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Calculation of Soil Cleanup Criteria for Volatile Organic Compounds as Controlled by the Soil-to-Groundwater Pathway: Comparison of Four Unsaturated Soil Zone Leaching Models

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ABSTRACT: Four computer models that predict leaching of chemicals in the unsaturated soil zone were used to calculate example soil cleanup criteria for volatile organic compounds, using a hypothetical environmental scenario. The criteria were calculated so that allowable groundwater concentrations for the chemicals were not exceeded. The models used were the Pesticide Root Zone Model (PRZM) and the Seasonal Soil Compartment Model (SESOIL) from the U.S. Environmental Protection Agency, the Sanitary Landfill Model (SLM1) from Oregon State University, and the Integrated Moisture and Aqueous Contaminant Transport model (IMPACT) under development for the State of New Jersey. The hypothetical scenario assumed a water table depth of 10 ft, a contaminated zone from 0 to 4 ft, and sandy loam soil properties. Transport times to groundwater were similar for all four models. The calculated soil criteria for many chemicals using the four models agreed to within an order of magnitude. In a few instances, SLM1 and PRZM predicted much lower cleanup criteria than the other two models because volatilization losses were not modeled. Calculated criteria were often quite low when degradation was assumed to be zero. When estimated degradation rates were employed, criteria were sometimes considerably higher.

KEY WORDS: soil, computer models, cleanup criteria, groundwater, volatile organic chemicals.

I. INTRODUCTION

Remediation of hazardous waste sites frequently requires an assessment of the extent of soil contamination and calculation of cleanup criteria to protect the groundwater from contamination. This often requires estimating the leaching potential of soil contaminants, the comparison of this potential with allowable groundwater concentrations, and the determination of acceptable levels of contaminants that may be left in the soil.

The use of computer simulation models is one option for assessing the potential for soil contaminants to leach to the groundwater. Numerous vadose zone models are available, all of which vary to some degree with regard to their formulation, assumptions, input requirements, output capabilities, and time resolution (EPA, 1987). The magnitude of the predicted leaching will depend to some extent on the model used. How much they will vary is unclear because comparison studies of different models have been limited. For this reason, it was felt that such a comparison would help determine whether or not the selection of one model over another would lead to substantially different results when using them to assess potential contaminant impact on groundwater. In this study, four computer simulation models that predict contaminant leaching in the unsaturated soil zone were compared to one another when run using a hypothetical environmental scenario. The models were used to calculate contaminant transport to the water table, and for purposes of this study, a dilution factor was applied to estimate resulting contaminant concentrations in groundwater. Example soil criteria were then determined. The compounds used for the comparison were volatile organic chemicals that are under consideration for regulation by the New Jersey Department of Environmental Protection. The four models chosen were the Sanitary Landfill Model -1 (SLM1; Elzy *et al*., 1974), the Pesticide Root Zone Model (PRZM; Carsel *et al*., 1984), the Seasonal Soil Compartment Model (SESOIL; Bonazountas and Wagner, 1984) as modified by Hetrick *et al*. (1989), and the Integrated Moisture and Aqueous Contaminant Transport model, Version 2.0 (IMPACT) under development for the State of New Jersey (Korfiatis *et al*., 1990; Korfiatis and Talimcioglu, 1991).

Two secondary objectives were also investigated. First, the effect that the contaminant degradation process had on model output was determined. This variable is the most uncertain of all the chemical input parameters due to its highly site-specific nature. Because of this uncertainty, it is frequently assumed that degradation does not occur when determining cleanup levels. It was desirable to see how large an impact this assumption had on the results. The second aspect investigated was whether or not models leaving out vapor phase processes entirely (diffusion and volatilization) would cause model results to be substantially different from those calculated using models that do include these processes. PRZM and SLM1 do not include vapor phase processes.

It was not the intent of this study to conduct sensitivity analyses for model input parameters. Such analyses should be included in model documentation (although this is not always the case) or carried out by potential model users. This study also was not concerned with comparison of the predicted results to field or laboratory data, although such comparisons are important. The focus in this study was on comparing the four models when they were run under the same environmental scenario.

II. PROCEDURES

A. Model Overview

PRZM and SESOIL were developed for the U.S. Environmental Protection Agency (EPA) and are well known, well documented, and widely used. PRZM was designed to calculate pesticide fate in agricultural fields in the root zone. However, its structure allowed adaptation to a hazardous waste site scenario because the effect of growing crops could be essentially eliminated. SESOIL is designed for general use in the unsaturated soil zone, for scenarios including hazardous waste sites. SESOIL was run using PCGEMS, a user-friendly operating system developed for the EPA that prepares input data files for several environmental computer models (General Sciences Corporation, 1989). SLM1 is a very simple compartmental model, and was chosen for purposes of comparison with the more complex models. SLM1 was designed for contaminant transport from landfills, but its structure was suitable for application to hazardous waste sites, where attenuation of the source concentration with time is desired. IMPACT is specifically designed for the calculation of soil cleanup criteria for hazardous waste sites as controlled by the soil-to-groundwater pathway.

Fundamental differences between the four models are highlighted in Table 1. These differences, and how the models were used, is discussed in more detail below.

B. Hypothetical Environmental Scenario

A single hypothetical environmental scenario was used for all model runs (Figure 1). Contamination was assumed to extend from the soil surface to a depth of 4 ft. Clean soil extended from 4 to 10 ft, and the water table depth was set at 10 ft. The soil organic carbon fraction was set to a conservative value of 0.001. Sandy loam soil texture was used for the simulation. Typical parameter values for this soil texture were obtained from the PRZM manual (Carsel *et al*., 1984). A dry bulk density of 1.3 g/cm^3 was assumed. Other environmental input parameters, and which models used them, are listed in Table 2. Several of these parameters are discussed below.

C. Water Application to Soil

SLM1 and PRZM require weekly and daily precipitation amounts, respectively. For SLM1, a constant 0.8 in./week was applied (42 in./year). For PRZM, another

TABLE 1

Mechanistic Features of the Four Unsaturated Zone Models

	Runoff	Infiltration	Evapotranspiration	Water transport	Contaminant partitioning	Contaminant transport	Vapor phase/ volatilization	Dispersion/ diffusion
SLM1	No	Infiltration rate specified by user	No	Drain to field capacity	Linear, rapid	Compartmental	No	Compartmental
PRZM	SCS curve no.	Precipitation minus runoff	Yes	Drain to field capacity	Linear, rapid	Compartmental	No	Compartmental
SESOIL	Eagleson model (statistical)	Precipitation minus runoff	Yes	Eagleson model	Linear/Freundlich, rapid	Retardation factor	Yes	Compartmental/ upward vapor diffusion
IMPACT	SCS curve no.	Precipitation minus runoff	Yes	Richards/Darcy equations	Linear, rapid	Advection/ dispersion equation	Yes	Included in advection/dispersion equation

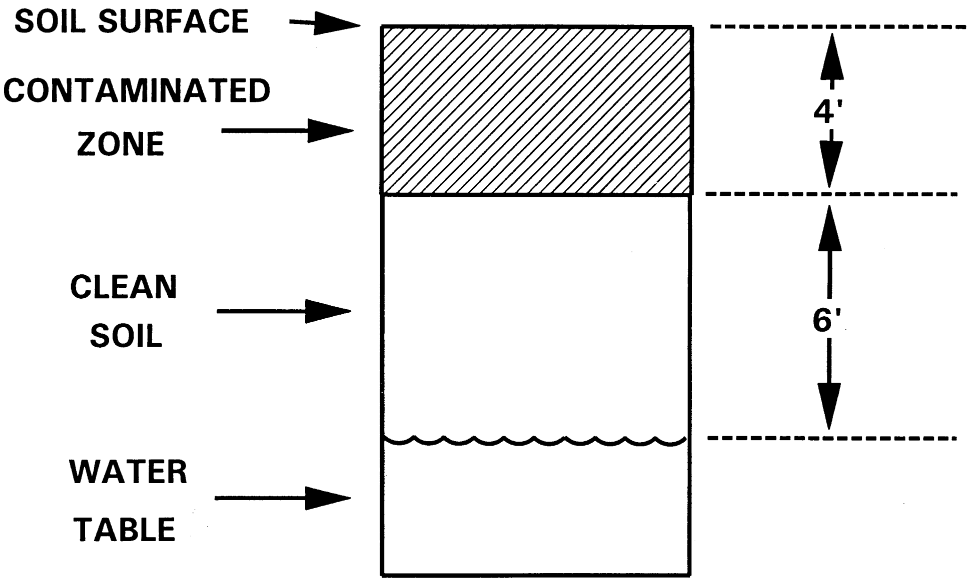

FIGURE 1. Hypothetical environmental scenario.

simulation model (Simulator for Water Resources in Rural Basins — Water Quality Version, SWRRB-WQ; Arnold *et al.*, 1991) was used to generate daily precipitation, using the weather generator contained in the model and the weather dataset for Newark, NJ, that was included with the model. Rainfall varied from 34 to 54 in./year, with an average of 42 in./year. SESOIL generates precipitation events based on monthly precipitation averages using a statistical formula. The climate dataset for Trenton, NJ, included with the PCGEMS package was used as source weather data. Total rainfall was 42 in./year. The IMPACT model uses a 30-year record of daily precipitation from the Newark, NJ, airport. While the average annual rainfall for this 30-year period was 43 in., the time period sampled had annual rates varying from 29 to 45 in./year, with an average of 39 in./year.

D. **Water Runoff and Infiltration**

SLM1 does not estimate water runoff; an infiltration rate is simply entered by the user. For this study, a 50% infiltration rate was used, which yielded a net annual recharge to groundwater similar to that of PRZM (see below). The PRZM and IMPACT models estimate surface runoff of water using the Soil Conservation Service runoff curve number (Soil Conservation Service, 1985); the remaining precipitation is assumed to infiltrate. The SESOIL model uses the water balance dynamics theory of Eagleson (1978) to calculate runoff and infiltration; the theory couples climatological and soil systems through a statistical dynamic water bal-

TABLE 2
Model Input Parameters

		SLM1	PRZM	SESOIL	IMPACT
Contamination depth range (ft)	0–4	x	x	x	x
Groundwater depth (ft)	10	x	x	x	x
Bulk density of dry soil, (g/cm^3)	1.3	x	x	x	x
Saturation volume of soil (v/v)	0.41	x	x		x
Field capacity of soil (v/v)	0.20	x	x		x
Wilt point of soil, (%, v/v)	9.5		x		x
Air dry moisture content (v/v)	0.05				x
Initial moisture content of soil (v/v)	0.20	x	x		x
Organic carbon content of soil (%, w/w)	0.1	[a]	[a]	x	x
Air diffusion coefficient of contaminant (m^2/d)	0.43			x	x
Water diffusion coefficient of contaminant (m^2/d)	4.3×10^{-5}				x
Soil layer depth		2′	5 cm	2′ and 4′	1′
SCS Runoff Curve number (AMC II)	82		x		x
Snow melt coefficient (cm/°C-d)	0.457		x		
Minimum depth to which evaporation is extracted (cm)	17.5		x		
Crop interception potential (cm)	0		x		
Maximum crop root depth (cm)	10		x		
Maximum areal crop coverage (%)	1		x		
Condition after harvest	Fallow		x		
Hydrodynamic dispersion (cm^2/d)	0		x		
Effective soil porosity (v/v)	0.20			x	
Intrinsic permeability (cm^2)	2e-9			x	
Disconnectedness index	6.33			x	
Freundlich exponent	1			x	
Saturated hydraulic conductivity (ft/d)	9.83				x
“m” Coefficient (Campbell’s hydraulic conductivity equation)	12.8				x
“b” Coefficient (Clapp and Hornberger’s soil diffusivity and soil moisture retention equations)	4.9				x
Saturation suction head (ft; Clapp and Hornberger equations)	0.72				x
Time increment (d)		7	1	1	1
Convergence criteria	0.001				x
Root zone depth (ft)	3				x
Soil dispersivity (ft)	1				x

[a] Model requires Kd (K_{OC} × fractional organic carbon).

ance formulation in order to calculate soil moisture behavior. Application of Eagleson’s approach in SESOIL is discussed in Bonazountas and Wagner (1984) and Hetrich *et al.* (1993).

SESOIL and PRZM have the capability to calculate the surface erosion of adsorbed contaminant through application of techniques based on the universal soil loss equation (Wischmeier and Smith, 1978); however, preliminary runs with PRZM indicated a negligible impact of this pathway due to the relatively low adsorption of the studied chemicals to soil, so this option was not used.

E. **Evapotranspiration**

SLM1 does not calculate evapotranspiration; all water that infiltrates reaches the water table. The other three models calculate evapotranspiration. PRZM estimates potential evapotranspiration using either temperature data or pan evapotranspiration data, and then adjusts for current soil moisture levels (Carsel *et al*., 1984). For this study, temperature data were used, generated using SWRRB-WQ as discussed above. In SESOIL, evapotranspiration is based on the model of Eagleson (1978). IMPACT uses the evapotranspiration procedure of Thornthwaite (1948), which calculates potential evapotranspiration as a function of temperature and percentage sunshine. The actual evapotranspiration is then calculated by the water balance method of Thornthwaite and Mather (1957).

F. **Soil Moisture Movement**

SLM1 and PRZM both use a simple, compartmental technique for calculating water transport. At each time step, any water present in a soil compartment above the field capacity volume drains to the next lower soil compartment. PRZM has an option for retarding this drainage for heavy soils; this option was not used. SESOIL and IMPACT each treat the soil column as a whole when calculating water transport, but use different techniques. SESOIL uses the model of Eagleson (1978) to calculate moisture movement, while the IMPACT model is based on the moisture form of the Richards' equation (Richards, 1931) and Darcy's law (Freeze and Cherry, 1979). In the IMPACT model, the hydraulic conductivity expression of Campbell (1974) is used, and soil moisture retention and soil diffusivities are calculated according to Clapp and Hornberger (1978).

G. **Capillary Rise**

The Eagleson water balance model contained in SESOIL determines capillary rise from the groundwater, a process not included in the other three models.

H. **Contaminant Partitioning**

All four models assume that equilibrium of contaminant is maintained between the sorbed and aqueous phases, and IMPACT and SESOIL also assume equilibrium between the aqueous and vapor phases (PRZM and SLM1 do not include the vapor phase). SLM1, PRZM, and IMPACT assume simple linear partitioning between soil and water using K_{oc} or K_d values. SESOIL allows the use of a Freundlich 1/n exponent; however, valves for this parameter are not generally available, so the coefficient for this study was set to one to achieve linear partitioning. IMPACT allows for the entry of a desorption coefficient; again, these parameters are not generally available, and this feature was not used. Henry's law constant is used for water-air partitioning in SESOIL and IMPACT. SESOIL checks calculated aqueous concentrations against the entered water solubility. If the solubility is exceeded, the excess chemical is maintained as a nonmobile, nonaqueous phase, which maintains the aqueous phase at the solubility limit until concentrations in the nonaqueous chemical is depleted in the soil layer of concern.

I. **Contaminant Degradation**

All models allow for first-order degradation in at least one phase of the soil compartment. SESOIL allows for degradation in either the aqueous or sorbed phases or both. SLM1 was modified to allow for the same flexibility. PRZM allows only for degradation of "total chemical" in a compartment (sorbed and aqueous phases combined), and IMPACT allows for degradation in the aqueous phase only. (SESOIL also allows for acidic, neutral, and basic hydrolysis, and IMPACT also allows for zero-order kinetics and Monod biodegradation kinetics, but these capabilities were not used in this study.)

J. **Volatilization**

SLM1 and PRZM do not include the vapor phase, and no volatilization is considered. IMPACT assumes that chemical reaching the soil surface volatilizes with no surface resistance, a procedure appropriate for volatile organic chemicals (Jury *et al*., 1990). The SESOIL model makes a similar assumption, but the process is applied to all chemical in the surface soil layer due to the compartmental nature of this model.

K. **Contaminant Transport**

SLM1 and PRZM calculate contaminant transport using a compartmental approach; any water in excess of field capacity that drains to the next lower soil layer will transport contaminant via aqueous bulk flow. PRZM has an option to enter a dispersion coefficient for the contaminant. However, the model's authors recommend simulating contaminant dispersion by using an appropriate soil layer thickness (see below), so this option was not used. Contaminant transport in

SESOIL is handled through the use of a retardation factor, derived from the adsorption coefficient, which is used to calculate the rate of contaminant movement relative to the water velocity. As in SLM1 and PRZM, any contaminant entering a soil compartment is assumed to be diluted into the entire compartment. In SESOIL, vapor-phase diffusion is calculated (but only in the upward direction) in order to allow chemical to be transported to overlying soil layers. The IMPACT model uses an advection-dispersion equation to calculate the transport of contaminants. This expression includes partitioning and degradation processes, and diffusive and dispersive processes of the contaminant in both the aqueous and vapor phases. One required parameter for the IMPACT model, soil dispersivity (used to calculate the dispersion coefficient), is not readily estimated without calibration data. For this study, an estimated value of 1 ft was determined by extrapolation of laboratory-measured dispersivities measured in soil column studies Williams *et al.*, 1994).

L. **Time Step**

The time step for SLM1 was set at 1 week. The time steps for SESOIL and PRZM are fixed at 1 d, although SESOIL's output is monthly. The time step for IMPACT is variable, but was set to 1 d for this study.

M. **Discretization of Soil Column**

The thickness of the soil layers varied among the four models, due to model formulation differences and recommendations of model authors. SLM1 has a set soil layer thickness of 2 ft. PRZM has a variable soil layer thickness, but it was set to a constant 5-cm thickness (for a total of 61 layers) because the model's authors recommended this thickness to simulate dispersion of contaminant in the soil column using "compartmental dispersion". For SESOIL, preliminary runs indicated that the soil layer (or sublayer) thickness did not have a large impact on results for the environmental scenario used in this study. Four soil layers were used; a 4-ft surface soil layer was followed by three 2-ft soil layers. IMPACT's soil layer thicknesses also do not have a large effect on results, although the model's authors recommend a relatively small increment. A 1-ft, layer thickness was used in this study.

N. **Miscellaneous Modeling Notes**

A minimum of one crop had to be specified when using the PRZM model. To minimize the effect of crops, one crop was set to emerge on day 1, mature on day

2, and be harvested on day 3 of the simulation. The contaminant was applied to the soil only and incorporated to a depth of 4 ft. A single soil horizon was assumed. For the IMPACT model, the top boundary condition was zero contaminant concentration in the liquid phase, and the bottom boundary condition was gravity flow.

O. The Contaminants

Several volatile organic compounds (VOCs) that are under consideration for regulation by the State of New Jersey were selected for study (Table 3). A majority are halogenated solvents, but a few oxygenated compounds and hydrocarbons are included. Solvents, with vapor pressures ranging from 50 to 600 mmHg at 25°C, include chemicals with a wide range of Henry's law constants (H). Acetone (dimensionless $H = 8.4 \times 10^{-4}$) strongly prefers the aqueous phase, while 1,1-dichloroethene ($H = 6.3$) displays significant vapor-phase behavior. Organics with intermediate volatility (1 to 10 mmHg) include bromoform, ethyl benzene, and 1,2-dichlorobenzene. The latter two compounds are rather strongly bound to soil (K_{oc}s of several hundred), while bromoform is only slightly sorbed ($K_{oc} = 60$). Acrylonitrile and the ketones, which are highly water soluble, are only minimally sorbed ($K_{oc} < 25$).

The reference for K_{oc} values for several of the most commonly occurring volatiles was a review by Uchrin (1991). Median K_{oc} values were picked from the range of values reported. K_{oc} values for compounds not included in this review were either obtained directly from Jury *et al*. (1990), Roy and Griffin (1985), EPA's Superfund Public Health Exposure Manual (EPA, 1986), or were estimated using a correlation equation of Hassett *et al*. (1983):

$$\log K_{oc} = 3.95\text{-}0.62 \log S$$

where S is the water solubility of the contaminant of interest (mg/l). The equation was developed using data from 107 nonpolar organics in water. Water solubilities were obtained from Mackay and Shiu (1981), except as noted.

Henry's law constants were obtained from a thorough literature survey by Mackay and Shiu (1981). A few were obtained from other sources, as noted in Table 3.

For purposes of this study, estimates of the half-lives of the chemicals in soil were taken from Howard *et al*. (1991). The upper estimate of the half-life range was used. The uncertainties of these numbers are substantial, for many of them are based on estimated aqueous aerobic half-lives. Most of the halogenated compounds, with the exception of methylene chloride and chloroform, had estimated half-lives of several months to 1 year. The nonhalogenated aromatic compounds, ketones, and acrylonitrile had estimated half-lives in soil of less than 1 month. The first-order degradation rates reported by Howard *et al.* were for total chemical in

TABLE 3
Chemical Properties of Compounds Studied

Chemical	CASRN	Water solubility (mg/l)[a]	K_{oc} (ml/g)	Henry's Law constant (25°C) (dimensionless)[a]	Half-life in soil (d)[b]
Acetone	67-64-1	Miscible	2.20e + 00[c]	8.42e – 04[c]	7
Acrylonitrile	107-13-1	79,000[c]	8.50e – 01[c]	3.61e – 03[c]	23
Benzene	71-43-2	1,780	1.00e + 02[d]	2.22e – 01	16
Bromoform	75-25-2	3,033	6.00e + 01[e]	2.50e – 02	180
2-Butanone (MEK)	78-93-3	2.68e+05[c]	4.50e + 00[c]	1.12e – 03[c]	7
Carbon tetrachloride	56-23-5	1,160	1.50e + 02[f]	8.07e – 01	360
Chlorobenzene	108-90-7	500	2.51e + 02[d]	1.41e – 01	150
Chloroform	67-66-3	7,900	3.00e + 01[e]	1.53e – 01	180
Chloromethane	74-87-3	5,350	6.00e + 00[g]	3.83e – 01	28
1,2-Dichlorobenzene	95-50-1	145	4.00e + 02[e]	7.66e – 02	180
1,3-Dichlorobenzene	541-73-1	123	4.00e + 02[e]	1.45e – 01	180
1,4-Dichlorobenzene	106-46-7	80	6.50e + 02[e]	6.69e – 02	180
1,1-Dichloroethane	75-34-3	5,100	4.60e + 01[g]	2.34e – 01	154
1,2-Dichloroethane	107-06-2	8,700	3.00e + 01[e]	4.44e – 02	180
1,1-Dichloroethene	75-35-4	400	2.00e + 02[e]	6.30e + 00	180
1,2-Dichloroethene (*trans*)	156-60-5	6,300	5.90e + 01[c]	2.70e – 01	180
1,2-Dichloroethene (*cis*)	156-59-2	3,500	4.90e + 01[c]	3.07e – 01	180
Ethylbenzene	100-41-4	167	3.80e + 02[c]	3.23e – 01	10
Methylene chloride	75-09-2	19,400	2.50e + 01[f]	1.05e – 01	28
4-Methyl-2-pentanone	108-10-1	19,000[f]	2.20e + 01[g]	2.10e – 03[g]	7
1,1,1,2-Tetrachloroethane	630-20-6	1,100	1.00e + 02[e]	1.14e – 01	66
1,1,2,2-Tetrachloroethane	79-34-5	3,000	5.00e + 01[e]	1.94e – 02	44
Tetrachloroethene	127-18-4	180	3.02e + 02[d]	9.28e – 01	360
Toluene	108-88-3	522	2.00e + 02[d]	2.70e – 01	22
1,1,1-Trichloroethane	71-55-6	720	1.00e + 02[d]	1.13e + 00	273
1,1,2-Trichloroethane	79-00-5	4,420	5.00e + 01[e]	4.84e – 02	365
Trichloroethene (TCE)	79-01-6	1,100	1.00e + 02[d]	3.65e – 01	360
o-Xylene	95-47-6	186	3.00e + 02[f]	2.02e – 01	28
m-Xylene	108-38-3	162	3.00e + 02[f]	2.82e – 01	28
p-Xylene	106-42-3	179	3.00e + 02[f]	2.86e – 01	28

[a] From Mackay and Shiu (1981) unless otherwise noted.
[b] From Howard *et al*. (1991).
[c] From EPA (1986).
[d] From Uchrin (1991).
[e] Calculated from water solubility and equation in Roy and Griffin (1985).
[f] From Roy and Griffin (1985).
[g] From Jury *et al*. (1990).

the soil, rather than for separate adsorbed and aqueous phases. For this study, these rates were also used as separate phase-degradation rates.

Air and water diffusion coefficients were taken as 0.43 and 4.3×10^{-5} m^2/d, respectively, per the recommendation of Jury *et al*. (1990), because the variation of these parameters among the compounds studied does not have a large impact on model results.

P. **Calculation of Example Soil Cleanup Criteria**

New Jersey groundwater standards for the compounds studied are indicated in Table 4. These criteria were recently adopted by the State of New Jersey for environmentally sensitive or potable aquifers (New Jersey Administrative Code, 1993). In this study, example soil cleanup criteria were calculated for each contaminant using the hypothetical environmental scenario and the four computer models, so that allowed groundwater concentrations were not exceeded. First, the aqueous concentration of the chemical just above the water table (soil layer immediately above water table) was taken as a function of time. For purposes of this study, a dilution factor of 100 was then applied to these aqueous concentrations to estimate dilution into groundwater. Although this factor is arbitrary, it has been used in the toxicity characteristic leaching potential procedure (TCLP) in site assessment (*Fed. Reg.*, 1990). To calculate example soil cleanup criteria, the maximum initial concentration in soil was determined for each contaminant that resulted in a peak groundwater concentration equal to its groundwater standard. Criteria above 500 ppm were not determined because aqueous solubility limits may be reached for some chemicals when the models calculate partitioning, and only the SESOIL model has a procedure for handling this situation. In addition, microbial activity may be inhibited at high levels of contaminant, and partition coefficients may become invalid due to the saturation of soil-binding sites.

III. **RESULTS AND DISCUSSION**

A. **Hydrology**

Table 5 summarizes the hydrological results for the four models, using the hypothetical environmental scenario. Average annual recharge to the water table, after allowing for runoff and evapotranspiration, were similar for SESOIL and IMPACT (14 and 15 in./year, respectively). PRZM calculated a higher average recharge (22 in./year). SLM1 recharge was set via the infiltration rate to approximate PRZM's recharge rate (21 in./year). The higher recharge rate for PRZM is largely due to its considerably lower calculated rate of evapotranspiration.

B. **Example Cleanup Criteria**

Example soil cleanup criteria were calculated using a hypothetical environmental scenario and the four unsaturated zone leaching models, assuming a dilution factor of 100 when the contaminant entered the water table (Table 4). Generally, there

TABLE 4

Example Soil Cleanup Criteria Calculated Using Four Unsaturated Zone Leaching Models and a Hypothetical Environmental Scenario

Contaminant	Groundwater std. (µg/l)	Degradation setting	Soil cleanup criteria (µg/g)			
			SLM1	PRZM	SESOIL	IMPACT
Acetone	700	No degradation	30	10	6	40
		Liquid phase only	>500		>500	>500
		Both phases	>500	>500	>500	
Acrylonitrile	50	No degradation	2	1	0.4	2
		Liquid phase only	200		50	500
		Both phases	200	300	50	
Benzene	1	No degradation	0.06	0.03	0.06	0.2
		Liquid phase only	10		100	20
		Both phases	90	>500	>500	
Bromoform	4	No degradation	0.2	0.1	0.06	0.3
		Liquid phase only	0.6		0.2	1
		Both phases	0.8	0.5	0.3	
2-Butanone (MEK)	300	No degradation	10	6	2	20
		Liquid phase only	>500		>500	>500
		Both phases	>500	>500	>500	
Carbon tetrachloride	2	No degradation	0.1	0.07	1	1
		Liquid phase only	0.2		2	2
		Both phases	0.4	0.2	3	
Chlorobenzene	4	No degradation	0.4	0.2	0.3	0.7
		Liquid phase only	1		0.6	2
		Both phases	5	5	10	
Chloroform	6	No degradation	0.3	0.1	0.1	0.6
		Liquid phase only	0.8		0.3	2
		Both phases	0.9	0.6	0.4	
Chloromethane	30	No degradation	1	0.6	2	5
		Liquid phase only	60		70	80
		Both phases	100	100	80	
1,2-Dichlorobenzene	600	No degradation	80	40	50	100
		Liquid phase only	200		90	400[a]
		Both phases	>500	>500	>500	
1,3-Dichlorobenzene	600	No degradation	80	40	70	200[a]
		Liquid phase only	200		100	400[a]
		Both phases	>500	>500	>500	
1,4-Dichlorobenzene	75	No degradation	10	6	8	20
		Liquid phase only	40[a]		10	60[a]
		Both phases	400	>500	400	
1,1-Dichloroethane	70	No degradation	3	2	3	10
		Liquid phase only	10		8	40
		Both phases	20	8	10	
1,2-Dichloroethane	2	No degradation	0.08	0.04	0.02	0.1
		Liquid phase only	0.2		0.06	0.5
		Both phases	0.3	0.2	0.08	
1,1-Dichloroethene	2	No degradation	0.2	0.08	>500	10
		Liquid phase only	0.5		>500	20
		Both phases	1	0.8	>500	

TABLE 4 (continued)

Example Soil Cleanup Criteria Calculated Using Four Unsaturated Zone Leaching Models and a Hypothetical Environmental Scenario

Contaminant	Groundwater std. (µg/l)	Degradation setting	Soil cleanup criteria (µg/g) SLM1	PRZM	SESOIL	IMPACT
1,2-Dichloroethene (*trans*)	100	No degradation	5	3	6	20
		Liquid phase only	20		10	50
		Both phases	20	10	20	
1,2-Dichloroethene (*cis*)	10	No degradation	0.5	0.2	0.6	2
		Liquid phase only	1		1	5
		Both phases	2	1	2	
Ethylbenzene	700	No degradation	90	40	100	200
		Liquid phase only	>500		>500	>500
		Both phases	>500	>500	>500	
4-Methyl-2-pentanone (MIBK)	400	No degradation	20	9	3	20
		Liquid phase only	>500		>500	>500
		Both phases	>500	>500	>500	
Methylene chloride	2	No degradation	0.09	0.05	0.03	0.2
		Liquid phase only	5		2	9
		Both phases	9	20	6	
1,1,1,2-Tetrachloroethane	10	No degradation	0.6	0.3	0.4	1
		Liquid phase only	6		3	20
		Both phases	20	20	30	
1,1,2,2-Tetrachloroethane	2	No degradation	0.09	0.04	0.02	0.1
		Liquid phase only	2		0.7	6
		Both phases	4	20	4	
Tetrachloroethene	1	No degradation	0.1	0.05	1	0.8
		Liquid phase only	0.2		2	1
		Both phases	0.5	0.3	6	
Toluene	1000	No degradation	90	40	100	200
		Liquid phase only	>500		>500	>500
		Both phases	>500	>500	>500	
1,1,1-Trichloroethane	30	No degradation	2	1	40	20
		Liquid phase only	4		70	30
		Both phases	6	3	100	
1,1,2-Trichloroethane	3	No degradation	0.1	0.08	0.04	0.2
		Liquid phase only	0.3		0.07	0.5
		Both phases	0.3	0.2	0.09	
Trichloroethene (TCE)	1	No degradation	0.06	0.03	0.1	0.2
		Liquid phase only	0.1		0.2	0.4
		Both phases	0.1	0.08	0.2	
o-Xylene	40	No degradation	4	2	4	10
		Liquid phase only	200[a]		200	>500[a]
		Both phases	>500	>500	>500	
m-Xylene	40	No degradation	4	2	6	10
		Liquid phase only	200[a]		200	>500[a]
		Both phases	>500	>500	>500	
p-Xylene	40	No degradation	4	2	6	10
		Liquid phase only	200[a]		200	>500[a]
		Both phases	>500	>500	>500	

[a] Calculated criteria are significantly affected by ignoring aqueous contaminant concentrations above the solubility limit. Criteria would be lower using a nonaqueous phase mechanism similar to that included in SESOIL.

TABLE 5
Hydrological Results from the Four Simulation Models

	Annual rainfall (in.)[a]	Annual runoff (in.)[a]	Annual evapotranspiration (in.)[a]	Annual recharge to groundwater (in.)[a]
SLM1	42	Not calculated	Not calculated	21
PRZM	34–54 (42)	4–9 (6)	13–17 (14)	16–29 (22)
SESOIL	42	<1	27	14
IMPACT	29–45 (39)	0.1–5 (3)	17–26 (21)	10–21 (15)

[a] Average values in parentheses.

was a linear relationship between the initial contaminant concentration and the resulting peak concentration in the groundwater. For the SESOIL model, there were a few exceptions. For compounds that had relatively high groundwater criteria (≥40 μg/l), the calculated soil-cleanup criteria were often relatively high (>100 μg/g). When this occurred with contaminants that had relatively low water solubilities (<1000 mg/l), aqueous concentrations at times exceeded the solubility limit. This situation occurred for some runs involving the dichlorobenzenes, ethyl benzene, toluene, and the xylenes. SESOIL has a mechanism that maintains chemical above the solubility limit as an immobile nonaqueous phase. Under these conditions, nonlinear behavior occurred with SESOIL in that increasing the initial soil concentration caused a larger-than-linear increase in the predicted groundwater concentrations. This resulted in lower soil-cleanup criteria than otherwise would have been calculated. Because maximum initial concentrations in the soil for this study were limited to 500 ppm, this deviation from linearity was minimal except for some model runs with the dichlorobenzenes and the xylenes, as noted in Table 4. In these cases, the cleanup criteria calculated by the other three models are higher than they would be had they used a procedure similar to SESOIL to handle the solubility limit.

The time at which the peak concentration in groundwater was reached for a particular contaminant was nearly identical with all four models (Figure 2). For one- or two-carbon halogenated solvents, where K_{oc}s are usually 100 or less, the peak concentration was usually reached in less than 2 years. This is illustrated for trichloroethene (Figure 2a), where the peak concentration was reached in about 500 d for all four models. For aromatic compounds, which usually have K_{oc}s between 100 and 600, the peak concentration was reached somewhat later, in 2 to 5 years. This is illustrated for 1,2-dichlorobenzene (in the absence of degradation), where the peak was reached in about 1100 d (Figure 2b). This uniform agreement in the time of maximum concentrations between the four models occurred despite differences in their hydrological and contaminant transport formulation, and also

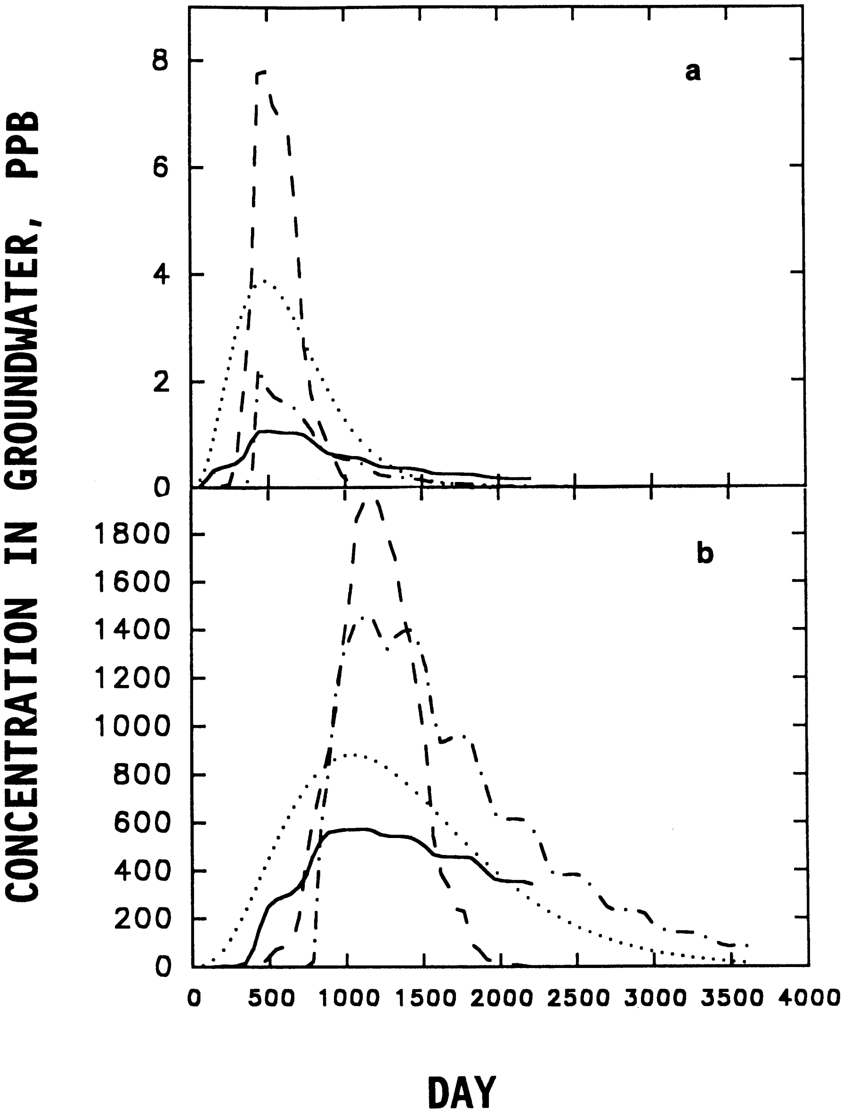

FIGURE 2. Simulated concentrations of contaminants in groundwater vs. time using four vadose zone leaching models. Degradation was set to zero. (a) Trichloroethene (0.25 μg/g initial concentration); (b) 1,2-Dichlorobenzene (125 μg/g initial concentration). — —, PRZM; ·····, SLM1; — · —, SESOIL; ——, IMPACT.

despite some differences in their calculated annual recharge to groundwater. This may be due to the relatively short transport times to groundwater for the chemicals studied (low K_{oc} values) and the relatively shallow water table used in the environmental scenario. This observation suggests that simplified treatment of water and/or contaminant transport may be adequate in some cases if only the time for the contaminant peak to reach groundwater is needed.

While the time for contaminant transport was nearly identical for all four models, the peak contaminant concentration in groundwater, and therefore the resulting soil cleanup criteria, varied depending on the model used (Figure 2). The model-based differences were not necessarily large, however. Frequently, the four models gave cleanup criteria that agreed to within an order of magnitude, and often the agreement was within a factor of two or three (Table 4). This occurred despite mechanistic differences between the four models, particularly the fact that two of the models, SLM1 and PRZM, do not include the vapor phase or volatilization mechanisms in their formulation. An estimate of the relative importance of volatilization vs. leaching to groundwater (in the absence of degradation) for these chemicals was made using the hypothetical environmental scenario and the screening model of Jury *et al*. (1983) (Table 6). Although volatilization of contaminant often accounted for a substantial fraction of the total fate of the chemical, this generally did not cause more than an order of magnitude difference between the cleanup criteria calculated using models that included volatilization (SESOIL and IMPACT) and those that did not (SLM1 and PRZM). The two most significant exceptions to this were the compounds 1,1-dichloroethene and 1,1,1-trichloroethane, which had cleanup criteria when determined by the SESOIL or IMPACT model that were usually more than an order of magnitude greater than those determined by SLM1 or PRZM. These two compounds have the largest Henry's law constants of all the chemicals studied, and volatilization was estimated to be 89 and 96% of the overall fate of 1,1,1-trichloroethane and 1,1-dichloroethene, respectively (Table 6). For these two compounds, using models that do not include the vapor phase is perhaps untenable.

PRZM always gave lower soil cleanup criteria than the SLM1 model because its predicted peak groundwater concentrations were higher (Figure 2). Neither of these models included vapor-phase transport or dispersion mechanisms. (PRZM allows the use of a dispersion coefficient, but the authors of PRZM recommended using instead a 5-cm layer depth to simulate dispersion compartmentally, as was done in this study.) Because both models calculate contaminant transport only via aqueous bulk flow, the primary variable responsible for the difference in the output between these two models is the thickness of the soil layer (five 2-ft layers in SLM1, and 61 5-cm layers in PRZM). An analogy can be made to chromatography in that the contaminant is migrating through more "theoretical plates" in the PRZM model than in the SLM1 model. This results in a sharper, higher peak concentration of contaminant when using the PRZM model. To confirm this, 1,2-dichlorobenzene was run using thicker soil layers in PRZM (Figure 3). Although the PRZM model would not run correctly with soil layers as thick as those used by SLM1 (2 ft), the model could be run using 16-cm (6.3-in.) layers. The 1,2-dichlorobenzene peak was broader and lower than when using 5-cm layers, and was closer in appearance to the SLM1 peak (Figure 3).

TABLE 6
Relative Importance of Leaching to Groundwater vs. Volatilizations for Volatile Organic Chemicals using Model of Jury *et al.* (1983) and a Hypothetical Environmental Scenario[a]

Contaminant	Percent leached to groundwater	Percent volatilized
Acetone	100	0
Acrylonitrile	99	1
Benzene	41	59
Bromoform	90	10
2-Butanone (MEK)	100	0
Carbon tetrachloride	15	85
Chlorobenzene	54	46
Chloroform	52	48
Chloromethane	27	73
1,2-Dichlorobenzene	71	29
1,3-Dichlorobenzene	54	46
1,4-Dichlorobenzene	75	25
1,1-Dichloroethane	39	61
1,2-Dichloroethane	82	18
1,1-Dichloroethene	4	96
1,2-Dichloroethene (*trans*)	35	65
1,2-Dichloroethene (*cis*)	32	68
Ethylbenzene	36	64
4-Methyl-2-pentanone (MIBK)	91	9
Methylene chloride	63	37
1,1,1,2-Tetrachloroethane	60	40
1,1,2,2-Tetrachloroethane	92	8
Tetrachloroethene	13	87
Toluene	35	65
1,1,1-Trichloroethane	11	89
1,1,2-Trichloroethane	81	19
Trichloroethene (TCE)	29	71
Xylenes	34	66

[a] A hypothetical environmental scenario illustrated in Figure 1. Degradation of contaminant not included.

Due to the "chromatography effect" previously discussed, the fact that PRZM did not include vapor-phase transport (which would broaden a contaminant peak due to diffusion) and also did not consider volatilization (which would decrease the amount of contaminant reaching the groundwater), this model most frequently gave the highest peak contaminant concentration in groundwater of the four models (which resulted in the lowest cleanup criteria). This was the case for about two thirds of the compounds studied. For the

chemicals on groundwater. While the actual degradation rate will be largely site specific, this conclusion is certainly true for certain environmental scenarios where microbial populations are known to be active. In these cases, it may be preferable to at least include a conservative estimate of degradation rates.

It was not the purpose of this study to include or discuss the field validation or field calibration of these models. Nonetheless, it is always recommended that field data be obtained (such as TCLP data, field-measured distribution coefficients, actual monitoring data, etc.). If such data are available, they should certainly be taken into consideration when using any simulation models to calculate the impact of soil contamination on groundwater.

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