

## Caution Against the Inappropriate Use of Analytical Fate and Transport Models to Estimate the Age and Risk of Petroleum Product Releases

by Pedro J.J. Alvarez

Analytical fate and transport models are often used to assess the age and stability of underground petroleum product releases. One common approach is to use the available data on the spatial distribution of the target contaminant(s) with appropriate hydrogeologic parameters to calibrate the model. Using standard data fitting techniques, such as nonlinear regression, ground water professionals can estimate site-specific migration and decay rates and, thus, the age of a release. The use of three-dimensional analytical fate and transport models, such as those depicted in Table 1, is likely to increase with the adoption of risk-based corrective action (RBCA) in the environmental protection rules of numerous states. Often, the new rules allow for the use of analytical models in Tier 2 and Tier 3 analyses to estimate site-specific levels of contamination at the source that do not create an "unreasonable risk to human health, safety, and the environment." Given the anticipated increase in modeling activity to determine the need for remedial action, there is a need to ensure that current modeling practices are adequate for protecting public welfare.

Hydrogeologists and environmental engineers should ascertain that the ground water flow and

contaminant behavior are consistent with the principles used in their analytical models. Unfortunately, this cardinal rule is often forgotten or ignored. Since model simulations are only as good as their input and assumptions, there is a potential for inadvertent misuse of models in negotiating litigation and site-specific target levels under RBCA.

The purpose of this article is to caution interested parties against the inappropriate use of analytical fate and transport models. A case study will be used to illustrate common faults and misjudgments associated with modeling petroleum product releases to ground water. This case study was abstracted from settled litigation. However, the modeling principles discussed apply as well to modeling done for RBCA assessments. This case study emphasizes modeling the fate of benzene, which is often the contaminant of greatest concern because of its potential to cause leukemia (*Federal Register* 1985).

### Case Study

#### General Background

This case involves a litigation with regard to ground water contamination by a leaking under-

ground storage tank (LUST). The facility under consideration had two different operators. Company X operated this facility until 1987. The current operator, Company Y, replaced X's underground storage tank system in 1987. The new system passed all annual tightness tests, and there are no reports of releases or overfills during Company Y's operation. In 1990, gasoline contamination was found by Company Y in an underlying silty bed; a site assessment ensued. Benzene was detected above its maximum contaminant level (MCL) of 5 mg/L in nearby monitoring wells. Nevertheless, no hydrocarbons were detected in the fill sand that surrounds the new UST system. This suggested that contamination occurred prior to the installation of the new UST system in 1987, while Company X operated the facility. Therefore, a cost recovery claim was filed against Company X.

In litigation, Company X argued that it was not liable for the contamination observed at this site and hired a consultant to support its defense against the cost recovery claim. The consultant used computer modeling analyses to determine the likelihood that contamination occurred while Company X operated the facility, prior to 1987. Based on a simple fate and transport model, they concluded that "... assuming a pulse source, a single release of benzene dissipates to below the MCL in less than a year. Therefore, any contamination from before 1987 would either have migrated off-site or degraded by the time samples were collected in 1990." As discussed below, this conclusion is questionable because of intrinsic limitations on the applicability of their analytical model and their choice of benzene biodegradation coefficient in their fate and transport simulations.

### **Intrinsic Limitations of the Analytical Model**

To simulate the fate of benzene, the consultant used an analytical solution to the three-dimensional advection-dispersion equation that

considers an instantaneous pulse source, local equilibrium with linear partitioning by sorption, and first-order biodegradation kinetics (Table 1, Equation 1). Similar to most analytical fate and transport models, the principal advantage of this model is its simplicity. This, however, is also its main weakness. While this model is relatively easy to use and requires minimum input of site-specific parameters, there are several intrinsic assumptions that should be fulfilled to ascertain its appropriateness and ensure the validity of its output. Nevertheless, data limitations (and perhaps also budgetary constraints) precluded the consultant from determining whether the contamination scenario and the ground water flow acted in a manner consistent with the principles used in the model. Four specific limitations are discussed below.

### **1. Contamination Source**

The consultant concluded that the benzene contamination detected within the site must have occurred after 1987 because any prior contamination should have migrated off-site by 1990. Nevertheless, the simulated contamination scenario assumed a single instantaneous pulse source. LUST contamination often resembles a constant source because tanks may leak for an extended period of time, and desorption of hydrocarbons from contaminated soil constitutes another source of sustained ground water contamination. Therefore, the pulse source assumption underestimates the time required for contamination to dissipate by physical processes. A constant source over a stipulated period may be a more representative way of modeling LUST contamination. It should be pointed out that the pulse source analytical solution requires knowledge of the volume of contaminant released. This is a common uncertainty associated with LUST contamination that introduces error in the time required for a plume to dissipate. The consultant assumed a release of 100 cubic feet, which may or

may not be accurate. Additional information would be required to determine whether this assumption was conservative.

### **2. Steady Flow**

The model used by the consultant is applicable only to steady flow fields (i.e., at any point in space, the flow does not vary in direction or velocity with respect to time). Often, however, the direction and velocity of ground water flow changes (at least seasonally). In the case under consideration, there was not enough data over time and space to evaluate the validity of the steady flow assumption. Unaccounted fluctuations in ground water flow direction and velocity could result in significant error.

### **3. Uniform Flow**

The simulations generated for this case assumed a uniform flow field (i.e., straight and parallel velocity vectors), which intrinsically assumes homogeneity of the porous medium. Nevertheless, the site under consideration is heterogeneous. Stratigraphic heterogeneities can result in unaccounted preferential flow pathways that transport contaminants faster than predicted and "dead spots" that hinder contaminant advection and dissipation.

### **4. Steady-State Plume**

Steady state was not an assumption made in this case. Nevertheless, this assumption deserves attention because it is commonly inherent to some fate and transport analytical models used for RBCA Tier 2 or Tier 3 analyses. By definition, a steady-state plume is one where, at any point, contaminant concentrations do not change with time. This occurs only under two ideal conditions: (1) the plume does not migrate and does not degrade, at least within the time frame of the investigation (i.e., the "trivial" solution); or (2) there is a constant source, and the migration rate equals the decay rate so that there is no net expansion or recession.

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sion. Often, steady state is assumed for simplicity without establishing the validity of this assumption. Validation of the steady state assumption can be costly because of extensive data requirements over sufficient time and space. Disregarding the validity of this assumption constitutes inappropriate modeling practice that could lead to significant error.

### Modeling of Benzene Biodegradation

Biodegradation is widely recognized as an important mechanism by which benzene is eliminated from LUST plumes (e.g., Barker et al. 1987; Lee et al. 1988; Thomas et al. 1990; Verheul et al. 1988; Werner 1985). While very small gasoline releases could dissipate solely by physical processes such as dilution, one must consider biodegradation to contemplate the possibility that benzene should disappear from typical LUST plumes. Indeed, mass balance studies have demonstrated that "passive" biodegradation (i.e., no biostimulation by oxygen or nutrients addition) is a significant attenuation mechanism in benzene transport (e.g., Chen et al. 1992; Chiang et al. 1989; Klecka et al. 1990; Zoetman et al. 1981). In such cases, biodegradation rates are typically controlled by oxygen diffusion from the atmosphere (Borden and Bedient 1986).

Biodegradation is the only "true" sink considered by most analytical codes. Adsorption, advection, and dispersion do not remove benzene from the aquifer, and volatilization is often (conservatively) ignored in analytical models because it is not a major benzene removal mechanism from dissolved LUST plumes (Chen et al. 1992). Therefore, choosing an appropriate biodegradation model and a reasonable decay rate coefficient is critical to the defensibility of the modeling results.

Biodegradation rates are best modeled using Monod kinetics because Monod's equation has a mechanistic (enzymological) basis and considers the active microbial

concentration. Therefore, most sophisticated (numerical) fate and transport models use Monod's equation. This equation, however, is hyperbolic and does not yield an explicit analytical solution for the contaminant concentration as a function of time and space. Therefore, simpler (analytical) fate and transport models use empirical kinetic expressions, such as first-order kinetics (i.e., the rate is proportional to the contaminant concentration) and zero-order kinetics (i.e., the rate is independent of the contaminant concentration). Although benzene biodegradation rates in aquifers have been reported to follow zero-order kinetics (Barker et al. 1987), first-order rates are more common. This is probably due to the fact that benzene is often present at trace concentrations, and Monod's equation reduces to a first-order expression whenever the target contaminant is present at levels much lower than the half-saturation Monod coefficient,  $K_s$  (Alvarez et al. 1991). This condition was met in the case under consideration, and the choice of first-order biodegradation kinetics was appropriate. The choice of first-order biodegradation coefficient, however, was inappropriate.

Following common practice, the consultant estimated a first-order biodegradation rate coefficient ( $\lambda$ ) of  $0.0462 \text{ day}^{-1}$  (i.e., a half-life of 15 days) using site-specific data, and "validated" this coefficient by comparison to values reported in the literature. Nevertheless, the literature values that they considered (Howard et al. 1991) reflect laboratory measurements. Benzene biodegradation in the field is much slower because it is often limited by the rate at which molecular oxygen diffuses into the plume. In situ rate coefficients are typically one order of magnitude lower than their estimated value. A recent paper by Rifai et al. (1995) presents a summary of first-order decay coefficients for benzene that have been measured at 12 sites under "passive" conditions. These literature values have an average

of  $0.0046 \text{ day}^{-1}$  (i.e., a half-life of 149 days) with a common range of 0 to  $0.0085 \text{ day}^{-1}$  and a geometric (log) mean of only  $0.0018 \text{ day}^{-1}$  (i.e., a half-life of 375 days). To put the magnitude of these coefficients in perspective, let us consider the time required for the benzene concentration to drop from  $10 \text{ mg/L}$  to the detection limit ( $1 \text{ }\mu\text{g/L}$ ) in a batch system. In this example, the time required would be 0.55 years using the consultant's estimated coefficient. This is consistent with the consultant's claim that contamination prior to 1987 would have been degraded by 1990. Nevertheless, a time of 14 years would be required if one uses the geometric mean of the literature values reported by Rifai et al. (1995). Therefore, common literature values did not support the consultant's claim of fast (intrinsic) biodegradation.

The discrepancy between the estimated and the commonly reported first-order decay coefficients casts doubt on the accuracy of the consultant's fate and transport simulations. While their estimate could have been high due to site-specific conditions (e.g., unlimited oxygen availability, which was not shown), this estimate was based on data from only three monitoring wells. Therefore, the standard error associated with their estimate was relatively large, and most of the literature values reported by Rifai et al. (1995) fell within the 95 percent confidence limit of their estimate. There was also some uncertainty regarding whether the consultant assumed that the concentration of benzene at the source was equal to its solubility in water (about  $1780 \text{ mg/L}$ ). If the source of benzene is gasoline, this assumption would lead to an overestimation of the decay coefficient because the decay curve is forced to begin at an unrealistically high concentration. According to Raoult's law, the concentration of benzene in ground water that is in equilibrium with gasoline cannot exceed the solubility of benzene in water times its molar fraction in gasoline (typically



about 0.01). This concentration is often less than 20 mg/L (Johnson et al. 1990), but benzene concentrations as high as 130 mg/L can be achieved with some gasoline formulations (Cline et al. 1991).

The dimensions of the contamination source were not relevant in this case because the simulated scenario assumed a pulse source. When a constant source is assumed, however, the area of the source can be an important factor in estimating the biodegradation coefficient. This situation is often encountered when using models for Tier 2 or Tier 3 (RBCA) analyses, where a finite planar source is often the most realistic geometry (e.g., Table 1, Equation 2). Care must be taken not to exaggerate the area of the source. This would overestimate the contaminant release rate (i.e., flux times area); thus, it would overestimate the decay coefficient necessary to simulate the observed contaminant distribution. Similarly, if steady state is assumed, an overestimation of the source area (and thus the release rate) results in an overestimation of the decay coefficient necessary to equalize the migration and degradation rates. An overestimation of the decay coefficient is conducive to underestimating the potential health risk associated with the release because model simulations would underestimate the contaminant concentration at a distant receptor.

The consultant did not evaluate whether their model was adequately calibrated with the estimated decay coefficient (i.e., goodness-of-fit). Furthermore, a sensitivity analysis was not conducted to assess the effect of varying the degradation coefficient within statistical error. Consequently, it could not be ruled out that the selected biodegradation coefficient overestimated the biodegradation rate and underestimated the age of the release.

Indeed, the best estimate of a given parameter is not necessarily precise or reasonable. This is known as the inverse problem, and it can lead to inaccurate use of mathematical models. To prevent this apparently

common problem, ground water professionals should consider adopting compatibility constraints that limit the input of decay coefficients. These limits of acceptability could be based on comparison with values that have been measured at similar sites and the relative standard error of the estimated decay coefficient that is necessary to meet case-specific precision requirements. Sensitivity analyses encompassing a reasonable range of reported values should also be conducted as routine practice.

## Conclusion

The modeling work presented by the consultant could not rule out the possibility that the observed contamination occurred prior to 1987, while Company X operated the facility. This conclusion is based on two facts: (1) there was not sufficient data to ensure that ground water contamination and flow acted in a manner consistent with the principles used in their mathematical model; and (2) the instantaneous pulse source assumption and a relatively high first-order decay coefficient are conducive to underestimating the age of the release. Therefore, the modeling defense by Company X was ineffectual.

Similarly, for fate and transport modeling under RBCA Tier 2 and Tier 3, the consultant must fully justify that modeling assumptions accurately reflect site conditions, that site-specific data used in modeling are valid, and that literature values abstracted for input are realistic and applicable. Without such detailed justification, risk from exposure to petroleum contamination will likely be erroneously assessed, and LUST site owners, operators, and consultants might find themselves in expensive litigation.

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Note: The table has been set on the Lino 2000 equipment. A galley will be run from imagesetter for drop-in. thanks . merry

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**Table 1**

**Commonly Used Three-Dimensional Analytical Fate and Transport Models for LUST Releases in Saturated, Homogeneous Porous Media (Adapted from Dominico and Schwartz 1990)**

**Instantaneous Point Source Model:**

$$C(x,y,z,t) = K \left[ \frac{M}{8 \sqrt{\alpha_x \alpha_y \alpha_z \pi^3 t^3 V_r^3}} \right] \exp \left[ -\frac{(x - v_r t)^2}{4 \alpha_x v_r t} - \frac{y^2}{4 \alpha_y v_r t} - \frac{z^2}{4 \alpha_z v_r t} - \lambda t \right] \quad (1)$$

Where

C = Contaminant concentration (mg/L) at a longitudinal distance of x feet, a transverse (lateral) distance of y feet, and a depth of z feet from the source, at time t (days) after the release

K = 16,019 (i.e., a factor to convert units from lb/ft<sup>3</sup> to mg/L)

M = Released mass of contaminant (lbs) (i.e., source concentration times volume released)

$\alpha_x$  = Coefficient of longitudinal hydrodynamic dispersion (ft), typically about 25 feet (EPRI 1985)

$\alpha_y$  = Coefficient of lateral hydrodynamic dispersion (ft), typically about 5 feet (EPRI 1985)

$\alpha_z$  = Coefficient of vertical hydrodynamic dispersion (ft), typically about 0.5 feet (EPRI 1985)

$V_r$  = Retarded velocity of the contaminant (ft/day) (i.e., the average, linear water velocity divided by the retardation factor)

$\lambda$  = Site-specific first-order decay coefficient (day<sup>-1</sup>)

**Constant Source Model:**

$$C(x,y,z,t) = \left( \frac{C_o}{8} \right) \exp \left\{ \left( \frac{x}{2\alpha_x} \right) \left[ 1 - \sqrt{1 + \frac{4\lambda\alpha_x}{V_r}} \right] \right\} \operatorname{erfc} \left[ \frac{x - V_r t \sqrt{1 + 4\lambda\alpha_x/V_r}}{2\sqrt{\alpha_x V_r}} \right] \\ \left\{ \operatorname{erf} \left[ \frac{(y + Y/2)}{2\sqrt{\alpha_y x}} \right] - \operatorname{erf} \left[ \frac{(y - Y/2)}{2\sqrt{\alpha_y x}} \right] \right\} \left\{ \operatorname{erf} \left[ \frac{(z + Z/2)}{2\sqrt{\alpha_z x}} \right] - \operatorname{erf} \left[ \frac{(z - Z/2)}{2\sqrt{\alpha_z x}} \right] \right\} \quad (2)$$

Where all variables are as previously defined and

$C_o$  = Contaminant concentration at source (mg/L)

Y = Source width (ft) (i.e., depth of the soil source, if contaminated soil exists, or the width of the tank excavation if no contaminated soil exists)

Z = Source depth (ft) (i.e., depth of the soil source, if contaminated soil exists, or the depth of the fill excavated below the tank if no contaminated soil exists)

erf = Error function

erfc = Complementary error function = 1 - erf