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Ms. Madhulla Logan Hazardous Materials Specialist Alameda County Health Agency 1131 Harbor Bay Parkway, 2nd Floor Alameda, California 94502

Subject: Results of Fate and Transport Modeling

Encinal Terminals Site, Alameda, California Re:

Dear Ms. Logan:

Woodward-Clyde Consultants (WCC), on behalf of Encinal Terminals Corporation (Encinal), is pleased to submit this letter describing the results of chemical fate and transport modeling at the Encinal Terminals site located at 1521 Buena Vista Avenue, Alameda, California (the site). The fate and transport modeling was performed to evaluate the potential for chemical migration in shallow groundwater from the site towards the bay. The modeling results are used to support decisions about the need (if any) and extent of additional remediation activities at the site, and ultimately to obtain a no further action (NFA) notice for the site.

EXECUTIVE SUMMARY

The site consists of an area where soil and shallow groundwater have been impacted by volatile organic compounds (VOCs), mainly 1,1-DCA. According to existing documentation, a considerable amount of investigation and remediation work has been performed at the site. That work included previous site soil and groundwater characterization by Geomatrix Consultants (Geomatrix 1995), and excavation and on-site stockpiling of several hundred cubic yards of impacted soil. In a letter from you to Mr. Wang of Encinal dated May 18, 1996, the Alameda County Department of Environmental Health (the County) required additional activities before issuing a NFA notice. The activities required include stockpile characterization, performance of chemical fate and transport modeling, additional remediation by excavation, and groundwater monitoring. This letter presents the site-specific approach, the input assumptions for this study, and the results of the modeling.

The chemical migration scenario to be modeled is represented by potential leaching of 1,1-DCA from soil into shallow groundwater, and subsequent horizontal migration of 1,1-DCA dissolved in the shallow groundwater as it naturally flows towards the harbor. Figure 1 presents a

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schematic plan view of the site, including the location of the residual 1,1-DCA in soil, and shallow groundwater average flow direction and gradient, based on measurements performed in 1996. It is important to point out that 1,1-DCA was never detected in monitoring well MW-10 that was installed as a "trigger point" downgradient of the source for early detection of migration towards the harbor.

In summary, the model estimated relatively low concentrations of 1,1-DCA in shallow groundwater at the bay before mixing into surface waters. The modeling results show that past excavation activities had a dramatic effect in reducing potential impact on the bay. The model shows that, due to degradation, concentrations of 1,1-DCA at the bay become undetectable within about 10 years after remediation. Due to the conservatism used in the model, and also based on the results of field sampling which indicate no detection at MW-10 and beyond, we conclude that no additional active remediation needs to be performed at the site. We recommend no further action based on the fact that:

- The active source has been removed
- Natural attenuation is significantly taking place at the site, effectively limiting the length of the residual plume by degradation of the chemical before reaching downgradient receptors
- The modeling and field sampling results indicate no significant impact on human health and the environment

Additional details about the fate and transport modeling are provided below.

MODELING ASSUMPTIONS AND EQUATIONS

Relevant processes governing the fate and transport of 1,1-DCA from the source (soil) to the potential receptor (water quality in the harbor) include: soil-water-air partitioning, vertical infiltration, mixing of leachate from soil into shallow groundwater, retardation due to adsorption to soil particles, chemical degradation over time, and finally mixing of shallow groundwater into the harbor's surface water (see Figure 2). We have developed a model that provides a conservative estimation of the potential water quality impact due to the residual concentration of 1,1-DCA in soil. The model is based on the fundamental equations for partitioning, infiltration, mixing, retardation, and degradation according to the American Society for Testing and Materials (ASTM) Risk-Based Corrective Action (RBCA) guidance (ASTM 1995), USEPA and other relevant exposure and risk assessment guidance, as appropriate. Site-specific input parameters based on field measurements or engineering judgment were used.



The chemical fate and transport model includes:

- Leaching of chemicals from the source located in the near-surface soil,
- Impact of chemicals on shallow groundwater quality upon entering the shallow saturated zone,
- Horizontal movement of chemicals in shallow groundwater governed by advection, retardation due to soil absorption, and longitudinal dispersion,
- Fate of chemicals in shallow groundwater governed by degradation during migration, and
- Impact of chemicals dissolved in shallow groundwater at the interface with surface water in the harbor.

Models describing the above processes are presented in Marino (1974), ASTM (1995) and in the manual for the USEPA's Multimed Model (USEPA 1990a and 1990b). We applied the appropriate models to estimate the chemical concentration in shallow groundwater at the interface with the harbor resulting from a given source concentration in soil. The modeling results were used to evaluate what residual soil concentrations are protective of water quality. The water quality protection criterion for 1,1-DCA is based on the standard USEPA method detection limit (MDL), corresponding to non detectable degradation of water quality.

The model was based on the following assumptions (see Figure 2 for a graphical illustration):

- The chemical source is assumed to have a spatially uniform concentration; transversal width of the source is conservatively assumed to be infinite (i.e., no lateral dispersion).
- Chemical concentration in water leaching from the source is estimated from the soil concentration based on equilibrium partitioning.
- Steady state migration of chemicals in the vadose zone is conservatively assumed to be governed by infiltration without retardation from soil adsorption and without attenuation due to dispersion or degradation. This would result in a leachate concentration at the water table conservatively equal to the concentration of leachate at the source.
- Concentration in the shallow groundwater after mixing with leachate beneath the source is conservatively assumed to be equal to the concentration in the leachate (i.e., no dilution is assumed for the leachate upon mixing into shallow groundwater).
- Degradation half-life of 1,1-DCA during migration in shallow groundwater is estimated based on conservative degradation rates from published literature (Howard et al. 1991).



The equations representing the processes outlined above, which were incorporated in the chemical fate and transport model, are presented below:

Soil-Water Partitioning:

Partitioning =
$$C_{leachate} / C_{soil} = \rho_b / (\rho_b K_d + \theta_{water} + H \theta_{air}) [(mg/kg)/(mg/L) \text{ or } cc/g]$$

Where:

 ρ_b = soil bulk density [g/cc]

 K_d = soil-water partitioning coefficient [cc/g] = $f_{oc} * K_{oc}$

 f_{oc} = total organic carbon fraction in soil (soil TOC) [--]

 K_{oc} = chemical-specific organic carbon partition coefficient [cc/g]

 $\theta_{\text{water}} = \text{water-filled porosity} [--]$

H = dimensionless Henry's constant [--]

 $\theta_{air} = air-filled porosity [--]$

Assuming conservatively no adsorption ($K_{oc} = 0$) and no volatilization (H = 0):

Partitioning =
$$C_{leachate} / C_{soil} = \rho_b / \theta_{water} [(mg/kg)/(mg/L)]$$

This concentration was assumed to occur in the shallow groundwater below the source.

Attenuation due to dispersion and degradation during shallow groundwater migration:

Attenuation during shallow groundwater migration was based on the solution of the transport equation by Marino (1974), described in detail in Attachment B. The Marino solution accounts for advection, dispersion, linear adsorption, first-order decay of the chemical, and exponentially decaying source for a solute migrating in groundwater within homogeneous and isotropic porous media in steady unidirectional flow fields. The Marino solution presented in eq. 44 of Marino (1974) is reported below (note that we have divided the fate and transport parameters by the retardation coefficient to account for the effect of linear adsorption):

$$C(x,t) = \frac{C_o}{2} \left\{ \exp\left[\frac{x(u-\mu)}{2D}\right] \cdot erfc\left(\frac{x-\mu t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u+\mu)}{2D}\right] \cdot erfc\left(\frac{x+\mu t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u+\mu)}{2D}\right] \cdot erfc\left(\frac{x(u+\mu)}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u+\mu)}{2(Dt)^{1/2}}\right] + \exp\left[\frac$$

$$-\exp(-\gamma t)\left[\exp\left[\frac{x(u-\phi)}{2D}\right]\cdot erfc\left(\frac{x-\phi t}{2(D t)^{1/2}}\right) + \exp\left[\frac{x(u+\phi)}{2D}\right]\cdot erfc\left(\frac{x+\phi t}{2(D t)^{1/2}}\right)\right]\right\}$$



where:

$$\mu = (u^2 + 4D\lambda)^{1/2}$$
$$\phi = \left[u^2 + 4D(\lambda - \gamma)\right]^{1/2}$$

C =Concentration of solute in liquid phase, mg/L

 $C_o =$ Reference concentration, mg/L

D =Retarded dispersion coefficient, m^2/yr

t = Time, yr

u =Retarded seepage velocity, m/yr

x =Coordinate parallel to flow, m

 γ = Retarded source decay constant, 1/yr

 λ = Retarded decay constant of the chemical, 1/yr

The above equation represents the receptor concentration resulting from a source that decays exponentially over time from an initial concentration C_0 . At the Encinal site, the source has been remediated by excavating soil with relatively high concentrations of 1,1-DCA (with maximum detections of approximately 10 mg/kg). Maximum residual concentrations in soil after remediation are approximately 2 mg/kg. The effect of source reduction due to remediation can be analyzed by appropriately superimposing three individual Marino solutions. The solutions can be superimposed thanks to the linearity of the transport equation. Assuming $M(x, t, \gamma_0, C_0)$ represents the receptor concentration estimated by the Marino solution at distance x and time t due to the initial source C_0 decaying at rate γ_0 , and assuming that remediation took place at time T_r reducing the chemical to a residual concentration C_1 , decaying at the rate γ_1 , then the receptor concentration due to the resulting decaying pulse source can be estimated by superposition as follows:

$$\begin{split} &C(x, t < T_r) = M(x, t, \gamma_0, C_0) \\ &C(x, t = T_r) = M(x, T_r, \gamma_0, C_0) \\ &C(x, t > T_r) = M(x, t, \gamma_0, C_0) - M\{x, (t - T_r), \gamma_1, [C_0 \exp(-\gamma_0 T_r)]\} + M[x, (t - T_r), \gamma_1, C_1] \end{split}$$

Figure 3 provides a schematic representation of the decaying pulse source. If we assume a unit initial concentration $C_0 = 1$ mg/L, then the above equation can be used to estimate the attenuation factor during migration in shallow groundwater:

Attenuation =
$$C_{water} / C_{source} = C(x, t>T_r) / C_0$$
 [--]



Where:

 C_{water} = shallow groundwater concentration at the bay [mg/L] C_{source} = shallow groundwater concentration beneath the source [mg/L]

Shallow Groundwater Seepage Velocity

 $U = Ki/\theta$

[m/yr]

K = hydraulic conductivity [m/yr]

i = hydraulic gradient [m/m]

 θ = average water-filled porosity [--]

MODELING CALCULATIONS, RESULTS AND CONCLUSIONS

Conservative but reasonable input parameters were used in the model's calculations. Field-measured parameters were used when available. This includes the distance from the source to MW-10 and the bay, and the groundwater velocity, which was based on field measured hydraulic gradient. Only high-end degradation half-lives from published literature were used in the modeling.

Page 1 of Attachment A presents the input parameters used in the groundwater model to estimate the potential impact of 1,1-DCA migration from the source to MW-10 and to the bay. The modeling parameters and rationale are discussed below:

• Initial source concentration (before remediation) was assumed equal to 64 mg/L to represent 1,1-DCA levels prior to the excavation based on maximum detections in soil samples of the order of magnitude of 10 mg/kg (Geomatrix 1995) and on partitioning as follows:

$$C_{leachate} = C_{soil} \rho_b / \theta_{water} = 10 * 1.6 / 0.25 = 64 \text{ mg/L}$$

- Residual concentration post remediation was assumed equal to 12.8 mg/kg based on maximum detected residual soil concentration of about 2 mg/kg, converted to leachate concentration according to the partitioning equation in the previous bullet.
- Distance from the source to MW-10 equal to 70 m (approximately 210 feet), and distance from the source to the bay is 165 m (approximately 550 feet).
- Chemical migration in shallow groundwater was assumed to take place principally in high permeability materials, with seepage velocity (u) equal to 14 m/yr based on conductivity of 350 m/yr (representing very permeable medium), measured gradient of 0.01 (Geomatrix 1995), and porosity of 0.25



- Dispersion coefficient (D) equal to 231 m²/yr based on the USEPA (1990a and b) recommendation of D = α * u with longitudinal dispersivity α = 1/10 of the distance from the source to the bay
- Source and chemical decay rate after remediation was assumed to be 0.693 1/yr, conservatively based on a half-life of one year, which is almost double the maximum reported in the literature (Howard 1991); 1,1-DCA is likely to degrade at much faster rate than in our model
- Source decay before remediation was conservatively assumed to be slower than after remediation and corresponding to a 5 year half-life
- It is assumed in the model that the source lasted 10 years before being remediated.

Attachment A provides detailed results of the model calculations. Page 1 of Attachment A shows the model inputs. Page 2 presents the calculation results. Pages 3 and 4 present charts of the estimated concentration at the bay over time, and of the estimated concentration over distance at time of 20 years, respectively.

In summary, the model estimated concentrations of 1,1-DCA in shallow groundwater at the bay always lower than 0.2 mg/L. The modeling results show that past excavation activities had a dramatic effect in reducing potential impact on the bay. The model overestimates current concentration detected at MW-10 by an order of magnitude, but this should be expected given the amount of conservatism applied. The model shows that, due to degradation, concentrations of 1,1-DCA at the bay become of the same order of magnitude of the detection limit (0.0025 mg/L by USEPA Method 8020) within about 10 years after remediation. Due to the conservatism used in the model, and also based on the results of field sampling which indicate no detection at MW-10 and beyond, we conclude that no additional active remediation needs to be performed at the site.

UNCERTAINTIES AND LIMITATIONS

The quantitative methods and procedures described in this document for evaluating potential environmental impact are based on a number of simplifying assumptions related to the characterization of the chemical sources and of the subsurface environment. The exposure models are based on descriptions of relevant physical/chemical phenomena. Any mechanisms that are neglected, such as neglecting attenuation due to lateral dispersion, result in predictions of exposure and risk that are conservative relative to those likely to occur. In other words, the models are biased towards predicting exposure concentrations in excess of those likely to occur (ASTM 1995). Uncertainty and variability affect the input parameters of all of the exposure and fate and transport models. Conservative values of those input parameters are selected to deal with this uncertainty and variability. Since the exposure models are multiplicative, conservatism is



compounded in the calculations. For this reason, the modeling results in this study are expected to overestimate exposure and risk, rather than underestimate the actual risk posed by the site. More detailed discussion of the exposure models assumptions and limitations is provided in ASTM (1995). In the application of fate and transport models to the site that is presented here, conservative but reasonable site-specific estimates of the input parameters have been selected. Rationales and references for input parameters estimated values used in the models are reported in the text and tables.

We appreciate your consideration of this report. If you have any questions, please do not hesitate to contact Marco at (510) 874-3254 or Al at (510) 874-3125.

Sincerely,

Marco C. Lobascio, R.E.A.

Mouromano

Project Manager

usew

Albert P. Ridley, C.E.G. Senior Consultant

cc: Mr. Chengben Wang, Encinal Terminal Co.

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FIGURES

FIGURE 1. SCHEMATIC SITE PLAN VIEW

FIGURE 2. ILLUSTRATION OF CHEMICAL MIGRATION MODEL

FIGURE 3. SCHEMATIC REPRESENTATION OF THE PULSE SOURCE

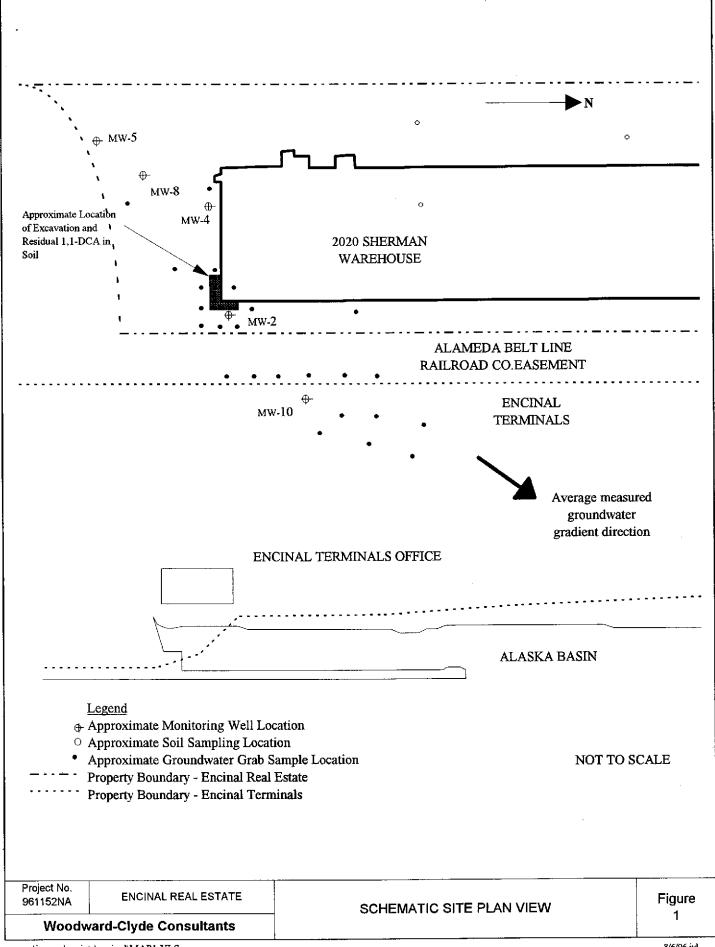
ATTACHMENTS

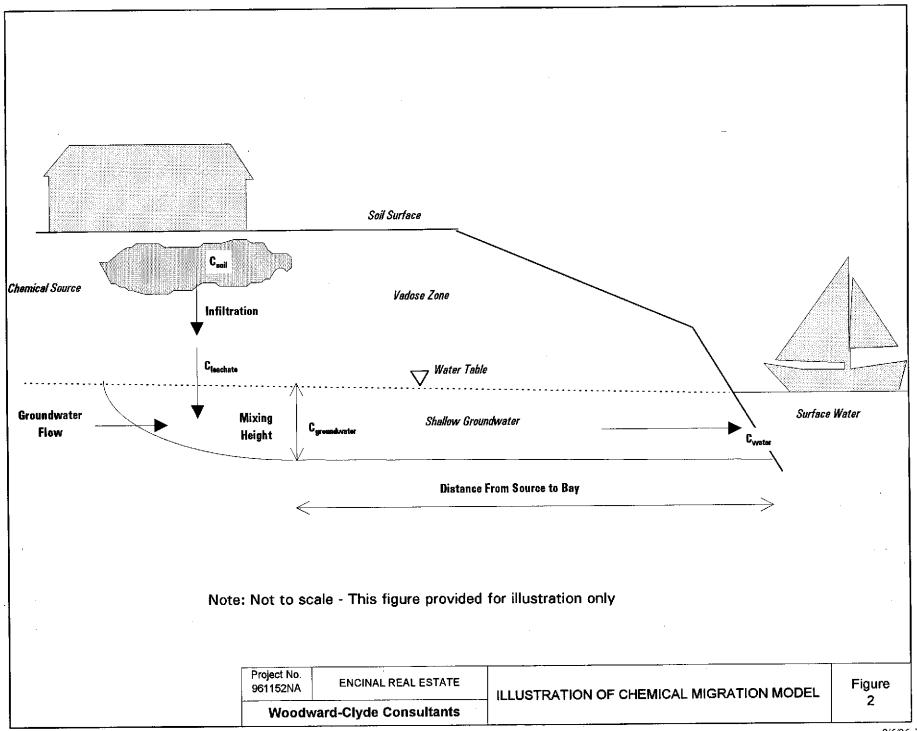
ATTACHMENT 1. GROUNDWATER MODELING CALCULATIONS

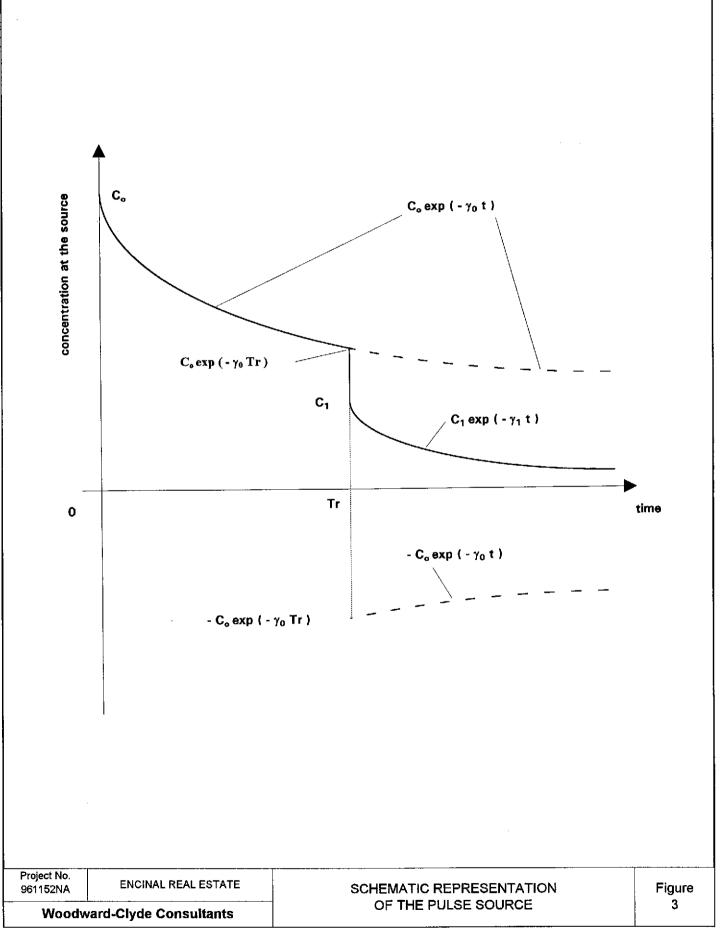
ATTACHMENT 2. PAPER BY MARINO (1974)

ATTACHMENT 3. DEGRADATION INFORMATION FOR 1,1-DCA (HOWARD 1991)









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ATTACHMENT 1 GROUNDWATER MODELING CALCULATIONS



GROUNDWATER MODEL OF CHEMICAL FATE AND TRANSPORT - DECAYING PULSE SOURCE

Model Input Parameters

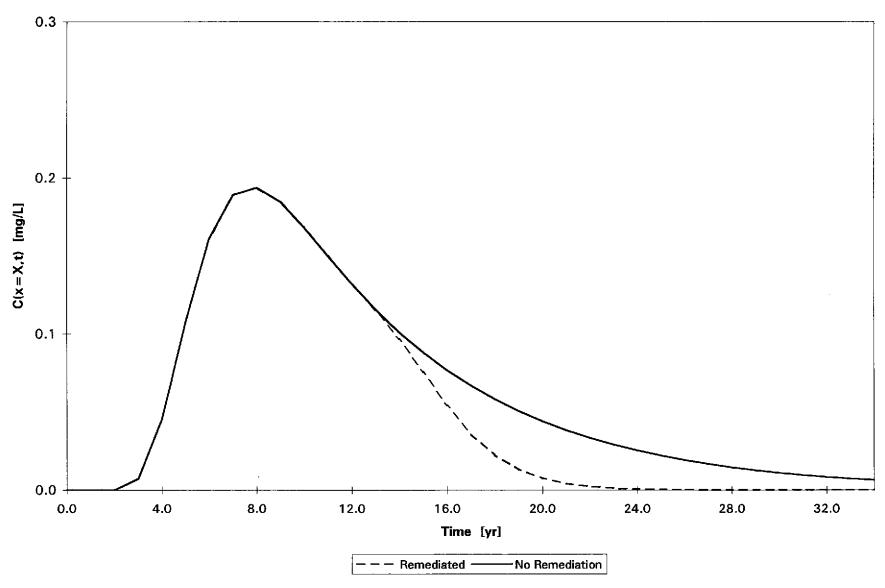
Parameter	Units	Name	Value	Remarks
Initial Sorce Concentration	[mg/L]	Ç	64	represents the source before remediation
Residual Concentration Post Remediation	[mg/L]	C ₁	12.8	assumed equal to the meximum detected residual soil concentration
Distance From Source to Receptor	[m]	x	165	550 feet distance from the source to the bay
Retarded Groundwater Seepage Velocity	[m/yr]	u	14	Darcy's law: $u = k^*i/n = 350^*0.01/0.25 = 14$
Retarded Dispersion Coefficient	[m²/yr]	D	231	$D = \alpha * u = X/10 * u = 165/10 * 14$
Retarded Source Decay Rate Before Remediation	[1/yr]	γο	0.139	5 years degradation half life - assumes slower decay before remediation
Retarded Source Decay Rate Post Remediation	[1/yr]	γ1	0.693	l year degradation half life (Howard 1991)
Retarded Chemical Degradation Coefficient	[1/yr]	λ	0.693	l year degradation half life (Howard 1991)
Time at Which Remediation Took Place	[yr]	Tpelse	10	age of the source when remediation took place
Calculation Time Step	[yr]	Δt	1	concentration will be calculated at distance X every Δt years
Time of Breakthough Calculation	[yr]	t*	20	concentration vs. distance will be calculated at time t*
Distance Step for Calculation	[m]	Δх	5,0	concentration will be calculated at time t* every \(\Delta \time \text{meters}\)

This model is based on the solution of the groundwater transport equation given by Marino (1974), adapted to a decaying pulse source to assess the effect of remediation on receptor concentration. 1-D advection and dispersion, retardation and first-order decay are considered.

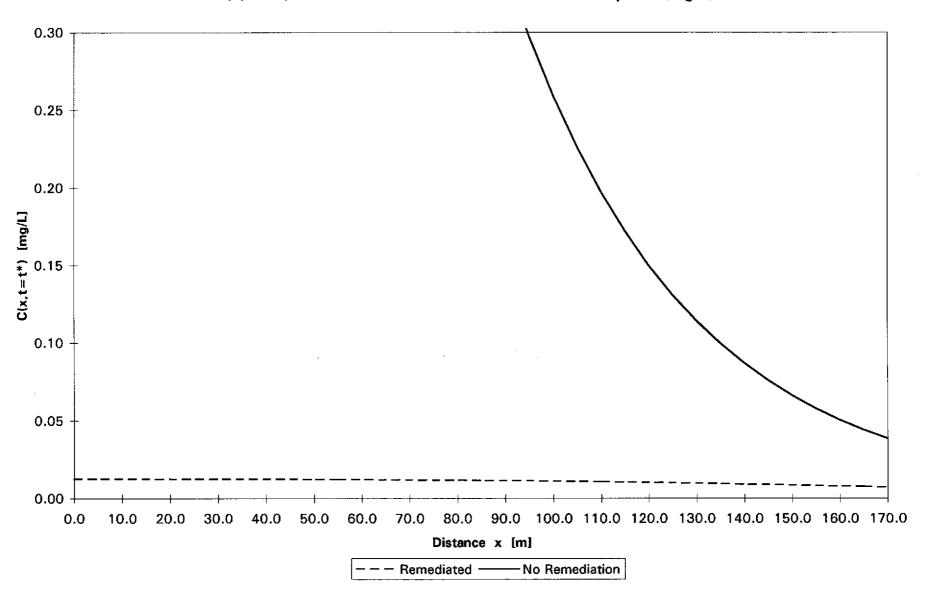
Marco Lobascio, San Francisco, California, August 1996.

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Receptor Concentration C(x = X,t) Vs. Time at X = 165 m [mg/L]



 $C(x,t=t^*)$ Vs. Distance From Source at Time $t^* = 20$ years [mg/L]



GROUNDWATER MODEL OF CHEMICAL FATE AND TRANSPORT - RESULTS

Distance from the source [m] =	165.0	Time of calculation [yr] =	20.0

Receptor Concentration Over Time

Breakthrough Concentration at t=t*

t		No Remed.	Remed.	I		No Remed.	Remed.
Time	Csource	C(x=X,t)	C(x=X,t)		Distance	$C(x,t=t^*)$	C(x,t=t*)
[yr]	[mg/L]	[mg/L]	[mg/L]		[m]	[mg/L]	[mg/L]
	1		, , , , , , , , , , , , , , , , , , ,	ĺ	7		. ,
0.0	64.00	0.000	0.000		0.0	3.970	0.013
1.0	55.69	0.000	0.000		5.0	3.464	0.013
2.0	48.46	0.000	0.000		10.0	3.022	0.012
3.0	42.17	0.007	0.007		15.0	2.637	0.012
4.0	36.70	0.045	0.045		20.0	2.301	0.012
5.0	31.94	0.107	0.107		25.0	2.007	0.012
6.0	27.79	0.161	0.161		30.0	1.751	0.012
7.0	24.19	0.189	0.189		35.0	1.528	0.012
8.0	21.05	0.194	0.194		40.0	1.333	0.012
9.0	18.32	0.184	0.184		45.0	1.163	0.012
10.0	12.79	0.168	0.168		50.0	1.015	0.012
11.0	6.40	0.150	0.150		55.0	0.885	0.012
12.0	3.20	0.132	0.132		60.0	0.772	0.012
13.0	1.60	0.116	0.115		65.0	0,674	0.012
14.0	0.80	0.101	0.097		70.0	0.588	0.012
15.0	0.40	0.088	0.075		75.0	0.513	0.012
16.0	0.20	0.077	0.054		80.0	0.448	0.012
17.0	0.10	0.067	0.036	•	85.0	0.390	0.012
18.0	0.05	0.058	0.022		90.0	0.341	0.011
19.0	0.03	0.051	0.013		95.0	0.297	0.011
20.0	0.01	0.044	0.008		100.0	0.259	0.011
21.0	0.01	0.038	0.004		105.0	0.226	0.011
22.0	0.00	0.033	0.002		110.0	0.197	0.011
23.0	0.00	0.029	0.001		115.0	0.172	0.010
24.0	0.00	0.025	0.001		120.0	0.150	0.010
25.0	0.00	0.022	0.000		125.0	0.131	0.010
26.0	0.00	0.019	0.000		130.0	0.114	0.010
27.0	0.00	0.017	0.000		135.0	0.100	0.009
28.0	0.00	0.014	0.000		140.0	0.087	0.009
29.0	0.00	0.013	0.000		145.0	0.076	0.009
30.0	0.00	0.011	0.000		150.0	0.066	0.009
31.0	0.00	0.010	0.000		155.0	0.058	0.008
32.0	0.00	0.008	0.000		160.0	0.050	0.008
33.0	0.00	0.007	0.000		165.0	0.044	0.008
34.0	0.00	6.3E-3	7.5E-7		170.0	3.8E-2	7.2E-3
Max. Time	Fi	nal Concentratio	ns]	Max distance	. <u>.</u> .	

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ATTACHMENT 2 PAPER BY MARINO (1974)



Distribution of Contaminants in Porous Media Flow

MIGUEL A. MARINO

Department of Water Science and Engineering, University of California, Davis, California 95616

A mathematical analysis is presented of simultaneous dispersion and adsorption of a solute within homogeneous and isotropic porous media in steady unidirectional flow fields. The dispersion systems are adsorbing the solute at rates proportional to their concentration and are subject to input concentrations that vary exponentially with time. Mathematical solutions are developed for predicting the concentration of contaminants in adsorbing and nonadsorbing porous media for prescribed media and fluid parameters.

The theory of dispersion of miscible fluids in porous media has received considerable attention during the past several years. It has been extensively studied in such processes as cation exchange chromatography and ion exchange in soils. Interest in dispersion in the water resource field has resulted from water quality considerations of artificial recharge and waste water disposal operations, seawater intrusion into coastal aquifers, and seepage from canals and streams into and through aquifers.

Solutions to miscible displacement problems in porous media have been obtained by many investigators. Common to these studies is the assumption of a step function for input concentration; that is, the concentration of the displacing fluid is changed instantaneously from zero to some value and is maintained at this value thereafter. In addition, it is commonly assumed that only mass transport by means of convection and dispersion takes place; that is, additional mass transfer mechanisms are neglected. The type of mass transfer by which dissolved substance is removed from the region occupied by the liquid (liquid phase) owing to the attraction between the solid matrix material of the porous medium (solid phase) and the substance is generally referred to as adsorption.

Analytical solutions for a longitudinal dispersion problem within a semi-infinite nonadsorbing porous medium in a steady unidirectional flow field have been obtained by *Ebach and White* [1958] for an input concentration that is a periodic function of time and by *Ogata and Banks* [1961] for a constant input concentration.

Hoopes and Harleman [1965] studied the problem of dispersion in radial flow from a well fully penetrating a homogeneous, isotropic, nonadsorbing confined aquifer. An approximate solution was obtained for the case of a step input of concentration. In addition, they studied dispersion between two wells, one pumping and the other one recharging at the same rate, fully penetrating the confined aquifer. For this case, three approximate solutions were obtained: one with no dispersion, one with only longitudinal dispersion, and one with only lateral dispersion.

Shamir and Harleman [1966] obtained analytical solutions for longitudinal dispersion in a semi-infinite nonadsorbing layered medium with flow perpendicular to the layers and for lateral dispersion with flow parallel to the layers. Both dispersion systems were subject to a constant input concentration. They also presented a numerical method for the solution of dispersion problems in steady two- and three-dimensional potential flow fields in porous media in which the miscible fluids have the same density and viscosity.

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Bruch and Street [1966] considered both longitudinal and lateral dispersion within a semi-infinite nonadsorbing porous medium in a steady unidirectional flow field. An analytical solution was developed for a constant input concentration.

Numerical simulation of dispersion in groundwater aquifers has been extensively studied by *Reddell and Sunada* [1970]. The numerical models were tested on some problems for which exact or approximate analytical solutions are available. Also dispersion along an intruded saltwater wedge was considered.

A physical chemical model for predicting and controlling the movement of contaminants in an isothermal groundwater system in which there are no chemical reactions was developed by *Bredehoeft and Pinder* [1973]. The model was solved numerically and was applied to a groundwater contamination problem in Brunswick, Georgia.

The theory of dispersion in porous adsorbing media has been extensively studied in chromatography [Bastian and Lapidus, 1956; Glueckauf et al., 1949; Eiester and Vermeulen, 1952; Lapidus and Amundson, 1952]. A recent review with applications to processes of ion exchange in soils is given by Reiniger and Bolt [1972].

Adsorption plays an important role in mass transport within natural flow systems. In general, the outcome of any contaminant introduced into the groundwater system is largely dependent on the capacity of the solid matrix material to adsorb the dissolved substance.

Banks and Ali [1964] presented a mathematical analysis of simultaneous dispersion and adsorption of a solute within a porous medium in a one-dimensional steady flow field subject to a constant input concentration. Solutions are presented for the case of longitudinal dispersion without adsorption and for the case of adsorption without dispersion. Numerous laboratory experiments were conducted.

Gershon and Nir [1969] studied the effects of boundary conditions of models on tracer distribution in flow through porous media. They give a solution for a one-dimensional dispersion problem within a semi-infinite adsorbing porous medium subject to a constant tracer mass flux. The solution, as reported by Bear [1972], is also presented by Carslaw and Jaeger [1959] for the case of heat conduction in a semi-infinite rod with radiation.

Ogata [1970] has presented various analytical solutions for dispersion problems within semi-infinite adsorbing porous media in unidirectional steady flow fields. The dispersion systems are subject to constant input concentrations.

This paper describes mathematical solutions to simplified dispersion problems involving simultaneous dispersion and adsorption of a solute in porous media flow and variable input concentrations of contaminants. In addition, solutions are

presented that take into account the decay of radioactive contaminants through nonadsorbing porous media. The dispersion systems are subject to input concentrations of contaminants that vary exponentially with time. The solutions predict the distribution of contaminants in saturated porous media resulting from the variable source concentrations.

DISPERSION EQUATION

The differential equation describing a homogeneous and isotropic convective dispersion system may be expressed [Bachmat and Bear, 1964; Bear, 1972; de Josselin de Jong and Bossen, 1961; Scheidegger, 1961] as

$$\frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C}{\partial x_i} - u_i C \right) = \frac{\partial C}{\partial t} \qquad i, j = 1, 2, 3 \tag{1}$$

in which C is the concentration of the dispersing mass (mass of solute per unit volume of fluid), D_{ij} are the components of the factor of dispersion (a second-rank symmetric tensor), u_i is the seepage velocity in direction i, and x_i are the Cartesian coordinates.

For a unidirectional steady flow field in the x direction, (1) becomes

$$D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$
 (2)

in which D_L and D_T are the longitudinal and transverse (lateral) dispersion coefficients, respectively.

If there is no lateral variation in concentration, then (2) reduces to

$$D_L \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$
 (3)

The first and second terms of (3) represent the transport of solute due to dispersion and convection, respectively. The right member indicates solute storage in the region occupied by the liquid (liquid phase).

To include chemical reactions and/or adsorption in the transport equation (3), it is generally assumed that changes in tracer concentration resulting from chemical reactions and/or adsorption are additional components in the dispersion equation. Thus the following extensions of (3) may be considered [Banks and Ali, 1964; Bear, 1972; Ogata, 1970].

Presence of adsorption. For an adsorbing dispersion system in which the concentration of the solute in the liquid and solid phases is denoted by C and S, respectively, (3) becomes

$$D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{1 - n}{n}\frac{\partial S}{\partial t}$$
(4)

in which n is the porosity of the porous medium. The last term of (4) represents solute storage in the region occupied by the particles (solid phase).

Adsorption equations that relate C to S under equilibrium or nonequilibrium conditions are available in the literature [Crank, 1956; Lapidus and Amundson, 1952; Ogata, 1970]. For example, we may use the equilibrium isotherm

$$S = a'C (5a)$$

or the nonequilibrium relationship

$$\partial S/\partial t = a(C - bS) \tag{5b}$$

in which a, a', and b are constants. Equation (5b) describes a first-order reversible reaction and is applicable to some ion exchange processes in fluids flowing in porous media. If $bS \ll C$, (5b) reduces to

$$\partial S/\partial t = aC$$
 (5c)

an expression that describes a first-order irreversible reaction.

It should be noted that the complete solution of a porous medium flow problem in which dispersion and adsorption of a solute take place involves the simultaneous solution of a pair of partial differential equations, say, (4) and any of the rate equations (5), for appropriate initial and boundary conditions on both C and S and for prescribed medium and fluid parameters.

Presence of radioactive decay. If a tracer undergoes radioactive decay as it is being transported through a nonadsorbing porous medium, then the resulting change in tracer concentration may be expressed as

$$\partial C/\partial t = -\lambda C \tag{6}$$

in which λ is the decay constant of the tracer equal to the reciprocal of the mean lifetime of the tracer. The dispersion equation (3) then becomes

$$D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t}$$
 (7)

In this case, the complete solution of a dispersion problem involves the solution of one partial differential equation, (7), subject to initial and boundary conditions on C provided that values for D, u, and λ are known.

Presence of adsorption and radioactive decay. If both radioactive decay and adsorption of a solute take place in the porous medium flow, then the concentration equation (3) becomes

$$D\frac{\partial^{2}C}{\partial x^{2}} - u\frac{\partial C}{\partial x} - \lambda C - \lambda \frac{1-n}{n}S = \frac{\partial C}{\partial t} + \frac{1-n}{n}\frac{\partial S}{\partial t}$$
(8)

Any appropriate rate equation, such as (5a), (5b), or (5c), may be used in conjunction with (8) for the solution of a porous medium flow problem in which dispersion, adsorption, and radioactive decay occur.

THEORY

The theory that follows is confined to simultaneous dispersion and adsorption in steady unidirectional scepage flows through semi-infinite, homogeneous, and isotropic porous media. However, the theory also includes the decay of a radioactive contaminant as it is being transported through nonadsorbing porous media. The dispersion systems to be considered are subject to input concentrations of contaminants that vary exponentially with time.

Case 1

Consider a semi-infinite porous medium in a unidirectional flow field in which the input tracer concentration is $C_0e^{\gamma t}$, where C_0 is a reference concentration and γ is a constant (Figure 1).

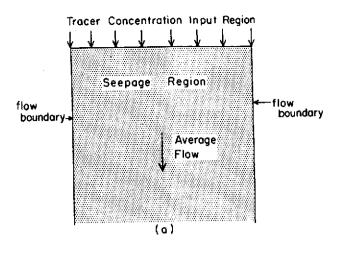
Adsorbing medium. The dispersion system is assumed to be adsorbing the solute at a rate proportional to its concentration. Thus the relation between the concentration of the solute

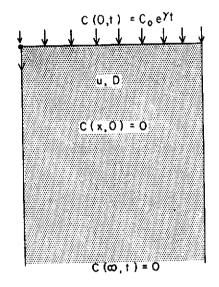
2 (c+ 12 pxdc) = 2c (n+1-x)

42 1-3 pxdc) = 2c (n+1-x)

42 1-3 pxdc

R 2c





(b)
 Fig. 1. Schematic representation of semi-infinite porous medium in unidirectional flow field. Source concentration is C₀e^{γt}.

in the liquid and that in the solid phase is of the non-equilibrium type.

The simultaneous dispersion and adsorption problem for the flow system under consideration may be expressed by the partial differential equations

$$D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{1 - n}{n}\frac{\partial S}{\partial t}$$
 (9)

and

h

`)

$$\partial S/\partial t = aC \tag{10}$$

subject to the following initial and boundary conditions on the concentration of the solute in the liquid phase,

$$C(x, 0) = 0$$
 $x \ge 0$ (11)

$$C(0, t) = C_0 e^{\gamma t}$$
 $t > 0$ (12)

$$C(\infty, t) = 0 \qquad t \ge 0 \tag{13}$$

and subject to the initial condition on the concentration of the solute in the solid phase,

$$S(x, 0) = 0 x \ge 0$$
 (14)

Conditions (11) and (14) indicate that the solute concentration in both phases is initially zero.

Thus the complete solution of the porous medium flow problem under consideration involves the simultaneous solution of (9) and (10) subject to conditions (11)-(14) for prescribed values of medium and fluid parameters.

Using the transformation

$$C(x, t) = C^*(x, t) \cdot \exp \left\{ \frac{ux}{2D} - \left[\frac{u^2}{4D} + \frac{a(1-n)}{n} \right] t \right\}$$
(15)

allows (9) and (10) to be rewritten as

$$\frac{\partial^2 C^*}{\partial x^2}(x, t) = \frac{1}{D} \frac{\partial C^*}{\partial t}(x, t)$$
 (16)

and (11)-(14) to be expressed as

$$C^*(x, 0) = 0 (17)$$

$$C^*(0, t) = C_0 \cdot \exp\left[\frac{u^2}{4D} + \frac{a(1-n)}{n} + \gamma\right]t$$
 (18)

$$C^*(\infty, t) = 0 \tag{19}$$

Applying the Laplace transformation with respect to t on the boundary value problem using (17) yields

$$\frac{d^2 \bar{C}^*}{dx^2}(x, p) - \frac{p}{D} \bar{C}^*(x, p) = 0$$
 (20)

$$\bar{C}^*(0, p) = C_0/p - \left[\frac{u^2}{4D} + \frac{a(1-n)}{n} + \gamma\right]$$
 (21)

$$\ddot{C}^*(\infty, p) = 0 \tag{22}$$

where the bar indicates the transformed function and p is the parameter of transformation.

It can be shown that a solution to (20) satisfying (21) and (22) is

$$\bar{C}^*(x, p) = C_0 \exp\left[-x(p/D)^{1/2}\right] \cdot \left\{ p - \left[\frac{u^2}{4D} + \frac{a(1-n)}{n} + \gamma\right] \right\}^{-1}$$
 (23)

Taking the inverse Laplace transformation of (23) gives

$$C^*(x, t) = \frac{C_0}{2} \left\{ \exp\left[\omega t - x \left(\frac{\omega}{D}\right)^{1/2}\right] \right.$$

$$\cdot \operatorname{erfc}\left[\frac{x - 2t(D\omega)^{1/2}}{2(Dt)^{1/2}}\right] + \exp\left[\omega t + x \left(\frac{\omega}{D}\right)^{1/2}\right]$$

$$\cdot \operatorname{erfc}\left[\frac{x + 2t(D\omega)^{1/2}}{2(Dt)^{1/2}}\right] \right\}$$
(24)

in which

$$\omega = \frac{u^2}{4D} + \frac{a(1-n)}{n} + \gamma \tag{25}$$

Substituting (15) into (24) finally gives

$$C(x, t) = \frac{C_0}{2} \exp{(\gamma t)} \left\{ \exp{\left[\frac{x(u - \alpha)}{2D}\right]} \right\}$$

$$\cdot \operatorname{erfc}\left(\frac{x - \alpha t}{2(Dt)^{1/2}}\right) + \exp{\left[\frac{x(u + \alpha)}{2D}\right]}$$

$$\cdot \operatorname{erfc}\left(\frac{x + \alpha t}{2(Dt)^{1/2}}\right)$$
(26)

in which

$$\alpha = \left\{ \frac{u^2 n + 4D[a(1-n) + \gamma n]}{n} \right\}^{1/2}$$
 (27)

Equation (26) predicts the concentration of a contaminant as a function of time and space within a semi-infinite adsorbing porous medium if the seepage flow, the source concentration, and the adsorption and dispersion coefficients are prescribed.

Nonadsorbing medium. If mass transfer from the liquid to the solid phase due to adsorption is neglected, then the concentration of the contaminant is given by

$$C(x, t) = \frac{C_0}{2} \exp \left(\gamma t\right) \left\{ \exp \left[\frac{x(u - \beta)}{2D} \right] \right.$$

$$\cdot \operatorname{erfc} \left(\frac{x - \beta t}{2(Dt)^{1/2}} \right) + \exp \left[\frac{x(u + \beta)}{2D} \right]$$

$$\cdot \operatorname{erfc} \left(\frac{x + \beta t}{2(Dt)^{1/2}} \right) \right\}$$
(28)

in which

$$\beta = (u^2 + 4D\gamma)^{1/2} \tag{29}$$

For a nonadsorbing porous medium subject to a constant input concentration C_0 , (28) simplifies to

$$C(x, t) = \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{x - ut}{2(Dt)^{1/2}} \right) + \exp \left(\frac{ux}{D} \right) \operatorname{erfc} \left(\frac{x + ut}{2(Dt)^{1/2}} \right) \right]$$
(30)

a result that has been obtained by Glueckauf et al. [1949] and by Ogata and Banks [1961].

Nonadsorbing medium with radioactive decay. If the pollutant undergoes radioactive decay as it is being transported through the nonadsorbing porous medium, the dispersion problem may be expressed by the partial differential equation

$$D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t}$$
 (31)

subject to the conditions

$$C(x,0) = 0 \tag{32}$$

$$C(0, t) = C_0 e^{\gamma t} \tag{33}$$

$$C(\infty, t) = 0 \tag{34}$$

Applying the Laplace transformation in the usual manner will ultimately yield

$$C(x, t) = \frac{C_0}{2} \exp (\gamma t) \left\{ \exp \left[\frac{x(u - \eta)}{2D} \right] \right.$$

$$\cdot \operatorname{erfc} \left(\frac{x - \eta t}{2(Dt)^{1/2}} \right) + \exp \left[\frac{x(u + \eta)}{2D} \right]$$

$$\cdot \operatorname{erfc} \left(\frac{x + \eta t}{2(Dt)^{1/2}} \right) \right\}$$
(35)

in which

$$\eta = [u^2 + 4D(\lambda + \gamma)]^{1/2}$$
 (36)

For a constant input concentration C_0 , (35) reduces to

$$C(x, t) = \frac{C_0}{2} \left\{ \exp\left[\frac{x(u - \mu)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x - \mu t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u + \mu)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x + \mu t}{2(Dt)^{1/2}}\right) \right\}$$
(37)

in which

$$\mu = (u^2 + 4D\lambda)^{1/2} \tag{38}$$

a result that has been obtained by Bear [1972, p. 630].

Case 2

The porous medium is represented in Figure 1a, but the source concentration of the contaminant is given by $C_0(1 - e^{-\gamma t})$.

Adsorbing medium. The dispersion system is considered to be adsorbing the solute at a rate proportional to its concentration. Thus the appropriate rate equation expressing solute transfer between the liquid and solid phases is (10).

The solution of the simultaneous dispersion and adsorption problem for the flow system under consideration is given by

$$C(x, t) = \frac{C_0}{2} \left\{ \exp\left[\frac{x(u-\rho)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x-\rho t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u+\rho)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x+\rho t}{2(Dt)^{1/2}}\right) - \exp\left(-\gamma t\right) \left[\exp\left[\frac{x(u-\sigma)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x-\sigma t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u+\sigma)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x+\sigma t}{2(Dt)^{1/2}}\right) \right] \right\}$$
(39)

in which

and

$$\rho = \left[\frac{u^2 n + 4 Da(1 - n)}{n} \right]^{1/2} \tag{40}$$

$$\sigma = \left\{ \frac{u^2 n + 4D[a(1-n) - \gamma n]}{n} \right\}^{1/2}$$
 (41)

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Nonadsorbing medium. If there are no chemical reactions, the distribution of the contaminant is given by

$$C(x, t) = \frac{C_0}{2} \left\{ \operatorname{erfc} \left(\frac{x - ut}{2(Dt)^{1/2}} \right) + \exp \left(\frac{ux}{D} \right) \right.$$

$$\cdot \operatorname{erfc} \left(\frac{x + ut}{2(Dt)^{1/2}} \right) - \exp \left(-\gamma t \right) \left[\exp \left[\frac{x(u - \xi)}{2D} \right] \right.$$

$$\cdot \operatorname{erfc} \left(\frac{x - \xi t}{2(Dt)^{1/2}} \right) + \exp \left[\frac{x(u + \xi)}{2D} \right]$$

$$\cdot \operatorname{erfc} \left(\frac{x + \xi t}{2(Dt)^{1/2}} \right) \right] \right\}$$

$$(42)$$

in which

$$\xi = (u^2 - 4D\gamma)^{1/2} \tag{43}$$

Nonadsorbing medium with radioactive decay. If the tracer under consideration continuously undergoes radioactive decay as it is being transported through the nonadsorbing medium, the tracer concentration is given by

$$C(x, t) = \frac{C_0}{2} \left\{ \exp\left[\frac{x(u - \mu)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x - \mu t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u + \mu)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x + \mu t}{2(Dt)^{1/2}}\right) - \exp\left(-\gamma t\right) \left[\exp\left[\frac{x(u - \phi)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x - \phi t}{2(Dt)^{1/2}}\right) + \exp\left[\frac{x(u + \phi)}{2D}\right] \cdot \operatorname{erfc}\left(\frac{x + \phi t}{2(Dt)^{1/2}}\right) \right] \right\}$$
(44)

in which

$$\mu = (u^2 + 4D\lambda)^{1/2} \tag{45}$$

and

$$\phi = [u^2 + 4D(\lambda - \gamma)]^{1/2}$$
 (46)

CONCLUDING REMARKS

Mathematical solutions have been developed for predicting the possible concentration of a given dissolved substance in steady unidirectional seepage flows through semi-infinite, homogeneous, and isotropic porous media subject to source concentrations that vary exponentially with time. The expressions take into account the decay of a radioactive contaminant as well as mass transfer from the liquid to the solid phase due to adsorption. For simultaneous dispersion and adsorption of a solute the dispersion system is considered to be adsorbing the solute at a rate proportional to its concentration.

Mass transfer due to adsorption plays an important role in mass transport within natural flow systems. In general, the outcome of any contaminant introduced into the groundwater system is largely dependent on the capacity of the solid matrix material to adsorb the dissolved substance. Approximation of the adsorption rate is used in the mathematical analysis for lack of better data that take into account the macroscopic aspects of adsorption in groundwater systems.

The analytical expressions developed herein should prove helpful in making quantitative predictions on the possible con-

tamination of groundwater supplies resulting from seepage of high salt concentrations in drainage ditches, canals, and streams and from groundwater movement through buried wastes. In addition, they should prove useful for other processes such as ion exchange in soils and decay of organic substances.

NOTATION

- constant in nonequilibrium adsorption equation, T^{-1} .
- constant in equilbrium adsorption equation. a'
- concentration of solute in liquid phase. \boldsymbol{C}
- reference concentration. C_{\circ}
- dispersion coefficient, L2T-1.
- porosity of porous medium.
- concentration of solute in solid phase.
- time, T.
- average seepage velocity, LT-1.
- coordinate parallel to flow, L.
- parameter defined by (27).
- parameter defined by (29).
- constant, T^{-1} .
- parameter defined by (36).
- decay constant of the tracer, T^{-1} .
- parameter defined by (38).
- parameter defined by (43).
- parameter defined by (40).
- parameter defined by (41).
- parameter defined by (46).
- parameter defined by (25).

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(Received July 20, 1973; revised May 14, 1974.)

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ATTACHMENT 3
DEGRADATION INFORMATION FOR 1,1-DCA (HOWARD 1991)



1,1-Dichloroethane

CAS Registry Number: 75-34-3

Half-lives:

· Soil:

High:

3696 hours

(22 weeks)

Low:

768 hours

(32 days)

Comment: Scientific judgement based upon methane acclimated soil grab sample data (low tuz: Henson, JM et al. (1989)) and sub-soil grab sample data from a ground water aquifer (high t₁₀: Wilson, JT et al. (1983)).

· Air:

High:

2468 hours

(103 days) (10.3 days)

Low: 247 hours Comment: Based upon photooxidation half-life in air.

Surface Water:

High: 3696 hours (22 weeks) (32 days)

Comment: Scientific judgement based upon estimated aqueous aerobic biodegradation half-life.

· Ground Water:

High:

Low:

8640 hours

768 hours

(22 weeks)

Low: 1344 hours (64 days)

Comment: Scientific judgement based upon estimated aqueous aerobic biodegradation half-life and sub-soil grab sample data from a ground water aquifer (high t_{1/2}: Wilson, JT et al. (1983)).

Aqueous Biodegradation (unacclimated):

· Aerobic half-life:

High:

3696 hours

(22 weeks)

Low:

768 hours

(32 days)

Comment: Scientific judgement based upon estimated methane acclimated soil grab sample data (low t₁₀: Henson, JM et al. (1989)) and sub-soil grab sample data from a ground water aquifer (high $t_{1/2}$: Wilson, JT et al. (1983)).

· Anaerobic half-life:

High: Low:

14784 hours

(88 weeks)

3072 hours

(128 days)

Comment: Scientific judgement based upon estimated aqueous aerobic biodegradation half-life.

· Removal/secondary treatment:

High: Low:

No data

Comment:

Photolysis:

Atmos photol half-life:

High: Low:

No data

Comment:

148

 Max light Comment:

· Aq photol

Comment:

Photooxidation

· Water:

Comment:

· Air:

Comment: 1 air (Atkınsor

Reduction half-li

Comment:

Hydrolysis:

· First-order Comment:

· Acid rate co Comment:

· Base rate co Comment:

weeks) 2 days)

imple data (low t_{in}: er aquifer (high t_{in}:

13 days)

.3 days)

: weeks)

32 days) iegradation half-life.

? weeks)

54 days) legradation half-life

1, JT et al. (1983)).

2 weeks)

32 days)

soil grab sample data ound water aquifer

8 weeks)

28 days) legradation half-life.

. Max light absorption (nm):

No data

Comment:

. Aq photol half-life:

High:

No data

Low:

Comment:

Photooxidation half-life:

· Water:

High:

No data

Low:

Comment:

· Air:

High:

2468 hours

(103 days)

Low: 247 hours

(10.3 days)

Comment: Based upon measured rate data for the vapor phase reaction with hydroxyl radicals in air (Atkinson, R (1985)).

Reduction half-life:

High:

No data

Low:

Comment:

<u>Hydrolysis:</u>

· First-order hydr half-life:

No data

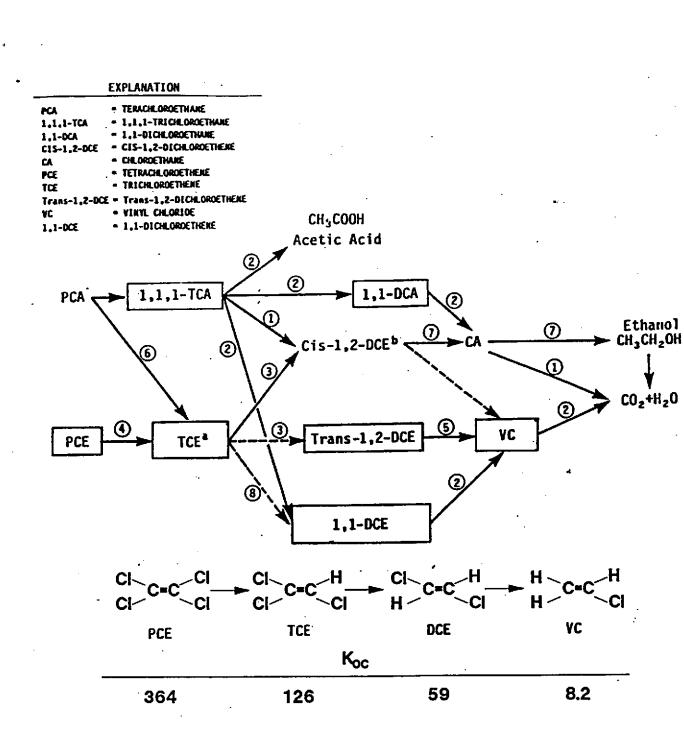
Comment:

· Acid rate const (M(H+)-hr)-1;

Comment:

· Base rate const (M(OH-)-hr)-1;

Comment:



PATH REFERENCE	MAJOR MECHANISM	<u>NOTES</u>
1 McCarty (1986)	Biodegradation	. —— Minor Paltway
2 Vogel & McCarly (1987 b)		Half life reaction rates detailed
(3) Kloepler et al (1985)		in Table 4-1
(4) Parsons et al (1984)	•	a Cis 1,2-DCE generated at approximately 30 times the
Barrio-Lage et al (1986)	1	concentration of Trans 1,2- DCE (3) and by a factor of
6 Cooper et a! (1987)	Abiotic Elimination	25:1 (8)
7 Vogel et al (1987)	Biodegradation	
8 Wood et al (1985)		•