Transport Model Parameter Sensitivity for Soil Cleanup Level Determinations Using SESOIL and AT123D in the Context of the California Leaking Underground Fuel Tank Field Manual

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ABSTRACT: The California Leaking Underground Fuel Tank Field Manual (LUFT Manual; WRCB, 1989) is used by the regulatory community, consultants, and industry in California to determine acceptable cleanup concentration goals for the remediation of hydrocarbon-affected soils. The LUFT methodology is a semiquanitative approach that uses rating tables that consider the effects of local precipitation and the depth to ground water from the deepest affected soils, as well as anthropogenic and geologic factors. The latter factors are evaluated subjectively, with only the effects of local precipitation and depth to ground water accounted for quantitatively. To assess the effects of these variables on the hydrocarbon concentrations that could be left in soil while protecting ground water quality, the state of California performed modeling using SESOIL and AT123D. The results from a small number of simulations covering a very narrow range of input parameter values were then extrapolated to form the LUFT Manual rating tables, which cover ranges in precipitation and depth to ground water of 0 to 40 in. per year and 5 to 150 ft, respectively. Although the use of these tables generally results in conservative cleanup level determinations, the extrapolation method used and the lack of consideration for extremely sensitive input parameters (other than precipitation and depth to ground water) in the development of the tables calls into question their validity. A sensitivity analysis on the model input parameters is presented that highlights several critical input parameters that greatly affect cleanup concentration determinations. The sensitivity analysis shows that certain parameters that were fixed at conservative levels for the development of the LUFT Manual rating tables (e.g., biodegradation rate and soil organic carbon content) are more sensitive than precipitation and the depth to ground water. In many cases, site-specific analysis will thus yield higher soil cleanup concentrations that are still protective of water quality. In addition, in some instances the cleanup concentrations in the LUFT Manual tables are not protective of water quality. To provide a firm basis for soil cleanup-level determinations, site-specific analysis is recommended whenever significant quantities of soil may require remediation. This will provide more cost-effective remediation and greater assurance of water quality protection.

KEY WORDS: cleanup level determinations, site-specific analysis, transport modeling, LUFT Manual, Total Petroleum Hydrocarbons (TPH), and benzene.

I. **INTRODUCTION**

The California Leaking Underground Fuel Tank Field Manual (LUFT Manual; WRCB, 1989) provides guidance on procedures to address environmental concern for water quality protection from gasoline or diesel leaks. Various tables and decision matrices were developed to simplify the risk analyses needed to determine (1) if a leak poses a health risk significant enough to require remedial evaluation and (2) the soil cleanup concentrations for benzene, toluene, xylene, and ethyl-benzene (BTXE).

The LUFT Manual tables were intended to approximate many complex phe-nomena that occur during the transport of diesel and gasoline. Petroleum and refined petroleum products (oils) are mixtures of petroleum hydrocarbons that vary widely in their individual properties. The subsurface transport behavior of petroleum hydrocarbons is dependent on the overall properties of the given mix-ture, as well as the properties of the soil matrix and the movement of soil water and gas surrounding the oil. Following a terrestrial oil spill, the oil mixture moves through the subsurface under the influences of gravity and capillarity until the oil is distributed in static or near-static mechanical equilibrium. After a static distribution has developed, the oil moves little as a bulk fluid, but the mobile components of the oil are transported away from the static oil dissolved in water or in the gas phase. Biological degradation rates for petroleum hydrocarbons in soil can be quite significant. Oil components move from the oil phase into the aqueous, gaseous, and adsorbed (soil) phases in the subsurface, and this con-stituent partitioning between phases, coupled with biodegradation and advective-dispersive movement in the soil water and gas, controls the fate and transport of the oil components.

A. **LUFT Manual Methodology**

The LUFT Manual Table 2-1 (reproduced here as Table 1), Leaching Potential Analysis for Gasoline and Diesel Using Total Petroleum Hydrocarbons (TPH) and Benzene, Toluene, Xylene and Ethylbenzene (BTXE), relates depth to ground water, precipitation, and unique manmade or geologic features to TPH and BTXE concentrations in soils that should not require remediation (WRCB, 1989). This screening-level table is incorrectly used throughout California by a wide variety of agencies and private entities to determine TPH and BTXE cleanup concentra-tions (RWQCB, 1988; Hubbard, 1991). If it is found during the screening step using Table 1 that additional detailed analyses are required, the LUFT Manual provides a more detailed analysis that compares "cumulative concentrations" of BTXE (the sum of BTXE concentrations detected in soil samples collected at 5 ft depth intervals) to compound-specific tables for determinations of appropriate cleanup levels. This second, more involved analysis, termed the General Risk Appraisal, is rarely performed or enforced. A more complete discussion of the

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TABLE 1
Recreation of Table 2-1 from LUFT (WRCB, 1989)

TABLE 2-1
Leaking Underground Fuel Tank Field Manual
Leaching Potential Analysis for Gasoline and Diesel
Using Total Petroleum Hydrocarbons (TPH)
and Benzene, Toluene, Xylene, and Ethylbenzene (BTX&E)

The following table was designed to permit estimating the concentration of TPH and BTX&E that can be left in place without threatening ground water. Three levels of TPH and BTX&E concentrations were derived (from modeling) for sites that fall into categories of low, medium, or high leaching potential. To use the table find the appropriate description for each of the features. Score each feature using the weighting system shown at the top of each column. Sum the points for each column and total them. Match the total points to the allowable BTX&E and TPH levels.

Site feature	Score 10 pts if condition is met	Score 9 pts if condition is met	Score 5 pts if condition is met
Minimum depth to ground water from the soil sample (ft)	>100	51–100	25–50[a]
Fractures in subsurface (applies to foothills or mountain areas)	None	Unknown	Present
Average annual precipitation (in.)	<10	10–25	26–40[b]
Man-made conduits that increase vertical migration of leachate	None	Unknown	Present
Unique site features: recharge area, coarse soil, nearby wells, etc.	None	At least one	More than one
Column totals → total pts	+	+	=
Range of total points	49 pts or more	41–48 pts	40 pts or less
Maximum allowable B/T/X/E levels (ppm)	1/50/50/50	0.3/0.3/1/1	NA[c]
Maximum allowable TPH levels (ppm)			
Gasoline	1,000	100	10
Diesel	10,000	1,000	100

[a] If depth is greater than 5 ft and less than 25 ft, score 0 points. If depth is 5 ft or less, this table should not be used.
[b] If precipitation is over 40 in., score 0 points.
[c] Levels for BTX&E are not applicable at a TPH concentration of 10 ppm.

use and application of the LUFT Manual can be found in Daugherty (1989). Finally, the LUFT Manual provides for Alternate Risk Appraisal using the models SESOIL and AT123D in lieu of the General Risk Appraisal methodology. This method is also applied rarely in California.

This paper examines the usefulness and validity of the screening and cleanup concentration tables of the LUFT Manual. First, the development and use of the LUFT Manual General Risk Appraisal tables and the Alternative Risk Appraisal will be described. Options for site-specific analysis available under the Alternative Risk Appraisal will then be discussed, with an evaluation of applicable chemical transport models. Input parameter assumptions used in the modeling performed to support the General Risk Appraisal tables of the LUFT Manual will be examined through sensitivity analyses to assess the usefulness and validity of these tables compared with site-specific modeling under the Alternate Risk Appraisal.

II. **LUFT MANUAL LEACHING POTENTIAL SCREENING**

A variety of factors were considered in developing the LUFT Manual's leaching potential screening analyses, including depth to ground water from the deepest affected soils, precipitation, geologic features affecting transport, chemical toxicity, migration potential, and analytical detection limits. As can be seen in Table 1, excluding unique site features, the greater the depth to ground water and the lower the precipitation rate, the higher the soil chemical concentrations deemed acceptable and nonthreatening to underlying ground water (WRCB, 1989).

If used as a screening technique, as intended, this semisubjective analysis seems reasonable. However, this table is applied inappropriately by many to determine specific soil cleanup concentrations throughout California. Perhaps most significant is the widespread application of cleanup concentrations for TPH. The LUFT Manual recognizes the lack of direct water quality threat posed by TPH alone, in the absence of BTXE. Thus, no cumulative concentration levels or cleanup concentrations for TPH are provided as part of the General Risk Appraisal in LUFT. TPH is viewed as a screening parameter that might indicate the presence of BTXE in gasoline- or diesel-affected soils. Since BTXE are the compounds with significant mobility and toxicity, the LUFT Manual focused on these compounds for cleanup concentration development under the General Risk Appraisal. In the absence of BTXE, the other compounds found in TPH generally have either minimal potential for migration or negligible toxicity. Hence, lacking significant concentrations of BTXE, TPH alone (in soil or asphalt roadways) would not warrant cleanup based on water quality concerns. The application of TPH cleanup concentrations to gasoline, diesel, waste oil, and crude oil does not reflect the intended application of the LUFT Manual or informed concern for water quality protection.

III. LUFT MANUAL GENERAL RISK APPRAISAL AND ALTERNATE RISK APPRAISAL PROCEDURES

Following the screening step using the Leaching Potential Analysis, the LUFT Manual provides two methodologies to determine appropriate cleanup concentrations for affected soils: the General Risk Appraisal and the Alternate Risk Appraisal. Both of these options are described below.

A. Cumulative Concentration Analysis Under the General Risk Appraisal

The cumulative concentration-level analysis provides a methodology for determining cleanup concentrations for BTXE in gasoline- and diesel-affected soils. It is based upon only eight SESOIL and AT123D model runs for four different locations in California with differing total annual precipitation rates (6.4, 12.2, 17.2, and 38.4 in.), with two depths to ground water from the lowermost affected soil (1 and 3 m) at each location modeled. These eight model runs were performed separately for each BTXE compound for use in developing the cumulative concentration analysis tables found in the LUFT Manual. Based upon the changes in output observed in these different model runs, extrapolations were made using a spreadsheet program to estimate changes in BTXE concentrations due to changes in precipitation and depth to the water table. Cumulative concentration tables covering the wide ranges of 0 to 40 in./year and 5- to 150-ft depth to ground water were developed from these extrapolations.

These tables consider the sum of each constituent found at intervals of 5 ft above the depth being considered, and provide an "acceptable cumulative concentration" as a cleanup level for soils. Implicit in this manipulation of sampling results is the erroneous assumption that BTXE concentrations will increase in a cumulative manner without an upper concentration limit as water percolates downward through source soils.

The model runs and extrapolations that formed the basis for the LUFT Manual tables were not well documented. Others have attempted to reproduce this work, with marginal success (Geotrans, 1987, 1988). A contributing factor is that SESOIL has been improved significantly from the version used in 1984 and 1985 to develop the LUFT tables. The version used in the development of the LUFT Manual overpredicted losses due to volatilization, making this part of the analysis nonconservative for the protection of water quality. In addition, the methods used for extrapolation of the SESOIL and AT123D results have been found to be highly questionable (Geotrans, 1987, 1988).

In addition to the contaminant-specific parameters, depth to ground water, and precipitation considered in the General Risk Appraisal, the SESOIL and AT123D models used to support the general rating tables require information on several other input parameters to evaluate accurately contaminant transport. These parameters include source area size and shape, soil chemical concentration, effective

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aqueous solubility, biodegradation rate, soil density, permeability, disconnectedness index, porosity, organic carbon content, aquifer thickness and width, hydraulic conductivity, dispersivities, soil/water partition coefficient, and hydraulic gradient. The assumed input parameter values used in the LUFT Manual modeling (upon which the General Risk Appraisal tables are based) are evaluated with the aid of sensitivity analyses following a discussion of the Alternate Risk Appraisal.

B. **Alternate Risk Appraisal**

As an alternative to the General Risk Appraisal, the LUFT Manual provides for the option of performing a site-specific analysis to determine appropriate soil cleanup levels. The LUFT Manual refers to this as an "Alternate Risk Appraisal", and recommends the use of the SESOIL and AT123D models for this purpose. Several computer models, however, are potentially applicable to the analysis of target cleanup levels in soils containing hydrocarbons. A brief review of these models is presented below, supporting the conclusion that SESOIL and AT123D are appropriate for use in the given application.

The determination of appropriate cleanup levels for hydrocarbon compounds in soils involves iterative modeling due to the inverse nature of the problem. The problem is inverse in nature because a specified target for the modeling output (acceptable chemical concentrations in ground water) is achieved by varying the model inputs (soil concentrations under the given site conditions) until the modeling yields acceptable output ground water concentrations. Due to the iterative nature of this modeling process, it may be necessary to complete many simulations to determine appropriate cleanup levels for a given set of site conditions. Thus, useful models for practical application should be efficient and user friendly.

C. **Computer Models**

Figure 1 is a schematic illustrating the modeling problem. In general, two models are needed, one for the vadose zone and one for the ground water zone. The vadose zone transport model must, at a minimum, be

- A one-dimensional vertical model that can be discretized into at least three layers, with varying soil properties and chemical loading concentrations by layer

- Capable of representing one mobile chemical component in three phases (adsorbed, aqueous, and gaseous)

- Capable of representing biodegradation, volatilization, and gaseous diffusion

- Capable of representing the variable effects of local climate (precipitation, temperature, etc.)
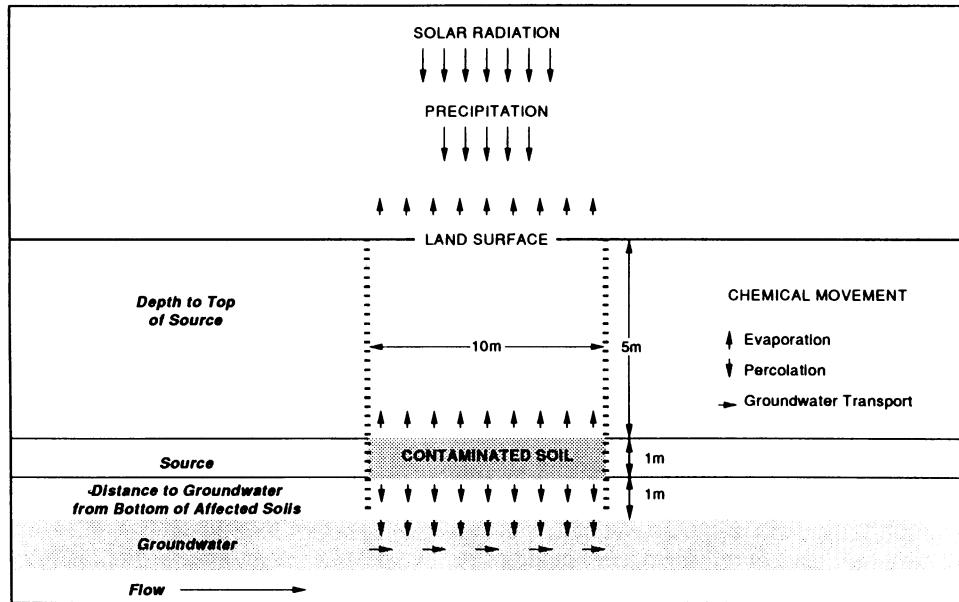
SOLAR RADIATION

↓↓↓↓↓↓↓

PRECIPITATION

↓↓↓↓↓

↑↑↑↑↑↑↑↑↑

— LAND SURFACE —

Depth to Top of Source

CHEMICAL MOVEMENT

←——10m——→ 5m

↑ Evaporation
↓ Percolation
→ Groundwater Transport

↑↑↑↑↑↑↑↑↑

Source CONTAMINATED SOIL 1m

Distance to Groundwater from Bottom of Affected Soils ↓↓↓↓↓↓↓↓↓ 1m

Groundwater ↓↓↓↓↓↓↓↓↓
→ → → → →

Flow ——————→

FIGURE 1. Schematic diagram of the base case. (Modified from Hubbard, 1987.)

Of the vadose zone transport models reviewed, only two models (MOFAT and SESOIL) meet all of the criteria listed above. This conclusion is based on a thorough review of available models, including:

- PRZM — Pesticide Root Zone Model (Carsel *et al.*, 1984, 1985)

- CMLS — Chemical Movement in Layered Soils (Nofziger and Hornsby, 1987)

- GLEAMS — Groundwater Loading Effects of Agricultural Management Systems (Leonard *et al.*, 1986)

- LEACHMP — LEAching estimation and Chemistry Model-Pesticides (Wagenet and Hutson, 1986)

- MOUSE — Method Of Underground Solute Evaluation (Pacenka and Steenhuis, 1984)

- PESTAN — PESTicide ANalytical model (Enfield *et al.*, 1982)

- Jury's analytical transport model (Jury *et al.*, 1983, 1990)

- MOFAT — Multiphase Organic Flow And Transport (ESTI, 1990)

- SESOIL — Seasonal SOIL compartment model (Bonazountas and Wagner, 1984; Hetrick *et al.*, 1989)

Volatilization and diffusive transport in the gas phase are represented only in the last three models in this list. Volatization and gaseous transport must be

represented to properly analyze petroleum hydrocarbons in the subsurface, where the fate and transport of alkanes and aromatics is critical. Thus, all but the last three models listed above were eliminated from further consideration.

Due to its analytical nature, Jury's model applies only to homogeneous soils with a uniform chemical distribution within a source layer. This limits its applicability to the subject problem, and therefore this model was also eliminated from further consideration.

MOFAT is a two-dimensional, finite-element modeling code recently developed by Ashok K. Katyal of the Virginia Polytechnic Institute (ESTI, 1990). MOFAT can represent the transport of up to five components between four phases (air, water, oil, and soil) and allows for up to ten soil layers of differing properties. MOFAT is not easy to use and has not yet been approved by the regulatory community in California. Thus, although this model is more powerful, it is currently less applicable than SESOIL.

SESOIL was developed for the U.S. Environmental Protection Agency (EPA) Office of Toxic Substances by Bonazountas and Wagner of Arthur D. Little, Inc. (Bonazountas and Wagner, 1984). Several shortcomings of the original SESOIL version were identified in a review by Watson and Brown (1985). Major revisions were made to SESOIL in 1986 at Oak Ridge National Laboratory (Hetrick *et al.*, 1989), and SESOIL has been incorporated into the EPA's Graphical Exposure Modeling System (GEMS). SESOIL allows the soil profile to be discretized into a maximum of four layers with varying soil properties and chemical loading concentrations. The model contains hydrologic routines to estimate infiltration and ground water recharge from monthly climate data and soil properties. The model represents transport of one chemical component through three phases (aqueous, gaseous, and adsorbed), with a fourth "pure chemical phase" represented as an immobile storage phase. Due to its wide regulatory acceptance and ease of use, SESOIL is currently the most practical vadose zone model to address this problem.

D. Ground Water Transport Modeling

The simulated mass flux rates at the bottom of the vadose zone must be routed into a ground water transport model to estimate resulting ground water concentrations. For ease of implementation, the ground water model should interface directly with the vadose zone model. The ground water transport model should handle variable-size source areas and be capable of representing biodegradation, adsorption, and advective-dispersive transport.

Although there are numerous ground water transport models (van der Heijde *et al.*, 1988), only a fraction of these are capable of representing both chemical retardation and degradation. Of those models with these required capabilities, only a few are publicly available, well-documented, PC compatible, and accepted by the scientific and regulatory communities. Due to the need for efficient, user-

friendly models, analytical models are preferred over numerical models to the extent that they can handle a reasonable degree of process complexity.

Ground water transport models that generally meet the above minimum requirements have been evaluated for their usefulness in solving the subject problem, including:

- MODFLOW/MT3D — MODular 3-dimensional ground water FLOW model (McDonald and Harbaugh, 1988)/Modular Transport in 3 Dimensions (Papadopulos & Associates, 1991)

- AT123D — Analytical Transport in 1, 2, and 3 Dimensions (Yeh, 1981)

MODFLOW is a widely used numerical ground water flow model developed by the USGS. It is quite useful in cases where complex hydrogeology must be represented to adequately simulate the given flow field. MT3D is a numerical model developed by Chunmiao Zheng of S. S. Papadopulos & Associates, Inc. This transport model is set up to interface directly with the MODFLOW code. MODFLOW output is used as input to MT3D, which solves the transport problem, given the source terms and the three-dimensional flow field(s) solved for by MODFLOW. These numerical models are more difficult to use and much more computationally demanding than AT123D, so they should be considered for use only where needed.

AT123D was developed by G. T. Yeh of the Oak Ridge National Laboratory (Yeh, 1981). It is a semianalytical model for transient simulation of the one-, two-, or three-dimensional transport of solutes in ground water. It can represent advective-dispersive transport with adsorption and biodegradation in homogeneous aquifers of simple geometry with uniform flow fields. It also can represent soil leachate loading at the water table, and is very flexible and user friendly. Thus, AT123D is most useful for general use on the subject problem.

In summary, SESOIL and AT123D meet the modeling requirements, and these models are also recommended in the LUFT Manual.

IV. **BASE CASE LUFT MODELING**

Our base case modeling scenario serves as the basis for comparisons in the sensitivity analysis described below. This base case uses the same input parameter values as the original modeling work performed to support the General Risk Appraisal rating tables of the LUFT Manual (Hubbard, 1987; Daugherty, 1989). Figure 1 is a cross-sectional schematic showing the basic features of the base case. The source of affected soil is 5 m from the land surface, the thickness of the affected soil is 1 m, and the water table is 7 m below the land surface. The transport of benzene from the source layer to underlying ground water as a result of diffusion in the soil air and advection in the soil water (as affected by retardation and degradation) is the primary transport pathway of interest in assessing potential

impacts on ground water quality. Of the BTXE compounds, benzene was selected for examination due to its greater mobility and high toxicity. Table 2 shows the physical, chemical, and biological parameters of the base case simulation.

TABLE 2
Input Values for the LUFT Manual Base Case

Parameter	Base case value
Chemical constituent	Benzene
Source area thickness	1 m
Depth to water table from affected soils	1 m
Organic carbon partition coefficient (Koc)	69 ml/g
Benzene solubility	1780 mg/l
Benzene diffusion coefficient in air	0.089 cm^2/s
Biodegradation rate	0.002/d (first order)
Henry's law constant	0.0055 atm m^3/mol
Molecular weight, benzene	78.11 g/mol
Soil bulk density	1.35 g/cm^3
Intrinsic permeability	2×10^{-9} cm^2
Disconnectedness index	6.3
Effective porosity	0.25
Soil organic carbon content	0.02%
Clay content	10%
Climate data	Los Angeles

The simulation period used for the base case was 10 years. Near the beginning of the simulated time, an initial mass of benzene is applied to the uppermost source layer as an "instantaneous" source available for transport. The initial chemical loading of 100 μg/(cm^2·month) is applied during the month of November in the first year of the simulation. (SESOIL simulations are performed on a water-year basis, with October 1 being the first of the year.) Based on an estimated wet soil bulk density of 1.5 g/cm^3 and the 1-m thickness of the source layer, this chemical loading rate corresponds to a soil concentration of approximately 0.67 mg/kg or 0.67 ppm. This chemical loading concentration is low in the context of this problem, especially when compared with the maximum acceptable cleanup levels of 100 ppm allowable under the General Risk Appraisal methodology of the LUFT Manual (WRCB, 1989).

To represent the effects of interacting processes governing the transport of benzene from the source layer to the water table, the benzene concentration in the soil water leachate at the water-table depth will be used. Figure 2 shows the benzene concentration in the leachate just before it enters the ground water for the base case simulation. The rise to a maximum concentration of 0.29 mg/l at 17 months and the gradual decline to zero illustrates the attenuation due to the many interacting processes. Note that the mass of benzene that ultimately reaches ground water can be substantially less than what was initially in the source soil layer due to biodegradation and volatilization losses.
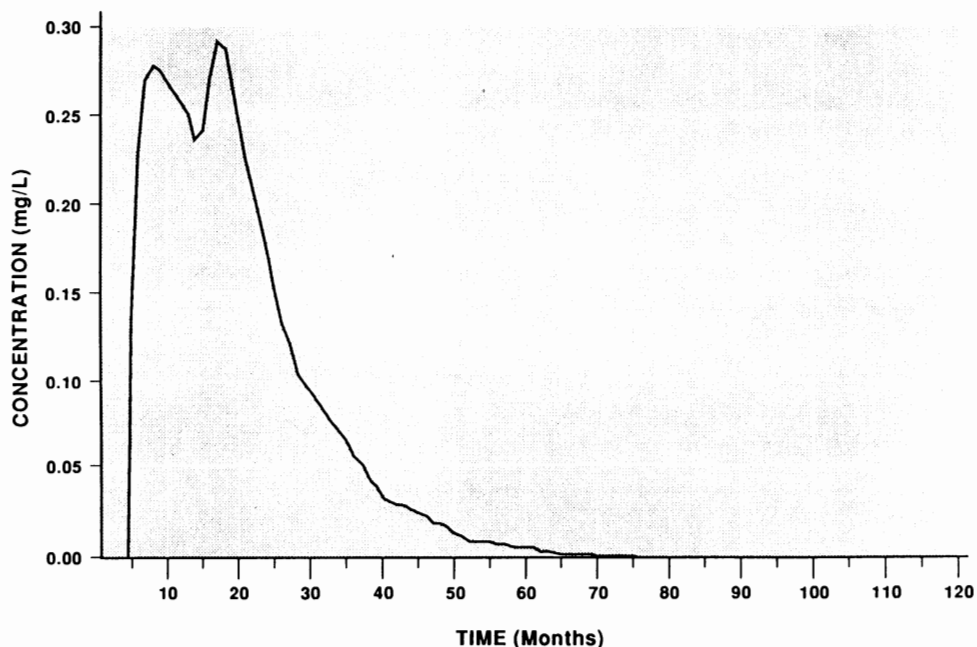
FIGURE 2. Benzene leachate breakthrough curve at the water table for the base case.

V. SESOIL SENSITIVITY ANALYSIS

The purpose of this section is to examine the sensitivity of SESOIL (used in the development of the LUFT Manual) to a range of values for site-specific input variables. The sensitivity of SESOIL to the variables listed in Table 2 was assessed in a simple manner, by varying the parameter values to reasonably high and low values about the base case parameter values shown in Table 2. All of the parameter values used in the sensitivity analysis fall within the range of typically observed values, based on field measurements. Some of the input parameters need to be supported by site-specific field and laboratory measurements, and others, such as compound-specific parameters, can be estimated from the literature. Only three of the variables considered in the sensitivity analysis here (local climate, the thickness of the source layer, and the depth to ground water from the deepest affected soils) were considered significant in the development of the LUFT Manual rating tables. (In the LUFT Manual, precipitation was the only climate variable actually considered, and significant effects of variable local evapotranspiration were neglected.) However, several of the remaining variables are shown to be highly significant in their effect on benzene transport form source soils to the water table.

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A. Depth to Ground Water from Deepest Affected Soils

Figure 3 shows that the distance to ground water is a fairly sensitive factor when assessing the risk to ground water quality. The model runs using 3- and 25-m depths affected substantially the transport of benzene compared with the base case 1-m depth. The peak leachate concentration decreased approximately an order of magnitude as the depth to the water table from the source bottom increased from 1 to 25 m. In addition, the peak concentration for the 25-m case occurred at 8 months, as opposed to 17 months for the base case depth of 1 m. The decreased concentrations result from the increased time for biodegradation and volatilization in the vadose zone. By comparing the three leachate breakthrough curves in Figure 3, it is evident that the peak leachate concentration calculated in the model is not a linear relationship with depth, making extrapolation over great depths difficult. This general finding is important because the LUFT tables extrapolated to greater depths from the 1- and 3-m computer simulations. Others have examined the LUFT Manual's extrapolation and found it to be highly questionable (Geotrans, 1987, 1988).
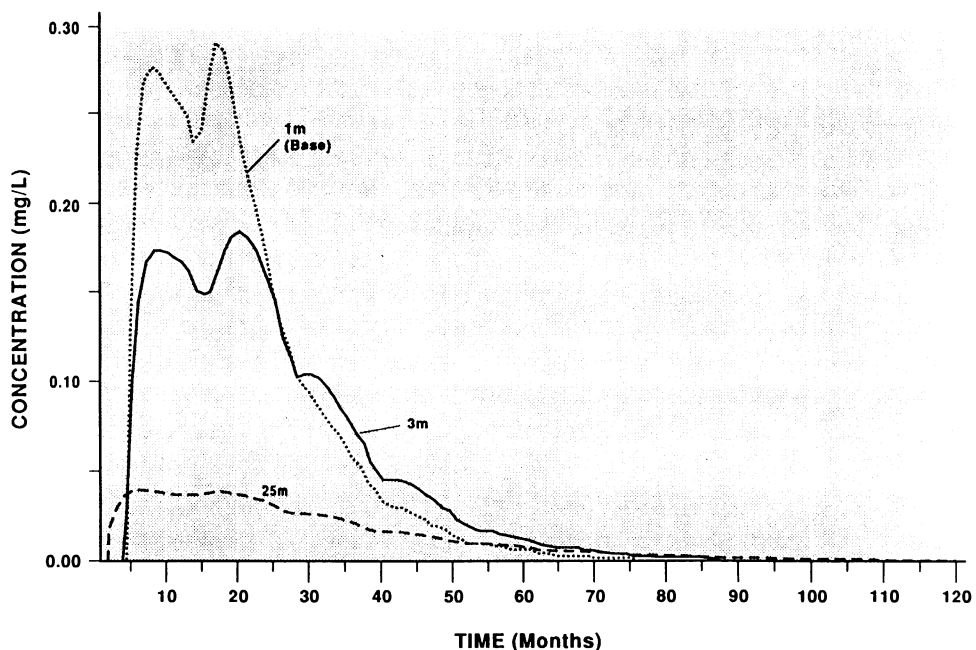

FIGURE 3. Benzene leachate breakthrough curves at the water table for different values of the distance to ground water from the deepest affected soils.

B. Different Climates in California

The climatic conditions at a hydrocarbon-affected site have a large effect on soil transport, as seen in Figure 4. Climate data from four different cities representing
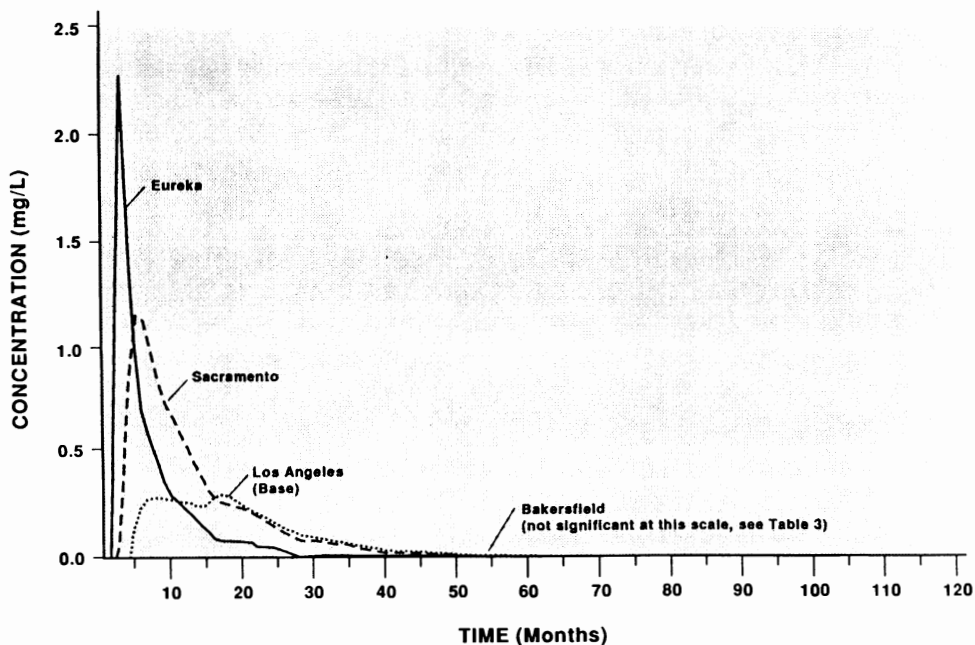
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FIGURE 4. Benzene leachate breakthrough curves at the water table for different California climates.

different regions in California were used in this analysis. The different climatic variables that were considered for each city were mean monthly temperature, fractional cloud cover, relative humidity, shortwave albedo of the surface, daily evaporation, monthly precipitation, mean duration of rainfall, mean number of storm events, and mean length of rainy season. The average annual precipitation in Bakersfield is 6.36 in., Los Angeles is 12.2 in., Sacramento is 17.22 in., and Eureka is 38.43 in. These areas represent arid to moderately wet climates throughout California. The four general regions of the state that these cities are representative of are the south interior, the south coastal, the north interior, and the north coastal, respectively. There was a difference of approximately two orders of magnitude in calculated/predicted peak leachate concentrations from the Eureka to the Bakersfield climate. In addition, increasing annual precipitation shortens the time to reach the peak concentration.

C. **Biodegradation Rate**

The sensitivity of the model results to the first-order biodegradation rate for benzene is shown by the curves in Figure 5. The biodegradation rate was found to be one of the most sensitive of all the variables examined in this paper. The general response of increased biodegradation was to lower the predicted maximum concentration in the liquid phase and reduce the time to peak concentration. The biodegradation rate in the base case was 0.002 d^{-1}, which is one half the rate
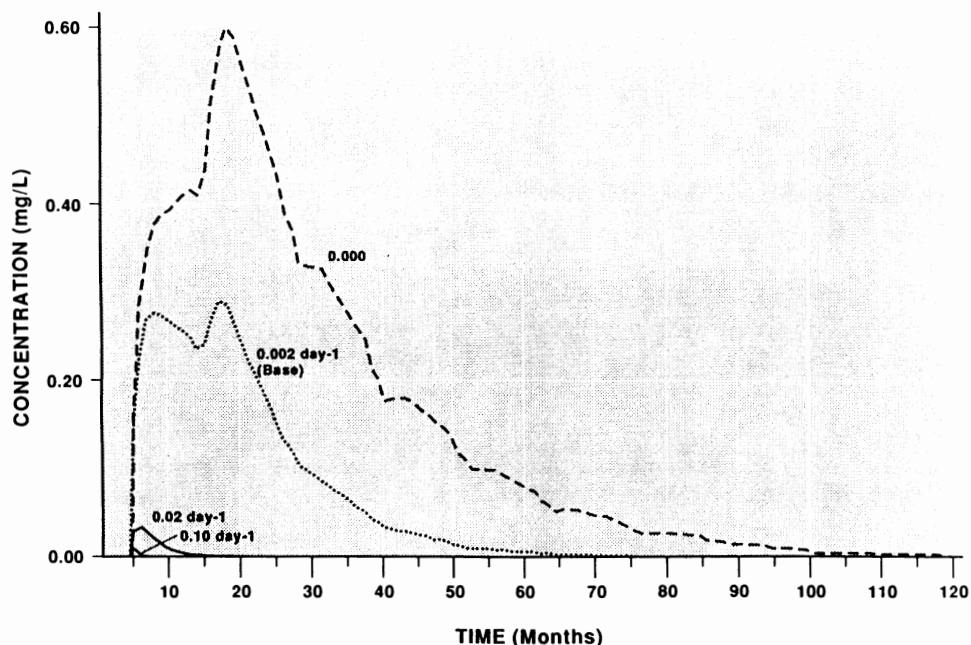
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FIGURE 5. Benzene leachate breakthrough curves at the water table for different values of the biodegradation rate.

of 0.004 d^{-1} reported by Rifai and Bedient (1990). Rifai and Bedient's reported degradation rate is extremely low compared with general literature values (Barker and Patrick, 1985). Howard *et al.* (1991) reported first-order degradation rates of 0.139 to 0.043 d^{-1}, which is a reasonable range considering the general literature. Therefore, in contrast to the arbitrarily selected low biodegradation rate used in the development of the LUFT Manual, the higher values of the first-order biodegradation rate used in this sensitivity analysis are well supported. The higher values of the biodegradation rate increased the removal of benzene from the leachate. Comparing the base-case curve to the results of the simulation with no biodegradation rate, the mass of benzene lost to biodegradation is very large, indicating the importance of estimating or measuring the degradation rate on a site-specific basis. *In situ* bioremediation is a rapidly expanding research and development area, for reasons clearly depicted by the results shown in Figure 5.

D. Fraction of Soil Organic Carbon

Figure 6 shows predicted breakthrough curves of benzene in the leachate at the water table for different fractions of soil organic carbon. The organic carbon content of soil is the primary governing factor for the adsorption/retardation of organic compounds in soils with relatively high organic carbon content. In soils with low organic carbon content (e.g., less than 0.1%; Karickhoff, 1984), sorption becomes affected significantly by the inorganic mineral surfaces of the soil. This
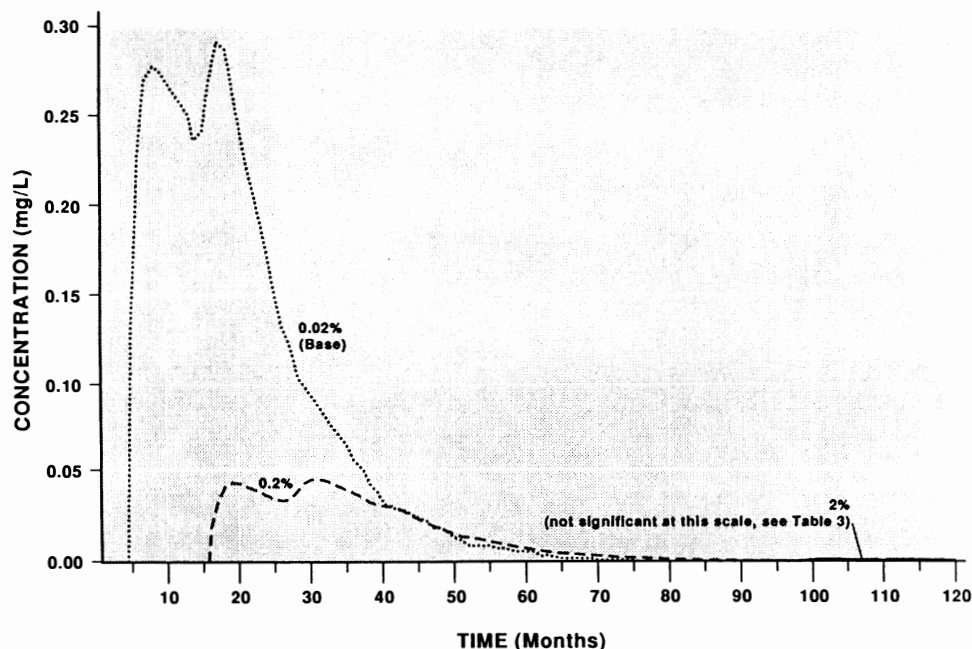
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FIGURE 6. Benzene leachate breakthrough curves at the water table for different values of soil organic carbon content.

is a current topic of much research, and it appears that the specific surface area, the presence of intragranular porosity, and the types of mineral surfaces are all significant factors controlling sorption in soils with low organic content (Vorst *et al.*, 1999; Hassett and Banwart, 1989; Pignatello, 1989; Roberts *et al.*, 1989). In the near future, correlations no doubt will become available to estimate partition coefficients based on these factors, in addition to the soil organic carbon content. However, such correlations are not available currently, and SESOIL accounts only for the partitioning effects due to soil organic carbon.

Assuming that sorption is dominated by the effects of soil organic carbon, SESOIL uses the following equation to relate the retardation factor to the fraction of organic carbon in the soil:

$$R = 1 + K_{oc}f_{oc} \, \rho_b/\theta_w + \theta_a \, K_H/\theta_w$$

where R is the retardation factor, K_{oc} the organic carbon/water partitioning coefficient, f_{oc} the organic carbon content, ρ_b the bulk density of the soil, θ_w the water content of the soil θ_a the air content of the soil, and K_H the dimensionless Henry's Law coefficient. The effects of three different percentages (0.02, 0.2, and 2%) of soil organic carbon were assessed, encompassing expected field values. Very few soils have soil organic carbon content as low as the 0.02% used in the base case. Increased retardation of benzene results in increased contact time with biodegrading organisms and allows greater time for volatilization, resulting in significantly lower leachate concentrations (see Table 3). Even though the bio-

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degradation rate used for these comparisons is extremely low, the significant effects of time lag and increased biodegradation and volatilization due to increased retardation are illustrated quite dramatically in Figure 6. It should be noted that the soil organic carbon content of 0.02% used in the LUFT modeling is unrealistically low for typical soils, and it is outside the range of where $K_d = K_{oc}f_{oc}$ is valid, as discussed earlier.

E. **Effective Solubility and Chemical Loading**

Although SESOIL is not designed to represent a multicomponent nonaqueous phase liquid (NAPL), such as a petroleum product, the 1986 revisions of Hetrick *et al.* (1989) included the provision to represent a pure chemical phase NAPL. If the aqueous benzene concentration calculated by the model exceeds the input solubility, then the model adds the mass of benzene in excess of the solubility limit to an immobile storage term. When the aqueous concentrations drop below the solubility limit, the pure phase can be depleted. However, the effective aqueous solubility of a chemical constituent in a multicomponent NAPL, such as a petroleum product, is orders of magnitude lower than the aqueous solubility of a chemical constituent in equilibrium with a pure chemical NAPL (e.g., 1780 mg/l for benzene). This fact seems to have been overlooked by the State of California in their development of the LUFT Manual rating tables.

Raoult's law states that the effective aqueous solubility of a mixture constituent, such as benzene, is equal to its aqueous solubility times the molar fraction of the constituent in the mixture. Feenstra *et al.* (1991) discuss the use of Raoult's law to estimate the effective solubility of BTXE in petroleum products. For gasolines, the molar fraction of benzene is about 2 to 5%. For diesel fuels and most crude oils, the molar fraction of benzene is at least an order of magnitude lower than this. Thus, to use SESOIL to represent the partitioning of benzene between a hypothetical diesel oil and the aqueous phase in this part of the sensitivity analysis, the input solubility was set to 5 mg/l, which represents a benzene molar fraction of about 0.3%.

To show clearly the effects of diesel NAPL in the soil, the base case chemical loading was increased 100 times for the simulation results shown in Figure 7. (This loading is equivalent to about 67 mg/kg or 67 ppm, and falls well within the range of concentrations dealt with in the LUFT rating tables.) The use of an effective solubility of 5 mg/l results in a dramatic change in transport behavior compared with using the aqueous solubility of benzene (1780 mg/l), as was done by the State of California in the development of the LUFT Manual rating tables.

F. **Intrinsic Permeability**

Figure 8 illustrates the sensitivity of SESOIL to the value of intrinsic permeability, which is a measure of the ease with which water passes through soil. The value
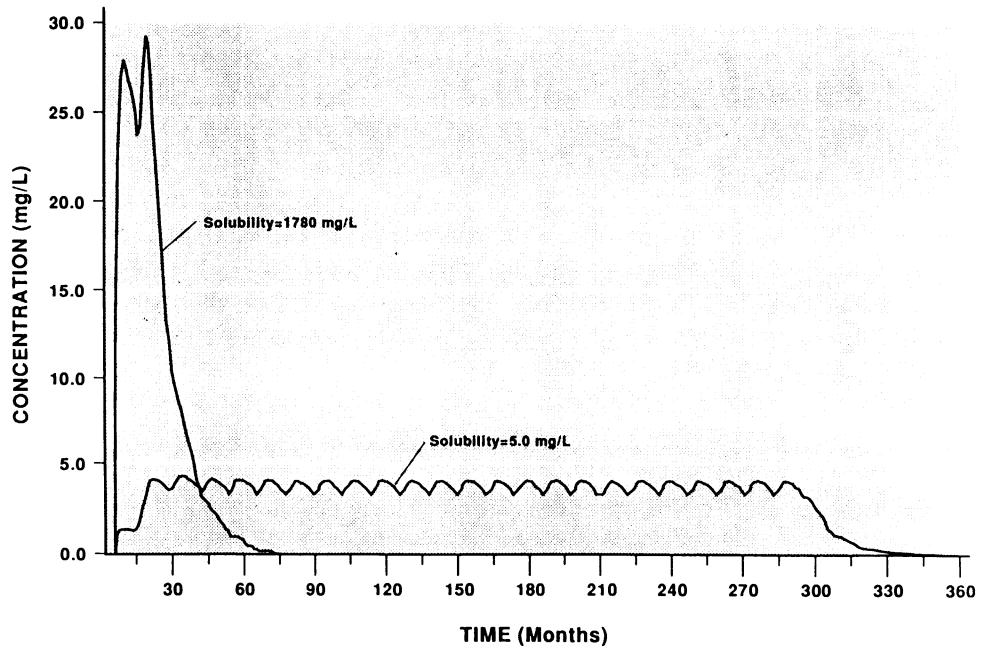
FIGURE 7. Benzene leachate breakthrough curves at the water table for different values of effective solubility at loading of 100 times the base case.
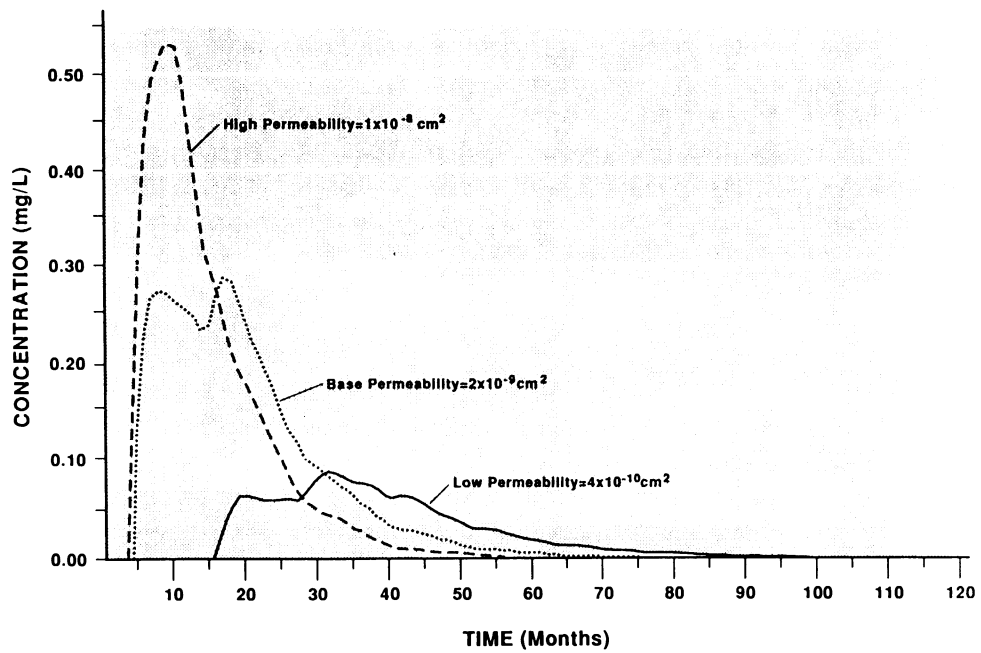

FIGURE 8. Benzene leachate breakthrough curves at the water table for different values of intrinsic permeability.

of the intrinsic permeability was varied by a factor of five. Increasing the permeability increased the predicted peak leachate concentration and decreased the time to peak. Lowering the intrinsic permeability decreased the maximum leachate concentration and increased the time at which the peak occurred. The lower permeability decreased the flow velocity through the soil, which resulted in increased-contact time with the bacteria and time for volatilization, reducing the leachate concentration and the total benzene mass entering the ground water. The LUFT Manual base case did not use a particularly high permeability $(2 \times 10^{-9}$ cm^2), and hence, for this parameter, the General Risk Appraisal is not conservative and may not be protective of water quality for sites with high-permeability soils.

G. Disconnectedness Index

Figure 9 suggests that soil transport is relatively sensitive to the hydrologic parameter termed the disconnectedness index. The disconnectedness index is the slope of the logarithmic hydraulic conductivity vs. the logarithmic moisture content curve. The sensitivity to the disconnectedness index is lower than the majority of the parameters examined in this article. The disconnectedness index is correlated (i.e., inversely proportional) to the intrinsic permeability. Therefore, in practical applications, a lowering of the disconnectedness index normally would be accompanied by increased intrinsic permeability. The LUFT Manual's limitations in this respect were addressed by the inclusion of a test to be used for
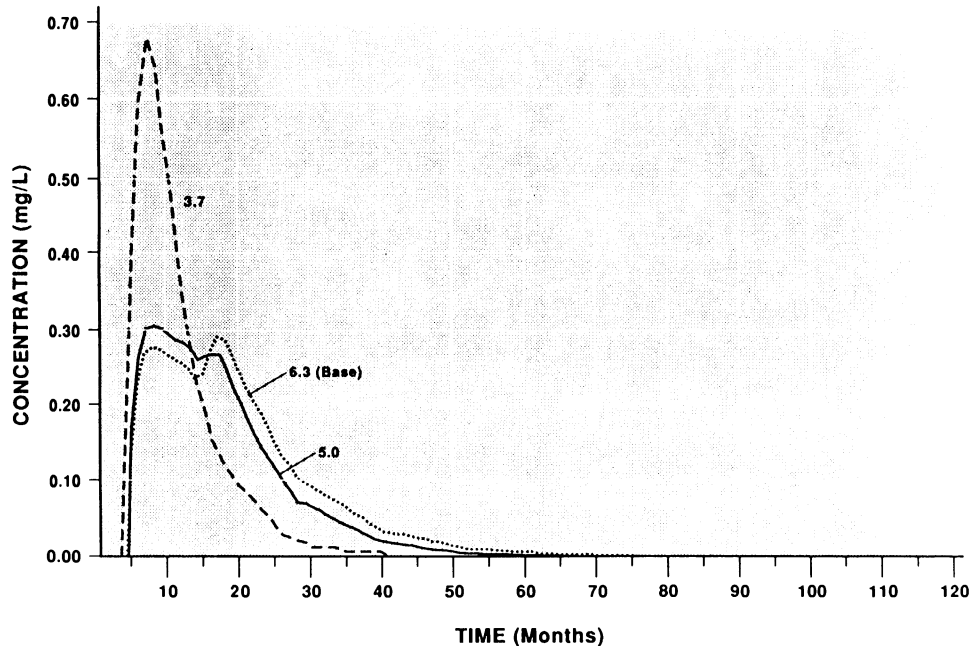

FIGURE 9. Benzene leachate breakthrough curves at the water table for different values of disconnectedness index.

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assessing the appropriateness of applying the LUFT methodology to specific cases.

H. Source Area Thickness

The effect of changing the thickness of the source area is summarized in Figure 10. The source thickness was increased to 3 and 5 m while preserving the same distance to ground water, reducing the thickness of the unaffected overburden. In addition, to preserve the same initial source soil concentration, the chemical loading per unit area was increased by three and five times that of the base case for the 3- and 5-m source thickness runs, respectively. The general effect of the increased source thickness is to increase slightly the predicted peak concentration and to increase the time to reach the water table. The results shown in Figure 10 indicate that this variable is not sensitive compared with others examined. The small decrease observed in the peak concentration from the 3- to the 5-m source thickness probably results from the increased volatilization with the reduced overburden thickness and increased biodegradation due to the increased time to peak concentration. The modeling results shown here are contrary to the LUFT Manual's cumulative concentration methodology, which holds that leachate concentrations should increase in an unlimited manner with increased source thickness. SESOIL suggests that the soil/water/contaminant concentrations equilibrate relatively quickly and do not increase in a linear manner, as suggested by the LUFT Manual methodology.
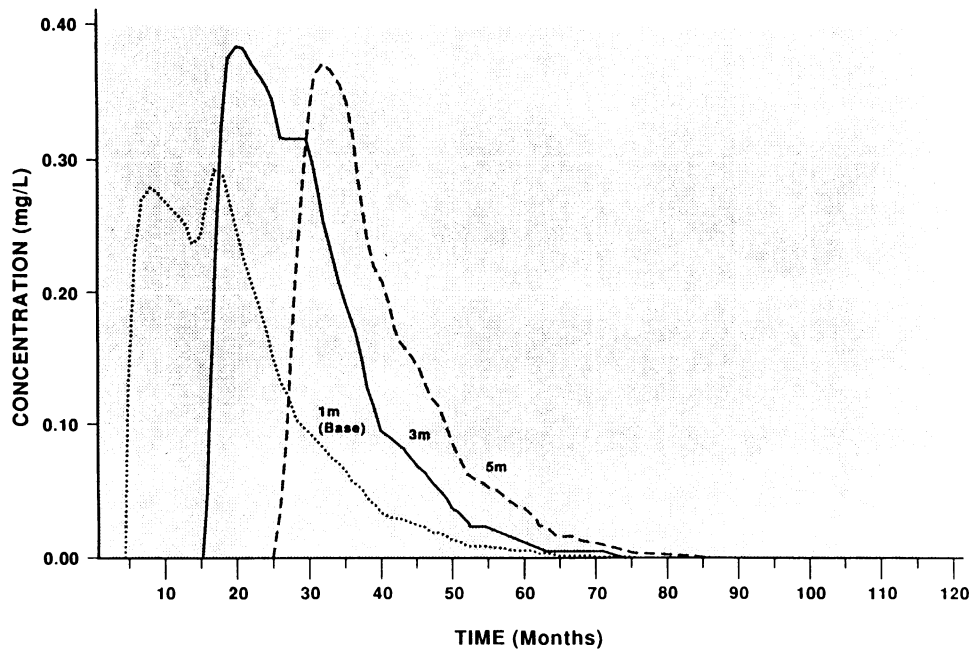

FIGURE 10. Benzene leachate breakthrough curves at the water table for different values of source thickness.

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VI. SUMMARY OF THE SESOIL SENSITIVITY ANALYSIS

A summary of all the computer simulation results discussed in this article appears in Table 3, with predicted peak leachate concentrations and the times to reach peak concentrations. The results in Table 3 indicate that several of the input variables are highly sensitive, and that these variables must be properly accounted for in site-specific analyses if accurate simulations of ground water quality threats are to be made. Of the eight variables examined in this article, it appears that biodegradation rate, climate, effective solubility, and soil organic carbon content are the most sensitive. The depth to ground water and intrinsic permeability are of intermediate sensitivity. Finally, the source thickness and disconnectedness index are the least sensitive. These determinations were made in the context of the LUFT Manual base case and should be viewed in that context.

TABLE 3
**Summary of Sensitivity Analysis in the Form
of Time to Predicted Peak and Maximum Leachate Concentration**

Parameter	Peak Concentration (mg/l)	Time to peak (months)
Base	0.29	17
Depth to groundwater from source bottom		
3 m	0.18	19
25 m	0.038	8
Climate		
Eureka	2.30	3
Sacramento	1.15	6
Bakersfield	0.010	32
Biodegradation rate		
0 d^{-1}	0.60	18
0.02 d^{-1}	0.033	6
0.10 d^{-1}	6.5×10^{-3}	5
Fraction of organic carbon content		
0.2%	0.045	32
2%	1.12×10^{-3}	103
Intrinsic permeability		
$1 \times 10^{-8} \text{ cm}^2$	0.53	9
$4 \times 10^{-10} \text{ cm}^2$	0.090	31
Disconnectedness index		
3.7	0.680	8
5.0	0.302	7
Source thickness		
3 m	0.385	20
5 m	0.375	32

VII. SUMMARY OF AT123D SENSITIVITY ANALYSIS

Numerous computer simulations were conducted to assess the sensitivity of AT123D to its various parameters, using as input the output from the base SESOIL case

just described. The aquifer parameters of hydraulic conductivity, longitudinal and transverse dispersivity, biodegradation rate, source configuration, and aquifer thickness were evaluated in terms of sensitivity. The general effects of changes in these variables are summarized below.

As might be expected, it is impossible to say which parameters are the most sensitive under all conditions, due to the great potential variability in site conditions. However, some general conclusions can be made regarding parameter sensitivity. The soil leachate usually derives significant dilution from the large lateral ground water flux under a source area. The magnitude of the dilution is directly proportional to the ground water flux, so in most cases the hydraulic gradient and hydraulic conductivity of the aquifer are highly sensitive variables.

The biodegradation rate also was found to be a highly sensitive ground water transport parameter. Increasing the first-order biodegradation rate lowered the plume concentration dramatically. As expected, increased longitudinal and transverse dispersivities increased ground water mixing and lowered the concentration compared with the base case. The source configuration can be a highly sensitive variable. If the source is long, narrow, and perpendicular to the flow direction, concentrations are lowered more substantially than when the long, narrow source is parallel to the flow direction. Finally, the aquifer thickness had very little effect at the plane of the water table near the source area. The effect of aquifer thickness becomes more important when transport in the vertical direction is of concern and ground water concentrations are evaluated further downgradient of the source area.

VIII. IMPORTANCE OF SITE-SPECIFIC MODELING AND RISK ASSESSMENT

Because of the sensitive parameters affecting chemical transport and ground water quality, site-specific modeling and risk assessment should be considered in cases where significant soil volumes might potentially require remediation. In most cases, the costs for site-specific modeling and the collection of field data to support it will be offset easily by reduced remediation costs and the associated reduction in liability due to improved remedial plans. Furthermore, water quality protection goals would be protected with a higher degree of certainty.

IX. SUMMARY

A detailed examination of the methodology presented in the LUFT Manual has revealed that the subjectively derived initial screening table is being misused throughout California to set cleanup concentrations, while the General Risk Appraisal methodology suggested by the LUFT Manual to set cleanup concentrations is seldom used. Further, this methodology only considers depth to ground water from affected soils, source thickness, and precipitation. These parameters were

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evaluated using sensitivity analyses referenced to the original LUFT Manual base-case simulations used to develop the LUFT rating tables. The sensitivity analyses suggest that these variables account for only a small fraction of the variability in site-specific transport behavior. Variation in other input parameter values analyzed significantly alters the output of the LUFT Manual modeling. Protection of water quality is not afforded consistently to all sites by the LUFT Manual methodology, but, generally, application of the LUFT methodology results in overprotective cleanup-level determinations that are not cost effective. A brief review of the modeling codes used in the development of the LUFT Manual supports their use in site-specific risk analysis. The work completed in this article suggests the desirability of using site-specific model input parameter determinations and modeling for larger remedial projects.

X. **CONCLUSIONS**

Based upon the work presented in this article, the authors offer the following conclusions for those in a position to affect the direction of soil remediations.

1. The LUFT Manual is being applied incorrectly throughout the State of California, causing large remedial expenditures to address soils affected by TPH, which, in the absence of BTXE, may not pose a significant water quality threat.

2. The methodology developed by LUFT to determine cleanup concentrations of soils can be highly overprotective or underprotective of water quality, depending on the given site conditions. To remediate larger sites in a manner that is both protective of water quality and cost effective, site-specific data collection and modeling assessment should be conducted on a case-by-case basis.

3. It is important to consider site-specific variables such as the biodegradation rate and soil organic carbon content, in addition to local climate and depth to the water table, in determining petroleum hydrocarbon cleanup levels.

4. SESOIL and AT123D are appropriate models for use in determining acceptable soil cleanup levels protective of water quality.

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