

MODEL FOR ESTIMATION OF CHLORINATED SOLVENT RELEASE FROM WASTE DISPOSAL SITES

JOHN C. WALTON, ARTHUR S. ROOD, ROBERT G. BACA and MARK D. OTIS
Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415 (U.S.A.)
(Received May 5, 1988; accepted September 25, 1988)

Summary

A mathematical model was developed to estimate the release and transport of chlorinated solvents from hazardous waste sites located in the vadose zone. The model formulation accounts for container degradation, interphase mass transfer, waste decomposition, soil temperature effects on physical and chemical properties of the waste, and mass transport through geologic media. Aqueous, nonaqueous, and vapor transport were considered. Calculations indicate the dominant transport mechanism is vapor diffusion to the surface and vadose zone. Model predictions also indicate an annual cycle of release caused by changes in soil temperature. The model was applied to an existing waste facility containing five chlorinated solvents. Reasonable agreement was found between model calculations and field data.

Introduction

Disposal of hazardous wastes has become a major environmental concern over the last two decades. In particular, past disposal practices have left a legacy of large amounts of hazardous materials disposed of in a manner and at locations which would not be acceptable by current standards. Management of these wastes and remedial action on these sites is often hampered by poor understanding of the basic processes which transport hazardous materials into the environment. Mathematical models are useful tools for understanding these processes and evaluating alternative remedial actions. A generalized modeling approach was used to examine the various environmental transport mechanisms which may have caused movement of the chlorinated solvents from a disposal site in eastern Idaho.

Projections of the concentrations and fluxes of organic solvents were of interest at this site and at other near surface disposal sites for volatile compounds. In particular, flux to the underlying aquifer was of concern because of its potential environmental impact. Flux to the atmosphere and the factors that control vapor emissions must be known in order to select potential remedial actions such as improved trench covers.

This paper focuses on the development of conceptual and mathematical models for the processes controlling vapor emissions and transport. The formulation considers waste release from buried containers, a calculation of vapor concentrations in the disposal pit itself, and transport of the chlorinated solvents away from the disposal site. The predictive capability of the model is demonstrated using available field data.

Waste site description

The disposal site considered is the Radioactive Waste Management Complex (RWMC), which is located at the Idaho National Engineering Laboratory in Southeastern Idaho. The RWMC comprises approximately 60 hectares of level ground in a shallow depression, about 1,500 meters above mean sea level and enclosed on three sides by low hills. The central and lowest part of this depression, where the burial ground is situated, has a surficial layer of heterogeneous water and wind-deposited sediments. The hydrogeology of the site is described in Barraclough et al. [1]. The burial ground is underlain by more than 600 meters of relatively thin horizontal basalt flows interbedded with lacustrine, fluvial, and windblown sediments. The upper 480 meters of basalt are relatively permeable and contain the Snake River Aquifer. The site receives an average of about 20 cm of precipitation per year with a range of 13 to 36 cm per year. Surface vegetation includes sagebrush and scrub pine.

Disposal records indicate that about 88,400 gallons ($\sim 33 \text{ m}^3$) of mixed organic wastes were disposed of at the RWMC during a five year period between 1966 and 1970. The waste was absorbed with calcium silicate and emplaced in sealed 55-gallon steel containers. The estimated inventory of organic waste deposited during the five year period [2] is presented in Table 1.

The waste containers were buried in trenches and pits within an enclosed area. Some trenches and pits were originally excavated down to the irregular surface of the basalt while others maintained a thin covering of soil over the

TABLE 1

Inventory of organic liquids (moles)

Organic liquid	Inventory	Mole fraction
1. Carbon tetrachloride	9.7×10^5	0.314
2. Machine oil	1.1×10^6	0.356
3. Trichloroethylene	2.7×10^5	0.087
4. Tetrachloroethylene	2.3×10^5	0.074
5. Chloroform	2.9×10^5	0.094
6. 1,1,1-Trichloroethane	2.3×10^5	0.074
Total	3.1×10^6	1.000

TABLE 2

Chemical data at 25°C

	H (dimensionless)	half life (years)	p^0 (bar)
1. Carbon tetrachloride	1.24	7,000	0.05
2. Machine oil	u/n ^a	u/n	0.00
3. Trichloroethylene	0.392	0.9-2.5	0.10
4. Tetrachloroethylene	0.723	0.7-6	0.026
5. Chloroform	0.150	1.3-3,500	0.25
6. 1,1,1-Trichloroethane	0.703	0.5-2.5	0.17

^au/n = unknown (assumed $H=0$, half life = ∞).

basalt surface. The waste was buried at an average depth of 2.5 meters with a surface cover of 1.5 meters. The surface area of the pits covers approximately 34,000 m² spread over a total area of 220,000 m².

The organic compounds of interest have relatively low solubility in water. Table 2 gives the Henry's law constants (H) of the contaminants [3], estimated abiotic decay rates [4], and the vapor pressure at 25°C [5].

The machine oil is a high naphthenic petroleum distillate (e.g., cycloalkanes) which is generally non-toxic [6]. This oil was not the pollutant of primary concern at this site but its presence in the inventory is important because of the influence it has on the vapor pressures of the chlorinated solvents with which the machine oil is mixed, and the viscosity of the organic liquid phase.

The machine oil, which constitutes the largest portion of the waste, has a very high viscosity at typical soil temperatures. The absorption of the organics with calcium silicate further tends to lower their ability to move as a separate phase. Consequently, the nonaqueous organic liquid phase is expected to have little potential for transport through the unsaturated zone.

Waste containment

The waste was initially present in waste containers (e.g., 55 gallon drums). Prior to release of solvents from the waste pits, it was presumed that the integrity of some fraction of the containers was lost. During emplacement, a proportion of the waste containers fail from dropping and/or crushing. This initial failure rate was assumed to be a constant. Subsequent to site closure containers may fail from corrosion processes. The failure rate was assumed to be a first order process. The mass balance equation governing the inventory of organics (Q_{di}) inside containers in the waste site is

$$\frac{dQ_{di}}{dt} = IX_{di}\epsilon - \lambda_d Q_{di} \quad Q_{di}(0) = (0) \quad (1)$$

where I = rate of waste input (mol s^{-1}), X_{di} = mole fraction of i_{th} component in containers, ϵ = portion of containers that do not fail at burial, and λ_d = container failure rate constant (s^{-1}).

There are two time periods of interest; the burial or emplacement period and post emplacement phase. Solution of the equation for these two periods gives

$$Q_{di} = \frac{K_i}{\lambda_d} \{1 - \exp(-\lambda_d t)\} \quad t < t_e, \quad (2)$$

$$Q_{di} = \frac{K_i \{1 - \exp(-\lambda_d t_e)\}}{\lambda_d} \exp(-\lambda_d \{t - t_e\}) \quad t > t_e. \quad (3)$$

where $K_i = X_{di}\epsilon$ and t_e = burial or emplacement time period. The release rate from the containers is thus

$$\zeta_i = IX_d(1 - \epsilon) + \lambda_d Q_{di} \quad t < t_e, \quad (4)$$

$$\zeta_i = \lambda_d Q_{di} \quad t > t_e. \quad (5)$$

The input data required for a simulation consists of the rate of waste input during emplacement (I), the proportion of containers which remained intact during emplacement (ϵ), the mole fraction of each constituent (X_{di}), and the container failure rate (λ_d).

The required data for the RWMC were obtained from internal reports and

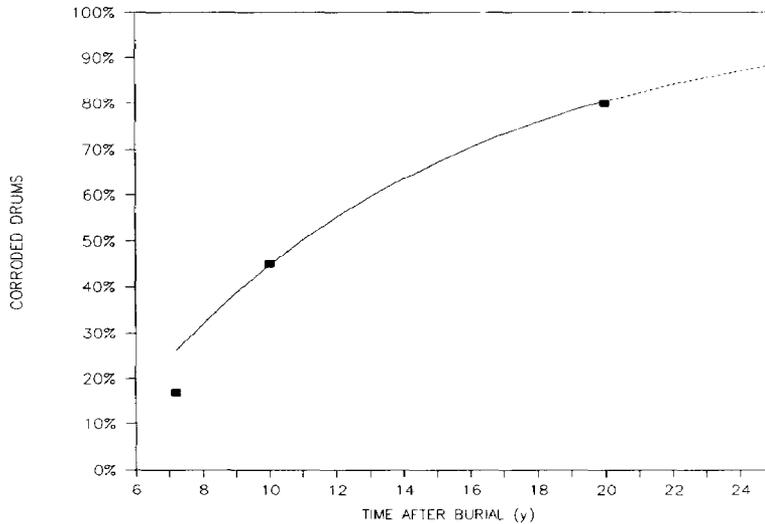


Fig. 1. Historical data (■) on container integrity over time fit to an exponential failure curve.

personal interviews with site personnel concerning the method of waste disposal and container integrity over time. The information suggested a high rate of initial container failure (i.e., drums were usually simply dumped into the pits and a cover bulldozed over the top) which was assumed to be 20%. Three estimates of container failure from corrosion over time were available from drum retrieval studies. These data appear to follow an exponential failure rate during later time periods (Fig. 1) with a failure rate of $\lambda_d = 3.2 \times 10^{-9} \text{ s}^{-1}$. The rate of waste input was estimated to be $26.9 \times 10^{-3} \text{ mol s}^{-1}$ over a depositional period of 5 years ($1.58 \times 10^8 \text{ s}$).

Contaminant concentrations in the disposal pit

Subsequent to release from the containers, the organic compounds are available for transport away from the waste disposal area and for decomposition. In general, transport of organic compounds can occur in a vapor, organic liquid, and/or aqueous phase. The dominant phase of transport is dependent upon the properties of the waste and hydrologic conditions of the site. The concentration of the chlorinated solvent at the disposal pit serves as a boundary condition for transport through the vadose zone. The concentration of each constituent is related to its vapor pressure and is estimated from soil temperature and mole fraction. Estimation of both vapor pressure and mole fraction requires information on constituents of the waste inventory other than the compound of interest.

The mass balance expression for contaminants in the pit but outside the containers is

$$\frac{dQ_{pi}}{dt} = \zeta_i - A(q_{di} + q_{ui}) - \lambda Q_{pi} \quad Q_{pi}(0) = 0, \quad (6)$$

where A = surface area of disposal area (m^2); q_{di}, q_{ui} = upward and downward flux of the i th compound (mol s^{-1}); and λ = decomposition rate (mol s^{-1}).

Vapor pressure estimation at source

The driving force for vapor transport from the source is the vapor pressure of the compound. Vapor pressure was estimated using Raoult's Law [7] which states that the vapor pressure (p_i) is given by the product of pure component vapor pressure (p_i°) and mole fraction (X_{pi}):

$$p_i = p_i^\circ X_{pi} \quad (7)$$

Pure component vapor pressures as a function of temperature are available from Perry and Chilton [5]. The data were fit to an empirical curve of the form [8].

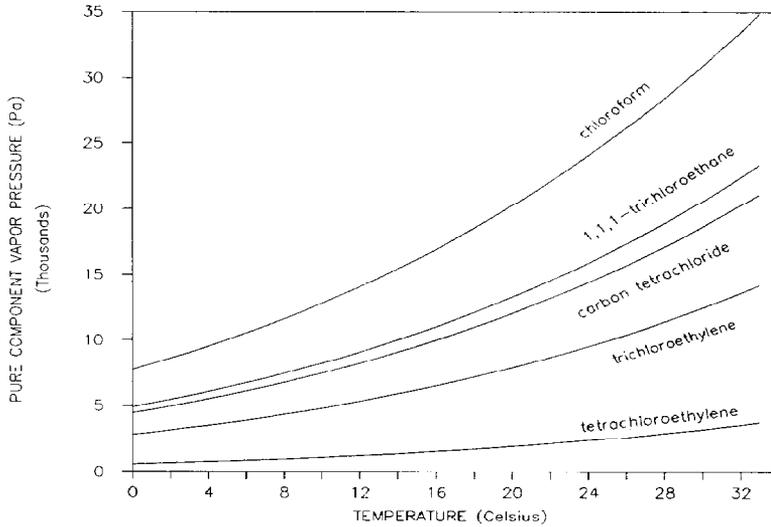


Fig. 2. Vapor pressure of chlorinated solvents of interest as a function of temperature.

$$\ln(p_i^o) = a_1 + \frac{a_2}{T} + a_3 T + a_4 \ln(T) + a_5 T^2 \quad (8)$$

The vapor pressure curves are illustrated in Fig. 2. Mole fractions are estimated from the equation:

$$X_{pi} = \frac{Q_{pi}}{\sum Q_{pi}} \quad (9)$$

In the specific case of the organic waste disposed at the RWMC, a significant quantity of machine oil served to dilute the organic solvents and had some predicted effect on the calculated vapor pressures. In the general case care must be taken to identify constituents of the inventory which will affect the vapor pressure of those compounds being modeled.

Temperature estimation

Estimation of pure component vapor pressure requires that the temperature be known. For compounds buried in disposal pits this requires estimating temperature as a function of depth in soil and time of year. The governing equation for heat conduction in a soil is [9]:

$$\frac{\partial T}{\partial t} = \nabla \cdot D_h \nabla T \quad T(0,z) = T_0(0,z) \quad T(t,0) = T_1(t,0) \quad T(t,\infty) = T_2 \quad (10)$$

where D_h = thermal diffusivity ($\text{m}^2 \text{s}^{-1}$), T = temperature (K), $T_{0,1,2}$ = boundary or initial temperatures (K), and t = time (s).

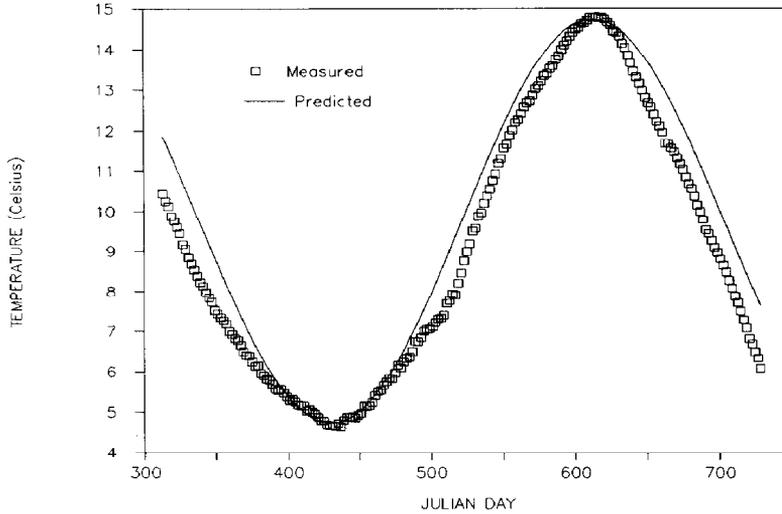


Fig. 3. Comparison of predicted and measured soil temperatures at the site.

For simplicity, the heat flux at the surface is assumed to follow a sine function with a period of one year that corresponds to seasonal variation in solar radiation. If T_{avg} is the average surface soil temperature and A_0 is the maximum seasonal variation then the surface soil temperature can be estimated by:

$$T(0,t) = T_{\text{avg}} + A_0 \sin \omega t \quad (11)$$

Assuming that the soil has a constant thermal diffusivity and is infinitely deep, the temperature at depth z is given by [9]:

$$T(z,t) = T_{\text{avg}} + A_0 \exp\left(\frac{-z}{z_d}\right) \sin\left(\omega t - \frac{z}{z_d}\right) \quad (12)$$

where z_d is the damping depth. To allow adjustment for $t=0$ to begin at any time of the year, a phase lag parameter is added inside the sine term. A phase lag of $-7\pi/12$ causes the simulation to begin on January 1. For site specificity, the general solution form can be fit to local soil temperature data by adjusting T_{avg} and A_0 as needed.

A comparison between fit and actual temperature data at the RWMC [2] is given in Fig. 3; T_{avg} was found to be 9.7°C with an amplitude of 12.7°C . A thermal diffusivity of $5.1 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ was used.

Transport from waste pit

To model contaminant transport from the disposal pit, boundary conditions were established at three locations: (1) the soil-atmosphere interface, (2) the

surface of the aquifer, and (3) the waste pit itself. Concentrations at both external boundaries were set to zero. The time variant concentration at the source was estimated by simultaneous solution of the coupled system of equations. Calculations of flux across these boundaries were simplified by considering only the dominant transport mechanisms for the compounds of interest at the RWMC.

Transport of organic contaminants from the waste pit can occur by advection, diffusion, and dispersion in three phases: vapor, aqueous liquid, and non-aqueous liquid solutions. Transport in the aqueous liquid phase is dependent, among other things, upon the solubility of the contaminant, soil moisture content, and flow rate. Water content and flow rate in the unsaturated zone are directly related to infiltration rates. For the RWMC, infiltration is quite low due to the arid nature of the climate (approximately 20 cm/y precipitation), however transport by dissolution in soil water may be important both for transport and as a means of retardation of contaminant movement.

Nonaqueous liquid phase movement is dependent upon the viscosity of the fluid. The wastes disposed at the RWMC were originally in a "semi-solidified" form (using calcium silicate) and contained a substantial amount of highly viscous machine oil [6]. The kinematic viscosity of the contaminants studied (~ 500 cSt or $5 \text{ cm}^2/\text{s}$) and pre-solidification of the waste resulted in very limited transport of liquids. Therefore, the nonaqueous liquid phase is, for all practical purposes, immobile.

Vapors move by advection, dispersion, and diffusion. Advection and dispersion of vapors can be caused by density differences and by mechanisms which can result in movement of subsurface air such as barometric pressure changes and changes in the water table depth. Some studies [10,11] suggest that vapor migration of fairly dilute contaminants is predominantly by simple molecular diffusion. Barometric pressure and wind effects typically dampen quickly with depth in the soil and density disparity induced velocities only become important at higher vapor concentrations than have been measured or predicted at the site.

Derivation of governing equations

The change in the total contaminant concentration (M) due to a flux (\mathbf{q}) of a contaminant can be obtained by mass balance:

$$\frac{\partial M}{\partial t} = -\nabla \cdot \mathbf{q} + R_R \quad (13)$$

where R_R is the rate of reaction. If ϕ_l , ϕ_g , ϕ_s are the liquid, gas and solid filled porosity and C, G and S are the soil water, soil gas and solid phase concentrations then the total mass per unit volume is:

$$M = (\phi_l C + \phi_g G + \phi_s S) \quad (14)$$

For compound degradation, the reaction rate is the rate constant times the concentration:

$$R_R = -\lambda M \quad (15)$$

The total flux leaving the waste pit is the sum of the liquid phase (\mathbf{q}_l) and gas phase (\mathbf{q}_g) fluxes,

$$\mathbf{q} = \mathbf{q}_l + \mathbf{q}_g \quad (16)$$

The flux of contaminant in the liquid phase is a result of advection, dispersion, and diffusion. Rates of contaminant dispersion in the unsaturated zone have been found to be fairly low [12]. Likewise, diffusion in the aqueous phase is approximately 4 orders of magnitude slower than vapor phase diffusion [5]. In the interest of simplification these minor terms are not considered, thus the important fluxes are advection in aqueous liquid

$$\mathbf{q}_l = \phi_l V_l \mathbf{C}, \quad (17)$$

and vapor diffusion

$$\mathbf{q}_g = \phi_g D \nabla G. \quad (18)$$

The vadose zone transport equation for an individual contaminant is then given by

$$\frac{\partial (\phi_l \mathbf{C} + \phi_g \mathbf{G} + \phi_s \mathbf{S})}{\partial t} = -\nabla \cdot (\phi_l v_l \mathbf{C} - \phi_g D \nabla G) - \lambda (\phi_l \mathbf{C} + \phi_g \mathbf{G} + \phi_s \mathbf{S}) \quad (19)$$

To solve the transport equation, relations are needed between the concentrations in the gaseous, aqueous, and solid phases. Partitioning of contaminant between the aqueous and vapor phases is assumed to obey Henry's Law ($G/C = H$). Partitioning of contaminants between the liquid phase and solid was assumed to follow linear reversible sorption with ($K \equiv S/C$) giving

$$\frac{\partial \phi_g \mathbf{G}}{\partial t} = \frac{1}{R_d} \left\{ \nabla \cdot \left(-\phi_l v_l \frac{\mathbf{G}}{H} + \phi_g D \nabla \mathbf{G} \right) \right\} - \lambda \phi_g \mathbf{G}, \quad (20)$$

$$G(0, z) = 0 \quad G(t, 0) = G_{\text{pit}}(t) \quad G(t, z_s) = 0$$

where the retardation factor is given by

$$R_d = \left(\frac{\phi_l}{\phi_g H} + 1 + \frac{\phi_s K}{\phi_g H} \right), \quad (21)$$

z_s is the atmosphere or aquifer surface, and G_{pit} is the contaminant concentration in the waste pit.

The relative importance of the two transport modes is highly dependent upon assumed infiltration rates and soil properties. In the arid climate considered, low infiltration rates (e.g., less than 5 cm/y) persist thus the vapor dif-

fusion term dominates the flux. Under these conditions the solution can be closely approximated by considering only vapor diffusion.

Variability in partitioning of the different waste constituents between the vapor, liquid, and solid phases (i.e., variability of K and H) can lead to separation of constituents during transport [13]. Although predicted by the model, sufficient data are not available to determine the degree to which this separation of contaminants is actually occurring at the site.

Parameter estimation

Sorption of organic solvents is related to the organic carbon content of the soil or rock material [14]. The site consists of relatively recent igneous rocks at a desert location. Organic carbon content of the materials is very low. Thus K was assumed to be negligible. This would not be the case at many wastes sites, thus sorption was included in the governing equations for completeness.

The diffusivity of vapors in porous media was estimated from diffusivity in air using the Millington formula [15]

$$D = D_0 \phi_v^{\frac{1}{2}} (\phi_v / \phi_t)^2 \quad (22)$$

The diffusivity of the contaminants in air is approximately $10^{-5} \text{ m}^2 \text{ s}^{-1}$ [5]. The total and vapor filled porosity of the cover materials have been estimated as [2] $\phi_t = 32\%$, $\phi_v = 15\%$. Porosity of the basalts based upon 61 laboratory analyses [16] was estimated as 8%. Separate modeling estimates of flow in the unsaturated zone at the site by the authors has suggested a moisture content of 1% in the basalt. The net infiltration rate for water at the site was assumed to be 5 cm/y giving a liquid pore velocity (v_l) of 625 cm y^{-1} .

The temperature dependence of the diffusion coefficient can be predicted from the kinetic theory of gases [17]:

$$D = D_0 (T / T_r)^{3/2} \quad (23)$$

where T_r is the reference temperature. This allows additional correction of the vapor diffusion coefficient from 25°C to the average temperature of the site (9.7°C).

Groundwater contamination

At the RWMC, contaminants have migrated through the vadose zone into the Snake River Aquifer which lies beneath the site. To model transport in the groundwater, the aquifer was modeled as a homogeneous porous medium of infinite lateral extent and finite depth. A uniform flow field was assumed to exist throughout the area studied. An analytical solution to ground water dispersion equation [18] was used to estimate concentrations down gradient from the disposal facility.

The equation for contaminant transport in groundwater is

$$\frac{\partial C}{\partial t} + \frac{\mathbf{v}}{R_d} \cdot \nabla C = \nabla \cdot D \nabla C - \lambda C, \quad C(0, x, y, z) = 0 \quad \frac{\partial C(t, x, y, z=0, b)}{\partial z} = 0 \quad (24)$$

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

For an impulse release of contaminant the solution is [18]

$$C(t, x, y, z) = \frac{M_i}{R_d} X(x, t) Y(y, t) Z(z, t), \quad (25)$$

where

$$X(x, t) = \frac{1}{2l} \left\{ \operatorname{erf} \frac{x + \frac{l}{2} - \frac{v_x t}{R_d}}{\sqrt{\frac{4D_x t}{R_d}}} - \operatorname{erf} \frac{x - \frac{l}{2} - \frac{v_x t}{R_d}}{\sqrt{\frac{4D_x t}{R_d}}} \right\} \exp(-\lambda t), \quad (26)$$

$$Y(y, t) = \frac{1}{2w} \left\{ \operatorname{erf} \frac{y + \frac{w}{2}}{\sqrt{\frac{4D_y t}{R_d}}} - \operatorname{erf} \frac{-y + \frac{w}{2}}{\sqrt{\frac{4D_y t}{R_d}}} \right\}, \quad (27)$$

$$Z(z, t) = \frac{1}{b}. \quad (28)$$

The solution was modified for a continuous time variant release by summing over a series of impulse releases. When the impulse spacing is kept small, relative to the standard deviation of the impulse at the receptor, a continuous time variant release can be simulated by [19]:

$$C(t, x, y, z) = \sum_{i=1}^k \frac{M_i}{R_d} X(x, t - t_i) Y(y, t - t_i) Z(z, t - t_i) \quad (29)$$

where b = aquifer thickness (300 m), $D_{x,y,z}$ = dispersion coefficients in the x , y , and z directions ($\text{m}^2 \text{s}^{-1}$), l = length of area source in x direction (469 m), M_i = amount of contaminant released in each pulse (mol), t = time (s), t_i = time of pulse release (s), and w = length of area source in y direction (469 m). The time variant flux of contaminant to the groundwater is obtained from the vadose zone transport code, then discretized into a number of impulse releases for use in eqn. (29). Modeled parameters were taken from Robertson, 1974 [20]. These parameters were: longitudinal dispersivity 91 m, transverse dispersivity 137 m, groundwater velocity 1.4×10^{-5} m/s, and aquifer thickness of 300 m.

Model application

Numerical solution

The governing equations presented above represent a system of differential equations describing release from the containment drums, mass balance of contaminants outside the drums but in the waste pits, transport of contaminants through the vadose zone, and transport through the aquifer. The solution methodology is best explained by considering the mass balance of contaminants in the pits but outside the drums (Fig. 4),

$$\frac{dQ_{pi}}{dt} = \zeta_i - A(-q_{di} + Q_{ui}) - \lambda Q_{pi} \quad (6)$$

Equation (6) represents a system of 6 coupled ordinary differential equations, one for each constituent. The system of 6 ordinary differential equations is solved by fifth order Runge–Kutta [21]. Solution of the system of equations requires estimates for release rate from the drums (ζ_i) and rate of mass transport from the pits (q_{di} , q_{ui}) as a function of time. Release rate from the drums is given by the analytical solution (eqns. 4–5).

The mass transport rate is obtained using an explicit solution to the one dimensional transport equation (eqn. 19). A standard finite difference method is used to solve the partial differential equation [22]. The Runge–Kutta and finite difference solving methods are coupled through the contaminant concentrations at the waste pits (G_{pit} , the boundary concentration for the trans-

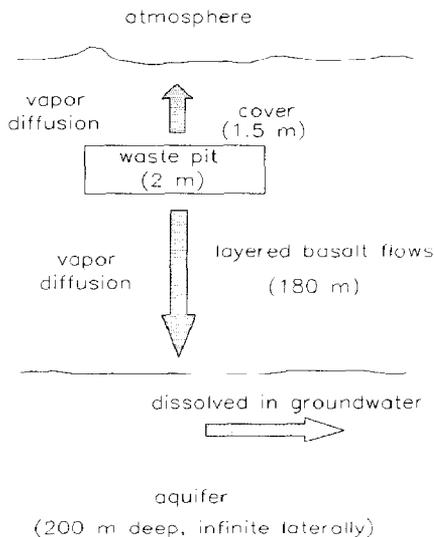


Fig. 4. Schematic of waste disposal site model showing direction of waste migration (arrows) and the thickness of the different submodel domains.

port calculation) and the transport flux ((q_{di}, q_{ui}) , required for obtaining a mass balance within the pits). The computational sequence involves alternating calls to the two routines. The contaminant flux is assumed constant during each call to the Runge–Kutta solver and the concentration in the pits is assumed constant during each call to the finite-difference solver. This methodology puts limitations on the length of the time steps which can be achieved, especially during early time periods when the rate of change is high. The flux of each contaminant to the groundwater at each time step is entered into the groundwater plume equation (29) as a single impulse release. The estimated groundwater concentration in three dimensions is then the sum of the contributions from all impulses.

Results

Release rate projections are highly dependent upon site properties, waste properties, and the compound of concern. The estimated release rate of carbon tetrachloride and tetrachloroethylene from the waste containers and the waste pits is illustrated in Figs. 5 and 6. In each figure, the smooth (solid) lines represent loss of containment from drum failures and the undulating (dashed) line represents the release rate from the waste pits.

Release rates from waste drums are a result only of the properties of the containers and are, therefore, similar for both compounds. During the initial five year disposal period, the inventories of both compounds increased as more containers were added to the pit. There was an initial container failure rate of 20% and an exponential container failure rate due to corrosion. Subsequent to the depositional period, only the exponential failure mechanisms operate to release material from buried drums.

Once solvents are released from the waste drums, release from the pit is driven by vapor pressure. The release rate from the waste pit is, therefore, a strong function of temperature with peaks of release during summer periods of warmer soil temperatures. This results in the sinusoidal cycles of release shown in Figs. 5 and 6. The amplitude of this cyclic variation is determined by site-specific meteorological conditions (annual seasonal temperatures), soil characteristics (thermal diffusivity), and the average depth of the waste pit. Within the time frame of interest, the average release rate of carbon tetrachloride is controlled by container failure rates.

The physical properties of the various chlorinated solvents can have a strong influence on the relative importance of release rates due to container failure and vapor phase transport away from the disposal pit. This can be seen by comparing the behavior of carbon tetrachloride and tetrachloroethylene as shown in Figs. 2, 5 and 6.

Carbon tetrachloride has a very high vapor pressure at all temperatures when compared to tetrachloroethylene (Fig. 2). Consequently, it can move as a vapor out of the waste quite rapidly. Figure 5 indicates that the average vapor

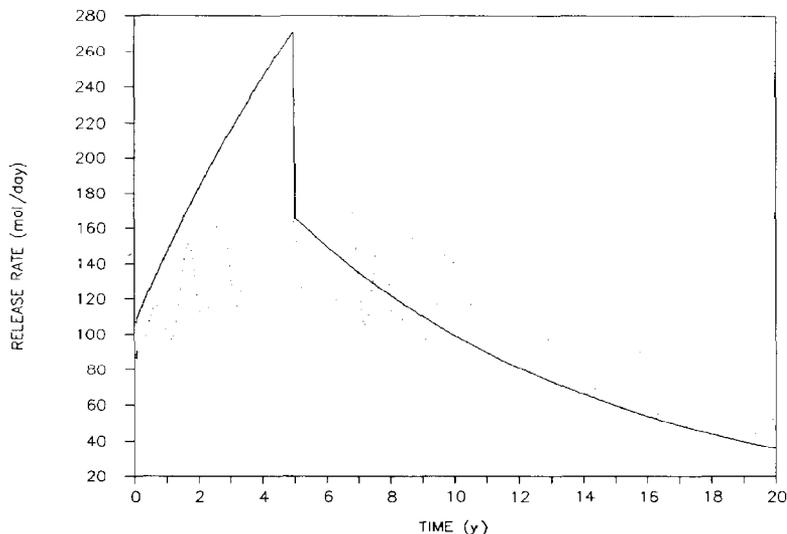


Fig. 5. Simulated release rates of carbon tetrachloride. The solid line represents release from the steel drums. The dashed line represents release from the waste pits.

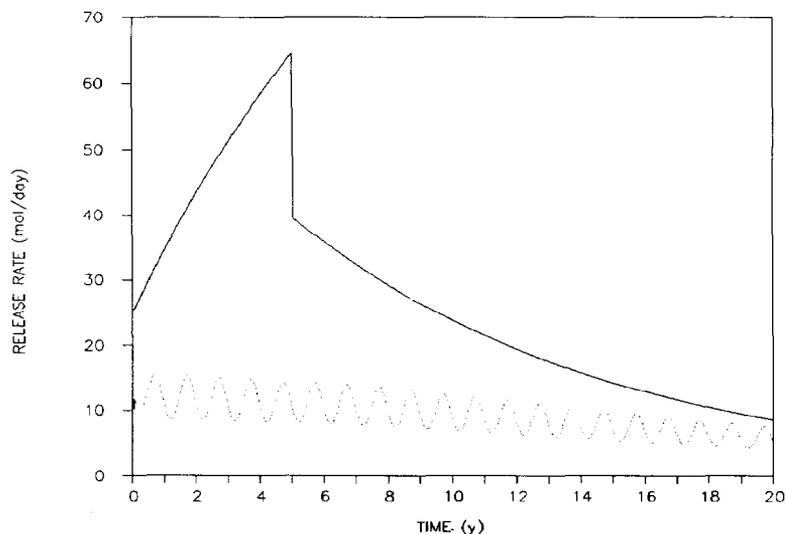


Fig. 6. Simulated release rates of tetrachloroethylene. The solid line represents release from the steel drums. The dashed line represents release from the waste pits.

phase release rate from the pit is always very close to the release rate from the waste containers. Container failure is, therefore, the limiting process for re-release of carbon tetrachloride.

Tetrachloroethylene, in contrast, has a lower vapor pressure and cannot move away from the disposal pit as quickly as it is released from failing containers.

This is clear from Fig. 6 in which the average release rate from the pit by vapor transport is everywhere lower than the release rate from the waste containers. From these two cases the behavior of the other constituents of the waste inventory can be anticipated (Fig. 2). Chloroform and 1,1,1-trichloroethane have vapor pressures even higher than carbon tetrachloride and will show a pattern of release rates similar to Fig. 5.

Figure 7 is an illustration of the integrated downward flux from the waste pit into the vadose zone. Flux upward to the atmosphere constitutes the remainder of the total. This figure clearly shows the influence on vapor pressure of annual variations in soil temperature even for cumulative releases. Although a significant fraction of the annual release moves toward the aquifer during early time periods, in the long run concentration gradients below the site increase, slowing the downward flux and leading to the dominance of atmospheric release. This has important consequences for evaluation of potential remedial actions. For example, addition of a high quality cover of the type designed to minimize water infiltration could decrease the flux to the atmosphere but result in an increase in the downward flux into the vadose zone, and eventually, the groundwater.

Predicted concentrations of carbon tetrachloride in the groundwater for the summer of 1987 (approximately 21 y after disposal began) are shown in Fig. 8. Also shown in Fig. 8 are measured concentrations of carbon tetrachloride from USGS monitoring wells [23]. The predicted results matched measured

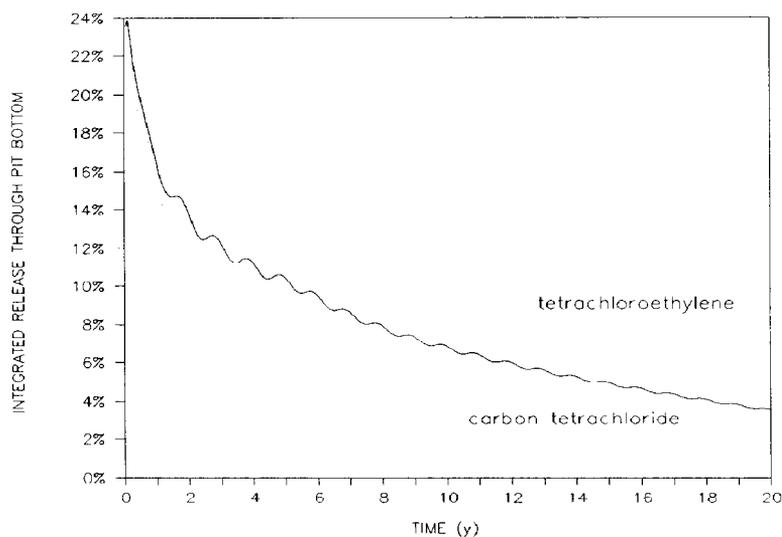


Fig. 7. Proportion of total release remaining in the subsurface. The graph compares the relative importance of flux to the atmosphere with transport into the vadose zone and groundwater. Most contaminants are released to the atmosphere.

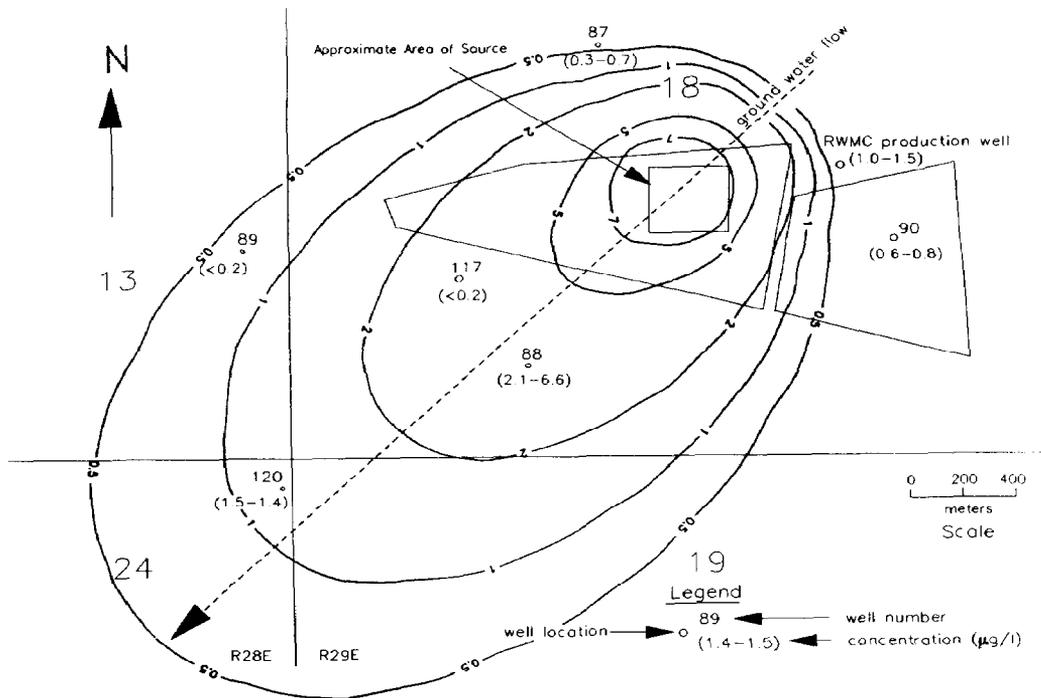


Fig. 8. Comparison of measured and calculated concentrations of carbon tetrachloride in the groundwater for 1987 (simulation time 21 years).

concentrations at wells 88 and 120, both of which are located down gradient from the RWMC. Well 117 was also located down gradient from the RWMC, however recent field data have shown no concentrations above $0.2 \mu\text{g}/\text{l}$.

The up gradient wells showed higher concentrations than predicted by the model. These wells included well 87, 90 and the RWMC production well. The model does not predict the concentrations in these wells for a number of reasons, some of which are 1) pumping from the production well was not included in the model, and 2) occasional seasonal gradient reversals in the ground water flow field [1] were not considered. While the model used in the analysis was adequate for downgradient predictions, up gradient predictions will require a more sophisticated groundwater model and supporting input data to accompany it. Considering the number of steps involved in the modeling process, the agreement between measured and predicted values is excellent.

Figure 9 gives the predicted flux of carbon tetrachloride to the groundwater as a function of time. Although the release rate from the disposal pits peaked approximately 15 years ago, the groundwater contamination problem is not expected to peak for another 25 years. The delay is a result of transport lag in

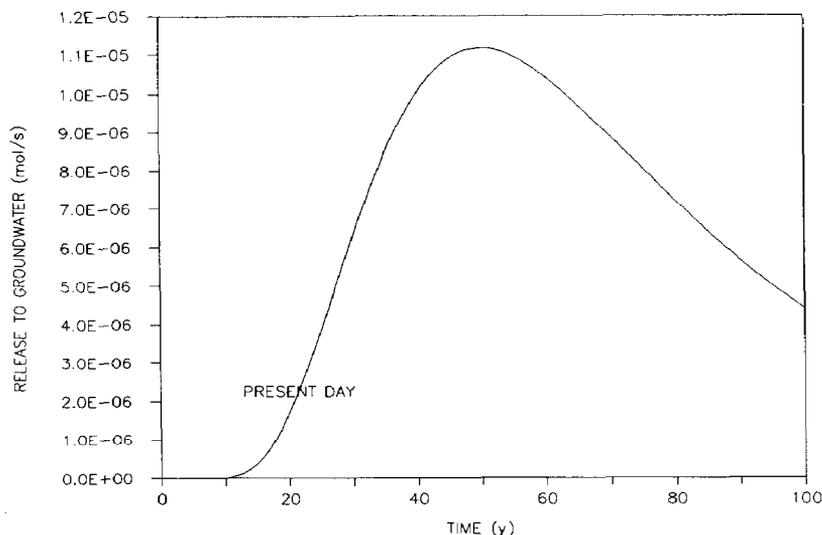


Fig. 9. Predicted time variant flux of carbon tetrachloride to the groundwater if no remedial actions are taken at the site. The model predicts that groundwater concentrations will peak 20–40 years in the future even though total releases from the waste pits (Figure 5) peaked 15 years ago back in 1972.

the vadose zone. These calculations clearly show that groundwater concentrations will increase if no remedial actions are taken at the RWMC.

Conclusions

A systematic approach has been developed for modeling organic contaminant release and transport from a hazardous waste site in an arid environment. The model theory predicts an annual cycle of vapor release induced by seasonal change in soil temperature. Container failure rates and diffusive mass transport have a significant effect on release from the pit. The release is also dependent upon the vapor pressure of the compound of interest and the hydrologic conditions of the site.

This work demonstrates that the first principles of chemistry and physics can be used to describe complex processes influencing organic contaminant releases from a disposal site. The model formulation can be greatly simplified by specializing the governing equations to apply to the unique site characteristics and properties of the compounds of interest. The model application to the RWMC provided the following information:

- a) The majority of the organic vapors released from the waste pits have been vented to the atmosphere.

- b) Release rates from the pits are primarily controlled by the container failure history and attenuated by the soil temperature cycle.
- c) Concentrations in the disposal pit reached a maximum about five years after start of disposal.
- d) Concentrations in the groundwater are projected to increase with time (if no remedial action is taken), with the peak occurring round about 2010 (25 years from present).

This information is being used in the selection and design of remedial actions that will be implemented at the RWMC.

Acknowledgement

Work performed under the auspices of the U.S. Department of Energy, DOE Contract No. DE-AC07-76IDO1570.

Notation

a_{1-5}	coefficients for vapor pressure equation
A	surface area of disposal area (m^2)
A_0	amplitude of temperature change at surface (K)
b	aquifer thickness (m)
c	concentration in soil moisture ($mol\ m^{-3}$ water)
D	coefficient of molecular diffusion in porous media ($m^2\ s^{-1}$)
D_h	thermal diffusivity ($m^2\ s^{-1}$)
D_0	coefficient of molecular diffusion in air ($m^2\ s^{-1}$)
$D_{x,y,z}$	dispersion coefficients in the x , y , and z directions = αv ($m^2\ s^{-1}$)
G	concentration in soil gas ($mol\ m^3$ soil gas)
H	Henry's law constant = G/C
I	rate of waste input (mol total organic s^{-1})
K	volumetric distribution coefficient = S/C
K_i	$IX_{di}\delta$ ($mol\ i\ s^{-1}$)
l	length of area source in x direction (469 m)
M	total contaminant concentration ($mol\ m^{-3}$ total volume)
M_i	mass of contaminant released in each pulse (mol)
ϕ_l, ϕ_g	liquid and gas filled porosity
p	pressure (Pa)
p_i^0	pure component vapor pressure of i (Pa)
p_i	actual vapor pressure of contaminant i (Pa)
q_{ui}	upward flux of contaminant ($mol\ m^{-2}\ s^{-1}$)
q_{di}	downward flux of contaminant ($mol\ m^{-2}\ s^{-1}$)
Q_{di}	moles of component i in buried containers
Q_{pi}	moles of component i in disposal area outside of containers
R_R	rate of reaction ($mol\ s^{-1}\ m^{-3}$)
R_d	retardation factor

S	concentration on soil solids (mol m^{-3} solids)
t	time (s)
t_0	length of emplacement period (s)
t_t	total time (s)
t_i	time of pulse release (s)
T	absolute temperature (K)
T_{avg}	annual average soil temperature (K)
T_R	reference temperature (K)
v_1	liquid pore velocity (m s^{-1})
x	distance in x direction (m)
X_{di}	mole fraction of component i in containers
X_{pi}	mole fraction of i outside container in disposal area
y	distance in y direction (m)
w	length of area source in y direction (469 m)
z	depth (m)
z_d	damping depth (m) $= \sqrt{2D_h/\omega}$
z_s	depth of aquifer/atmosphere surface relative to waste pits (m)
α	dispersivity (m)
ϵ	proportion of containers which do not fail at initial burial
ζ_i	release rate of component i from containers (mol s^{-1})
λ_d	container failure rate subsequent to burial (s^{-1})
λ	decomposition rate (s^{-1})
ω	angular frequency $= 2\pi$ divided by the period (one year) (s^{-1})

References

- 1 J.T. Baraclough, J.B. Robertson and V.J. Janzer, Hydrology of the Solid Waste Burial Ground, as Related to the Potential Migration of Radionuclides. Idaho National Engineering Laboratory, U.S. Geological Survey Open Report 76-471, 1976.
- 2 P.T. Laney, S.C. Minkin, R.G. Baca, D.L. McElroy, J.M. Hubbell, L.C. Hull, B.F. Russel, G.J. Stormberg and J.T. Pittman, Subsurface Investigations Program at the Radioactive Waste Management Complex of the Idaho National Engineering Laboratory, Annual Progress Report: FY-1987, DOE/ID-10183, 1988.
- 3 J.M. Gossett, Measurement of Henry's Law constants for C_1 and C_2 chlorinated hydrocarbons, Environ. Sci. Technol., 21 (2) (1987) 202-209.
- 4 T.M. Vogel, C.S. Criddle and P.L. McCarty, Transformations of halogenated aliphatic compounds, Environ. Sci. Technol., 21(8) (1987) 722-736.
- 5 R.H. Perry and C.H. Chilton, Chemical Engineers' Handbook, 5th ed. McGraw-Hill, New York, NY, 1973.
- 6 Texaco Inc., Regal Oil, Industrial Hygiene, Toxicology, and Material Safety Data Sheet, Texaco, Inc., Beacon, NY, 1987.
- 7 I.M. Klotz and R.M. Rosenberg, Chemical Thermodynamics - Basic Theory and Methods. W.A. Benjamin, Inc., Menlo Park, CA, 1974.

- 8 J.M. Prausnitz, T.F. Naderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria. Prentice-Hall, Englewood Cliffs, NJ, 1980.
- 9 D. Kirkham and W.L. Powers, Advanced Soil Physics. Wiley-Interscience, New York, NY, 1972.
- 10 D.D. Evans, Gas movement, in: C.A. Black (Ed.), Methods of Soil Analysis, American Society of Agronomy, Madison, WI, 1965, pp. 319-330.
- 11 V.C. Rogers, K.K. Nielson, G.B. Merrell and D.R. Kalwarf, The Effects of Advection on Radon Transport Through Earthen Materials. NUREG/CR-3409, 1983.
- 12 M.Th. van Genuchten, J.C. Parker and J.B. Kool, Analysis and prediction of water and solute transport in a large lysimeter, in: E.P. Springer and H.R. Fuentes (Eds.), Modeling Study of Solute Transport in the Unsaturated Zone. NUREG/CR-4615, 1987.
- 13 A.L. Baehr, Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor Phase Partitioning, Water Resour. Res., 23 (10) (1987) 1926-1938.
- 14 M.R. Mehran, R.L. Olsen and B.M. Rector, Distribution Coefficient of Trichloroethylene in Soil-Water Systems, Groundwater, 25 (3) (1987) 275-292.
- 15 R.J. Millington, Gas Diffusion in Porous Media, Science, 130 (1959) 100-102.
- 16 A.I. Johnson, Laboratory Report on the Hydrologic and Physical Properties, Snake River Basalt, Idaho, Hydrologic Laboratory, U.S. Geological Survey, Denver, CO, 1960.
- 17 R.B. Bird, W.E. Stewart and E.N. Lightfoot, Transport Phenomena. John Wiley and Sons, New York, NY, 1960.
- 18 R.B. Codell and J.D. Duguid, Transport of radionuclides in groundwater, in: J.E. Till and H.R. Meyer (Eds.), Radiological Assessment-A Textbook on Environmental Dose Analysis, NUREG/CR-3332, 1983.
- 19 J.C. Walton, M.S. Bensky, M.E. Mease and T.J. Bander, Sensitivity of Radionuclide Transport in Groundwater to Source and Site Characteristics, Waste Management 88, University of Arizona, AZ, 1988.
- 20 J.B. Robertson, Digital Modeling of Radioactive and Chemical Waste Transport in the Snake River Plain Aquifer at the National Reactor Testing Station, Idaho. IDO-22054, USGS, Water Resources Division, Idaho Falls, ID, 1974.
- 21 W.H. Press, B.P. Flannery, S.A. Teuklsky and W.T. Vetterling, Numerical Recipes-The Art of Scientific Computing. Cambridge Univ. Press, Cambridge, MA, 1985.
- 22 B. Carnahan, H.A. Luther and J.O. Wilkes, Applied Numerical Methods. John Wiley and Sons, New York, NY, 1969.
- 23 L.J. Mann and L.L. Knober, Purgeable Organic Compounds in Groundwater at the Idaho National engineering Laboratory, Idaho. USGS Open File Report 87-766, ID, 1987.