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EXPLANATION OF SIGNIFICANT DIFFERENCES
HAGEN FARM SUPERFUND SITE
SOURCE CONTROL OPERABLE UNIT
STOUGHTON, WISCONSIN

Introduction

On September 17, 1990, the United States Environmental Protection Agency ("U.S. EPA"), issued a Source Control Operable Unit Record of Decision ("ROD"), in which U.S. EPA, with concurrence of the State of Wisconsin, determined the remedy to be implemented for the remediation of contaminated soils and waste materials found at the Hagen Farm Superfund site, located in Dane County, Wisconsin (the "Site"). Since the signing of the ROD, U.S. EPA has received information making it appropriate for U.S. EPA, with the concurrence of the State of Wisconsin (the "State"), to revise the methodology to be used in calculating the Clean-up Standard for the waste refuse and sub-surface soils ("Waste/sub-Soils") at the Site. In accordance with Section 117(c) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, as amended ("CERCLA") and to the extent practicable, the National Contingency Plan, U.S. EPA has determined that the revised methodology for calculating the Clean-Up Standard for the Waste/sub-Soils, as discussed below, constitutes a significant change to a component of the remedy in the 1990 ROD. CERCLA Section 117(c) requires that U.S. EPA publish an Explanation of Significant Differences from the 1990 ROD. The purpose of this document is to provide a brief background of the Site, and to present this Explanation of Significant Differences, which explains how the revised methodology for calculating the Clean-Up Standard was arrived at, and how it differs from the Clean-Up Standard described in the ROD signed on September 17, 1990.

This Explanation of Significant Differences ("ESD") and the corresponding supporting documents are available for public review in the Hagen Farm Administrative Record, which is located at the following information repository:

Stoughton Public Library
304 S. 4th Street
Stoughton, Wisconsin 53589

SITE BACKGROUND

The Site is located at 2318 County Highway A, approximately one mile east of the City of Stoughton, Dane County, Wisconsin. The 10-acre Site is situated in a rural surrounding that is dominated largely by sand and gravel mining and agriculture.

The Site was operated as a sand and gravel pit prior to the late 1950s. The gravel pit was then used for disposal of waste material from the late 1950s to the mid-1960s. During the period that the Site was operated as a disposal facility the property was owned by Nora Sundby, who is now deceased. The Site was operated by City Disposal Corporation ("City Disposal"), a predecessor corporation of the current Site owner, which is Waste Management of Wisconsin, Incorporated ("WMWI"). City Disposal accepted municipal wastes, waste solvents and other various organic materials including acetone, butyl acetate, 1-2-dichloroethylene, tetrahydrofuran, solid vinyl, sludge material containing methylethyl ketone and xylenes, and toluene for disposal at the Site. In a 103(c) notification submitted to the U.S. EPA by Uniroyal, Inc. ("Uniroyal"), in June 1981, Uniroyal indicated that F003 and F005 wastes, which are hazardous wastes within the meaning of the Resource Conservation and Recovery Act (RCRA), 42 U.S.C. 6901, also were disposed of at the Site. WMWI and Uniroyal are the two Potentially Responsible Parties ("PRPs") that have been identified in connection with the Site.

Beginning in November 1980, in response to complaints received from local residents, the Wisconsin Department of Natural Resources ("WDNR") began conducting groundwater sampling at nearby private water supply wells. Sampling of the on-Site monitoring wells during the period 1980-1986 indicated certain organic compounds were present in the groundwater, including benzene, ethylbenzene, tetrahydrofuran, xylenes, and toluene. In addition, nearby private water supplies on adjacent properties have also shown detectable levels of volatile organic compounds ("VOCs"). The private wells located at the Site have been impacted by acetone, tetrahydrofuran, vinyl chloride, xylene, trans 1,2-dichlorethene, and trichloroethylene. These private wells are no longer in use.

The Site was proposed for inclusion on the National Priorities List ("NPL") on September 18, 1985. The Site was placed on the NPL in July of 1987. Subsequently, WMWI and Uniroyal, the two PRPs named by U.S. EPA in connection with the Site, entered into an Administrative Order by Consent (U.S. EPA Docket No. VW 87-C-016, dated September 14, 1987) ("Consent Order") with U.S. EPA and WDNR. In the Consent Order, WMWI and Uniroyal agreed to conduct a Remedial Investigation and Feasibility Study ("RI/FS") at the Site. Accordingly, in July of 1988, upon U.S. EPA approval, in consultation with the WDNR, of the required Work Plans, fieldwork at the Site commenced.

Two operable units, which are being conducted concurrently, have been defined for the Site. Operable Unit ("OU") I, which is the Source Control Operable Unit ("SCOU"), is intended to address Waste/sub-Soils at disposal area A and the two smaller disposal areas B and C. OU II, which is the Groundwater Control Operable Unit ("GCOU"), is intended to address the contaminated groundwater at the Site. This approach was agreed upon after discussions among U.S. EPA, WDNR, and the PRPs during the early phase of the implementation of the Work Plan for the RI for the SCOU.

The RI for the SCOU was completed in early 1989, and the Technical Memorandum for the SCOU was submitted in March 1989. The RI for the GCOU was initiated in July 1989 and the Technical Memorandum for GCOU was submitted in February 1990. Currently, additional field activities to define the extent of plume migration are ongoing. The RI report for the GCOU, including the Endangerment Assessment, is scheduled for completion in July 1991. The Record of Decision for the GCOU is scheduled for early 1992.

In June, 1990, U.S. EPA provided the FS and the Proposed Plan for the source control remedial action to the public. An opportunity for public comment was provided. Comments were to be submitted in writing to the U.S. EPA by August 10, 1990, or orally at the public meeting held in Stoughton, Wisconsin, on August 2, 1990.

The ROD for the SCOU was signed on September 17, 1990. Special Notice and a Consent Decree for Remedial Design and Remedial Action ("RD/RA") for the Site was issued to the PRPs on October 31, 1990. The PRPs did not submit a good faith offer within the statutorily mandated time period. Accordingly, on March 7, 1991, U.S. EPA issued to the PRPs a unilateral administrative order ("UAO") pursuant to Section 106 of CERCLA. The PRPs have agreed to comply with the terms and requirements of the UAO.

Remedial Investigation/Feasibility Study

Analyses of soils, waste, and fill materials performed during the RI revealed the presence of numerous hazardous substances including ethylbenzene, toluene, xylene, 2-butanone, tetrahydrofuran, vinyl chloride, arsenic, lead, and mercury. These contaminants are present in the subsurface soils at and above the water table and continue to be released into the groundwater.

Contaminants are being released to the environment through the following pathways: volatilization of contaminants through the soil to the air; direct contact; and release of contaminants from waste, and soils to the groundwater. These releases provide potential for exposure of VOCs to humans as well as terrestrial and aquatic life.

The level of contaminants found at the source characterization wells far exceed Federal and State standards. For the case of tetrahydrofuran, the most frequently detected compound at the Site, the level (630 parts per billion (ppb)) is 12,600 times higher than the State groundwater enforcement standard (50 ppb). This data clearly indicated that the Waste/sub-Soils are acting as a source of groundwater contamination. This source will continue to load contaminants to the groundwater unless addressed by remedial action.

Record of Decision

Considering the Proposed Plan for remedial action and the public comments received, U.S. EPA, with concurrence by the State, selected a source control remedy for remediation of on-site waste and sub-surface soils at the Site. U.S. EPA's decision is summarized in the ROD signed by the U.S. EPA Regional Administrator on September 17, 1990. The selected remedy includes the following: consolidation of non-native materials from disposal areas B and C into disposal area A with subsequent backfilling of disposal areas B and C with clean soil material; installation of a WDNR NR 504 solid waste cap over disposal area A after consolidation; In-situ vapor extraction of the waste refuse and sub-surface soils in disposal area A; off-gas treatment through carbon adsorption; installation and maintenance of a fence around disposal areas A, B, and C during remedial activities; and deed and access restrictions to prevent installation of drinking water wells within the vicinity of the disposal areas and to protect the cap.

U.S. EPA's ROD includes a discussion of U.S. EPA's reasons for the selection of the source control remedy. The remedial action ("RA") has been determined to be a cost-effective remedial action which provides adequate protection of public health, welfare, and the environment, and meets all Federal and more stringent State ARARs.

Description of Significant Differences and the Basis for those Differences

The description of the selected remedy in the ROD, Section X, Selected Remedy, states that "the goal of the ISVE extraction will be 90 percent removal of VOCs in the Waste/sub-Soils". Information became available to U.S. EPA and WDNR after the ROD was signed which allows U.S. EPA to further refine the Clean-Up standard. Because in this case there is no standard accepted method to collect and analyze the waste from this Site which would yield statistically reliable and representative results, U.S. EPA has determined that the Waste/sub-Soils Clean-Up standard be based upon a reduction of the soil-gas VOC concentrations. Based upon a literature survey (see Attachment A) and discussions with U.S. EPA's Environmental Research Laboratory, Ada, Oklahoma (see Attachment B), U.S. EPA, with State concurrence, has determined that it is more appropriate to use a state-of-the-art Groundwater/Soil-gas Model ("Model") for each VOC detected in the Waste/sub-Soils and/or the groundwater during the remedial investigation to determine the Clean-Up standard for the Waste/sub-Soils. Using this Model to determine the Clean-Up standard will ensure clean-up levels that are measurable and reliable, as well as consistent with the National Contingency Plan.

The Scope of Work that has been prepared for the implementation of the remedy selected in the ROD, as modified by this ESD, states that the PRPs shall submit a state-of-the-art Groundwater/Soil-gas Model to provide U.S. EPA with the data on which to base a soil-gas Clean-up Standard in the Waste/sub-Soils. It further states that the Groundwater/Soil-gas Model shall be used to determine the concentration of VOCs in the Waste/sub-Soils necessary to achieve the protective level of VOCs in the groundwater.

Wisconsin Department of Natural Resources Comments

WDNR has been given an opportunity to comment on this ESD. Their comments have been addressed and the State is in agreement with the revised Clean-up Standard under this ESD.

Affirmation of the Statutory Determination

Considering the new information that has been developed and the change that has been made to the methodology for calculating the Clean-Up standard component of the selected remedy, the U.S. EPA, with the concurrence of the State, believes that the remedy remains protective of human health and the environment, complies with Federal and State requirements that are applicable or relevant and appropriate to this remedial action, and is cost-effective. In addition, the remedy and the revised methodology for calculating the Clean-Up standard utilizes permanent solutions and alternative treatment technologies to the maximum extent practicable for this Site.

ATTACHMENT A

Modeling of Ground-Water Contamination Caused by Organic Solvent Vapors

by Carl A. Mendoza[a] and Todd A. McAlary[b]

Abstract

Mathematical models are used to evaluate the potential for ground-water contamination resulting from vapor transport of volatile organic solvents in the unsaturated zone. A two-dimensional numerical model for density-driven flow and transport of vapors shows that trichloroethylene (TCE) vapors can be expected to spread rapidly from a residual source above an unconfined aquifer in an unsaturated, sandy deposit. Sensitivity analyses show that the shape of the vapor plume is particularly sensitive to the ground surface boundary condition and the material permeability. The shape of the vapor plume is insensitive to the mass flux by diffusion through the capillary fringe, although the flux may be significant in terms of ground-water quality because the drinking-water standard is very low. The vapor plume simulations and a plug-flow infiltration model are *used to calculate a source function for a ground-water transport model in order to estimate the potential for ground-water* contamination. Ground-water simulations show that an impermeable surface cover could reduce the flux of contaminants to the aquifer by preventing infiltration through the vapor plume. However, for the conditions modeled, significant ground-water contamination can be expected to occur regardless of whether the ground surface is covered or not. Contaminants can reach the saturated zone from a residual source either by liquid-phase diffusion through the capillary fringe or by migrating as a vapor beyond the lateral limits of a cover and subsequently dissolving and being flushed to the saturated zone by infiltration.

Introduction

Vapor transport in the unsaturated zone has an important influence on the fate of volatile organic compounds released into the subsurface. Schwille (1988) suggested that vapors from solvents may spread laterally by diffusion and density-driven advection in the unsaturated zone and lead to ground-water contamination; however, there are few quantitative analyses of the problem presented in the literature. An understanding of the transport *processes involved is important for the determination of the* extent of contamination and for the design of remedial measures.

Discrete solvent releases in the subsurface move primarily downward through the unsaturated zone, leaving behind a trail of liquid solvent which occupies a small fraction of the pore space. Although this residual solvent is immobilized by capillary forces, the contaminant may reach the saturated zone by dissolving in the soil moisture and being transported by infiltration, liquid-phase diffusion, or a fluctuating water table. Since infiltration is generally the most important of these processes, it is common practice in remedial programs to place an impermeable cover on the ground surface over the residual solvent to minimize ground-water contamination. Many hydrophobic organic solvents, however, will vaporize readily and migrate through *the gas phase in the unsaturated zone*, which constitutes an alternative pathway to the saturated zone. Dissolution of the vapors in the soil moisture creates an effective source of ground-water contamination which can spread so quickly that the liquid residual itself is soon insignificant by comparison (Sleep and Sykes, 1989). In these cases, a surface cover over the residual solvent alone may not provide adequate protection from ground-water contamination.

The objective of this study was to simulate the ground-water contamination resulting from vapor transport, dissolution, and infiltration for a hypothetical case where a *residual solvent source occurs above the water table in a* sandy unconfined aquifer. A two-dimensional finite-element model was used to simulate vapor transport of trichloroethylene (TCE) from a residual source in the unsaturated zone and to conduct sensitivity analyses for the influence of the ground surface and water-table boundary conditions and the permeability of the geologic material. The results of the unsaturated zone model were used to define a source for a ground-water transport model to evaluate the potential for ground-water contamination from spreading solvent vapors. The models were used collectively to simulate the effect of placing a low-permeability cover over a solvent spill site in an attempt to diminish the severity of ground-water contamination.

The rationale for choosing TCE as the compound was that it is one of the most common organic contaminants *found in ground water. Since many other chlorinated* solvents have properties similar to those of TCE, the general results of the study apply to many cases where volatile chlorinated solvents are accidentally released into the unsaturated zone.

The approach of using decoupled models for the unsaturated and saturated zones was chosen to give an acceptable balance between the accurate representation of the physical processes and the appropriate level of mathematical complexity justified for the hypothetical scenario being considered. Decoupling results in more efficient models since the spatial and temporal scales of transport in

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the two zones are different. One-dimensional transport models have been developed by Weeks *et al.* (1982) and Baehr and Corapcioglu (1987); however, two dimensions are required to represent the lateral spreading of the vapors. The two-dimensional models of Abriola and Pinder (1985) and Baehr (1987) do not consider advection in the gaseous phase, and so were not suitable for this study since density-driven advection may be important for chlorinated solvents. The model developed by Sleep and Sykes (1989), which considers advection and dispersion in both the gaseous and aqueous phases, was not available at the time of this study. Thus, a new model, based partly on that of Allan (1986), was developed to simulate the transport of vapors in the unsaturated zone. Existing flow and transport models were used for the saturated zone.

Mass Transport Modeling in Porous Media

The mathematical simulation of subsurface contaminant plumes is obtained by solving the partial differential flow and transport equations, subject to boundary and initial conditions. The general mathematical equations describing fluid and mass transport in granular materials are applicable to both the gaseous and aqueous phases (Bear, 1972). In this study, transport in the saturated and unsaturated zones was simulated separately since gaseous phase transport is restricted to the unsaturated zone and we assumed that aqueous phase transport dominates only in the saturated zone.

Some general assumptions were made which apply to the governing equations for both fluid phases. Chemical and biological transformations were not considered, so the results are restricted to compounds that are not degraded over the time scales of the simulations. The gas, liquid, and solid phases were all assumed to be essentially incompressible and under isothermal conditions. The temperature was chosen to be 20°C. Additional assumptions are discussed later.

Flow and Transport in the Unsaturated Zone

In the unsaturated zone, gas flow may result from pressure gradients or density gradients within the vapor plume. Pressure gradients due to vacuum extraction were not considered in this study and the effects of barometric pressure fluctuations were assumed to be negligible. Density gradients were considered as a function of molecular weight and vapor concentration relative to natural soil gas. Density flow can be modeled using the same mathematical formulation as for the density-dependent ground-water flow model presented by Frind (1982). To maintain numerical efficiency, an equivalent head (h^*) and relative density (ρ_r) may be defined:

$$h^* = \frac{P}{\rho_a g} + z \qquad \rho_r = \frac{\rho}{\rho_a} - 1 \qquad (1a,b)$$

where ρ is the density of the gas mixture, ρ_a is the density of uncontaminated air, P is the fluid pressure, and g is the gravitational constant.

In the absence of large pressure gradients, the gas phase may be assumed incompressible, and density is then a function of concentration only (Sleep and Sykes, 1989). The two-dimensional flow equation for the vapor phase is then:

$$\frac{\partial}{\partial x}\{k_x^* \frac{\rho_a g}{\mu} \frac{\partial h^*}{\partial x}\} + \frac{\partial}{\partial z}\{k_z^* \frac{\rho_a g}{\mu}(\frac{\partial h^*}{\partial z} + \rho_r)\} = S_s \frac{\partial h^*}{\partial t} \qquad (2)$$

where k_x^* and k_z^* are the principal directions of effective permeability (assumed to be horizontal and vertical), and μ is the gas mixture viscosity. In this study, the effective gas permeability is taken as being 80% of the intrinsic permeability. The specific storage is defined by:

$$S_s = \theta_g \rho_a g \gamma \qquad (3)$$

where γ is the macroscopic compressibility of the gas phase, and θ_g is the gas-filled porosity.

The unsaturated zone transport equation developed here ignores transport in the aqueous phase by assuming that the soil moisture is held motionless by capillary tension. This is reasonable if infiltration, evapotranspiration, and water-table fluctuations are negligible over the period of time represented by the vapor transport simulation. The vapor transport equation for static moisture conditions may be written as:

$$\frac{\partial}{\partial x}\{\theta_g(D_{xx}\frac{\partial c}{\partial x} - D_{xz}\frac{\partial c}{\partial z})\} + \frac{\partial}{\partial z}\{\theta_g(D_{zx}\frac{\partial c}{\partial x} + D_{zz}\frac{\partial c}{\partial z})\}$$

$$- v_x \frac{\partial}{\partial x}(\theta_g c) - v_z \frac{\partial}{\partial z}(\theta_g c) = \frac{\partial}{\partial t}(\theta_g R_v c) \qquad (4)$$

where c is the concentration, and v_x and v_z are the velocities. The vapor dispersion tensor is:

$$D_{ij} = \alpha_T |v| \delta_{ij} + (\alpha_L - \alpha_T)\frac{v_i v_j}{|v|} + D_a^* \delta_{ij} \quad (i,j = x,z) \qquad (5)$$

with α_L and α_T being the longitudinal and transverse dispersivities, respectively, and δ_{ij} is the Kronecker delta.

For nonreactive vapors in moist granular soils, Millington and Quirk (1961) showed that the effective *diffusion coefficient (D_a^*) can be calculated from the* free-air diffusion coefficient (D_a) using the relationship:

$$D_a^* = \frac{\theta_g^{7/3}}{\theta_t^2} D_a \qquad (6)$$

where θ_t is the total porosity.

The effects of sorption and dissolution reactions can be accounted for by using a vapor retardation factor of the form suggested by Weeks *et al.* (1982). The retardation factor for the vapor phase is then:

$$R_v = 1 + \frac{\theta_w}{\theta_g} K_h + \frac{\rho_b}{\theta_g} K_h K_d \qquad (7)$$

where K_h is the inverse dimensionless Henry's Law constant (mg/l liquid per mg/l gas), K_d is the solid-liquid partitioning coefficient (mg/g solid per mg/ml liquid), ρ_b is the bulk density of the soil, and θ_w is the water-filled porosity. The first term in (7) accounts for mass removed by dissolution into the soil moisture assuming two-phase equilibrium described by Henry's Law; the second term accounts for sorption onto the solids from the aqueous phase assuming a linear sorption isotherm. These phase transfer reactions are assumed to be essentially instantaneous. This formulation is not valid for very dry soils where sorption increases dramatically and becomes strongly nonlinear (Chiou and Shoup, 1985), nor for highly advection-dominated situations where reaction kinetics should be considered (Johnson *et al.*, 1987). The geologic setting used here is expected to satisfy the above constraints, but more research is needed to determine the range of conditions under which these assumptions are valid.

Flow and Transport in the Saturated Zone

Ground-water flow was simulated at steady-state by neglecting temporal flow variations and the effects of the solvent on the physical properties of the aqueous solution. The solubility of TCE in water is low enough for the second assumption to be valid. In terms of hydraulic head (h), the two-dimensional steady-state flow equation for water in the saturated zone is:

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) = 0 \qquad (8)$$

where K_x and K_z represent the principal directions of hydraulic conductivity.

For saturated transport, the advection-dispersion equation is:

$$\frac{\partial}{\partial x}\left(D_{xx}\frac{\partial c}{\partial x} + D_{xz}\frac{\partial c}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_{zx}\frac{\partial c}{\partial x} + D_{zz}\frac{\partial c}{\partial z}\right)$$

$$- q_x \frac{\partial c}{\partial x} - q_z \frac{\partial c}{\partial z} = \theta_w R_d \frac{\partial c}{\partial t} \qquad (9)$$

where R_d is the retardation factor for dissolved solutes, and q_x and q_z are the Darcy fluxes. The aqueous dispersion term is defined as:

$$D_{ij} = \alpha_T |q| \delta_{ij} + (\alpha_L - \alpha_T)\frac{q_i q_j}{|q|} + D_w^* \delta_{ij} \quad (i,j = x,z) \qquad (10)$$

where D_w^* is the effective aqueous diffusion coefficient.

Boundary and Initial Conditions in the Unsaturated Zone

The upper and lower boundary conditions for the unsaturated domain were modeled using theoretical methods of estimation for the boundary mass transfer coefficients. Since these estimation methods have not been verified experimentally, a sensitivity analysis was conducted for each boundary condition. The ground surface boundary was simulated as: (1) an impermeable boundary intended to represent a building foundation, pavement, or frozen ground, or (2) a permeable boundary with vegetative cover. The impermeable boundary was simulated by specifying zero gradients of head and concentration normal to the boundary. The permeable boundary was simulated using the boundary layer theory of Thibodeaux (1981). If a stagnant layer of air of thickness h_{gs} exists above the ground surface, the steady-state diffusive flux across the layer can be described by:

$$\theta_g D_n \frac{\partial c}{\partial n} - \theta_g v_n c = \frac{D_a}{h_{gs}} c_{gs} \qquad (11)$$

where c_{gs} is the vapor concentration at the ground surface boundary, D_n is the normal dispersion coefficient within the domain, v_n is the normal velocity within the domain, and n is the unit normal to the boundary. The concentration in the atmosphere is assumed to be zero. The head along the permeable boundary was constrained to correspond to constant atmospheric pressure.

The top of the saturated zone has been assumed to be impermeable to transport in most previous vapor models; however, a diffusive flux must be considered if a concentration gradient exists between the unsaturated and saturated zones. Assuming that the rate limiting mass transfer process is aqueous phase diffusion through a horizontal flow layer of thickness h_{wt} near the capillary fringe, the steady-state boundary flux can be described by an equation similar to that used by Weeks *et al.* (1982):

$$D_n \frac{\partial c}{\partial n} = \frac{D_w^*}{h_{wt}} c_{wt} \qquad (12)$$

where c_{wt} is the aqueous phase concentration at the top of the boundary layer. The concentration at the bottom of this boundary layer is assumed to be zero. Since this boundary is impermeable to gas flow, the head gradient was specified to be zero.

The initial condition for flow was a static air phase everywhere. For transport, zero concentration was specified everywhere but the source.

Numerical Method of Solution

The Galerkin finite-element method was applied using triangular elements and linear basis functions. Details of the method were presented by Wang and Anderson (1982) and Huyakorn and Pinder (1983). The vapor flow equation was solved using implicit time-weighting, while the vapor and aqueous transport equations were solved using the Crank-Nicolson time-weighting scheme. Stability and accuracy problems were controlled by satisfying the Peclet and Courant criteria (Daus *et al.*, 1985).

In the vapor model, the flow and transport equations are not independent because the velocities from equation (2) are required for the solution of equation (4), yet the velocities depend on the concentrations calculated from (4). An iterative solution was used therefore to solve repeatedly the flow and transport equations until the concentrations converged to within 0.001% of the source concentration between iterations. With TCE as the solvent, only two iterations were generally necessary, except at early times where three to five iterations were required because of high-density gradients.

Output from the vapor model was compared to simple linear analytical solutions of the diffusion and advection-dispersion equations to verify that the basic equations were being solved correctly. The conservation of mass was shown to be acceptable by mass balance calculations, which compared the mass input to the domain, to the difference between the mass stored within the domain and the mass transported across the boundaries. Experimental data that definitively exhibit density-driven advection do not yet exist (Sleep and Sykes, 1989), so the model could not be rigorously validated.

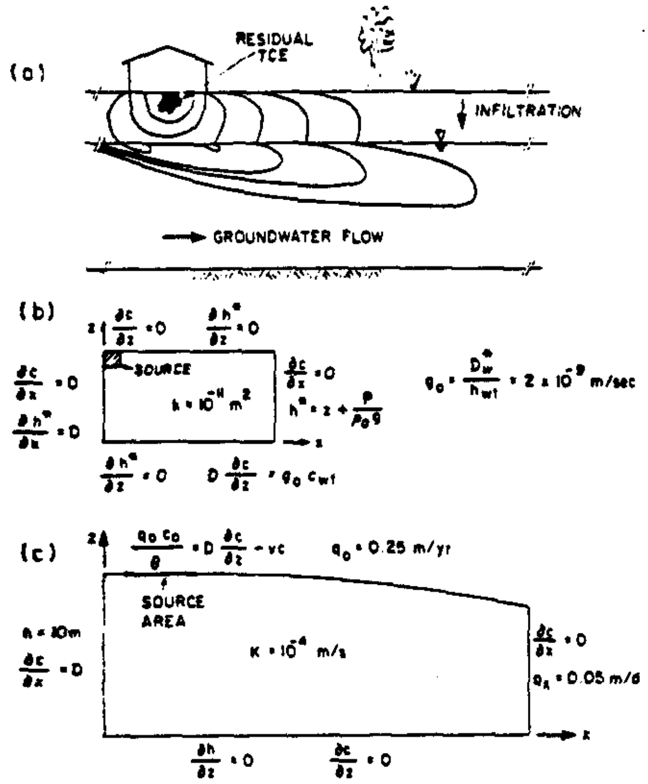

Fig. 1. (a) Schematic representation of hypothetical setting. *Domain and boundary conditions for (b) the unsaturated* zone base case, and (c) the saturated zone.

The ground-water flow equation was solved *using* a potential/stream function model (FLONETS) based on the dual formulation of flow (Frind and Matanga, 1985). Only a single solution of the flow equation was required for each simulation because the ground-water flow was assumed to *be at steady-state. The transport equation* was *then* solved using a general purpose solute transport model (FEMTRAN). These models, developed by E. O. Frind and E. A. Sudicky at the University of Waterloo, have been tested extensively and applied to a number of situations.

Physical Setting

The vapor and ground-water models were applied to a hypothetical geologic setting in a humid, temperate climatic region intended to be representative of south-central Canada or the northeastern United States. Although the models will accommodate heterogeneity and anisotropy, a simple setting of an unconfined aquifer in a homogeneous, isotropic, medium-grained, sandy deposit was considered sufficient to show the potential impact of vapor plumes on ground-water quality. A schematic representation of the setting, with postulated vapor and ground-water plumes, is shown in Figure 1 along with the domains and boundary conditions for the simulations. The physical properties for both domains are summarized in Table 1.

The soil moisture content throughout the unsaturated zone was assumed to be uniform at a field capacity of 6% of bulk volume. In reality, there is a transition zone of gradually increasing moisture contents above the saturated zone, but this was ignored here to avoid extremely small elements near the capillary fringe. Increased moisture contents near the bottom of the unsaturated zone would be expected to reduce vapor transport rates and increase mass partitioning to the aqueous phase.

The source of organic vapors was assumed to originate from a hypothetical surface spill of 200 l (approximately one barrel) of trichloroethylene (TCE) which spread out uniformly over a 1 m by 3 m area and infiltrated until it reached residual saturation. Assuming that the residual saturation was uniform at 15% of the pore volume, which is within the range reported by Schwille (1988) for medium sand, the residual liquid solvent would penetrate to a depth of 1.2 m. We assume that vaporization was fast enough so that the local soil gas was continually saturated with TCE vapors, and thus the vapor source would have a constant concentration of 7.9% (by volume) and a relative density (compared to air) of 1.3. The coexisting aqueous phase at *equilibrium would be saturated with TCE at a concentration* of about 1100 mg/l.

Results of Unsaturated Zone Modeling

The results of the vapor model are shown as plots of one-half of the unsaturated domain because of the symmetry about the residual solvent source. The fate of TCE was calculated for the half domain and is summarized in Table 2 for each of the vapor simulations. Mass balance errors were less than 0.01% of the vaporized mass.

The contours in Figures 2, 3, and 4 show the vapor concentration expressed as a fraction of the source vapor concentration (430 mg/l gas). From Henry's Law and the *assumption of equilibrium between the gas and* liquid phases, the vapor contours correspond to aqueous concen-

Table 1. Simulation Parameters

Unsaturated zone (base case)	
Effective permeability, k^*	8.0×10^{-12} m^2
Bulk-water content, θ_w	6%
Porosity, θ_t	30%
Bulk density, ρ_b	1.65 g/ml
Effective diffusion coefficient, D_a^*	3.2×10^{-6} m^2/s
Longitudinal dispersivity, α_L	1.0 m
Transverse dispersivity, α_T	0.1 m
Inverse Henry's constant, K_h	2.56
Partitioning coefficient, K_d	0.01 ml/g
Calculated retardation factor, R_v	1.8
Water-table diffusion thickness, h_{wt}	0.3 m
Domain dimensions	4 by 24 m
Domain discretization	11 by 31 nodes 600 elements
Saturated zone	
Hydraulic conductivity, K	1.0×10^{-4} m/s
Porosity, θ_t	30%
Effective diffusion coefficient, D_w^*	3.0×10^{-10} m^2/s
Longitudinal dispersivity, α_L	2.0 m
Transverse dispersivity, α_T	0.1 m
Assumed retardation factor, R_d	1.0
Domain dimensions	10 by 224 m
Domain discretization	21 by 71 nodes 2800 elements
Both zones	
Temperature, T	20°C

trations in the soil moisture as a fraction of the solubility. Although the drinking-water standard for TCE is about five orders of magnitude lower than the solubility, only the first three orders of magnitude are shown on the plots since numerical dispersion may cause significant errors at lower levels.

Base Case

The base case simulation shows the vapor plume development for the medium-grained sand deposit described in the previous section. It is intended to be used as a basis for comparing the results of the sensitivity analyses. It was also used to generate the source function for the ground-water zone modeling.

The base case vapor plume after 45, 90, and 135 days is shown in Figure 2. The shape of the base case plume is very similar to simulations conducted using a zero density gradient (see Figure 4) which indicates that diffusion is the dominant transport mechanism. The effect of density-driven advection is barely detectable, but it results in the contours extending slightly further from the source near the bottom of the domain. Again, it should be noted that vapor migration just above the water table would be expected to be slower than shown because of the increased retardation with increasing moisture content that was not accounted for in the simulations.

The base case simulations indicate that vapor transport can cause rapid spreading of contaminants from a residual solvent source in unsaturated sand. The source of potential ground-water contamination expands with the vapor plume since the vapors will dissolve into the local soil moisture and can be transported later to the saturated zone by aqueous-phase diffusion, infiltration, or a fluctuating water table.

Sensitivity Analysis

1. Ground Surface Boundary

The sensitivity analysis on the ground surface boundary condition shows the effect of natural venting to the atmosphere. The shape of the vapor plume after 135 days is shown in Figure 3 for the cases of an impermeable ground surface cover, a permeable ground surface with a thick boundary layer (h_{gs} = 1 m), and a permeable ground surface with a thinner boundary layer (h_{gs} = 25 cm). The thickness of the boundary layer of air above the ground surface corresponds to about two-thirds the height of the vegetative cover (Oke, 1978). For each of the permeable cases, the ground surface was modeled as being impermeable to a distance of 6 m from the source to show the effects of passive venting at the edge of a cover.

Both of the permeable ground surface simulations show that venting to the atmosphere can be an important attenuation mechanism for vapor plumes, although the effect diminishes with depth below the surface. An impermeable surface cover minimizes natural venting, thereby maximizing the areal extent of the effective source of ground-water contamination. Vapors will eventually spread beyond the limits of a surface cover where infiltration can transport dissolved contaminants to the water table, thereby counteracting the remedial effects of the surface cover.

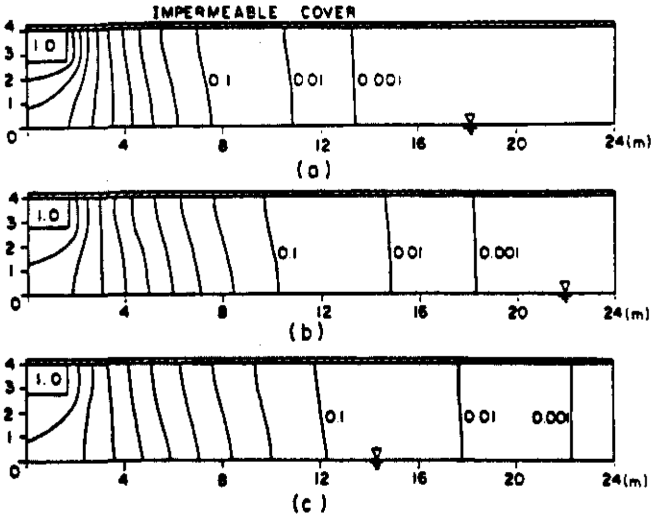

Fig. 2. Base case TCE vapor plume development: (a) 45, (b) 90, and (c) 135 days. Contours represent vapor concentrations relative to the source vapor concentration, or equivalently, soil moisture concentrations relative to saturation.

This study did not consider some factors which may affect the ground surface boundary flux. Barometric pressure fluctuations might increase vertical dispersion near the ground surface resulting in increased venting of TCE to the atmosphere. A rising water table would also increase venting to the atmosphere. Organic-rich soil layers near the ground surface would decrease venting through an increase in sorption. Similarly, sorption onto mineral surfaces has been shown to increase dramatically at very low moisture contents which can occur near the ground surface (Chiou and Shoup, 1985).

2. Water-Table Boundary

A sensitivity analysis on the water-table boundary condition was conducted to determine the effect of diffusion

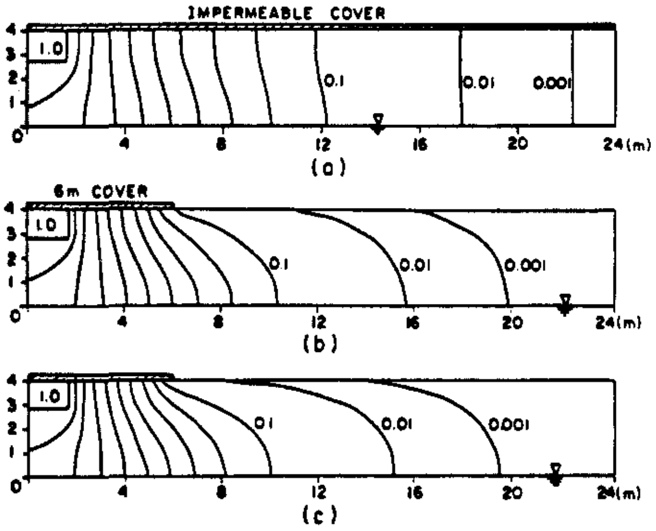

Fig. 3. Effect of the ground surface boundary condition on TCE vapor plumes after 135 days: (a) impermeable surface (base case), (b) a thick boundary layer (h_{gs} = 1.0 m), and (c) a thinner boundary layer (h_{gs} = 0.25 m).

Table 2. Mass Fate for Vapor Transport Simulations

Simulation	*Source vaporization (kg)*	*Vapor phase (kg)*	*Retarded phase (kg)*	*Atmospheric losses (kg)*	*Water-table losses (g)*
Base case:					
90 days	4.02	2.23	1.79	0.00	2.68
135 days	4.79	2.66	2.13	0.00	5.09
Ground surface sensitivity (135 days):					
$h_{gs} = 1.0$ m	5.05	2.12	1.70	1.24	4.76
$h_{gs} = 0.25$ m	5.15	2.03	1.62	1.50	4.68
Water-table sensitivity (135 days):					
$h_{wt} = 3.0$ m	4.79	2.66	2.13	0.00	0.509
$h_{wt} = 0.03$ m	4.81	2.56	2.12	0.00	50.5
Permeability sensitivity (90 days):					
Diffusion only	3.47	1.98	1.59	0.00	2.03
$k^* = 8 \times 10^{-11}$ m^2	7.55	4.19	3.35	0.00	7.34

Values are for the half domain, 1-m wide in the third dimension.

into the saturated zone. Vapor transport simulations were conducted with three different mass transfer coefficients which correspond to boundary layer thicknesses (h_{wt}) of 3, 30, and 300 cm. In all cases, the mass flux across the water table was small enough to have a negligible effect on the shape of the vapor plume; however, it might have a considerably more important effect on ground-water quality. The mass fate values in Table 2 confirm that there was little effect on the vapor plume, but the mass transported into the saturated zone by diffusion alone was between 0.5 and 50 g for the half domain after 135 days. This may be a considerable load since the U.S. EPA drinking-water standard for TCE is 5 μg/l. Ground-water contamination may therefore occur even in the absence of infiltration or water-table fluctuations. Thus, the water table should not be considered an impermeable boundary for contaminant transport from solvent vapors if ground-water contamination is the primary concern.

3. Material Permeability

The sensitivity analysis of material permeability shows the potential effects of density-driven vapor advection. The vapor plumes after 90 days are shown in Figure 4 for a pure diffusion case with density gradients removed, the base case, and a high-permeability case with an order of magnitude increase in permeability relative to the base case. The high-permeability material is equivalent to a clean coarse sand (aqueous hydraulic conductivity, $K = 10^{-3}$ m/s), whereas the material of the base case is equivalent to a clean medium sand ($K = 10^{-4}$ m/s).

Based on the similarity between the base case and the pure diffusion simulations, it is evident that molecular diffusion is the dominant vapor transport mechanism for TCE in a medium sand deposit. Advection becomes increasingly important as the permeability increases, although diffusion still dominates near the periphery of the vapor plume because the density gradient diminishes at lower concentrations. For chemicals whose vapor density is significantly different from air, subsurface vapor advection should be considered until it is shown to be negligible for the specific chemical and geological conditions. Models which neglect advection may underestimate the rate of vapor transport and fail to provide conservative estimates for the protection of ground-water resources.

Results of Saturated Zone Modeling

The saturated zone simulations show the effect of placing an impermeable cover on the ground surface over the residual solvent in an attempt to reduce ground-water contamination by controlling infiltration. In the first case, a 13-m long impermeable cover was placed over the center of the vapor plume, and infiltration was restricted to the uncovered areas. In the second case, the ground surface boundary was completely uncovered.

Ground-Water Flow

The steady-state ground-water flow model was used to calculate the velocities needed to solve the transport equation. The flow model solved iteratively for the position of the water table based on a prescribed head value of 10 m

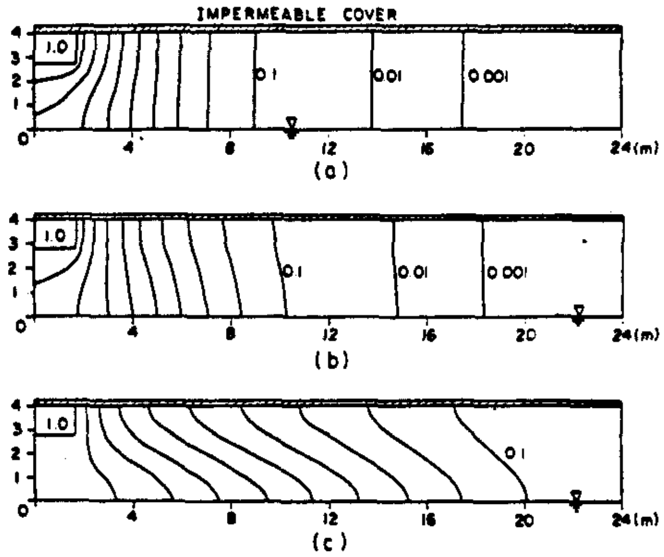

Fig. 4. Effect of density-driven advection on TCE vapor plumes after 90 days: (a) pure diffusion, (b) 8×10^{-12} m^2 permeability (base case), and (c) 8×10^{-11} m^2 permeability.

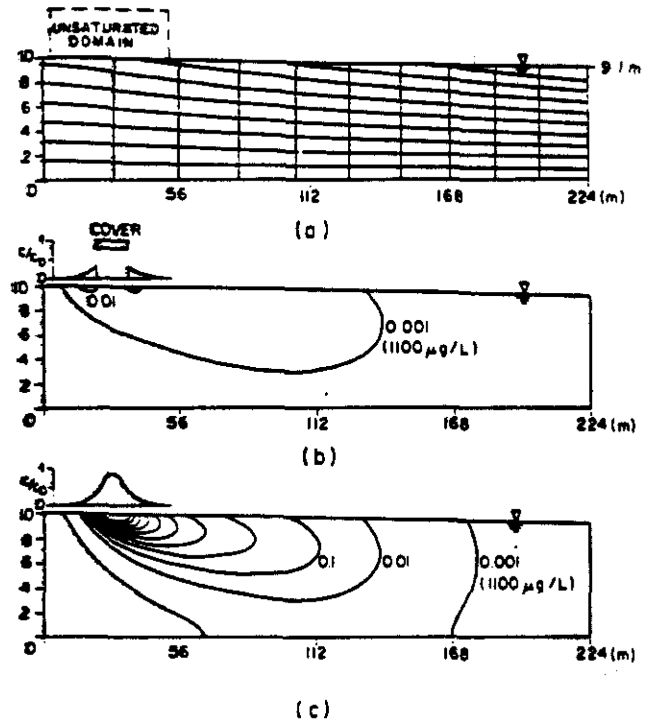

Fig. 5. (a) Saturated zone flownet for the uncovered case showing the location of the model domain for the vapor simulations. TCE ground-water plumes after three years and input concentration functions for (b) the covered case, and (c) the uncovered case. Contours represent aqueous concentrations relative to saturation (1100 mg/l).

on the left boundary and a prescribed Darcy flux of 0.05 m/d on the right boundary. The lower boundary was impermeable. Infiltration was considered constant at 25 cm/yr over the uncovered portions of the upper boundary. For both cases, the resulting horizontal velocities ranged from about 0.08 m/d (30 m/yr) near the left boundary to 0.14 m/d (50 m/yr) near the right boundary, and the elevation of the upper right corner of the domain was 9.12 m. Figure 5(a) shows the flownet for the uncovered case. The covered case flownet was very similar in appearance.

Ground-Water Transport

The input of TCE to the saturated zone was calculated using a simple plug-flow infiltration model. The mass flux was defined by multiplying the infiltration rate by the aqueous TCE concentration at the water table. The diffusive flux through the capillary fringe was considered to be negligible by comparison. For the covered case, the flux beneath the cover was specified to be zero. The aqueous concentration at the water table was selected from the base case vapor simulation at 135 days. The base case scenario was used since the concentration distribution at the water table was not particularly sensitive to the ground surface boundary condition. The time of 135 days was chosen so that the rate of net mass input by vaporization into the unsaturated zone was of the same order as the rate of mass removed by infiltration into the ground-water zone, a condition which would correspond to stabilization of the unsaturated zone plume. Although the actual concentration distribution at the water table changes over time, this snapshot was considered sufficient to show the effects of controlling infiltration through a vapor plume. The water-table concentration distributions used for each case are shown on Figures 5(b) and 5(c).

Figures 5(b) and 5(c) show the dissolved plumes after three years for the covered and uncovered cases, respectively. Since the contours represent aqueous concentrations relative to saturation, *the outermost contour represents a concentration* of 1.1 mg/l. This concentration is still several orders of magnitude greater than the U.S. EPA drinking-water standard of 5 µg/l, and thus, the zone of contamination actually extends for some distance beyond this outer contour. Limitations on the accuracy of numerical model simulations prevent a full description of the problem to concentrations as low as the drinking-water standard.

For these three-year simulations, the mass input to the ground-water zone for the uncovered case was 6.15 kg, whereas the input for the covered case was only 0.93 kg. *While the extent of ground-water contamination is less* severe in the covered case, infiltration beyond the limits of the cover still causes extensive ground-water contamination. Considering the low drinking-water standards for TCE, alternative remedial measures would be required if the aquifer was to be used for a drinking-water supply. Ground surface covers therefore should be considered only as a partial form of remediation for vadose zone solvent spills and should be supplemented with vapor control systems or alternative remedial strategies for maximum effectiveness.

Conclusions

Vapor transport and subsequent dissolution of volatile organics have been shown to be potentially important sources of ground-water contamination. For a spill of TCE in a permeable sandy material, a vapor plume will spread a few tens of meters through the unsaturated zone within a few months by molecular diffusion and possibly by density-driven advection. Phase transfer reactions will contaminate the soil moisture within the vapor plume and significantly increase the size of the potential source of ground-water contamination. The dissolved TCE may be transported to the saturated zone by infiltration, water-table fluctuations, or liquid-phase diffusion across the capillary fringe.

The ground surface boundary condition is a sensitive parameter for vapor transport. A permeable ground surface allows natural venting to the atmosphere which reduces the lateral extent of the unsaturated zone vapor plume; however, it also allows infiltration which can flush contaminated soil moisture into the saturated zone. An impermeable cover over the ground surface will reduce surface venting and increase the lateral migration of the vapor plume.

The water-table boundary should not be considered impermeable to mass transport when investigating the potential for ground-water contamination from solvent vapor plumes. Liquid-phase diffusion can cause a flux of volatile organics across the capillary fringe. The mass flux by diffusion alone is generally too small to affect the shape of the vapor plume; however, it may cause significant contamination in the ground-water zone.

Ground-water simulations demonstrate that a cover at the ground surface can greatly reduce the flux of solvent mass to the saturated zone by preventing infiltration through the residual source and the concentrated regions of a vapor plume. However, because of infiltration beyond the limits of a surface cover and the low concentrations of concern, the reduction in mass flux does not lead to a comparable reduction in the size of the ground-water plume. Surface covers therefore are not considered to be effective remedial measures for the protection of ground-water quality.

Although the simulations presented here are for TCE, the results generally can be expected to apply to other volatile chlorinated solvents. Similar behavior is expected since many other solvents have high vapor pressures and Henry's constants, which favor vapor phase transport in the unsaturated zone. In addition, small amounts of solvent can contaminate large volumes of ground water to undesirable levels because drinking-water standards are generally very low. For example, 1,1,1-trichloroethane, which has a Henry's constant twice that of TCE, will migrate faster in the unsaturated zone. Dichloromethane has a Henry's constant that is one-quarter that of TCE, so migration will be slower; however, its high solubility will place large amounts of mass in the soil moisture that can then be transported to the ground-water zone.

More research is required in order to more fully understand the processes by which aquifers can become contaminated through vapor transport. In particular, experimental data are necessary to validate the theoretical basis for the density-driven advection of vapors, and additional chemicals and geological settings should be investigated.

Acknowledgments

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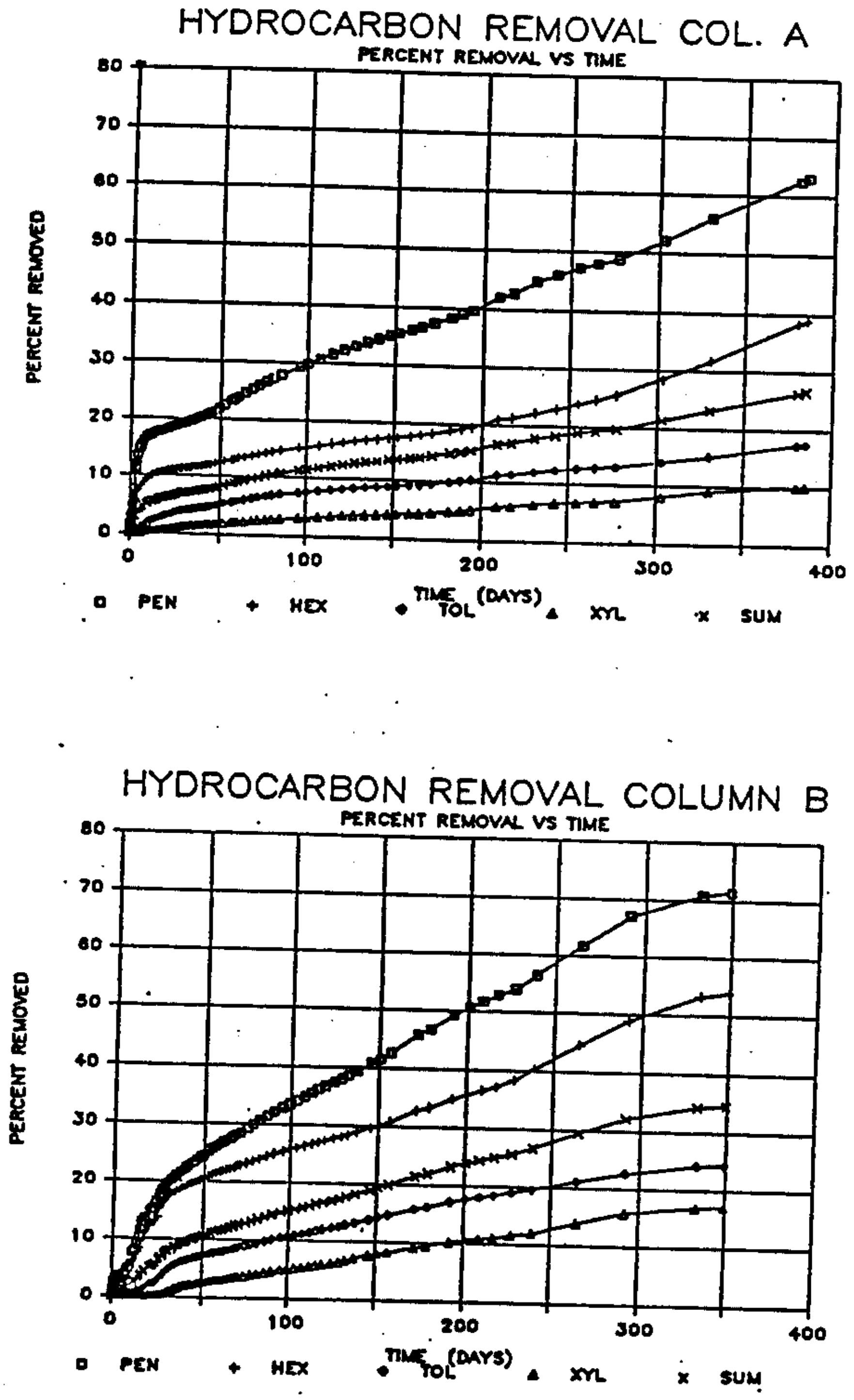

Figure 3. Hydrocarbon Removal Results through August 31, 1988

LARGE-SCALE LABORATORY EXPERIMENTS FOR FORCED AIR VOLATILIZATION OF HYDROCARBON LIQUIDS IN SOIL

Ken Rainwater, Billy J. Claborn, Harry W. Parker,
Douglas Wilkerson and Mohammad R. Zaman

Texas Tech University Water Resources Center
Lubbock, Texas

ABSTRACT: The process of in situ volatilization of liquid hydrocarbon pollutants has been and continues to be applied successfully at field sites around the country. The technique utilizes air vacuum wells which remove hydrocarbon vapors from the subsurface, and may also include air injection wells to complete the flow circuit. Current design practice for these systems consists of pilot-scale operation in a small portion of a polluted site to establish operational parameters, followed by scaling up the process to restore the entire site. Little work has yet been done to describe the volatilization mechanisms in porous media for development of an accurate model for design of these systems. Use of field data for this purpose is limited due to lack of control of initial and boundary conditions. This research project was formulated to answer this need. Two soil columns, 10 feet in height by 3 feet in diameter, were assembled and filled with a fine sand. The moisture content of the sand was set at field capacity. A mixture of pentane, hexane, toluene, and xylene was used to represent a petroleum fuel. The hydrocarbon mixture was introduced to set an initial condition in the unsaturated zone with residual water and hydrocarbons. Forced radial air flow was caused by a vacuum pump connected to a well in the center of each column. Bulk liquid movement was monitored with gamma density measurements, and hydrocarbon on concentrations in the removed air were analyzed by gas chromatography. This paper provides a report of the removal data and description of preliminary modeling efforts.

INTRODUCTION

Restoration of contaminated groundwater sites is a major current environmental concern. Infiltration of organic

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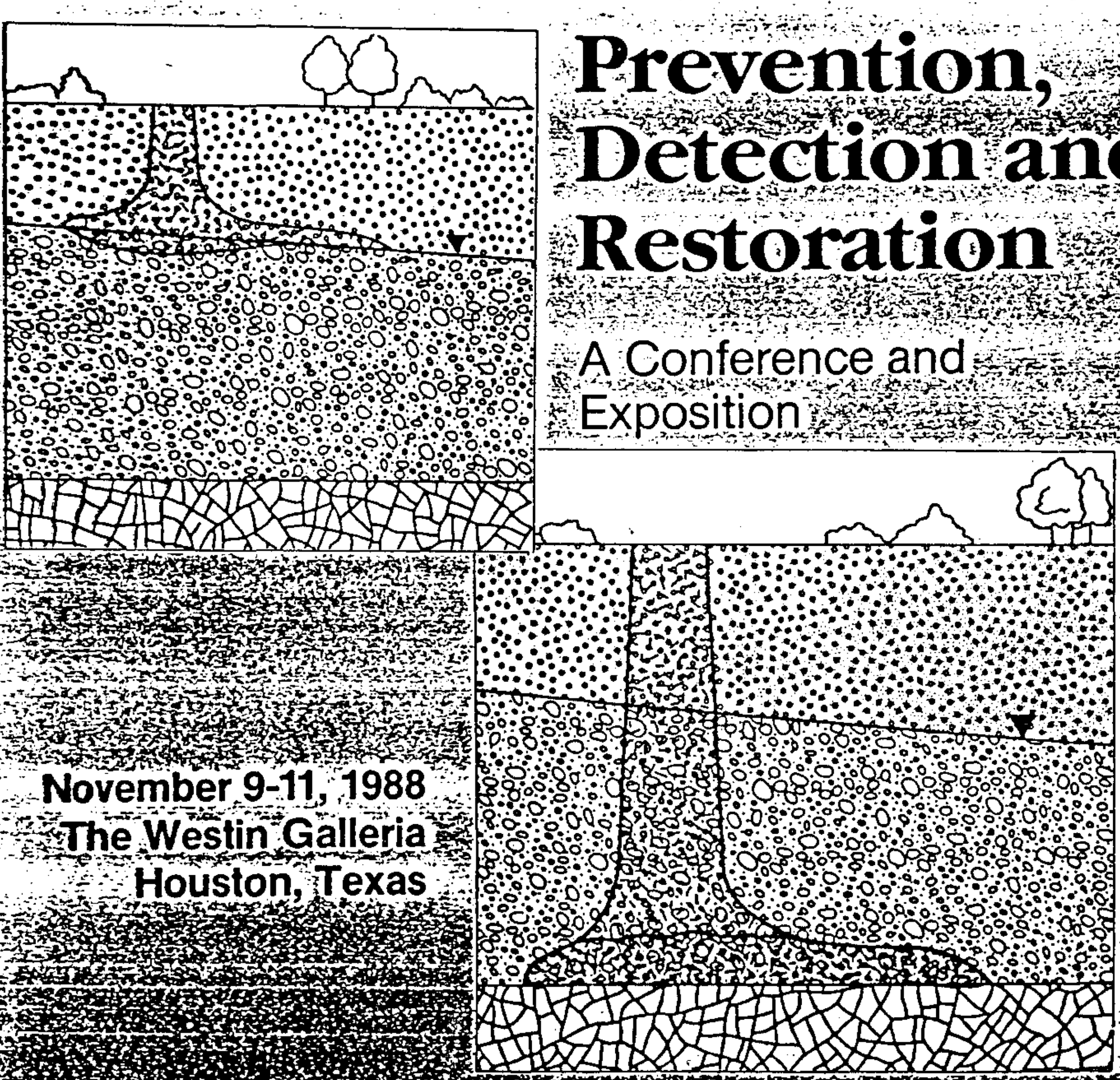
Exposition



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Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils

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■ An experiment was conducted to evaluate the effects of sample disturbance, container headspace volume and integrity, and sample preservation on volatile organic compound (VOC) measurements in contaminated soil. A sandy soil was contaminated under controlled conditions at 10 °C by an aqueous solution containing six target VOCs: methylene chloride (157.5 mg/L), 1,2-dichloroethane (130 mg/L), 1,1,1-trichloroethane (16 mg/L), trichloroethane (12.8 mg/L), toluene (4.5 mg/L), and chlorobenzene (2.85 mg/L). Replicate soil samples were then collected by different methods at an air temperature of 20 °C. For all VOCs, the highest concentrations were measured in undisturbed soil samples immediately immersed in methanol in Teflon-sealed glass bottles. With these measurements as a reference, the relative negative bias was highest for container integrity (up to 100%) and lack of methanol immersion (up to 81%) and considerably lower for container headspace volume (up to 17%) and soil disturbance (up to 15%). The potential for negative bias appeared to be correlated with the VOC soil sorption affinity (i.e., low K_h and high K_{ow}). For accurate measurements of the more volatile compounds, rigorous sampling procedures are necessary.

Introduction

Volatile organic compounds (VOCs) such as trichloroethylene and toluene are present in diverse products found throughout society and are commonly among the controlling contaminants in site remediation projects. Since decisions regarding the significance of contamination and the extent of cleanup have far-reaching effects, it is essential that they be based on accurate measurements of the VOC concentrations present. Unfortunately, this is difficult to achieve as the sampling process is subject to numerous sources of random and systematic errors. Sample collection and handling activities can contribute relatively large errors compared to the analysis itself (*1*). Of these, negative bias (i.e., measured value less than true value) is perhaps the most significant and most difficult to delineate and control. This error is principally caused by volatilization losses during soil sample collection, storage, and handling.

There are currently no standardized procedures for sampling soils for VOC analyses. In the United States, disturbed soil samples are often containerized in Teflon-sealed glass jars and refrigerated at 4 °C. However, practical experience and some recent field research has suggested that simple procedures such as these may lead to substantial error when sampling soils for VOCs and alternative procedures are now being promoted (*2*). Yet controlled research has so far been limited, due in part to a lack of a methodology for effective analysis of this problem. In the experiment described herein, a methodology was developed and used to determine the VOC measurement effects of several key sampling method attributes. This paper presents a synopsis of this research while details may be found elsewhere (*3*).

Experimental Methods

Experimental Approach. To enable the evaluation of sampling method effects, it was necessary to have a volume of soil uniformly contaminated with VOCs. Due to anticipated problems with uncontrolled field conditions, an experimental approach was conceived which included a laboratory soil column contaminated by VOCs during saturated upflow of an aqueous solution containing a number of target compounds. After desaturation and equilibration, sampling the column by methods with different attributes would enable determination of their relative effects on VOC measurements. The attributes chosen for evaluation were sample disturbance, sample container headspace volume and integrity, and sample preservation.

Column Apparatus. Soil for this experiment was collected from the upper 50 cm of a glaciofluvial deposit near Mysen, Norway. The field moist soil was sieved (4-mm mesh) and then a composite sample was characterized as a sand (USDA texture) with 1% silt plus clay content, an ambient water content of 8.6% (dry weight basis), pH of 5.21, organic carbon content of 0.44% (dry weight basis), and cation exchange capacity of 4.0 mequiv/100 g (*4, 5*).

Each of two glass columns (one control and one test column) was packed with 3.6 kg of moist soil yielding a moist bulk density of 1.64 g/cm^3, total porosity of 43.5%, and a water filled porosity of 32% of total porosity (Figure 1). Each column was scanned with a computer-assisted X-ray tomograph (Siemens Somatom 2) to determine spatial uniformity as measured by relative density (i.e., density relative to water) (*3, 6*). The tomography analyses (visual and quantitative) revealed no spatial heterogeneities that would confound the interpretation of the experimental results.

The target VOCs were methylene chloride (MC), 1,2-dichloroethane (DCA), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), toluene (TOL), and chlorobenzene (CB) (Table I). The VOC concentrations in the column feed solution were selected to saturate the VOC retention capacity of the soil column at a likely cleanup action level (*e.g., 1–10 $\mu g/g$) with a workably small volume of feed* solution (e.g., <20 L). The appropriate VOC concentrations were established by an iterative analysis involving consideration of the soil column characteristics and a series of empirical relationships for VOC distribution between the soil liquid, vapor, and solid phases (*3, 7–9*). Based on this analysis, the VOC concentrations chosen for the feed solution were as follows: [MC] = 200 mg/L, [DCA] = 125 mg/L, [TCA] = 25 mg/L, [TCE] = 20 mg/L, [TOL] = 7.5 mg/L, and [CB] = 5.0 mg/L. These concentrations were inversely proportional to the soil sorption potential and ca. 1–2% of the VOC water solubilities (Table I). The feed

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†Institute for Georesources and Pollution Research.

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Table I. Characteristics of the Target VOCs[a]

characteristics	MC	DCA	TCA	TCE	TOL	CB
MW	84.9	99.0	133.4	131.5	92.1	112.6
specific gravity, g/cm^3	2.32	1.25	1.35	1.46	0.87	1.11
water solubility (10 °C), g/L	11.09	10.55	1.40	1.50	0.58	0.41
water solubility S_w (10 °C), mol/L	0.131	0.107	0.0105	0.0114	0.0062	0.0036
molar vol V, L/mol	0.064	0.079	0.099	0.090	0.105	0.101
vp (20 °C), mmHg	349	61	100	60	22	8.8
K_{ow}, mL/g	17.8	30.2	148	195	490	692
K_h (10 °C)	0.060	0.050	0.415	0.232	0.164	0.105
K_{om}, mL/g	4.96	4.92	27.1	27.4	39.6	63.6
K_d, mL/g	0.036	0.036	0.197	0.199	0.288	0.463
RF	1.12	1.12	1.68	1.68	1.99	2.59

[a] Data and empirical relationships from refs 13–15: K_{ow}, octanol/water partition coefficient, mL/g; K_h, Henry's law constant, dimensionless; $\log K_{om} = -0.813 \log (S_w V) - 0.993$; K_{om}, organic matter partition coefficient; soil distribution coefficient, $K_d = 1.72 f_{oc} K_{om}$, with fractional soil organic carbon content, $f_{oc} = 0.00423$; retardation factor, $\mathrm{RF} = 1 + K_d[\rho_b/\theta]$ with dry bulk density, $\rho_b = 1.5$, and volumetric water content, $\theta = 0.436$.

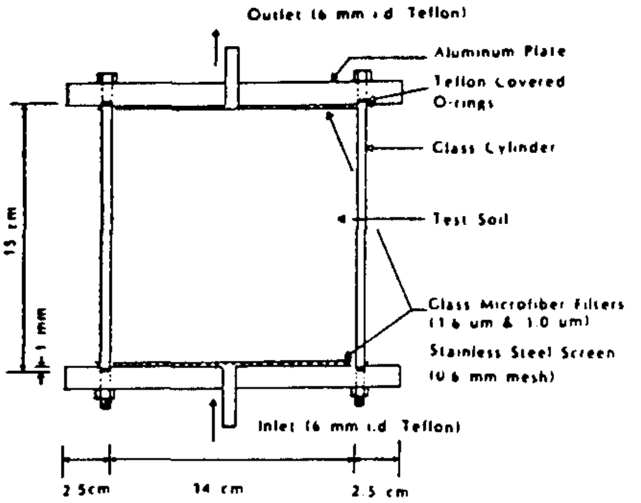

Figure 1. Characteristics of the soil column apparatus.

solution volume required to saturate the VOC retention capacity was, in every case, estimated to be less than 3 pore volume (PV) equivalents.

The feed solution was prepared by diluting stock solution containing the six target VOCs (1000×, ethanol matrix) in "reconstituted freshwater" (RFW) (*10*). The RFW, prepared by adding salts to distilled water (96 mg/L $NaHCO_3$, 60 mg/L $CaSO_4 \cdot 2H_2O$, 60 mg/L $MgSO_4$, 4.0 mg/L KCl), had a pH of 7.0 and specific conductance (EC) of 290 μS/cm.

The test soil column was connected to the rest of the experimental apparatus in a laboratory at 10 °C (Figure 2). Then ca. 25 mL of the VOC stock solution was added to the RFW in the feed reservoir and the two gas-washing reservoirs. After mixing for ca. 1 h, 1 L of solution from the feed reservoir was used to fill the two, 0.5-L gas washing bottles. Tritiated water (5 mL) was next added to the feed reservoir as a hydraulic tracer (feed concentration 170 Bq/mL). Following a few minutes of mixing, flow through the test column was initiated. After initial saturation, 15 PVs of feed solution was passed through the column at a hydraulic gradient of ca. 1.5. The column was then desaturated under a tension of approximately 50 cm with the pore replacement gas derived from the gas-washing system. After drainage ceased (<1 h), the colur was sealed and allowed to equilibrate at 10 °C overnig… (ca. 17 h) prior to soil sampling. The control soil column was treated in a similar fashion, except the target VOCs and tritiated water were not added to the RFW feed solution and the control column run occurred the day preceding the test column run.

Sample Collection and Analyses. During contamination of the test column, samples of the feed and outflow solutions were collected periodically. Following contamination, desaturation, and equilibration, the test column was partially embedded (50% of length) in ca. 10 kg of 10 °C soil to provide support and maintain the soil temperature during sampling. The column was then moved from the laboratory at 10 °C to one at 20 °C to simulate field conditions where cool soil is removed into a warmer am-

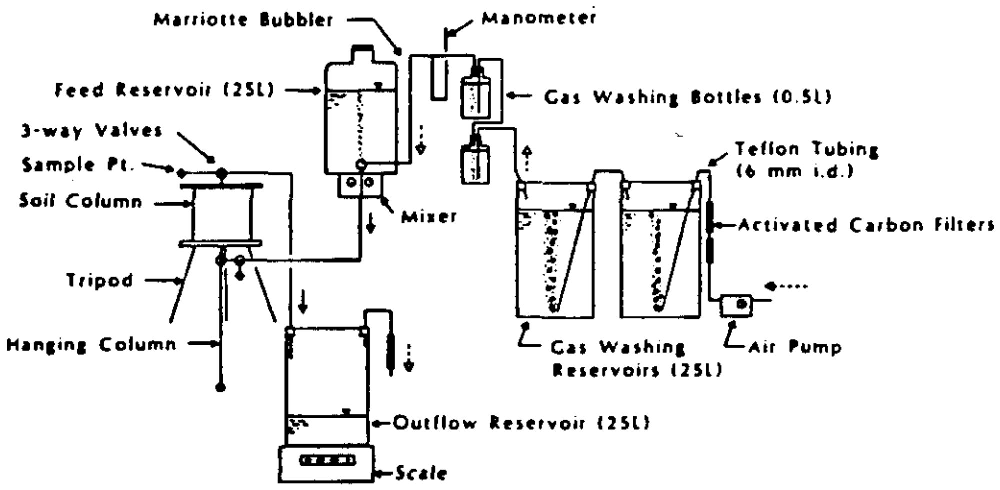

Figure 2. Soil column flow system apparatus.

Table II. Characteristics of the Soil Sample Collection Methods

- A. undisturbed samples in glass bottles with high headspace (A, A′)
  - 1.5 cm i.d., 10 cm long core (ca. 17 mL, 29 g) extruded directly into a Teflon-sealed glass bottle (128 mL) with headspace volume of ca. 85% of container volume
- B. undisturbed samples in glass bottles with low headspace (B, B′)
  - 3.0 cm i.d., 10 cm long core (ca. 75 mL, 125 g) extruded into a Teflon-sealed glass bottle (128 mL) with headspace volume of ca. 40% of container volume
- C. undisturbed samples immersed in methanol in glass bottles (C, C′)
  - 3.0 cm i.d., 10 cm long core (ca. 75 mL, 125 g) extruded into a Teflon-sealed glass bottle (250 mL nominal, 300 mL actual) with 100 mL of reagent grade methanol added and headspace volume of ca. 40% of container volume
- D. disturbed samples in glass bottles with low headspace (D, D′)
  - 3.0 cm i.d., 10 cm long core (ca. 75 mL, 125 g) emptied in 7–10 aliquots with a stainless steel spoon and deposited into a Teflon-sealed glass bottle (128 mL) with headspace volume of ca. 40% of container volume
- E. disturbed samples in empty plastic bags with low headspace (E, E′)
  - soil sample (ca. 40 mL, 70 g) removed directly from the column in 7–10 aliquots with a stainless steel spoon and deposited into a laboratory-grade plastic bag (12 × 18 cm, 0.5 L nominal) with zip closure and headspace volume of ca. 40% of container volume

bient air temperature environment. The column top was removed and replaced with a sampling template to maintain the centerpoint of each sampling location at the same radius within the column. Duplicate soil samples were then collected at diametrically opposite positions within the column according to the methods described in Table II. All of the stainless steel sampling tubes were inserted simultaneously with the tops covered with aluminum foil. Then the samples were collected sequentially in a clockwise fashion (A to E, A′ to E′), with each sample containerized and refrigerated prior to collecting the next sample. Each sample was collected with separate, precleaned utensils and bottles (all at 20 °C). The first sample from the test column (A) was collected 6.2 min after removal of the column top plate, while the last sample (E′) was collected 10.3 min later. Samples for soil water content and organic carbon content were then collected from each column at 0–5 and 5–10 cm depth increments at two (test column) or three (control column) horizontally separate locations.

Solution samples were analyzed for pH, specific conductance, tritium, and the six target VOCs. Analyses for pH and specific conductance were made onsite electrometrically. Tritium was determined by liquid scintillation counting of a 1-mL subsample. Analyses for each of the target VOCs were made by extraction and gas chromatography (GC). A subsample (4.0 mL) of each solution sample was spiked with 40 μg of bromotrichloromethane as an internal standard and then extracted with 4 mL of pentane. The pentane extract was recovered and dried with sodium sulfate prior to GC analysis. Analyses of the four halocarbons were made using a GC apparatus (Hewlett-Packard Model 5730) equipped with a 60 m long, 0.25 mm i.d. J&W fused-silica capillary column and an electron capture detector (^{63}Ni). Analyses of the two aromatics were made on a GC apparatus (Hewlett-Packard Model 5890) equipped with a 30 m long, 0.32 mm i.d. J&W fused-silica capillary column and interfaced with a mass selective detector (5970 series) operated in the single-ion-monitoring mode. For all GC runs, the injection volume was 2 μL.

Soil samples were analyzed for soil water content, total organic carbon, and the target VOCs. Soil water content was determined gravimetrically and total organic carbon content was determined by dry combustion. VOC analyses of soil samples A, A′, B, B′, D, D′, E and E′ were made as follows. The refrigerated soil sample was homogenized in the sample container and a weighed amount (10 g) was transferred to a test tube. After addition of 40 μg of the internal standard, the soil was extracted with a mixture of 10 mL of 2-propanol and 4 mL of pentane. The solvent mixture was transferred to a small separatory funnel, and the extraction was repeated with 5 mL of 2-propanol and 4 mL of pentane. The extracts were combined, and the pentane phase was isolated by extraction with deionized water. The pentane extract was washed with 2 mL of water and dried with sodium sulfate prior to gas chromatographic analyses as described above. The water content of each sample was determined on a separate aliquot of soil and VOC concentrations were expressed on a dry soil basis. The analytical detection limits (μg/g) were as follows: [MC] = 0.4, [DCA] = 0.1, [TCA] = 0.01, [TCE] = 0.004, [TOL] = 0.05, and [CB] = 0.01.

VOC analyses of samples C and C′ (both immersed in methanol) were made differently. The methanol/soil sample was mechanically shaken for 20 min and settled for 30 min, after which an aliquot of the methanol was removed and centrifuged at 3000 rpm for 5 min. A 4.0-mL sample of the methanol phase was then spiked with 40 μg of the internal standard, 2.0 mL of water and 2.0 mL of pentane were added, and the mixture was shaken. The pentane phase was removed and the extraction repeated. The two pentane extracts were combined and washed with 2 mL of deionized water and then dried with sodium sulfate prior to GC analyses as above. The VOC results were converted to a dry soil basis. The analytical detection limits (μg/mL) were as follows: [MC] = 0.1, [DCA] = 0.05, [TCA] = 0.005, [TCE] = 0.002, [TOL] = 0.04, and [CB] = 0.03.

For quality control purposes, all reagents were glass-distilled or GC grade and the sodium sulfate was heated at 550 °C overnight. All reagents were stored at 4 °C. All glassware was precleaned by washing, rinsing with deionized water, and drying overnight at 550 °C. VOC analyses of the 2-propanol and pentane revealed trace concentrations of TCA, TCE, and TOL, but no MC, DCA, or CB. These trace concentrations were near the analytical detection limits and were subtracted from all sample analyses. Soil samples collected from the control soil column by methods A, B, and C revealed no detectable concentrations of the target VOCs. Analyses of clean soil and the methanol used for infield preservation similarly yielded no detectable target VOCs. A sample of the clean soil was spiked with the target VOCs and analyses revealed the following recoveries: [MC] = 77%, [DCA] = 73%, [TCA] = 100%, [TCE] = 112%, [TOL] = 115%, and [CB] = 95%. Replicate analyses were made on ca. 50% of the soil samples, revealing negligible differences in the concentrations measured for each respective sample.

During preanalytical holding, all samples were stored at 2–4 °C. During all analyses, the samples and extracts were kept in ice baths. All samples for VOC analyses were extracted within 14 days of sample collection. GC analyses were completed within 48 h of the extractions.

Results and Discussion

Column Dynamics. The test column was initially saturated by upward flow. Then saturated upflow oc-

Table III. VOC Concentrations As Measured by Different Sampling Methods[a]

	Sampling Method[b]						
	E	A	D	B	C		
disturbance	yes	no	yes	no	yes		
headspace	low	high	low	low	low		
container	bag	glass	glass	glass	glass		model
methanol	no	no	no	no	yes	*LSD*[c]	estimate *(3)*
MC, μg/g	<0.4	1.75	6.10	4.90	7.2	6.66	24.5
DCA, μg/g	<0.1	5.15	5.15	6.70	18.72	1.14	22.6
TCA, μg/g	<0.01	0.20	0.28	0.36	1.87	0.08	6.6
TCE, μg/g	0.01	0.32	0.42	0.55	2.27	0.136	4.7
TOL, μg/g	0.06	0.37	0.39	0.49	0.70	0.062	1.7
CB, μg/g	<0.01	0.56	0.58	0.69	0.76	0.072	1.5

[a] The values shown are averages of single analyses of duplicate samples. [b] Refer to Table II for a description of each sample method. [c] LSD (95%), least significant difference at 95% confidence level.

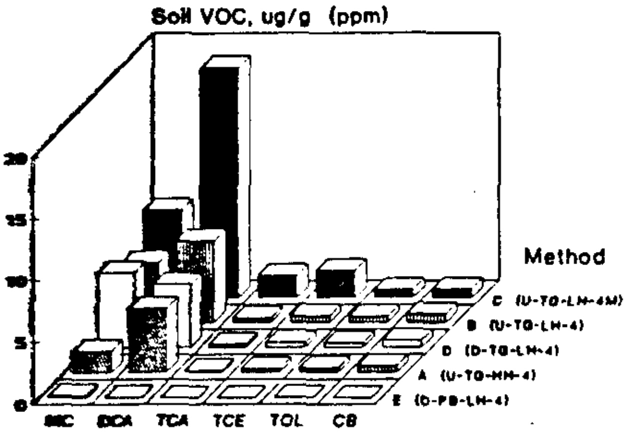

Figure 3. Average concentrations of soil VOCs as a function of sampling method. (See Table II for sampling method descriptions and Table III for numerical results.)

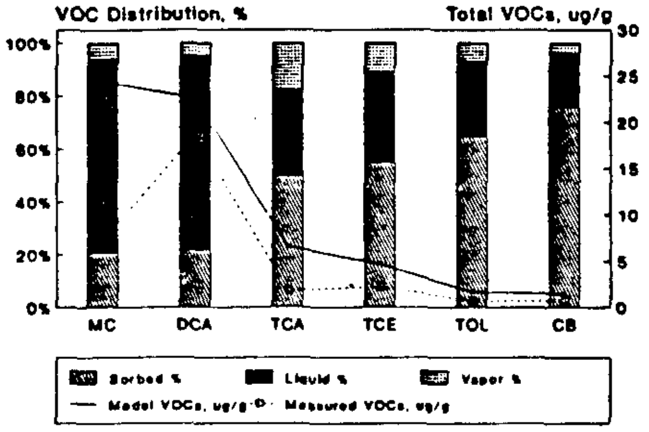

Figure 4. Model-estimated VOC concentration and phase distributic within the test column and the highest VOC concentration measure (i.e., by method C with methanol immersion).

curred over a 2.5-h period at a flux of 870 cm/day, yielding an average hydraulic retention time in the column of ca. 10.4 min. The results of the tritium tracer study indicated that the feed solution both bypassed and mixed with the soil pore water in the initially unsaturated column. For the test column, by 1.1 PVs of outflow (1.8 PVs of column feed) the outflow to inflow ratio (C_o/C_i) approached unity (0.96). The final concentrations of the target VOCs in the feed solution (mg/L) were as follows: [MC] = 157.5, [DCA] = 130, [TCA] = 16, [TCE] = 12.8, [TOL] = 4.5, and [CB] = 2.85. As predicted, there was little retardation of the target VOCs within the sandy soil under the conditions of this experiment. By three PVs of outflow, the VOC concentrations in the outflow solution were substantially similar to those in the feed solution (i.e., 84–106%).

Soil water content analyses indicated an increasing water content with depth in the test soil column, but similar results at horizontally separate spatial locations. The water content trend with depth (9.6% at 0–5 cm to 12.3% at 5–10 cm) is probably due to moisture drainage and redistribution following the contamination phase. The total organic carbon content was consistent regardless of depth or location [average 0.423% (dry weight basis); SD = 0.015%; n = 4].

Soil Sampling Method Effects. The soil samples collected by the different sampling methods yielded markedly different soil VOC concentrations (Figure 3, Table III). An analysis of variance revealed that sampling method had a significant effect on the determinations of all six VOCs. The effects were highly significant ($p >$ 99.5%) for all VOCs but MC (p = 75%). The lack of a highly significant effect for MC may have been due in part to sample replicate variability as well as the analytical difficulties often associated with quantitation of this compound.

The undisturbed soil samples collected with infield immersion in methanol (method C) consistently yielded the highest VOC concentrations. However, even these concentrations were only 28–83% of the model-estimated soil-associated concentrations at the time of sampling (Figure 4). This discrepancy may be due to some undefined negative bias due to volatilization losses during soil column exposure and sample collection. Error due to sample storage and laboratory subsampling would presumably be limited due to the methanol immersion, as would measurement error associated with irreversible sorption. Alternatively, the estimates of VOC retention may have been too high due to inaccuracies in the empirical VOC distribution relationships used or due to the absence of equilibrium conditions due to the high flux of contaminant solution. The above discrepancies illustrate the difficulties in accurately predicting soil-associated VOC concentrations, even in a relatively simple soil system.

Given that the highest concentrations measured may have deviated from the "true" value by an appreciable but unknown negative bias, it was still possible to make comparisons of the relative negative bias associated with different sampling method attributes. This was done by using the highest measured concentration as a reference (i.e., method C) and comparing sampling methods with different attributes (methanol equals method B vs C; soil disturbance equals method D vs B; headspace volume

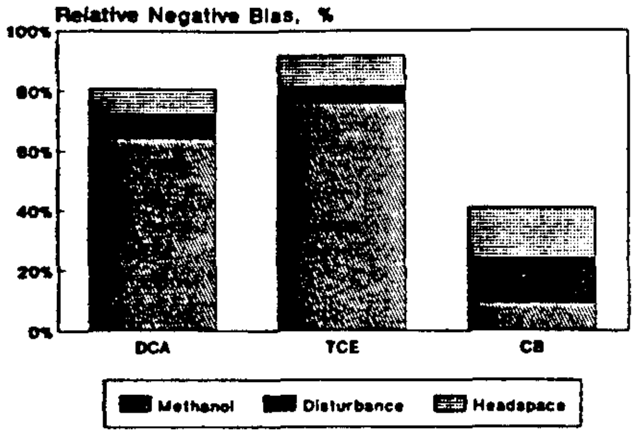

Figure 5. Relative negative bias associated with sampling method attributes. (Relative negative bias is computed with the VOC concentration in the sample immersed in methanol as a reference.)

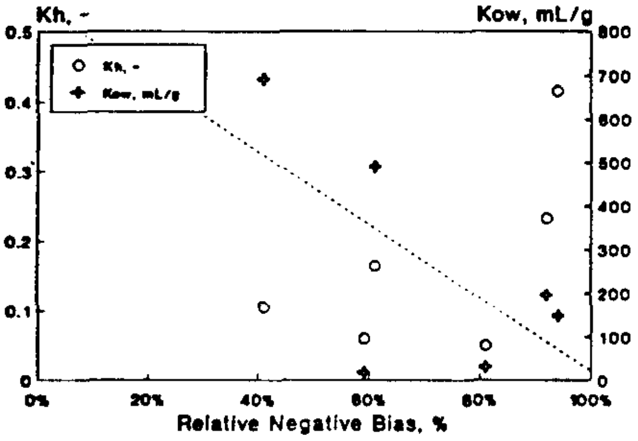

Figure 6. Relative negative bias as a function of VOC properties: Henry's law constant (K_h) and octanol/water partition coefficient (K_{ow}).

equals method A vs B; container integrity equals method E vs D). By this analysis, for soil samples containerized in Teflon-sealed glass jars, the relative bias contributions were highest for lack of infield immersion in methanol (up to 81%), followed by considerably lower contributions by headspace volume (up to 17%) and soil disturbance (up to 15%) (Figure 5). For soil samples containerized in plastic bags there was substantial relative negative bias (up to 100%). In general, sampling bias declined with increasing soil sorption affinity of the target VOC (i.e., lower Henry's constant, K_h, and higher distribution coefficient, K_d) (Figure 6). For example, the relative bias for TCA was considerably higher than that for CB.

The principal mechanism underlying the sampling method effects observed is believed to be volatilization. For all sample collection methods, there was likely some negative bias associated with column exposure and sample collection. Additional bias during storage and laboratory subsampling would be minimized in samples immediately immersed in methanol (i.e., method C). Additional negative bias in undisturbed samples containerized in Teflon-sealed glass jars without methanol (method B) was likely due to a combination of volatilization losses during storage and subsampling in the laboratory. Additional bias was caused by increasing soil disturbance and headspace volume (methods D and A), attributes that would enhance volatilization losses. The substantial negative bias associated with collection of a disturbed sample in the plastic bag (E) was probably exacerbated by sorption and vapor leakage through the polyethylene bag during preanalytical holding.

The research results indicating enhanced VOC recoveries with methanol preservation are consistent with those reportedly recently by Urban et al. based on field experience with TCE and 1,1-dichloroethene (*2*). These investigators found that VOC concentrations in soil samples collected from a standard split-spoon sampler and containerized in 40-mL VOC vials with Teflon-lined caps typically were only 20% or less of those measured in split samples immediately immersed in methanol in glass bottles with Teflon-lined caps. The research results suggesting VOC losses from samples stored in plastic bags are supported by data of Slater et al., which indicated substantial leakage of TCE through multiple polyethylene bags used to encase soil samples contained in Teflon-sealed glass vials (*11*). For all methods, transformation losses during preanalytical holding were probably low, based on recent research where good stability was observed for VOCs in water samples during holding at 4 °C for up to 28 days (*12*).

Practical Implications. It is clear that standardized procedures are needed that account for the special properties and behavior of VOCs in soils. However, procedures must also account for the difficult situations in which samples are often collected (e.g., wet/cold weather, dirty/dusty environments, high hazard locations) and the costs associated with sample collection. Ideally, standardized procedures should provide for an acceptable accuracy and precision by a sample collection process that is as workable and efficient as possible. There are a wide variety of sample collection procedures currently in routine use, others being promoted, and still others under development. These include procedures employing basic soil-sampling concepts as well as those based on more sophisticated materials and methods (e.g., specialized minicore extractors, infield containerization in special purge and trap vessels, or infield solvent immersion). Adoption of standardized procedures, particularly if they involve complicated and costly apparatus and methods, should ideally be based on scientific evidence justifying the need. The research described conducted herein has provided the following practical information toward this goal.

Collection of soil samples with containerization in plastic bags is unacceptable where analyses for VOCs are intended. Containerization in a Teflon-sealed glass jar is workable and appropriate, but decisions regarding sample disturbance, headspace volume, and infield methanol preservation appear subject to considerations associated with target VOC properties and contamination levels. For analyses of VOCs with relatively high soil sorption affinities (e.g., CB), collection of a disturbed sample with containerization in a Teflon-sealed glass jar and refrigeration at 4 °C would usually provide an accuracy similar to that of more complex methods. For such samples, equally accurate results are produced by collecting a disturbed sample and completely filling a sample container as by collecting an undisturbed sample that yields a high headspace volume in the container. For analyses of VOCs with relatively low soil sorption affinities and particularly where concentrations are anticipated in the range of a cleanup action level (e.g., TCA at ca. 1 μg/g), enhanced accuracy may require the collection of an undisturbed sample with infield immersion in methanol in a Teflon-sealed glass jar and refrigeration at 4 °C.

Conclusions

The methodology developed in this experiment appears workable and appropriate although some refinements are under consideration. In an initial experiment, the effects on soil VOC measurements of several sampling method attributes (i.e., soil disturbance, container headspace volume, container integrity, and sample preservation) were observed to be significant and to result in potentially serious systematic error or bias (up to 100%). The potential for negative bias appeared to be correlated with the soil sorption affinity of the target VOC (i.e., low K_h and high K_{ow}). Clearly, great care must be exercised when sampling soils for VOC measurements and more sophisticated sampling procedures may be required to control sampling errors, particularly with the more volatile VOCs. Further research is necessary to study other organic compounds, soil conditions, and sampling environments. This information is needed to facilitate the development and implementation of standardized sampling procedures for VOC measurements in soils.

Registry No. MC, 75-09-2; DCA, 107-06-2; TCA, 71-55-6; TCE, 79-01-6; TOL, 108-88-3; CB, 108-90-7.

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MEASUREMENT ERROR POTENTIAL AND CONTROL WHEN QUANTIFYING VOLATILE HYDROCARBON CONCENTRATIONS IN SOILS [1]

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INTRODUCTION

Due to their widespread use throughout commerce and industry, volatile hydrocarbons such as toluene, trichloroethene and 1,1,1-trichloroethane routinely appear as principal pollutants in contaminated sites throughout the U.S. and abroad. As a result, quantitative determination of soil system hydrocarbons is necessary to confirm the presence of contamination and its nature and extent; to assess site risks and the need for cleanup; to evaluate remedial technologies; and to verify the performance of a selected alternative. Decisions regarding these issues have far-reaching impacts and ideally should be based on accurate measurements of soil hydrocarbon concentrations. Unfortunately, quantification of volatile hydrocarbons in soils is extremely difficult and there is normally little understanding of the accuracy and precision of these measurements. Rather, the assumption is often implicitly made that the hydrocarbon data are sufficiently accurate for the intended purpose. This paper presents a discussion of measurement error potential when quantifying volatile hydrocarbons in soils and outlines some methods for understanding and managing these errors.

ENVIRONMENTAL MEASUREMENTS IN SOILS

Basic Concepts

Environmental measurements in soils must account for the extreme variability which characterizes a natural soil system [1-4]. Variations in natural soil properties which affect water movement and contaminant transport and fate can be substantial. Spatial variations predominate and include short-range (e.g. < 1m) and long-range effects. It is common for coefficients of variation for soil properties to vary from a few percent to several hundred percent, although 10 to 100 percent may predominate for many situations [2,3]. Temporal variations can also occur although these are less well characterized. It has long been recognized that these natural variations can lead to sampling errors which can be substantially greater than analytical errors. As early as 1944, it was acknowledged that "the limit of accuracy was determined by the sample, not by the analysis" and this remains true even today [1].

When making measurements in a contaminated soil, the process is even more complicated. Contamination incidents with unknown characteristics and transport and fate processes

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which are highly nonlinear and poorly understood, create problems and often leads to data deficiencies for normal measurement programs. In fact, it might be argued that a contaminated soil system may be so "chaotic" that accurate and precise characterization over space and time may be impossible.

It is important to explicitly define the objectives and scope of a environmental measurement program and specify the requisite type, quantity and quality of the data to be generated. According to the U.S. EPA, data quality objectives (DQOs) should be explicitly stated a priori and include the desired data accuracy, precision, representativeness, completeness and comparability [4]. Accuracy defines the bias in a measurement system while precision defines the reproducibility of measurements under set conditions. Representativeness expresses the degree to which sample data accurately and precisely define the true characteristic in question. Completeness is defined as the percentage of measurements made which are judged to be valid. Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. Common to all of the DQOs *is an understanding of the nature and magnitude of any measurement errors.* It is essential to data analysis and hypothesis testing that the measurement errors on the average be sufficiently small that they may be ignored when analyzing and interpreting measurement data (e.g. measurement error variance = <10% of total variance between measurements) [4]. Moreover, since measurement error as bias is elusive if not impossible to determine, it is often necessary to presume that it is absent.

When sampling contaminated sites, soil samples are collected according to various statistical designs (e.g. random, systematic, judgemental) under a wide variety of soil conditions (e.g. soil texture, depth, water content, temperature). The collection process may often be hindered by adverse site conditions (e.g. health and safety hazards requiring personal protective apparel and equipment). Sampling involves a wide variety of classical methods to expose the soil volume to be sampled (e.g. shovel, power auger, backhoe) and to remove and containerize a sub-sample for analysis (e.g. utensils, hand implements, thin-walled tubes). Qualitative analyses of soil sub-samples have often been made in the field by test kits while quantitative analyses of separate sub-samples have been made in an onsite or remote laboratory. Determination of measurement error variance has normally focused on laboratory operations with analyses of a wide variety of quality assurance/quality control (QA/QC) samples (e.g. spiked sample analyses, blank samples, duplicate analyses). Field operations are less well addressed with field "duplicates" (separated in space by some distance) and decontamination rinses the only common field QA/QC samples.

Volatile Hydrocarbon Measurements

Beyond the problems associated with natural soil variability and site contamination, quantitative characterization of soil volatile hydrocarbons, or VOCs are they are often called (volatile organic compounds), is complicated by the complex and highly unpredictable behaviors of these hydrocarbons [5,6]. For example, there are ca. 35 hydrocarbons categorized as VOCs in the U.S. EPA hazardous substance list (HSL). These compounds have widely different physical and chemical properties (Table 1) and in soil systems, VOCs can be present in the liquid (dissolved or non-aqueous phase), solid (sorbed) and gas (vapor) phases. The biodegradability of these compounds varies from readily degradable (e.g. toluene) to recalcitrant (e.g. tetrachloroethylene).

Quantification of soil system VOCs requires conduct of a series of tasks as illustrated in Figure 1. In practice, quantification of soil VOCs has been achieved by various means often driven by laboratory convenience, regulatory requirements or personal preferences. Materials and methods for collecting and containerizing soil samples are often similar to those used for basic sampling of soil and geologic materials. Numerous methods have been used to reach and expose the point of sampling (e.g. hand implements, backhoes, power augers, drilling rigs) as well as to remove a bulk volume to be sampled (e.g. hand utensils, push probes, thin-walled tubes, split-spoons). Methods to extract and containerize a soil sub-sample (e.g. 25 to 100 g) for later analysis have also been varied (e.g. spatulas and spoons, trowels, coring devices). Qualitative analyses of soil sub-samples have often been made in the field by hand-held detectors (e.g. photoionization or flame ionization units) while quantitative analyses of separate sub-samples been made in a remote laboratory. Analyses of the containerized soil samples are normally accomplished by removing 1 to 5 g from the field subsample and immersing this soil in water or methanol. The soil/liquid sample undergoes extraction, purge and trap concentration followed by gas chromatography or gas chromatography/mass spectrometry and up to 35 VOCs are identified and quantified. More recently, there has been increased use of field portable laboratory instruments for quantitative field analyses, often employing head-space techniques, principally to provide real-time data.

VOLATILE HYDROCARBON MEASUREMENT ERRORS

Measurement Error Potentials

Efforts to interpret and draw conclusions from soil VOC data are often frustrated by apparent data quality problems. For example, it is common for laboratory data to correlate poorly if at all with the field screening measurements made by photoionization or flame ionization detectors [8] Moreover, "duplicate" samples collected within 10 cm of each other from a given field sample (e.g. from a split-barrel sampler) can yield VOC results which vary by one or more orders of magnitude. These results are not totally surprising given the highly variable nature of contaminated soils and the multi-phase, dynamic behavior of soil VOCs. However, an alternative explanation for these types of data quality problems is that quantitative measurements of soil VOCs can be subject to serious *measurement error potential.* In the context of this discussion, measurement error potential means the tendency for a VOC measurement at a given location and time, to have a measurement error variance and/or bias which is statistically unacceptable for the purpose for which the data was collected. While practitioners have wondered about the measurement errors associated with sampling and analysis of VOCs in soils, only recently has research begun to elucidate the measurement error potential associated VOC quantification and provide guidance on improved methodologies. Highlights of some of this work are summarized in Tables 2 and 3. In addition to the work outlined in Tables 2 and 3, additional efforts are in progress by the ASTM and U.S. EPA to assess and develop new standardized procedures and/or modify existing ones.

The existing database (Tables 2 and 3), while limited, suggests that soil VOC measurements may be subject to substantial measurement error potentials when samples are collected and analyzed by classical methods. A measurement error variance (as coefficient of variation) of 10 to 100% can reasonably be expected. More important and of greater concern is the measurement error bias which can be in the range of -100% to +25%. Siegrist and Jenssen (1990) concluded that measurement error potential was strongly influenced by the phase distribution of a given VOC. Increasing error potential was correlated with increasing VOC Henry's Constant (K_h) and decreasing soil sorption affinity (K_d). These error potentials have significant implications given the vast numbers of soil VOC measurements that have been and are being made and the far-reaching decisions being reached based on an assumed acceptable data quality.

Despite the results of recent research, much uncertainty remains regarding the nature and magnitude of soil VOC measurement errors. There are a wide variety of soil and site conditions and volatile hydrocarbons yet to be studied. In addition, compilation and integration of sample collection and analytical errors is virtually impossible with the limited existing database. Research conducted to date has dealt with either the sample collection or the sample analyses components and has not integrated the error potential across the entire measurement process. Finally, potential short-range temporal and spatial variability has not been accurately characterized for soil VOCs.

Controlling Measurement Errors

Given the measurement error potential for volatile hydrocarbons in soils, effective procedures for error management and control are needed. With the current understanding of measurement errors, the greatest improvements in accuracy and precision can be made by using more rigorous materials and methods for sampling. Ideally, the measurement process should involve assessment of measurement error potential for a given sampling scenario to yield the required rigor for the measurement procedures. An example of this integration is illustrated in Table 4. It is emphasized that further work is necessary to better define the categories and factors in Table 4 and determine their significance to the measurement error management task.

At this time, two measurement approaches have been developed and shown to reduce measurement error potentials. These involve collection of undisturbed soil cores and either infield containerization in a purge and trap vessel or infield immersion in methanol. The purge and trap vessel method has the advantage of simplicity, maintaining low detection limits and not requiring field handling of chemicals. However, the sample volume analyzed is quite small (1 to 5 g) and compositing of soil samples is precluded. The methanol protocol has the advantage of increasing the sample size analyzed (thereby attenuating short-range spatial variability) and it also enables sample compositing. However, the methanol addition can increase the detection limits by a factor of 10 to 100 and requires field handling of chemicals.

In addition to more rigorous methods for sample collection and analysis, sampling designs should include more close-range sampling points (e.g. <10 cm separation) to help define short-range spatial variability and its contribution to measurement error variance identified through duplicate sample analyses. QA/QC procedures need to be developed which account for the measurement error potential of volatile hydrocarbons. In addition to field duplicate and laboratory split samples, it is recommended to include field blank and audit soil samples. The field blank samples would consist of a similar but clean soil matrix while the field audit samples would consist of the clean soil matrix spiked with a suite of compounds similar to those anticipated in the field. Both types of samples would be carried from/to the laboratory and handled similarly to the field collected soil samples. These samples would enable determination of measurement error bias.

Finally, minimizing the pre-analytical holding time and variability of holding conditions should be accomplished where measurement error potentials are high. Improved and expanded use of infield analytical instrumentation and procedures may provide great benefits here. However, the contribution of field quantitation to reducing measurement error potentials is yet to be determined.

Development and implementation of methods to control measurement error potential must recognize the limitations associated with sample collection and analysis. For example, samples are often collected under adverse field conditions where cumbersome collection procedures might be impractical, if not impossible to implement. Also, since laboratory capacity is often limited, rapid sample analyses are impossible and samples are often held for many days prior to sub-sampling and analysis.

CONCLUSIONS

Despite the sophistication and cost of sample collection and analyses, there remains substantial and significant uncertainty associated with soil VOC measurement data. Interpretation of existing VOC data must include careful analysis of sample collection, handling and analysis procedures. Early VOC characterization data may be more suspect than recent data due to recently improved sampling practices. In general, measurement error can be assumed to be significant, comprised of both simple error variance and negative bias. The measurement error potential is particularly high for the more volatile compounds with low aqueous solubilities. When prescribing procedures for VOC measurements, consideration must be given to the measurement error potential of a given measurement scenario and available measurement methodologies as well as the application of the data and the seriousness of a data-quality related incorrect decision. More rigorous methods are available and/or under development which can reduce as well as delineate measurement error variance and bias when quantifying soil VOCs. Further research is necessary to elucidate the measurement errors involved in quantifying volatile hydrocarbons in soils and to facilitate continued development and refinement of sampling and analysis methods and QA/QC procedures.

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Figure 1. Sampling process for volatile hydrocarbon measurements in contaminated soil and quantification error components.

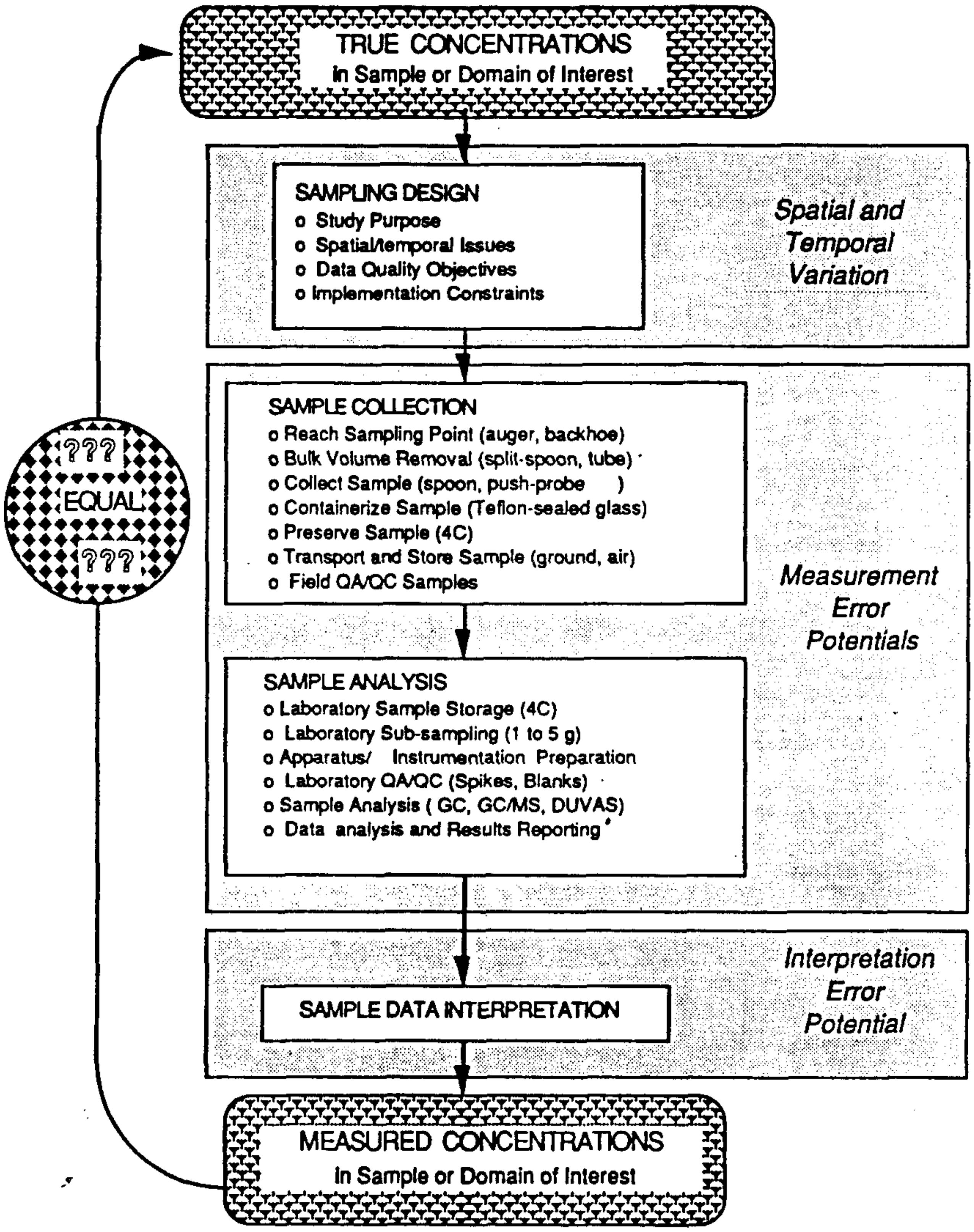

Table 1. Volatile hydrocarbons included within the Hazardous Substance List (HSL) in the USA and their occurrence at U.S. EPA Superfund Sites.

	Properties[1]				Hazardous
Compound	Molecular Weight	Boiling Point	Vapor Pressure	Aqueous Solubility	Waste Site Rank and Prevalence[2]
	g/mol	°C	mm	mg/L	
Chloromethane	51	-24	3800	4000 *	
Bromomethane	95	4.6	-	900	
Vinyl Chloride	62	-13.9	2660 (25°C)	1100 (25°C)	23 [8%]
Chloroethane	64.5	12.4	1000	5740	
Methylene Chloride	85	40	349	20000	18 [10%]
Acetone	58	56.2	270 (30°C)	Miscible	
Carbon Disulfide	76.1	46.3	260	2300 (22°C)	
1,1-Dichloroethene	97.0	31.9	500		20 [9%]
1,1-Dichloroethane	99.0	57.3	180	5500	19 [10%]
trans-1,2-Dichloroethene	97.0	48	200 (14°C)	600	17 [12%]
Chloroform	119.4	62	160	8000	6 [20%]
1,2-Dichloroethane	99.0	83.5	61	8690	25 [7%]
2-Butanone	72.1	79.6	78	353000 (10°C)	
1,1,1-Trichloroethane	133.4	71/81	100	4400	8 [17%]
Carbon Tetrachloride	153.8	76.7	90	800	27 [7%]
Vinyl Acetate	86.1	73.0	83	25000	
Bromodichloromethane	163.8	90.0			
1,2-Dichloropropane	113.0	96.8	42	2700	
trans-1,3-Dichloropropene	111.0	112	34 (25°C)	2800	
Trichloroethene	131.5	86.7	60	1100 (25°C)	1 [35%]
Dibromochloromethane	208.3	116-122			
1,1,2-Trichloroethane	133.4	113.7	19	4500	
Benzene	78.1	80.1	76	1780	5 [23%]
cis-1,3-Dichloropropene	111.0	104.0	43 (25°C)	2700	
Bromoform	252.8	149	5.6 (25°C)	3190 (30°C)	
4-Methyl-2-Pentanone	100.2	116/119	6	17000	
2-Hexanone	100.2	128	2	35000	
Tetrachloroethene	165.8	121.4	14	150 (25°C)	9 [17%]
1,1,2,2-Tetrachloroethane	167.9	146.4	5	2900	
Toluene	92.1	110.8	22	515	3 [27%]
Chlorobenzene	112.6	132	8.8	500	26 [7%]
Ethylbenzene	106.2	136.2	7	152	15 [12%]
Styrene	104.1	145.2	5	300	
m-Xylene	106.2	139	6		14 [13%]
o-/p-Xylene	106.2	144.4	5	175	*

[1] Properties are at 20°C unless another temperature is shown in ( ).

[2] Rank (highest = 1) and prevalence (% of sites) based on a total of 466 different substances found at the 888 Superfund sites (as of October 1986).

Table 2. Measurement error associated with sampling practices for soil VOCs.[1]

Study and Location	Conditions	VOCs Studied	Findings
Siegrist and Jenssen [8] Aas, Norway	Natural Sand from 0-50 cm depth Laboratory controlled contamination Samples collected with thin-walled tubes to evaluate: 1.Container 2.Disturbance 3.Headspace 4.Methanol preservation	Methylene Chloride 1,2-dichloroethane 1,1,1-trichloroethane Trichloroethene Toluene Chlorobenzene	VOCs measured = 0 to 83% of model estimate Highest VOCs in samples infield immersed in methanol Measurement coefficient variation always <66% and typically < 15% Relative negative bias of 15 to 100% (compared to highest measured value) Bias correlated with sampling method and VOC K_h and K_d VOC recoveries in matrix spikes = 57 to 125%
Urban et al. [9] Pennsylvania, USA	Silty clay- clayey silt Uncontrolled hazardous waste site Field collected samples from split-barrel samples to evaluate: 1.Conv. EPA process 2.Methanol preservation	Trichloroethene 1,1-dichloroethene	Highest VOCs in samples infield immersed in methanol Measurement coefficient variation <17% Relative negative bias compared to methanol was typically >80%. VOC recoveries in matrix spikes = 31 to 96%
Maskarinec et al. [10] Tennessee, USA	Soil spiked with mixture of VOCs Samples collected by two methods to evaluate sub-coring device and direct containerization in a purge and trap vessel	19 VOCs on U.S. EPA HSL	Negative bias varied with VOC Eliminating the laboratory sub-sampling and container transfer using direct containerization in purge and trap vessels can reduce negative bias from an average of 89% to 29%.

Table 3. Measurement error associated with sample analyses for soil VOCs (after 11).[1]

Hydrocarbon	Measurement Error Component			
	Intra-Laboratory Precision			
	Number of Duplicate Pairs	Mean Relative Standard Deviation	QC Recovery Limits	Contract Detection Limit
1,1-Dichloroethene	353	8.9 %	59 - 172 %	5 ug/kg
Trichloroethene	438	7.8 %	59 - 139 %	5 ug/kg
Chlorobenzene	432	6.7 %	60 - 133 %	5 ug/kg
Toluene	376	7.4 %	59 - 139 %	5 ug/kg
Benzene	411	7.4 %	66 - 142 %	5 ug/kg

	Inter-Laboratory Precision and Bias			
	Number	Mean Relative Standard Deviation	Bias	QC Recovery Limits
Toluene-d8	10399	13.2 %	+ 2.0 %	88 - 110 %
4-Bromofluorobenzene	10395	15.9 %	- 1.7 %	86 - 115 %
1,2-Dichloroethane-d4	10402	18.1 %	- 3.2 %	76 - 114 %

	Method Bias (Blind Sample Analyses)		
	Number	Mean Relative Standard Deviation	Bias
Chloroform	9	8.0 %	- 0.1 %
1,2-Dichloroethane	14	13.1 %	+ 11.1 %
Dibromochloromethane	9	35.0 %	- 12.0 %
Benzene	9	32.1 %	- 10.3 %
Bromoform	10	16.6 %	- 12.1 %
2-Hexanone	6	16.6 %	- 45.5 %
Toluene	10	13.8 %	+ 13.7 %
Chlorobenzene	10	21.2 %	+ 13.2 %

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[1] Data based on analyses conducted under U.S. EPA Contract Laboratory Program during Dec. 1984 and November 1985. All results based on analyses of spiked soil samples.

Table 4. Example integration of measurement error potential and measurement rigor for quantification of soil VOCs.[1]

	Relative Error Potential or Measurement Rigor [2]		
Element	Low	Moderate	High
Measurement Error Potential	VOCs of low K_h and high K_{ow} (e.g. chlorobenzene) Soils with high TOC (e.g. surface soils of various textures) Low ambient air temperatures (e.g. <10°C) Undisturbed samples can be collected easily (e.g. surface soils)	VOCs of moderate K_h and K_{ow} (e.g. toluene) Soils with low TOC but high clay content (e.g. clays) Moderate ambient air temperatures (e.g. 10-20°C) Undisturbed samples can usually be collected (e.g. shallow subsoils)	VOCs with high K_h and low K_{ow} (e.g. trichloroethene) Soils with low TOC and clay content (e.g. subsoils of clean sand) High ambient air temperatures (e.g. >20°C) Undisturbed samples are hard to collect (e.g. deep subsoils, saprolites and rock material)
Appropriate Measurement Rigor	Disturbed samples containerized in Teflon-sealed glass jars with low head-space and preserved at 4°C QA/QC requires only routine laboratory QA/QC samples and analyses	Undisturbed samples containerized in Teflon-sealed glass jars with low head-space and preserved at 4°C QA/QC requires field duplicate samples and a field audit sample is recommended along with other routine laboratory QA/QC samples and analyses	Undisturbed samples containerized infield in purge and trap devices or immersed in methanol and preserved at 4°C QA/QC requires field duplicate samples and field audit sample as well as other routine QA/QC samples and analyses

[1] Information provided in this table is for illustrative purposes only. Further research and development is needed to define the error and measurement rigor categories and the factors involved.

[2] K_h = Henry's Constant, K_{ow} = octanol/water partition coefficient, TOC = soil total organic carbon content.

MODELING POTENTIAL MIGRATION OF PETROLEUM HYDROCARBONS FROM A MIXED-WASTE DISPOSAL SITE IN THE VADOSE ZONE

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ABSTRACT

Environmental monitoring of a mixed-waste disposal site at the Idaho National Engineering Laboratory has confirmed release and migration into the vadose zone of: (1) chlorinated hydrocarbons in the vapor phase and (2) trace levels of certain transuranic elements. The finding has prompted an evaluation of the potential role of waste petroleum hydrocarbons in mediating or influencing contaminant migration from the disposal site. Disposal records indicate that a large volume of machine oil contaminated with transuranic isotopes was disposed at the site along with the chlorinated solvents and other radioactive wastes.

A multiphase flow model was used to assess the possible extent of oil and vapor movement through the 177 m thick vadose zone. One-dimensional simulations were performed to estimate the vertical distribution of the vapor phase, the aqueous phase, and immiscible free liquid as a function of time. The simulations indicate that the oil may migrate slowly through the vadose zone, to potentially significant depths. Calculated transport rates support the following ranking with regard to relative mobility: vapor phase > aqueous phase > free liquid.

INTRODUCTION

Subsurface contamination by mixtures of organic chemicals and radionuclides associated with energy-related activities has been identified as a major environmental problem (U. S. Department of Energy, 1984; 1988). Past disposal practices of mixed wastes associated with national defense programs were not subject to current environmental regulations, with the result that problems of migration of organic and radionuclide co-contaminants are arising at numerous mixed-waste disposal sites. In some cases, the remediation of mixed-waste sites is made more difficult by the synergistic effects of co-contaminant migration. A further difficulty is encountered when mixed-waste contamination occurs in variably saturated, interbedded porous and fractured media.

In the western United States, arid waste disposal sites were originally selected on the basis of climatic and hydrogeologic conditions considered best suited to the avoidance of contaminant migration. It is often more difficult to model any contaminant transport that occurs at disposal sites located in arid regions, because there is a smaller set of data for understanding co-contaminant flow and transport in areas with low recharge and thick vadose zones of variable permeabilities.

In order to effectively mitigate contamination at a mixed-waste disposal site located in an arid environment, it is necessary to develop a fundamental understanding of the hydrological and geochemical processes that affect organic co-contaminant migration, transport, and chemical reaction in the subsurface. Computer models of contaminant releases from mixed-waste sites can be used to provide insight to the processes controlling co-contaminant release and transport.

This paper presents the application of computer models to a case study of the movement of chlorinated hydrocarbon solvents, petroleum hydrocarbons, and transuranic (TRU) radionuclides from a mixed-waste disposal site located over a 177 meter thick vadose zone at the U. S. Department of Energy's Idaho National Engineering Laboratory (INEL) in southeastern Idaho. Ongoing site characterization has demonstrated that chlorinated solvents and transuranic radionuclides have migrated through the vadose zone (Laney *et al.*, 1988). The fate of the co-disposed petroleum hydrocarbons is less certain. Therefore, modeling was conducted to evaluate the relative mobility of the co-contaminants in the subsurface and to determine the possible contribution of the petroleum hydrocarbons to radionuclide migration.

The paper includes a brief description of the site hydrogeology and the nature and extent of the co-contaminant migration. The conceptual and mathematical basis for the modeling approach is presented. The paper presents results of computer simulations of petroleum hydrocarbon migration, and a discussion of the aspects of the model that warrant further evaluation.

SITE HYDROGEOLOGY

As part of past waste disposal practices at the INEL in southeastern Idaho, transuranic and low-level nuclear wastes mixed with hazardous constituents have been disposed in a shallow landfill, the Subsurface Disposal Area (SDA). The INEL is located in a shallow basin in the north-central part of the eastern Snake River Plain and the SDA is sited at the Radioactive Waste Management Complex in the southwestern corner of the INEL (Figure 1).

The INEL is underlain by Pleistocene basalt flows and intercalated sedimentary units that host the Snake River Plains aquifer. The unsaturated zone separating the SDA disposal site from the Snake River Plain aquifer is approximately 177 meters thick and basalts constitute approximately 95% of the stratigraphic section. Alluvial sediments of Holocene age occur in a band that extends across the site from northeast to southwest, and are associated with the flood plain of the Big Lost River.

The subsurface geology of the unsaturated zone at the INEL and the SDA is well-characterized as a result of data collected by the United States Geological Survey and site contractors from numerous monitoring wells on the INEL site. The SDA is located in several meters of surficial alluvium. Beneath the SDA, basalt flows range in thickness from 2 meters to 20 meters, with an average thickness of approximately eight meters (U. S. Department of Energy, 1983). The flows are interlayered with unconsolidated cinders and volcanic breccia, and fluvial, lacustrine, and aeolian sediments.

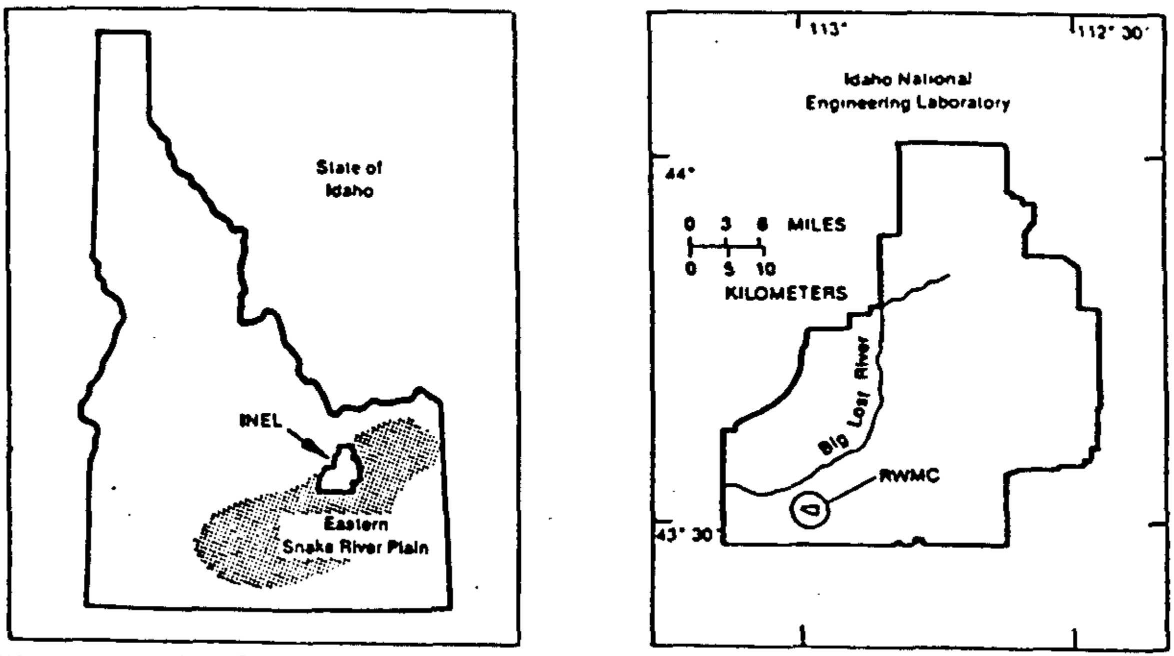

Figure 1. Location of the Radioactive Waste Management Complex at the INEL.

Two major interbeds occur beneath the SDA, at depths of 34 meters (110 ft) and 73 meters (240 ft) (U. S. Department of Energy, 1983). A discontinuous interbed at approximately 9-10 meters (30 ft) has also been identified. The clay minerals that are found in the alluvium and sediments are predominantly illite, mixed illite/smectite, and smectite, with minor kaolinite. Concentrations of organic carbon are less than 0.5 weight percent (Rightmire and Lewis, 1987). A summary of the lithology and mineralogy of the vadose zone units (alluvium, basalts, and sedimentary interbeds) is given in Rawson and Walton (1989).

Fractures in basalt are commonly filled with clay- and silt-sized phyllosilicates and caliche where the basalt was previously exposed to the surface. Several basalts are locally very highly fractured, with fracture fillings of loess that signify a long period of exposure at landsurface. Some of the fracture infilling material may have been transported into fractures by suspension in water and downward infiltration of the water through the fracture network (Rightmire and Lewis, 1987). As the water evaporates in the unsaturated zone, thin layers of clays are either deposited from suspension or precipitated from solution. Fractures and vesicles both exhibit some layering of the fracture fill material (Rightmire and Lewis, 1987).

Hydrology of the unsaturated zone at the INEL is controlled in part by the average precipitation. Precipitation on the INEL site is in the range of 13 to 36 centimeters per year, with an average of 20 cm per year (Barraclough *et al.*, 1976). Snowfall accounts for 30% of the annual precipitation. In areas of thick alluvial fill, evapotranspiration exceeds 95% of the precipitation. The average annual infiltration rate ranges from 5-10% of the precipitation.

NATURE AND EXTENT OF CONTAMINATION

The SDA consists of trenches and pits, some of which were originally excavated down to basalt. A soil buffer that ranged from 0.67 to 1 meter thick was left between the waste and the uppermost basalt flow. Between 1952 and 1970, approximately 96,300 cubic meters (3.4×10^6 ft^3) of transuranic and low-level radioactive wastes were emplaced on the soil buffer and covered with a soil cap. Further burial of transuranic waste was prohibited by regulation in 1970, but disposal of low-level waste has continued until present.

Surface and subsurface environmental monitoring for radionuclides at the SDA has been conducted since the 1960s. Recently, monitoring for the migration of transuranic radionuclides established the presence of environmental concentrations of plutonium and americium (activities up to picocuries/gm) at a depth of 34 m below land surface (Laney *et al.*, 1988). The contaminant migration problem was exacerbated by the discovery of elevated levels of hazardous volatile organic compounds (VOCs) in the Snake River Plain aquifer beneath the SDA in 1987 (Mann and Knobel, 1987). Corrective action required by the Resource Conservation and Recovery Act (RCRA) has been implemented at the site (EG&G, 1988).

Although detectable quantities of carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, and chloroform were measured in monitoring wells in the aquifer in 1987, the concentrations of all but one of the contaminants were below the maximum EPA allowable concentration of 5µg/l. Carbon tetrachloride concentrations in a single sample were above allowable levels (6.6µg/l) during only one sampling period (Mann and Knobel, 1987).

Maximum concentrations of VOCs detected by aquifer sampling, and soil gas surveys of the surface alluvium and deep borehole gases are shown in Table 1. The most extensive contamination is related to vapor plumes of carbon tetrachloride, trichloroethylene, chloroform, 1,1,1-trichloroethane, and tetrachloroethylene in the vadose zone (EG&G, 1988). Partitioning of VOCs from a vapor into the perched water and the aquifer is assumed responsible for the indicated aqueous concentrations.

The RCRA corrective action prompted by release of hazardous VOCs into the vadose zone at the SDA included an effort to establish a complete inventory of the hazardous materials that were disposed at the site. Disposal records indicate that approximately 334,000 liters (88,400 gallons) of TRU- contaminated, mixed-waste sludges from a national defense plant were disposed in several pits and trenches at the SDA between 1966 and 1970 (EG&G, 1988). Prior to disposal, the wastes were absorbed on calcium silicate and emplaced in 208 liter (55 gallon) steel drums that were subsequently sealed. An additional 89,000 liters (23,400 gallons) of oil contaminated by unidentified radionuclides were also disposed at the SDA.

The defense plant sludges consisted of mixtures of a light machine oil and various chlorinated solvents contaminated with transuranic radionuclides. According to disposal records, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane comprised the bulk of solvents disposed during 1966-1970(Laney *et al.*, 1988). The generator of the defense plant sludges provided information indicating that the lathe coolant used in foundry operations consisted of 60% machine oil and 40% carbon tetrachloride (EG&G, 1988). As much as 148,000 liters of machine oil were disposed, bringing the total volume of disposed petroleum hydrocarbons to approximately 237,000 liters.

Transuranic radioactivity, hazardous organic wastes, and petroleum hydrocarbons are assumed to be co-contaminants, because a significant volume of the organic sludges from the defense plant was used in plutonium foundry operations and component fabrication (EG&G, 1988). The chemical form of the plutonium used in foundry operations and component fabrication is assumed to be plutonium metal, based on the unclassified information discussed by Baldwin and Navratil (1983). The plutonium recovery operations at the defense plant involved purification of the metal and impure

TABLE 1. MAXIMUM CONCENTRATIONS FOR VOCs RELEASED FROM SDA[1]

VOLATILE ORGANIC COMPOUNDS	VADOSE ZONE SOIL GAS (mg/M^3)	VADOSE ZONE BOREHOLE GAS (mg/M^3)	VADOSE ZONE PERCHED WATER (µg/L)	SNAKE RIVER PLAIN AQUIFER (µg/L)
Carbon tetrachloride	1400	1000	1200	6.6
Chloroform	ND[2]	230	650	1.0
Trichloroethylene	690	380	860	1.4
Tetrachloroethylene	40	62	110	<3.0
1,1,1-Trichloroethane	310	120	140	0.9
Dichloroethane	NA[2]	3	13	<3.0

[1] Data from EG&G, 1988.

[2] ND = not detected. Analytical interference with carbon tetrachloride. NA = not analyzed

plutonium oxides (Baldwin and Navratil, 1983). The plutonium associated with the organic sludges is assumed to have initially been physically entrained in the sludge as small particles from foundry operations. Contaminated acids and solvents from the plutonium recovery operations may also contain lesser amounts of particulate plutonium in the oxide form.

Of the radionuclides disposed at the SDA, detectable quantities of plutonium-238, plutonium-239+240, americium-241, strontium-90, cesium-137, cobalt-60, and europium-154 have been reported from surficial sediments (Laney *et al.*, 1988). Plutonium-238, plutonium-239+240, and americium-241 have also been detected in the 34m interbed (Laney *et al.*, 1988). The mode of radionuclide transport is currently being investigated as part of an ongoing study of the SDA subsurface (Rawson *et al.*, 1989).

A conceptual model for the release of VOCs was developed to describe the evolution of the soil gas plumes and the subsequent aquifer contamination (Baca *et al.*, 1988; Walton *et al.*, 1989b). Processes considered in the model of VOC migration include aqueous flow, vapor transport by gaseous diffusion, and nonaqueous fluid phase flow. The observed migration of VOCs was modeled previously using one and two dimensional flow and transport codes to describe vapor generation and transport (Walton *et al.*, 1989b; Baca *et al.*, 1988). The models of VOC migration indicate vapor transport is the predominant mode for chlorinated solvent transport.

Likewise a similar model for the migration of the radionuclides in the unsaturated zone was developed, and preliminary calculations on aqueous flow and solute transport were performed using a three-dimensional flow and transport code (Walton *et al.*, 1989a). The majority of transuranic radionuclides are assumed to migrate as colloids that undergo no retardation during transport (Rawson *et al.*, 1989).

To evaluate the possible role of the machine oil in the migration of both VOC contaminants and radionuclides from the SDA, the primary mechanism for petroleum hydrocarbon migration must be established. The remainder of the paper reports results of modeling oil flow in the unsaturated zone at the SDA.

MODELING PROCESS

The possible extent of migration of the machine oil relative to the other contaminants has been evaluated by the application of a model for multiphase flow and transport, described below. A systematic approach was applied in all the modeling studies that were used to evaluate the relative mobility of the co-contaminants in the subsurface. The approach is summarized below:

1. Determine the key physical and chemical properties of the organic and radionuclide contaminants
2. Develop a conceptual framework to describe the controlling processes and driving forces
3. Formulate mathematical models for vapor generation and transport, aqueous flow and transport, and multiphase fluid flow and transport
4. Implement the mathematical models with general computer codes
5. Check the transport model predictions using available data for organic and radionuclide contaminants
6. Predict the fate of the co-disposed machine oil
7. Evaluate the relative rates of contaminant migration

Because models of VOC vapor transport and radionuclide aqueous transport have been previously presented (Baca *et al.*, 1988; Walton *et al.*, 1989b), the modeling process as applied to the petroleum hydrocarbon migration is the only facet of the modeling effort discussed here.

Physical and Chemical Properties of Machine Oil

The key physical and chemical properties of the machine oil were developed as part of the current study. Characterization of the oil disposed between 1966 and 1970 has involved certain assumptions due to the difficulty in obtaining detailed compositional information on any machine oil. Most lubricating oil fractions contain normal alkanes (n-alkanes) in the range of C_{22}-C_{40}, as well as a wide range of branched alkanes, cycloalkanes, and mono- and polynuclear aromatics (Kinghorn, 1983). The most common cycloalkanes or napthenes in lubricating oil consist of one to five rings of carbon. The aromatics are primarily of the fused-ring type, with phenanthrene derivatives more common than anthracene-based compounds (Kinghorn, 1983).

Heteroatomic compounds containing nitrogen, sulphur, and oxygen are more prevalent in lubricating oils, and are also more reactive. Usually it is the medium chain length alkanes that impart the lubricating properties while the cyclic compounds are detrimental to these properties. Only n-alkanes have been isolated as pure compounds from the lubricating oil fraction, although many compound types have been identified by mass spectrometry (Kinghorn, 1983).

The machine oil used at the defense plant was a mixture of several base oils that were either solvent-dewaxed, paraffinic oils or napthenic oils. Because 32- to 68-weight oils are used in current machining operations at the defense plant, the oil used between 1966-1970 was assumed to fall in this category. The manufacturer of the machine oil was unable to provide information on the proportion of paraffinic to napthenic oils used to generate the machine oil produced in the late 1960s, so general chemical characteristics were estimated from data on machine oil currently in use. The hydrocarbon compounds in machine oil are assumed to be approximately 64-70% paraffinic hydrocarbons (mostly branched), 21-29% napthenic hydrocarbons, and 8-9% aromatic hydrocarbons.

A 68-weight oil has a kinematic viscosity of 64.5 cSt at 40°C and one of 489 cSt at 10°C. The kinematic viscosity of 32-weight oil at 40°C is 30.5 and at 10°C is approximately 230 cSt. Data for the 32 weight oil were used in simulations to ensure the most conservative case was modeled.

Conceptual and Mathematical Models

The conceptual model of petroleum hydrocarbon migration in the unsaturated zone considered multiphase transport. The co-contaminants were modeled as coexisting immiscible liquids and a vapor phase. The process chosen for simulation was the simultaneous movement of water, machine oil, and air in the SDA unsaturated zone.

The computer code MOFAT developed by Parker and Kaluarachchi (1989) was used in the oil migration simulations. MOFAT is a two-dimensional, multiphase Galerkin finite element code. The code is implemented on the INEL Cray and on a SUN Workstation. The non-linear nature of the governing equations extracts a high cost in computer resources for the simulations.

The continuity equations for multiphase flow are:

$$\Phi \frac{\partial \rho_w S_w}{\partial t} = \frac{\partial}{\partial x} \rho_w K_{wx} \left(\frac{\partial}{\partial x} h_w \right) + \frac{\partial}{\partial z} \rho_w K_{wz} \left(\frac{\partial}{\partial z} h_w + \rho_{rw} \right) \tag{1}$$

$$\Phi \frac{\partial \rho_o S_o}{\partial t} = \frac{\partial}{\partial x} \rho_o K_{ox} \left(\frac{\partial}{\partial x} h_o \right) + \frac{\partial}{\partial z} \rho_o K_{oz} \left(\frac{\partial}{\partial z} h_o + \rho_{ro} \right) \tag{2}$$

$$\Phi \frac{\partial \rho_a S_a}{\partial t} = \frac{\partial}{\partial x} \rho_a K_{ax} \left(\frac{\partial}{\partial x} h_a \right) + \frac{\partial}{\partial z} \rho_a K_{az} \left(\frac{\partial}{\partial z} h_a + \rho_{ra} \right) \tag{3}$$

where:
K = fluid conductivity
ρ = density
S = fluid saturation
Φ = porosity
t = time

h = fluid pressure head $= P/\rho_w g$
<u>*subscripts*</u>
w, o, a = water, oil, air
r = reference

The gas phase has a much lower viscosity than the two immiscible liquid phases. For this reason pressure gradients in the gas phase will generally be low and can frequently be ignored when calculating migration of the liquid phases. Elimination of the gas flow equation is referred to as the Richards approximation.

When several fluids coexist in a porous medium, the fluids become arranged in the pores according to wettability for the solid phase. The fluid with preferential wettability will occupy the smallest pores and the fluid with least wettability will occupy the largest pores. In the water/oil/air system, the water occupies the smallest pores and the air occupies the largest pores. The oil phase occupies pores of intermediate dimension. The relationship between the three components is illustrated in Figure 2.

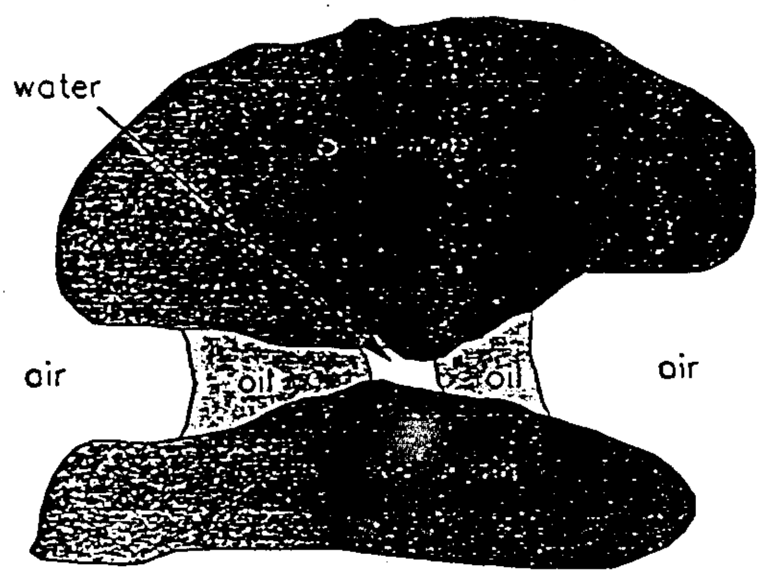

Figure 2. Arrangement of water, oil, and air phases in soil pores.

In the governing equations (Equations 1-3), the liquid saturation (S) and the fluid conductivity (K) are dependent upon the relative amounts of water, oil, and air in the pores. Constitutive relations for the multiphase system were derived using the van Genuchten (1980) model, where the saturation versus pressure head relation for an air-water system is:

$$\bar{S}_w = (1+(\alpha h_{aw})^n)^{-m} \qquad m = 1-\frac{1}{n} \qquad \text{for} \quad h_{aw} > 0 \qquad (4)$$

$$\bar{S}_w = 1 \qquad \text{for} \quad h_{aw} \leq 0$$

where:

$$\bar{S}_w = \frac{S_w - S_m}{1 - S_m}$$

S_m = residual water saturation

When modeling a multiphase system, it is assumed that the relation given in Equation 4 represents a pore size distribution of the medium which is fluid-independent. This assumption allows the relation to be generalized to a three-phase system.

$$\bar{S}_w(\beta_{ow} h_{ow}) = \bar{S}_w(h_{aw}) \qquad \bar{S}_t(\beta_{ao} h_{ao}) = \bar{S}_w(h_{aw}) \qquad (5), (6)$$

$$\beta_{ao} = \sigma_{aw}/\sigma_{ao} \qquad \beta_{ow} = \sigma_{aw}/\sigma_{ow} \qquad (7), (8)$$

$$h_{ao} = h_a - h_o \qquad h_{ow} = h_o - h_w \qquad h_{aw} = h_a - h_w \qquad (9), (10), (11)$$

The relative permeability of each phase is also a function of the amounts of each phase present. Relative permeability is estimated using the Mualem (1976) integral. These integrals are evaluated analytically using the van Genuchten (1980) expressions giving explicit relations between saturation and relative fluid conductivity.

The source of contaminants must be characterized as input to the model. A total of 237 cubic meters of TRU-contaminated machine oil and unspecified oils in absorbents were estimated to have been disposed at the RWMC. The total area of the disposal pits is approximately 30,000 square meters. Assuming oils were disposed as free liquids, an average oil depth in the pits of 0.75 cm can be calculated from these data. For disposal, the oils were solidified by addition of calcium silicate; however, no credit is given in the modeling for this solidification.

Since the distribution of the oil is unlikely to be uniform, greater amounts are expected to be present in some areas. The simulations performed as part of this study assumed the availability of up to 15 cm of oil in the pits.

Information concerning the viscosity of machine oil was obtained from the manufacturer as described above. In the interest of conservatism, the behavior of 32 weight machine oil is simulated in the analysis. The ratio of oil/water viscosity is then approximately 150. Heavier oils will migrate more slowly than the oils modeled in this example. B_{ow} (Eq. 8) was assumed equal to 2.25.

TABLE 2. HYDROLOGIC PROPERTIES USED IN SIMULATIONS

LAYER	SATURATED HYDRAULIC CONDUCTIVITY	VAN GENUCHTEN α (Eq. 4)	VAN GENUCHTEN n (Eq. 4)	RESIDUAL SATURATION (Eq. 4)	POROSITY
Sedimentary interbeds	25 cm/hr	0.0108	1.38	0.06	0.476
Basalts	5 cm/hr	0.161	2.11	0.062	0.28

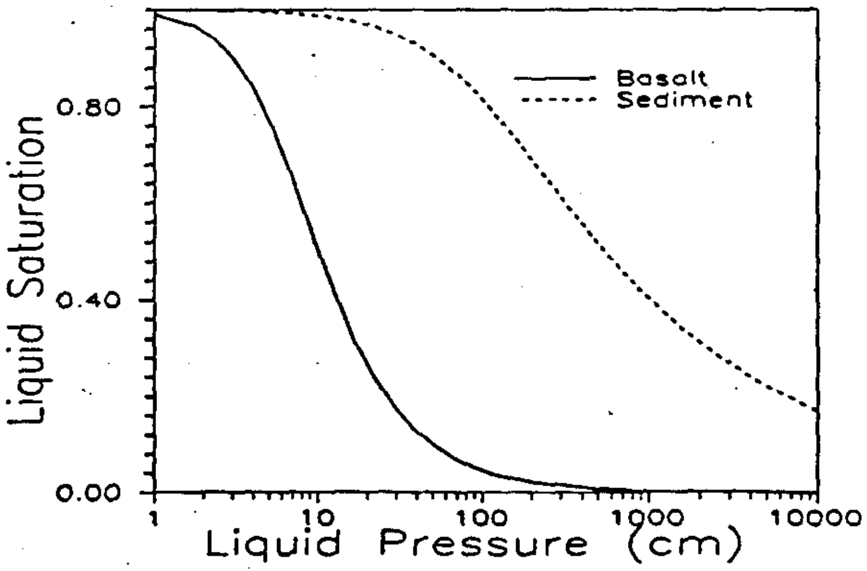

Figure 3. Relationship between liquid saturation and liquid pressure. Note the large differences between the basalt and sedimentary materials.

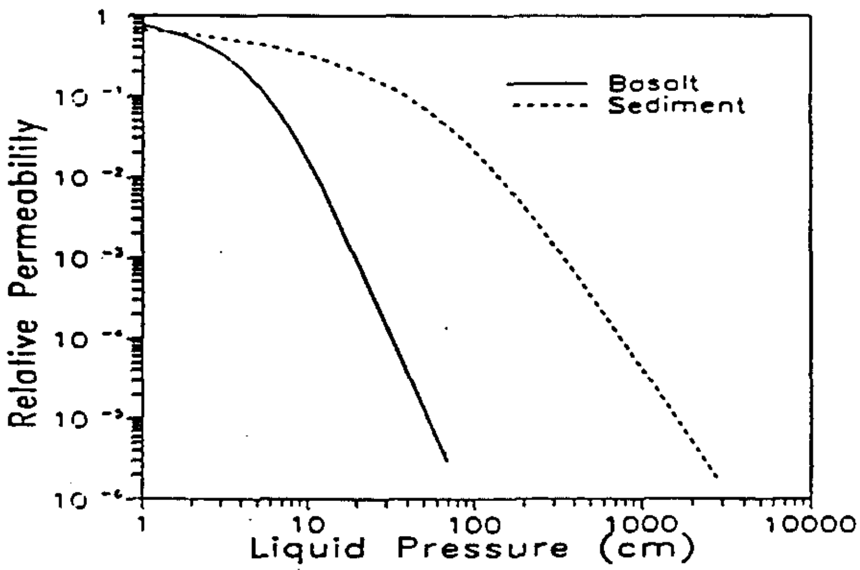

Figure 4. Relationship between relative permeability and liquid pressure.

Additional model inputs include the hydrologic properties of the sediments and basalts that control the amount of water and oil that will infiltrate the SDA unsaturated zone. The material properties assumed for the sedimentary materials and basalts from the SDA unsaturated zone are given in Table 2 and Figures 3-4. The properties for basalt are modeled as a combination of fractured and porous media. Fracture properties are derived from fracture properties for tuff (Wang and Narasimhan, 1985), and porous properties for basalt matrix were determined by TerraTek on basalt sample RWMC-1 collected from beneath the SDA. Fracture porosity was assumed to be 5% and matrix porosity was 23%. The final curve represents a summation of matrix and fracture properties. A linear interpolation was used to estimate matrix properties for low suctions. Note that the residual saturation for each lithology was calculated from Equation 4.

The model domain was broken into 158 finite elements with 318 nodes making a one-dimensional simulation. The medium was modelled as two discrete layers. The sediments were assumed to cover the basalt to a depth of 5 meters. The grid spacing was nonuniform with a greater concentration of elements near the sediment/basalt interface where numerical problems are greatest.

RESULTS OF SIMULATIONS

The simulation of oil migration was performed for a period of 10, 20, and 30 years. Net percolation of water through the pits was assumed to be 5 cm/yr, with 15 cm of total oil available for transport. The results of the simulations are shown in Figures 5 - 7.

In Figure 5, oil pressure head is plotted as a function of depth into the subsurface for times of 10, 20, and 30 years. Starting from initial conditions as a 15 cm layer within the pit, the oil moves downward as a front under a positive pressure head. The front advance appears to slow once the oil has entered the basalt, but the simulation suggests that the machine oil could penetrate 1-2 meters into the basalt in a 30 year time frame.

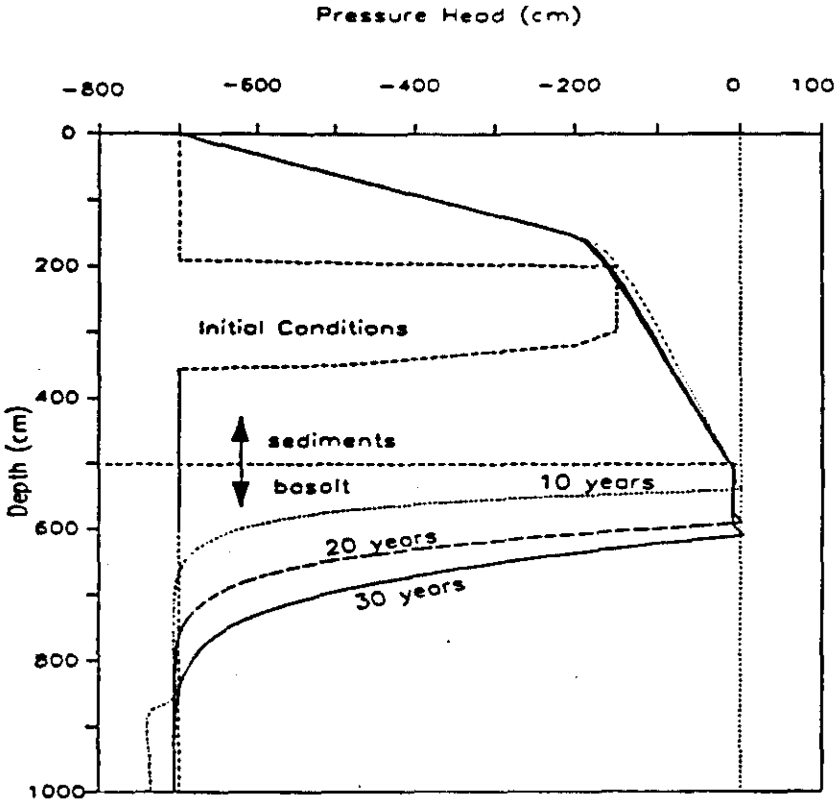

Figure 5. Simulated oil pressure head as a function of time and distance. The oil is predicted to move through the basalts as a front under positive pressure.

Figure 6 depicts the degree of oil saturation as a function of depth for times of 10, 20, and 30 years. Again, the oil phase moves downward as a front near total saturation. A residual saturation of up to 10% oil is left behind in the unsaturated sediments after 10 years, but is reduced below 6% after 30 years. This result is comparable to residual saturation values obtained experimentally for other organic liquids migrating in the unsaturated zone (Wilson *et al.*, 1988) The residual oil saturation in the basalt ranges from 20% at 10 years to approximately 10% after 30 years and is expected to further decrease over time. The oil front at near-saturated conditions penetrated over 1 meter into the basalt over 30 years.

Figure 7 shows the simulated degree of total saturation (machine oil plus water) as a function of depth for times of 10, 20, and 30 years. The oil front moves downward as a front, as was shown in Figure 6. An interesting effect is the development of capillary perching of water at the interface between the sediment and the basalt. Residual saturations of water plus oil in the unsaturated sediments were approximately 70% at the base of the pits after 10, 20, and 30 years, and increased to approximately 95% at the interface between the surface soil and the basalt. Total residual saturation left behind the oil fronts in the basalt varied from approximately 20-35%.

DISCUSSION

The results of the numerical simulations suggest that the potential for a significant amount of petroleum hydrocarbon migration exists at the SDA. The amount of machine oil that actually migrates in the system is currently unknown and

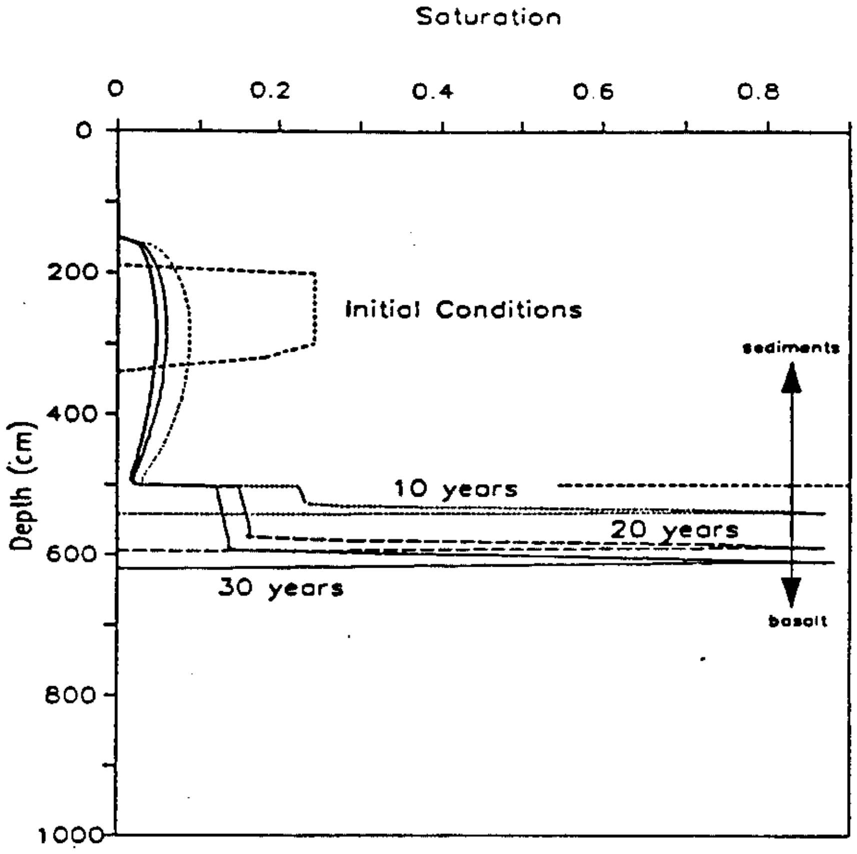

Figure 6. Simulated oil saturation as a function of time and distance. The oil moves through the basalts as a front near saturation. Lower amounts of oil, which drain more slowly, are left behind the advancing oil front.

simulations conducted to date do not account in any way for the chemical degradation of the oils. However, the simulations performed as part of this study indicate that oil could have moved from the pits within a 10 year time frame.

The machine oil is predicted to migrate as a front that will have moved approximately four meters from the base of the pits in 30 years after disposal. If the VOCs are associated with the oil by cosolvency, the migration distance is still too low to account for the observed extent of migration of the VOCs through the vadose zone to the aquifer. Likewise if the machine oil has moved as predicted, it is not responsible for the presence of transuranic radionuclides in the 34m interbed.

It is considered unlikely that movement of the petroleum hydrocarbons has had any significant impact on the extent of migration of the VOCs or the radionuclides. The presence of the oil affects the VOCs by increasing their residence time, by cosolvency, in the source area. However, the predicted migration of machine oil from the pits changes the residence time of VOCs in the source area only slightly from original predictions. The migration of VOCs is still best explained by diffusion in the vapor phase. The earlier modeling studies indicate that the VOCs reached the aquifer within 10 years of release from containment in the pits (Baca *et al.*, 1988; Walton *et al.*, 1989b).

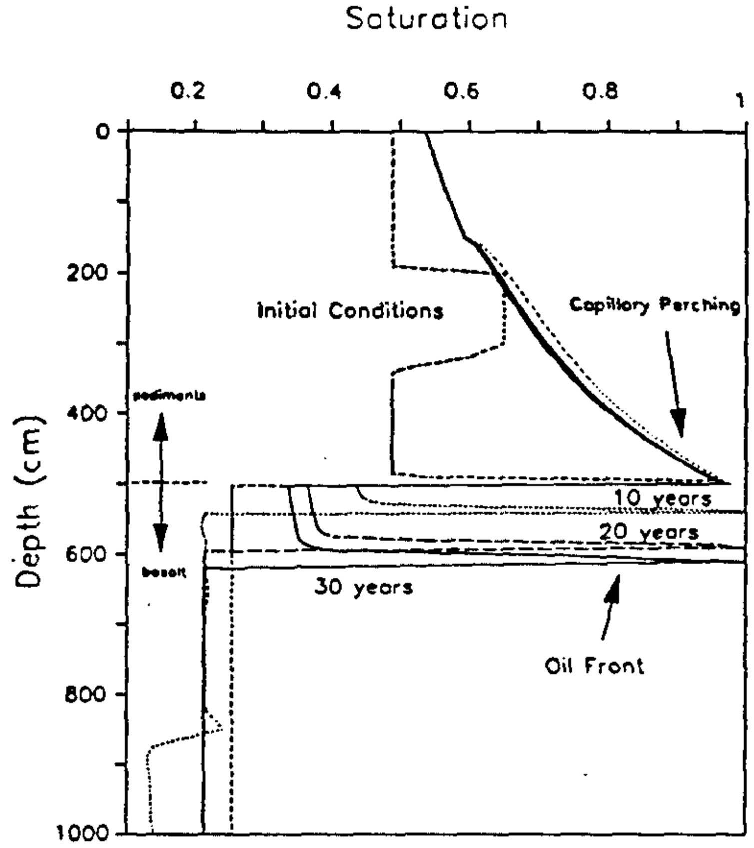

Figure 7. Simulated total saturation (oil + water) as a function of time and distance. Note the capillary perching of water in the sediments just above the basalt.

Entrained radionuclides will migrate with the machine oil. The issue of most concern regarding the interaction of radionuclides with the petroleum hydrocarbons is the possibility of radiolytical degradation of oil contributing to complexation of radionuclides in a form soluble in the aqueous phase (Rawson and Walton, 1989). Studies are ongoing to assure that solubilization of plutonium by organic degradation products of the machine oil is not occurring.

Because any oil that has migrated into the basalts will likely contain entrained radionuclides, the potential exists for introducing a significant residual radionuclide source term to the vadose zone. While the predicted migration distance of radionuclides associated with the oil is insignificant in relation to distance to the groundwater table, such a source term could prove difficult to remediate due to the difficulty of applying current technologies to basalt.

An ongoing field investigation is being conducted at the site, and it is planned to obtain samples from the soil buffer that exists beneath the base of the pits. Any samples taken beneath the waste pits will be analyzed for the presence of petroleum hydrocarbons to determine if the simulated migration of oil is actually occurring. Further study of the effect of microbial and radiolytic degradation of oil is underway to evaluate remedial actions should the predicted migration of petroleum hydrocarbons be confirmed.

ACKNOWLEDGEMENTS

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BIOGRAPHICAL SKETCHES:

Shirley A. Rawson is a Senior Scientist at the Idaho National Engineering Laboratory (INEL). Dr. Rawson has a Ph. D. in Geology, with specialization in geochemistry, from the University of Oregon. Her research includes geochemical aspects of nuclear and hazardous waste disposal and experimental and modeling studies of radionuclide and metal solubility and sorption as related to solute transport. She has published studies on chemical reaction and mass transfer in water-rock systems.

John C. Walton is a Senior Scientist at the INEL. Mr. Walton holds M.S. degrees in Environmental Science from the University of Virginia, and Chemical Engineering from the University of Washington. His research is in the areas of contaminant transport, multiphase fluid flow, performance assessment, and corrosion studies. He has publications in the areas of hazardous waste, nuclear waste, and corrosion.

Robert G. Baca is the Technical Leader for Fluid and Contaminant Transport modeling at the INEL. Mr. Baca holds an M.S. degree in Mechanical Engineering from Washington State University and an M.S. degree in Nuclear Engineering from the University of Washington. His expertise includes development and application of computer models to problems of hazardous and nuclear waste disposal. He has published numerous papers on hydrological and environmental modeling.

ATTACHMENT B

90-R05-012

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
P. O. BOX 1198
ADA, OKLAHOMA 74820

January 9, 1991

SUBJECT: Review of SOW for Operation of Soil Venting at Hagen Farm

FROM: Dom DiGiulio,
Applications and Assistance Branch

TO: Jae Lee, RPM
U.S. EPA - Region V
Chicago, IL

THRU: Jerry Thornhill, Deputy Chief
Applications and Assistance Branch

As requested, I have reviewed the proposed Scope of Work for Remedial Design at the Hagen Farm Site and comments by the potentially responsible parties (PRPs). My comments are as follows:

1.0 Cleanup Standard

I agree with the PRPs that a cleanup standard based on mass removal is for all practical purposes infeasible. The PRPs expressed concern on the difficulty of sampling and analyzing landfill waste material. Another concern is the ability in general to accurately determine contaminant mass at a hazardous waste site. Subsurface conditions, especially contaminant concentration, is often so spatially variable that a very large number of samples would be required to determine contaminant mass with any degree of certainty.

The PRPs propose as an alternative to base remediation on a 90% reduction of initial offgas total volatile organic compound (VOC) concentration. I suggest that remediation be based on static (i.e., soil venting system not operating) vapor concentrations of individual constituents. Static vapor measurements are more indicative of the presence and location of contaminant mass in soils. Offgas measurements represent averaged gaseous concentration levels from extraction wells drawing air from large volumes of soil. Offgas levels represent integrated volumes rather than discrete areas of soil or waste contamination. Also, offgas measurements do not adequately account for air phase VOC re-equilibration observed under static conditions. Vapor phase re-equilibration is thought to be primarily caused by diffusion of VOCs from less permeable to more permeable areas. In regard to monitoring total VOC concentration as an indication of remediation, I suggest monitoring individual constituents. Risk is based on the carcinogenicity or toxicity of individual compounds, thus performance should also be based on individual constituents. I recommend that remediation be based on static levels of individual constituents at concentrations indicative of acceptable soil-water levels. Published values for Henry's Constants and soil-water partition coefficients based on organic carbon content can be used to evaluate soil-gas levels indicative of acceptable soil-water concentrations. Acceptable soil-water concentrations can be determined using appropriate vadose zone modeling or if soils are excessively heterogeneous (waste) by using a simple water balance method.

2.0 Pilot Scale Test

Objective identified in the SOW for the pilot scale test include determining efficient design parameters for full-scale venting implementation and evaluation of soils cleanup standard. I agree that pilot testing should determine the initial number of extraction/injection wells, well spacing, and pumping rates. A pneumatic pump test could be conducted to determine air permeability under steady state conditions. The PRPs state that a short term field test will not predict the long-term effectiveness of a vacuum extraction system. I agree with this conclusion but add that, if properly designed, a long term (3 to 6 months) pilot test could determine the feasibility of meeting proposed cleanup standards. In conducting a field test to evaluate long term effectiveness, a small area of the site could be isolated through the use of passive inlet wells and air exchange maximized (i.e. high soil-gas velocity). Within a relatively short period of time (weeks to months) the system would be driven to diffusion limited transport which in effect determines remediation time.

3.0 Venting Enhancement

The SOW states that during the first 6 months of full-scale operation, the PRPs shall examine the feasibility of enhancing microbial degradation. The PRPs state that the effectiveness of bioenhancement can be determined by having the system operational long enough to evaluate the system's capability. I suggest evaluating the feasibility of bioventing during pilot testing. Pilot testing on bioventing have been completed at a number of sites by Battelle. Procedures used by Battelle can easily be adapted for the Hagen Farm site.

Summary

1. Base remediation standards on static vapor concentration of individual constituents and at levels indicative of acceptable soil-water concentrations.
2. Conduct pneumatic testing at steady-state conditions to determine venting design parameters.
3. If long term evaluation of venting effectiveness is required, conduct a long-term field test by isolating a small area of the site and maximizing air exchange.
4. Evaluate enhanced biodegradation via venting during pilot testing.

cc: Dick Scalf, RSKERL
Rich Steimle, OS-110
Doug Yeskis, Region V