

**SEEPAGE AND DRAINAGE FROM  
THE UNSATURATED ZONE AT THE  
PNM PERSON GENERATING STATION**

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WATER RESOURCES

GROUND-WATER POLLUTION WASTE  
UNIT

**Person Generating Station**

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EXECUTIVE SUMMARY

A previous investigation showed that unsaturated sediments beneath a waste tank at Public Service Company of New Mexico's Person Generating Station are contaminated by chlorinated organic solvents, primarily tetrachloroethylene (PCE). At the time of sampling, over 99% of the solvent was contained within the upper 20 meters. The depth to the water table is approximately 33.5 meters below land surface. At present most of the land surface above the contaminated zone is covered with low-permeable asphalt and concrete, which reduces infiltration and the rate of contaminant movement.

A mathematical analysis was used to determine future impacts of the contaminants in the unsaturated zone on the underlying aquifer. The analysis relies on determinations of the hydraulic conductivity of the unsaturated sediments, which were calculated from laboratory measurements of moisture retention. At the average field water content, the estimates of hydraulic conductivity may vary by two orders of magnitude, and therefore predicted rates of fluid flow through the unsaturated zone may also vary by this amount.

The mathematical analysis shows that if an impermeable surface covering were used to prevent natural infiltration, practically all of the contaminants would be retained in the unsaturated zone. Under this case, the maximum flux of PCE to the aquifer would occur in about 80 years and would be about  $7 \times 10^{-5}$  kg/yr. At this rate, concentrations of PCE in the aquifer

would be less than one part per billion below the present tank area.

An analysis was also made of a hypothetical situation in which the existing asphalt and cement cover around the tank area deteriorated and the land surface around the tank reverted to native conditions. It is estimated that 1% of the precipitation would infiltrate through the contaminants in the unsaturated zone, in this scenario. The time for infiltration to dissolve all the contaminants from the unsaturated zone would be on the order of seven thousand years if no other chemical or physical transformations occur, and the maximum flux of PCE would be about  $1.35 \times 10^{-2}$  kg/yr. Using a solute transport model for the aquifer, concentrations up to 20 ppb could extend about 85 meters down gradient from the present waste tank area. However, the actual concentrations could be considerably lower since numerous conservative assumptions were made to compute the mass flux of PCE which could drain from the unsaturated zone into the aquifer.

INTRODUCTION

Daniel B. Stephens and Associates was contacted to evaluate the rate of movement of organic constituents through the vadose zone to the water table at the PNM Person Generating Station. The data base for making these assessments was contained in the report "Final Soil Contamination Assessment and Preliminary Ground Water Contamination Assessment, PNM Person Generating Station," February 29, 1984, by Geoscience Consultants, Ltd., Albuquerque, New Mexico. That report defined the nature of the problem, and the extent of the contamination from sampling in the unsaturated zone. Most of these data were collected during the late fall of 1983 and winter of 1984.

The site under study is located in T9N.R3E.Sec.8, in Albuquerque, New Mexico, northeast of the intersection of Rio Bravo and Broadway boulevards. The waste tank was previously used by the Public Service Company of New Mexico to collect spent solvents, greases, oils, and steam cleaner condensate from a machine washing area. Chlorinated organic solvents were used in this cleaning operation for about six years. The waste tank was taken out of service in 1983 when it was found to be leaking. Most of the soil underlain by contamination is presently covered by pavement and concrete which have low permeability and restrict infiltration of natural precipitation.

Our first objective was to assess the significance of variability in available hydraulic properties of the unsaturated zone. The second objective was to calculate the seepage rate

from the unsaturated zone by estimating the mass flux of contaminants for two scenarios: 1) assuming that an impermeable cover exists at the tank area and prevents infiltration of precipitation; and 2) assuming that the present cover around the tank area deteriorates and returns to native conditions that allow infiltration of precipitation.

CHARACTERISTICS OF THE UNSATURATED ZONE

Hydrogeology

Nineteen coreholes and three observation wells have been drilled in the immediate area of the waste tank. Logs of these holes are given in the report by Geoscience Consultants Ltd. (1984). Briefly, the waste tank area is underlain by approximately 33.5 meters of unsaturated, relatively uniform, medium- to coarse-grained, fluvially-deposited sand with small amounts of clay and gravel. The clay and gravel lenses are reported to not exceed 20 centimeters in thickness. A more detailed description of the site geology is given in the report mentioned previously by Geoscience Consultants, Ltd.(1984).

In the unsaturated zone, disturbed samples have been collected from the coreholes every 1.5 to 3.0 meters to a total depth of 27.4 meters in most of the holes (Geoscience Consultants Ltd., 1984). The samples were analyzed for gravimetric water content and concentration of PCE (tetrachloroethylene). The average bulk density at field moisture content of these samples is about 1.61 g/cc. The arithmetic mean of reported volumetric water contents is about 0.074 cm<sup>3</sup>/cm<sup>3</sup>. The moisture content distribution for these coreholes appears to be relatively uniform, with only slight deviations from the mean water content value which presumably are due to stratification. We infer from this that the variability of the particle size throughout the profile is small. There do not appear to be any zones of anomalously high moisture content which might indicate that a

wetting front is still advancing through the profile after the washdown practices ceased.

The fact that the profile is relatively uniform in moisture content may suggest that a state of dynamic equilibrium exists in the profile. A dynamic equilibrium in this unsaturated zone implies that there is a balance between inflow to the profile from the infiltration of natural precipitation and outflow from the profile as recharge to the aquifer. Under this condition, the seepage rate through the unsaturated zone would be approximately equal to the hydraulic conductivity at the insitu water content. Insitu pore fluids and contaminants could be displaced into the aquifer by infiltrating precipitation.

On the other hand, a state of static equilibrium could also be inferred from available moisture content data. A static equilibrium condition would represent the moisture distribution above the water table when drainage ceases and vertical hydraulic gradients are zero. A static equilibrium condition could develop beneath an impermeable surface cover. At static equilibrium, the flow rate in the unsaturated zone is zero and permanent waste storage in the unsaturated zone could occur. Given the relatively uniform, low moisture content observed in the profile, it is difficult to distinguish between a state of dynamic and static equilibrium on the basis of water content. Substantial variations in pressure head and hydraulic gradient may occur without a substantial change in water content under the relatively dry field conditions. In this report both dynamic and static

equilibrium conditions will be discussed.

Distribution of Contaminants

The samples obtained from the coreholes for chemical analyses by Geoscience Consultants Ltd. were frozen after collection. The laboratory performing the analyses thawed the samples and a portion of the sample was used for methanol extraction. The extract was then analyzed using gas chromatography with electron capture detection. The results are reported as parts per million (ppm) of PCE; that is, grams of PCE per million grams of sample from the field. Figure 1 shows average concentration profiles of PCE. This figure was compiled by averaging PCE concentrations at each depth. The chemical analyses indicate that more than 99% of the total amount of PCE in the 33.5 m thick unsaturated zone is contained within the upper 20 m of the profile. Below about the 20 m depth, PCE concentrations average about 0.013 ppm and are reported not to exceed 0.084 ppm.

For our assessment, the volume of contaminated soil was estimated from the cross-sectional area within which the PCE concentration exceeds 0.01 ppm for each depth in the profile from which samples were taken. The average horizontal area containing these levels of PCE between the 3.0 and 27.4 m depths is 45.6 m<sup>2</sup>. This horizontal area ranges from 4.8 m<sup>2</sup> at 27.4 m depth to 72 m<sup>2</sup> at 9.1 m depth (Table 1). Within the 33.5 m depth of unsaturated sediments, there would be approximately 103 kg of PCE in the soil assuming a field bulk density of about 1.61 g/cc. The

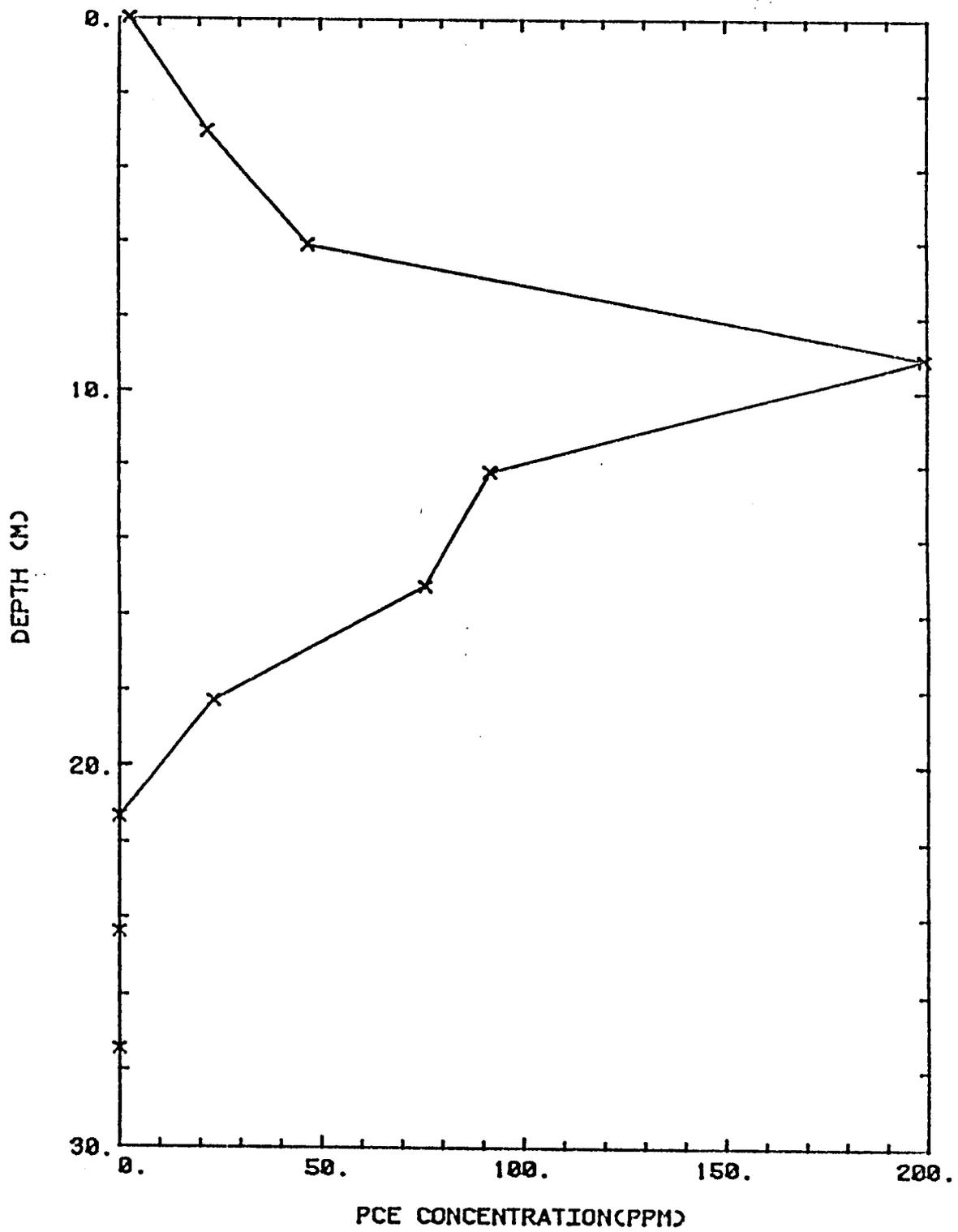


Figure 1. -- Concentration profile of PCE.

Table 1. -- Horizontal area within which PCE exceeds 0.01 ppm.\*

<u>Depth (m)</u>	<u>Area (m<sup>2</sup>)</u>
3.0	67.61
6.1	65.97
9.2	71.91
12.2	51.69
15.2	71.38
18.3	34.26
21.3	23.84
24.4	18.89
27.4	4.82

\* Basic Data From Geoscience Consultants, Ltd. (1984).

fact that lateral spreading of contaminants is a maximum at intermediate depths and diminishes with increasing depth, suggests that stratification and capillarity have significant effects on the direction and rate of PCE migration. Without stratification to create essentially an anisotropic medium, the plume of contamination in the unsaturated zone would be expected to expand with depth.

The solubility limit of PCE in water is reported to be about 150 mg/l at 20 degrees celsius (Hughes et al., 1985); this would correspond to about 6.9 ppm of PCE on a field weight basis when the average volumetric water content is 0.074 cm<sup>3</sup>/cm<sup>3</sup>. Above a depth of about 20 m, PCE concentrations in the soil exceed the solubility limits in the pore water. In this zone, PCE is either dissolved in other liquids or it exists in its own phase as a so-called non-aqueous phase liquid. Below about 20m, concentrations are less than the solubility limits. Thus PCE in other phases appears to be lagging behind the aqueous phase PCE in the vadose zone. Owing to the nature of geologic heterogeneity, capillary effects, and characteristics of the various organic fluids in the waste, the non-aqueous phase PCE may be much less mobile compared to the aqueous phase, based on the observed vertical distribution of PCE. It is possible at the relatively low moisture contents measured in the field that PCE above 20m may be mostly in a discontinuous phase, trapped in narrow pore throats and held at the so-called residual saturation. That is, there may not be a means for PCE to flow from one pore to another

under present conditions. It may be expected that water will preferentially wet the soil matrix relative to PCE as a non-aqueous phase and tend to cause blobs of PCE to become isolated. However, if PCE does exist as a discontinuous fluid phase, infiltration of precipitation may still move through the profile and dissolve PCE to the limit of its solubility, about 150 mg/l.

Depending upon the relative wettability of the PCE and the water, it is also possible that some PCE which exists as a non-aqueous phase or in solution with another fluid may be displaced by infiltrating precipitation. This would be more likely to occur if the infiltration rate were large.

To explain the observed variability of PCE in the unsaturated zone in Figure 1, either the strength of the source of contamination was highly variable, or physiochemical processes have selectively retarded or retained the non-aqueous phase above 20m. Liquid and vapor diffusion are also mechanisms which would transport relatively small amounts of PCE in the unsaturated zone. PCE has a fairly strong tendency to be retained by soils, according to Griffin and Roy (1985). After PCE is dissolved, its velocity is significantly retarded with respect to pure water. Durant and McKay (1985) report retardation factors for PCE in a stratified sandy aquifer to range from 5.39 to 27.34. (The retardation factor is the ratio of the water velocity to the contaminant velocity.) McCarty et al. (1984) and Griffin and Roy (1985) indicate that PCE may be biodegradable under anaerobic conditions, making it possible for PCE to be broken down into

other products. PCE also will volatilize. In aqueous solutions open to the atmosphere, PCE has a residence half-life of about 30 minutes (Hughes et al., 1985). Thus, PCE should not move through the unsaturated zone as rapidly as predicted by analytical models used in our analyses.

Hydraulic Properties

Three disturbed samples of unsaturated sediments were obtained by Geoscience Consultants Ltd. from the PS-4 corehole at the 7.6, 12.2, and 21.4 meter depths, for analyzing hydraulic properties. The samples were sent to the New Mexico Tech Soil-Water Research Laboratory for analysis. Each sample was re-packed into a 100 cc stainless steel ring to a dry bulk density of 1.55 g/cc. The saturated hydraulic conductivity of the samples was determined in a laboratory permeameter. The average saturated hydraulic conductivity was approximately  $9.07 \times 10^{-3}$  cm/sec. The samples were subsequently placed in a hanging column apparatus to determine moisture retention characteristics (the water content [ $\theta$ ] versus pressure head [ $\psi$ ] relationship) for both drainage and imbibition. The moisture retention results for drainage were then used to calculate unsaturated hydraulic conductivity,  $K$ , with a model by Mualem (1976) and computer procedure by van Genuchten (1978). One of the parameters, WCR, is specified by the model user, and van Genuchten's program fits the other two parameters,  $\alpha$  and  $n$ , to cause the best fit of the measured retention data to the func-

tional relationship:

$$\theta = \text{WCR} + \frac{\theta_s - \text{WCR}}{(1 + (\alpha\psi)^n)^m} \quad (1)$$

$$m = 1 - 1/n \quad (0 < m < 1; n > 1)$$

where  $\theta_s$  is saturated water content. The resulting curve-fit parameters are then used to predict the relationship between unsaturated hydraulic conductivity and water content or pressure head in the following relation:

$$K_r(\psi) = \frac{(1 - (\alpha\psi)^{n-1} (1 + \alpha\psi^n)^{-m})^2}{(1 + (\alpha\psi)^n)^{m/2}} \quad (2)$$

The resultant K-theta or K-psi relationship can be very sensitive to the specified model parameter, WCR, as shown by Stephens and Rehfeldt (1985) for a fine sand similar to the one at the PNM site. This fact will be illustrated graphically later on.

Initial model results for the theta-psi and K-psi relationships were shown in the Geoscience Consultants, Ltd. (1984) report for each of the three soil samples. The theta-psi relationship for the 21.4 meter depth samples was considered questionable, owing to the relatively low saturated water content; therefore, only the 7.6 and 12.2 meter depth samples were chosen for use in a sensitivity analysis. Our analysis was limited to drainage data because, on the average, this curve should provide conservatively large values of K for a particular value of pressure head.

Figure 2 shows the measured theta-psi values obtained for

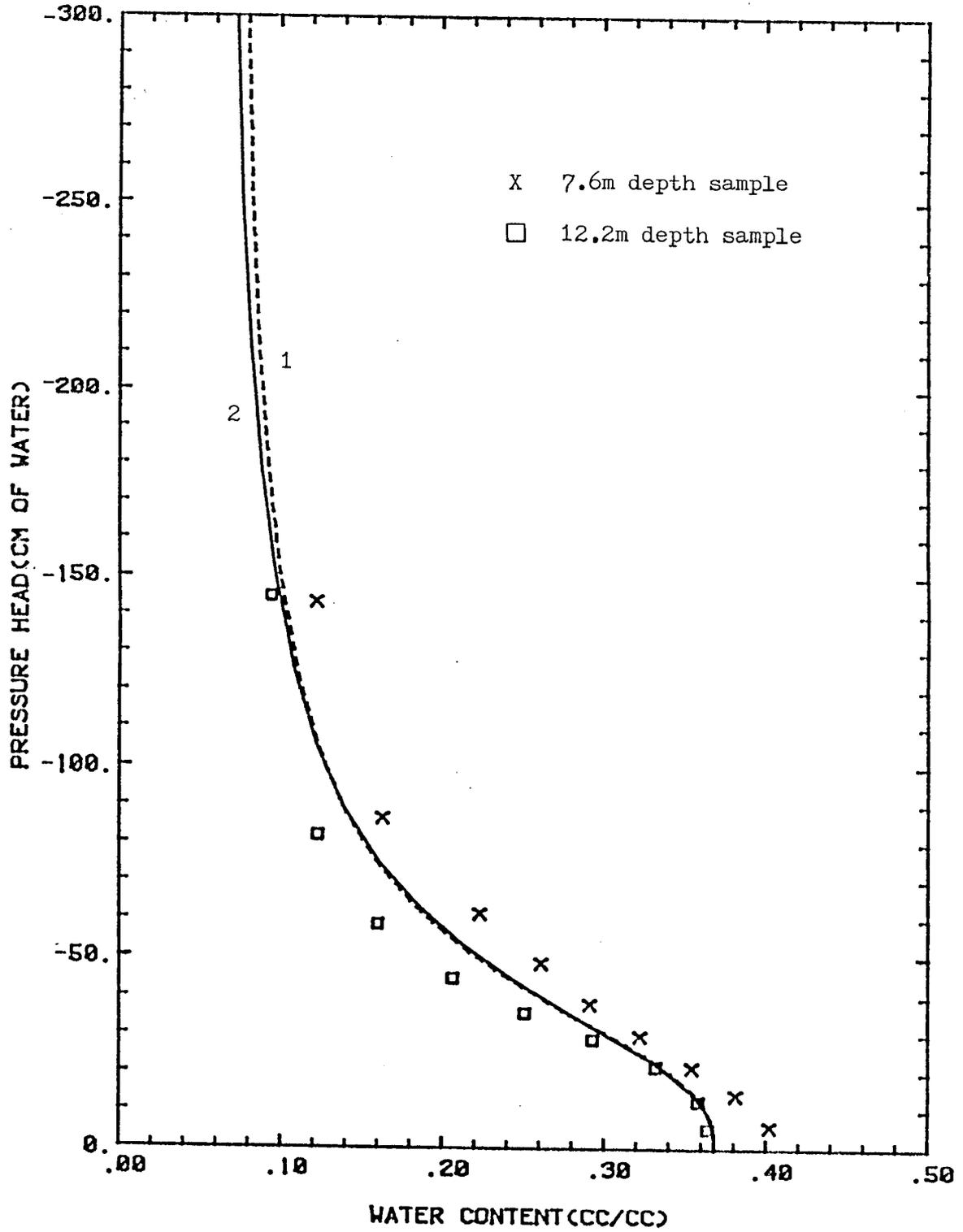


Figure 2. -- Moisture retention characteristics. Mualem's model results versus laboratory results. Curve 1 is for WCR = 0.07 cc/cc; curve 2 is for WCR = 0.06 cc/cc.

both the 7.6 and 12.2 meter depth samples. Also shown on Figure 2 are two curves fit through the combined measured data, as determined by the van Genuchten procedure. These two curves illustrate the difference in the predicted theta-psi relationship for two separate specifications of the fitting parameter:

WCR = 0.07 cm<sup>3</sup>/cm<sup>3</sup> (hydraulic conductivity relationship 1) and WCR = 0.06 cm<sup>3</sup>/cm<sup>3</sup> (hydraulic conductivity relationship 2). These two values of WCR were selected based on laboratory measurements of water content at high negative pressure heads. Stephens and Rehfeldt (1985) concluded that improved accuracy in the calculated unsaturated conductivity may be obtained when WCR is set equal to the water content measured at high negative pressure head. In order to calculate conductivities in the range of water contents observed in the field, WCR must be less than the average field water content, 0.074 cm<sup>3</sup>/cm<sup>3</sup>.

The calculated K-theta relationships for WCR equal to 0.07 and 0.06 cm<sup>3</sup>/cm<sup>3</sup> in Figure 3 are substantially different at low moisture content. For example, at the field water content of 0.074 cm<sup>3</sup>/cm<sup>3</sup>, the corresponding K values are 1.52 x 10<sup>-2</sup> cm/yr and 9.85 x 10<sup>-1</sup> cm/yr for the cases where WCR is 0.07 and 0.06 cm<sup>3</sup>/cm<sup>3</sup>, respectively. There is almost two orders of magnitude difference in predicted K values near the average field water content.

To determine whether these K-theta curves are reasonable, we will invoke the assumption that the soil profile is in dynamic equilibrium. Under this condition, Darcy's equation can be used

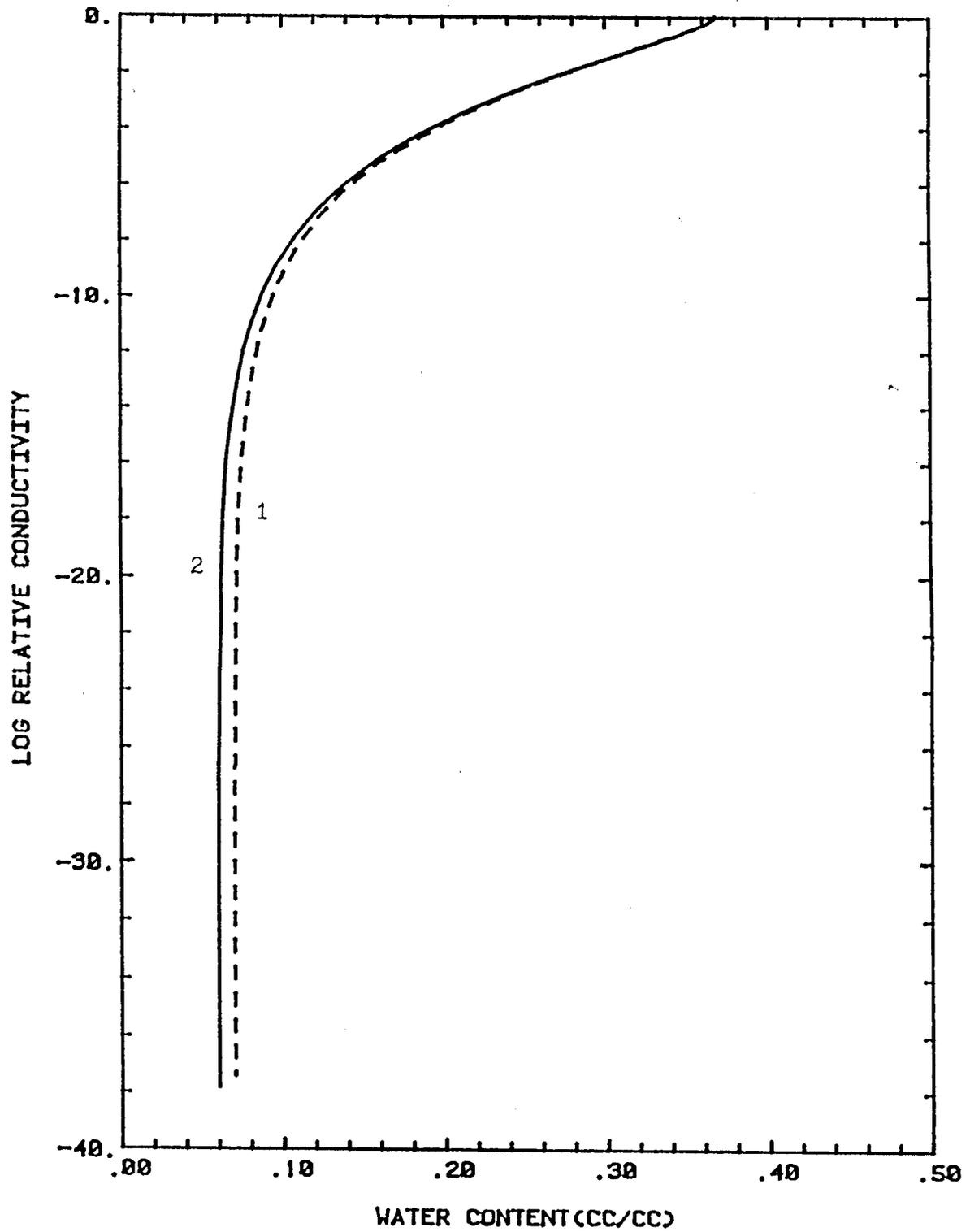


Figure 3. -- Calculated unsaturated conductivity from Mualem's model.  
 Curve 1 is for WCR = 0.07 cc/cc; curve 2 is for WCR = 0.06 cc/cc.

to calculate the soil water flux,  $q$ , through the unsaturated sediments, assuming they are uniform. Darcy's equation can be represented as:

$$q = K (\theta) \times i \quad (3)$$

where  $K (\theta)$  is the unsaturated hydraulic conductivity as a function of water content, and  $i$  is the hydraulic gradient. For our assumed state of dynamic equilibrium and uniform water content,  $i$  is equal to unity. Therefore, from Equation 3 and the two estimates of  $K$  at the average field water content, the flux would be 0.015 cm/yr for conductivity relationship 1 and 0.985 cm/yr for conductivity relationship 2. The National Oceanic and Atmospheric Administration's annual summary of 1982 indicates the 1941-1970 average annual precipitation is 19.7 cm/yr for Albuquerque. The flux estimates would then correspond to a recharge rate that was 0.08% or 5.0% of the precipitation rate for the cases of WCR equal to 0.07 and 0.06 cm<sup>3</sup>/cm<sup>3</sup>, respectively. These calculated fluxes are considered to be within the range typical of natural recharge rates in sandy soils of this arid region.

The land surface near the waste tank is already covered over a substantial area with asphalt and concrete which restrict infiltration. If any natural recharge does occur in the immediate vicinity of the waste tank, the recharge rate is undoubtedly lower than would occur beneath native material. Thus, conductivity relationship 1 is probably more representative of the profile. If the existing cover were partially destroyed or decomposed in future years, then an upper limit to recharge of

perhaps 1% of precipitation could be expected.

The range of darcian flux values discussed above can be translated into a range of particle velocities by dividing by the average water content in the profile,  $0.074 \text{ cm}^3/\text{cm}^3$ . The average fluid particle velocity would therefore be between 0.21 and 13.3 cm/yr for the recharge rates of 0.08 and 5.0% of precipitation. For a recharge rate corresponding to 1% of precipitation, the average water particle velocity would be about 2.7 cm/yr.

CONTAMINANT TRANSPORT THROUGH THE UNSATURATED ZONE

Two cases were analyzed to predict the rate at which PCE will move through the unsaturated zone. In the first, we assume that an impermeable cover is placed over the land surface to prevent any infiltration. In this case, all the seepage to the aquifer is by slow drainage of fluids in the profile at present. This case corresponds most closely with existing conditions, based on available data. For the second case, we assume that the existing cover material in the tank area deteriorates, and has little effect on reducing the natural recharge through the profile.

Impermeable Cover

For this case, we assume that an impermeable cover is placed over the affected area to prevent infiltration of precipitation. The analytical approach taken here to evaluate this scenario is a variation of a method described by Hillel et al. (1972), called the instantaneous profile method, which was originally a field and laboratory method to determine unsaturated hydraulic conductivity. In the instantaneous profile method, the soil is flooded over a large area until the profile is deeply wetted. The water supply is closed and the surface is covered to prevent evaporation. Measurements of moisture content and pressure head during drainage are used to calculate K.

This procedure just described is analogous to the infiltration events at the site beneath an impermeable surface cover.

However, in the present case, the assumption is made that the hydraulic conductivity is known. We want to predict the rate of fluid drainage from the unsaturated zone with a surface cover in place. In the first step of the calculation, the darcian velocity as a function of time is determined according to:

$$\int_0^z \frac{\partial \theta}{\partial t} dz = q = K(\theta_{avg}) i \quad (4)$$

The hydraulic conductivity during a discrete time interval of drainage corresponds to the average water content during that interval. We assume the hydraulic gradient,  $i$ , is equal to unity, and therefore the hydraulic conductivity is directly proportional to the change in water content with time. Furthermore, if the profile drains uniformly with depth, then the left side of the equation above can be integrated over the entire vertical profile in one increment. These assumptions are often made without substantial loss in accuracy. However, in our analysis of solute transport, the profile is discretized into eleven cylindrical cells three meters thick. During a discrete time interval, each cell loses moisture at the same rate. The fluid drained from the bottom of the column of cells at any time is equal to the sum of the drainage leaving each of the cells. In the second step of the calculation, the mass of solute leaving a cell per unit time,  $M$ , is calculated from:

$$M(t) = C A q(t) \quad (5)$$

where  $C$  is the average concentration of solute in the pore fluid,

A is the cross-sectional area within which flow is occurring, and q is obtained from Equation 4 for each cell. Each cell is assigned an initial concentration which approximates the field conditions shown in Figure 1. During any time step, the concentration in each cell changes due to the instantaneous mixing of drainage fluid from the cell directly above it. Therefore, at the end of a time step, the concentration in a particular cell is calculated according to:

$$C = \frac{(\text{mass of PCE in cell}) + (\text{mass of PCE drained into cell})}{(\text{volume of fluid in cell}) + (\text{volume of fluid drained into cell})} \quad (6)$$

Before the next time step, concentrations of PCE in each cell are reinitialized based on the water content, and losses and gains of PCE from the cell. This procedure is carried out until the estimated particle velocity is negligible and the profile approaches static equilibrium. The PCE which actually drains into the aquifer occupies voids in the lower portion of the unsaturated zone. This approach produces mass flux estimates for a draining profile, based on the assumption that dispersion and retardation are negligible and that advection is the primary mechanism of transport in the unsaturated zone.

Table 2 shows the rate of drainage and mass flux of PCE out of the profile characterized by hydraulic conductivity relationship 1. Practically all the PCE is still in the profile after equilibrium is reestablished, based on the assumptions and analyses. Nearly the same result is achieved with hydraulic

Table 2. -- Analysis of outflow from the unsaturated zone for impermeable surface cover case, assuming unsaturated hydraulic conductivity relationship 1.

Time (yrs)	Water Content (cm <sup>3</sup> /cm <sup>3</sup> )		q (cm/s)	Mass Flux (kg/yr)	Mass Drained (kg)
	Begin- ning of Time Step	End of Time Step			
1.397E+02	.0740	.0735	3.807E-10	5.787E-07	8.086E-05
3.760E+02	.0735	.0730	2.251E-10	3.525E-07	1.641E-04
8.123E+02	.0730	.0725	1.219E-10	2.055E-07	2.538E-04
1.724E+03	.0725	.0720	5.835E-11	1.118E-07	3.557E-04
4.018E+03	.0720	.0715	2.318E-11	5.358E-08	4.787E-04
1.191E+04	.0715	.0710	6.739E-12	1.975E-08	6.346E-04
6.332E+04	.0710	.0705	1.035E-12	3.978E-09	8.390E-04
2.971E+06	.0705	.0700	1.829E-14	9.387E-11	1.112E-03

conductivity relationship 2 (Table 3). The reasons for this are attributed to the low hydraulic conductivity during drainage from insitu moisture content and the low concentrations in the lower regions of the unsaturated zone.

As a simple check on the analyses in Tables 2 and 3, note that the total drainage from the profile is 6.1 and 21.3 m<sup>3</sup> of fluid for conductivity models 1 and 2, respectively. Assuming the average volumetric moisture content is 0.074 cm<sup>3</sup>/cm<sup>3</sup> in a vertical cylinder having a cross-sectional area of 45.6 m<sup>2</sup>, then the fluid which drains would be contained in the lower 1.8 and 6.3m of the cylindrical profile for conductivity models 1 and 2, respectively. The average concentration of PCE in this zone is less than about 0.2 mg/l. Thus, the total mass of PCE drained from the profile would be about 0.0012 and 0.0042 kilograms for conductivity models 1 and 2, respectively. These quantities are negligible compared to the 103 kilograms in the unsaturated zone.

#### Native Cover

Piston Displacement Approach. For comparative purposes of evaluating the benefits of an impermeable surface cover, we also studied the worst-case scenario, that is, complete displacement by infiltration of all PCE, regardless of its phase. Such a scenario could occur if the existing asphalt/concrete around the tank deteriorates in future years and the area eventually returns to native conditions.

For the computations, a simple piston displacement model was

Table 3. -- Analysis of outflow from the unsaturated zone for impermeable surface cover case, assuming unsaturated hydraulic conductivity relationship 2.

Time (yrs)	Water Content (cm <sup>3</sup> /cm <sup>3</sup> )		q (cm/s)	Mass Flux (kg/yr)	Mass Drained (kg)
	Begin- ning of Time Step	End of Time Step			
1.823E+00	.0740	.0735	2.918E-08	4.437E-05	8.086E-05
3.917E+00	.0735	.0730	2.539E-08	3.976E-05	1.641E-04
6.338E+00	.0730	.0725	2.197E-08	3.703E-05	2.538E-04
9.152E+00	.0725	.0720	1.890E-08	3.623E-05	3.557E-04
1.244E+01	.0720	.0715	1.616E-08	3.736E-05	4.787E-04
1.632E+01	.0715	.0710	1.373E-08	4.023E-05	6.346E-04
2.091E+01	.0710	.0705	1.157E-08	4.449E-05	8.390E-04
2.641E+01	.0705	.0700	9.674E-09	4.964E-05	1.112E-03
3.305E+01	.0700	.0695	8.017E-09	5.514E-05	1.478E-03
4.113E+01	.0695	.0690	6.578E-09	6.036E-05	1.966E-03
5.109E+01	.0690	.0685	5.339E-09	6.475E-05	2.611E-03
6.352E+01	.0685	.0680	4.280E-09	6.779E-05	3.453E-03
7.924E+01	.0680	.0675	3.384E-09	6.912E-05	4.540E-03
9.943E+01	.0675	.0670	2.634E-09	6.849E-05	5.923E-03
1.258E+02	.0670	.0665	2.014E-09	6.585E-05	7.662E-03
1.611E+02	.0665	.0660	1.508E-09	6.129E-05	9.823E-03
2.093E+02	.0660	.0655	1.103E-09	5.508E-05	1.248E-02
2.772E+02	.0655	.0650	7.835E-10	4.763E-05	1.571E-02
3.761E+02	.0650	.0645	5.380E-10	3.942E-05	1.961E-02
5.262E+02	.0645	.0640	3.543E-10	3.102E-05	2.427E-02
7.664E+02	.0640	.0635	2.214E-10	2.298E-05	2.979E-02
1.178E+03	.0635	.0630	1.294E-10	1.580E-05	3.628E-02
1.947E+03	.0630	.0625	6.907E-11	9.855E-06	4.387E-02
3.583E+03	.0625	.0620	3.252E-11	5.385E-06	5.268E-02
7.785E+03	.0620	.0615	1.266E-11	2.419E-06	6.284E-02
2.265E+04	.0615	.0610	3.577E-12	7.844E-07	7.451E-02
1.242E+05	.0610	.0605	5.239E-13	1.311E-07	8.782E-02
6.411E+06	.0605	.0600	8.460E-15	2.406E-09	1.029E-01

employed to estimate the mass flux of PCE exiting from the unsaturated zone for a worst case scenario, in which infiltration of precipitation occurs as though no asphalt or cement cover material are present. This model assumes that there eventually will be complete displacement of the insitu pore fluids by infiltrating precipitation. There would be a unit displacement of PCE-laden water at the water table for every unit inflow of fresh water at the top of the soil profile. The rate of displacement is calculated from the average fluid particle velocities determined at insitu moisture content. This method therefore assumes that no dispersion or retardation occurs. This approach is consistent with the concept of dynamic equilibrium in the unsaturated profile. This approach assumes that PCE in its own phase as well as PCE in solution with water or other chemicals will be displaced equally. As previously discussed, this assumption is considered to be conservative, in that known concentrations shown in Figure 1 suggest that PCE above 20m is either dissolved in fluids other than water or exists as a non-aqueous phase liquid, whereas PCE below this depth may be dissolved in water, based on solubility limits.

In the piston displacement calculation, the initial concentration in the profile is variable and approximates the observed concentrations (Figure 4). For each case, the mass of PCE arriving at the aquifer each year is predicted for the two K-theta relationships discussed previously.

In this piston displacement approach, the initial concentra-

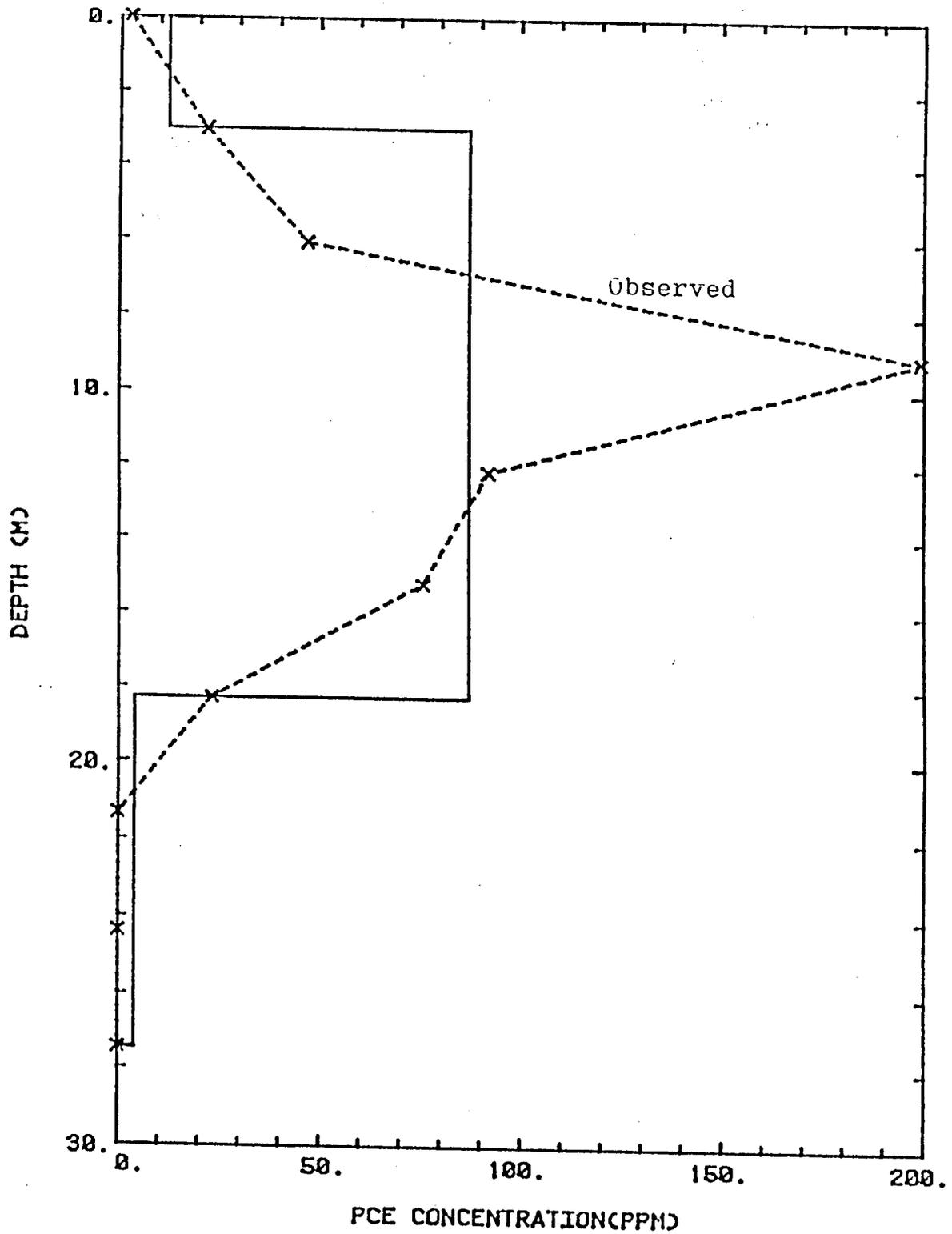


Figure 4. -- Assumed initial distribution of PCE for piston displacement analysis and observed concentrations.

tions of PCE vary step-wise with depth, in approximation of observations in the field. From land surface to 3.1 meters the average concentration is approximately 12.3 ppm on a field weight basis, or 268 mg/l in the pore fluid. The 3.1 to 18.3 meter depth interval has markedly higher concentrations of PCE than the rest of the profile (Figure 4). The average concentration within this zone is approximately 87.3 ppm or 1900 mg/l. The average concentration below this zone, from 18.3 to 33.5 meters depth, is about 2.3 ppm, or 50.7 mg/l. The assumption is made in the piston flow model that these average concentrations contained in discrete depth intervals will remain intact as they are displaced downward toward the water table under a constant velocity associated with the natural recharge.

For the case where the recharge rate is approximately 0.08% of the precipitation rate (conductivity relationship 1), the mass flux would initially be about  $3.53 \times 10^{-4}$  kg/yr for about 7403 years. During the next 7403 years the mass flux would be about  $1.32 \times 10^{-2}$  kg/yr. Subsequently, the flux would decrease to about  $1.86 \times 10^{-3}$  kg/yr for the final 1481 years. The total time of displacement would be about 16,287 years. Figure 5 shows these results graphically.

For the case where the recharge flux was 5.0% of the precipitation rate (conductivity relationship 2), the mass flux behavior for this model would be represented by Figure 6. The initial mass flux is estimated at  $2.28 \times 10^{-2}$  kg/yr for a period of 115 years. The main peak of PCE entering the saturated zone

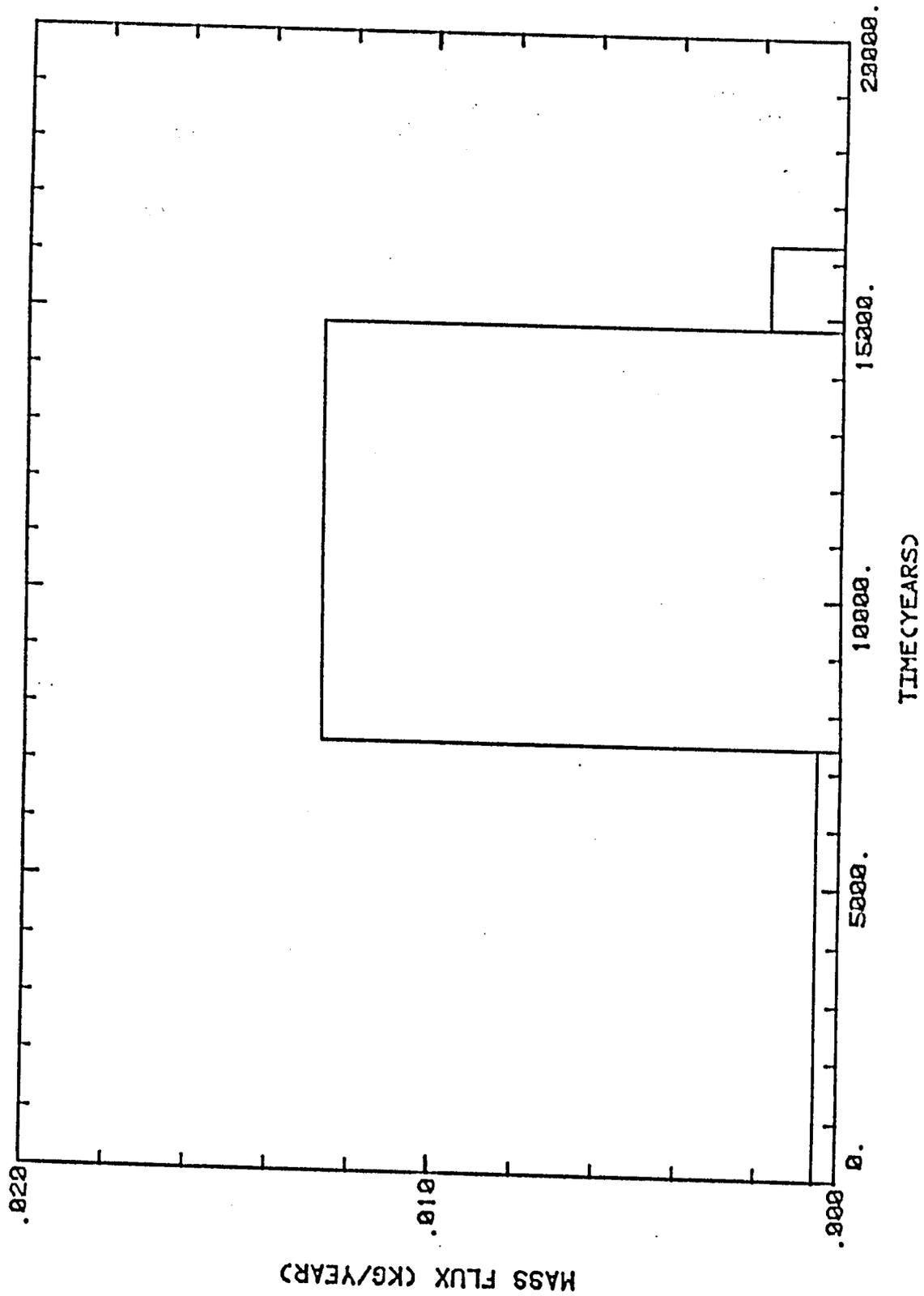


Figure 5. -- Mass rate of PCE outflow from the unsaturated zone assuming piston displacement and hydraulic conductivity relationship 1. Native cover case.

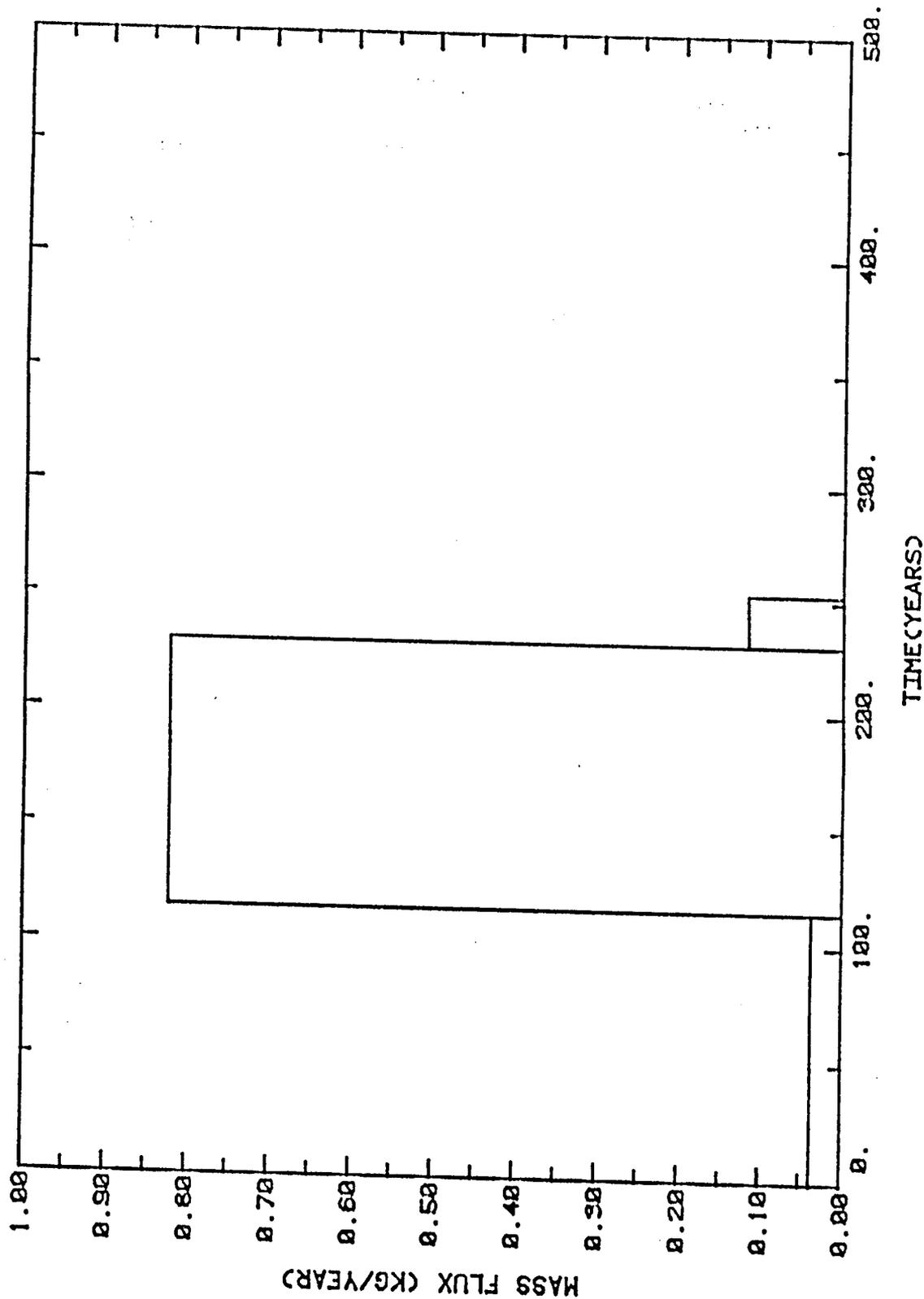


Figure 6. -- Mass rate of PCE outflow from the unsaturated zone assuming piston displacement and hydraulic conductivity relationship 2. Native cover case.

would be at 0.853 kg/yr for the 115 years following the first pulse. For about 23 years after this, the mass flux would be about 0.120 kg/yr. Therefore, this model predicts a total time of 253 years to displace 103 kg of PCE from the unsaturated zone.

We expect that the probable condition for the native cover scenario (ie., degradation of existing asphalt and cement cover and return to native conditions) would fall somewhere between conductivity relationship 1 (0.08% infiltration of precipitation) and conductivity relationship 2 (5% infiltration of precipitation). We have selected a conductivity relationship in which infiltration is 1% of precipitation as the probable condition for the native cover case. For this condition, the average initial flux of PCE to the aquifer would be about  $4.6 \times 10^{-3}$  kg/yr for 573 years. The peak loading rate would be approximately 0.171 kg/yr averaged over the next 573 years. The average PCE loading during the final phase would be about  $2.40 \times 10^{-2}$  kg/yr for 115 years.

In providing a worst-case analysis, dispersive and sorptive processes have been neglected and a maximum vadose zone cross-sectional area which could contribute significantly to the contaminant flux was assumed. Just above the water table, the area containing more than 0.01 ppm of PCE is only 4.82 m<sup>2</sup>, whereas we assumed that the contaminant flux would flow through a cross-sectional area of 45.6 m<sup>2</sup>. This assumption alone may cause an over estimation of the loading on the aquifer by nearly an order of magnitude. Actual concentrations in the discharge are

expected to be smaller because of dispersion, and the arrival of solutes to the aquifer would be delayed because of sorption.

Dissolution Approach. Because there is some evidence that the PCE above 20 m may be relatively immobile owing perhaps to capillary effects, displacement of PCE by infiltrating precipitation at low moisture contents and small fluid velocities may not actually occur to a significant extent. If this is true, then the worst-case would become that of precipitation leaching through the PCE-rich zone and slowly dissolving it. The maximum concentration of PCE in displaced fluid would be the limit of PCE solubility in water, about 150 mg/l. The contaminant loading would be simply the product of the recharge rate times the cross-sectional area times 150 mg/l. For the recharge rates of 0.08, 1.0 and 5.0 % of precipitation, the mass flux would be about  $1.036 \times 10^{-3}$ ,  $1.346 \times 10^{-2}$ , and  $6.731 \times 10^{-2}$  kg/yr, respectively. Very rough estimates of the time required to dissolve 103 kilograms from the profile at these recharge rates, would be 99000, 7652, and 1530 years, corresponding to the three recharge rates above.

Sensitivity to Dispersion and Retardation

Inasmuch as the analytical methods used to assess contaminant movement have ignored the diluting effect of the dispersive mechanisms and the retardation of solutes due to sorptive mechanisms, an analytical solution was utilized to evaluate the importance of these processes. Owing to the lack of data on the

precise distribution of the seepage rates from the waste tank, this model was not used to reproduce observed field conditions. Instead, a simple demonstration is provided to illustrate the significance of dispersion and sorption for the native cover case where the average fluid particle velocity,  $v$  is 13.3 cm/yr. For the sensitivity demonstration, it is assumed that the profile is initially at a constant concentration throughout and water having zero concentration infiltrates the upper part of the column.

The analytical solution selected is for one-dimensional convective-dispersive solute transport (van Genuchten and Alves, 1982). The governing transport equation has the form:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (7)$$

where  $R$  is the retardation coefficient,  $D$  is the dispersion coefficient,  $v$  is the particle velocity,  $x$  is distance,  $t$  is time, and  $C$  is the concentration of outflow from the unsaturated zone. The initial concentration in the model was set to  $C/C_i = 1.0$ .

The value of the retardation factor essentially gives the ratio of the velocity of water relative to the solutes; for example, for  $R = 30$ , the solutes move 30 times slower than the average fluid particle, owing to sorption on solid particles.

First, a sensitivity analysis on the dispersion coefficient was carried out. The retardation coefficient was set to 1.0 (no retardation). The dispersion coefficient was estimated from

results of van Genuchten (1981, 1982) to be within the range of 1.49 to 59.4 cm<sup>2</sup>/d. These two values and a mean value of 30.54 cm<sup>2</sup>/d were used in the model. From Figure 7, the differences in predicted concentration outflows from the vadose zone for varying dispersion coefficients are relatively small compared to the perturbation in the dispersion coefficient. For example, after about 200 years the relative outflow concentration would be 0.8 if dispersion were small and 0.2 if it were quite significant (Figure 7).

To evaluate the sensitivity to sorption, measurements of distribution coefficients or retardation factors are required. These may be specific to individual solutes and organic compounds. No data are available for PCE in partially saturated media. However, the range of estimated retardation coefficient values for PCE was found by Durant and McKay (1985) to be about 5.39 to 27.34 in a stratified sandy aquifer. This range of values was used in the model, along with an average value of  $R = 16.37$ . The average estimated dispersion coefficient of 30.45 cm<sup>2</sup>/d was used in each case. Figure 8 shows that there is a significant difference in the potential mass flux for varying retardation coefficients.

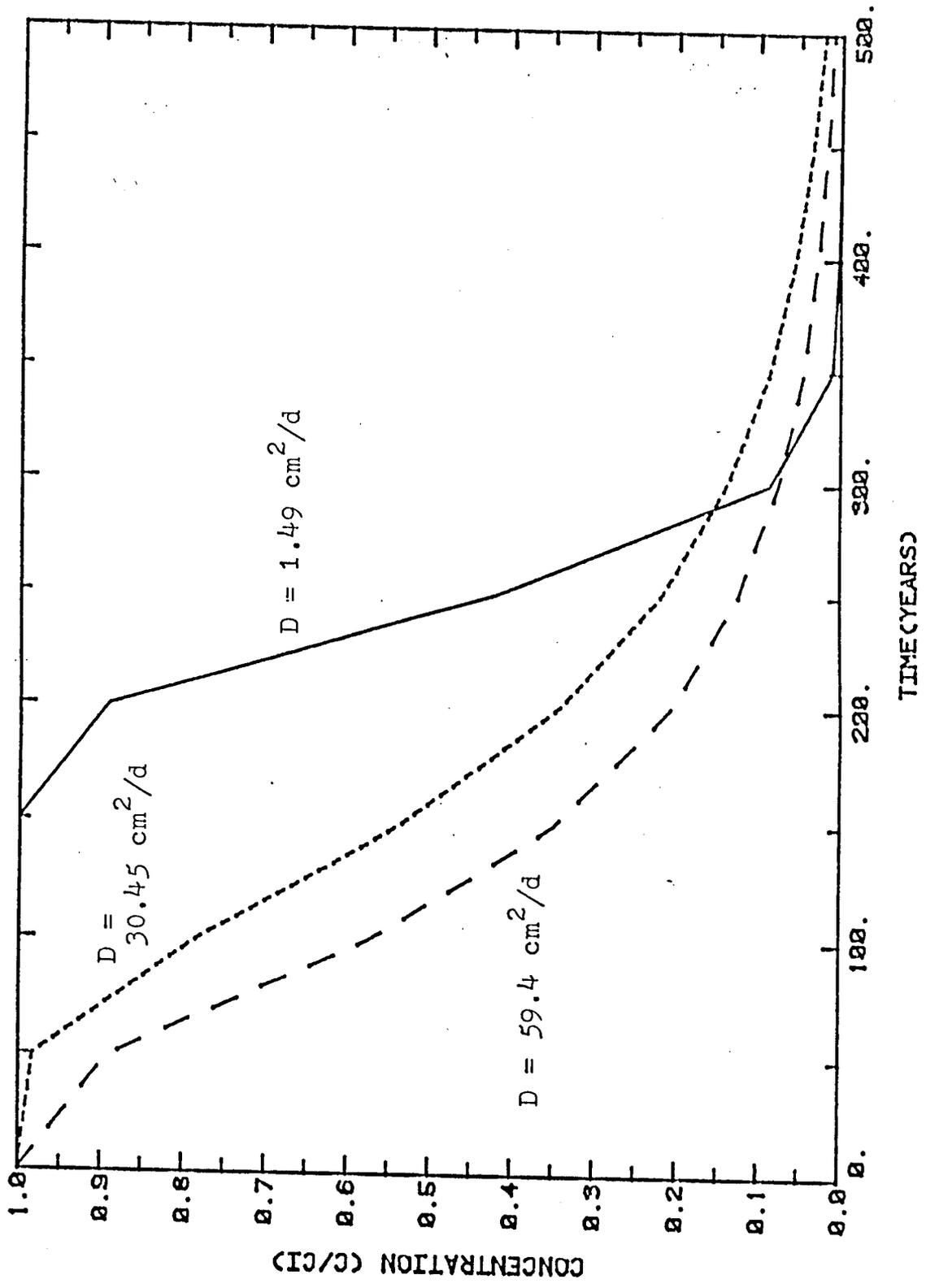


Figure 7. -- Ratio of concentration in outflow from the unsaturated zone to the initial average concentration for miscible displacement model without sorption;  $v = 13.3 \text{ cm/yr}$ . Native cover case.

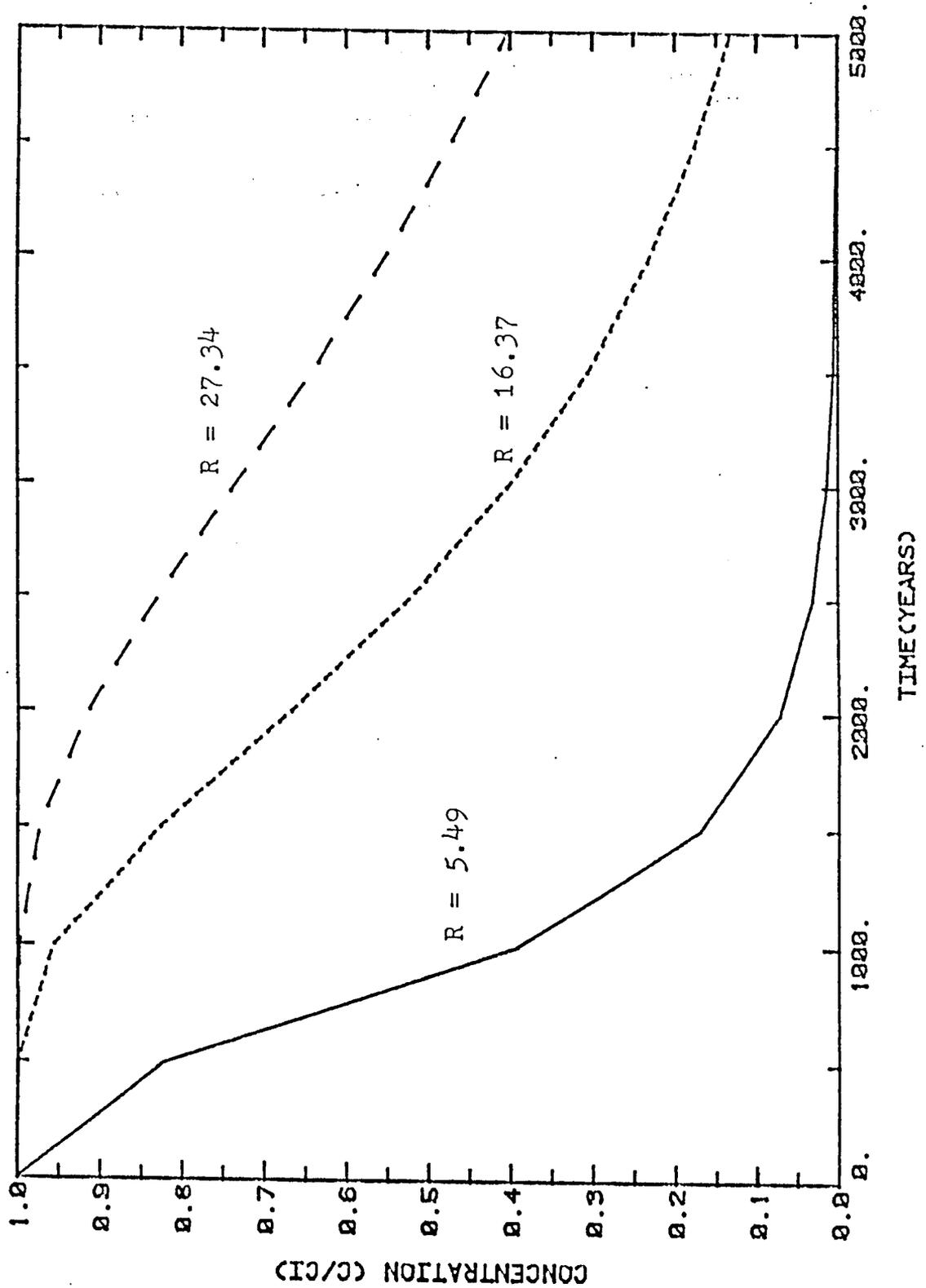


Figure 8. -- Ratio of concentration in outflow from the unsaturated zone to the initial average concentration for miscible displacement model with  $D = 30.45 \text{ cm}^2/\text{d}$ ;  $v = 13.3 \text{ cm/yr}$ . Native cover case.

ANALYSIS OF EFFECT ON THE AQUIFER

To evaluate the significance of the discharges from the unsaturated zone, a two-dimensional solute transport model by Wilson and Miller (1978) was used to predict PCE concentration in the aquifer. The model applies to the case of solute injection at a constant rate along a vertical line source. The aquifer flow field is assumed to be uniform and unidirectional. The aquifer is homogeneous, isotropic, infinite in areal extent, and has finite thickness. Dispersion is permitted in the longitudinal and transverse directions to flow.

The model was applied to the field study area using aquifer characteristics provided to us by PNM. For the analysis we assumed the aquifer is 6.09 m thick, the hydraulic conductivity is 1.0 m/d, the hydraulic gradient is 0.009, and the longitudinal and transverse dispersivities are 5.0 and 1.0 m, respectively. The model may tend to overestimate actual concentrations owing to dispersion which will occur in the vertical direction in an aquifer which is actually much thicker than 6.1 m. Therefore, concentrations near the source will be overestimated, because actually the PCE which drains from the unsaturated zone would be spread out over a much larger area of the aquifer. The model options we selected neglected retardation effects, in order to be conservative in the analysis.

To separate the impact of PCE now in the unsaturated zone from that already present in the groundwater, the initial

condition for the analysis assumes that PCE presently in the aquifer has been completely flushed from the system. The PCE loading rates to the aquifer were obtained from the previous analyses of contaminant transport through the unsaturated zone.

Impermeable Cover

Concentrations of PCE in the aquifer are estimated for the mass flux rates calculated for the two permeability cases used in the drainage model analysis. During the first 100 years, mass flux from the unsaturated zone averaged  $5.8 \times 10^{-7}$  and  $6.0 \times 10^{-5}$  kg/yr for permeability models 1 and 2, respectively (Tables 2 and 3). Using these mass flux rates in the solute transport model for the aquifer, the predicted PCE concentrations are on the order of  $5 \times 10^{-6}$  and  $3 \times 10^{-4}$  mg/l just one meter from the source after 100 years, for the respective unsaturated conductivity conditions. The maximum loading rate is calculated to be  $6.9 \times 10^{-5}$  kg/yr after about 80 years (Table 3). At this rate, the aquifer concentration of PCE would be less than about  $4 \times 10^{-4}$  mg/l, or 0.4 ppb, one meter down gradient from the point of injection.

Native Cover

For this case, the PCE loading was calculated using the condition that infiltration will be 1% of precipitation and PCE will arrive at the aquifer in solution at 150 mg/l.

For these assumptions, the loading on the aquifer would be

0.0135 kg/yr. Computations were carried out to 100 years, at which time the concentrations in the area of interest were practically steady. The maximum extent of the 0.02 mg/l PCE concentration is predicted to be about 85 meters down gradient from the present tank area.

DISCUSSION

In summary, one of the principal objectives of our study was to assess the effect on contaminant transport of an impermeable surface cover that would restrict the rate of drainage from the unsaturated zone to the aquifer. Two markedly different unsaturated hydraulic conductivity relationships were applied in the analysis. In each case, the surface cover is clearly effective in reducing seepage. That is, the effectiveness of such a surface cover is not sensitive to the unsaturated hydraulic conductivities described herein. With a surface cover which prevents infiltration of precipitation and surface runoff, the profile will approach a static equilibrium condition with the water table. In this condition, almost all contaminants (ie., PCE) presently in the unsaturated zone would remain there. An analysis was also made of the hypothetical situation where the present asphalt and concrete near the tank deteriorated and the land area returned to native cover. Under this scenario, a dynamic equilibrium flow condition exists and all PCE would eventually be transported out of the unsaturated zone over a time period in excess of 1000 years. The mass fluxes calculated for the surface cover case are a few orders of magnitude less than the peak loading rates predicted for the native cover case.

The analyses applicable to the dynamic equilibrium assumption of flow in the unsaturated zone provide worst-case results. However, it must be emphasized that there are a number of

assumptions which were made that would tend to cause the actual contaminant flux to be less than the calculated flux for these hypothetical cases. First, the land surface around the tank is presently covered over much of the immediate area by asphalt and concrete which restricts the natural infiltration. As a result, hydraulic gradients may be less than the assumed value of unity and the profile may be approaching static equilibrium. Second, dispersion and sorption mechanisms have been ignored in the unsaturated zone. Third, the actual area contributing contaminants to the aquifer may be approximately nine times smaller than the area used for calculations. Fourth, lateral spreading of contaminants has been neglected.

The last two points cited above need clarification. The size of the areas containing most of the contaminants varies with depth, as shown in Table 1. Owing to capillarity, horizontal stratification, and contrasts in the unsaturated hydraulic conductivity between layers of slightly different texture, fluids spilled from a point source often tend to migrate laterally from the source. The depths at which the contamination is most extensive are at 9 m and 15 m below the surface in the tank area. Below 15 m, the zone of contamination becomes smaller; at 27 m, about 7 m above the water table, the area containing more than 0.01 ppm of PCE is only 4.82 m<sup>2</sup>. In our calculations, we assumed that the crosssectional area through which PCE flowed into the aquifer was 45.6 m<sup>2</sup>. Thus, our conservative estimate for the cross-sectional area may over predict mass fluxes by

nearly an order of magnitude.

Contrasts in unsaturated hydraulic properties between layers not only tend to cause lateral spreading, but they also cause the effective average vertical unsaturated conductivity to decrease. Thus, the actual rates of recharge and drainage would tend to fall near the low end of the range of the calculations.

In summary, taking into consideration the numerous conservative assumptions, the impact of PCE in the unsaturated zone on the aquifer could be even less than predicted herein, using the maximum hydraulic conductivities for the case of a native cover material.

CONCLUSIONS

1. For the sands at the site, the methods used to calculate unsaturated hydraulic conductivity from moisture retention data obtained in the laboratory are sensitive to small changes in the specified parameter, WCR.

2. At the average field moisture content, the rate of natural recharge is estimated to range between about 0.01 and 1.0 cm/yr; this range corresponds to about 0.08 to 5.0% of the mean annual precipitation rate.

3. For the hypothetical situation where the present surface cover deteriorates and the land surface returns to native cover, the time required to completely displace all the PCE by natural infiltration is estimated to be on the order of a thousand years. The time required to dissolve all the PCE in infiltrated precipitation is approximately seven thousand years.

4. With a surface cover (ie., asphalt or concrete) in place to prevent natural infiltration, practically all of the PCE will be retained in the profile and only trace concentrations would occur in the aquifer.

5. Predicted levels of PCE concentration greater than 0.02 mg/l in the aquifer would not extend more than 85 m down-gradient from the waste tank, for the probable worst-case condition in which infiltration percolates through the unsaturated zone at a rate equal to 1% of the mean precipitation rate.

6. The distribution of mass flux of PCE inflow to the aquifer from the unsaturated zone is very sensitive to sorption

on soil particles. Dispersive mechanisms diminish the peak concentrations. Both sorption and dispersion in the unsaturated zone were neglected in order to determine worst-case impacts to the aquifer.

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