ESTIMATING THRESHOLD VALUES FOR THE LAND DISPOSAL OF ORGANIC SOLVENT-CONTAMINATED WASTES

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Summary

This paper describes conceptual and mathematical modeling approaches to evaluate environmentally suitable waste management practices that prevent ground water pollution from landfill disposal of solid wastes contaminated with organic solvents. Threshold values for disposal of solid wastes contaminated with acetone, nitrobenzene, chlorobenzene, and carbon tetrachloride were estimated using a disposal site model using a two-dimensional advection–dispersion solute transport computer code. For example, the threshold value for disposal of carbon tetrachloride at the site model was approximately 600 g/acre, while the value for acetone was limited only by the characteristics of the waste to prevent free drainage of liquid solvent. The study indicated that the toxicity, mass loading rate, and the mass of solvent initially disposed are critical parameters determining the relative success of a given site to attenuate contaminants to environmentally acceptable levels.

Introduction

The movement and fate of organic solvents dissolved in leachate in ground water may be estimated or predicted by computer-assisted models, based on the hydrogeology of a given site, and the geochemistry of the leachate–aquifer system. A significant environmental application of such models is to evaluate the ability of a site to attenuate or reduce the concentration of contaminants to environmentally acceptable levels.

If the attenuation capacity of a site has been studied, this body of information can be used to make decisions as to what wastes might be disposed of in landfills, and at what concentrations of solvent in a given waste, can be safely accepted at a given site. It is the purpose of this paper to illustrate how an understanding of the attenuation capacity of a waste-disposal site can be used to estimate threshold values for the disposal of solvent-contaminated solid wastes. These threshold values would then represent the maximum amount of waste that could be placed into the disposal site without exceeding its attenuation capacity.

In this analysis, it was assumed that the environmentally acceptable con-

TABLE 1

Description of the four organic solvents

Solvent	Aqueous solubility[a] (mg/L)	MPC (mg/L)	Mobility[b] classification	Partition[c] coefficient (K_d)
Acetone (CH_3COCH_3)	miscible	750	very highly mobile	0.003
Nitrobenzene $(C_6H_5NO_2)$	2000 (20°C)	19.8	highly mobile	0.121
Chlorobenzene (C_6H_5Cl)	448 (30°C)	0.488	medium mobility	0.572
Carbon tetrachloride (CCl_4)	800 (25°C)	0.004	medium mobility	0.418

[a]Griffin and Roy [3].
[b]Roy and Griffin [4].
[c]Griffin and Roy [5].

centrations of an organic solvent in potable ground water near the site should be less than the acceptable daily intake (*ADI*) value, that is, the concentration below which the solvent is considered nontoxic to human health in potable water. The selection of such values for most organic solvents is not a simple task, primarily because of a lack of toxicity data. The U.S. EPA is currently attempting to establish standards for acceptable contaminant levels, and the standards are in a state of flux [1]. For the objectives of this paper, the maximum permissible concentration (*MPC*) of a solvent in ground water at a compliance point on a site boundary was defined as the ADI value for noncarcinogenic solvents, and for known carcinogens, the *MPC* was the 10^{-6} lifetime cancer-risk level.

In this study, four organic solvents were used as examples; acetone, nitrobenzene, chlorobenzene, and carbon tetrachloride. Acetone is the least toxic, while carbon tetrachloride is the most toxic of the four solvents and is a known carcinogen [2]. Based on the toxicity data given in George et al. [2], *MPC*s for each solvent were selected for this study (Table 1). As additional data becomes available, these *MPC*s, or analogous contaminant ceilings can of course be used in similar studies.

It is the premise of this type of study that a given disposal site must reduce (attenuate) the concentrations of the solvents to concentrations that are less than the *MPC* of each solvent at all points of compliance. If this condition is met, then the disposal operation of the solvent-contaminated waste is said to be environmentally acceptable. To facilitate discussion, it may be helpful to briefly review the mechanism of attenuation used in this analysis.

Attenuation mechanisms

Before considering situations where attenuation takes place, the "no attenuation case" should be considered. This case is where the concentration of an

organic solvent in leachate does not decrease while it migrates away from the disposal area. Thus, the maximum concentration of the solvent that can be placed in a trench is the maximum permissible concentration (*MPC*) of that solvent. In other words, requiring that the initial solvent concentration be zero (i.e., banned altogether from landfill disposal) has little meaning, even in a system where no attenuation takes place.

Dilution by ground water

Leachate generated in a waste trench will tend to move from the site and be mixed with ground water. This mixing may or may not dilute the concentration of the leachate to acceptable levels. As discussed in Griffin and Roy [5], as the quantity of ground water increases, an increase in the initial (predilution) concentration of the leachate can be environmentally tolerated. As the toxicity and/or the aqueous solubility of the organic solvent increases, then so does the dilution factor necessary to dilute the contaminants to acceptable concentrations.

Adsorption

Adsorption is a physical–chemical process whereby solvent molecules are concentrated at solid–liquid interfaces. The adsorption of solvent molecules by natural materials such as soil components may retard the movement of the solvent as the leachate migrates from the disposal site. Roy and Griffin [4] concluded that acetone has essentially no tendency to be adsorbed by soils or aquifer materials. Nitrobenzene does not have a strong tendency to be adsorbed, but the amount that is retained will increase as the organic carbon content of the aquifer materials increases. The same trend can be expected for both chlorobenzene and carbon tetrachloride. The latter two solvents have a moderately strong tendency to partition to the organic matter in soil materials.

Dispersion

Dispersion is a physical process where a liquid moves through a porous medium at different velocities due to a number of factors. These include density and viscosity gradients, and to variation of pore sizes available to conduct the liquid. This attentuation mechanism is a type of dilution in that it has the effect of spreading solutes in the porous material thereby reducing their concentrations at a given point over time. Dispersion should be considered when assessing the arrival times of contaminants at a compliance point to accurately predict solute migration. Dispersion will cause relatively low levels of contaminants to arrive at a compliance point far in advance of the center of mass projected by computations not considering the effects of dispersion.

Degradation

Solvent degradation during the movement of a leachate represents the combined effects of solvent hydrolysis, and biodegradation. Hydrolytic reactions
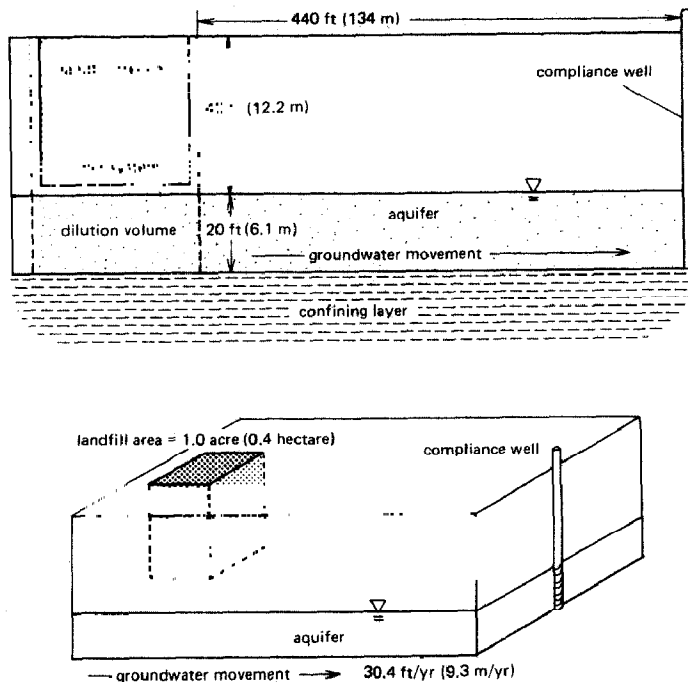
Fig. 1. Waste disposal site model with the following properties: saturated hydraulic conductivity, 10^{-3} cm/s; horizontal hydraulic gradient, 0.01 cm/cm; total porosity, 0.36 cm^3/cm^3; effective porosity, 0.35 cm^3/cm^3; dry bulk density, 1.7 g/cm^3; percent organic matter, 0.18.

are chemical reactions whereby the solutes react with water forming weak acids or bases. Biodegradation is a biochemical process whereby micro-organisms (e.g. bacteria, actinomycetes, fungi, and algae) break down organic solvents yielding other compounds or products. The four solvents (acetone, nitrobenzene, chlorobenzene, and carbon tetrachloride) do not hydrolyze readily [6,7]. Studies cited in Griffin and Roy [5] indicate that there is very little detailed information on the biodegradation of organic solvents, but acetone is generally not persistent in the environment, and nitrobenzene and chlorobenzene are moderately persistent. Carbon tetrachloride may not be readily biodegradable in aquifers. In the next section, the impact of these attenuation mechanisms on the solution concentrations of organic solvents in ground water will be examined. The summation of these individual attenuation mechanisms constitute the overall attenuation capacity of a given site.

Solvent migration simulations

To illustrate the concept of modeling as a tool in threshold value estimations, a hypothetical disposal site was defined (Fig. 1). In this scenario, the aquifer

is composed of sandy materials that are 20 ft (6.1 m) thick. The direction of groundwater flow is from left to right, and is perpendicular to the flow boundary (Fig. 1). A disposal trench covers a cross sectional area of 1 acre (0.4 hectare), and is 40 ft (12.2 m) deep. The trench is lined with a synthetic-compacted clay double liner (RCRA design shown in detail in Griffin and Roy [5]). The base of the sandy aquifer is defined by virtually impermeable shale. The edge of the trench is 440 ft (134 m) from a monitoring well. This well serves as a compliance point for the disposal facility model.

In saturated, homogeneous materials that are subjected to steady-state flow conditions, the change in solute concentration as a function of time may be generalized [8–10] by a two-dimensional advection–dispersion equation containing adsorption and degradation terms, viz.,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X_i} \left(D_{ij} \frac{\partial C}{\partial X_j} \right) - \frac{\partial}{\partial X_i} \left(C \, V_i \right) - \frac{\rho}{\theta} \frac{\partial S}{\partial t} - \lambda C \tag{1}$$

where C is the concentration of the solvent in solution, t is time, D_{ij} is the i,j component of the hydrodynamic dispersion tensor, V_i is the mean value of the ith component of flow velocity of water, X_i, X_j are space coordinates, ρ is the dry bulk density of the aquifer materials, θ is the volumetric water content of the aquifer materials, S is the amount of solute adsorbed per mass of adsorbent, and λ is the rate of degradation.

The solution to this equation is given in Bumb et al. [11], and forms the basis of the two-dimensional solute transport computer program PLUME (Version 2.0, Insitu, Inc., Laramie, WY, Bumb et al. [11]). The program PLUME was used in this study to conduct simulations with the site model (Fig. 1), using infinite-length boundary conditions, viz.,

$C(x,y,0) = 0$

$C(0,0,t) = C_0$, the initial solute concentration

$C(\infty,\infty,t) = 0$

The input parameters necessary to implement the program PLUME are the hydrogeologic characteristics of the disposal site (summarized in Fig. 1) and the physical–chemical characteristics of the solvents (Table 1). The basis and rational for these parameters are given in Griffin and Roy [5].

In this specific application, an adsorption term in eqn. (1) (S) for each solvent was calculated from single-solute partition coefficients (Table 1). Hence the movement of each solvent was modeled as a single-solute system for the purpose of illustration. Moreover, it was assumed that the adsorption of each solute conformed to a linear isotherm. Leachates however at actual disposal sites will contain a mixture of solutes that may exhibit competitive interactions for adsorption sites, and cosolvent interactions. Furthermore, the

adsorption of many solutes do not conform to linear isotherms. In applications of modeling to actual disposal sites, adsorption data should be collected using in situ leachates or laboratory extracts of the wastes to more accurately mimic these complex multicomponent systems (see Roy et al. [12] for suggested methods).

In each subsequent analysis, the volume of leachate breaking through the liner as a function of time was determined. Mitchell [13] conducted a number of linear leakage studies under various conditions, using the RCRA double-liner system. The results of Mitchell [13] were incorporated into this study with respect to estimating seepage rates. Briefly, it was assumed that the hydraulic conductivity of the geomembrane liner was 1×10^{-11} cm/s, the clay liner was 1×10^{-7} cm/s. The hydraulic conductivity of a clay liner will vary considerably, but the 10^{-7} cm/s value should represent a maximum conductivity. The trench in Fig. 1 was completely filled with leachate, and thus, there was a 40 ft (12.2 m) head providing the maximum gradient possible for driving the leachate through the liner system. In other words, a worst-case assumption was imposed; the RCRA drainage system has either failed or has been abandoned. Mitchell [13] concluded that under these conditions, the leachate is computed to break through the liner in 82 years at a rate of 12,000 gal/year-/acre (112 kL/year/hectare).

It was assumed in this study that the leachate breaking through the liner was saturated with respect to each solvent. In other words, the initial (pre-attenuated) concentration of each solvent is limited by its aqueous solubility (Table 1). Acetone is miscible in water, and thus it was assumed that there was 5% acetone in solution. Higher concentrations seemed unlikely given the probability of dilution by water percolating through the solid wastes containing the acetone. It was further conservatively assumed that the concentrations of the solvents in the leachate breaking through the liner were not affected by passage through the liner (i.e., no dilution, adsorption, or degradation in the liner).

It was also assumed that the solvents did not influence the saturated hydraulic conductivity of the liner. As discussed by Griffin and Roy [3], studies have shown that pure solvents may increase the hydraulic conductivity of some clays and soils, but there is little evidence that dilute solvent solutions (such as those used in this analysis) also produce similar effects.

Given that the volume of leachate seeping through the liner, and the concentration of each solvent in the leachate are known, the mass loading rate of each solvent to the aquifer was calculated. For example, the aqueous solubility of nitrobenzene in water at 20°C is 2000 mg/L, hence

$$M_r \text{ (mass loading rate)} = \text{(volume)(concentration)} \tag{2}$$

$$M_r = 12{,}000 \text{ gal/yr/acre} \times 3.785 \text{ L/gal} \times 2000 \text{ mg/L} \tag{3}$$
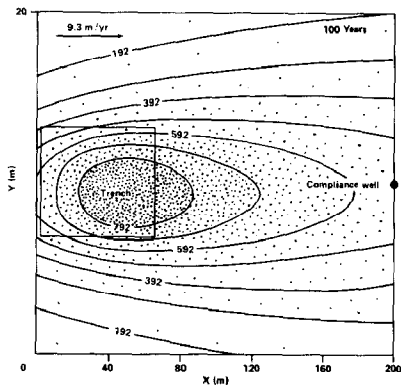$$= 90.72 \text{ kg/yr/acre.}$$

Fig. 2. Plan view of the disposal site model showing the predicted distribution and concentration of acetone (mg/L) in the aquifer 100 years after liner breakthrough.

The mass loading rates of acetone, chlorobenzene, and carbon tetrachloride were: 2,268; 20.32; and 36.29 kg/yr/acre, respectively.

The model PLUME used these mass loading rates in calculating the down-gradient concentrations of each solvent. PLUME "moves" the leachate from the trench into the aquifer and instantaneously mixes the mass of solvent with a volume of ground water that is moving directly beneath the trench (see Fig. 1, dilution volume) at a rate of 30.4 feet/year (9.3 meters/year). Consequently dilution by ground water was approximated. The assumption of complete mixing may not be valid when there is a marked difference in density between the leachate and the ground water. In such situations, down gradient solute concentrations will be greater than those predicted. The assumption of complete mixing appears to be valid for relatively thin aquifers (i.e., less than about 6 meters) where the thickness of the aquifer is less than 10% of the length of the leachate source, i.e., the waste trench. The assumption was validated by comparisons with 3-dimensional transport models (Y.M. Sternberg, personal communication, 1986, University of Maryland).

As discussed previously, it was estimated that the leachate would break through the liner in 82 years. If the mass loading rate remains constant, the predicted distribution and concentration of acetone in the model site 100 years after breakthrough is shown in Fig. 2. In this simulation, the degradation rate constant was conservatively taken as zero, i.e., acetone was not allowed to degrade during the 100 year simulation even though it is known to be nonpersistent. Since acetone has very little tendency to be adsorbed by aquifer materials, its velocity of migration was comparable to that of water. Consequently, the only attenuation mechanisms that could reduce the concentration of the acetone were dilution and dispersion. The simulation suggested (Fig. 2) that acetone would be present in the aquifer over a large area, including the compliance well. However, the concentrations of acetone in the well would be less
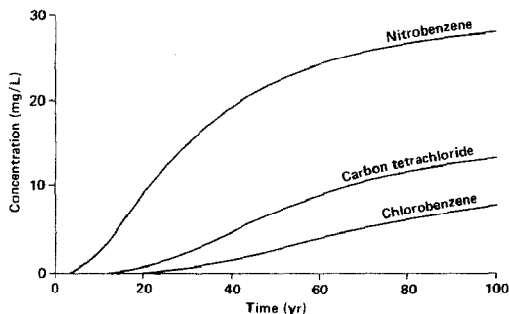
Fig. 3. The predicted concentrations of nitrobenzene, carbon tetrachloride, and chlorobenzene (mg/L) in the monitoring well at the disposal site model as a function of time in years after liner breakthrough.

than 600 mg/L, which is below the *MPC* for acetone of 750 mg/L. Thus, under the conditions described, the attenuation capacity of the model site appeared to be adequate for the disposal of acetone for long periods.

The predicted concentrations of nitrobenzene, carbon tetrachloride, and chlorobenzene at the monitoring well as a function of time are shown in Fig. 3. The concentration of each solvent in the well gradually increased during the 100 year simulation period. As before, the solvents were assumed to not degrade. One hundred years after liner breakthrough, the concentration of chlorobenzene was predicted to be approximately 8 mg/L which was well above its *MPC* of 0.488 mg/L. Moreover, the concentration of nitrobenzene was approximately 28 mg/L, exceeding its *MPC* of 19.8 mg/L. Approximately 100 years after liner breakthrough, the simulation suggested that the concentration of carbon tetrachloride in the well would be far greater than its *MPC* of 0.004 mg/L (Fig. 3).

This simulation (Fig. 3) suggested that, under the conditions imposed, the attenuation capacity of the site was inadequate for chlorobenzene, nitrobenzene, and carbon tetrachloride; that is, the attenuation capacity of the site has been exceeded for these solvents. Thus, the simulation identified a waste management problem with respect to solid wastes containing these compounds. There are essentially two approaches to resolve this problem. One avenue is to reduce the mass loading rate. However, the state-of-the-art technology (i.e., the RCRA double-liner system) has been applied. Consequently, the mass loading rate is probably as low as economically feasible. The second possible solution is to reduce the mass of solvent buried at the disposal site.

Previous simulations such as Figs. 2 and 3, assumed that the amount of solvent available for leaching was essentially infinite. Figure 4 displays a family of curves indicating the concentration of carbon tetrachloride in the monitoring well as a function of time. Each curve corresponds to a different mass of carbon tetrachloride placed in the trench. In each case, the concentration of
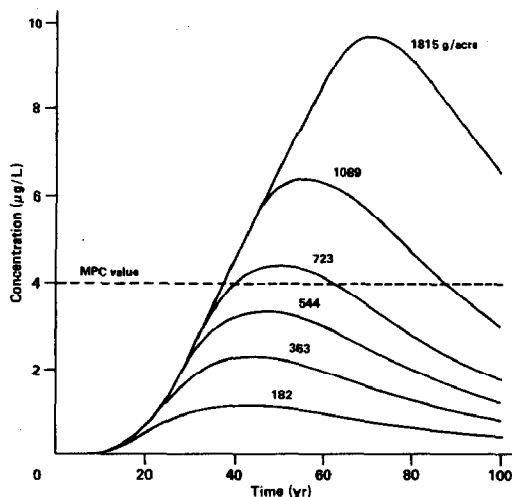
Fig. 4. The predicted concentration of carbon tetrachloride (μg/L) in the monitoring well as a function of time after liner breakthrough. Each curve corresponds to a different initial mass of carbon tetrachloride (g/acre) placed in the disposal trench.

carbon tetrachloride steadily increased as before, but in Fig. 4, reached a maximum value, then declined. This behavior is due to the fact that the amount of carbon tetrachloride is now limited; as the amount of the solvent available to leach is exhausted, the concentration of carbon tetrachloride in the monitoring well decreases.

In this scenario, a mass of 723 g carbon tetrachloride per acre resulted in carbon tetrachloride concentrations in the monitoring well that exceeded the *MPC* (Fig. 4). However, the simulation suggested that a mass of 544 g/acre of carbon tetrachloride was sufficiently low that the attenuation capacity of the model site was not exceeded. Therefore, a mass of 544 g carbon tetrachloride per acre could be considered as a conservative estimate of the threshold value for landfilling this solvent in the site trench. This threshold value for carbon tetrachloride is very low, an amount comparable to about 1 gallon of pure solvent spread over each acre of the site. The same type of analysis could be applied to chlorobenzene and nitrobenzene to estimate threshold values. It is proposed here that this type of analysis can be used to estimate solvent threshold values for actual sites.

These types of simulation analyses may be enhanced by conducting sensitivity analyses to help establish safety margins. For example, in these simulations the dispersion coefficient was approximated by

$$D_x \simeq \alpha \ V_x \tag{4}$$

where D_x is the dispersion–diffusion coefficient, V_x is the mean ground water flow velocity, and α is the dispersivity.
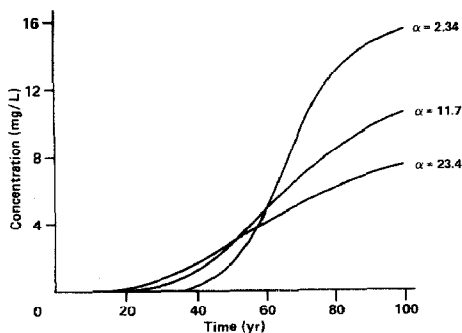
Fig. 5. The predicted concentration of chlorobenzene (mg/L) in the monitoring well at the disposal site model as a function of time after liner breakthrough. Each curve corresponds to a different dispersivity (α) value.
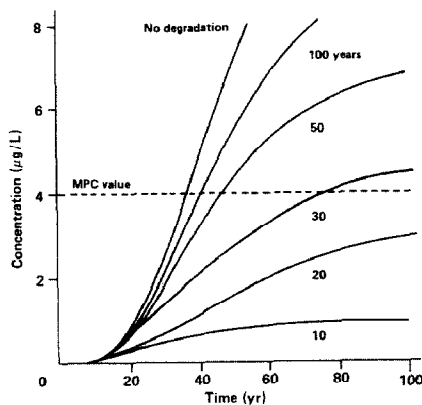
Fig. 6. The predicted concentration of carbon tetrachloride (μg/L) in the monitoring well at the disposal site model as a function of time after liner breakthrough. Each curve corresponds to a different degradation half-life value.

The dispersivity term (α) is a proportionality constant relating the mean velocity of the water to the dispersion coefficient. The quantification of dispersion is difficult. Since dispersion is an important mechanism leading to decreases in solute concentration, dispersion estimates should be carefully addressed (see Freeze and Cherry [10]). The dispersivity has been found to be scale dependent, and is estimated to be about 10% of the total distance of movement in the analysis [14]. In Fig. 5, the longitudinal dispersivity was varied from 2.3 to 23 m. The transverse dispersivity was assumed to be 15% of the longitudinal value in each case. The mass of chlorobenzene was infinite. As shown, the concentration of chlorobenzene in the monitoring well decreased with increasing dispersivity, i.e., it was reduced by greater dispersion. It is also important to note that the time of first arrival of the contaminant at the monitoring well is shorter for larger dispersivities (Fig. 5).

In the previous simulations, including the threshold analysis, the solvents were not allowed to degrade. Such simulations may be more accurate by taking degradation into account. In this study, solvent attenuation by degradation was estimated by assigning a half-life value for the solvent. The results for carbon tetrachloride assuming no degradation and half-life values of 100, 50, 30, 20, and 10 years, respectively, are shown in Fig. 6. As the half-life of carbon tetrachloride decreased, the concentration of the solvent at the monitoring well decreased. According to the simulation, the concentration of carbon tetrachloride in the well did not exceed it's *MPC* when the half-life was 10 years, but did when the half-life was 50 years. Thus, if 10 to 30 years was an accurate

range for the half-life, the conclusion reached from Fig. 4 could be revised; that is, the mass of carbon tetrachloride placed in the trench could be increased without exceeding the *MPC* because of the added attenuation due to degradation. In this particular case however, the available data indicates that it is problematic that carbon tetrachloride would be degraded that quickly in a ground water environment.

Conclusions

The basic theorem of this study was that an integrated evaluation of the overall attenuation capacity of a site is the key to determining threshold values for the land disposal of organic solvent-contaminated wastes. The computer code PLUME was used to simulate the movement of organic solvents, dissolved in solution, from a disposal site model into a sandy aquifer. This equation was used via sensitivity analyses to estimate threshold values. For example, the threshold value for disposal of carbon tetrachloride at the site model was approximately 600 g/acre, while acetone was limited only by the ability of the waste matrix to preclude drainage of free liquid solvent.

It is proposed that this approach can be applied to actual sites using similar computer codes to make estimations of threshold values. The study indicated that the toxicity, mass loading rate, and the mass of solvent initially disposed are critical parameters determining the relative success of a given site to attenuate contaminants to environmentally acceptable levels.

Acknowledgments

References

1   ENR, Tracing risk in the water we drink, Eng. News-Record, 215 (1985) 42–48.
2   W.J. George, L.A. Martin and L.E. White, Toxicity profiles of selected organic solvents, Environmental Institute for Waste Management Studies, Open File Report, P.O. Box 2310, University of Alabama, Tuscaloosa, AL 35403, 1985.
3   R.A. Griffin and W.R. Roy, Interaction of organic solvents with saturated soil–water systems, Environmental Institute for Waste Management Studies, Open File Report, P.O. Box 2310, University of Alabama, Tuscaloosa, AL 35403, 1985.
4   W.R. Roy and R.A. Griffin, Mobility of organic solvents in water-saturated soil materials, Environ. Geol. Water Sci., 7 (1985) 241–247.

5   R.A. Griffin and W.R. Roy, Feasibility of land disposal of organic solvents: Preliminary assessment, Environmental Institute for Waste Management Studies, Open File Report, P.O. Box 2310, University of Alabama, Tuscaloosa, AL 35403, 1986.

6   J.C. Harris, Rate of hydrolysis, Handbook of Chemical Property Estimation Methods, McGraw-Hill, New York, 1982, Chap. 7.

7   W.R. Mabey, J.H. Smith, R.T. Podoll, H.L. Johnson, T. Mill, T.W. Chou, J. Gates, I.W. Partridge, H. Jaber and D. Vandenberg, Aquatic fate process data for organic priority pollutants, U.S. Environmental Protection Agency, EPA-440/4081-014, 1982.

8   A. Ogata, Theory of dispersion in a granular medium, U.S. Geological Survey Professional Paper 411-I, 1970.

9   J. Bear, Dynamics of Fluids in Porous Media, American Elsevier, New York, 1972.

10 R.A. Freeze and J.A. Cherry, Groundwater, Prentice-Hall, Englewood Cliffs, NJ, 1979.

11 A.C. Bumb, C.R. McKee, J.M. Reverand, J.C. Halepaska, J.I. Drever and S.C. Way, Contaminants in groundwater: Assessment of containment and restoration options, Conference on Management of Uncontrolled Hazardous Materials Control Research Institute, Washington, DC, 1984.

12 W.R. Roy, I.G. Krapac, S.F.J. Chou and R.A. Griffin, Batch-type adsorption procedures for estimating soil attenuation of chemicals, Technical Resource Document, U.S. Environmental Protection Agency, in press.

13 J.K. Mitchell, unpublished open file report, Environmental Institute for Waste Mangement Studies, P.O. Box 2310, University of Alabama, Tuscaloosa, AL 35403, 1985.

14 L.W. Gelhar and G.J. Axness, Stochastic analysis of microdispersion in 3-dimensionally heterogeneous aquifers, Report no. 8, Hydrologic Research Program, New Mexico Institute of Mining and Technology, Soccoro, NM, 1981.