the estimation of soil sorption from water solubility or octanol-water partitioning, but these are based primarily on data for pesticides. Since pesticides are generally designed to be immobile on soil, they may not provide a good model for VOC. The lack of relevant data for many compounds makes prediction of vapor-phase migration of VOC through soil difficult.

Once VOC have migrated through soil into the vicinity of houses, either by gas-phase or aqueous transport, and are in the gas phase, they are potentially available for transport into these houses. The entry of soil gas into houses has been studied in relation to the issue of indoor radon. It has been demonstrated that advective flow of soil gas into substructures is the primary source of radon gas in single-family residences with elevated concentrations (D'Ottavio *et al.*, 1987 and Sextro *et al.*, 1987). This flow is driven by depressurization of the substructure with respect to the surrounding soil. In non-mechanically ventilated buildings, depressurization of a few Pascals results from the stack effect caused by thermal differences between indoors and outdoors and from the Bernoulli effect due to wind loading on the building superstructure (Nazaroff *et al.*, 1985 and Nazaroff *et al.*, 1987). In extreme weather conditions, this depressurization can approach -10 Pa (Sextro *et al.*, 1987). If the below-grade leakage area of the substructure is sufficient and if the soil is sufficiently permeable, a persistent pressure differential can draw soil gas bearing contaminants into a house at a higher rate than would be predicted by diffusion alone. In one field study, pressure coupling between basements and surrounding soil was measured, and the entry of soil gas was demonstrated using a tracer-gas technique (Nazaroff *et al.*, 1987). While significant differences from radon are expected due to differences in the physical and chemical properties of VOC, it is clear that VOC in soil gas can enter houses via the same advective-flow pathway.

STUDY OBJECTIVES

The primary objective of this investigation was to establish, by direct measurement at a field site, that pressure-driven flow of soil gas can result in the transport of VOC from soil into a house. To accomplish this objective, extensive field experiments were conducted at a house which had a basement and which was located adjacent to a covered municipal landfill. The specific objectives of the experiments conducted at this site were:

1. To characterize the relevant soil parameters;
2. To measure the pressure coupling between the building substructure and the surrounding soil;
3. To measure the entry rate of soil gas as a function of depressurization of the substructure;
4. To measure the concentrations of VOC in soil gas, outdoor air, indoor air and well water;
5. To determine the entry rate of VOC into the house due to the pressure-driven flow of soil gas; and
6. To compare potential inhalation exposures to VOC resulting from the entry of VOC from the soil and from the household use of contaminated water.

In conjunction with the field experiments, an apparatus and method were developed to measure the pressure-driven flow of gas and VOC through soil in the laboratory under controlled, well-characterized conditions. The apparatus and method were used:

1. To compare sulfur hexafluoride and hexafluorobenzene as potential tracers for gas-phase migration of VOC in soil; and
2. To preliminarily investigate the process of gas-phase migration of VOC.

ORGANIZATION

This report is organized into seven chapters. The theory of gas-phase migration of VOC in soil, which is essential for interpreting the results of the laboratory experiments, is developed in Chapter 2. In this chapter, a one-dimensional, time-dependent advection-diffusion equation is derived for gas-phase migration of VOC. The derivation results in the definition of a retardation factor for contaminant velocity with respect to the velocity of the bulk soil gas. Chapters 3, 4, and 5, which present the laboratory and field experiments, are written to describe each phase completely.

The results of the laboratory experiments are presented in Chapter 3. The behavior of the two proposed tracer gases are compared with the behavior predicted from the theory in Chapter 2. Chapter 4 presents the field experiments on the entry of VOC from soil gas into the basement of the house. Investigation of the physical mechanisms of soil-gas transport near and into the house consisted of a study of the pressure coupling between the basement and the surrounding soil, and a tracer-gas study of the entry of soil gas into the basement during basement depressurization. The concentrations of VOC in soil gas, outdoor air and indoor air were measured, and the entry rate of VOC into the house via the soil gas was estimated. In Chapter 5, soil gas and contaminated water used for showers are compared as sources of indoor inhalation exposure to VOC in the house.

Chapter 6 summarizes the conclusions drawn from the laboratory and field studies and makes recommendations for further study. The references for the entire report are contained in Chapter 7.

The research presented in Chapters 2 and 3 and a portion of the research presented in Chapter 4 were conducted by one of us (K. Garbesi) as partial fulfillment of the requirements for a Master of Science degree at the University of California, Berkeley (Garbesi, 1988). Chapter 4 was accepted for presentation at the 81st annual meeting of the Air Pollution Control Association (Hodgson *et al.*, 1988).

DISCLAIMER

Although there is reason to believe that VOC measured in the soil gas at the field site originated in the adjacent landfill, no attempt was made to study the long-distance transport of VOC from the landfill to the house. In addition, no evaluation was made of the effectiveness of the air-injection pumps installed between the landfill and the house to block the migration of methane from the landfill. Concentrations of VOC in the soil gas at the site may or may not have been altered by the operation of the pumps. Therefore, the measured concentrations are not necessarily representative of exposures to the former occupants of the house, and no attempt was made to evaluate potential health hazards to the former occupants based on the exposures estimated in the present study.

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CHAPTER 2

THEORY OF GAS-PHASE MIGRATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL

INTRODUCTION

The mechanisms of advection, diffusion, and contaminant retardation, as they apply to the migration of volatile organic compounds (VOC) in soil, are described in this chapter. Darcy's Law, which governs pressure-driven advective flow, and Fick's Law of molecular diffusion are outlined. The various physical and chemical factors influencing VOC retention and retardation with respect to the flow of the bulk gas through the soil are discussed. In particular, equilibrium partitioning between the gas, aqueous, and solid phases of soil is discussed. In addition, the distinction between mineral surface adsorption and partitioning into organic carbon is clarified.

A one-dimensional, time-dependent advection-diffusion equation for the transport of gas-phase VOC through soils is developed. The equation assumes equilibrium partitioning of VOC between the gas, aqueous, and solid phases of soil. That is, although a concentration gradient might exist along the transport path, equilibrium partitioning is assumed to apply at each point. Making use of equilibrium partitioning relationships in a complex multi-phase medium greatly simplifies the theoretical analysis of the transport problem. However, transfer kinetics cannot be neglected in situations in which the equilibrium assumption is not valid.

Cases in which an equilibrium model does not apply have been reported for aqueous systems. Adsorption equilibrium for some VOC on aqueous sediments can take from days to months (Wu and Gschwend, 1986; Karickhoff, 1984). Wu and Gschwend (1986) reported cases where physical mixing processes exposed sediments to contaminants at rates exceeding the mass-transfer rate. Under such conditions the equilibrium assumption will not apply.

However, in soil systems, the use of an equilibrium model is probably justified since there is evidence that equilibrium develops rapidly. In experiments by Chiou and Shoup (1985) on the gas-phase adsorption of five VOC onto soil, sorption equilibrium was generally achieved within four hours. This is quite rapid in comparison with the low-flow regimes expected due to a pressure buildup in a landfill, for example.

The one-dimensional model derived here is applicable to the soil-column experiments discussed in Chapter 3. A three-dimensional equivalent would be needed to describe the gas-phase migration of VOC from a landfill under the influence of methane pressure buildup in the landfill or the migration of VOC from a leaky underground storage tank under the influence of a pressure field developed around the basement of a house, as examples.

DARCY'S LAW

The pressure-driven flow of a fluid through a porous medium, such as soil, is governed by Darcy's Law. For a gas, the one-dimensional equation has the form:

$$v_d = \frac{-k}{\mu} \frac{dP}{dx} , \tag{2.1}$$

where v_d, referred to as the Darcy velocity, is the volumetric gas flux resulting from the pressure differential dP/dx; k (length squared) is the intrinsic permeability of the soil; and μ (mass per length per time) is the absolute viscosity of the gas. The velocity, v_d, is the approach velocity of the gas to the porous medium. The average flow velocity in the medium, v_x, is faster, such that $v_x = v_d/a$, where a is the air-filled fraction of the soil.

Darcy's Law applies under conditions of laminar flow. This criteria is satisfied if the Reynold's number, Re, does not exceed a number on the order of one. Bear (1972) reports that, for porous media, Re takes the form:

$$Re = \frac{v\,d}{\nu} , \tag{2.2}$$

where v is the fluid velocity and ν is the kinematic viscosity (absolute viscosity divided by fluid density). The parameter d, characteristic of the grain dimension, has different accepted forms. Sometimes d_{10} (or d_{50}) is used, defining the size d such that 10 (or 50) percent of the mass of the soil has a grain size less than d.

FICK'S LAW

Molecular diffusion in air is governed by Fick's Law:

$$F = -D_a \, dC_a/dx \, , \tag{2.3}$$

where F is the mass flux; D_a is the diffusion coefficient of the contaminant in air; and dC_a/dx is the concentration gradient of the contaminant in air. In order to account for the increased path length of a molecule diffusing in soil, D_a is divided by a tortuosity factor τ, to obtain an effective diffusion coefficient:

$$D_{eff} = D_a/\tau \, , \tag{2.4}$$

where τ is always greater than 1 and can be greater than 2 (Hillel, 1980, pg. 177). Typical values for tortuosity in soil are 1.5 or 1.6.

EQUILIBRIUM PARTITIONING

Volatile organic compounds of interest as environmental contaminants typically have low water solubilities, have high vapor pressures, are uncharged, and are relatively nonpolar. These properties govern their partitioning behavior among the three phases of the soil medium. Air-water partitioning in soil is governed by Henry's Law. Air-solid and water-solid partitioning are more complex phenomena. The solid phase can act as a two-phase medium, such that VOC sorption to the solid phase can occur via mineral surface adsorption or by absorption into organic matter (Chiou *et al.*, 1988).

Contaminant partitioning between the vapor and aqueous phases at low aqueous concentrations is described by Henry's Law:

$$C_a = H\,C_w\,, \tag{2.5}$$

where, C_a is the concentration of the contaminant in air; C_w is the concentration in water; and H is the Henry's Law constant. Henry's Law constants are experimentally determined or can be estimated from vapor pressure and solubility data. For VOC which are low solubility liquids at ambient temperatures, Henry's Law constants are obtained by dividing the saturation vapor pressure by the solubility, where both quantities are taken at the system temperature. In practice, there has been considerable confusion over the calculation of Henry's Law constants for compounds which are gases under ambient conditions, and much of the published data are conflicting. Mackay and Shiu (1981) provide a detailed reference on the calculation of Henry's Law constants and a compilation of Henry's Law constants for many VOC which occur as environmental contaminants.

Historically, partitioning between the fluid and solid phases has been explained as a surface-adsorption phenomenon. Chiou *et al.* (1979) first suggested that partitioning of aqueous-phase, non-ionic, organic compounds into soil organic matter was a dissolution process rather than a surface adsorption-phenomenon. This process was found to be linear and correlated with the weight fraction of organic carbon in the soil, such that:

$$C_s = f_{oc}\,K_{oc}\,C_w\,, \tag{2.6}$$

where C_s is the concentration of VOC immobilized by the organic carbon; f_{oc} is the weight fraction of organic carbon in the soil; and K_{oc} is the temperature-dependent, contaminant-specific, adsorption coefficient.

Few direct measurements have been made of sorption coefficients for the myriad VOC found as environmental contaminants. However, correlations have been found between the sorption coefficient and water solubility, S. Lyman *et al.* (1982, Chapter 4) provide an excellent summary of these studies, all of which report a relationship of the form:

$$\log K_{oc} = a + b \log S . \tag{2.7}$$

Most of the reported regressions are, however, based on data for pesticides. Because pesticides are generally designed to be persistent on soils, these data regressions are probably not a good model for the behavior of VOC.

Chiou *et al.* (1979) measured K_{oc} for 15 chlorinated hydrocarbons, only two of which were low-boiling VOC, and obtained the relationship below. This relationship has been rewritten as a function of K_{oc} in the manner suggested by Lyman *et al.* (1982, pp. 4-9).

$$\log K_{oc} = 4.277 - 0.557 \log S , \tag{2.8}$$

with a coefficient of determination (r^2) of 0.99, where S has units of micromole L^{-1}, and K_{oc} is unitless.

Chiou and Shoup (1985) demonstrated the importance of mineral surface adsorption in dry soils in a series of experiments in which the vapor-phase uptake of VOC onto soil was determined as a function of relative humidity (RH) of the soil gas. Their work indicates that soil acts as a dual sorbent for VOC from the gas phase. The charged mineral surface and the organic matter provide two types of sorption sites with distinctly different properties. The mineral surface acts as a conventional surface-phenomenon adsorber, while the the organic fraction behaves as a partitioning medium (Chiou *et al.*, 1988). The authors found that at low RH, VOC sorbed to both the mineral surface and the organic fraction. The adsorption isotherms measured at low RH were found to be distinctly nonlinear. At higher RH, water vapor began to displace VOC on the mineral surface sites. At RH greater than 90 percent, VOC sorption was essentially confined to the organic fraction, with the total amount of sorption significantly lower than that at low RH. At high RH, the normalized vapor-phase isotherms (C_s vs. P/P_{sat}) had fallen into the range of aqueous isotherms (C_s vs. $C_w/C_{w,sat}$), where P_{sat} and $C_{w,sat}$ represent the saturation vapor pressure and the saturation water solubility, respectively.

The RH of soil gas in natural soils is normally 98-100 percent, while the RH in air-dry soils is approximately 50 percent due to the retention of capillary water (H. Donner, UCB, personal communication). Therefore, in the natural environment, organic carbon content should be the soil characteristic which dominates the sorption of VOC. This considerably simplifies the transport analysis in that: 1) vapor-solid sorption need not be considered separately from water-solid sorption; and 2) an analytically simpler, linear sorption isotherm may be used. Accordingly, substitution of Equation 2.5 into 2.6 gives the vapor-solid partitioning equation:

$$C_s = (f_{oc} K_{oc}/H)C_a . \tag{2.9}$$

However, Karickhoff *et al.* (1979), who investigated the sorption of hydrophobic compounds onto different particle-size fractions of pond and river sediments, demonstrated that not all organic carbon behaves equally. They found the organic carbon on sands to be 50-90 percent less effective as a sorbent than the organic carbon on the silt and clay. This effect has been ignored in the development of the time-dependent, advection-diffusion equation since the errors in the predicted adsorption coefficients are expected to be as large as those resulting from the differences in the distribution of organic carbon among particle size fractions of the soil. In addition, mineral surface adsorption has been ignored since it is assumed to only be important for soil with a very low organic carbon content.

TIME-DEPENDENT, ADVECTION-DIFFUSION EQUATION

A time-dependent advection-diffusion equation can be developed for the movement of a gas-phase contaminant through soil using the equilibrium-partitioning relationships discussed above. The soil is treated as a three-phase medium with n as the soil porosity (volume of non-solid divided by volume of soil) and s as the water-filled fraction of n (volume of water divided by pore volume). Therefore, 1-s is the air-filled fraction. The fractional pore volume for soil is typically in the range of 0.3 to 0.6 (Hillel, 1980, pg. 11). The water-filled fraction is more variable. The one-dimensional, partial differential equation is derived through mass balance. For a given volume element, the mass entering by advection, at velocity v_x, plus the mass entering by diffusion, with flux F_{eff} (where $F_{eff} = D_{eff} dC_a/dx$), is set equal to the mass leaving by advection and diffusion plus the change in concentration in each of the three phases.

$$\begin{aligned} &C_a(x)v_x An(1-s)\Delta t + F_{eff}(x)n(1-s)A\Delta t = \\ &C_a(x+\Delta x)v_x(x+\Delta x)An(1-s)\Delta t + F_{eff}(x+\Delta x)n(1-s)A\Delta t + \\ &\Delta C_a(x)n(1-s)A\Delta x + \Delta C_w(x)nsA\Delta x + \Delta C_s(x)\rho_b A\Delta x , \end{aligned} \tag{2.10}$$

where A is the area of the volume element, Δx is the element width, Δt is the time increment, and ρ_b is the bulk density of the soil. $F_{eff}(x)$ and $F_{eff}(x+\Delta x)$ represent the diffusive fluxes entering and leaving the element, respectively. A similar convention is used for concentration. The last three terms on the right hand side of Equation 2.10 are the changes in concentration in each of the phases (air, water, and solid) of the volume element. Substituting in Equations 2.3, 2.5, and 2.9, rearranging terms, and taking the limit in which Δx and Δt go to zero, give the advection-diffusion equation:

$$\frac{\partial C_a}{\partial t} = \frac{-1}{R} \frac{\partial (C_a v_x)}{\partial x} + \frac{D_{eff}}{R} \frac{\partial^2 C_a}{\partial x^2} , \tag{2.11}$$

where the retardation factor, R, is defined by:

$$R = 1 + \frac{s}{H(1-s)} + \frac{\rho_b f_{oc} K_{oc}}{Hn(1-s)} . \tag{2.12}$$

Assuming a constant advective velocity,

$$\frac{\partial C_a}{\partial t} = \frac{-v_x}{R} \frac{\partial C_a}{\partial x} + \frac{D_{eff}}{R} \frac{\partial^2 C_a}{\partial x^2} . \tag{2.13}$$

The first term on the right-hand-side of Equation 2.13 is the advective contribution to transport, while the second term is the contribution by molecular diffusion. The form of the equation suggests the function of R, the retardation factor. It is the factor by which contaminant velocity is slowed with respect to the velocity of the bulk soil gas; it also serves to increase the diffusion time. As shown in Equation 2.12, a contaminant with a large adsorption coefficient combined with a small Henry's Law constant is expected to have a relatively large retardation. Retardation in the natural environment is expected to be subject to temporal variation, since both H and K_{oc} are temperature dependent and s can vary with precipitation.

Using the Peclet number, Pe, from fluid mechanics, Equation 2.13 can be simplified for situations in which either diffusion or advection can be neglected.

$$Pe = \frac{v\,L}{D} \quad , \tag{2.14}$$

where, in porous media, v is the velocity of the bulk fluid, D becomes the effective diffusion coefficient, D_{eff}, of the compound of interest, and L is the distance scale. For example, in the laboratory experiments described in Chapter 3, L is the length of the soil column, the distance over which the test-gas contacts the soil. In situations in which Pe is much greater than one, diffusion is insignificant. If diffusion can be neglected and advection is governed by Darcy's Law, then the equation for pressure-driven flow of VOC in soil, from Equation 2.13, becomes:

$$\frac{\partial C_a}{\partial t} = \frac{-v_d}{R} \frac{\partial C_a}{\partial x} \quad , \tag{2.15}$$

which is solvable exactly if R is constant in space and time.

CHAPTER 3

LABORATORY COMPARISON OF TRACER GASES FOR STUDIES OF GAS-PHASE MIGRATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL

INTRODUCTION

In this phase of the investigation, an experimental apparatus and a method were developed for the direct observation of the pressure-driven flow of gas and volatile organic compounds (VOC) through soil under controlled laboratory conditions. The apparatus and method were used to compare the transport of two tracer gases, sulfur hexafluoride (SF_6) and hexafluorobenzene (HFB), proposed for use in the subsequent field study. The retardation factors of these two compounds were measured and compared with the retardation factors predicted from the theory developed in Chapter 2. The observation of tracer-gas transport in both air-dry and wetted soil enabled a qualitative comparison between mineral surface adsorption and organic carbon absorption.

The apparatus and method developed for these experiments can be applied to the study of the long-distance transport of VOC through soil. The retardation factors are applicable to a situation in which contaminated soil gas moves into a region of soil not already in equilibrium with the inflowing soil gas. In the case of gas-phase VOC migrating away from a landfill on a methane gas plume, for example, the relative retardations of various VOC give an estimate of which VOC will move the fastest and farthest through the soil.

The apparatus and method can also be used to provide information about the potential variation in the sorptive capacity of a given soil as a function of temperature and moisture content. This information is particularly applicable to the study of the entry of VOC into houses. On a short time scale, the concentrations of VOC in the soil gas around a house are expected to remain relatively constant. However, on a seasonal scale, the concentrations are expected to vary due to changes in meteorological conditions which will alter the parameters controlling the partioning of VOC among the soil phases.

METHODS

Soil-Column Apparatus

The soil-column apparatus was designed to be non-contaminating, to have low reactivity with VOC, and to have interchangeable columns of soil of various lengths. A regulated flow of test gas is passed through the column while measuring the flow rate of the gas and the pressure differential across the soil. The relative humidity of the test gas is controlled and monitored. Concentrations of VOC in the test gas are monitored as the gas exits the column. Soil properties are varied by using soils with a range of organic-carbon content and particle-size distribution and by adjusting the water content of the soil before packing. The soil column is packed homogeneously in a reproducible manner with the aid of a mechanical device. The importance of incorporating temperature control was not fully realized until near the end of this phase of the study. At that time, temperature probes were added to the extensions above and below the soil column in order to correlate observed effects with temperature.

Figure 3.1 is a schematic diagram of the soil-column apparatus. The apparatus consists of three sections constructed of nickel-plated brass. The central section, constructed of 9.4-cm ID pipe, is the soil column. Columns of various lengths are used to facilitate observation of compounds with different retardation factors. The columns have a screen on the bottom with 50-micron stainless-steel mesh. The mesh, which supports the soil, is fine enough to contain the clays in a static environment after soil packing, but offers no significant resistance to gas flow. The top and bottom extensions are sealed to the soil column with Viton O-rings set into bolted flanges. The extensions are provided with ports for the entry and exit of the test gas and for insertion of pressure and temperature probes.

Soil Characterization

Three Northern California soils were collected to represent a range of particle-size distribution and organic-carbon content. The classifications of these soils according to the U.S. Department of Agriculture Soil Survey are Panoche Soil, Yolo Loam, and Delhi Sand. The soils were spread thinly and air dried for several days and were then passed through a 2-mm sieve to remove coarse particles. Each soil was analyzed for particle-size distribution and organic-carbon content. Particle-size distribution was determined for the silt and clay fractions by standard hydrometer-method sedimentation analysis and for the sand fraction by sieving (Day, 1965). Organic-carbon content was measured with the Walkley-Black procedure (Nelson and Sommers, 1982) which uses dichromate ion from $K_2Cr_2O_7$ to oxidize the organic carbon. The remaining dichromate ion is determined by titration with Fe(II). The mass of organic carbon is then determined from the difference between the original and the remaining amounts of dichromate ion.

Soil Packing

Soil columns were packed with the aid of a mechanical device based on the design of Reeve and Brooks (1953) and illustrated in Figure 3.2. An extension is bolted onto the top of the soil column. Soil is dropped into the extension-column assembly from a reservoir with a perforated bottom. While the soil is falling, the perforated bottom is rotated, resulting in evenly distributed, lightly packed soil. The column and extension are then fastened onto a platform and light pressure is applied to the top of the soil with a spring loaded disk. The entire assembly is repeatedly dropped a distance of 2.5 cm onto a rubber-covered platform using a motor-driven, spiral cam to create a reproducible, homogeneously packed sample. The extension is then rotated off the column so that the surface of the soil is smooth.

Soil Wetting

In order to vary the water content of the soil while leaving all other soil variables unchanged, several methods of wetting soil already packed in columns were attempted. Passing air saturated with water vapor through the soil column was unsatisfactory because of the excessive length of time required to wet the soil. Methods in which water was added directly to the column also proved to be unsatisfactory because soils treated in this manner contracted from the walls of the column leaving a short circuit for the test gas to flow around the soil.

Therefore, the following procedure was adopted of wetting the soil before packing. Several kilograms of air-dried soil are divided into four parts and spread thinly on a heavy plastic sheet. The soil in each of the four parts is then sprayed with a fine mist of water and stirred. This process is repeated until the soil just starts to clump. The four parts are then mixed and placed in a sealed container and tumbled overnight. In the morning, the soil is removed from the container and passed though a 2-mm sieve. Packing of the column with soil proceeds as described above resulting in a uniformly packed, low-density, highly permeable soil. The moisture content of the soil is determined by weighing a sample of the wetted soil before and after drying in an oven to constant weight at 110°C.

Measurement of Soil Permeability

After assembling the apparatus as shown in Figure 3.1, the permeability of the soil is measured by passing a regulated flow of air through the column while monitoring the pressure drop across the soil. The flow rate of air is regulated with an electronic mass-flow controller and the pressure differential is measured with a variable-reluctance pressure transducer (Model DP103, Validyne Instr., Inc.). Rearranging Equation 2.1 for Darcy's Law and rewriting the flux in terms of the volumetric flow rate, Q, per soil-column area, A, the permeability is:

$$k = \frac{-\mu Q}{A} \frac{\Delta L}{\Delta P} , \tag{3.1}$$

where k (cm^2) is the intrinsic permeability, μ (1.84×10^{-4} g cm^{-1} s^{-1}) is the viscosity of air, Q (cm^3 s^{-1}) is the flow rate of the test gas, A (cm^2) is the area of the soil column, ΔP (dyne cm^{-2}) is the pressure drop across the column; and ΔL (cm) is length of the soil column.

Preparation of Test Gases

The test gases used for the transport experiments were prepared in the following manner. A small injection of pure HFB liquid was diluted with pure air to 100 ppm in a Tedlar gas-sampling bag. The SF_6 tracer was a commercially prepared, pressurized cylinder of 190 ppb SF_6 in pure air. Test gases used in experiments with wetted soil were humidified before entry into the soil column by passing the gas stream over boiling water and then through a condenser with glass wool to remove liquid-phase water. The outflow from the condenser was then passed through a coil of Teflon tubing to equilibrate the gas to ambient temperature before inletting it to the soil column. Relative humidity of the gas stream was measured periodically during the experiments both upstream and downstream of the soil column with a dewpoint hygrometer (Model 911, EG&G, Inc.).

Analysis of Test-Gas Concentrations

Concentrations of SF_6 and HFB in the test gas were measured with a gas chromatograph (GC) (Model 1030A, Baseline Industries, Inc.) equipped with an electron capture detector and an automatic sampling valve. The valve was set to sample at one-minute intervals. The GC was configured with two ten-port valves to accommodate simultaneous operation of two columns, one for SF_6 and the other for HFB. A molecular sieve (5A) column (0.32 cm OD, 0.22 cm ID x 2.4-m) was used for SF_6. The HFB column was 100/120 mesh Chromosorb G with OV-101 silicone coating (0.32 cm OD, 0.22 cm ID x 0.41 m). The GC was operated isothermally at 150°C with the detector at 240°C. The carrier gas was Argon with seven percent methane, and was run at a flow rate of 50 cm^3min^{-1}. Under these conditions, the retention times were five seconds for HFB and 28 seconds for SF_6.

Peak height rather than peak area was used for the calibration of the two test gases. Concentrations of SF_6 were linear with peak height up to 200 ppb, with a resolution of 0.5 ppb. Concentrations of HFB were nonlinear with peak height up to 8 ppm, and linear between 8 and 100 ppm. The nonlinearity at low concentrations did not significantly affect the results of the experiments and was, therefore, ignored.

Experimental Setup and Procedures

Figure 3.3 is a schematic diagram of the experimental setup for the transport experiments. The flow rate of the test gas entering the soil column was regulated and measured with an electronic mass-flow controller (0 - 100 cm^3min^{-1}). One test gas was introduced into the soil column at a time. Either SF_6 was delivered under pressure to the mass flow controller from the gas cylinder, or HFB, contained in the gas-sampling bag, was delivered to the mass-flow controller with a peristaltic pump and a in-line 5-L pressure capacitor to dampen the pressure fluctuations due to the pump. The gas stream then either passed through the humidifier for experiments with wetted soil or entered the soil column directly. Test gas exiting the soil column was sampled by the GC and the excess gas was vented to a laboratory hood.

A transport experiment was initiated by introducing the test gas through a port in the base of the soil-column apparatus at time zero. Test gas exiting the column was monitored by the GC, and the flow rate of the test gas and the pressure across the soil column were monitored as in the soil-permeability measurements. During experiments lasting several hours, the concentration of the test gas at the column inlet was periodically measured. When the concentration at the outlet was equal to the concentration at the inlet, pure air was substituted for the test gas, and the decay in concentrations at the outlet was monitored over time.

Experiments were performed during which first SF_6 and then HFB were passed through soil columns packed with air-dry Delhi Sand, air-dry Yolo Loam, air-dry Panoche Soil, and Panoche Soil with 8.6 percent water by weight. A 5-cm soil column was used in all experiments to minimize the time required for outflow concentrations to equal inflow concentrations. The gas flow rate was 100 cm^3min^{-1} in all experiments so that the retardation factors for the tracer gases could be directly compared.

RESULTS AND DISCUSSION

Soil Characterization

Table 3.1 summarizes the results of the analyses of particle-size distribution and organic-carbon content. All soils were low in organic carbon. There was, however, an approximate ten-fold spread in organic-carbon content, with Panoche Soil and Yolo Loam having about 0.2 percent carbon by weight, and Delhi Sand having 0.03 percent. All of the soils had sand contents of 69 percent or more. There was a reasonable spread in clay content, with the Panoche Soil having 17 percent clay and the Delhi Sand having three percent. The cumulative particle-size distributions for each of the three soils are presented in Figure 3.4.

Soil Packing

The procedure using the soil-packing device produced satisfactorily reproducible results. The amount of packing achieved was determined by measuring the permeability of the packed columns. Figure 3.5 shows permeability versus the number of impacts used to pack Yolo Loam in a 16-cm column. Constant permeability was obtained to within approximately ten percent when 350 or more impacts were used. Consequently, 400 impacts were used to pack the soil for the transport experiments.

Soil Permeability

The permeability of air-dry Yolo Loam packed in a 16-cm column was measured at various applied pressures. The results presented in Figure 3.6 show that the apparent Darcy permeability, calculated using Equation 3.1, decreased with increasing applied pressure. In another experiment using Yolo Loam with 1.9 percent water packed in a 16-cm column, permeability increased with increasing applied pressure; however, the magnitude of the effect was smaller than for air-dry soil (Figure 3.7). Additional experiments using Yolo Loam with 8.8 percent water and Panoche Soil with 8.6 percent water packed in a 5-cm column showed no measureable change in permeability with applied pressure.

According to the original formulation of Darcy's Law, permeability should be constant with applied pressure. Three separate calculations were made to ensure that Darcy's Law applied to the experimental system. First, the Reynold's Number was calculated using Equation 2.2. With d = 100 μm, $\nu = 0.144\ \text{cm}^2\ \text{s}^{-1}$, and $v_x = 0.06\ \text{cm s}^{-1}$, corresponding to the highest flow rates used in the experiments, Re is 4×10^{-3}, well within the required flow regime. Second, the permeability data were entered into the Darcy's Law equation for a compressible gas (Scheidegger, 1974) to determine if compressibility could account for the observed deviation.

$$v = \frac{-k}{\mu} \frac{(P_t^2 - P_b^2)}{2 P_b L}, \tag{3.2}$$

with P_b and P_t equal to the pressure at the bottom and top of the column, respectively. At a pressure of 400 Pa, well above that applied in the experiments, the correction for compressibility is only 0.2 percent which does not explain the observed deviation. Third, the hypothesis of imperfect fluid viscosity at the soil surface was tested. Klinkenberg (1941), assuming the fluid to have small, but finite velocity at the media surface, calculated the relationship between the apparent and true permeabilities:

$$K_a = K\ (\ 1 + b/P\ ) \tag{3.3}$$

where K is the true, constant permeability, K_a is the measured permeability, and P is the mean pressure of the gas in the column. A plot of experimental values of K_a versus 1/P does not linearize the data and, therefore, the Klinkenberg effect does not account for the observed deviations.

Data similar to those in Figure 3.6 have been repeatedly recorded when making permeability measurements in the field (R. Sextro, unpublished data). Our conclusion is that the effect is due to a change in the porous medium itself. We hypothesize that as applied pressures are increased in dry soil, the fine particles are forced into the interstices of the medium resulting in a systematic increase in resistance to flow. Resistance will become asymptotic at high pressures when no more rearrangement can occur. This effect is reduced in wetter soils as the fine particles become aggregated in the presence of water. The increase in permeability with pressure shown in Figure 3.7 might be explained by water bubbles, fixed in the pore spaces, being broken as applied pressure is increased resulting in increased permeability.

However, for environmental applications, the uncertainty in the measured permeability will, in general, be insignificant. A two- or three- fold uncertainty due to the variation inherent in the measurement technique is generally insignificant since this parameter ranges over seven orders of magnitude. In addition, the observed variation in permeability due to small-scale heterogeneity in natural soils is larger than this uncertainty.

Comparison of SF_6 and HFB

Table 3.2 compares the measured breakthrough times of SF_6 and HFB for pressure-driven transport through the various soils. The breakthrough time is defined as the time required for the concentration of the compound at the outlet of the column to reach $1-e^{-1}$ of the concentration at the inlet. Figures 3.8 through 3.13 show the concentrations of SF_6 and HFB at the outlet of the column for these experiments, where outlet concentrations have been normalized with respect to inlet concentrations. As discussed above, the anomalous results for HFB at low concentrations are due to the nonlinearity of the calibration below 8 ppm.

In all of the experiments, HFB was found to be retarded with respect to SF_6 (Table 3.2, Figures 3.8 - 3.13). This was most notable with the air-dry soils. For example, in air-dry Panoche Soil, the breakthrough time of HFB was a factor of 30 longer than that of SF_6 (Figures 3.8 and 3.9), while in wetted Panoche Soil, there was less than a two-fold difference (Figure 3.13). This result is in agreement with the finding of Chiou and Shoup (1985) that, at the high soil-gas relative humidity expected in wet soils, water displaces hydrophobic organic compounds on mineral surface sites resulting in significantly decreased total sorption. Therefore, the large retardation of HFB in air-dry soil was probably due to mineral surface adsorption, whereas the greatly reduced sorption in wetted soil is explained by the uptake of HFB by the organic carbon fraction alone.

Assuming that the retardation of HFB in air-dry soil was due primarily to mineral surface adsorption, the greatest retardation would be expected in the soil with the highest clay content. Delhi Sand, with the lowest clay content of three percent, did produce the lowest retardation, but Yolo Loam, with seven percent clay, produced higher retardation than Panoche Soil, with 17 percent clay (Table 3.2, Figures 3.8 - 3.12). The lack of temperature control during these experiments (discussed in more detail below) may account for this result.

A retardation factor was calculated for HFB using Equation 2.12 and the conditions of the experiment with wetted Panoche Soil. The numerical values of the parameters used in this calculation are presented in Table 3.3. The predicted retardation factor is 3.2. A retardation factor was also calculated for SF_6. Assuming K_{oc} for SF_6 equals zero, Equation 2.12 becomes:

$$R = 1 + \frac{s}{H(1-s)} . \qquad (3.4)$$

For a low solubility gas at atmospheric pressure, H can be calculated by dividing atmospheric pressure by the water solubility of the gas at one atmosphere (Mackay and Shiu, 1981).

Using a solubility of 4.1×10^{-5} g(SF_6)-cm^{-3}(H_20) at 20°C (Horvath, 1975), H is 150 cm^3(H_2O)-cm^{-3} (air), which makes the second term in Equation 3.4 negligible. Therefore, R for SF_6 can be taken as one, and SF_6 can be used as a reference gas to measure the retardation of HFB.

In order to obtain the experimental retardation of HFB relative to SF_6, a correction must be applied to the breakthrough-time data to account for the mixing time of the compounds in the soil-column extensions. The mixing time associated with the volume of the extensions to the soil column (Figure 3.1), as determined by a well-mixed-box model, is V/Q, where V is the total volume of the extensions and Q is the flow rate of the test gas. Using Q for the experiment with wetted Panoche Soil, the mixing time is 6.9 minutes. Subtracting this time from the measured breakthrough time for SF_6 of 10.3 minutes (Table 3.2) results in an effective breakthrough time of 3.4 minutes. Similarly, the effective breakthrough time of HFB is 15 minus 6.9 minutes, or 8.1 minutes. Using SF_6 as a reference, the measured retardation factor for HFB for this experiment is 8.1 divided by 3.4, or 2.4. Considering the uncertainty in the estimation of K_{oc} for HFB (Equation 2.8), the predicted retardation factor of 3.2 is in good agreement with the experimental value.

The large effect of temperature on the sorption of HFB on soil was demonstrated during the experiment with air-dry Yolo Loam. In this experiment, the temperatures of the test gas in the extensions above and below the soil column were monitored continuously (the temperatures in the two extensions were the same within experimental uncertainty). As shown in Figure 2.13, there was an eight-hour time lag after introducing HFB to the column before any appreciable increase in the concentration of HFB was measured at the outlet. During this period in which the normalized outlet concentration remained less than 0.1, the temperature of the test gas was steadily decreasing. As temperature decreases, the sorption coefficient and the total sorptive capacity of the soil increase. Had the experiment been conducted isothermally, the breakthrough time for HFB would certainly have been shorter. The reverse effect of temperature was observed at hour 13 when the temperature rose, and the concentration of HFB at the outlet exceeded the inlet concentration. This effect was further demonstrated during the transport of HFB across air-dry Panoche Soil (not shown). When the outlet concentration had reached a steady state, the soil column was rapidly heated with a heat gun. Almost instantaneously, the outlet concentration rose to well above the inlet concentration. These results indicate that the lack of temperature control in the experiments could account for the longer breakthrough time of HFB in Yolo Loam than in Panoche Soil even though the clay content of Panoche Soil is higher.

The relative magnitude of the retardation of HFB in Delhi Sand versus the retardations in Yolo Loam and Panoche Soil is not readily explained. The retardation in Delhi sand is approximately a factor of ten less than the retardation in the other two soils, yet the clay content of Delhi Sand is relatively close to that of Yolo Loam. A more detailed understanding of the effects of soil parameters on retardation would require further experimentation using a range of compounds in a temperature controlled system with soils having a wider range of particle-size distributions and organic-carbon contents.

CONCLUSIONS

The soil-column apparatus and method proved to be suitable for evaluating the behavior of tracer gases proposed for use in the field to measure the pressure-driven flow of VOC through soil. The breakthrough times of SF_6 and HFB in three soils at two conditions of soil moisture were measured and compared. The SF_6 tracer gas was not lost by sorbtion to any of the soils. The flow of HFB tracer gas was always retarded relative to the flow of SF_6, and HFB was strongly sorbed by two air-dry soils. The measured and predicted retardation factors for HFB in a wetted soil, more typical of soils in the natural environment, had a value of approximately three. Based on these results, SF_6 appears to be a good tracer gas for use in the field to measure the advective flow of the bulk soil gas, at least over the relatively short distances applicable to the investigation of soil-gas entry into houses. Because HFB is sorbed onto the soil, it would not be a good tracer gas to use for this application. However, since its behavior in soil may be similar to that of other VOC, it might be possible to use it to study the advective transport of certain VOC. Comparisons of the behavior of HFB with the behavior of VOC of interest could be made with this apparatus and method. The major disadvantages of a tracer gas, such as HFB, that is sorbed by soil are that considerable mass could be lost to the soil and its residence time in soil might be unacceptably long.

Table 3.1. Particle-size fractions and organic carbon content of soils by weight.

Soil	Clay (%)	Silt (%)	Sand (%)	OC[a] (%)
Panoche Soil	17	14	69	0.24
Yolo Loam	7	15	78	0.23
Delhi Sand	3	3	94	0.03

a. organic carbon

Table 3.2. Measured breakthrough times of SF_6 and HFB for pressure-driven flow across a 5-cm soil column.

Soil	Soil Water (%)	k[a] (m^2)	τ_{SF_6}[b] (min)	τ_{HFB}[b] (min)
Panoche Soil	AD[c]	2×10^{-11}	11	340
Panoche Soil	8.6	1×10^{-11}	10	15
Yolo Loam	AD	1×10^{-11}	10	720
Delhi Sand	AD	2×10^{-11}	11	60

a. Permeability

b. Time for outlet concentration to reach $1 - e^{-1}$ of inlet concentration

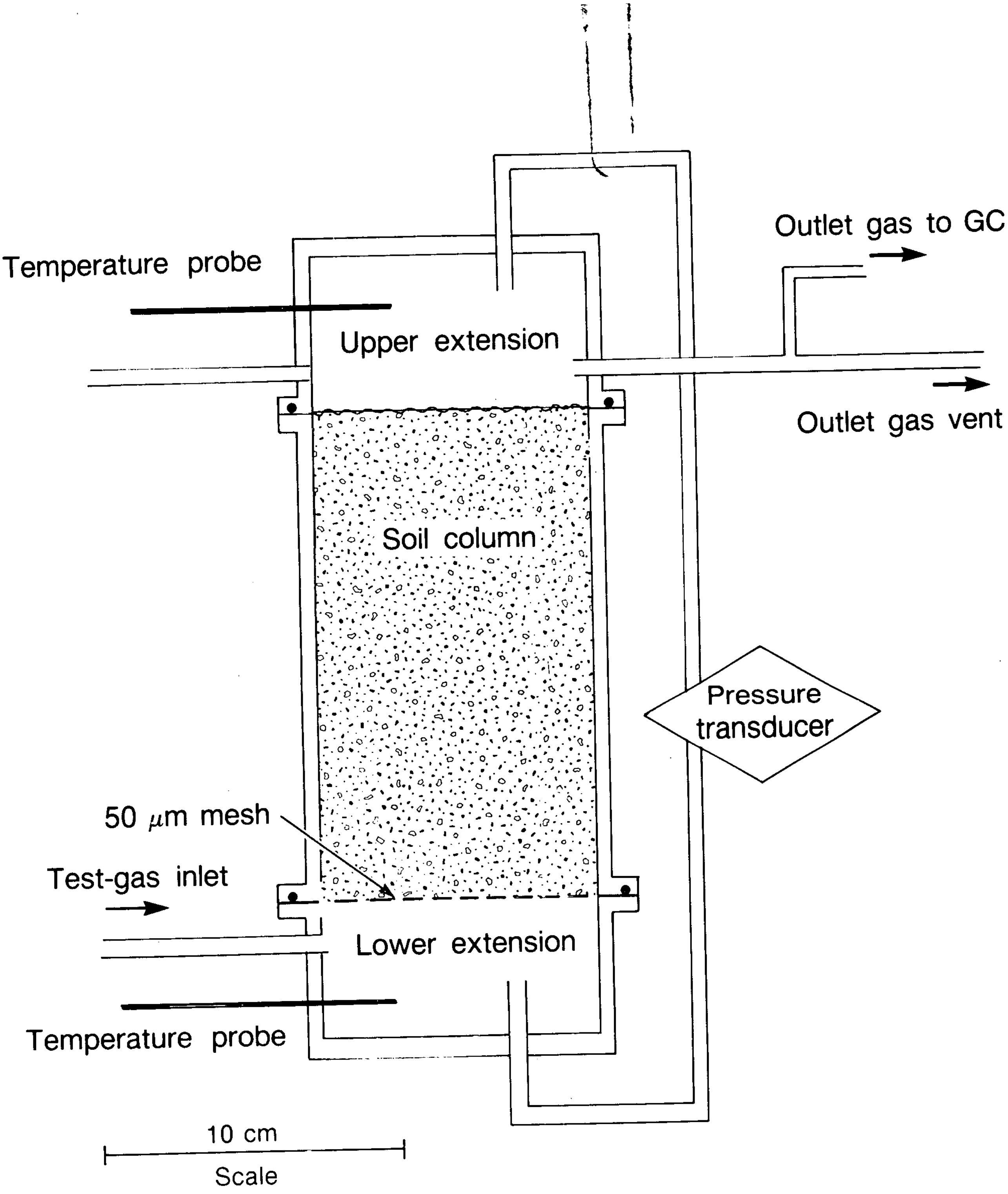
c. Air dry

Table 3.3. Parameter values used to calculate theoretical retardation factor for HFB.

Parameter	Value	Source
n	0.4	estimated
s	0.25	estimated
ρ_b	$1.12(g \cdot cm^{-3})$	measured
f_{oc}	0.0024	measured
H	0.71[a]	*Eichler et al.*, 1986
K_{oc}	135[b]	calculated from Eq. 2.8 using data for S from *Eichler et al.*, 1986

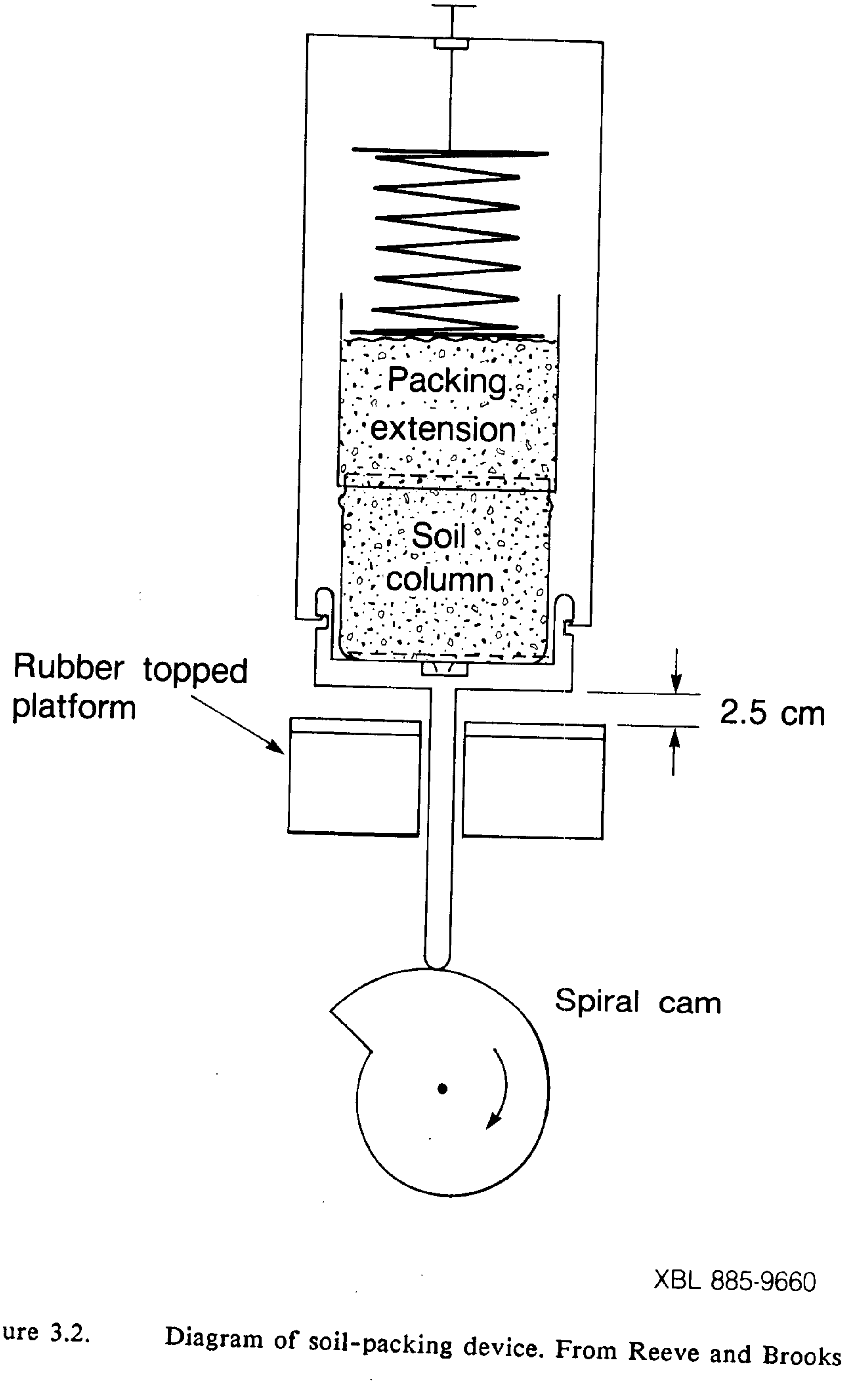
a. The effective units of H are $cm^3 (H_2O)$-cm^{-1} (air).

b. The effective units of K_{oc} are $cm^3 (H_20)$-g^{-1} (organic carbon), or equivalently, in unitless form, $g^3 (H_2O)$-g^{-1} (organic carbon).



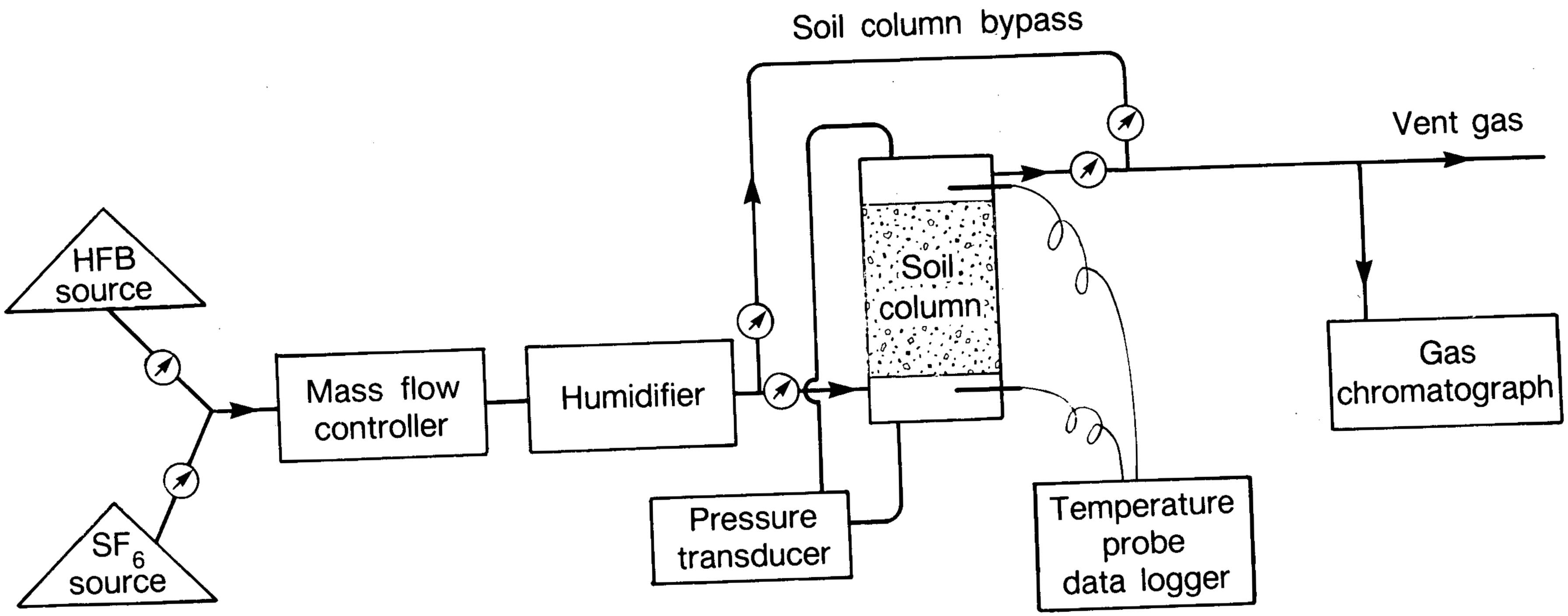
XBL 885-9661

Figure 3.1. Diagram of soil-column apparatus.



XBL 885-9660

Figure 3.2. Diagram of soil-packing device. From Reeve and Brooks (1953).



XBL 885-9659

Figure 3.3. Schematic diagram of experimental setup.

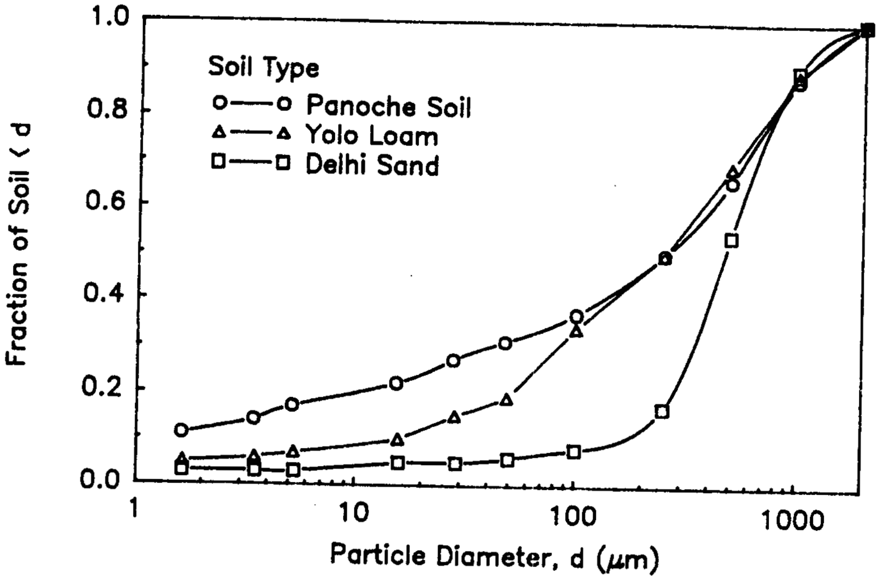


Figure 3.4. Cumulative particle-size distributions of soils.

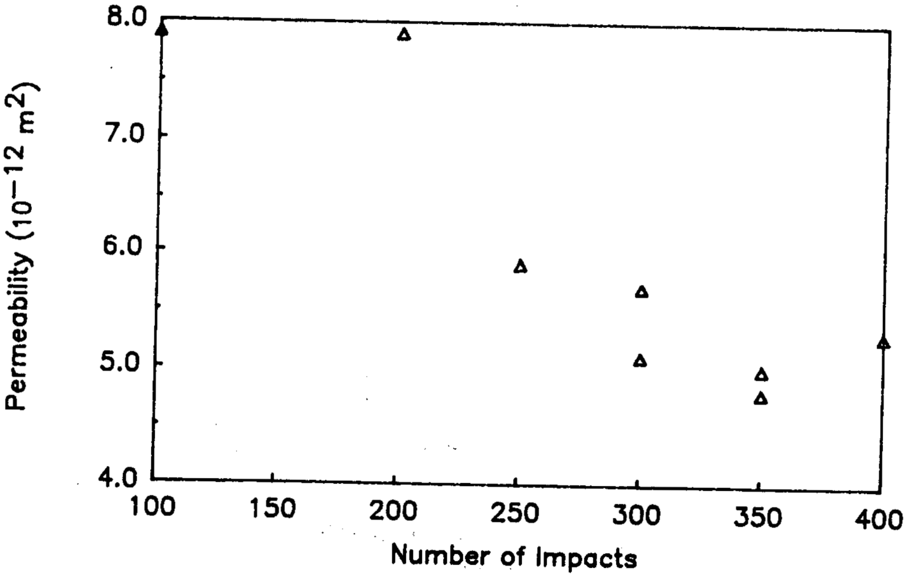


Figure 3.5. Permeability of Yolo Loam in 16-cm column versus number of impacts.

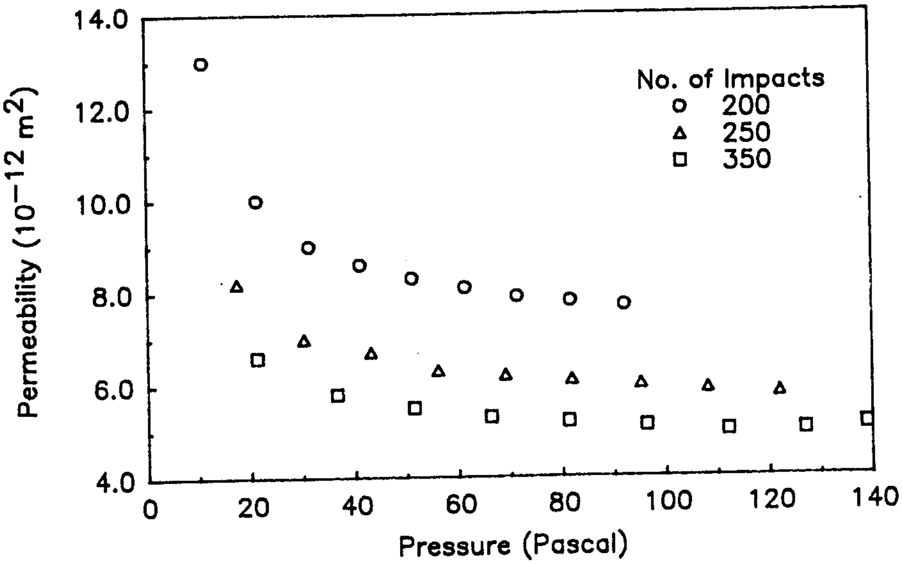


Figure 3.6. Permeability of air-dry Yolo Loam in 16-cm column versus pressure differential across column.

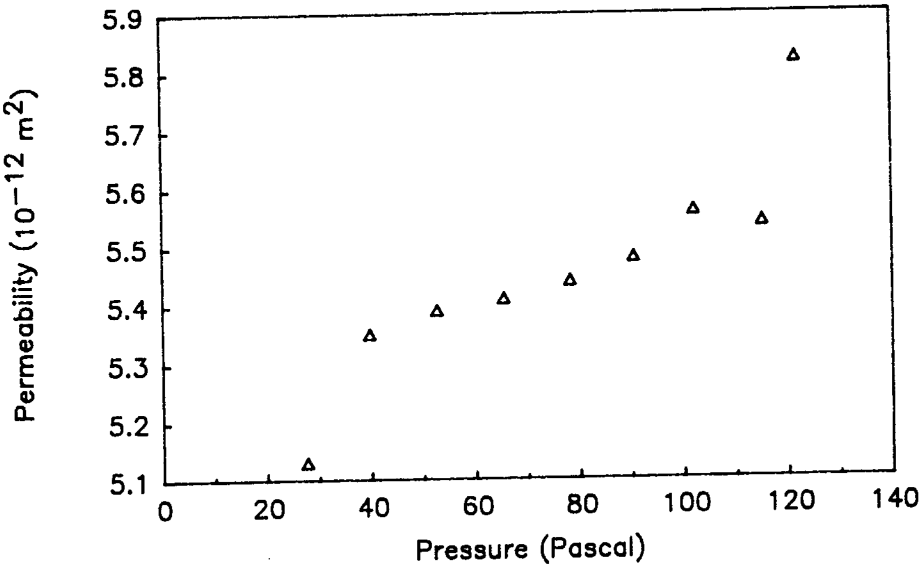


Figure 3.7. Permeability of moist Yolo Loam (1.9 percent water) in 16-cm column versus pressure differential across column.

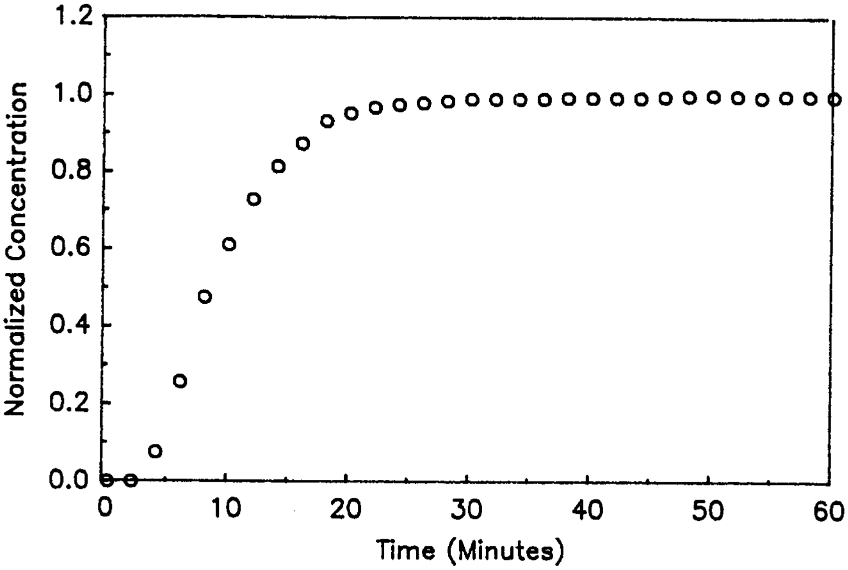


Figure 3.8. Breakthrough of SF_6 on air-dry Panoche Soil. The plot shows outlet concentration normalized to inlet concentration.

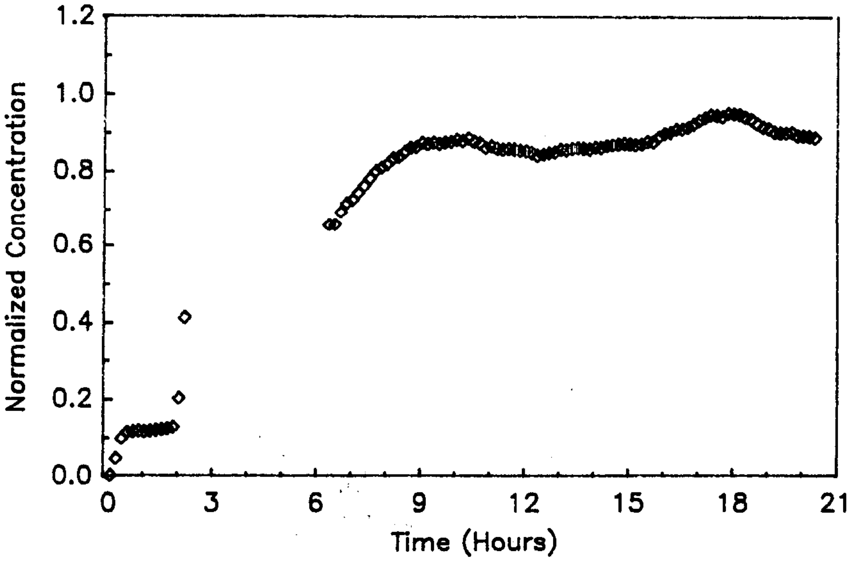


Figure 3.9. Breakthrough of HFB on air-dry Panoche Soil. The plot shows outlet concentration normalized to inlet concentration. Missing data points resulted from failure of GC automatic sampling valve.

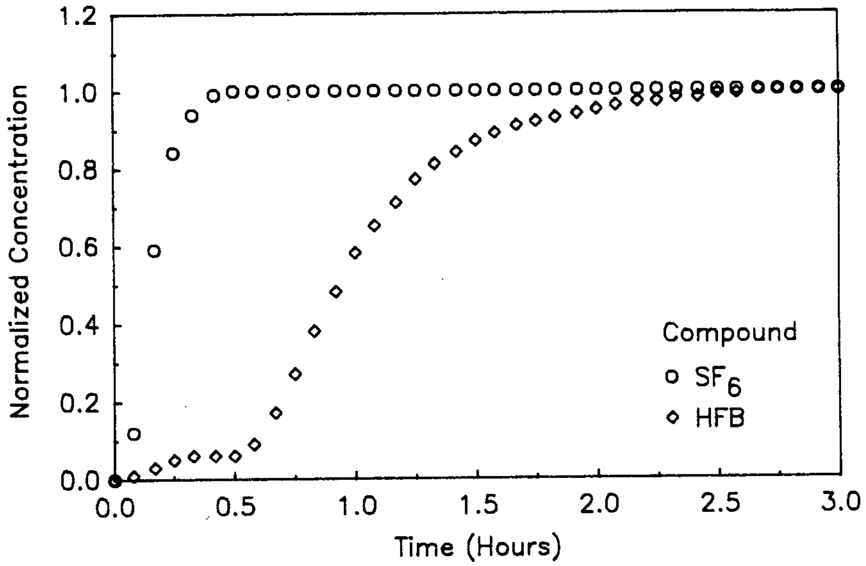


Figure 3.10. Breakthrough of SF_6 and HFB on Dehli Sand. The plots show outlet concentrations normalized to inlet concentrations.

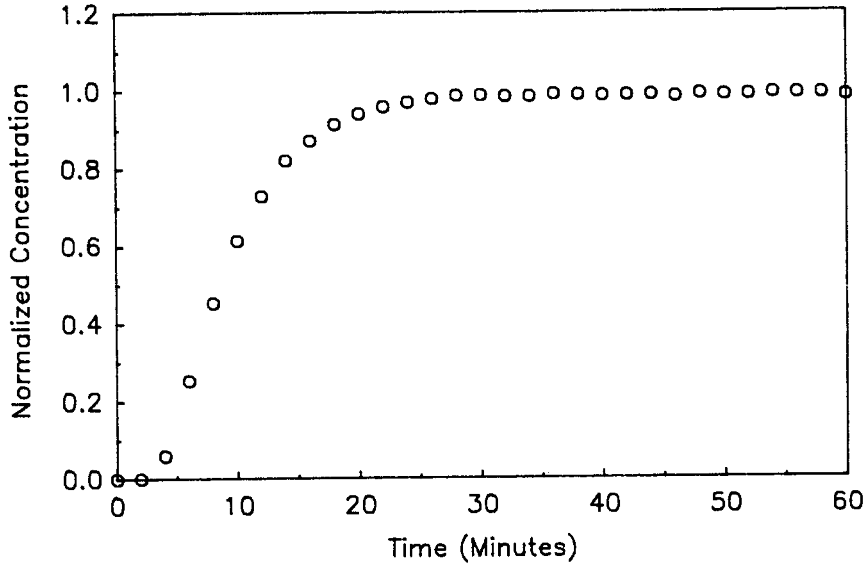


Figure 3.11. Breakthrough of SF_6 on air-dry Yolo Loam. The plot shows outlet concentration normalized to inlet concentration.

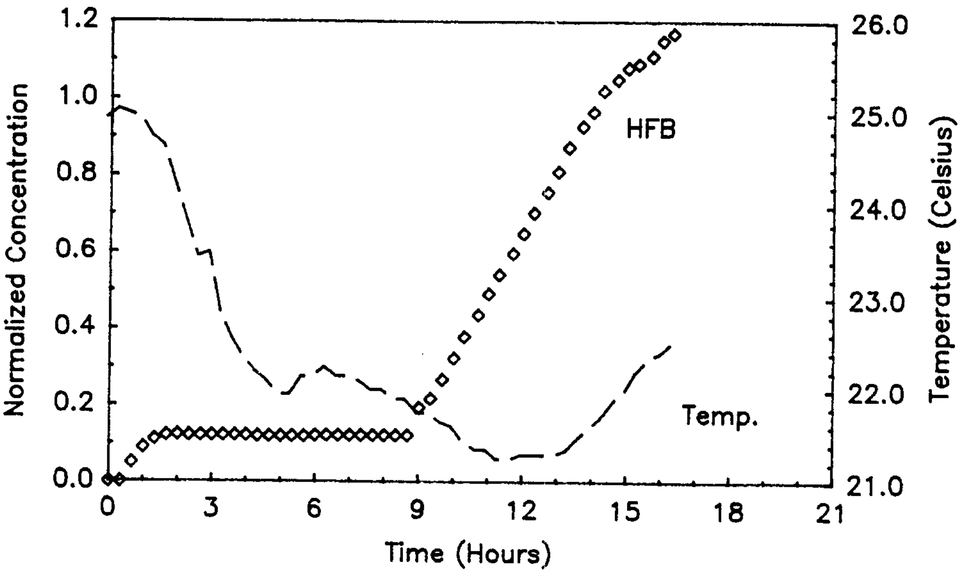


Figure 3.12. Breakthrough of HFB on air-dry Yolo Loam. Outlet concentration normalized to inlet concentration is plotted along with average temperature of the soil column.

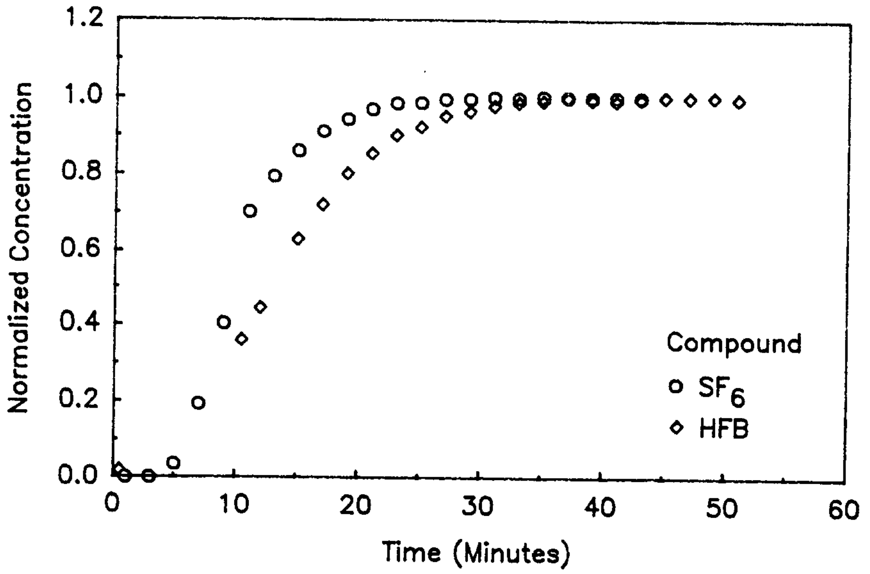


Figure 3.13. Breakthrough of SF_6 and HFB on wetted Panoche Soil (8.6 percent water). The plots show outlet concentrations normalized to inlet concentrations.

CHAPTER 4

TRANSPORT OF VOLATILE ORGANIC COMPOUNDS FROM SOIL INTO A RESIDENTIAL BASEMENT

INTRODUCTION

The primary objective of this phase of the investigation was to assess the importance of pressure-driven flow of soil gas in the entry of volatile organic compounds (VOC) into a house with a basement. This house was located adjacent to a covered municipal landfill. The study consisted of two interrelated components. In the first, the physical mechanisms of soil-gas entry were investigated using two techniques: 1) measurement of the pressure field developed in the soil around the house while the basement was depressurized with an exhaust fan, and 2) monitoring of the movement of a tracer gas from the soil into the depressurized basement. Contamination of soil gas and indoor air were examined in the second component by means of measurements of VOC in soil gas, outdoor air and indoor air.

METHODS

Description of Study Site

The study house was a vacant single-family residence in Central California. There was previous evidence of migration of landfill gas and VOC from the landfill to the site. In 1983, the county, which operates the landfill, installed air-injection pumps at the perimeter of the landfill to contain methane which was detected at this house and other nearby residences. Samples of well water collected by several agencies at the site from 1985 through 1986 were found to contain Freon-12, Freon-11, tetrachloroethylene, and other halogenated compounds.

The house was constructed in 1977 after the landfill had begun operation. It is a three-bedroom, one-story structure built over a garage and a basement which is almost entirely below grade. The foundation and basement of the house were constructed by excavating the soil, pouring a cement slab and building up a cement-block wall on top of the slab. The cavities in the wall were backfilled with cement, and the exterior of the wall was sealed with an asphalt-based product. The interior of the wall and the floor were painted. The areas of the first floor and the basement are 183 and 103 m^2, respectively. A plan view of the house and site is shown in Figure 4.1. The berm containing the landfill is approximately 70 m to the west of the house at its closest point. The land between the berm and the house is flat and covered with grass. The land immediately to the east of the house slopes steeply downward for a vertical drop of approximately 10 m. The prevailing wind during the study was from the direction of the landfill.

Investigations at the site were conducted over a period of about four months from late July through early November, 1987. Thus, the study was largely conducted during the hot, dry summer season. There was only 1.5 cm of rainfall which occurred in the last two weeks of October. Rainfall during the preceding winter was low.

Sampling and Characterization of Soil

In late October, eighteen soil samples were extracted by bucket auger from three vertical profiles located 0.8, 4.3 and 10.7 m from the west basement wall. Sampling depths ranged between 0.3 and 2.8 m. The samples were sealed in moisture proof containers at the time of collection and were refrigerated within six hours. The moisture content of the samples was determined by weighing subsamples before and after drying to constant weight at 110^{o}C. Samples were analyzed for particle-size distribution using standard sieving and hygrometer-technique sedimentation analyses (Day, 1965).

Construction and Installation of Soil Probes

Soil probes were installed at the site and were used in experiments to determine in-situ permeability of the soil, pressure coupling between the basement and the soil, soil-gas entry into the basement, and concentrations of VOC in soil gas. Thirty probes were installed around the house at distances ranging from 0.5 to 12 m from the basement wall and at depths ranging between 1 and 3 m (Figure 4.1). The majority of these probes terminated at a depth of 1.5 m and were located to the west of the house between the house and the landfill. No probes were installed to the south of the house which was distant from the basement. Two probes were installed through the basement floor to a depth of 3.2 m below the grade level of the soil.

The soil probes were identical to those used in a study of radon entry into houses (Turk *et al.*, 1987). They consisted of 2- or 3-m lengths of 13-mm OD, 9-mm ID galvanized steel pipe open at both ends with the outlet end threaded to accommodate pipe-to-tube connectors. A guide hole was drilled in the soil prior to installation of a probe in order to minimize disturbance of the soil. A stainless-steel rod was inserted into the probe so that it extended 1 cm beyond the inlet end. The pair was then driven into the soil to the desired depth using a sledge hammer. After installation, the center rod was removed, and the inlet was augured to break up compacted soil. During both drilling and hammering, distinct soil layers offering greater or less resistance were detected. Probes were generally terminated in a relatively low resistance, presumably more permeable, layer. Soil probes were capped at the outlet when not in use.

Measurement of In-situ Permeability

The in-situ permeability of the soil was measured at the soil probes using the technique suggested by DMSA (1983). Because there is no discrimination in flow direction, this technique gives an effective permeability. In brief, a regulated flow of compressed air was directed into the soil through a probe while measuring the air flow rate and the pressure difference between the soil and the ambient air. A diaphragm differential-pressure gauge (0-125 Pa, Dwyer Instr., Inc.) and either a microflowmeter (0-15 cm^3 min^{-1}) or a rotameter (0-450 cm^3 min^{-1}) were used to measure pressure and flow rate. Permeability, which assumes Darcy flow, is calculated from:

$$k = \frac{Q\mu}{4\pi P r}, \tag{4.1}$$

where:

k = permeability (m^2);
μ = viscosity of air (1.83×10^{-5} kg m^{-1} s^{-1});
P = probe pressure (Pa);
Q = flow rate (m^3 s^{-1}); and
r = radius of the probe (4.5×10^{-3} m).

Permeabilities down to as low as approximately 10^{-14} m^2 can be determined at which point the flow rates become too small to measure at reasonable applied pressures. The measurements are accurate to better than a factor of two, with some variation in apparent permeability with applied pressure observed (see Chapter 3).

Measurement of Pressure Coupling

Pressure coupling between the basement and the soil was determined using the technique of Nazaroff *et al.* (1987). A large exhaust fan (blower door), typically used to make leakage-area measurements in houses, was installed in the doorway between the basement and the garage (Figure 4.1). With the garage door open, the door between the basement and the upper floor closed, and the windows and doors on the upper floor open, the fan was operated to achieve a basement depressurization with respect to outdoor air of -25 Pa. This pressure was measured with a diaphragm differential-pressure gauge (0-60 Pa) and was maintained to within 2 Pa. With the basement at the desired pressure, differential pressures with respect to outdoor air were measured in the soil probes using a variable reluctance pressure transducer (Model DP103, Validyne Instr., Inc.). The pressure transducer was calibrated in the field and was periodically checked during use with a micromanometer.

Estimation of Soil-gas Entry into the Basement

An experiment was conducted to estimate the entry rate of soil gas into the basement as a function of basement depressurization. The purpose of this experiment was to obtain an order-of-magnitude estimate of pressure-driven inflow of soil gas under typical operating and environmental conditions. Pure sulfur hexafluoride (SF_6) was injected into the soil around the house to provide a source of labeled soil gas. In September, a total of 490 cm^3 of SF_6 was injected into five soil probes to the north and west of the house (probes AN2, AW2, BW3, BW4, and BW5) in approximately equal portions. The experiment was conducted one month later in October after the SF_6 had diffused over most of the soil-probe field.

Shortly before beginning the experiment, duplicate samples of soil gas were collected from each probe using plastic syringes. The concentrations of SF_6 and Freon-12, a soil-gas contaminant present at the site at relatively high concentrations, were measured with an on-site, transportable gas chromatograph (GC) (Model 1030A, Baseline Industries, Inc.) equipped with an electron capture detector (ECD), a gas sampling loop and valve, and a molecular sieve (5A) column. Before the samples were collected, a volume of air equal to two probe volumes was withdrawn from the probe and discarded.

Meanwhile, the basement was thoroughly ventilated by running the exhaust fan at high speed for an extended period with the interior door to the upper floor and all windows and doors on the upper floor open. Then the door to the upper floor and all of the heating ducts in the basement were closed, and the GC-ECD was set up to automatically sample and analyze basement air for SF_6 and Freon-12 at one-minute intervals. The exhaust fan was operated to produce pressures in the basement of -20, -30, -40, and -50 Pa relative to ambient pressure. Each stage of depressurization was maintained long enough to achieve near steady-state conditions.

Sampling and Analysis of VOC

Samples of soil gas, outdoor air, and indoor air for qualitative and quantitative analysis of VOC were collected and analyzed using previously described methods (Hodgson *et al.*, 1986; Hodgson and Girman, In press). Samples were collected on multisorbent samplers containing Tenax-TA, Ambersorb XE-340 and activated charcoal (Part No. ST-032, Envirochem, Inc.). Sampling flow rates were 113 cm^3 min^{-1} (20^oC, 760 torr). Flow rates were regulated with electronic mass-flow controllers placed between the samplers and a diaphragm vacuum pump. Sample volumes for soil gas, outdoor air and indoor air were typically 0.23, 5.6 and 2.5-5.6 L, respectively. Single samples were collected for qualitative analyses at each sampling location. For quantitative analyses, duplicate samples were collected. Before samples of soil gas were collected from a soil probe, a volume of air equal to two probe volumes was withdrawn and vented. Soil gas was then drawn through either one or two parallel, in-line samplers.

Samples for VOC were collected on three occasions during the study. A preliminary survey was conducted in July in which samples for qualitative analysis only were obtained from two soil probes, from outdoor air between the house and the landfill, and from basement air. In September, samples for both qualitative and quantitative analyses were collected. Qualitative samples were obtained from one soil probe, from outdoor air, and from basement air with the basement at ambient pressure and at a depressurization of -20 Pa relative to ambient pressure. Quantitative samples were collected from three soil probes, from outdoor air, and from basement air at ambient pressure. In the final sampling period in October, samples for quantitative analysis only were collected from four soil probes and from indoor air in both the basement and the upper floor of the house. Prior to this period, the house had been closed for four weeks with the door between the basement and the upper floor closed. Samples were collected immediately after entering the house and before significant ventilation due to opening and closing of doors had occurred.

For analysis, a sample is thermally desorbed from the sampler and introduced into a capillary GC with a UNACON Model 810A (Envirochem, Inc.) sample concentrating and inletting system. Sample components are resolved with a GC (5790A Series, Hewlett-Packard Co.) equipped with liquid nitrogen subambient cooling and a fused-silica capillary column (DB-1701, J & W Scientific, Inc.). The GC is connected via a direct capillary interface to a 5970B Series Mass Selective Detector (MSD) (Hewlett-Packard Co.). For qualitative analyses, the MSD is continuously scanned from m/z 33 to m/z 250. For quantitative analyses the MSD is operated to monitor multiple, individually selected mass ions.

RESULTS AND DISCUSSION

Soil Characteristics

The range of soil type at the site as characterized by the sieving and sedimentation analyses is loamy sand to silt loam according to the U.S. Soil Classification System. Samples taken from the vertical profile 0.8 m distant from the basement wall were of a single soil type, loamy sand, which is predominantly sand. Uniformity of soil type in this profile was expected since the profile was within the region that was backfilled after construction of the basement wall. Some horizontal layering of the soil was evident in the vertical profiles 4.3 and 10.7 m distant from the house. Above the 2.4 m horizon, the layers variously alternated between loamy sand and sandy loam, which has more fine particles. Below 2.4 m, the soil was the less permeable silt loam, which is predominantly silt. The water content of the soil increased from approximately two to four percent by weight over a depth range of 0.5 to 2 m. The water content of the deep silt-loam layer was approximately 12 percent.

The in-situ soil permeabilities calculated from the field data using Equation 4.1 are presented in Table 4.1. The mean permeability at a depth of approximately 1.5 m is 2.5 x 10^{-12} m^2 with a range of 0.3-20 x 10^{-12} m^2. The permeability at the three, 3-m deep probes is not appreciably different. Since the soil probes were terminated in soil layers of apparent higher permeability, based upon resistance to insertion, the calculated mean permeability may somewhat exceed the actual average permeability of the soil. The range of permeabilities measured at the site is in agreement with the particle-size composition of the soil described above. Nazaroff *et al.* (1986), for example, report that permeabilities for uniform fine sands to uniform silts are typically in the range of 5×10^{-12} to 5×10^{-14} m^2.

Pressure Coupling between the Basement and Soil

With the basement depressurized, a pressure field was propagated through the soil around the house and was measured at the soil probes. Pressures in the probes are presented in Table 4.1 as percentages of basement depressurization. Pressure coupling 0.5 m from the basement wall was typically 30-40 percent, and, as expected, there was a general decrease in pressure coupling with increasing distance from the basement wall. Significant pressure coupling, in excess of ten percent, was observed 7 to 12 m away from the house. Similar results were reported for a house situated in soil with a uniform permeability of approximately 6×10^{-11} m^2 in which pressure coupling of about eight percent was observed 5 m away from the house (Sextro *et al.*, 1987).

On a number of occasions during the experiment, the exhaust fan in the basement was abruptly switched on or off to verify that the underpressures measured at the probes resulted from the depressurization of the basement. In each case, the soil pressure reached equilibrium within seconds of turning the fan on or off. Soil depressurization was measured as a function of basement depressurization at probes AN3, BW4, and DE1. Figure 4.2 shows that the soil pressures at these locations were quite linear with the pressure in the basement. Pressures at probe AN3, only 0.5 m from the basement wall, were most strongly coupled. Within the uncertainty in the measurements, the intercepts of the slopes incorporate the origin.

VOC in Soil Gas

The composition of VOC in soil gas that was sampled from several soil probes in July and

September is shown in Table 4.2. A total of 26 individual compounds were identified in these samples. Identifications were determined using mass spectral data bases and were confirmed, in many cases, by analyses of standards. No attempt was made to analyze compounds with very low boiling points (most Freons and C_4-C_5 hydrocarbons) in July. There was no major qualitative difference in the composition of the other compounds between July and September. In general, halogenated and oxygenated compounds were the dominant classes, both in terms of the numbers of compounds detected and relative peak heights. Compounds with distinctly high peak heights were dichlorodifluoromethane (Freon-12), trichlorofluoromethane (Freon-11), 1,1,1-trichloroethane, tetrachloroethylene, 2-propanone (acetone), 4-methyl-3-penten-2-one (mesityl oxide), and 2-ethyl-1-hexanol.

The concentrations of 14 compounds which were measured by GC-MSD in soil gas collected at several probes in September and October are presented in Table 4.3. Both the ranges of concentrations and the mean concentrations are shown since there were large quantitative differences among the probes in each sampling period. The generally larger variations in September may have been due to the inclusion of data from a 3-m deep probe with data from two 1.5-m deep probes, while the four probes sampled in October were all 1.5-m deep. Nevertheless, even in October, concentrations of individual compounds generally ranged over a factor of three to five among the probes. There were also major differences in the concentrations of the compounds between the two sampling periods. In September, the dominant compounds were Freon-12, Freon-11, and tetrachloroethylene. These compounds still had relatively high concentrations in October, while the concentrations of five other compounds increased considerably from September to October. These compounds were dichloromethane, 2-propanone, hexanal, 2-methylbutane, and toluene. These changes occurred over a period in which there was a general decrease in average ambient temperature and some precipitation (1.5 cm). However, these factors would not be expected to alter soil parameters at the sampling depth.

In October, Freon-12 was quantified at all probe locations by GC-ECD. Considerable spatial variability was observed. The average concentration of Freon-12 for the site is 630 ppb with concentrations in the individual probes ranging from 100 to 2100 ppb. Concentrations in the 1.5-m deep probes on the west side of the house average 250 ppb and are distinctly lower than concentrations in the other probes. The average concentration for the 3-m deep probes, including the basement probes, is 1500 ppb, and the average concentration for all probes (1.5-m deep) to the north and east of the house is 1000 ppb. If the landfill is the source of Freon-12, higher concentrations of Freon-12 on the north side of the house suggest that this area may be closest to the path of migration of landfill gas. The considerably higher concentrations at depth suggest the possible presence of a layer of soil of lower permeability lying between 1.5 and 3 m and limiting diffusion to the atmosphere.

Gas in the landfill adjacent to the study site was not analyzed, and, in general, there are few data on the composition of the minor constituents of landfill gas. Nevertheless, it is probable that many, if not all, of the dominant compounds in the soil gas around the house originated from the landfill.

Brookes and Young (1983) present a list with some quantitative data of compounds that were detected in soil gas at six landfills in Great Britain. More than 100 compounds encompassing all of the major classes of organic compounds were detected and either identified or partially classified. Thirteen of the compounds found in soil gas in the present study (Tables 4.1 and 4.2) appear in this list. In most cases their concentrations in the landfill gas were greater than several ppm. At one of the six landfills, oxygenated compounds, halogenated compounds and alkanes were the dominant classes both in terms of numbers of compounds and concentrations. Similarly, oxygenated and halogenated compounds are dominant in the present study.

If conditions are favorable, VOC contained in landfills can be transported away from the site by subsurface water and by subsurface gas-phase migration. Gas-phase migration of VOC into surrounding areas was detected at two sites included in a survey of 20 nontoxic, municipal landfills in Southern California (Wood and Porter, 1987). At one location where methane was detected in nearby houses at concentrations approaching one percent, a sample of migrating gas was taken from a gas well outside the periphery of the landfill and another sample was taken from under the kitchen sink of a house approximately 180 m away. Tetrachloroethylene and 1,1,1-trichloroethane were detected at both locations. Concentrations at the entry point into the house were about two orders of magnitude lower than in the well. At another location, qualitative changes in the composition of soil gas with distance beyond the landfill perimeter were investigated. The first compounds to disappear with distance were the oxygenated compounds followed by the aromatic compounds, the other hydrocarbons and the polar halogenated compounds. Tetrachloroethylene, a dominant compound in the present study, was one of the most persistent compounds.

Entry of Soil Gas into the Basement

The concentrations of SF_6 and Freon-12 measured by GC-ECD in samples of soil gas collected from the soil probes closest to the house are summarized in Table 4.4. As indicated by the averages and ranges for soil probes on the two sides of the house, the spatial variability in the concentrations of both of these compounds was large. This variation occurred in an area of relatively uniform soil. An examination of all of the data for SF_6 revealed that concentrations predictably decreased with increasing distance from the points of injection. As shown in the table, concentrations of SF_6, 0.5 m from the basement wall, were somewhat higher on the west side of the house than on the north side. In contrast to SF_6, the concentrations of Freon-12 were higher on the north side of the house than on the west side by about a factor of four. For both compounds, the highest concentrations occurred in the two probes penetrating the basement floor.

After thorough ventilation, the concentrations of SF_6 and Freon-12 in the basement at the beginning of this experiment were 0 and 1 ppb, respectively. Volumes of air equivalent to 4.8, 3.0, 5.9, and 5.6 basement volumes were respectively exhausted from the basement at depressurizations of -20, -30, -40, and -50 Pa. Figure 4.3, which shows concentrations of SF_6 in the basement at -20 Pa as a function of time, demonstrates that near steady-state conditions were achieved within about one hour at this pressure. Concentrations of SF_6 and Freon-12 in air sampled in the open upper floor of the house and outdoors near the basement sill plate were 0 and 1 ppb, respectively.

Direct evidence of the entry of soil gas into the basement was obtained from the experiment. During depressurization, air flow into the basement was detected at the electrical outlet boxes which were recessed into cavities cut into the cement block wall approximately 45 cm above the floor. The average concentrations of SF_6 and Freon-12 in air samples collected from the cavities on the west wall were about 90 and 200 ppb, respectively. These concentrations are similar to the average concentrations measured in the adjacent soil outside the wall. Air flow into the basement was also detected at the sill plate running around three sides of the basement at a height of about 30 cm above the surface of the soil. This location may serve as a major entry pathway for outdoor air.

A simple mass-balance model assuming steady-state conditions was applied to the concentration data obtained at the end of each depressurization stage. Setting the mass flow of a tracer gas in the exhaust air equal to the mass flow of the gas in the air entering the basement gives:

$$Q_f C_\infty = C_s Q_s + C_o Q_o. \tag{4.2}$$

The C_∞ is the final concentration of the tracer gas in the basement at equilibrium, and C_s and C_o are the concentrations in the soil gas and the outside air, respectively. The corresponding flow rates of soil gas and outside air are Q_s and Q_o. The ventilation rate of the basement, Q_f, is simply the calibrated flow rate of the exhaust fan. Solving for Q_s, and letting

$Q_f = Q_s + Q_o$ yields:

$$Q_s = Q_f \frac{C_\infty - C_o}{C_s - C_o}. \tag{4.3}$$

It was assumed that any soil gas entering the basement would be drawn from near the basement wall. Therefore, the averages of concentrations of SF_6 and Freon-12 in probes 0.5 m from the west and north walls and in the two basement probes were selected as the best estimates of concentrations for use in the mass-balance model. This results in values of C_s of 230 and 780 ppb for SF_6 and Freon-12, respectively. There is, however, considerable uncertainty in the estimates due to the large spatial variations which were observed (Table 4.4) and the lack of data for soil gas close to the east wall of the basement. As a result, the effective concentrations in soil gas entering the basement could vary from these values by a factor of two or more. The uncertainty in the concentrations due to spatial variations is compounded by the fact that the distribution of the pathways for entry of soil gas into the basement is unknown. Together, these factors introduce considerable uncertainty into the estimation of entry rates.

The entry rates of soil gas into the basement as a function of basement depressurization which were estimated from the SF_6 and Freon-12 concentration data are shown in Figure 4.4. The relationship is linear for both compounds. The divergence between the two slopes, which is undoubtedly due to the large uncertainties discussed above, emphasizes the limitations of the experiment. Clearly, only order-of-magnitude estimates of entry rates of soil gas can be obtained by this method. However, despite the limitations, the regressions suggest that the entry rate of soil gas due to pressure-driven flow would be less than 1 $m^3\ h^{-1}$ at a typical basement depressurization of a few Pascals which would result from wind and an indoor-outdoor temperature differential (Nazaroff *et al.*, 1988). This estimated rate is probably an upper limit since these natural phenomena actually produce a vertical pressure gradient with the maximum depressurization at the basement floor while this experiment was conducted with the basement uniformly depressurized. For comparison, the infiltration rate of outdoor air for the whole house was calculated for possible winter conditions by the method of Sherman and Grimsrud (1980). Using the measured leakage area of the house and assuming a wind speed of 4 m sec^{-1} and an indoor-outdoor temperature differential of 22°C, this infiltration rate would be approximately 500 m^3 h^{-1}, or almost three orders of magnitude higher than the estimated soil-gas entry rate. For moderate weather conditions, both basement depressurization and the infiltration rate would be reduced so that the soil-gas entry rate would be expected to remain relatively insignificant.

VOC in Indoor Air

The compositions of VOC in the basement of the house in July and September are compared to the compositions of VOC in outdoor air and soil gas in Table 4.2. For September, the compositions in the basement with the basement both at ambient pressure and at a depressurization of -20 Pa are presented. In July, only a few compounds were detected in the basement, and the composition is similar to that of outdoor air. Most of the oxygenated compounds present in soil gas did not appear indoors. In September, many more compounds were detected in the basement. Most of the halogenated compounds in soil gas appeared indoors, and more oxygenated compounds were detected indoors in this month. A number of alkane and aromatic compounds, e.g. n-hexane, methylcyclopentane, n-decane, n-undecane, and trimethylbenzenes, were detected only in the basement, suggesting indoor sources for these compounds in this month, perhaps due to the activities of the researchers. No significant increase in the number of compounds was observed when the basement was depressurized. However, seven of the compounds decreased to concentrations that were near their detection limits. This decrease was due to the dilution of basement air with infiltrating outdoor air.

The concentrations of VOC in the house in September and in October are compared to the concentrations in outdoor air and soil gas in Table 4.3. Thirteen of the 14 compounds quantified in soil gas appeared indoors, and eight of these were also present in outdoor air. In general, the concentrations of VOC in the house were very low, particularly in September when they typically ranged from less than one to a few parts per billion. In this month, acetone had the highest indoor and outdoor concentrations; Freon-12 had very high concentrations in the soil gas, but its concentration in indoor air was relatively low. Concentrations in outdoor air, with the exception of acetone, were all less than 1 ppb. Concentrations of VOC in the house in October were, with the exception of one compound, higher than they were in September by a factor of two or more. This increase may have been due to the additional care which was taken in October not to disturb the ventilation of the house prior to collecting samples. In this sampling period, concentrations of VOC in the basement were compared to concentrations in a bedroom on the upper floor. The concentration of acetone in the basement approached the mean soil gas concentration and was much higher than the concentration in the bedroom. All of the other compounds had nearly equivalent concentrations in the basement and bedroom, with the possible exception of Freon-12 which was somewhat higher in the basement. Ignoring the unexplained anomalous results for acetone, this similarity suggests that well-mixed, steady-state conditions had been reached. Since the house was unfurnished and unoccupied, the outdoor concentrations were typically very low, and there were no other obvious sources, it was, therefore, assumed that soil gas was the primary source of most of these compounds.

CONCLUSIONS

The measurement of significant pressure coupling at a distance of 12 m from the west side of the house demonstrates that soil gas can be drawn by depressurization of the basement from a large area that extends out from the house toward the landfill. The significant pressure coupling that was measured on three sides of the house suggests that the pathway for the entry of soil gas into the basement is distributed around this house rather than located in one or a few penetrations. This is consistant with the observed lack of penetrations in the basement. The similarity of concentrations of tracer gas and Freon-12 in air coming from cavities on the inside of the cement-block wall when the exhaust fan was operating and in the adjacent soil outside the wall provided direct evidence of the entry of soil gas. However, the actual entry pathway for this soil gas is unknown. Garbesi (1988) has applied the pressure field data from this study to an existing fluid-transport model to obtain a more detailed understanding of the effect of soil macro-structure and basement leakage geometry on the pressure field and the entry of soil gas into the house.

The advective flow of soil gas into the basement of this house due to a pressure differential of a few Pascals, a pressure that would result from typical wind and indoor-outdoor temperature differences, is estimated to be less than 1 m^3h^{-1}. This is only a small fraction, less than one percent, of the estimated inflow of air into the house due to infiltration under similar conditions. Consequently, the infiltrating air would significantly dilute the concentrations of any contaminants entering from the soil. Since the basement is well coupled with the soil gas and the soil is moderately permeable (about 2×10^{-12} m^2, on average), the pressure-driven entry of soil gas is probably limited by the low below-grade leakage area. For houses with higher below-grade leakage areas, soils of equal or greater permeability, and low infiltration rates, the relative contribution of pressure-driven inflow to total inflow can be much higher. For example, in a study of radon entry into houses in Spokane, Washington, the soil-gas entry rate ranged from 0.4 to 39 m^3h^{-1}, and the estimated range of soil gas entry to total infiltration was 1 to 20 percent (Turk *et al.*, 1987). It is concluded that advective transport can be an important entry mechanism for VOC in those houses which have high relative inflow rates of soil gas.

The concentrations of Freon-12 and other VOC in soil gas were found to be highly variable in the vicinity of the house in an area of relatively uniform soil. It is probable that these variations arose from a combination of interrelated factors, such as the degree of coupling with the source, the presence of boundaries limiting transport to the surface, and spatial variations in the sorptive capacity of the soil for VOC.

Some VOC, which were significantly elevated in soil gas relative to outdoor air, also occurred in indoor air at higher concentrations than in outdoor air. Since the house was unfurnished and unnoccupied and there were no other obvious sources, it was concluded that the source of these compounds in indoor air was the soil gas. However, the exact entry mechanism for these VOC cannot be determined since the natural depressurization of the basement and the infiltration rate were not measured. Although pressure-driven entry of soil gas is expected to be very low for the unoccupied summer conditions of the study, a slight depressurization of the basement could develop due to indoor-outdoor temperature differences. This could provide the driving force for the entry of soil gas and VOC. Since infiltration is also expected to be low for these conditions, pressure-driven flow cannot be ruled out as the cause of the observed indoor concentrations. However, the data can also be explained by diffusion of VOC from soil through the basement wall. It is possible for this house, particularly at the conditions of the study, that diffusion is the dominant entry mechanism for VOC.

TABLE 4.1 Soil permeability and pressure coupling of soil gas with basement air at soil-probe locations.

Probe ID	Distance from House[a] (m)	Depth[a] (m)	Soil Permeability[b] (m^2)	Pressure Coupling[c] (%)
AW1	0.5	1.5	2.2×10^{-13}	30±6
AW2	0.5	1.5	2.1×10^{-12}	33±4
AW3	0.5	1.5	1.0×10^{-12}	37±6
AW4	0.5	1.5	4.9×10^{-13}	33±13
AW5	0.5	1.5	1.1×10^{-12}	27±6
AW6	0.5	1.5	2.6×10^{-12}	4±3
AN1	0.5	1.5	5.8×10^{-13}	44±6
AN2	0.5	1.5	5.3×10^{-13}	37±6
AN3	0.5	1.5	3.9×10^{-13}	23±4
BW1	1.5	1.5	1.1×10^{-12}	17±5
BW2	1.5	1.5	3.4×10^{-12}	17±3
BW3	1.5	1.5	4.2×10^{-12}	20±3
BW4	1.5	3	1.6×10^{-11}	6±1
BW5	1.5	1.5	2.0×10^{-13}	28±6
BN1	1.5	1.5	2.7×10^{-13}	25±6
CW1	3	1.5	9.3×10^{-13}	12±3
CW2	3	1.5	3.0×10^{-11}	14±3
CW3	3	3	3.8×10^{-12}	18±3
CW4	3	1.5	6.6×10^{-13}	14±4
DW1	5	1.5	1.5×10^{-12}	10±2
DW2	5	1.5	2.4×10^{-12}	9±2
DW3	5	3	2.7×10^{-13}	21±5
DE1	5	1.5	2.3×10^{-13}	10±7
DE2	5	1.5	3.9×10^{-13}	7±7
EW1	7	1.5	1.1×10^{-12}	7±2
EW2	7	1.5	2.6×10^{-13}	17±5
EW3	7	1.5	1.3×10^{-12}	10±3
FW1	12	3	1.9×10^{-13}	16±3
FW2	12	2	5.6×10^{-14}	-[d]
FW3	12	1	2.1×10^{-13}	-
B1	0	3.2	2.1×10^{-11}	-
B2	0	3.2	1.6×10^{-13}	-

a. Distances and depths are approximate

b. Uncertainty is x/÷2

c. As percent of basement depressurization of -25 Pa; uncertainty is based upon instrumental noise

d. No data

TABLE 4.2 Composition of VOC in soil gas, indoor air and outdoor air in July and September. "X" = present; "XX" = very high concentration; "t" = trace concentration and "-" = not detected.

	July			September			
Compound	Soil-Gas[a]	Basement	Outdoor Air	Soil-Gas[b]	Basement Ambient	Basement -20 Pa	Outdoor Air
HALOGENATED							
Dichlorodifluoromethane	ND[c]	ND	ND	XX	X	X	t
Chlorodifluoromethane	ND	ND	ND	X	-	X	-
Dichlorotetrafluoroethane	ND	ND	ND	X	-	-	-
Trichlorofluoromethane	ND	ND	ND	XX	X	X	t
Trichlorotrifluoroethane	X	-	-	-	-	-	-
Dichloromethane	-	X	t	-	X	t	t
1,1,1-Trichloroethane	XX	X	X	X	X	X	t
Tetrachloroethylene	XX	-	t	XX	X	X	t
OXYGENATED							
2-Propanone	XX	X	X	X	X	X	X
2-Propanol	X	-	-	-	-	-	-
2.4-Dimethyl-2-pentanol	-	-	-	X	-	-	-
Acetic acid	-	X	t	X	X	X	X
Hexanal	X	t	-	X	X	X	-
4-Methyl-3-penten-2-one	XX	-	-	X	-	-	-
3-Methyl-3-penten-2-one	-	-	-	X	-	-	-
3-Heptanone	X	-	-	X	X	X	-
2-Heptanone	X	-	-	X	-	-	-
Heptanal	X	-	-	X	t	t	-
2-Butoxyethanol	X	-	-	-	-	-	-
6-Methyl-2-heptanone	X	-	-	X	-	-	-
2-Ethyl-1-hexanol	-	-	-	XX	-	-	-
Nonanal	X	-	-	-	-	X	-
Decanal	X	-	-	-	X	t	X

TABLE 4.2 (Continued)

		July			September		
	Soil-Gas[a]	Basement	Outdoor Air	Soil-Gas[b]	Basement Ambient	Basement -20 Pa	Outdoor Air
Compound							
ALKANE AND CYCLOALKANE							
2-Methylpropane	ND	ND	ND	X	t	X	-
2-Methylbutane	ND	ND	ND	-	X	X	t
n-Hexane	-	-	t	-	X	t	-
Methylcyclopentane	-	-	t	-	X	t	-
n-Heptane	-	t	t	-	X	t	X
n-Decane	-	-	-	-	X	t	-
n-Undecane	-	-	-	-	X	-	-
AROMATIC							
Toluene	X	X	X	X	X	X	X
Ethylbenzene	-	-	t	-	X	X	-
1,3- 1,4-Dimethylbenzene	-	t	X	t	X	X	t
1,2-Dimethylbenzene	-	-	t	X	X	X	t
Trimethylbenzene	-	-	t	-	X	X	-
Trimethylbenzene	-	-	-	-	X	t	-
Trimethylbenzene	-	-	-	-	X	X	-

a. Soil probes CW3 and DW3

b. Soil probe CW2

c. No data

TABLE 4.3 Concentrations of VOC in soil gas, indoor air and outdoor air in September and October.

	Concentration, ppb							
	September				October			
	Soil Gas				Soil Gas			
Compound	Range	Mean[a]	Basement	Outdoor Air	Range	Mean[b]	Basement	Bedroom
HALOGENATED								
Dichlorodifluoromethane	230-920	490	2.3	0.2	110-340	190	15	10
Trichlorofluoromethane	7.6-110	46	0.8	0.3	42-230	140	2.0	3.3
Dichloromethane			1.2	0.1	50-200	120	9.6	13
1,1,1-Trichloroethane	1.4-11	4.9	0.7	0.3	2.8-9.4	6.1	1.5	1.6
Tetrachloroethylene	23-150	70	0.7	0.1	26-79	56	2.0	1.9
OXYGENATED								
2-Propanone	16-27	20	12	4.9	90-370	250	200	38
Hexanal	3.3-7.9	6.1	1.0		37-52	42	3.7	4.8
4-Methyl-3-penten-2-one	0-10	3.4						
3-Heptanone	0-6.8	4.2	0.6		7.8-15	9.9		
ALKANE AND AROMATIC								
2-Methylbutane			5.2	0.3	14-74	36	11	12
Toluene	1.4-35	13	4.3	0.9	41-92	66	12	11
Ethylbenzene			0.6		2.8-3.7	3.3	2.0	1.8
1,3- 1,4-Dimethylbenzene	0-0.9	0.1	1.9		9.3-12	11	6.8	5.9
1,2-Dimethylbenzene	0.2-1.7	0.7	1.0		3.4-7.2	5.8	3.9	3.0

a. Soil probes AW2, CW2 and B2

b. Soil probes AW2, CW2, CE1 and CE2

TABLE 4.4 Concentrations of SF_6 and Freon-12 in soil probes adjacent to the basement. Probes to the North and West were ~0.5 m from the basement wall and ~1.5 m deep.

Probe Location	Concentration, ppb Mean	Range	No. of Probes
SF_6			
North	56	30-84	3
West	130	55-200	6
Basement	800	710-890	2
Freon-12			
North	1100	560-1700	3
West	270	160-450	6
Basement	2100		2

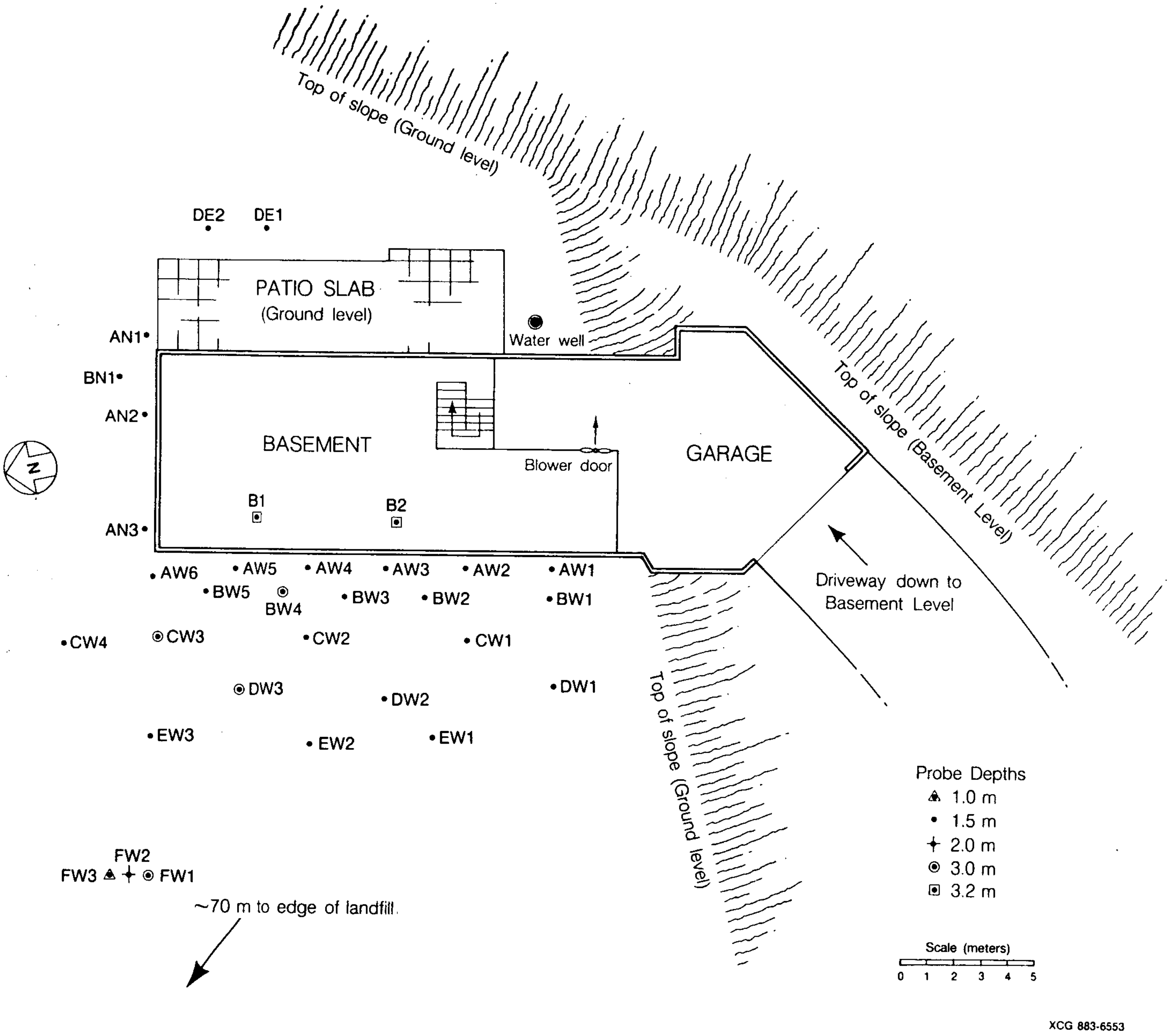
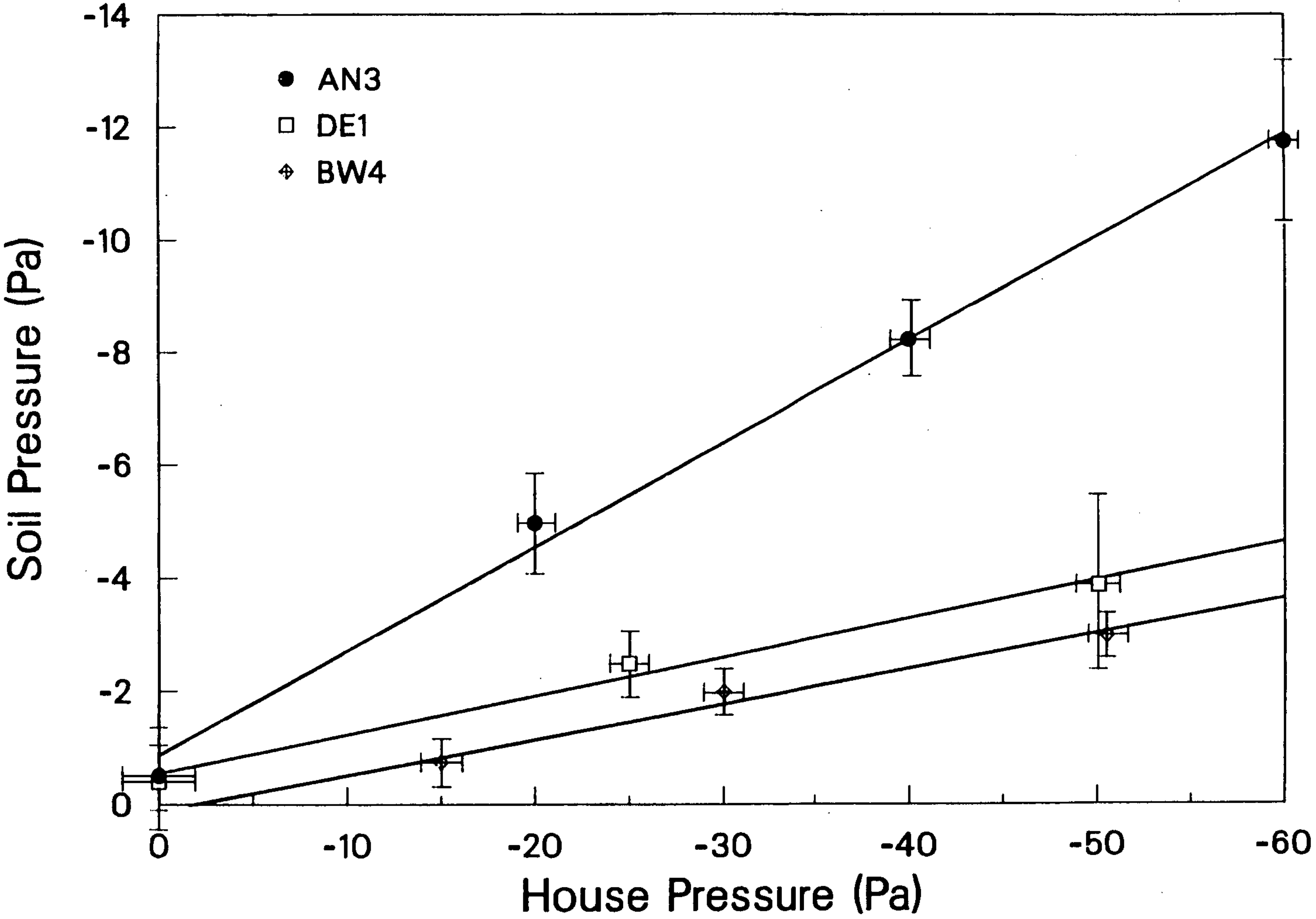
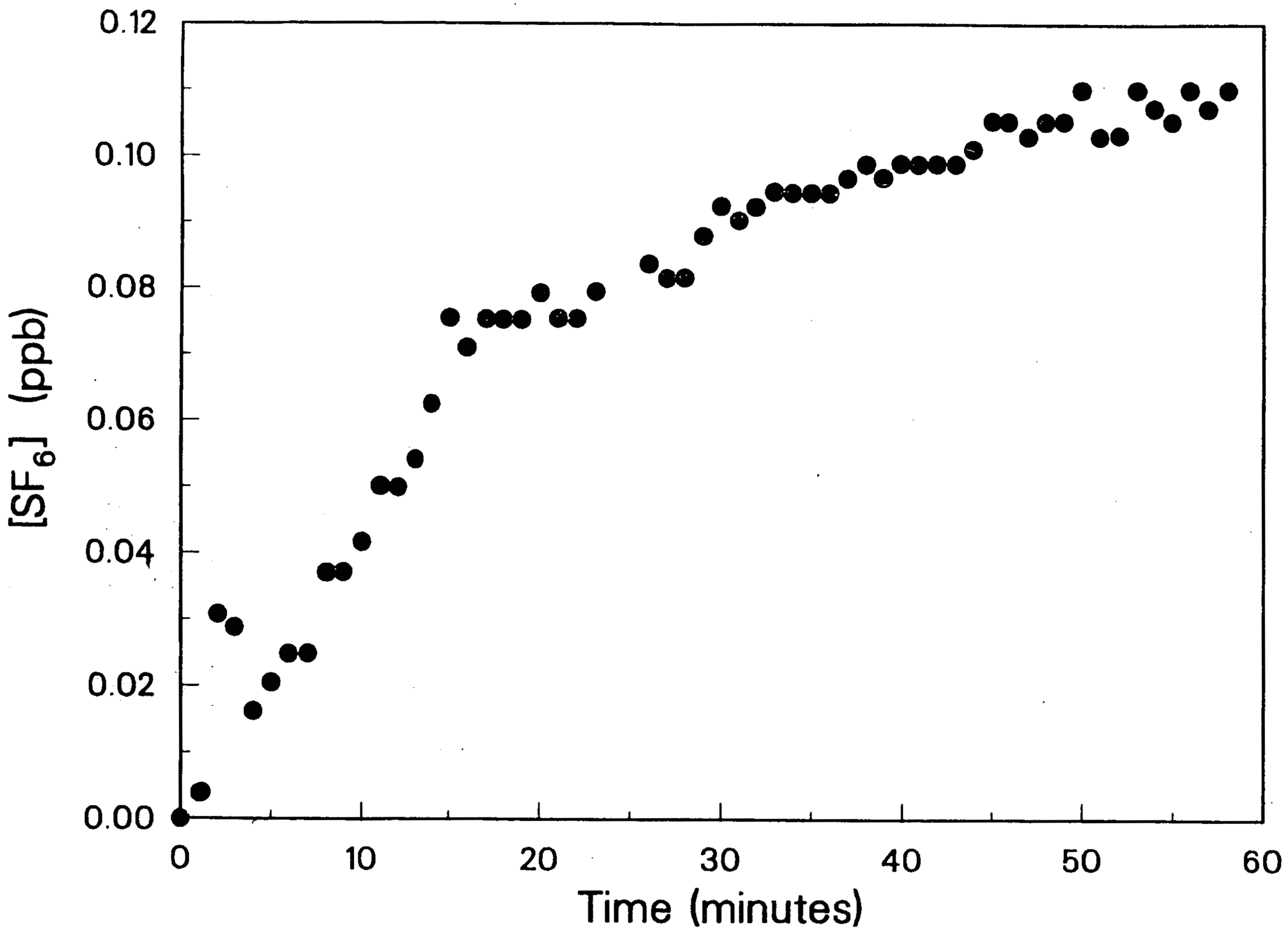


Figure 4.1 Plan view of the study site and the basement level of the house showing the locations and depths of the soil probes.



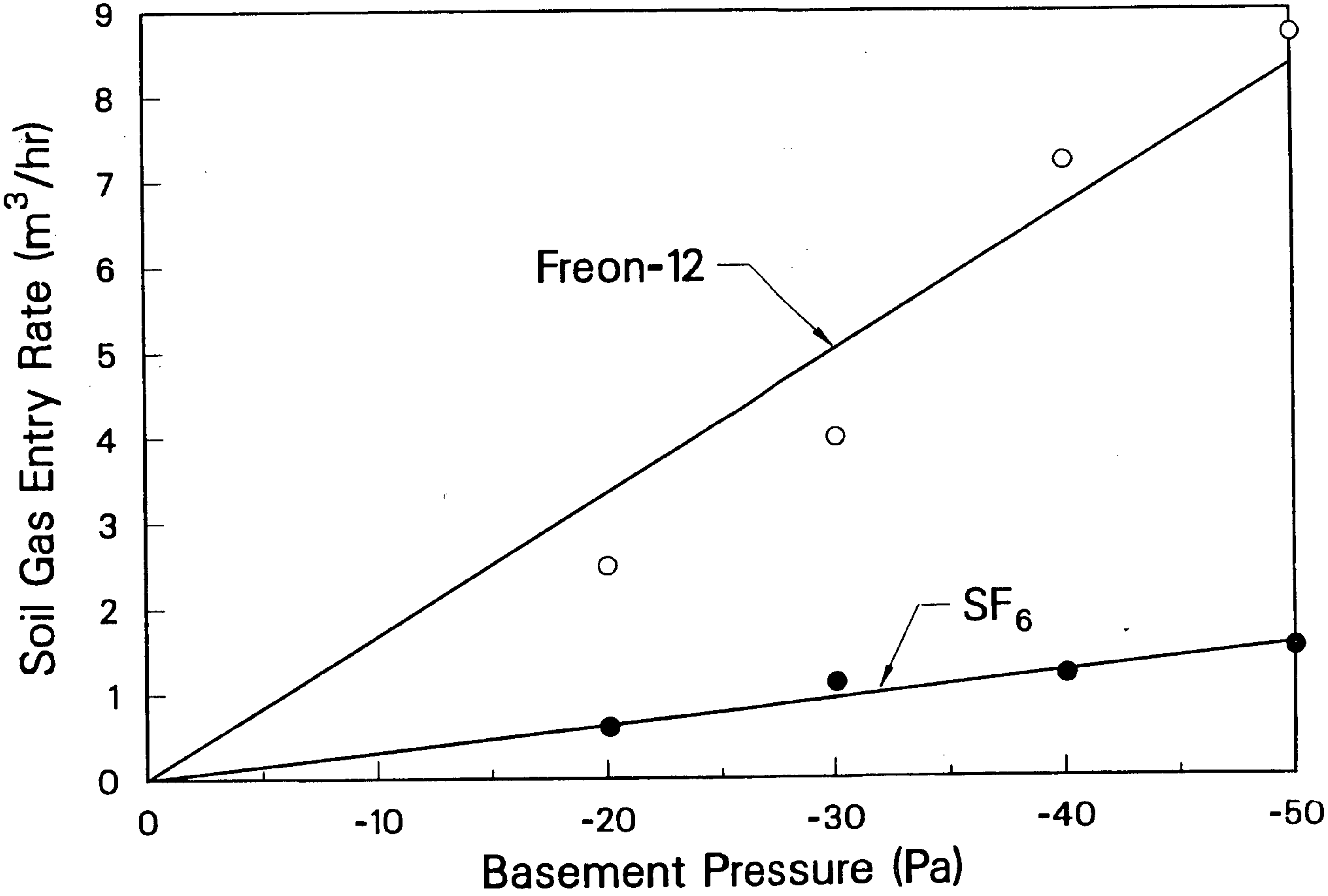
XCG 883-6558
3/10/88

Figure 4.2 Depressurization of the soil as a function of basement depressurization at three soil probes. The error bars represent the uncertainties in the measurements due to instrumental noise. Linear regressions fitted to the data are shown as solid lines.



XCG 883-6559
3/10/88

Figure 4.3 Concentrations of SF$_6$ tracer gas in the basement as a function of time with the basement at a depressurization of -20 Pa.



XCG 883-6564
3/15/88

Figure 4.4 Entry rates of soil gas into the basement as a function of basement depressurization estimated using a mass-balance model and concentrations of Freon-12 and SF_6 tracer gas in basement air, outdoor air, and soil gas adjacent to the house. Linear regressions fitted to the data are shown as solid lines.

CHAPTER 5

COMPARISON OF CONTAMINATED WATER AND SOIL GAS AS SOURCES OF INDOOR INHALATION EXPOSURE TO VOLATILE ORGANIC COMPOUNDS

INTRODUCTION

Household use of water contaminated with volatile organic compounds (VOC) for showers, baths, toilets, dishwashers, washing machines, and cooking can result in human inhalation exposures to these compounds that are as great or greater than the exposures that occur due to typical ingestion of water from the same source. The dominant inhalation exposures to VOC from use of water occur in showers since relatively large volumes of water are used in a confined space under conditions that favor mass transfer from water to air.

Andelman (1985a,b) investigated the transfer of trichloroethylene from water to air using a model shower enclosure. Concentrations of trichloroethylene in shower air increased with water temperature, length of drop path, and water concentration. He demonstrated that indoor inhalation exposures can be six times higher than ingestion exposures, given his assumptions regarding shower use and a daily ingestion of two liters of water. The question of relative absorption and potency from air and water media was not addressed. Foster and Chrostowski (1987) developed a theoretical model for estimating exposures to VOC in showers and validated it using Andelman's experimental data. They adjusted for relative potency and estimated that, for many VOC, the risk associated with inhalation in the shower may be as large as the risk associated with ingestion assuming a daily consumption of two liters of water. McKone (1987) developed a multi-compartment mass-balance model for estimating exposures to VOC from showers and other uses of water. With this model, more than one-half of the daily inhalation exposure was projected to occur in the shower, and the inhalation exposure was estimated to be between 1.5 and 6 times the exposure from drinking the water.

Inhalation exposures to VOC in houses also result from emissions of these compounds from interior finish materials and furnishings and from use of consumer products containing solvents. Under special circumstances, the soil around a house may also contribute to VOC concentrations in indoor air (Chapter 4).

This phase of the investigation was conducted at the same house described in Chapter 4. Since the experimental data for transfer of VOC from water to air from use of showers are scant, the primary objective was to measure the transfer efficiencies of several VOC under real conditions of shower use. From these data and air concentration data, indoor inhalation exposures resulting from household water use were estimated and were compared to exposures estimated to result from the entry of VOC into the house from soil gas.

METHODS

Water for household use is supplied by a well on the east side of the house. The depth of this well is approximately 20 m. A large tank in the basement serves as a water-storage reservoir. Samples of water collected from the well by several agencies from 1985 through 1986 were found to contain Freon-12, Freon-11, tetrachloroethylene and other halogenated compounds.

Experiments were conducted in the bathroom adjoining the master bedroom. This bathroom contains a vanity with two sinks, a toilet, and a 0.9 x 1.5 m stall shower. The sliding glass shower door extends to within 0.5 m of the ceiling. There is one interior door and one exterior window. Both the door and the window were closed during the experiments.

Two nearly identical experiments were conducted. The physical parameters for these experiments are summarized in Table 5.1. All conditions were the same for the two experiments except that in Experiment A the shower stall was unoccupied during the shower while in Experiment B there was a showering individual.

The ventilation rate of the bathroom in the closed condition was determined immediately prior to the experiments by the technique of tracer-gas decay. A small volume of pure sulfur hexafluoride (SF_6) was injected into the bathroom, and the air in the bathroom was mixed with a room fan. Then the fan was turned off, and the concentration of the tracer gas in an air sample drawn continuously from a location over the vanity at a height of 1.5 m from the floor was measured at one-minute intervals with an on-site gas chromatograph (see Chapter 4 for a description of this instrument). The slope of a plot of the natural log of concentration versus time is the ventilation rate. The air-exchange rate between the shower stall and the rest of the bathroom was not measured.

The temperatures of the shower water and the bathroom air were monitored during the experiments with thermister probes and were recorded with a data logger. The flow rate of the shower water, with the single lever faucet set at the desired temperature and the maximum flow rate, was determined immediately prior to the experiments by collecting water in a graduated beaker over a timed interval. Five replicate measurements of flow rate were made. The same shower temperature and water-flow rate were used during the experiments.

Experiments consisted of a ten-minute shower, followed by a ten-minute period during which the bathroom remained closed. Air samples for quantitative analysis of VOC were collected in the ten-minute periods immediately before, during, and after the shower. Samples were drawn through Teflon tubing from a point over the vanity at a height of 1.5 m from the floor. Each sample was collected and analyzed in duplicate using the procedures described in Chapter 4.

Samples of feed water were collected during each experiment in cleaned glass septum vials from a short length of Teflon tubing connected to a metering valve installed immediately upstream of the shower head. Drain water was collected in a shallow, foil-lined tray placed on the floor of the shower so that it collected water as it fell. At the end of the shower, the water in the tray was transferred to a glass beaker and then poured into the sample vials. The vials were capped so that there was no entrapped air and were refrigerated until analysis.

Samples of water were analyzed for 30 halogenated VOC by EPA Method 601 (EPA, 1982).

RESULTS AND DISCUSSION

Table 5.2 summarizes the physical properties of the five compounds investigated in these experiments, Freon-11, Freon-12, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene, using data from Mackay and Shiu (1981) and Roberts and Dandliker (1983). For all compounds having Henry's constant, H, greater than about 5×10^{-3} atm-m^3-mol^{-1}, the overall water-to-air transfer efficiency is dominated by liquid-phase resistance to mass transfer (Roberts and Dandliker, 1983). All of the compounds considered here satisfy this condition. Since the diffusion coefficients in water for these compounds are similar, their transfer efficiencies from water to air are also expected to be similar. Murphy (1987) estimated that compounds with H larger than 1.5×10^{-3} atm-m^3-mol^{-1} would be mostly volatilized from water during a shower. The actual amount volatilized will depend on the temperature of the shower water, the diameter of the water droplets, and the fall time of the droplets. Non-droplet air-water surfaces also increase the residence time during which volatilization can occur. Consequently, water running down walls, the showering individual, and draining from the shower bottom is expected to contribute significantly to air concentrations of VOC in the shower (Foster and Chrostowski, 1987).

Transfer efficiencies from water to air for the five compounds in the two experiments were calculated as the differences between the feed concentrations in the water at the shower head and the concentrations in the drain water divided by the feed concentrations (Table 5.3). As expected, the results for all compounds were quite similar. Also, the results for the two experiments were similar, indicating that the additional surface area of a showering individual had little effect on water-to-air transfer. The mean transfer efficiency and the 95 percent confidence limits of the mean are 0.84 ± 0.1. This mean value exceeds the transfer efficiencies that have been determined from direct water analyses for several inorganic chemicals. Prichard and Gesell (1981) measured radon transfer from water to air for various household water-use activities. For showers, the radon transfer efficiency was 63 percent. Giardino *et al.* (1988), using a full-size experimental shower with SF_6 as a surrogate for volatilization of VOC, found that typically 50 percent of the SF_6 volatilized during a 17-minute shower.

The air concentrations of the four compounds measured in bathroom air for the pre-shower, shower and post-shower periods are also presented in Table 5.3. Air concentrations of trichloroethylene were not measured. There is good agreement between the two experiments for all compounds except 1,1,1-trichloroethane which was present at low concentrations. The concentrations measured before the experiments began are assumed to represent steady-state background concentrations for the house due to the entry of VOC from soil gas, as discussed below.

Source strengths of the compounds due to operation of the shower can be estimated from both the water and air concentration data (Table 5.4). For water, the source strength for a compound was estimated to be the mass of the compound released from the water during the shower (feed concentration minus drain concentration times the water volume) divided by the time of the shower. For air, the source strength was estimated simply as the post-shower air concentration minus the pre-shower concentration multiplied by the bathroom volume and divided by the time of the shower. Since the ventilation rate was low (0.28 h^{-1}), removal due to ventilation during the 20-minute experiment was small and is ignored in this calculation. Source strengths estimated from air concentrations are approximately 15 percent of source strengths estimated from water concentrations. This large difference may be due to several causes. Although errors in sampling or analyses cannot be entirely discounted, the good replication between the two experiments for both water and air concentrations lends confidence to the data. It is possible that the source strengths calculated from the water data are overestimated. The in-shower residence time of the water captured in the tray on the shower floor was longer than the average residence time of the water used in the shower. Therefore, a larger percentage of the VOC may have been transferred from the water in the tray, which was only a small portion of the total amount of water used, than from the rest of the shower water. Source strengths calculated from air concentrations could be underestimated due to losses of VOC to surfaces. However, using Henry's Law, an estimation of the uptake of VOC by shower water condensed on bathroom surfaces indicates that this effect would be negligible.

A probable explanation for at least part of the discrepancy between the estimates of source strengths is incomplete mixing of the bathroom air. McKone (1987) proposed a multi-compartment mass-balance model for estimating exposures due to showers and calculated air concentrations for a hypothetical case in which he assigned the shower an air exchange rate of 3 h^{-1} and the bathroom an air exchange rate of 2 h^{-1}. The resulting concentrations were about five times higher in the shower than in the rest of the bathroom. Empirical evidence for incomplete mixing comes from the experiment of Andelman (1985a,b) in which he measured concentrations of trichloroethylene in a model shower. After running the shower for 55 minutes, air concentrations in the shower at a "lowered sampling position" were about 40 percent higher than concentrations at the "normal sampling position."

The maximum possible concentrations of the compounds in the shower stall at the end of the showers were estimated based on the assumption of incomplete mixing of air between the stall and the rest of the bathroom. These concentrations were calculated as the differences between the masses released from the water and the masses in the air in the bathroom during the post-shower period, exclusive of the stall, divided by the volume of the stall. Masses in the air due to background sources were excluded from the calculations. The resulting estimated concentrations in the shower stall are compared to the concentrations in the rest of the bathroom in Table 5.5. Concentrations in the stall generally exceed concentrations in the bathroom by a factor of 20 or more.

Inhalation exposures for a ten-minute shower followed by a ten-minute period in the closed bathroom were calculated using the estimated airborne concentrations for the shower and the bathroom (Table 5.5). Although concentrations actually increase and decrease exponentially, it was assumed that concentrations increased linearly during the shower and remained constant during the post-shower period. This simplification is valid because the ventilation rate was low and the duration of the exposure was short. Since it is likely that the water-transfer efficiencies were overestimated, the calculated exposures are probably overestimated and, therefore, represent maximum upper limits which would not be exceeded. The predicted exposures for a single shower which are shown in Table 5.6 are dominated by the exposures that occur in the stall. Exposures to Freon-12 and tetrachloroethylene for a single shower are estimated to be 54 and 11 ppb-h, respectively.

Estimated inhalation exposures due to showers are compared to inhalation exposures that might result from other sources of VOC in the house given an occupancy pattern that is assumed to be relatively common for working adults (Table 5.6). Household uses of water other than showers also release VOC to the air. Although no release data are available for VOC, radon transfer efficiencies from these sources have been measured and range from 30 percent for sinks and toilets to almost 100 percent for dishwashers (Prichard and Gesell, 1981). Exposures due to these other uses of water were estimated for a continuous 14-hour period representing an evening and night at home. These exposures were calculated by integrating the results of a single-compartment, mass-balance model which describes the average volume concentration of an airborne pollutant in an enclosed space (see McKone, 1987, for an example of a multi-compartment mass-balance model). The model incorporated the following assumptions: 1) water use for five hours at a continuous rate of 40 L h^{-1} followed by a period of nine hours with no water use; 2) water concentrations equal to those in the shower experiments and an average transfer efficiency of 85 percent; 3) perfect mixing throughout a house volume of 400 m^3 with a ventilation rate of 0.5 h^{-1}; and 4) no adjustment for reduced respiration volume while resting. Exposures in the morning prior to a ten-hour period away from the house were assumed to be dominated by the exposures received in the shower. Although the estimates are very approximate, exposures due to other household uses of water are predicted to be less than the maximum exposures due to showers by a factor of four or more. This dominance of shower exposures is consistent with the predictions of McKone (1987) for his hypothetical occupancy and water-use scenario.

The surrounding soil gas as a potential source of indoor VOC is of particular interest for this house since all of the VOC measured in well water, with the exception of trichloroethylene, were also detected in the soil gas. In Chapter 4, it was shown that pressure-driven flow of soil gas into the house is expected to be low under most operating and meteorological conditions. Nevertheless, some entry of VOC from soil gas is expected either by this pathway or by diffusion through the basement wall.

Prior to the shower experiments, air samples were collected from the basement and the master bedroom after the house had remained closed for four weeks and before there was significant ventilation due to opening and closing of doors and windows. The air concentrations of the compounds of interest in the basement and the bedroom are presented in Table 5.6. As noted in Chapter 4, it was assumed that the soil gas was the primary source of these compounds since the house was unfurnished and unoccupied, the outdoor concentrations of these compounds were very low, and there were no other obvious sources. The concentrations of the compounds were similar in basement and bedroom air suggesting that well-mixed, steady-state conditions had been reached. Inhalation exposures for a 14-hour period of occupancy, equivalent to that used above, were estimated from the concentrations that were measured in the bedroom and are shown in Table 5.6. These exposures, which range between 9 and 57 ppb-h, are equivalent to the exposures that are estimated for the shower. Actual exposures due to soil gas would be lower if the ventilation rate of the house was higher during occupancy due to the occupants' activities. However, since the shower exposures are probably overestimated to a larger extent, soil gas appears to be as least as an important source of exposure to VOC as water use for showers in this house.

CONCLUSIONS

The inhalation exposures to halogenated VOC that might occur in this house both from household use of water and from entry of VOC in soil gas are estimated to be very low. For example, the exposure to tetrachloroethylene from all of these sources over a period of one year is predicted to be 10 ppm-h, or less. The occupational eight-hour, time-weighted-average, threshold limit value for this compound is 50 ppm resulting in a maximum exposure of 400 ppm-h per work day (ACGIH, 1987). This comparison is useful because it puts the estimated exposure into perspective. It is not, however, intended to be a health risk assessment since occupational guidelines are probably not appropriate for the general population.

Although a number of papers have appeared in the literature on the subject of inhalation exposures to VOC due to household uses of water, these experiments present some of the few actual measurements of the transfer of VOC from water to air during a shower. The measured transfer efficiency of about 84 percent, based on water concentrations, is higher than the values used or predicted in published models for indoor exposure (Foster and Chrostowsk, 1987; McKone, 1987; Murphy, 1987). This is significant since these models are relatively sensitive to this parameter (McKone, 1987). The inconsistency between the water and the air concentration data is hypothesized to be due to the incomplete mixing of air between the shower stall and the rest of the bathroom, and, possibly, to differences in the transfer efficiency from the bulk of the shower water and from the sample of drain water.

The exposure estimates derived from these experiments should be used with caution because they can be significantly affected by a number of factors, such as, water concentrations, amount of water used per shower, volume of shower stall, duration of shower, and other occupancy factors. However, they do establish that the entry of VOC from soil gas is a relatively important source of inhalation exposure in this house even though the entry rate of soil gas is low. For a house with similar concentrations of VOC in soil gas and a higher entry rate of soil gas, the exposures to VOC from soil gas could be even more important.

Table 5.1. Physical data for shower experiments.

Parameter	Value[a]
Shower water temperature (°C)	40 ± 2
Shower water flow rate ($L \cdot min^{-1}$)	13.7 ± 1.0
Shower head height (m)	1.6
Shower duration (min)	10
Duration after shower (min)	10
Shower stall volume (m^3)	2.8
Bathroom total volume (m^3)	10.9
Bathroom ventilation rate (h^{-1})	0.28 ± 0.10
Bathroom air temperature (°C)	25 ± 2

[a] Average ± 95% confidence interval if applicable

Table 5.2. Physical properties of VOC studied.

Compound	Formula	MW $g \cdot mol^{-1}$	P_{20}[a] atm	H[b] $atm \cdot m^3 \cdot mol^{-1}$	d_w[c] $m^2 \cdot s^{-1}$
Freon-11	CCl_3F	137.4	0.88	0.41	NA[d]
Freon-12	CCl_2F_2	120.9	5.7	0.81	1.02
1,1,1-Trichloro-ethane	CH_3CCl_3	133.4	0.13	2.8×10^{-2}	0.83
Trichloroethylene	$CHCl{=}CCl_2$	131.4	0.079	9.0×10^{-3}	0.86
Tetrachloroethylene	$CHCl_2{=}CCl_2$	165.8	0.18	2.3×10^{-2}	0.79

[a] Vapor pressure at 20°C from Mackay and Shiu (1981)

[b] Henry's constant from Mackay and Shiu (1981)

[c] Diffusivity in water as presented in Roberts and Dandliker (1983)

[d] Not available

Table 5.3. Concentrations of VOC in shower water and bathroom air.

Compound	Exp.	Water Concentration Feed $\mu g \cdot L^{-1}$	Water Concentration Drain $\mu g \cdot L^{-1}$	Transfer Efficiency %	Air Concentration Pre-Shower $\mu g \cdot m^{-3}$	Air Concentration Shower $\mu g \cdot m^{-3}$	Air Concentration Post-Shower $\mu g \cdot m^{-3}$
CCl3F	A	11	1.0	91	4.0	11.0	16.0
	B	9.4	1.8	81	4.5	12.0	18.5
CCl2F2	A	73	10	86	4.2	43.3	138
	B	94	18	81	6.6	67.4	129
CH3CCl3	A	3.4	0.5	85	1.4	6.6	5.7
	B	3.1	0.8	74	6.6	9.6	12.3
CHCl=CCl2	A	2.7	0.4	85	ND[a]	ND	ND
	B	3.0	0.4	87	ND	ND	ND
CCl2=CCl2	A	18	3.2	82	6.0	25.4	44.0
	B	29	4.2	86	3.6	21.6	45.0

[a] No data

Table 5.4. Source strengths of VOC from shower use calculated from water and air concentration data.

Compound	Exp.	Source Strength Water mg·h^{-1}	Source Strength Air mg·h^{-1}	Air/Water %
CCl3F	A	8.23	0.78	10
	B	6.26	0.92	15
CCl2F2	A	51.6	8.75	17
	B	62.6	8.00	13
CH3CCl3	A	2.38	0.28	12
	B	1.89	0.37	20
CHCl=CCl2	A	1.89	ND[a]	--
	B	2.15	ND	--
CHCl2=CCl2	A	12.1	2.49	21
	B	20.5	2.71	13

[a] No data

Table 5.5. Estimated air concentrations of VOC in shower stall and rest of bathroom.

		Estimated Concentration	
Compound	Exp.	Shower Stall $\mu g \cdot m^{-3}$	Bathroom $\mu g \cdot m^{-3}$
CCl3F	A	450	12
	B	330	14
CCl2F2	A	2700	130
	B	2400	120
CH3CCl3	A	130	4.3
	B	96	5.7
CHCl=CCl2	A	--[a]	--
	B	--	--
CCl2-CCl2	A	610	38
	B	1100	41

[a] Not available, no data for air

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

It is just beginning to be recognized that landfills have the potential to be relatively important sources of indoor exposures to volatile organic compounds (VOC) for residents of nearby houses. Gas-phase advective transport of VOC through unsaturated soil, which has not been extensively studied, is a potential mechanism of VOC migration away from landfills. Diffusive flow can also play a role in this migration, as can aqueous transport through soil, about which more is known. Once VOC have migrated into the vicinity of houses and are in the gas phase, they are potentially available for transport into these houses. In studies of indoor radon, it has been shown that advective flow of soil gas into substructures is the primary source of radon gas in residences with elevated concentrations. This flow is driven by the depressurization of the substructure with respect to the surrounding soil. In non-mechanically ventilated buildings, depressurization results from the stack effect caused by thermal differences between indoors and outdoors and from the Bernoulli effect due to wind loading on the building. Although the physical and chemical properties of VOC are different from radon, it is clear that VOC in soil gas can enter houses by the same advective flow pathway.

In order to assess the potential for VOC to migrate from landfills into the vicinity of houses and how the properties of soil will affect this migration and the availability of VOC for entry into houses, it is necessary to understand the mechanisms of advection, diffusion, and retardation of VOC in soil. This theoretical basis was developed in Chapter 2. Using the theory of fluid mechanics and empirical relations for equilibrium partitioning of VOC between gas, aqueous, and solid phases of soil, a one-dimensional advection-diffusion equation for the transport of gas-phase VOC through soil was derived. This derivation results in the definition of a retardation factor which describes the velocity of VOC through soil with respect to the velocity of the bulk soil gas.

An experimental apparatus and accompanying method were developed for the direct observation of pressure-driven transport of gases through soil under controlled laboratory conditions (Chapter 3). The apparatus and method were used to compare the transport of sulfur hexafluoride (SF_6) and hexafluorobenzene (HFB) through several soils. These compounds were proposed for use in the subsequent field study as tracer gases to study the pressure-driven flow of soil gas and the advective transport of VOC.

The soil-column apparatus and method were suitable for evaluating the two proposed tracer gases. In experiments with three soils and two conditions of soil moisture, SF_6 was not lost by sorption to any of the soils. The flow of HFB was always retarded relative to the flow of SF_6, and HFB was strongly sorbed by two air-dry soils. In one air-dry soil, HFB was retarded with respect to SF_6 by a factor of 30, while when the same soil was wetted, there was less than a two-fold difference. This result supports the theory that at the typically high relative humidities found in soil, water displaces hydrophobic VOC on surface sites resulting in greatly decreased total sorption. The measured retardation factor for HFB in the wetted soil was in good agreement with the retardation factor predicted from the theory developed in Chapter 2. It was concluded that since uptake of SF_6 by soil was not detected, SF_6 is a good tracer gas for use in the field to measure the pressure-driven flow of soil gas, at least over the relatively short distances applicable to the investigation of soil-gas entry into houses. Because HFB is sorbed by soil, it was rejected as a tracer gas for the measurement of the pressure-driven flow of soil gas. However, since its behavior in soil may be similar to that of other VOC, it might be possible to use it to study the advective transport of certain VOC. Comparisons of the behavior of HFB with the behavior of VOC of interest could be made using the soil-column apparatus and method.

The primary objective of this study, that of measuring the pressure-driven flow of soil gas into a house, was addressed in field experiments conducted at a house with a basement located adjacent to a municipal landfill (Chapter 4). Thirty-two soil probes were installed in and around the house and were used in experiments to: 1) determine the in-situ permeability of the soil, 2) measure the pressure coupling between the basement and the soil, 3) determine the entry rate of soil gas into the basement due to depressurization of the basement, and 4) identify and quantify VOC in the soil gas. The average permeability of the soil at a depth of 1.5 m was about 2.5×10^{-12} m^2. This permeability is about an order of magnitude lower than that observed in a radon study in Spokane, Washington (Turk *et al.*, 1987) and is similar to permeabilities measured in another radon study in New Jersey (R.G. Sextro, unpublished data). There was significant pressure coupling between the basement and the soil on the three sides of the house where measurements were made. This result demonstrated that soil gas can potentially be drawn from a large area around the house and that the entry pathway for soil gas is distributed around the house rather than located in one or a few penetrations. This is consistent with the observed lack of obvious penetrations in the basement.

Although the basement is well-coupled with the soil gas, the pressure-driven entry of soil gas is relatively low. The advective flow of soil gas into the house due to depressurization of the basement was estimated using SF_6, a tracer gas injected into the soil around the house, and Freon-12, a soil-gas contaminant. The similarities of concentrations of SF_6 and Freon-12 in air coming from cavities on the inside of the cement-block wall to concentrations in the adjacent soil outside the wall provided direct evidence of the entry of soil gas, although the exact entry pathway was undetermined. Nevertheless, the entry rate of soil gas due to pressure-driven flow was estimated to be less than 1 m^3 h^{-1} at a basement depressurization of a few Pascals, a pressure that would result from typical wind and indoor-outdoor temperature differentials. This is less than one percent of the estimated inflow of outdoor air into the house due to infiltration under similar conditions. However, for houses with higher below-grade leakage areas, soils of equal or greater permeability and low infiltration rates, the relative contribution of pressure-driven inflow to the total inflow of air can be much higher. For example, the estimated soil-gas entry rates for the houses in the Spokane radon study ranged from 0.4 to 39 $m^3 h^{-1}$, and the estimated range of soil gas entry to total infiltration rate was 1 to 20 percent (Turk *et al.*, 1987). It is concluded that advective transport can be an important entry mechanism for VOC in those houses which have high relative inflow rates of soil gas.

Halogenated and oxygenated compounds were the dominant classes of VOC in the soil gas both in terms of numbers of compounds and concentrations. Compounds with relatively high concentrations in soil gas were Freon-11, Freon-12, dichloromethane, tetrachloroethylene, acetone, hexanal, and toluene. The concentrations of most compounds in the soil gas were highly variable in an area of relatively uniform soil. Some VOC, which were significantly elevated in soil gas relative to outdoor air, also occurred in indoor air at higher concentrations than in outdoor air, suggesting that the source of these compounds in the house was the soil gas. It was not possible to determine the exact entry mechanism for VOC from soil. However, the data for this house at the natural conditions of the study can be explained either by pressure-driven inflow of soil gas or by diffusion of VOC through the basement wall.

A number of papers have appeared in the literature on the subject of inhalation exposures to VOC due to household uses of water. These papers conclude that showers have the highest potential for exposure to VOC in contaminated water. Nevertheless, very few empirical data are available. This study presents some of the few actual measurements of the transfer of VOC from water to air and of the airborne concentrations of VOC in a bathroom due to a shower.

Two shower experiments were conducted under realistic conditions in the study house. The transfer efficiencies from water to air for Freon-11, Freon-12, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene (present in the water as contaminants at ug L^{-1} concentrations) for a ten-minute shower were all about 84 percent based on water data. This is higher than the values used or predicted in the published models for indoor exposure.

Source strengths estimated for the individual compounds from the air-concentration data were approximately 15 percent of source strengths estimated using the water-to-air transfer efficiencies. This inconsistency is hypothesized to be due to the incomplete mixing of air between the shower stall and the rest of the bathroom and, possibly, to uncertainties in the experimental method.

From the data, inhalation exposures to halogenated VOC were estimated for a ten-minute shower combined with a ten-minute period in the closed bathroom following the shower. Estimated exposures to Freon-12 and tetrachloroethylene for this period were 54 and 11 ppb-h, respectively. Estimated exposures to the other compounds were lower. Assuming an occupancy pattern that is typical for working adults, inhalation exposures were also estimated for other sources of these VOC in the house. Exposures due to household uses of water other than showers were predicted to be less than the maximum exposure due to showers by a factor of four or more. Exposures due to entry of VOC into the house from the soil gas were estimated to be equivalent to the exposures due to showers. All of these estimates of exposure, which are quite low, are subject to considerable uncertainty because they can be significantly affected by a number of factors. Nevertheless, they do suggest that for this house, entry of VOC from soil gas is a relatively important source of inhalation exposure compared to the household use of water.

RECOMMENDATIONS FOR FURTHER STUDY

Solid-Vapor Phase Sorption and Kinetics

The apparatus and method developed for the soil-column experiments are suitable, with appropriate modification for temperature control, for measuring the relative retardation factors for VOC found or likely to occur in soil gas. The relative advective mobility of these VOC could then be estimated. The apparatus and method are also well suited for investigating the effects of varying soil parameters on the retardation of these compounds. For a more detailed understanding of the mechanisms of retardation and retention of VOC in soil, it is recommended that the solid-vapor phase transfer kinetics of VOC also be investigated. If the transfer kinetics for these compounds are found to be rapid, then soil-column experiments can provide a measure of the soil-sorption coefficient (Equation 2.11).

Because of the lack of good soil-sorption data for VOC, and the uncertainty of the data regression used for the calculation of the sorption coefficient, it is recommended that more sorption isotherms be measured for these compounds and the results be compared with the existing data regression (Equation 2.8). These sorption data could then be used in conjunction with soil-column experiments to test the model for pressure-driven transport (Equation 2.15).

Development of Sampling Strategies and Methods for VOC in Soil Gas

At the field site, large spatial and temporal variabilities in the concentrations of VOC in soil gas were encountered in relatively uniform soil. Additional sampling strategies and analytical methods for quantifying VOC in soil gas are needed to evaluate these variations and to adequately characterize VOC concentrations at a site. A method for the rapid onsite analysis of a broad spectrum of VOC would be useful for evaluating spatial variability because this method would allow relatively large numbers of samples to be analyzed less expensively than the current method. A transportable gas chromatograph equipped with multiple columns and detectors should be suitable for this application. A method for compositing or combining samples of soil gas prior to analysis would reduce the number of samples needed to characterize the concentrations of VOC at a site. The present multisorbent sampler technique might be adapted to such a strategy. Relatively long-term integrated samples useful for evaluating changes in concentrations of VOC which may occur over periods of weeks or months at a site, might be collected using passive devices which sample by diffusion. The suitability of available diffusive samplers for this application should be evaluated. Since VOC are also sorbed onto particles and an equilibrium is established between gas and solid phases, there is a need to develop methods for collecting and preserving soil samples for subsequent analysis of sorbed VOC.

Development of Models

Measurement of pressure coupling between the basement and the surrounding soil revealed significant coupling (>10 percent) 12 m from the basement wall. A finite element model has been used to examine the soil parameters and leakage characteristics of the basement which resulted in this relatively large zone of influence (Garbesi, 1988). The results of this preliminary modeling effort suggest that soil layering was important in determining the shape and extent of the pressure field. Since macro-structure of the soil, such as layering, will always affect the pressure-driven flow of soil gas, there is a need to develop and/or evaluate methods for rapidly determining the macro-structure at a site. It is also recommended that mathematical models be further evaluated as tools for understanding the pressure-driven flow of soil gas and the entry of VOC into houses.

Exposure Assessment

Models for the pressure-driven flow of soil gas and the entry of VOC into houses can additionally be incorporated into exposure models for VOC. In this way, the possible ranges of indoor inhalation exposures to VOC at waste disposal sites could be estimated. The data currently being gathered on the gas-phase, subsurface migration of VOC at California landfills could be analyzed within the context of this methodology for the purpose of identifying sites which have high potential for exposing nearby residents to VOC.

CHAPTER 7

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