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PARAMETER CHARACTERIZATION FOR SOLUTE TRANSPORT IN GROUND WATER

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LIST OF NOTATIONS AND SYMBOLS

Δx	Length of the elementary volume in x-direction	$[L]$
Δy	Length of the elementary volume in y-direction	$[L]$
Δz	Length of the elementary volume in z-direction	$[L]$
ΔV	Elementary volume	$[L^3]$
c	Concentration of dissolved pollutants	$[ML^{-3}]$
n	Porosity	$[-]$
t	Time	$[T]$
D_m	Coefficient of molecular diffusion	$[L^2T^{-1}]$
J_m	Diffusive flux	$[ML^{-2}T^{-1}]$
H	Aquifer thickness	$[L]$
x_i	$_i$ = tensor = 1,2,3. $x_1 = x$; $x_2 = y$; $x_3 = z$.	$[L]$
v_i	Velocity tensor	$[LT^{-1}]$
D_L	Coefficient of longitudinal dispersion	$[L^2T^{-1}]$
D_T	Coefficient of transversal dispersion	$[L^2T^{-1}]$
D_{ij}	Coefficient of dispersion tensor	$[L^2T^{-1}]$
	(when, i=1=x; i=2=y; i=3=z and when, j=1=x; j=2=y; j=3=z. e.g	
	D_{xz} ⇒ Coefficient of dispersion in x-direction due to a gradient in z-direction)	
α_L	Longitudinal dispersivity	$[L]$
α_T	Transversal dispersivity	$[L]$
$\lvert v \rvert$	Magnitude of local groundwater velocity	$[LT^{-1}]$
c_i	Concentration of pollutant in infiltrated water	$[ML^{-3}]$
q_{3i}	Volumetric infiltration (+ = infiltration)	$[T^{-1}]$
q_{3a}	Volumetric abstraction (+ = abstraction)	$[T^{-1}]$
λ_c	Decay constant for dissolved pollutants	$[T^{-1}]$
$T_{1/2}$	Half life of a pollutant	$[T]$
ξ_c	Volumetric reaction rate of dissolved pollutants	$[ML^{-3}T^{-1}]$
c_s	Concentration of adsorbed pollutants	$[MM^{-1}]$
ρ_s	Density of solids (grains)	$[ML^{-3}]$
f_s	Rate of mass transfer from dissolved to adsorbed phase	$[ML^{-3}T^{-1}]$
λ_s	Decay constant for adsorbed pollutants	$[T^{-1}]$
ξ_s	Volumetric reaction rate of adsorbed pollutants	$[ML^{-3}T^{-1}]$
K_d	Distribution coefficient	$[L^3M^{-1}]$
	(ratio of adsorbed and dissolved concentration)	
R	Retardation factor	$[-]$
L	Average distance travelled by groundwater flow	$[L]$
σ	Standard deviation	
t_h	time to reach half the maximum concentration	$[T]$

ABSTRACT

Scarcity of surface water and increasing threat of pollution to the surface water bodies, have given rise to more pressure on the groundwater resources. Resulting effects are being experienced in many spheres; such as: threat of continuous depletion of groundwater tables, intrusion of saline water in costal aquifers, more pronounced entry of contaminants from surface to the groundwater reservoirs etc. When the demand of water is on the rise and availability is a limiting factor, the planning strategy should be scientific and efficient management of available resources.

Management of groundwater resources is becoming a complicated task due to overwhelming pressure on the groundwater and changing scenario of groundwater quality (physical, chemical and biological). True picturization of spatial and temporal variation of groundwater both in terms of quantity and quality can only be made once causes of the problem are well understood and addressed properly. Groundwater flow and transport modelling can assist as an aid to attempt such kind of problems.

Hydraulics of groundwater is governed by many bounded and unbounded factors. To obtain an accurate groundwater flow model, appropriate skill of the modeller is required. Modelling of the fate of contaminant's transport in groundwater further needs more expertise, particularly in understanding the kinetics of flow and transport behaviours of contaminated water. Mixing of constituent in groundwater is another important factor which shape the occurrence of constituents in any precise location at a given time.

A mathematical model for the transport of a solute in groundwater can be developed by taking the mass balance of the dissolved pollutant over a static elementary volume in three cartesian co-ordinates. Solutions of equation both analytical and numerical are also well established. Analytical solution is only available for one-dimensional case while numerical solutions are available for 1-D, 2-D and 3-D cases. Despite well established theory of contaminant's transport in groundwater, there is a common tendency of simplification of a 2-D or a 3-D problem to a 1-D problem. As a consequence, a good agreement between the observed and computed values do not comprehend in many cases.

The present study is an attempt to evaluate the behaviour of constituents/pollutants moving with groundwater. Three hypothetical examples having relevance to the field conditions have been demonstrated to satisfy the study. Dispersivity, adsorptivity and decay which are the primary parameters affecting the transport phenomena have been considered. The dispersivity which is the main characterizing parameter in transport problems, have been considered for sensitivity analysis. It is also attempted to quantify errors involved when a 3-D problem is simplified to a 2-D problem and a 2-D problem to a 1-D problem.

On comparison of solution of a 1-D transport problem involving advection, dispersion, adsorption and decay solved through analytical procedure and numerical flow/transport model MODFLOW/MT3D, an excellent match was found between the two solution. The effect of varying dispersivity (longitudinal, transverse and vertical) on the concentration profile was also attempted by taking a 2-D and a 3-D case example.

1.0 INTRODUCTION

1.1 Groundwater Scenario and Problem

Groundwater is a valuable source for producing sound drinking water besides its use in industrial, agricultural sectors and domestic purposes. Because of large underground travel times, groundwater in general has a constant composition and possesses a high quality, at least, until a few decades ago. During recent times due to over use and abuse of ground water resources and also because of dynamic population pressure, the stresses imposed on the groundwater system have increased steadily. Not only a quantitative over exploitation has occurred, but also a qualitative assault on groundwater bodies have occurred that resulted in depletion of groundwater resources. It has further led to lowering of water table, intrusion of salt water in the aquifer, and reduction in agricultural production etc.

Depletion of ground water tables in productive reservoirs have been reported in many places. On the other hand, degradation of ground water quality due to agricultural return flows, disposal of domestic and industrial wastes in land fills, ponds, low lands, rivers, streams have further lead to environmental catastrophe. Activation and presence of toxic elements in the sub-surface litholog and groundwater, originating due to abuse on the surface are an additional graving problem that requires attention of researchers. In fact, picturization of space-time distribution of ground water level intended to demarcate the safe zone for a production well is a complicated task, however, contamination in ground water is another additional complication.

1.2 Problems in Simulating Groundwater Flow and Transport

Contaminant's transport in ground water is largely governed by the parameters which also shape the flow equation. In addition, it is governed by the factors : i) advection of the constituent with the water flowing through the aquifer, ii) dispersion of the constituent, and iii) sources and sinks of the constituent within the volume. Without solving ground water flow equation, the contaminant transport equation can not be solved.

Numerous analytical and numerical models are available to simulate the behaviour of groundwater with contaminants in the aquifer system. The basic concept of solving flow and transport equation is the mass-balance equation. Analytical models although can be used to simulate groundwater flow and transport for aquifers with simple initial and boundary conditions - but - for most cases of practical interest, the analytical methods were observed unrepresentable because of heterogeneity of aquifer parameters, irregular shape of the domain boundaries and temporal and spatial distributions of the various sink-sources functions. Even if the flow modelling is done, numerical modelling of contaminant transport in groundwater is considerably more difficult.

To simplify the flow and transport problems, the most common assumptions are : i) consideration of one-dimensional flow and transport equation assuming thoroughly mixed reservoir and homogeneous nature of transport medium, ii) constituents are assumed to have same properties and their decay and absorption/adsorption rate are constant within a specific time period. Due to these simplifications, in most of the cases, a good agreement between observed and computed values do not comprehend. One needs to work out the errors committed when a problem is simplified from 3-dimensional to a 2-dimensional to a 1-dimensional problem. Common problems in groundwater transport modelling is the absence of direct means for determination of dispersivity in the field, ignorance of adsorption and absorption of constituents, lack of knowledge of exact chemical reactions occurring during movement of constituents etc.

1.3 Present Study and Objectives

The present study is an attempt to evaluate the behaviour of constituents/pollutants moving with groundwater. Three hypothetical examples having relevance to the field conditions have been demonstrated to satisfy the study. Dispersivity, adsorptivity and decay affecting the transport phenomena have been considered. The sensitivity of parameter mainly dispersivity which characterize the transport problems, have been worked out. It is also attempted to quantify errors involved when a 3-D problem is simplified to a 2-D problem and a 2-D problem to a 1-D problem.

In the first case example, a simple one-dimensional transport problem involving advection, dispersion, adsorption and decay is considered. Results obtained by analytical procedure and by the well known flow/transport model MODFLOW/MT3D are compared to quantify the disagreement in solutions. Later, the same problem is expanded to a two-dimensional case, by considering the effect of transverse dispersivity, to evaluate the quantum of deviation in the concentration profile as compared to the result obtained in one-dimensional case.

The second case example deals with a source and sink problem. A two-dimensional case with contaminants forcing into the aquifer through an injection well for a given time is assumed as source, and pumped out from the same well is considered as sink. The effect of variation of longitudinal and transverse dispersivities on the concentration in time and space has also envisaged.

The third case example explains deals with a three-dimensional problem which addresses the behaviour of constituent's transport from a waste dump site. Here, the migration of pollutant is analyzed by assuming different longitudinal and also considering both the transverse (horizontal and vertical) dispersivities. It aims at studying the effect of transverse dispersivities at a distance from the source (i.e whether it dominates over the longitudinal dispersivity considered alone).

2.0 CONTAMINANT TRANSPORT IN GROUNDWATER

The movement of contaminants in unsaturated soil is a complicated hydrologic problem. Figure-1 shows a region of contaminated soil and the factors and processes that affect the fate and transport of chemicals. As rainfall percolates or any recharge takes place into the soil, the dissolved chemicals released from wastes at the land surface and hydrocarbon from surface washoff migrates through the pores of the soil media. Percolated water drives contaminant into the soil through vadose zone which extends from the ground surface to the water table.

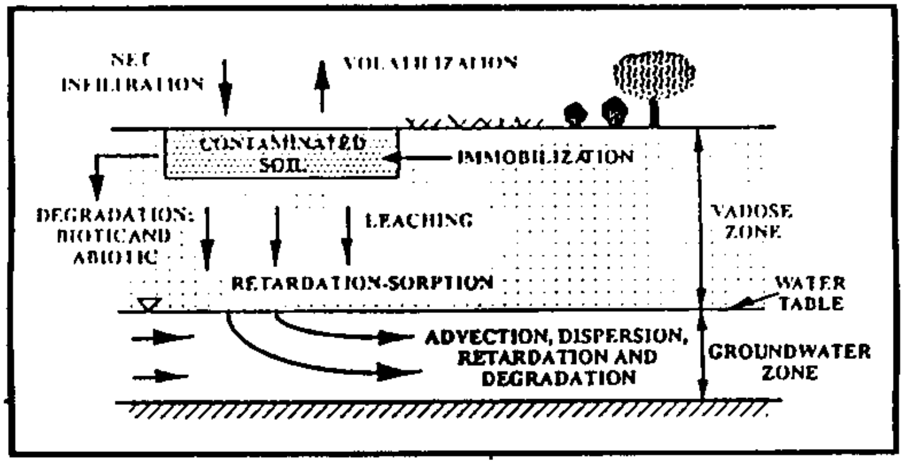

Figure 1: Processes which affect the movement and fate of contaminants in the subsurface environment.

Once the water from unsaturated zone, containing dissolved constituents, is captured in the saturated groundwater zone it is transported due to groundwater flow and disperses in all directions. It is necessary to estimate the travel time for solutes from ground surface to the water table, and the rate at which leachate leaves the unsaturated zone to become ground water contamination.

Contaminated water when reaches the groundwater zone, its actual velocity and direction depend on the hydrogeological properties of the soil in combination with hydrological stresses acting on the groundwater system, such as precipitation, discharge by the rivers, abstraction by wells, etc. Groundwater flow and movement changes if one of these factors change.

2.1 *Principles of Contaminant Transport*

When describing groundwater flow we are used to work with Darcy's velocities. These Darcy velocities present average flow rates. The specific discharge is computed if there is no soil matrix. In reality, however, groundwater must flow through open space between the grains that constitute the soil. This causes a velocity differentiation on a microscopic level (Figure 2).

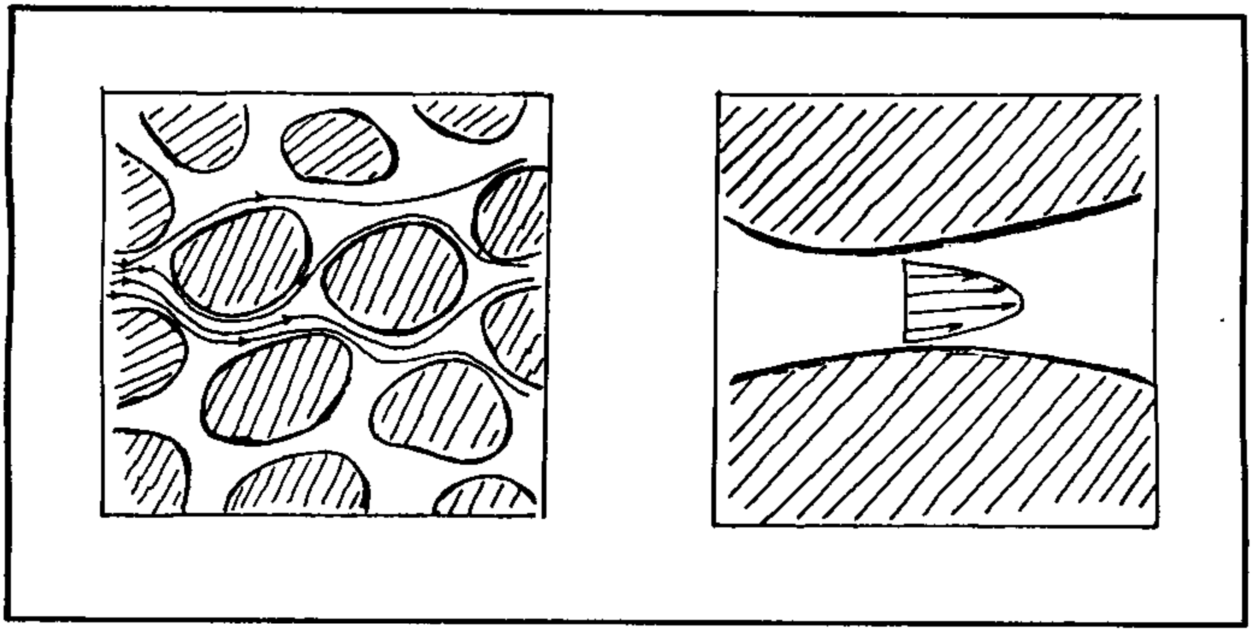

Figure 2: Deviation from the average flow velocity.

- In a flow tube groundwater particles will move faster in the centre of the tube than on the sides, near the solid phase.
- Some groundwater particles will take the 'short cut' around an obstacle (grain) while others will take their time and choose an easy way out.
- The pores between the grains will sometimes be large, enabling high maximum flow rates, while in other cases velocity is low due to a narrow pore-space.

These variations in velocity will induce differences in travel times of water particles to move from one point in space to another. In this way, an initially sharp pollution front will be spread. The spreading will be dominant in the direction of flow because the velocity variation in this direction are the largest. Nevertheless, also some spreading perpendicular to the direction of groundwater flow will take place as a result of differences in streamlines.

Also, on a macroscopic scale velocity differences are present, e.g. caused by the differences in hydraulic permeability. If we know these heterogeneities we can describe the resulting flow field. In reality, however, we mostly lack the information we need to accurately describe the velocities on this macroscopic scale. Again, we can only describe the average groundwater velocity.

As stated earlier, deviation from the average flow velocity cause a spreading of pollutant (Figure 3). This spreading is very similar to a diffusion process. Therefore, in solute transport modelling, groundwater flow will be described by two terms:

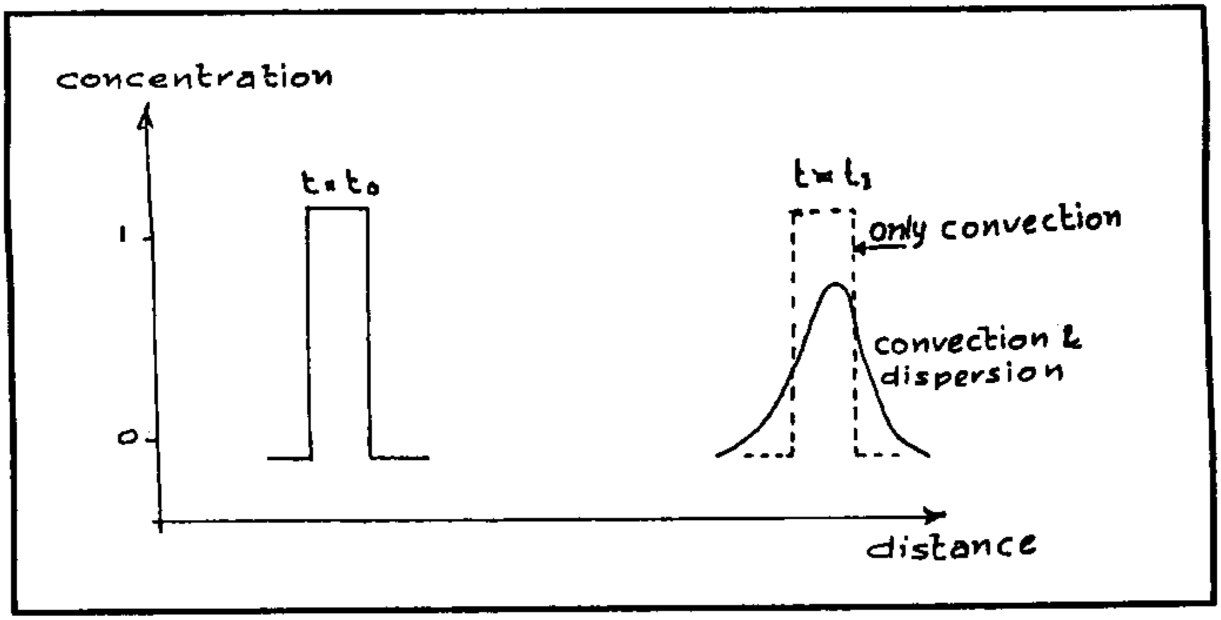

Figure 3. Concentration change as a result of groundwater flow.

transport by the local average groundwater velocity (convection).
transport by deviations from the average groundwater velocity, similar to diffusion.

The second term is referred as dispersion. Difference is made between the spreading in the direction of groundwater flow (*longitudinal dispersion*) and the direction perpendicular to groundwater flow (*transversal dispersion*).

2.1.1 Diffusion

The random movement of molecules in a fluid causes a solute flow from regions with high to regions with low concentrations. Hence, diffusion causes a spreading and levelling of solute concentrations. Diffusion acts independent of groundwater flow. *Even in no-flow conditions diffusion occurs.* The broad transition zones that can exist between fresh and salt water sometimes are a result of diffusion over many centuries.

Diffusion is a slow process. In most practical situations the spreading by variations in groundwater flow is much larger than spreading by diffusion. Yet, especially in a direction perpendicular to groundwater flow, diffusion can be of importance.

2.1.2 Adsorption

Groundwater flow and diffusion are processes that control the distribution of solutes, but they do not affect the total amount of pollutant mass in the groundwater. Adsorption is a process that can influence the dissolved pollutant mass. Solute from groundwater can adhere to the soil matrix. Reversely, adsorbed substances can dissolve into the groundwater. The rate of adsorption (or desorption) and the direction depend on the concentrations of pollutant in the water and on soil matrix.

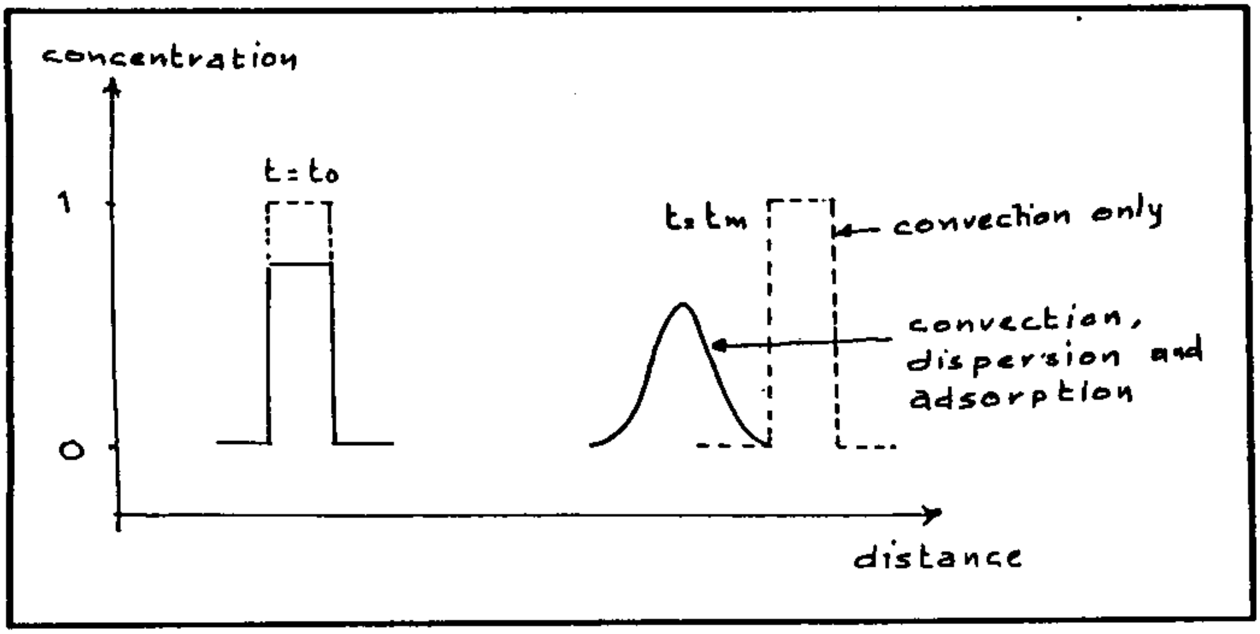

Figure 4. Concentration change as a result of groundwater flow and adsorption.

To fully describe the adsorption process one has to keep track of the concentration of pollutant in both the water phase and the solid phase. However, if one assumes instantaneous adsorption to an equilibrium level between dissolved and adsorbed pollutant, then both concentrations can be described by one variable, commonly taken as the concentration of dissolved pollutant.

It should be noted that if a dissolved pollutant is directly introduced into the saturated groundwater zone, e.g. by infiltration wells, the solute concentration will decrease due to adsorption. Thus, only a fraction of the infiltrated pollutant will be present in the dissolved phase (Figure 4). Adsorption tends to reduce the velocity with which a pollutant moves through the soil.

2.1.3 Decay

Decay reduces the solute concentration in the course of time. Many substances are subjected to decay by radio-active, biological or chemical mechanisms. The decay rate is taken proportional to the solute concentration and can depend largely on the circumstances. A high decay rate is advantageous in pollutant problems (Figure 5). Large travel times between infiltration and abstraction can secure a low solute concentration in the abstracted groundwater. It has to be noted that metabolites that are formed during decay can also be hazardous.

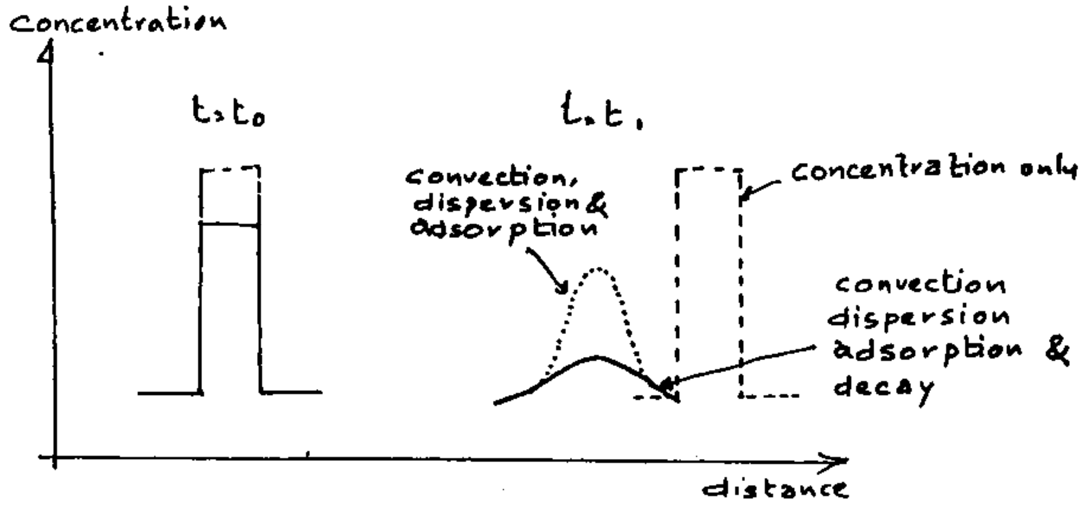

Figure 5. Concentration change as a result of groundwater flow, adsorption and decay.

2.1.4 Reaction

A solute in groundwater can also be subjected to chemical reactions. Not only with other solutes in the groundwater, but also with fractions of the soil material or adsorbed matter. To describe these reactions, a book-keeping of a vast amount of solutes would be necessary. In practice, if a regional description of a pollutant concentration is desired, only a limited number of solutes can be considered (for each solute a complete model must be built).

3.0 MATHEMATICAL FORMULATION OF TRANSPORT EQUATION

3.1 Mass Balance Equation Over a Control Volume

A mathematical model for the transport of solute in groundwater can be derived by taking the mass balance of the dissolved pollutant over a static elementary volume, $\Delta V = \Delta x \Delta y \Delta z$. Expressed in words the equation can be written as:

Change in solute mass stored =

excess solute mass diffusion into volume

+ excess solute mass inflow over outflow or mass transport by Convection

+ solute mass added by injection/infiltration

- solute mass lost by withdrawal

- solute mass lost by decay

- solute mass lost by reaction

- solute mass adsorbed on solid interface.

3.1.1 Change in solute mass stored

Let us denote the solute concentration by 'c' [ML^{-3}] and the porosity by 'n'. The total solute mass contained in the elementary volume then equals $nc\Delta V$. The change of solute mass stored within this volume per unit of time can be expressed as:

$$\frac{\partial (nc)}{\partial t}\Delta V \qquad (1)$$

3.1.2 Excess solute mass diffusion into volume

The transport of solute by diffusion is described by Fick's law which states that the diffusive flux is proportional to the gradient in concentration. The constant of proportionality is called diffusion coefficient D_s [L^2T^{-1}]. For the flux in x-direction we can write:

Solute mass flux (Diffusive flux, J_s) in x-direction:

$$J_s = -D_s \frac{\partial c}{\partial x} \qquad (2)$$

where, $\partial c/\partial x$ is the concentration gradient along the flow direction.

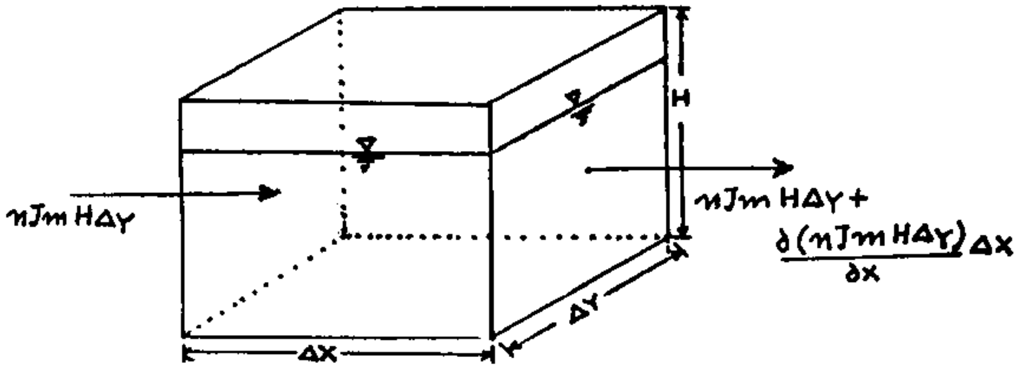

Figure 6. Transport by Diffusion at the control volume.

Change in diffusive flux in x-direction = In - Out =

$$-\frac{\partial}{\partial X}(nJ_m H\Delta y)\Delta x \tag{3}$$

where, 'H' is the aquifer thickness [L].

From (2) and (3), In - Out =

$$\frac{\partial}{\partial X}\left(nD_m\frac{\partial C}{\partial X}H\Delta y\right)\Delta x - \frac{\partial}{\partial X}\left(nD_m\frac{\partial C}{\partial X}\right)\Delta V \tag{4}$$

Diffusive flux in x,y and z direction =

$$\frac{\partial}{\partial_{x_i}}\left(nD_m\frac{\partial C}{\partial_{x_i}}\right)\Delta V \tag{5}$$

3.1.3 Mass transport by Convection (average groundwater flow)

The pollutant mass flux as a result of average groundwater flow, determined by Darcy,s law is given in figure 6. In x-direction the mass flux over an area $\Delta y \Delta z$ amounts to $nv_x c.\Delta y\Delta z$; where, v_x is the x-component of groundwater velocity [LT^{-1}], which is 1/n times the specific discharge. If, v_y and v_z are the 'y' and 'z' component of groundwater velocity, similar expression can be written for y and z-direction.

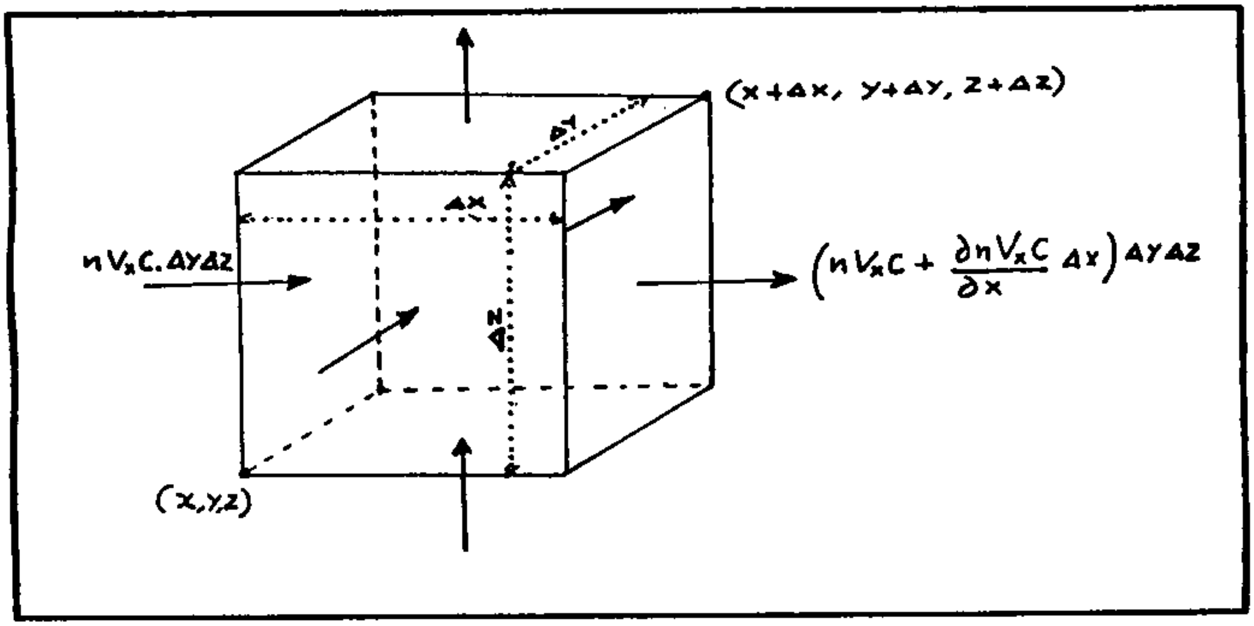

Figure 7. **Mass transport by average groundwater flow at the control volume.**

∴ Change in solute mass flow in x-direction $= - \partial/\partial_x(n.v_x.c)\Delta V$
Similarly, change in solute mass flow in y-direction $= - \partial/\partial_y(n.v_y.c)\Delta V$
& Change in solute mass flow in z-direction $= - \partial/\partial_z(n.v_z.c)\Delta V$

Combining,

Change in solute mass flow in the control volume =

$$-\left[\frac{\partial(nV_xC)}{\partial X}+\frac{\partial(nV_yC)}{\partial Y}+\frac{\partial(nV_zC)}{\partial Z}\right]\Delta V = -\left[\frac{\partial}{\partial X_i}(nV_iC)\right]\Delta V \tag{6}$$

Dispersion

Deviation from the average groundwater flow also give rise to mass transport by Dispersion similar to diffusion. It is proportional to the gradient of solute concentration and is directed from high to low concentrations. Assuming v_x is parallel to x axis (i.e $v_x = v$) and $v_y=v_z=0$, the Dispersive flux in 'x' direction is given by:

$$J_{disp.x} = -D_L\frac{\partial C}{\partial X} \tag{7}$$

$$J_{disp.y} = -D_T\frac{\partial C}{\partial Y} \tag{8}$$

Where,

D_L = Longitudinal dispersion coefficient.
D_T = Transversal dispersion coefficient.

The excess dispersive mass inflow over the dispersive mass outflow in one direction when v_I is parallel to 'x' axis is give by:

$$(In\text{-}Out)_x = \frac{\partial}{\partial x}\left(nD_L\frac{\partial C}{\partial x}\right)\Delta x\Delta y\Delta z \tag{9}$$

$$(In\text{-}Out)_y = \frac{\partial}{\partial y}\left(nD_T\frac{\partial C}{\partial y}\right)\Delta x\Delta y\Delta z \tag{10}$$

If the flow is not aligned with one of the principal axis, the dispersion coefficient takes the form of a tensor[1]. The dispersive flux in x-direction is then written as:

$$-\left(D_{xx}\frac{\partial C}{\partial x}+D_{xy}\frac{\partial C}{\partial y}+D_{xz}\frac{\partial C}{\partial z}\right) \tag{11}$$

and the excess dispersive mass inflow over outflow in x,y and z direction is written as:

$$(In\text{-}Out)_x = \frac{\partial}{\partial x}\left(n\left(D_{xx}\frac{\partial C}{\partial x}+D_{xy}\frac{\partial C}{\partial y}+D_{xz}\frac{\partial C}{\partial z}\right)\right)\Delta x\Delta y\Delta z \tag{12}$$

$$(In\text{-}Out)_y = \frac{\partial}{\partial y}\left(n\left(D_{yx}\frac{\partial C}{\partial x}+D_{yy}\frac{\partial C}{\partial y}+D_{yz}\frac{\partial C}{\partial z}\right)\right)\Delta x\Delta y\Delta z \tag{13}$$

$$(In\text{-}Out)_z = \frac{\partial}{\partial z}\left(n\left(D_{zx}\frac{\partial C}{\partial x}+D_{zy}\frac{\partial C}{\partial y}+D_{zz}\frac{\partial C}{\partial z}\right)\right)\Delta x\Delta y\Delta z \tag{14}$$

Expressing in the form of tensors, above three equations combinely can be written for all mass fluxes across the edges of a control volume ΔV as:

$$(In\text{-}Out)_{x_i} = \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial C}{\partial x_j}\right)\Delta V \tag{15}$$

The value of dispersion coefficient D_{ij} depends on several factors:

- The magnitude of groundwater velocity (magnitude of D_{ij} is proportional to the average groundwater velocity).
- The direction of groundwater flow (magnitude of D_{ij} is larger in the average direction of flow).
- The size of inhomogenities in the aquifer.

In an *isotropic* medium the second factor leads to the definition of two dispersion coefficient: longitudinal dispersion coefficient D_L in the direction of

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[1] A tensor relates two vectors.

average groundwater flow and transversal dispersion coefficient D_T (figure 8)

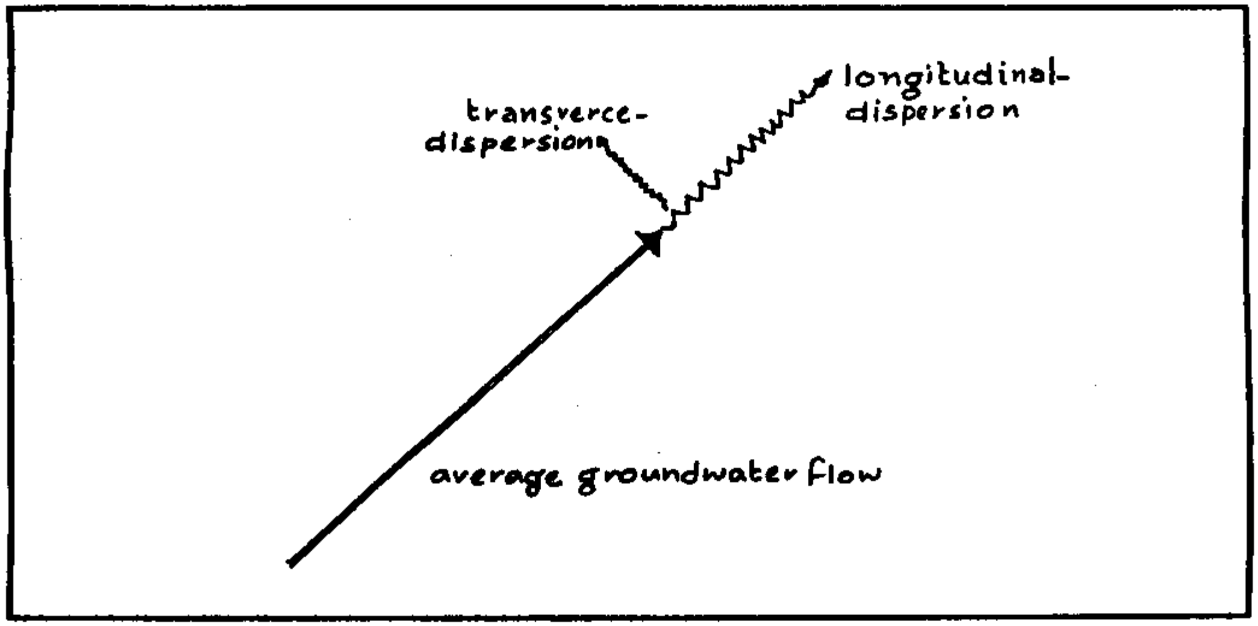


Figure 8. Longitudinal and transversal dispersion.

$$D_L = \alpha_L|v|$$
$$D_T = \alpha_T|v|$$

α_L and α_T are called *longitudinal dispersivity* [L] and *transversal dispersivity* [L]. They indicate the size of the inhomogenities that are 'polished' during averaging. $|v|$ is the magnitude of the local average groundwater velocity. Transverse dispersivities are usually smaller than longitudinal dispersivities (α_T = 0.1 - 0.01 α_T). But, α_T should not be neglected since spread of pollutants is due to α_T.

If average groundwater flow is aligned with the x-axis, the dispersion tensor can be written as:

$$D = \begin{bmatrix} D_{XX} & D_{XY} & D_{XZ} \\ D_{YX} & D_{YY} & D_{YZ} \\ D_{ZX} & D_{ZY} & D_{ZZ} \end{bmatrix} = \begin{bmatrix} D_L & 0 & 0 \\ 0 & D_T & 0 \\ 0 & 0 & D_T \end{bmatrix} = \begin{bmatrix} \alpha_L|V| & 0 & 0 \\ 0 & \alpha_T|V| & 0 \\ 0 & 0 & \alpha_T|V| \end{bmatrix} \qquad (16)$$

If groundwater flow is *not* aligned with one of the principal co-ordinate axes, the off-diagonal elements of the dispersion tensor will generally be non-zero (Bear & Verruijt, 1987):

$$D_{xx}=\alpha_L\frac{V_x^2}{|V|}+\alpha_T\frac{V_y^2}{|V|}+\alpha_T\frac{V_z^2}{|V|}\qquad D_{yy}=\alpha_L\frac{V_y^2}{|V|}+\alpha_T\frac{V_x^2}{|V|}+\alpha_T\frac{V_z^2}{|V|}$$
$$D_{zz}=\alpha_L\frac{V_z^2}{|V|}+\alpha_T\frac{V_x^2}{|V|}+\alpha_T\frac{V_y^2}{|V|}\qquad D_{xy}=D_{yx}=(\alpha_L-\alpha_T)\frac{V_xV_y}{|V|}\qquad (17)$$
$$D_{xz}=D_{zx}=(\alpha_L-\alpha_T)\frac{V_xV_z}{|V|}\qquad D_{yz}=D_{zy}=(\alpha_L-\alpha_T)\frac{V_yV_z}{|V|}$$

In *anisotropic media*, the expressions for the coefficient of dispersion will become even more complex. As can be seen from equation (17) all coefficient of the dispersion tensor can be determined if the values for α_L and α_T are available. The value of the dispersivity is usually related to the size of the area to be modelled and grows with increasing model-area. Kinzelbach (1986) shows the relation between dispersivity and model-area, as deduced from numerical pollution model (figure 9).

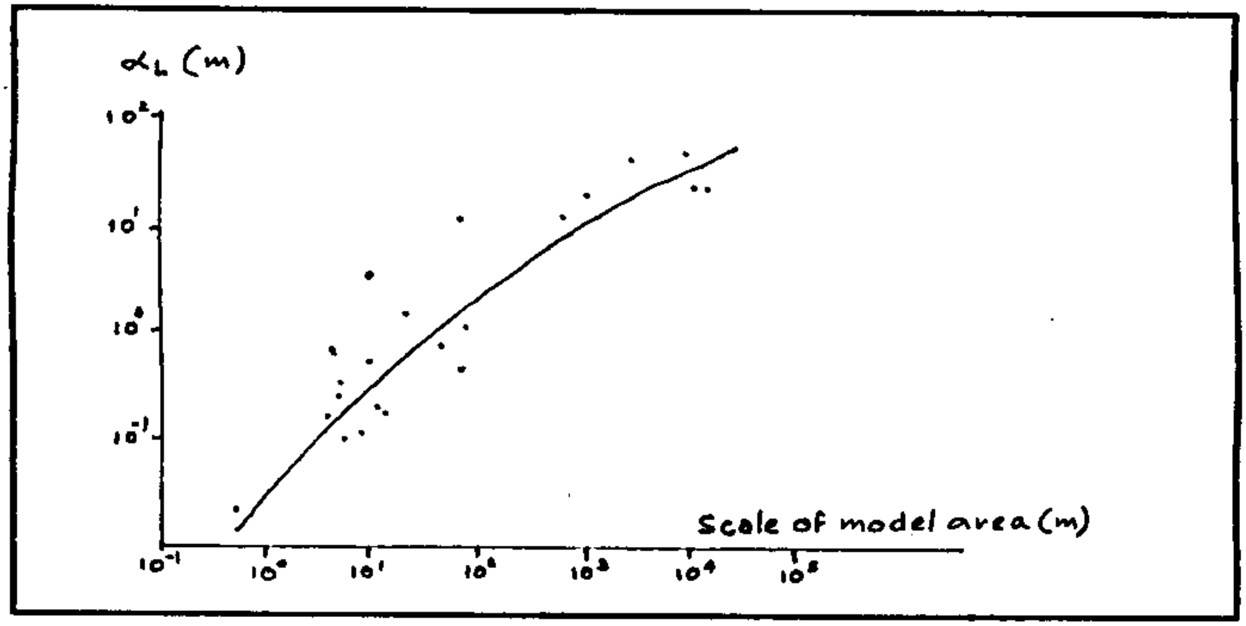


Figure 9. Scale dependence of longitudinal dispersivity. Each dot represents a numerical study.

3.1.4 Solute mass added by injection/infiltration

If the volumetric strength of the infiltrated source of water is denoted by q_{ji} $[L^3L^{-3}T^{-1}]$, and the infiltrated water has a solute concentration 'c_i', then the solute mass added to the control volume ΔV per unit time equals:

$q_{ji}c_i\Delta V$ In case of infiltration (18)

Here, q_{ji} is positive in case of infiltration. In case, there is no infiltration but abstraction, the same expression holds, except that the concentration c of the local water is involved.

$-q_{ja}c\Delta V$ In case of abstraction (19)

where, q_{ja} = volumetric abstraction $[L^3/(L^3T)]$.

3.1.5 Solute mass lost by decay

For decay, the rate of concentration reduction is proportional to the concentration 'c' itself

i.e $-\partial c/\partial t \ \alpha \ c \Rightarrow \partial c/\partial t = \lambda_c c$

where, λ_c = Decay constant of the solute [1/T].

Integrating, $c(t) = c_0 e^{-\lambda_c t}$

where, c_0 = Initial concentration.

The initial concentration c_0 is reduced to half its original value by decay in time $t = T_{\frac{1}{2}}$ (i.e half life period).

$$\frac{1}{2}C_o = C_o e^{-\lambda_c T_{1/2}} \Rightarrow T_{1/2} = \frac{\ln 2}{\lambda_c}$$

$$\text{Decay} = -n\lambda_c c \Delta V \tag{20}$$

3.1.6 Solute mass lost by reaction

The solute mass in the control volume can diminish by reaction at a rate $= -n\zeta_c \Delta V$ (21)

where, ζ_c = volumetric reaction rate of dissolved pollutant $[ML^{-3}T^{-1}]$.

3.1.7 Solute mass adsorbed on solid interface

Adsorption is expressed as concentration of adsorbed mass per unit mass of soil grains. Adsorption reduces the solute concentration within the liquid phase. The adsorption rate depends on the solute concentration 'c' and on the concentration of adsorbed pollutant 'c_s' on the solid interface.

Mass balance equation for the adsorbed pollutant can be written in the following way:

Mass of solid = $(1-n)\rho_s \Delta V$; where, ρ_s = density of grains.
Mass of pollutant adsorbed = $c_s(1-n)\rho_s \Delta V$
Change of pollutant mass/unit time in the elementary volume 'ΔV' coming from the dissolved phase i.e the rate of adsorption = $\partial/\partial t[(1-n)\rho_s c_s \Delta V]$

Adsorption mass *per unit volume* is equal to the flux 'f_s' of the solute from the liquid phase to the solid interface diminished by adsorbent lost by decay and reaction i.e

$$\frac{\partial}{\partial t}[(1-n)\rho_s c_a] = f_a - \lambda_a(1-n)\rho_s c_a - (1-n)\xi_a \tag{22}$$

where, λ_a = Decay constant for adsorbed pollutant [1/T].
ξ_a = Volumetric reaction rate of adsorbed pollutant $[ML^{-3}T^{-1}]$.

The flux 'f_a' of solute from the liquid phase to solid interface is the adsorption term that must be substituted (i.e subtracted) in the balance equation for the solute i.e:

$$f_a = \left[\frac{\partial}{\partial t}((1-n)\rho_s c_a) + \lambda_a(1-n)\rho_s c_a + (1-n)\xi_a\right] \tag{23}$$

3.2 General Mass Balance Equation

General mass balance equation per unit volume per unit time can be written from equations: (1),(5),(6),(15),(18),(19),(20),(21) and (23):

Change in storage = Diffusion + Convection + Dispersion + Infiltration + Withdrawal + Decay + Reaction + Adsorption.

$$\begin{aligned}\frac{\partial(nC)}{\partial t} = {} & \frac{\partial}{\partial x_i}\left(nD_m\frac{\partial C}{\partial x_i}\right) - \frac{\partial}{\partial x_i}(nv_iC) + \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial C}{\partial x_j}\right) + q_{3i}C_i - q_{3a}C \\ & -n\lambda_c C - n\xi_c - \left[\frac{\partial}{\partial t}((1-n)\rho_s c_a) + \lambda_a(1-n)\rho_s c_a + (1-n)\xi_a\right]\end{aligned} \tag{24}$$

The variables c and c_a are most frequently related by the linear equilibrium isotherm:

$c_a = K_d c$; where K_d = Distribution coefficient.

By assuming: $\lambda_c = \lambda_a$ and no reaction takes place i.e $\xi_c = \xi_a = 0$ equation (24) reduces to:

$$\begin{aligned}\frac{\partial(nC)}{\partial t} = {} & \frac{\partial}{\partial x_i}\left(nD_m\frac{\partial C}{\partial x_i}\right) - \frac{\partial}{\partial x_i}(nv_iC) + \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial C}{\partial x_j}\right) + q_{3i}C_i - q_{3a}C \\ & -n\lambda C - \left[\frac{\partial}{\partial t}((1-n)\rho_s K_d C) + \lambda(1-n)\rho_s K_d C\right]\end{aligned}$$

$$\Rightarrow \frac{\partial}{\partial t}[c(n+(1-n)\rho_s K_d)] = \frac{\partial}{\partial x_i}\left(nD_m \frac{\partial c}{\partial x_i}\right) - \frac{\partial}{\partial x_i}(n v_i c) + \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial c}{\partial x_j}\right)$$
$$+ q_{3i}c_i - q_{3a}c - \lambda c[n+(1-n)\rho_s K_d]$$

$$\Rightarrow \frac{\partial}{\partial t}\left[nc\left(1+\frac{1-n}{n}\rho_s K_d\right)\right] = \frac{\partial}{\partial x_i}\left(nD_m \frac{\partial c}{\partial x_i}\right) - \frac{\partial}{\partial x_i}(n v_i c) + \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial c}{\partial x_j}\right)$$
$$+ q_{3i}c_i - q_{3a}c - n\lambda c\left[1+\frac{1-n}{n}\rho_s K_d\right]$$

$$\Rightarrow \frac{\partial}{\partial t}(nRc) = \frac{\partial}{\partial x_i}\left(nD_m \frac{\partial c}{\partial x_i}\right) - \frac{\partial}{\partial x_i}(n v_i c) + \frac{\partial}{\partial x_i}\left(nD_{ij}\frac{\partial c}{\partial x_j}\right)$$
$$+ q_{3i}c_i - q_{3a}c - n\lambda(Rc)$$

where, R = 1 + $\rho_s K_d$(1-n)/n = Retardation factor.

$$\Rightarrow \frac{\partial}{\partial t}(nc) = \frac{\partial}{\partial x_i}\left(n\frac{D_m}{R}\frac{\partial c}{\partial x_i}\right) - \frac{\partial}{\partial x_i}\left(n\frac{v_i}{R}c\right) + \frac{\partial}{\partial x_i}\left(n\frac{D_{ij}}{R}\frac{\partial c}{\partial x_j}\right)$$
$$+ \frac{q_{3i}c_i - q_{3a}c}{R} - n\lambda c \qquad (25)$$

In the above equation, the convective term describing the transport by average groundwater flow, the velocity 'v' reduces to 'v/R'. Similar effect appears in the diffusive and dispersive terms. Hence, the total effect of groundwater flow 'v' on the solute transport is *reduced by the adsorption process* to such a level as if groundwater was flowing with a velocity 'v/R'. Adsorption also influences the effect of external sources and sinks (infiltration or abstraction). If by an external source, a mass 'M' of pollutant is introduced, then an amount of 'M/R' will be present in the dissolved phase, the rest (M-M/R) being adsorbed on the solid matrix.

The value of 'R' can vary significantly depending on solute and soil properties: R=1 (no adsorption) for Chlorides to for instance, R=12,000 for polychlorinated by phenols (PCB) in soils containing 0.3% organic matter (Appelo, 1988)

3.2.1 Characteristic equation for 1-D solute transport

General mass balance equation for 3-D solute transport per unit volume per unit time is given as:

$$\frac{\partial(nc)}{\partial t} = \frac{\partial}{\partial x_i}\left(n\cancelto{=0}{D_m}\frac{\partial c}{\partial x_i}\right) - \frac{\partial}{\partial x_i}(n\cancelto{v}{v_i}c) + \frac{\partial}{\partial x_i}\left(n\cancelto{D}{D_{ij}}\frac{\partial c}{\partial x_j}\right) + \cancelto{=0}{q_{3i}}c_i - \cancelto{=0}{q_{3a}}c$$
$$-\cancelto{=0}{n\lambda_c}c - \cancelto{=0}{n\xi_c} - \left[\frac{\partial}{\partial t}((1-n)\rho_s c_a) + \lambda_a\cancelto{=0}{(1-n)}\rho_s c_a + \cancelto{=0}{(1-n)}\xi_a\right] \tag{26}$$

By assuming

i. 1-D solute transport;
ii. Constant porosity;
iii. Aquifer thickness is constant;
iv. Convective velocity 'v' is constant (steady state groundwater flow;
v. Since 'v' is constant and $D = \alpha_L|v| \Rightarrow$ D is constant;
vi. Molecular diffusion is very very small ⇒ Diffusion may be neglected;
vii. No decay; and
viii. No reaction, the above equation reduces to:

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} - \frac{\partial}{\partial t}\left(\frac{1-n}{n}\rho_s c_a\right) \tag{27}$$

⇒ Two unknown variables 'c' and 'c_a'.

$$\Rightarrow \frac{\partial}{\partial t}\left[c + \frac{1-n}{n}\rho_s k_d c\right] = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} \tag{28}$$

⇒ One unknown variable 'c'.

$$\Rightarrow \frac{\partial}{\partial t}\left[c\left(1 + \frac{1-n}{n}\rho_s k_d\right)\right] = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2}$$

$$\Rightarrow \frac{\partial}{\partial t}(Rc) = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2}$$

$$\Rightarrow \frac{\partial c}{\partial t} = -\frac{v}{R}\frac{\partial c}{\partial x} + \frac{D}{R}\frac{\partial^2 c}{\partial x^2}$$

$$\Rightarrow \frac{\partial c}{\partial t} = -\frac{v}{R}\frac{\partial c}{\partial x} + \alpha_L\frac{|v|}{R}\frac{\partial^2 c}{\partial x^2} \tag{29}$$

The solution of the above equation for the boundary condition (Ogata and Banks, 1961)

at: $t \to \infty$; $x \to \infty \Rightarrow c = 0$
at: $t \to \infty$; $x \to -\infty \Rightarrow c = c_0$

Solution is:

$$c(x,t) = \frac{1}{2} c_0 \, erfc\left[\frac{x-\frac{v}{R}t}{2\sqrt{\alpha_L \frac{|v|}{R} t}}\right] \tag{30}$$

where, 'erfc' is the complementary error function defined by:

$$erfc(x) = 1-erf(x) = 1-\frac{1}{\sqrt{\pi}}\int_0^x e^{-t^2}\, d\xi$$

The solution for this problem lead to some easy to use conclusions:

- Since erfc(0)=1, the point in x direction with a concentration of $c=0.5\ c_0$ can be found at x=vt. The centre of the front progresses with average groundwater flow.
- From the analogy between the solution of 1-D transport problem and a *probability density function*, one can deduce that the distribution of the front can be described by a standard deviation 'σ' that amounts to:

$$\sigma = \sqrt{2\alpha_L vt} = \sqrt{2\alpha_L L} \tag{31}$$

Where 'L' is the displacement of the centre of the front by average groundwater flow (Bear 1979). 68% of the front width lies within the interval of [L−σ; L+σ] and 95% of the front within [L−2σ; L+2σ] (Figure 10). Now if we compute transport of pollutant by convection only, we can give a fairly good estimate of the front width by using the above expression.

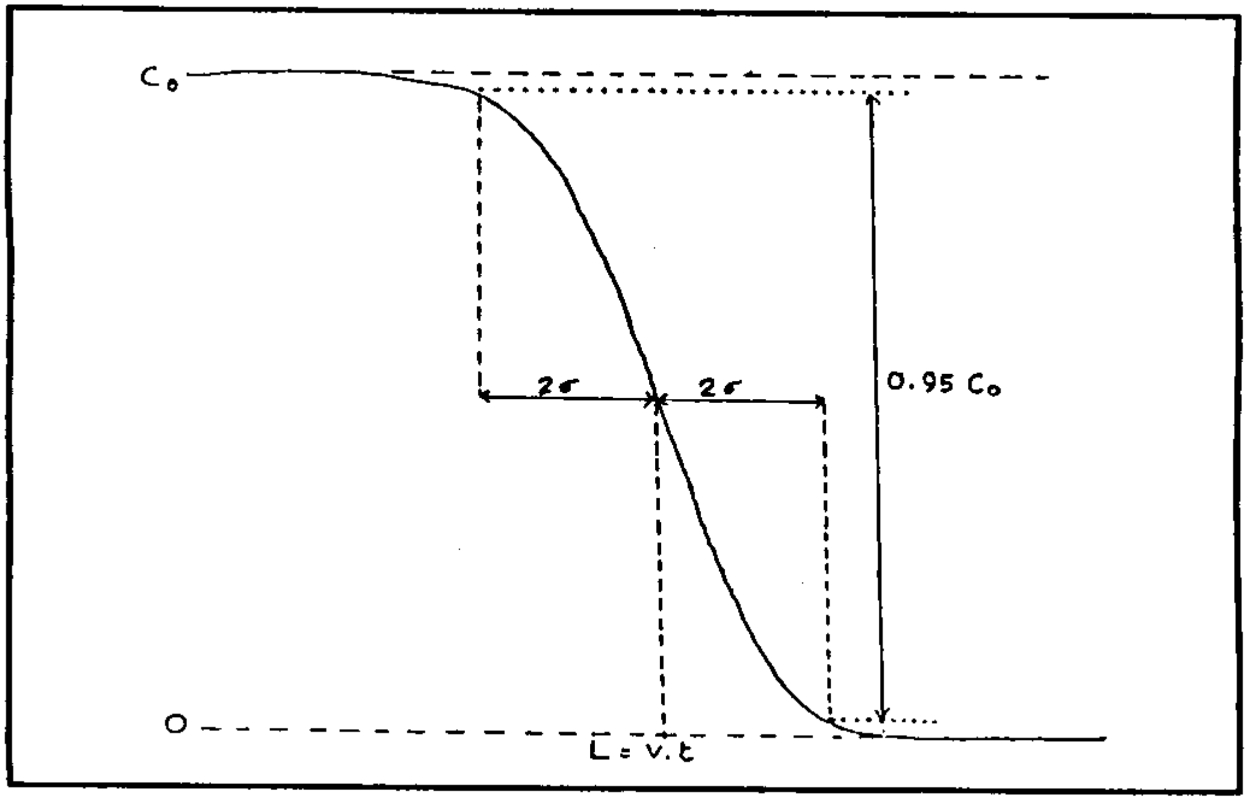


Figure 10. Shape of pollutant front after a time 't' and interpretation of the standard deviation 'σ'.

The indication of the front width by 'σ' can also be used for an instantaneous point injection of pollutant and for 2-D situations. In this case [L-σ; L+σ] denotes the interval in which 68% of the total pollutant mass can be found; 95% of the total mass can be found within [L-2σ; L+2σ].

If a uniform flow and a 1-D distribution of solute concentration is present, e.g near a river bank - after a sudden pollution of the river water, the longitudinal dispersivity can be calculated from measurements in an observation well near the river bank.

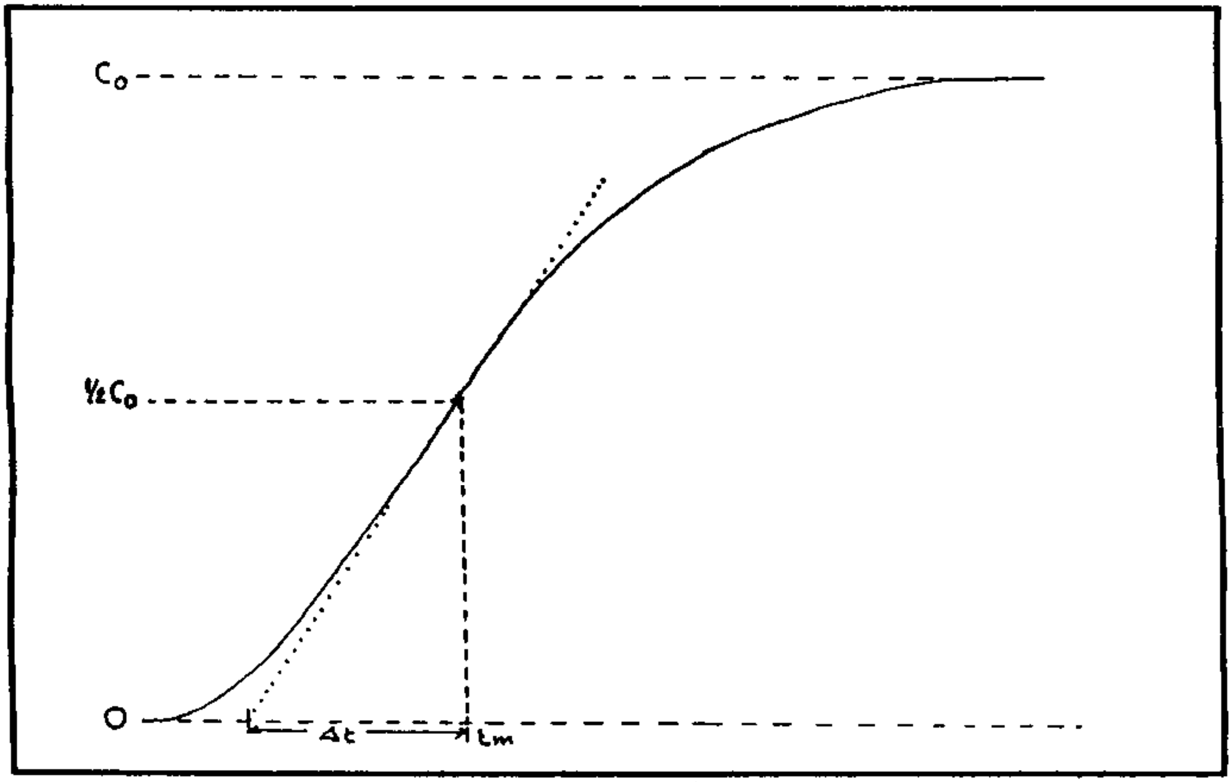


Figure 11. Breakthrough curve at an observation well.

First it is required to draw the breakthrough curve of pollutant in the observation well (Figure 11). Next the time gradient of the concentration at time level 't_m', when the concentration has reached half the maximum level. This measured gradient equals approximately

$$\frac{\partial}{\partial t}c(L,t)\Big|_{t=t_m} = \frac{C_0}{2\Delta t} \qquad (32)$$

The time derivative of equation (30) at a distance $L=vt_m$ is:

$$\frac{\partial}{\partial t}C(L,t)\Big|_{t=t_m}=\frac{C_o}{2}\frac{v}{\sqrt{\pi\alpha_L v t_m}} \qquad (33)$$

From above two equations:

$$\frac{C_o}{2}\frac{v}{\sqrt{\pi\alpha_L v t_m}}=\frac{C_o}{2\Delta t}$$

$$\Rightarrow \alpha_L=\frac{\Delta t^2}{\pi t_m}v \qquad (34)$$

Which is a direct relation between measured data and 'longitudinal dispersivity'.

4.0 THE MODEL

A model is a device that represents an approximation of a field situation. Models provide a framework for synthesizing field information and for testing of ideas about how the system works. Use of groundwater model enables one to make an informed analysis or prediction about the consequences of a proposed action.

Numerous models (MODFLOW/MT3D, SUTRA, ASM, AQUA, FE3DGW, CTRAN/W etc.) are available to study the contaminant's transport in groundwater for 1-D, 2-D and 3-D cases. The MT3D compatible with MODFLOW has successfully been used over the world to study the flow and transport phenomena in groundwater. MODFLOW, MODPATH and MT3D integrated in a package named PM (Processing Modflow) has also been applied for the present study.

4.1 Processing Modflow (PM)

Processing Modflow (PM) is designed to help the modeller to perform groundwater flow and transport simulations with the USGS groundwater flow model MODFLOW (McDonald and Harbough, 1988), computation of pathline with the particle tracking program MODPATH (Pollock, 1988) and the transport model MT3D (Zheng, 1992). PM performs four tasks: Modelling, Simulation, Analysis and Data control. The tasks performed by each are as follows:

i) Modelling
- Input of model data is performed (i.e the dimensions of the model domain, the initial conditions, the physical properties, data of selected packages etc) by using a graphical model designer.
- Drawing and editing a digitized map.
- Importing a digitized map.
- Checking of input data for errors before simulation.

ii) Simulation
- Simulates three dimensional groundwater flow model using MODFLOW.
- Computes pathline using MODPATH.
- Simulates groundwater transport in three dimensions using MT3D.

iii) Analysis
- Graphically represents the simulated heads in the form of isolines.
- Draws two and three dimensional pathline from the result of MODPATH.

- Draws concentration distribution in space and time using the result of MT3D.
- Computes water balance and mass balance of concentration for a desired sub-region and for the whole area.

iv) Data control

Displays input data in the form of contours or classes.

4.2 MODFLOW

The model MODFLOW simulates flow in three dimensions. The program uses a modular structure wherein similar program functions are grouped together.

The programme has been divided into a main program and a series of independent subroutines called modules. The modules, in turn, have been grouped into 'packages'. A package is a group of modules that deals with a single aspect of the simulation. For example, the option 'Well package' simulates the effect of wells, the 'River package' simulate the effect of river etc.

4.2.1 Mathematical Background

The three dimensional movement of groundwater of constant density through porous earth material under equilibrium conditions in a heterogenous anisotropic medium can be described by the following partial differential equation:

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right) - W = S_s\frac{\partial h}{\partial t} \tag{35}$$

Where,

$K_{xx}(x,y,z)$, $K_{yy}(x,y,z)$, $K_{zz}(x,y,z)$ are values of hydraulic conductivity along x, y and z coordinate axes, which are assumed to be parallel to the major axes of hydraulic conductivity [LT^{-1}];

$h(x,y,z,t)$ is the piezometric head [L];

$W(x,y,z,t)$ is the volumetric flux per unit volume and represents sources and/or sinks of water [T^{-1}];

$S_s(x,y,z)$ is the specific storage of the porous material [L^{-1}] and,

t is the time [T].

MODFLOW discretizes the model domain with a mesh of blocks called cells, the location of which are described in terms of rows, columns, and layers.

The period of simulation is divided into a series of 'stress period' within which stress parameters are constant. Each stress period, in turn, is divided into a series of time steps. The user specifies the length of the stress period, the number of time steps at each stress period, and the time step multiplier. Using these terms, the program calculates the length of each time step in the stress period. Thus, within a simulation, there are three nested loops: a stress-period loop, within which there is a time-step loop, which in turn contains an iteration loop.

With above discretization in space and time, equation (1) will lead to system of simultaneous linear algebraic equations. MODFLOW utilizes iterative methods to obtain the solution of the system's equation.

4.3 MODPATH

Modpath is a Particle tracking program. It generates three dimensional path line, position of pollutant (solute) at a specified point of time, computes ending point coordinates and the total time of travel for each particle by using the simulated output from a *steady state groundwater flow model* MODFLOW. The method is based on the assumption that directional velocity component varies linearly within a grid cell in its own coordinate direction. Areas contributing flow to a pumping wells (i.e capture zone of a pumping well), contours of equal traveltime of particles can be estimated along the flow path. Delineation of capture zone can aid in designing a monitoring network as part of a comprehensive wellhead protection program to protect the quality of a groundwater supply.

Particle tracking takes into account the advective component of the transport only. Particles are tracked through a flow field explicitly by computing the directional components of velocity at a particle's current position and moving the particle to a new location. The new position of the particle in terms of x, y, and z coordinate is obtained by multiplying the velocity components by a finite time step. Every new position of the particle is a function of time.

4.4 MT3D

Numerical modelling of contaminant transport is considerably more difficult than computation by analytical procedures. Numerical modelling is more vulnerable to numerical errors such as; numerical dispersion and artificial oscillation.

The transport model referred as MT3D, is a 3-dimensional computer model which can be used to simulate changes in concentration of *single species* miscible contaminants in groundwater considering advection, dispersion and some *simple chemical reactions* with various types of boundary conditions and external sources or sinks. It uses modular structure similar to that of MODFLOW. The modular structure of the MT3D transport model makes it possible to simulate advection, dispersion, source/sink mixing, and chemical reactions independently. After a flow model is developed and calibrated, the information needed by the transport model is saved in files which are then retrieved by the transport model.

Currently, MT3D accommodates the following spatial discretization capabilities and transport boundary conditions: i) confined, unconfined or semi-confined aquifer layers; ii) inclined model layers and variable cell thickness within the same layer; iii) specified concentration or mass flux boundaries; and iv) effects of external sources and sinks such as wells, drains, areal recharge and evapotranspiration.

4.4.1 Solution techniques

The model MT3D uses mixed Eulerian-Lagrangian approach to the solution of the advective-dispersive-reactive equation, based on a combination of the method of characteristics and the modified method of characteristics. This approach combines the strength of the method of characteristics for eliminating numerical dispersion and the computational efficiency of the modified method of characteristics.

In the Eulerian approach, the transport equation is solved with a fixed grid method such as the finite-difference or finite-element method. This approach handles dispersion/reaction dominated problems effectively. For advection dominated problems requiring small grid spacing and time steps this method is susceptible to excessive numerical dispersion or oscillation. The Lagrangian approach provides an accurate and efficient solution to advection dominated problems with sharp concentration fronts. However, a Lagrangian method can lead to numerical instability and computational difficulties in nonuniform media with multiple sink/sources and complex boundary conditions. The mixed Eulerian-Lagrangian approach adopted in MT3D attempts to combine the advantages of both the Eulerian and the Lagrangian approaches. It solves the advection term with a Lagrangian method by employing the forward-tracking method of characteristics (MOC), the backward-tracking modified method of characteristics (MMOC), or a hybrid of these two methods (HMOC). The dispersion and reaction term is solved with an Eulerian method by utilizing a conventional block-centred finite-difference method.

4.4.2 Governing equations

The partial differential equation describing three-dimensional transport of contaminants in groundwater can be written as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{n}C_s + \sum_{k=1}^{N} R_k \qquad (36)$$

Where,

C is the concentration of contaminants dissolved in groundwater, $[ML^{-3}]$;

t is time, $[T]$;

x_i is the distance along the respective Cartesian coordinate axis, $[L]$;

D_{ij} is the hydrodynamic dispersion coefficient, $[L^2T^{-1}]$;

v_i is the seepage or linear pore water velocity, $[LT^{-1}]$;

q_s is the volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative), $[T^{-1}]$;

C_s is the concentration of sources or sinks, $[ML^{-3}]$;

n is the porosity of the porous medium, [];

$\sum_{k=1}^{N} R_k$ is the chemical reaction term, $[ML^{-3}T^{-1}]$.

Assuming that only equilibrium-controlled linear or non-linear sorption and first-order irreversible rate reactions are involved in the chemical reactions, the chemical reaction term in equation (36) is expressed as:

$$\sum_{k=1}^{N} R_k = -\frac{\rho_b}{n}\frac{\partial \bar{C}}{\partial t} - \lambda\left(C + \frac{\rho_b}{n}\bar{C}\right)$$

$$\sum_{k=1}^{N} R_k = -\frac{\rho_b}{n}\frac{\partial C}{\partial t}\frac{\partial \bar{C}}{\partial C} - \lambda\left(C + \frac{\rho_b}{n}\bar{C}\right) \qquad (37)$$

Where,

ρ_b is the bulk density of the porous medium, $[ML^{-3}]$;

$\bar{C}$ is the concentration of contaminants sorbed on the porous medium, $[MM^{-1}]$;

λ is the rate constant of the first-order rate reactions, $[T^{-1}]$.

substituting equation (37) in (36) gives:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{n}C_s - \frac{\rho_b}{n}\frac{\partial \bar{C}}{\partial C}\frac{\partial C}{\partial t} - \lambda\left(C + \frac{\rho_b}{n}\bar{C}\right) \qquad (38)$$

Moving the fourth term on the right hand side of equation (38) to the left hand side, equation (38) becomes:

$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{n}C_s - \lambda\left(C + \frac{\rho_b}{n}\bar{C}\right) \tag{39}$$

where, R is called the retardation factor, defined as

$$R = 1 + \frac{\rho_b}{n}\frac{\partial \bar{C}}{\partial C} \tag{40}$$

Equation (39) is the governing equation underlying the transport model. The transport equation is linked to the flow equation through the relationship:

$$v_i = -\frac{K_{ii}}{n}\frac{\partial h}{\partial x_i} \tag{41}$$

Where, K_{ii} is a principal component of the hydraulic conductivity tensor, $[LT^{-1}]$;

h is hydraulic head, [L].

4.4.2.1 Eulerian-Lagrangian approach

Applying Chain rule to the advection term in the equation (39):

$$\frac{\partial}{\partial x_i}(v_i C) = v_i\frac{\partial C}{\partial x_i} + C\frac{\partial v_i}{\partial x_i} = v_i\frac{\partial C}{\partial x_i} + C\frac{q_s}{n} \tag{42}$$

substituting the advective term from above and dividing both sides by the retardation factor, the governing equation (39) becomes:

$$\frac{\partial C}{\partial t} = \frac{1}{R}\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \overline{v_i}\frac{\partial C}{\partial x_i} - \frac{q_s}{Rn}(C - C_s) - \frac{\lambda}{R}\left(C + \frac{\rho_b}{n}\bar{C}\right) \tag{43}$$

$\overline{v_i} = \frac{v_i}{R}$, represents the "retarded" velocity of a contaminant particle.

Equation (43) is an Eulerian expression in which the partial derivative, $\partial C/\partial t$, indicates the rate of change of solute concentration (C) *at a fixed point in space*. Equation (43) can also be expressed in the Lagrangian form as:

$$\frac{DC}{Dt} = \frac{1}{R}\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{q_s}{Rn}(C - C_s) - \frac{\lambda}{R}\left(C + \frac{\rho_b}{n}\bar{C}\right) \tag{44}$$

where, the substantial derivative,

$$\frac{DC}{Dt} = \frac{\partial C}{\partial t} + \overline{v_i}\frac{\partial C}{\partial x_i}$$

indicates the rate of change in solute concentration (C)* along the pathline of a contaminant particle.

By introducing the finite-difference algorithm, the substantial derivative in equation (44) can be approximated as:

$$\frac{DC}{Dt} = \frac{C_m^{n+1} - C_m^{n'}}{\Delta t} \tag{45}$$

so that equation (44) becomes

$$C_m^{n+1} = C_m^{n'} + \Delta t * RHS \tag{46}$$

Where

C_m^{n+1}	is the average solute concentration for cell m at the new time level (n+1);
$C_m^{n'}$	is the average solute concentration for cell m at the new time level (n+1) due to advection alone, also referred as to as the intermediate time level (n');
Δt	is the time increment between the old time level (n) and the new time level (n+1);
RHS	represents the finite-difference approximation to the terms on the right-hand side of equation (44). The finite-difference approximation is explicit if the concentration at the old time level C^n is used in the calculation of RHS; it is implicit if the concentration at the new time level C^{n+1} is used.

Equation (46) constitutes the basic algorithm of the mixed Eulerian-Lagrangian method used in the MT3D transport model. In this method, the term $C_m^{n'}$ in equation (46), which accounts for the effect of advection, is solved with a Lagrangian method on a moving coordinate, while the second term in equation (46), which accounts for the effect of dispersion, sink/source, and chemical reactions, is solved with a finite-difference method on the fixed Eulerian grid.

5.0 CASE EXAMPLES

5.1 1-D, 2-D Case Problem

In order to demonstrate the quantum of errors involved when a 2-D or a 3-D problem is simplified to a 1-D problem, a case example is studied. The test problem reads as follows:

The steady state condition of flow domain consists of 100 columns, 1 row and 1 layer. The input parameters for flow and transport simulation are :

For flow:

- Cell width along rows (Δx) = 25m.
- Cell width along column (Δy) = 25m.
- Layer thickness (Δz) = 25m.
- Aquifer type = unconfined.
- Porosity (n) = 0.25.
- Homogenous hydraulic conductivity (k) = 40m/day.
- Constant head cell at (1,1) and (100,1) with head = 70m and 60 m respectively.
- No external stresses (viz. well, drains, river, evapotranspiration, aerial recharge, stream aquifer relation) considered.

For transport:

- The cell in the first column (1,1) is treated as a constant concentration cell with concentration = 1kg/cum.
- Starting concentration at all other cell = 0kg/cum.
- Longitudinal dispersivity (α_L) = 20m, Retardation factor (R) = 5 and Decay or the rate constant of the first order rate reaction (λ) = 0.002 day^{-1}.

First, a 1-D transport problem involving advection, advection + dispersion, advection + dispersion + adsorption and advection + dispersion + adsorption + decay are solved separately by analytical procedure suggested by Ogatta and Banks (1961). In this problem, only the *longitudinal dispersivity* is considered. The same problem is also solved numerically using MT3D model. Comparison of results are given in figure 12. The result (concentration v/s distance) shows an excellent match between the analytical and numerical solution which eventually show that the transport phenomena can well be represented by the 1-D model.

Next, the same example is expanded to a 2-D case with 100 X 100 grids. The first and the last column is assumed to be constant head cells for flow simulation. For simulation of constituent's transport, only Cell (1,51) is assumed to be a constant concentration cell. The transverse dispersivity is assumed to be half of the longitudinal dispersivity. All other parameters of flow and transport are kept same. In fact, situation in a real field problem involves spreading of concentration in all directions. These spreading reduces the concentration at a point as compared to a 1-D problem. The simulated results (concentration profile) advocating the effect of advection + dispersion in a 2-D test case is shown in figure 13. The results of the 1-D case for advection + dispersion is also shown in the same figure for comparison. The results reflect an appreciable reduction in concentration with distance in each cell along the rows of 1-D case. This difference (reduction) in concentration is due to spreading of pollutants along the transverse direction.

Similar type of concentration profiles are also seen from the result of simulation involving advection + dispersion + adsorption and advection + dispersion + adsorption + decay (figure 14 and 15)

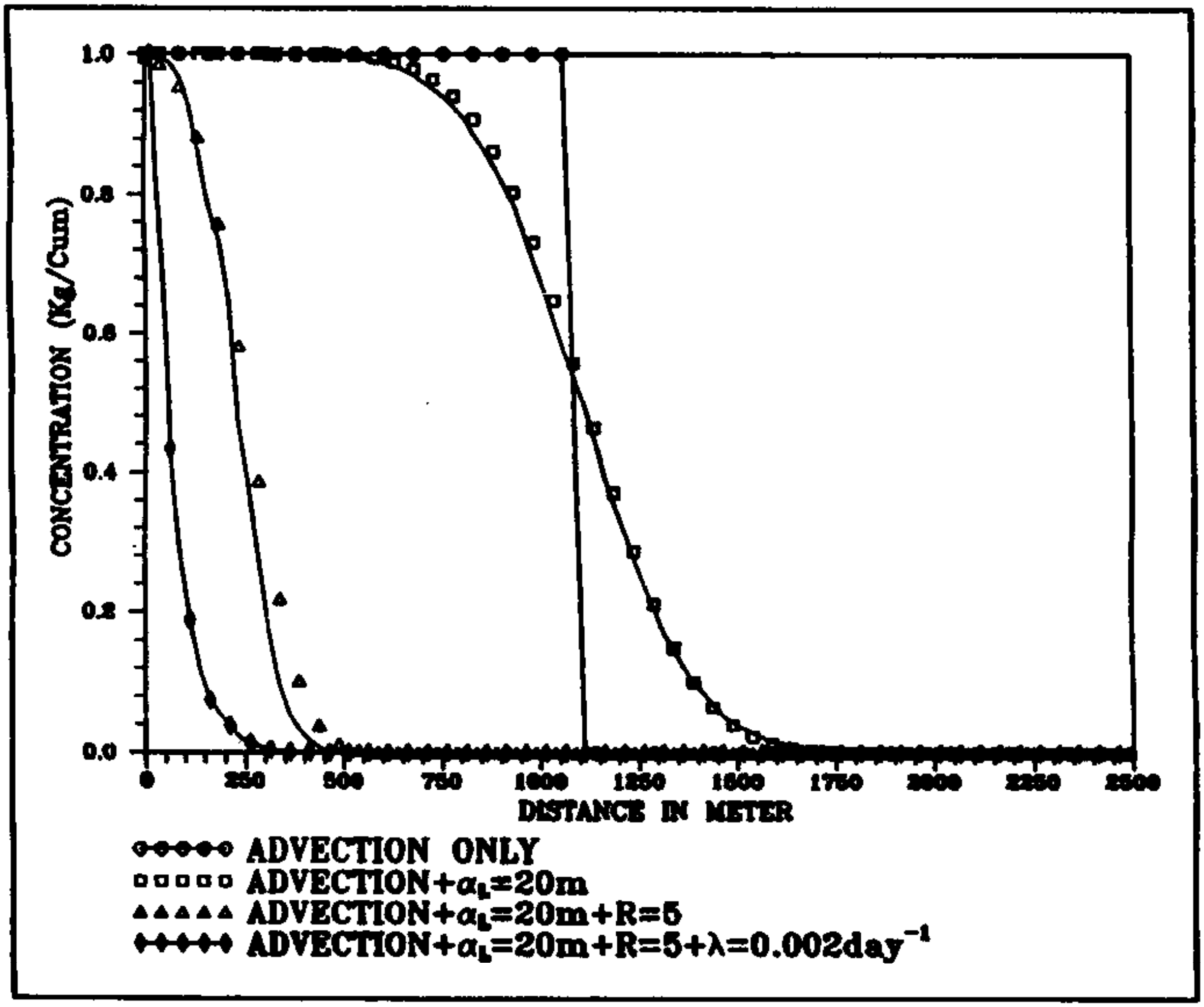


Figure 12: Effect of Advection, Dispersion, Adsorption and Decay on the Concentration Profile in an 1-D Problem (line ⇒ Numerical solution and point ⇒ Analytical solution)

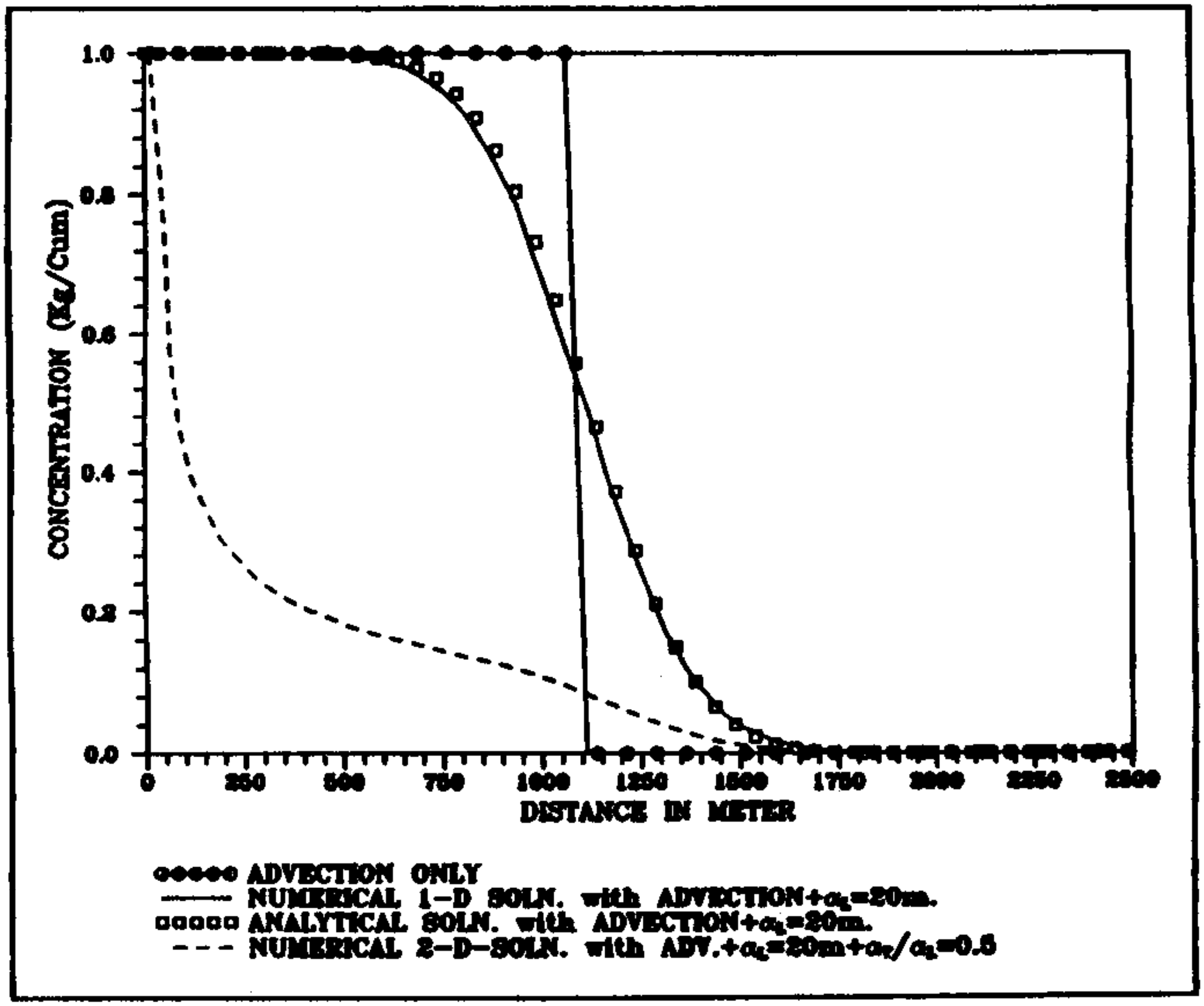


Figure 13: Comparison of Advection + Dispersion on the Concentration Profile in a 1-D and 2-D Problem (line ⇒ Numerical 1-D solution and dashed line ⇒ 2-D solution)

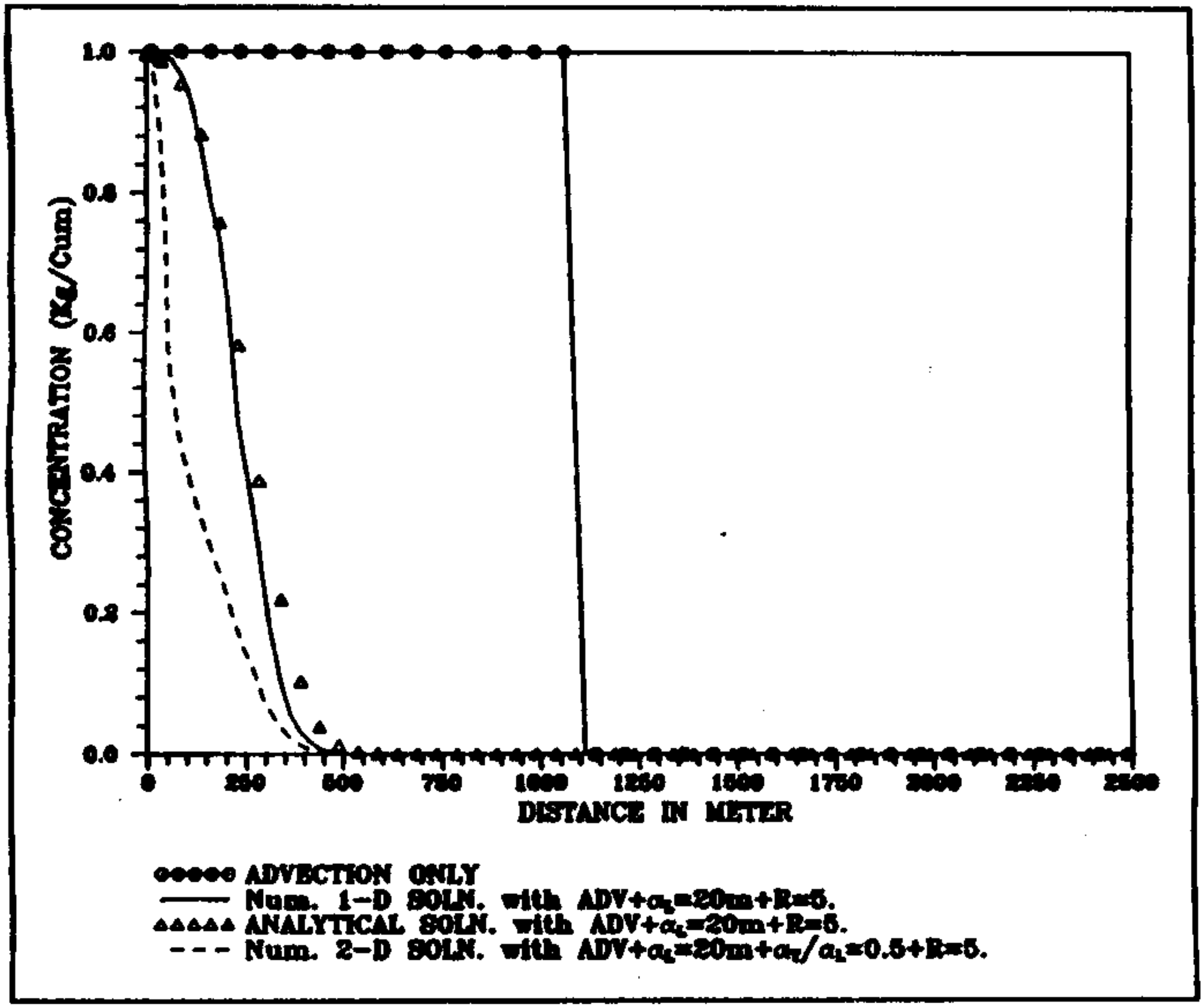


Figure 14: Comparison of Advection + Dispersion + Adsorption on the Concentration Profile in a 1-D and 2-D Problem (line ⇒ Numerical 1-D solution and dashed line ⇒ 2-D solution)

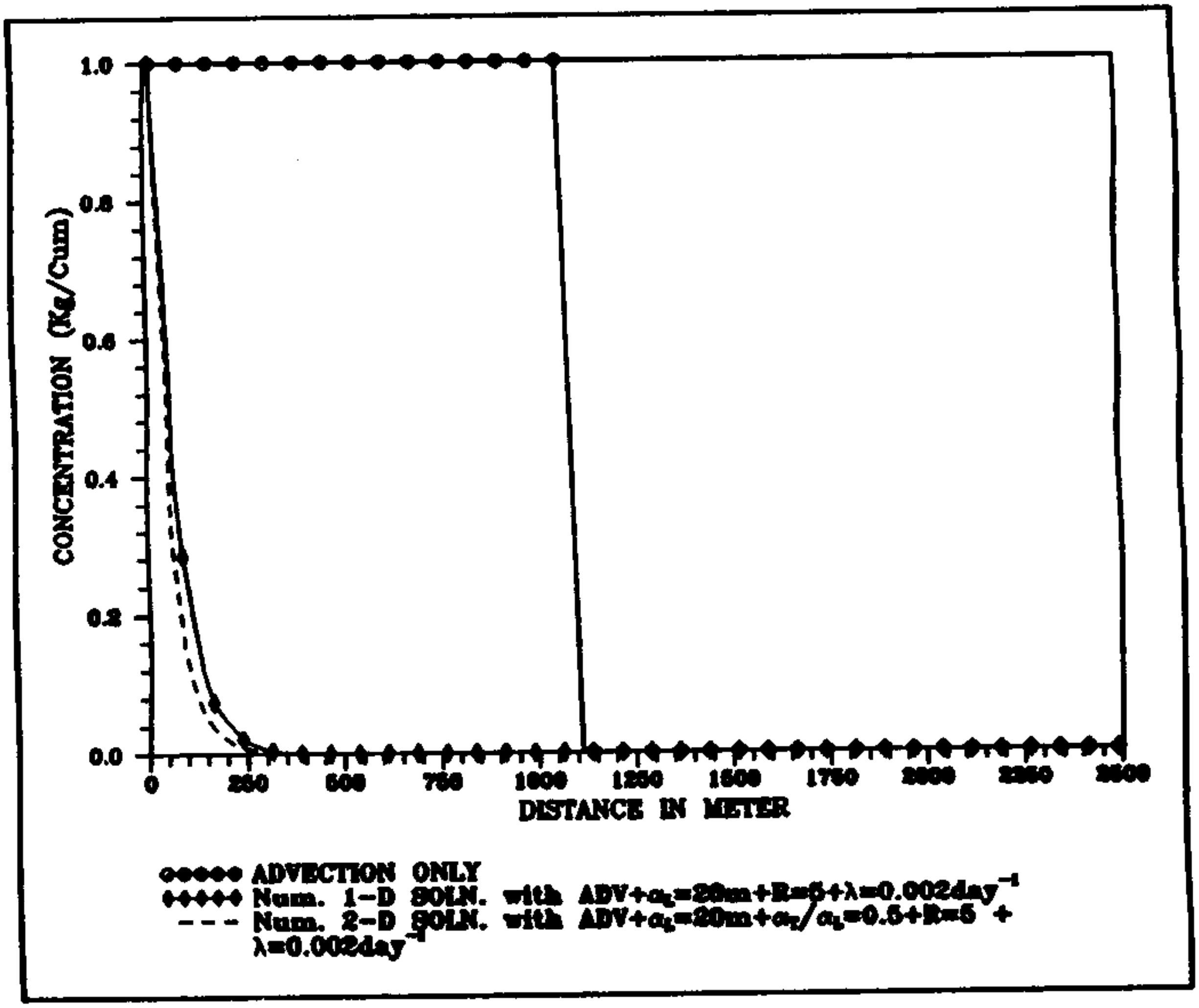


Figure 15: Comparison of Advection + Dispersion + Adsorption + Decay on the Concentration Profile in a 1-D and 2-D Problem (line, ⇒ Numerical 1-D solution and dashed line ⇒ 2-D solution)

5.2 Injection/Pumping Well Problem

Basically, the magnitudes of constituent's concentration and their *space-time* distribution and occurrence are shaped by the properties of injection wells and production wells. Injection wells and production wells which primarily act as sources and sinks of contaminants respectively, are meant/used for injection and sweeping of contaminants in/from groundwater. To evaluate the effectiveness of remedial alternatives, it is always necessary to demonstrate the concentration at the close proximity of the injection /extraction wells.

A problem involving an injection/pumping cycle for a fully penetrating well in a confined aquifer is used to test the potentiality of transport in MT3D model. Since the dispersivity cannot be determined by direct means during field observations, its value is estimated by indirect means, which, ofcourse, will have some uncertainty in prediction. In order to examine the effects of variation of input value of ***longitudinal dispersivity*** on the simulated concentration v/s time profiles at various distances from the pumping well, an example problem with following assumed field setup has been studied.

Water of constant concentration is injected into the well. After certain period of time, the flow is reversed and the contaminated water is pumped out. In these two stress periods, the simulated concentration profile is noted for analysis.

The transient 2-D case taken for modelling consist of 51 rows, 51 columns and 1 layer with a well located at the centre of the area in the cell (26,26). The well is used as an injection well during the first stress period and as a pumping well during the second stress period. The input data for flow and transport simulation are as follows:

For flow:

- 1st stress period (Injection)	= 910 days ≈ 2.5 years.
- 2nd stress period (Pumping)	= 2740 days ≈ 7.5 years.
- Cell width along rows (Δx)	= 100m.
- Cell width along column (Δy)	= 100m.
- Layer thickness (Δz) (Top RL = 100m & Bottom RL = 80m.)	= 20m.
- Aquifer type	= Confined.
- Porosity (n)	= 0.30
- Homogenous hydraulic conductivity (k)	= 50m/day.

- Constant head cell at four sides of the boundary. At corners it is 103m and at the centre of four sides it is 101m.

- Injection rate = 2500cum/day.
- Pumping rate = 2500cum/day.
- Other external stresses are ignored.

For transport:

- All cells are considered as variable concentration cell with starting concentration as zero.
- In the well package, concentration of the injected water is taken as = 100g/cum.
- Advective and Dispersive transport is assumed. No chemical reaction is considered.
- Longitudinal dispersivity (α_L) considered = 10m, 50m and 75m.
- Model is also simulated for α_T/α_L = 1 i.e Transversal dispersivity and Longitudinal dispersivity are same.
- Observation points are chosen at the well and at 100m, 200m, 300m, 500m and 800m from the well.

Results of flow simulation reveals that during the injection period, the flow is out of the well towards the boundary sides, and during pumping period, the flow is towards the well. This is also evident from the isoline of simulated piezometric head elevation (Figure 16 and 17).

After defining the flow domain, transport model is simulated for advective transport, and afterwards with different values of longitudinal dispersivity. In order to examine the effect of transverse dispersivity on the concentration profile, transverse dispersivity is considered to be equal to the longitudinal dispersivity (i.e α_T/α_L = 1.0) and the model is simulated. The breakthrough curves (time-concentration profile) at different observation points located at specified distances from the well is plotted for different values of longitudinal dispersivity and for α_T/α_L = 1.0 (Figure 18 to 23). From these figures, it is evident that concentration profiles show a representable differences as one move away from the well. This leads one to draw the following inferences:

i. With increase in value of the longitudinal dispersivity, reduction of concentration of constituents occurs upto a certain distance from the well (upto 300m in the present case).

ii. For larger value of dispersivity, the fall of concentration during the pumping cycle is gradual i.e the concentration reduces at a slower rate for larger value of dispersivity. Thus, concentration profile extends for a longer duration for higher value of dispersivity.

iii. The effect of transverse dispersivity, when $\alpha_T/\alpha_L = 1.0$, becomes significant at a longer distance from the well. In the case example it started becoming apparent at 300m from the well as seen in figure 7. In the closer proximity of the well, the difference in the effect of longitudinal dispersivity and transverse dispersivity is insignificant.

iv. More to the close of the well, the influence of advective transport is dominant and the influence decreases with increase in distance from the well and for larger distance it becomes insignificant. Beyond certain distance from the well (in the example case from a distance of 500m from the well), the dispersion phenomena dominates and the concentration profile shows a reverse trend i.e more the dominancy of longitudinal dispersivity, more is the concentration. This can well be explained from figure 8 and 9.

v. Dominancy of dispersive transport over the advective transport shifts the peak of concentration profile (Figure 8 and 9).

To supplement above points, isolines of concentrations in the model area are also plotted at the end of two stress periods with the simulated results for the following cases:

- considering advective transport only.
- considering different longitudinal dispersivities with the advective transport.
- considering same value of transverse dispersivity and longitudinal dispersivity with the advective transport.

The distribution of concentrations in space in the form of isolines for the above cases are shown in figures 24 to 27. Gridal network is shown from cell (15,15) to (36,36). These figures indicate the following:

i. If only advective transport is considered, there is no indication of the presence of pollutants at the end of simulation (Figure 10(b)). Whereas, when dispersive transport is considered with the advective transport the presence of pollutants become apparent.

ii. With the increase in dispersivity (both longitudinal and transverse), concentration near the well also increases at the end of the second stress period.

iii. With the increase in dispersivity, concentration reduces, to a lesser magnitude at the end of the first stress period.

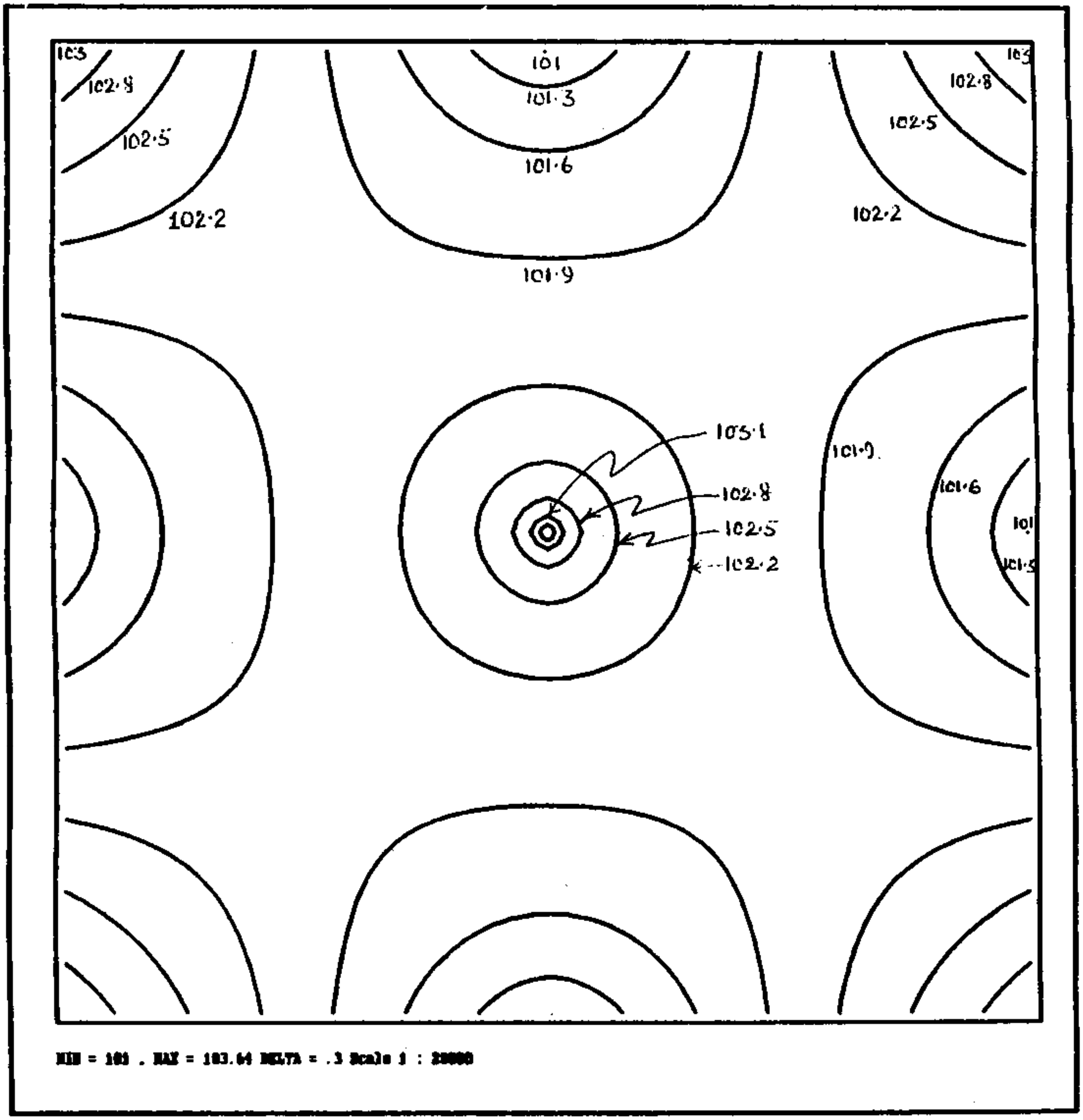


Figure 16: Isolines of piezometric head at the end of the first stress period (Injection).

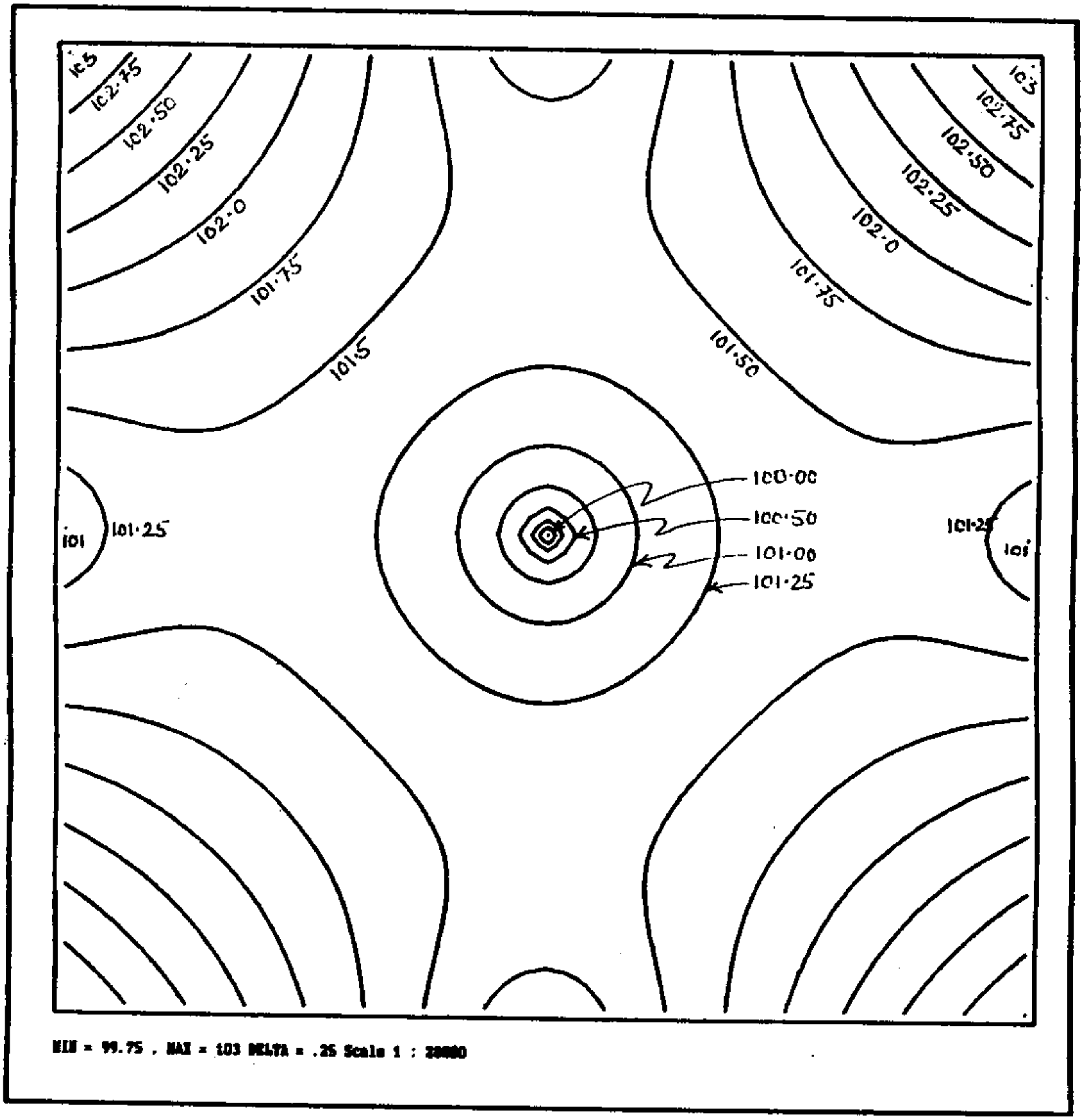


Figure 17: Isolines of pieżometric head at the end of the second stress period (Pumping).

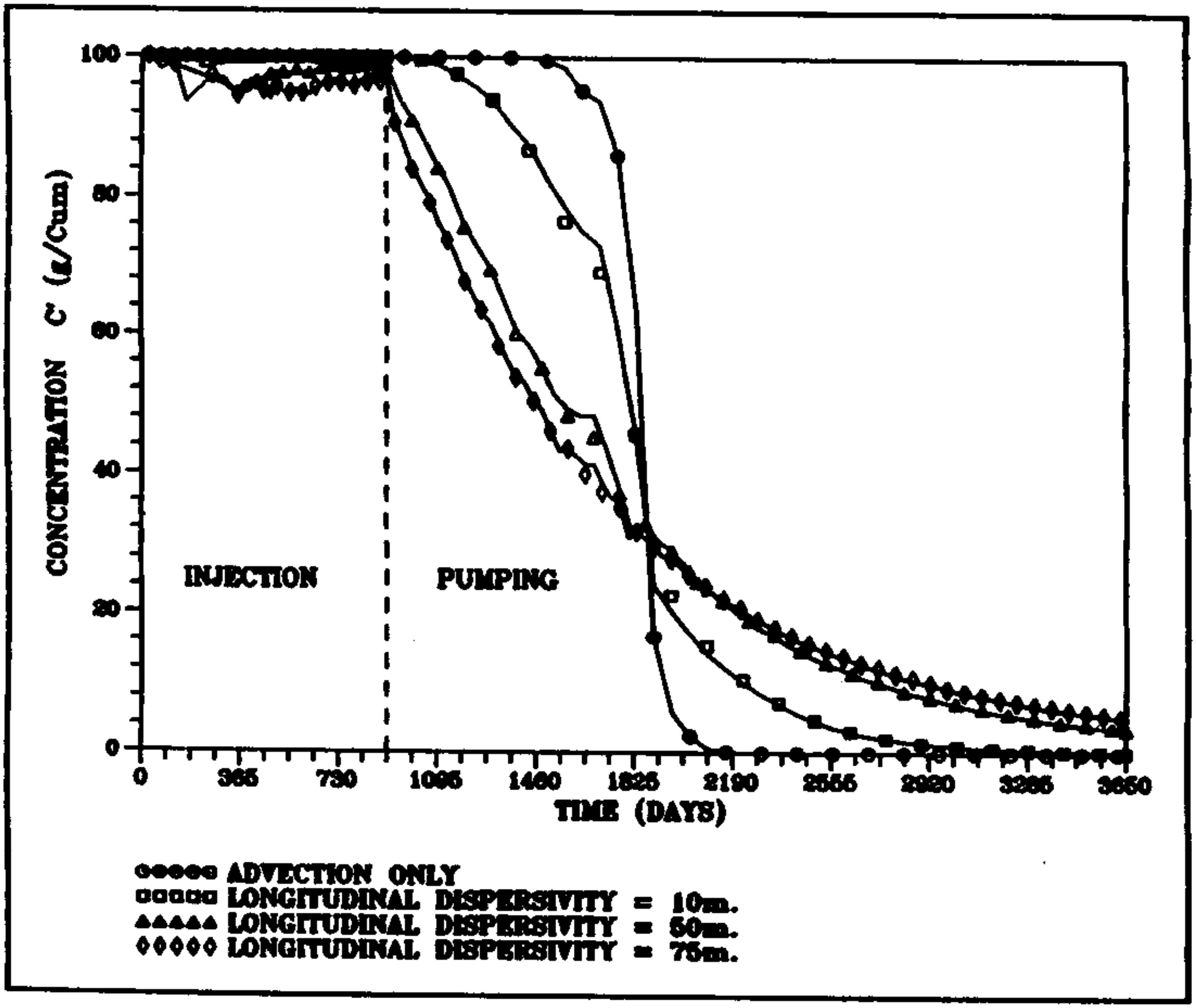


Figure 18. Breakthrough curves at the injection/pumping well with Advection and different values of Longitudinal Dispersivity (line ⇒ with Longitudinal dispersivity; symbols ⇒ $\alpha_T/\alpha_L = 1.0$).

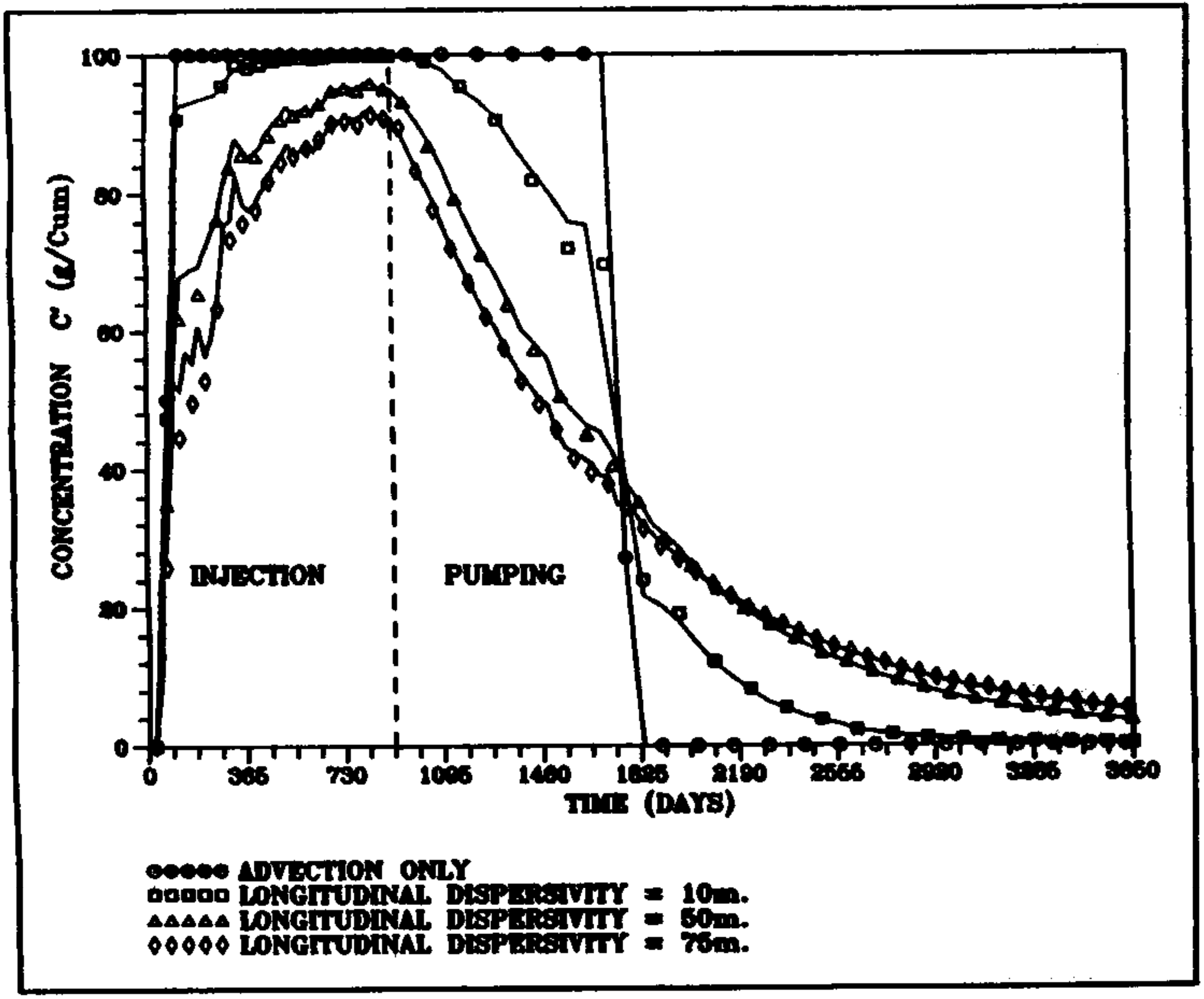


Figure 19. Breakthrough curves at 100m from the well with Advection and different values of Longitudinal Dispersivity (line ⇒ with Longitudinal dispersivity; symbols ⇒ α_T/α_L = 1.0).

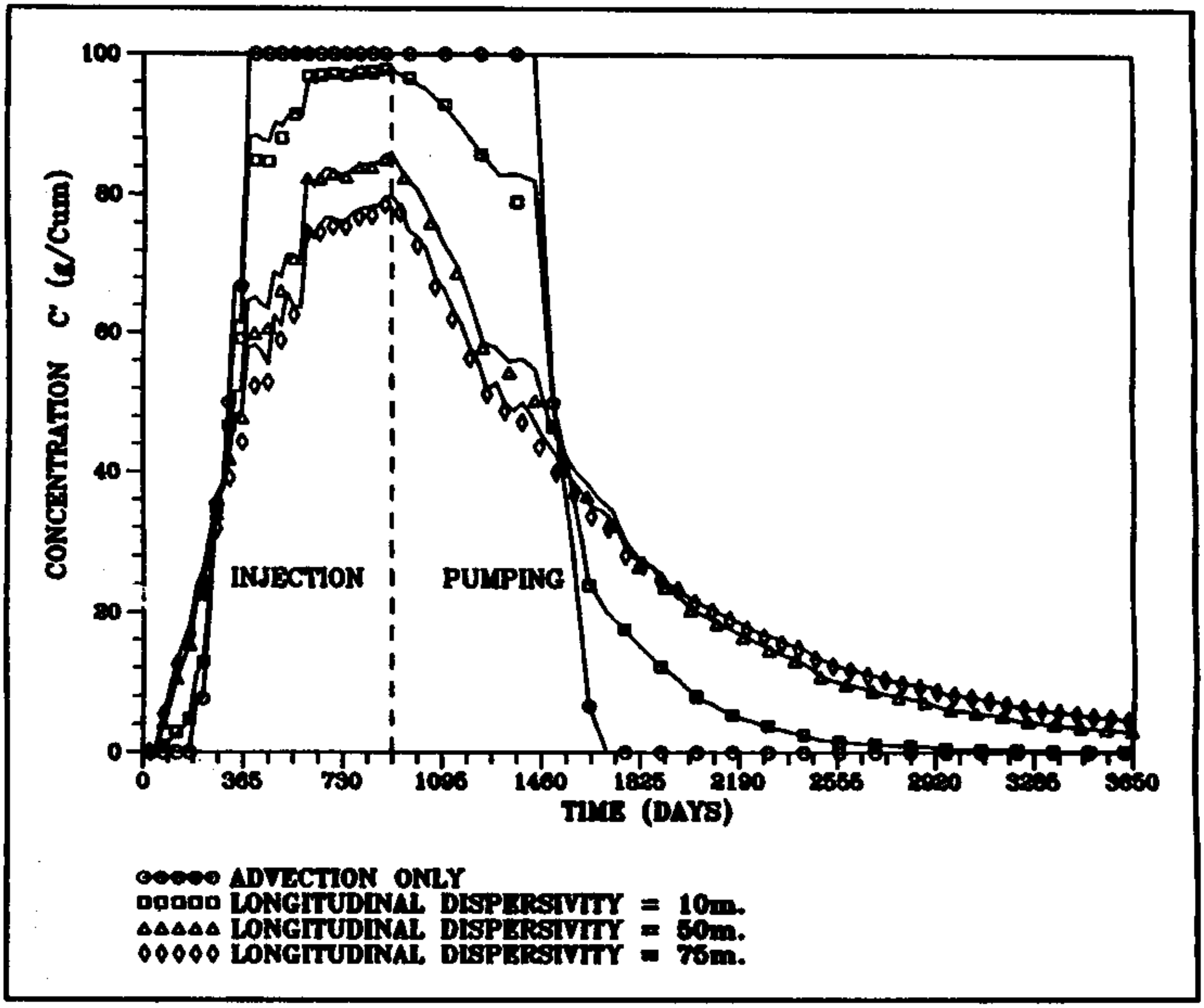


Figure 20. Breakthrough curves at 200m from the well with Advection and different values of Longitudinal Dispersivity (line ⇒ with Longitudinal dispersivity; symbols ⇒ α_T/α_L = 1.0).

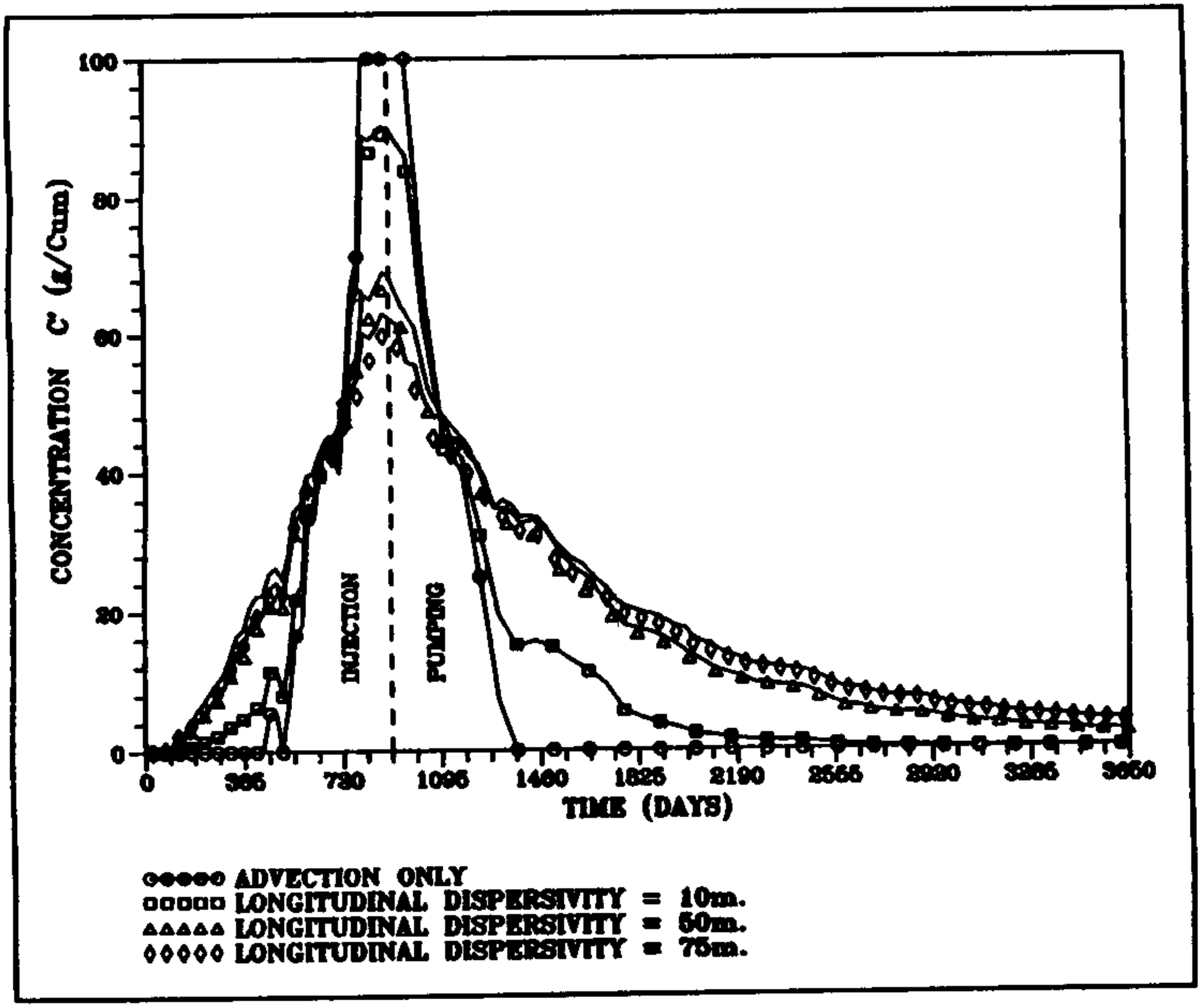


Figure 21. Breakthrough curves at 300m from the well with Advection and different values of Longitudinal Dispersivity (line ⇒ with Longitudinal dispersivity; symbols ⇒ α_T/α_L = 1.0).

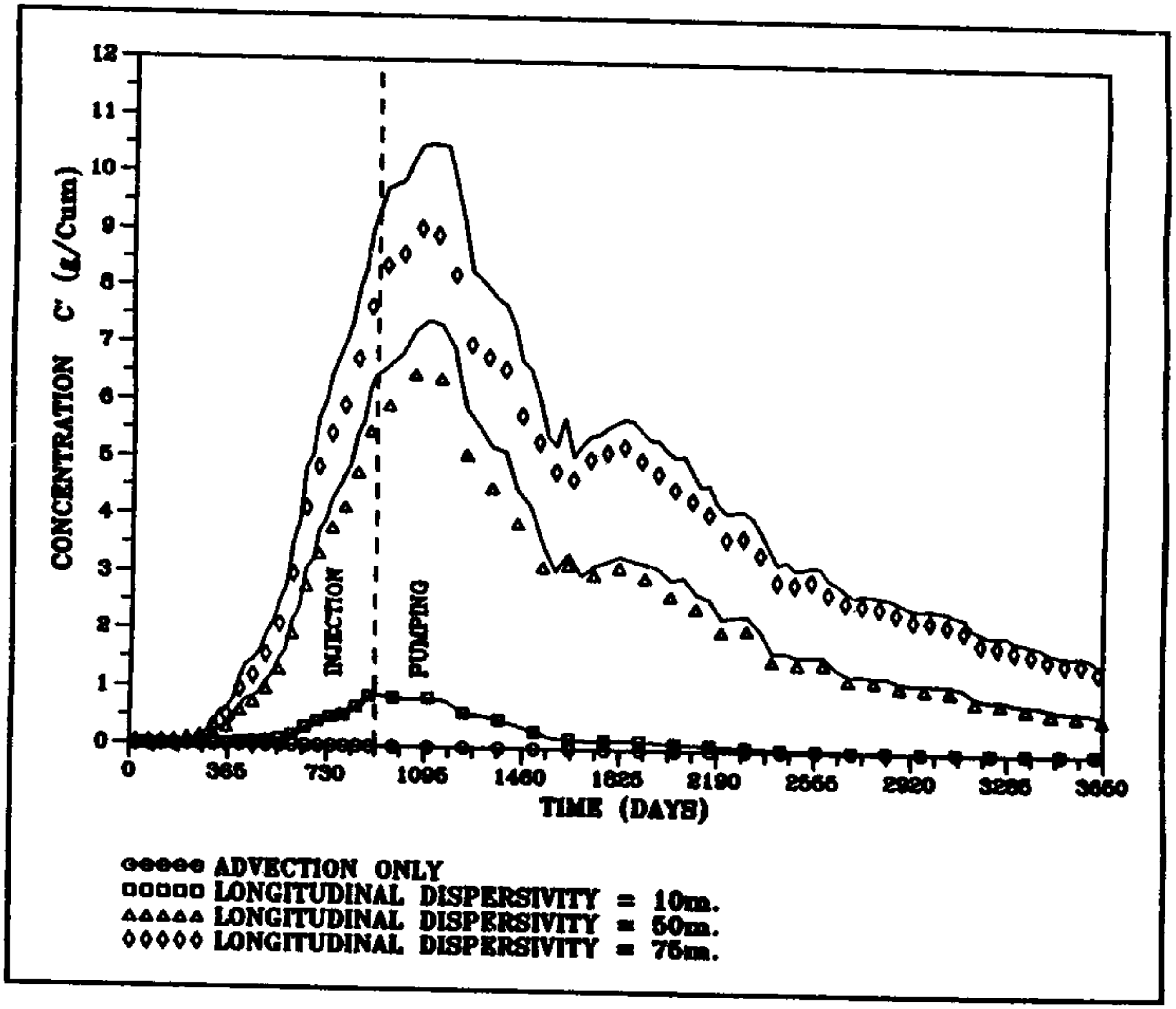


Figure 22. Breakthrough curves at 500m from the well with Advection and different values of Longitudinal Dispersivity (line ⇒ with Longitudinal dispersivity; symbols ⇒ $\alpha_T/\alpha_L = 1.0$).

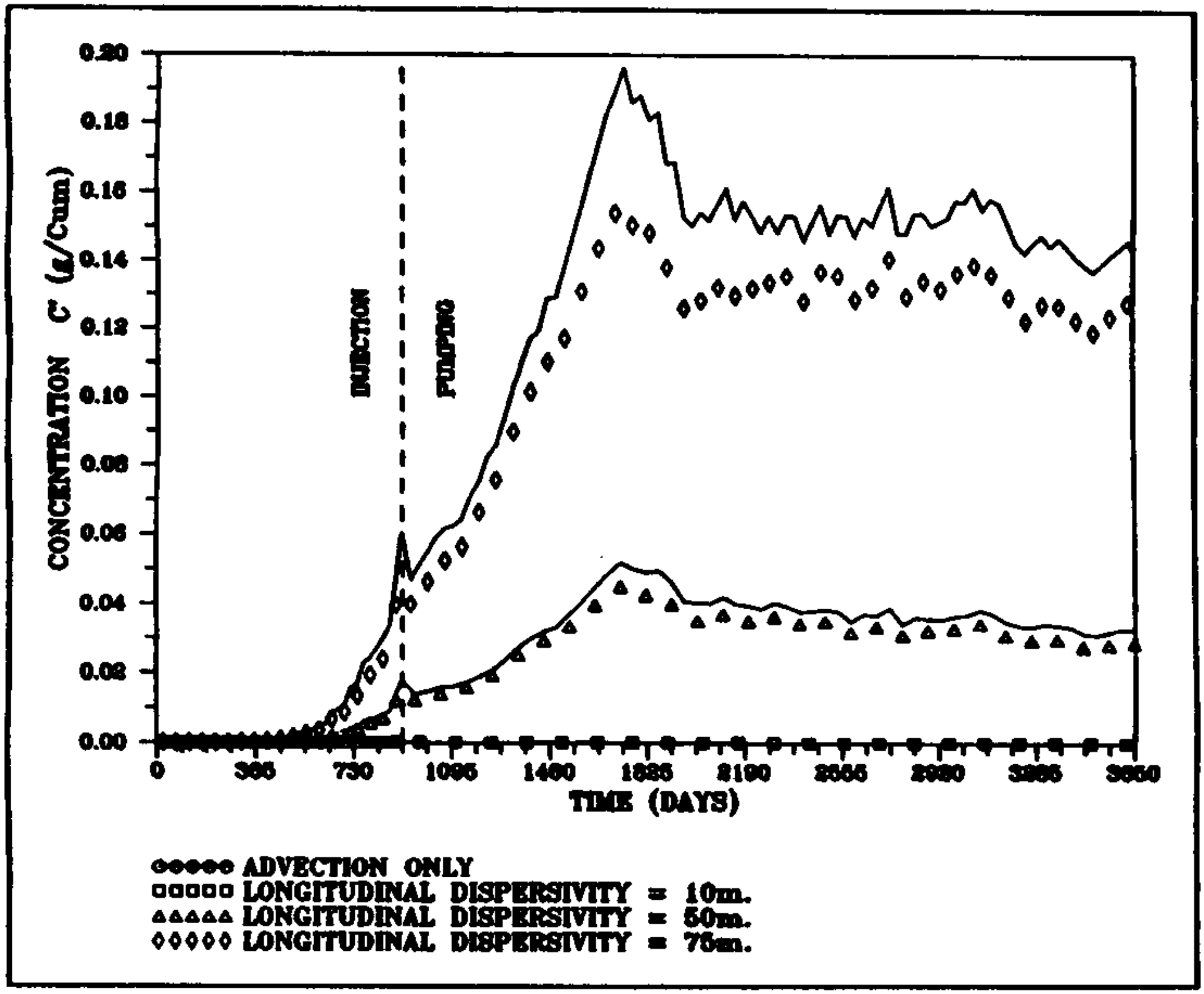
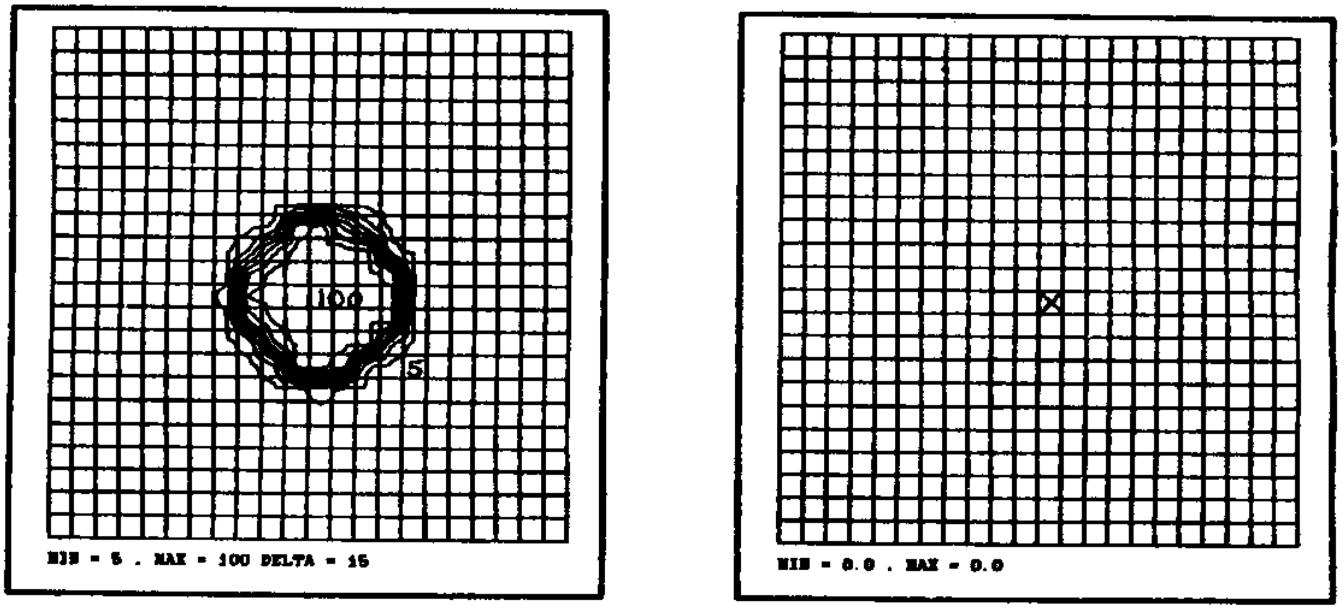


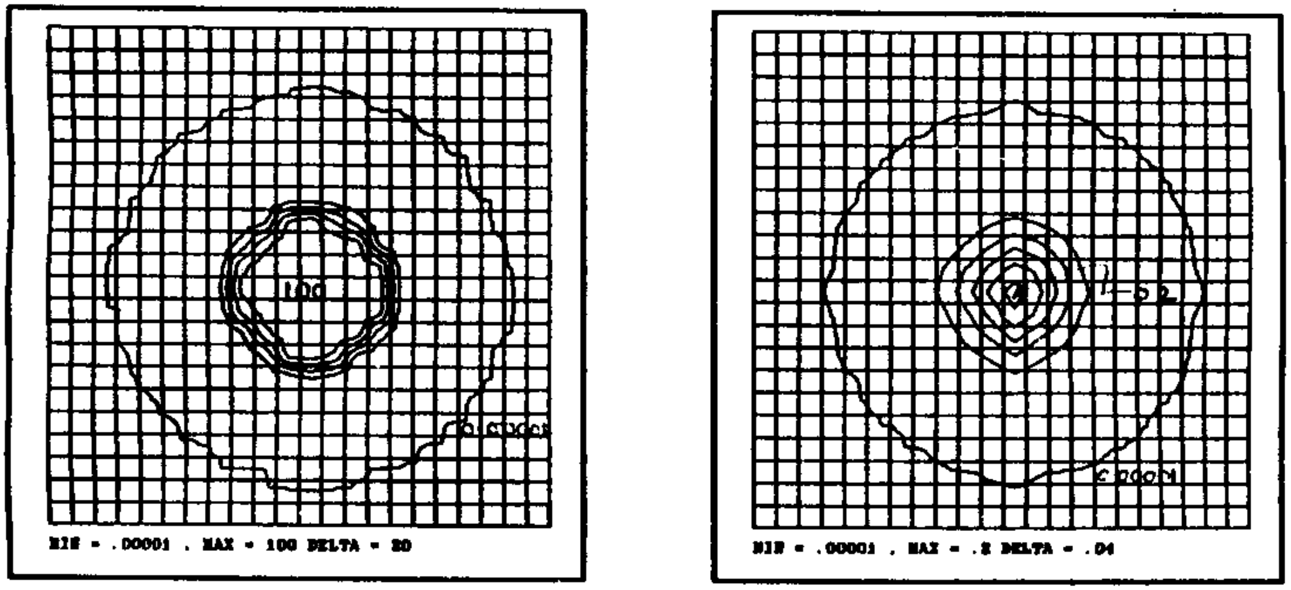
Figure 23. Breakthrough curves at 800m from the well with Advection and different values of Longitudinal Dispersivity (line ⇒ with Longitudinal dispersivity; symbols ⇒ α_T/α_L = 1.0).



Concentration after 2.5 years with advection only

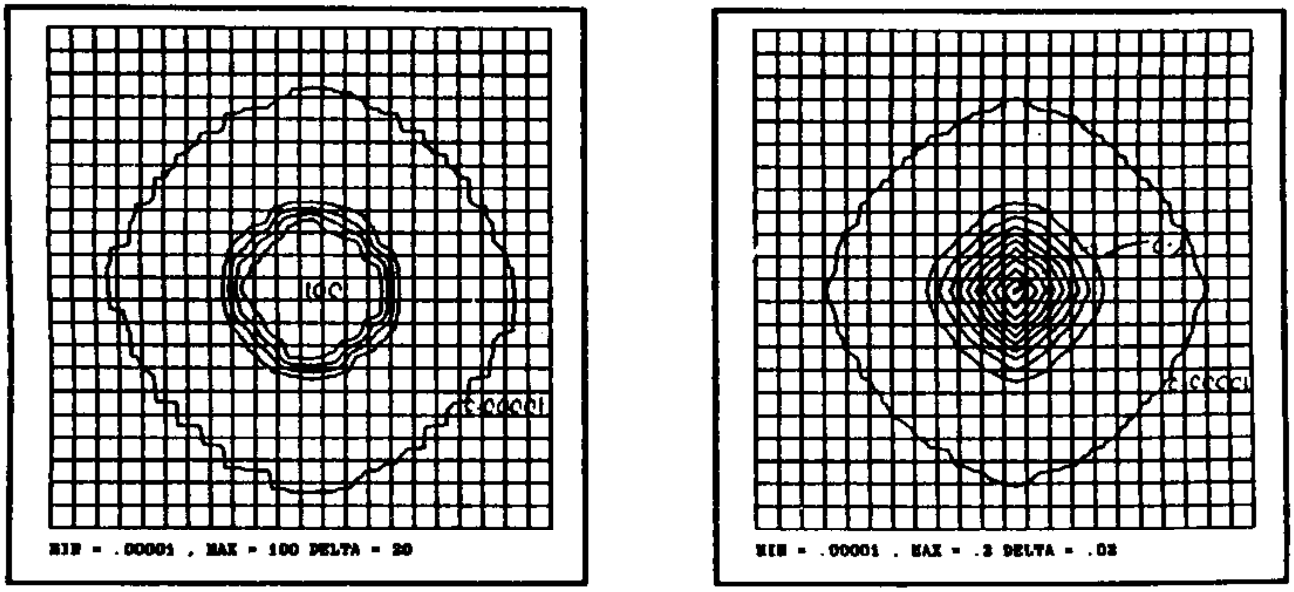
Concentration after 10 years with advection only

Figure 24. Effect of Injection and Pumping from the same well (26,26) considering advective transport only (gridal network shown is from (15,15) to (36,36).



Concentration after 2.5 years with α_L = 10 m.

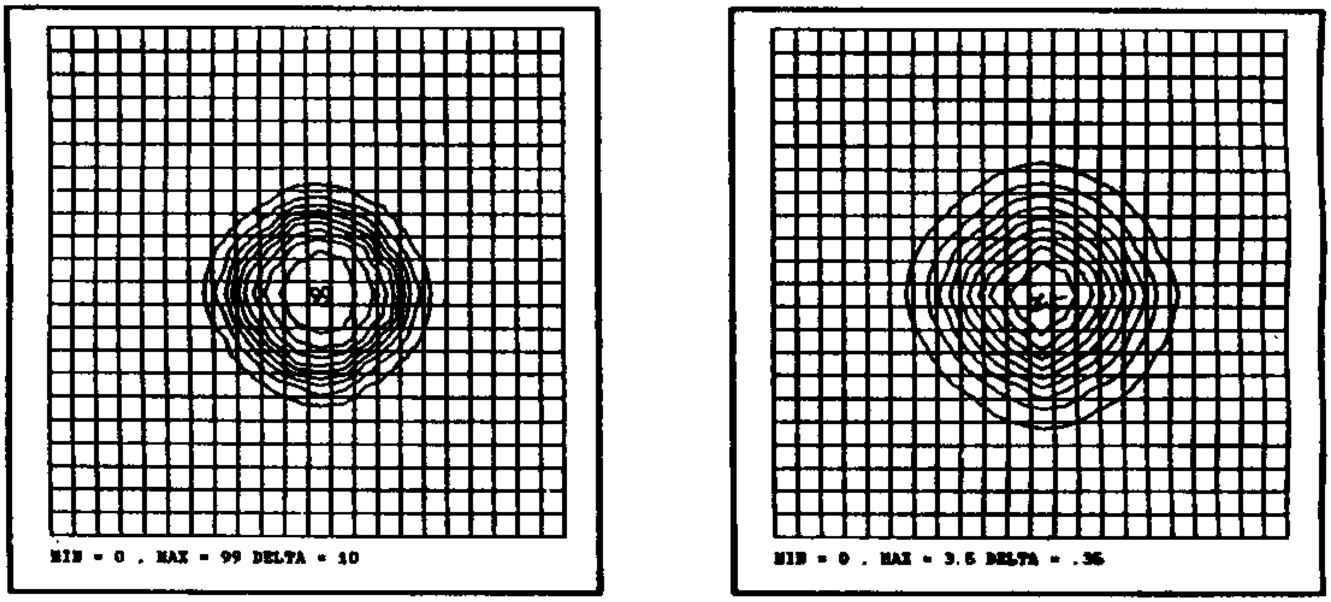
Concentration after 10 years with α_L = 10 m.



Concentration after 2.5 years with α_L = 10m and α_T/α_L = 1.0.

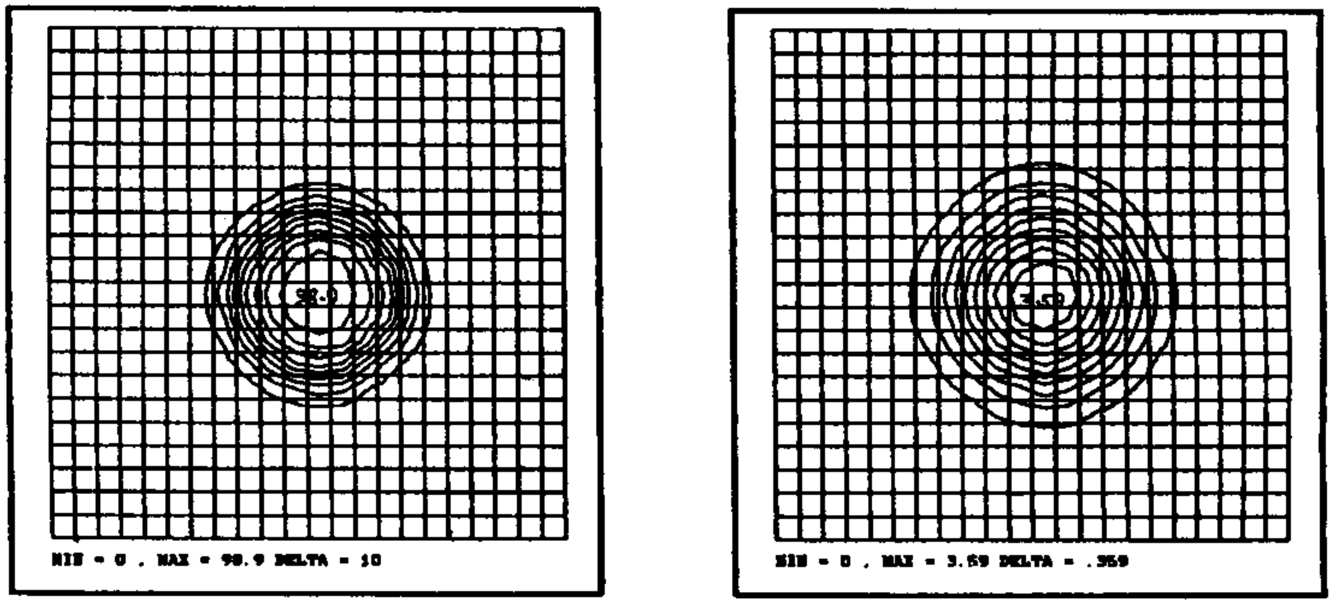
Concentration after 10 years with α_L = 10m and α_T/α_L = 1.0.

Figure 25. Effect of Injection and Pumping from the same well (26,26) considering advective and dispersive (longitudinal and transverse) transport (gridal network shown is from (15,15) to (36,36).



Concentration after 2.5 years with α_L = 50m.

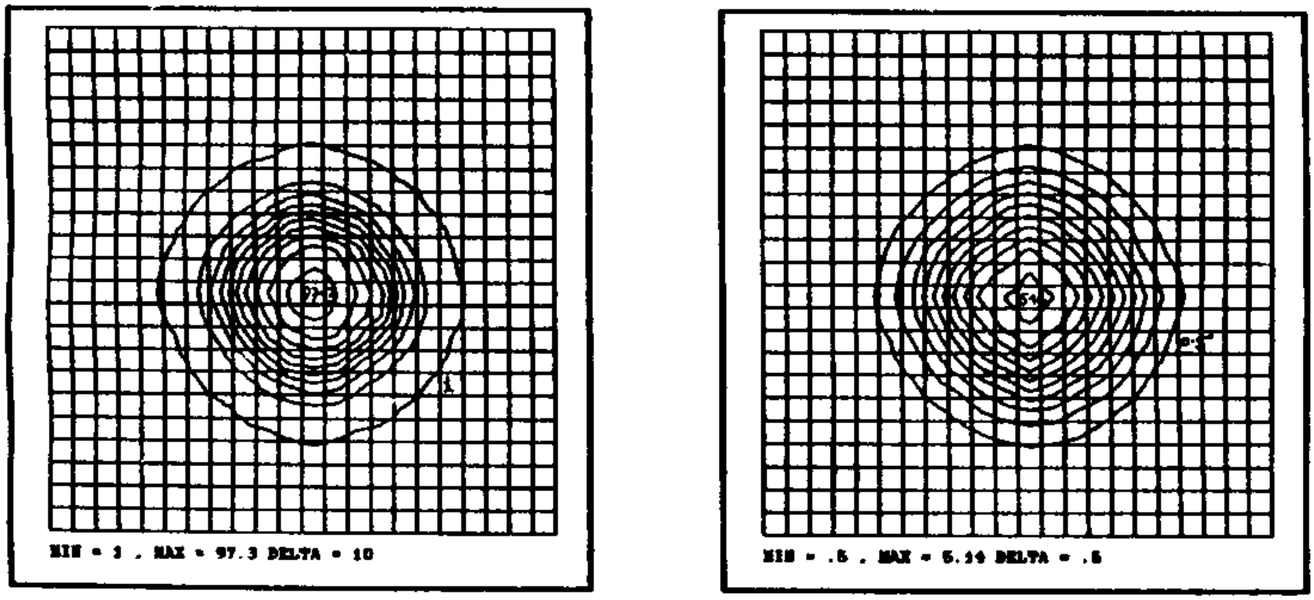
Concentration after 10 years with α_L = 50m.



Concentration after 2.5 years with α_L = 50m and α_T/α_L = 1.0.

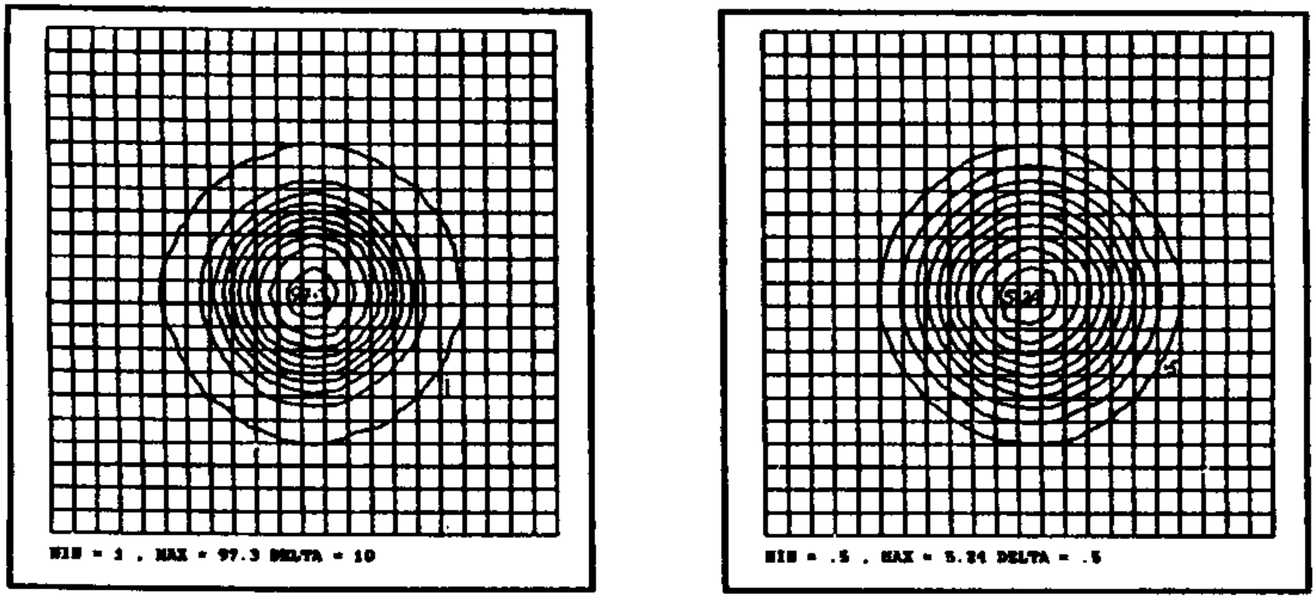
Concentration after 10 years with α_L = 50m and α_T/α_L = 1.0.

Figure 26. Effect of Injection and Pumping from the same well (26,26) considering advective and dispersive (longitudinal and transverse) transport (gridal network shown is from (15,15) to (36,36).



Concentration after 2.5 years with α_L = 75m.

Concentration after 10 years with α_L = 75m.



Concentration after 2.5 years with α_L = 75m and α_T/α_L = 1.0

Concentration after 10 years with α_L = 75m and α_T/α_L = 1.0

Figure 27. Effect of Injection and Pumping from the same well (26,26) considering advective and dispersive (longitudinal and transverse) transport (gridal network shown is from (15,15) to (36,36).

5.3 3-D Waste Dump Problem

To study the behaviour of constituent's transport in a 3-dimensional case, a study area as shown in figure 28 is considered. It is assumed that a deposit of Benzene in dissolved form lies in the central part of the area covering cells shown in figure 28. The pollutant in dissolved form enters the aquifer system with a concentration equal to 0.0001 kg/cum. Assuming a steady state condition of flow for the area with the following input data and boundary conditions, the time-concentration profile at a number of observation points located at different distances from the dump site for 20 years after beginning of benzene migration in the aquifer is analyzed.

The aquifer is assumed to be of two layers of confined in nature. The model area is discretized into 55 rows and 57 columns as shown in figure 28. The boundaries of the model area in the north-east, east, south-east and south-west sides are defined by canal which are in full hydraulic contact with the aquifer. They can be treated as fixed head boundaries as shown in figure 28. Other boundaries are defined by stream lines and are therefore impervious (no-flow boundaries). The input data, aquifer parameters and solute properties are assumed constant everywhere as defined below:

For flow:

- Thickness of the first aquifer = 8m.
- Thickness of the second aquifer = 7m.
- Cell width along rows (Δx) = 100m, 25m and 100m.
- Cell width along columns (Δy) = 100m, 25m and 100m.
- Porosity (n) = 0.2.
- Horizontal hydraulic conductivity = 69m/day.
- Vertical hydraulic conductivity = 1/20 of Hoz. hydraulic conductivity.
- Aerial recharge = 0.00216 m/day.

For transport:

- All cells in the model area are considered as active or variable concentration cells.
- Concentration of pollutants = 0.0001 kg/cum entering with the recharge water.
- Advection, dispersion and chemical reaction have been assumed.
- Longitudinal dispersivity (α_L) = 5m, 10m and 20m.
- The ratio of horizontal and vertical transverse to longitudinal dispersivity in both layers is assumed to be 0.5

- Distribution coefficient (k_d) of Benzene = 0.0002 cum/kg.
- Bulk density of the porous medium in the aquifer = 1700 kg/cum.

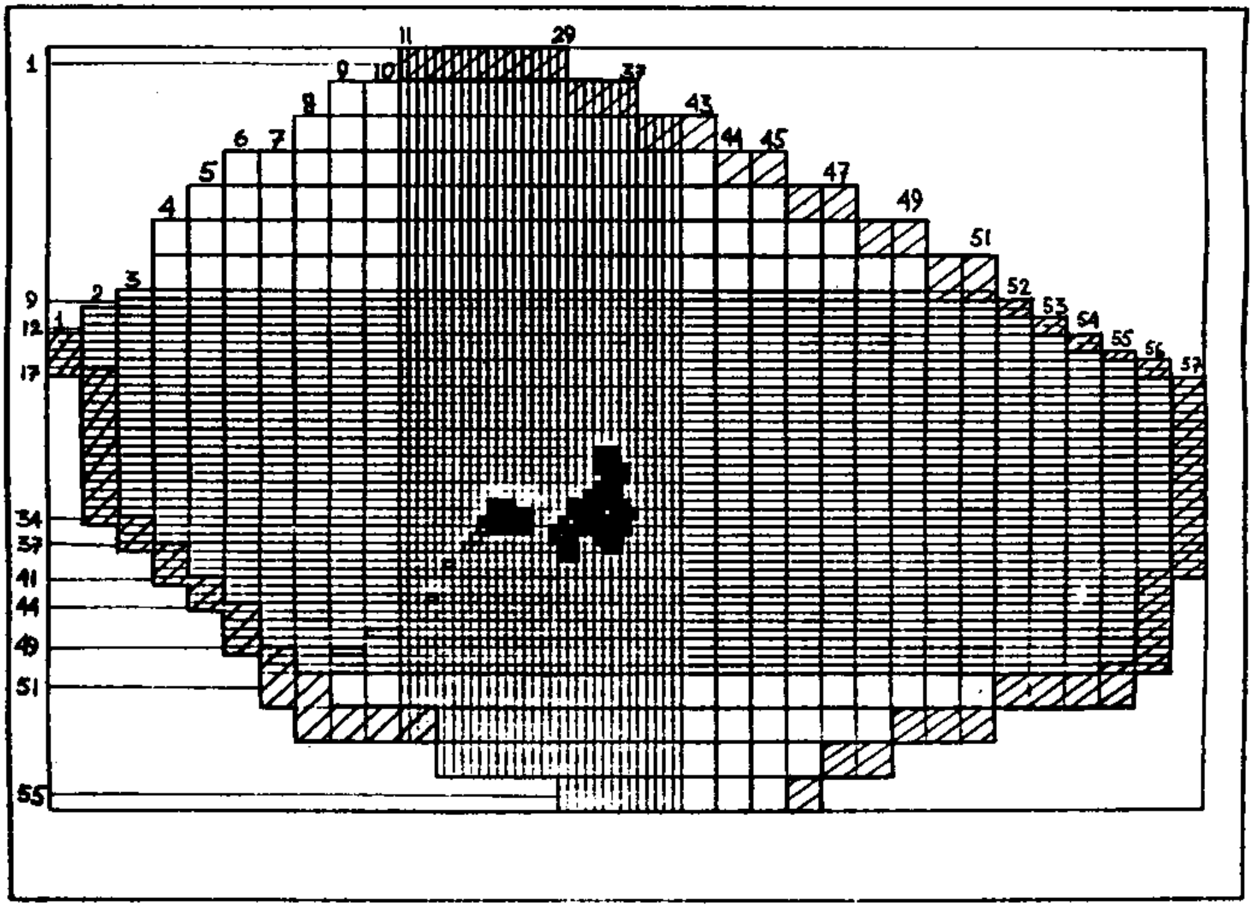
The flow is simulated assuming steady state condition and the simulated isolines of piezometric head for two layers are shown in figure 29 and 30. These isolines indicate an outflow towards the south-western side i.e towards canal boundaries. To demonstrate the transport behaviour, four observation points at cells (22,35), (21,36), (18,39) and (14,43) are chosen in both layers of the aquifer.

Responses of concentrations at cell (22,35) over different time are shown in figures 31 and 32 which (22,35) reveals that:

i. Increase in longitudinal dispersivity decreases the concentration.
ii. Combined effect of longitudinal and transverse (horizontal and vertical) dispersivity reduces the concentration further.
iii. In the first aquifer where the dump site is located, the spread of pollutant influence both by the longitudinal and transverse (horizontal and vertical) dispersivities.
iv. In the second layer the occurrence of pollutant concentration is dominated by the combined effect of longitudinal and transverse dispersivity. The effect of longitudinal dispersivity alone, is negligible.

Similar inferences can also be drawn for cell (21,36) from figures 33 and 34 excepting that concentration reduces with increase of distance from the dump site.

A reverse trend is observed for cell (18,39) shown in figure 35 in the first layer. In this case, the concentration due to advective transport becomes insignificant and with increase in dispersivities, the concentration also increases. It means - the occurrence of pollutant at a farther distance is influenced by the dispersion phenomena and the concentration increases with dispersivity. In the second layer also (figure 36), similar trend is observed, in which the effect of horizontal and vertical transverse dispersivity is more to the concentration and more so for higher dispersivity. Similar conclusion is also evident at cell (14,43) as shown in figures 37 and 38.



Active cell = ▦

Constant head cell = ▨

Inactive cell = □

Pollutant source = ■

Observation points = ▦

Figure 28: Gridal network of the model area showing Active, Constant, Inactive cells, dump site and observation points.

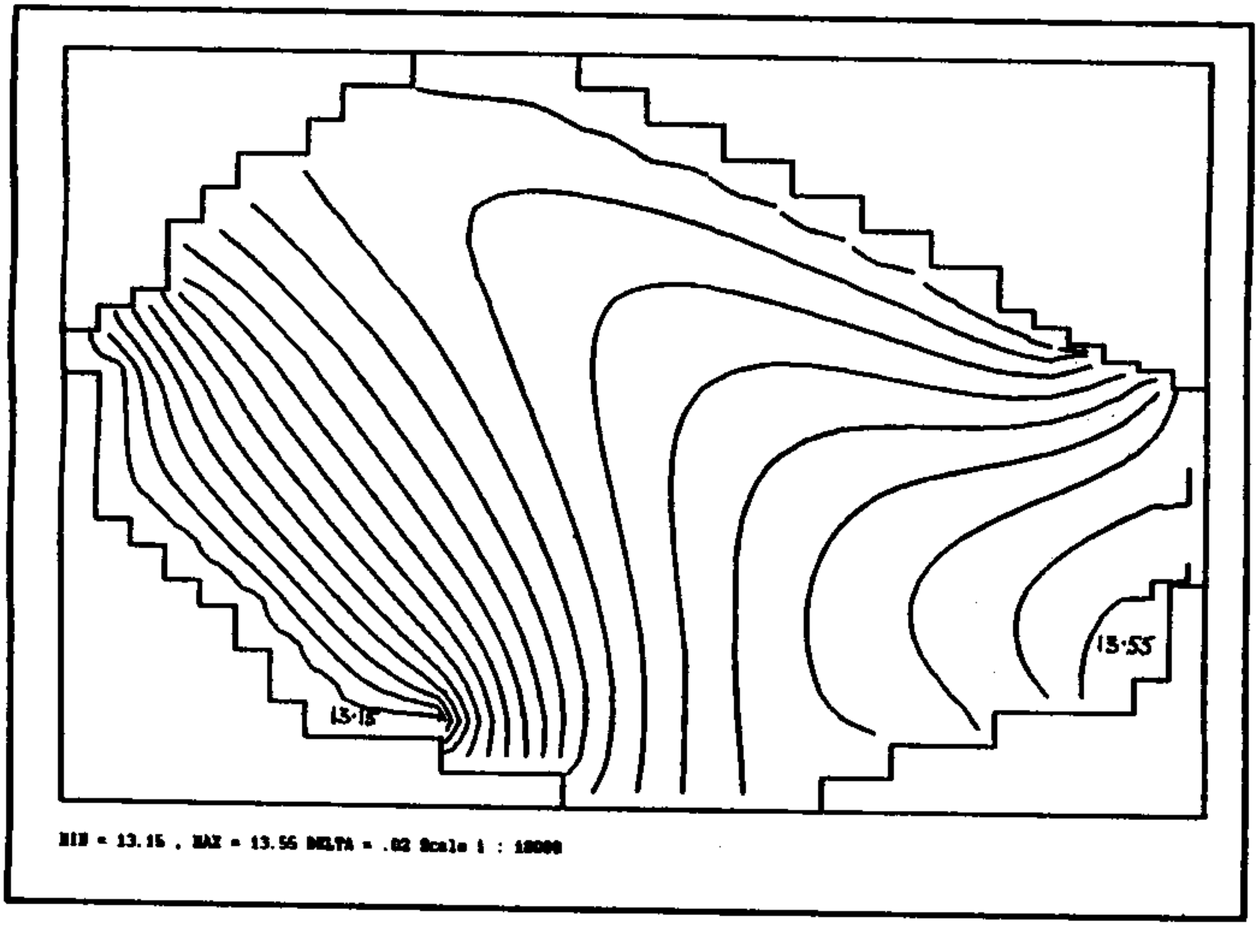


Figure 29: Isolines of piezometric head for the first aquifer.

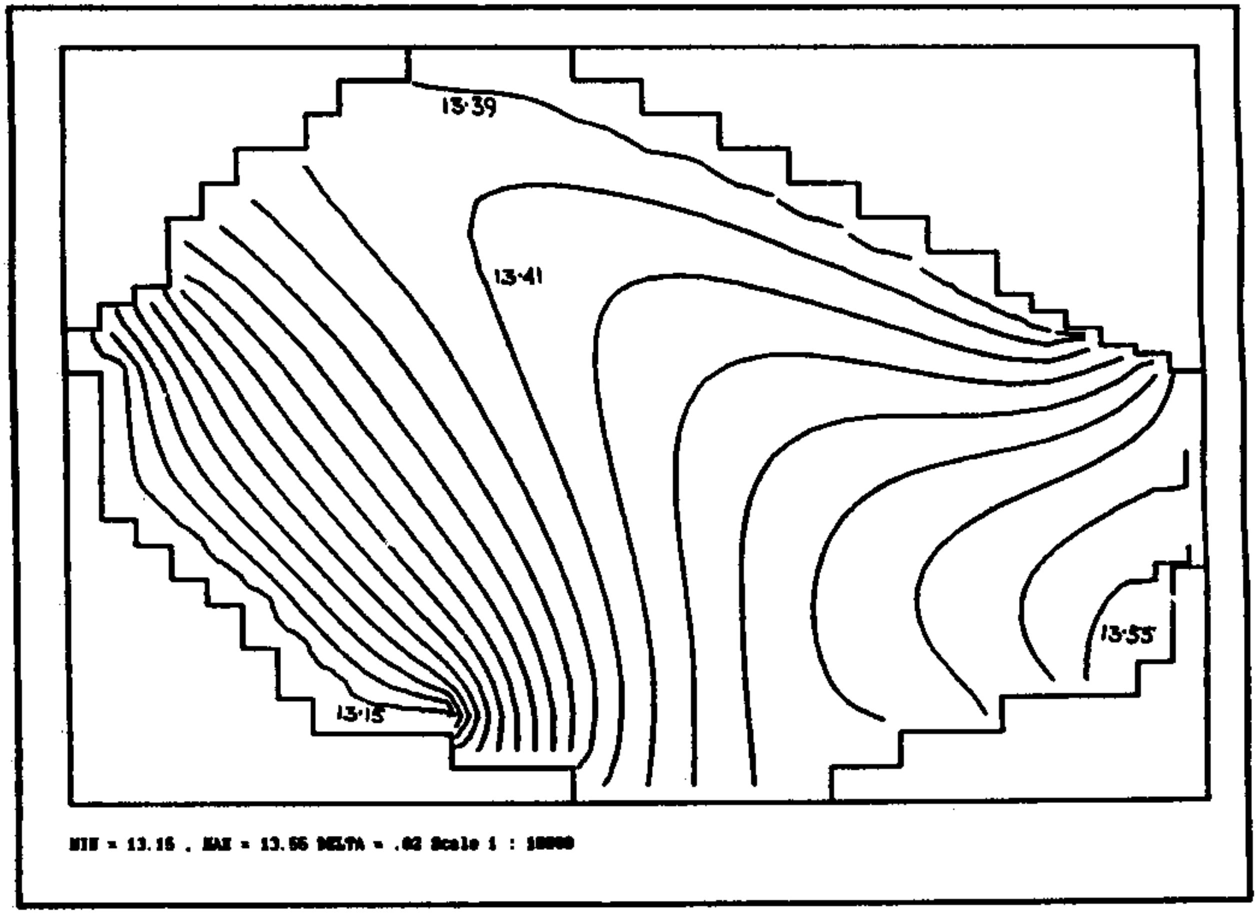


Figure 30: Isolines of piezometric head for the second aquifer.

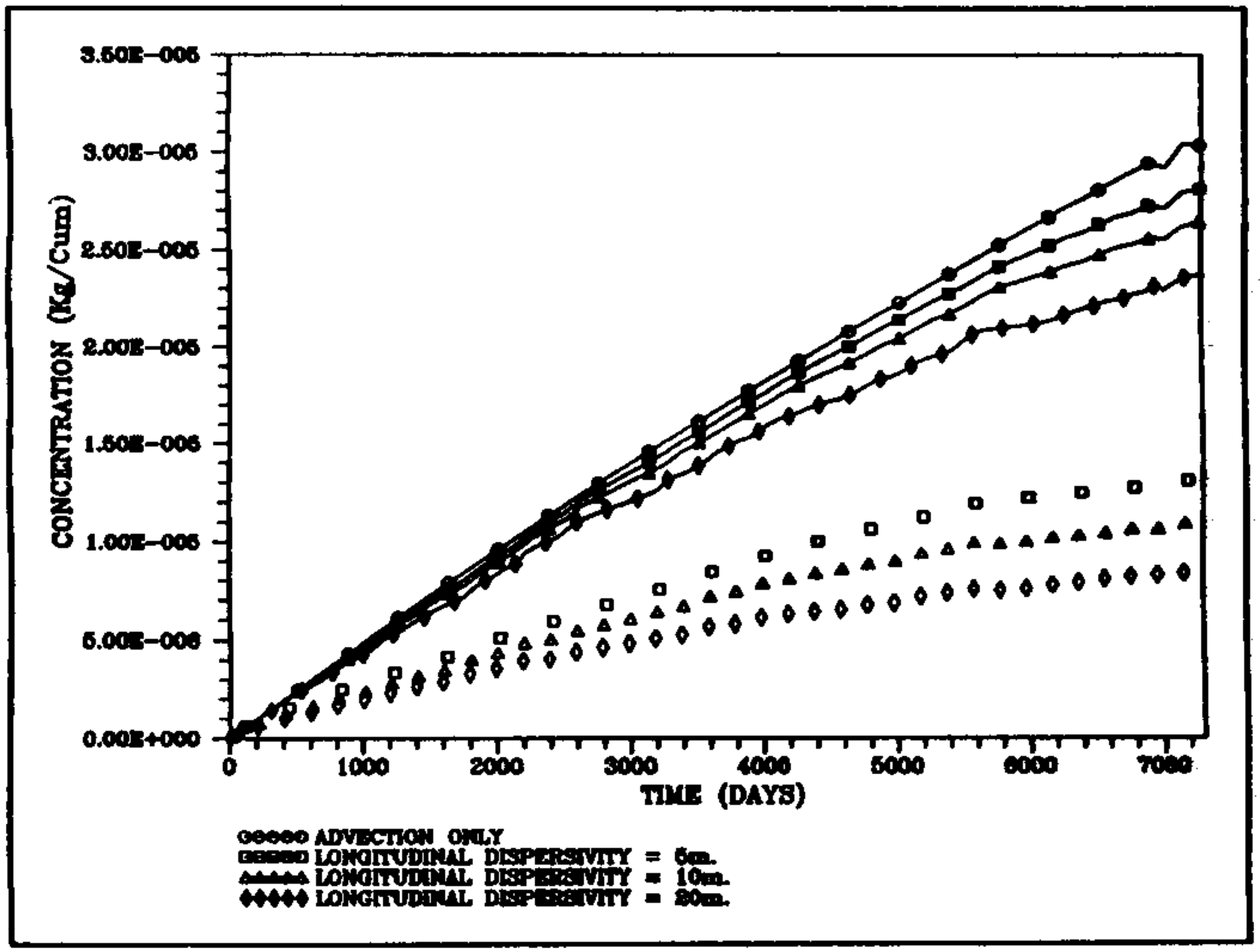


Figure 31: Breakthrough curves at cell (22,35) for the first layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ $\alpha_T/\alpha_L = 0.5$ and $\alpha_V/\alpha_L = 0.5$).

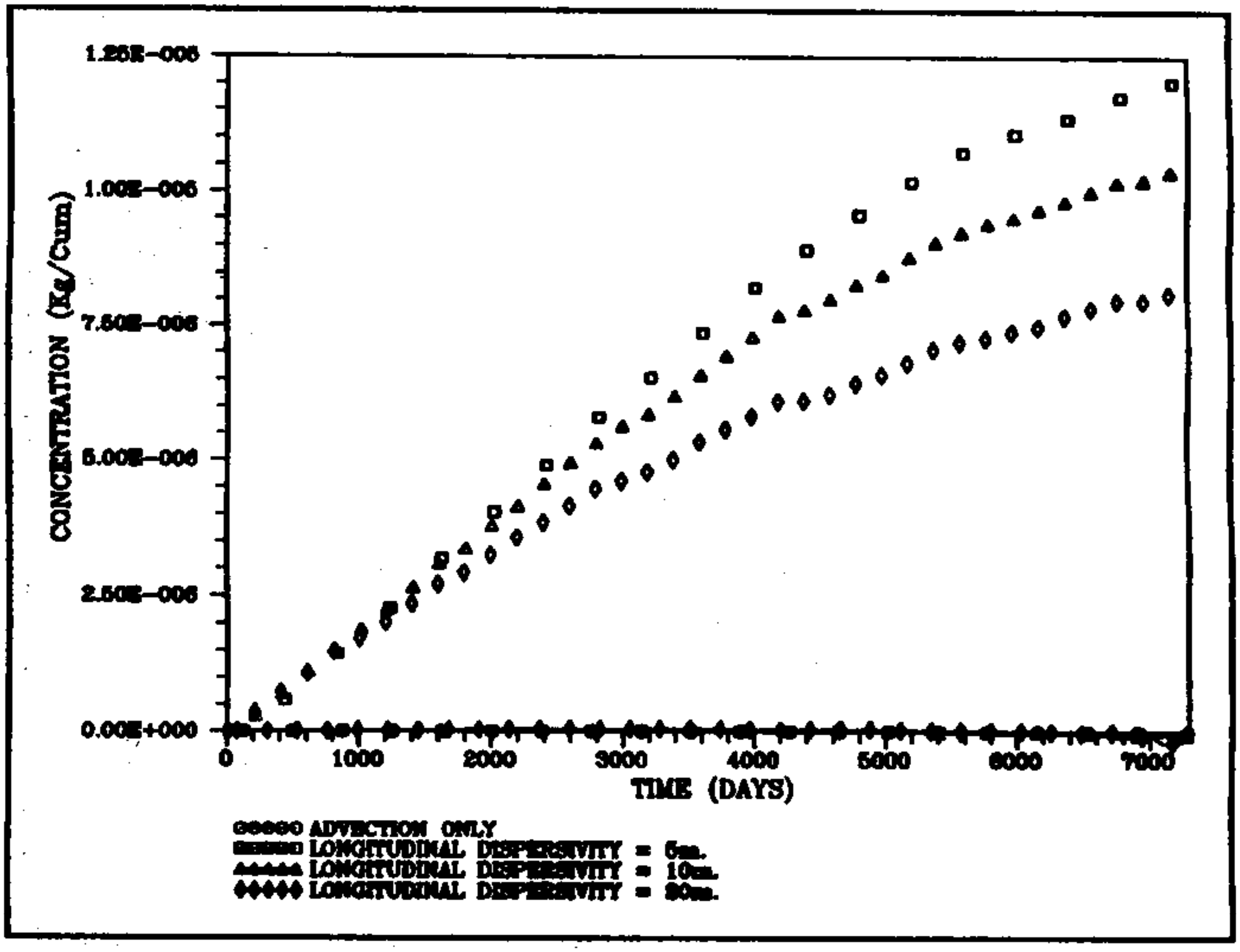


Figure 32: Breakthrough curves at cell (22,35) for the second layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ α_T/α_L = 0.5 and α_T/α_L = 0.5).

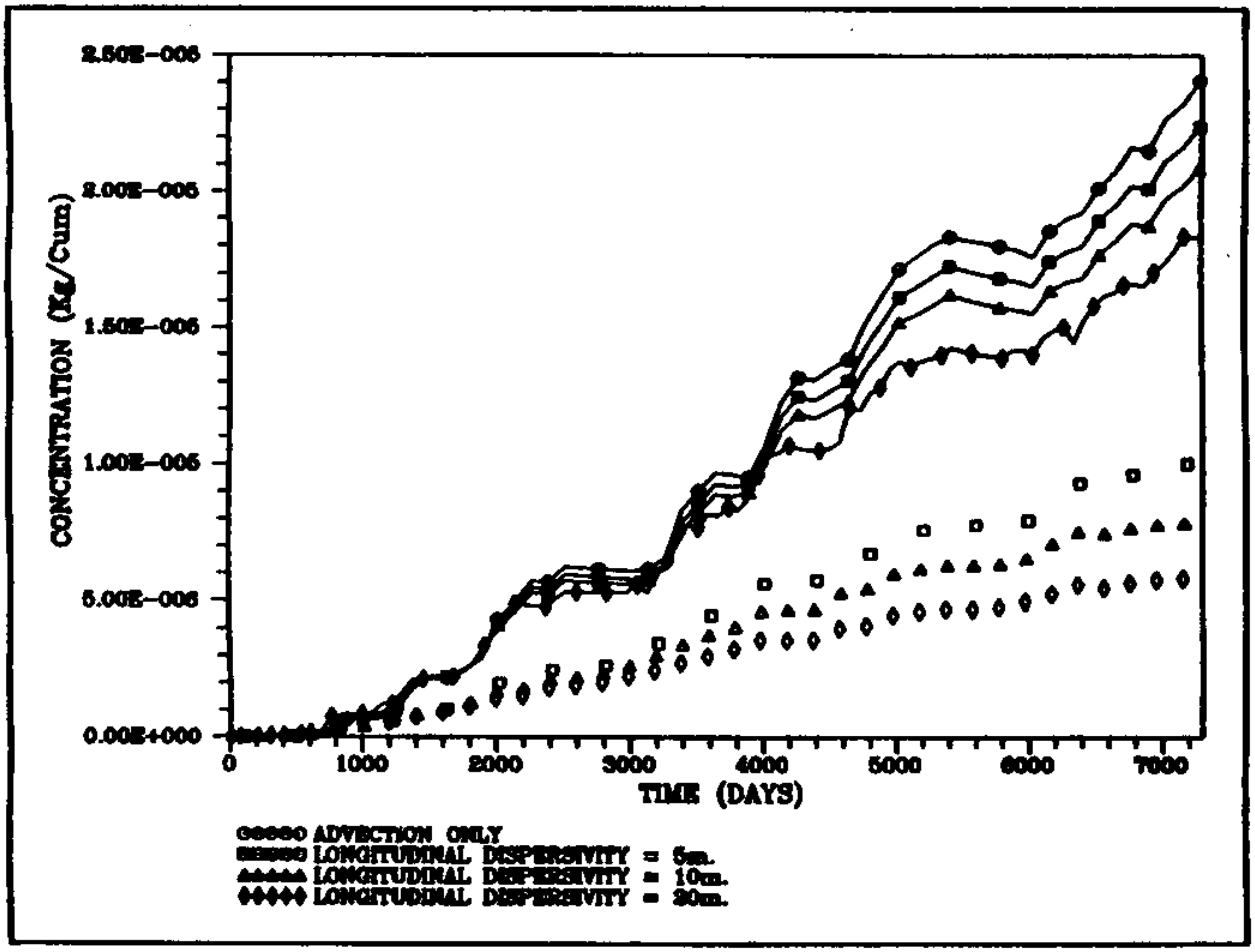


Figure 33: Breakthrough curves at cell (21,36) for the first layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ α_T/α_L = 0.5 and α_V/α_L = 0.5).

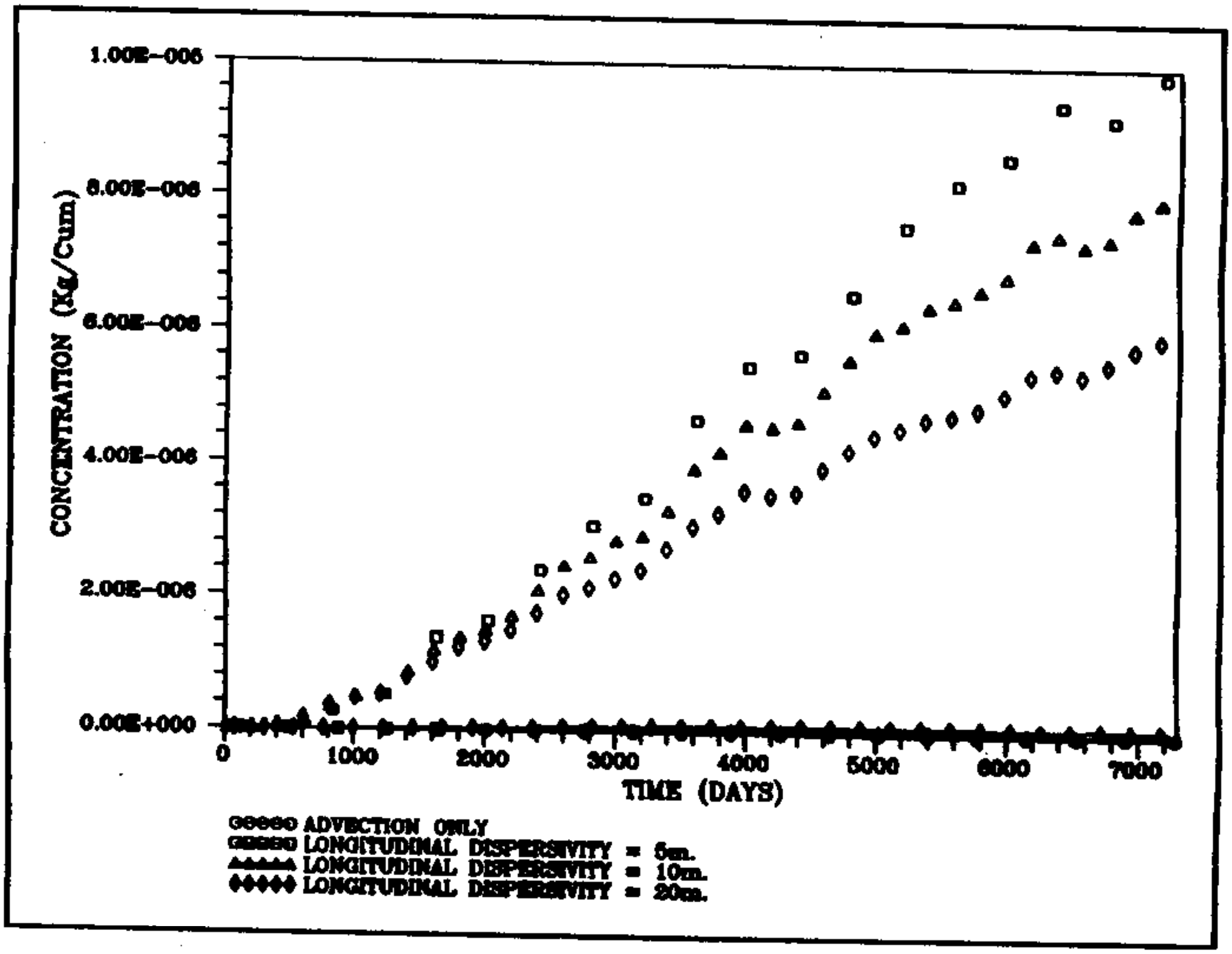


Figure 34: Breakthrough curves at cell (21,36) for the second layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ α_T/α_L = 0.5 and α_V/α_L = 0.5).

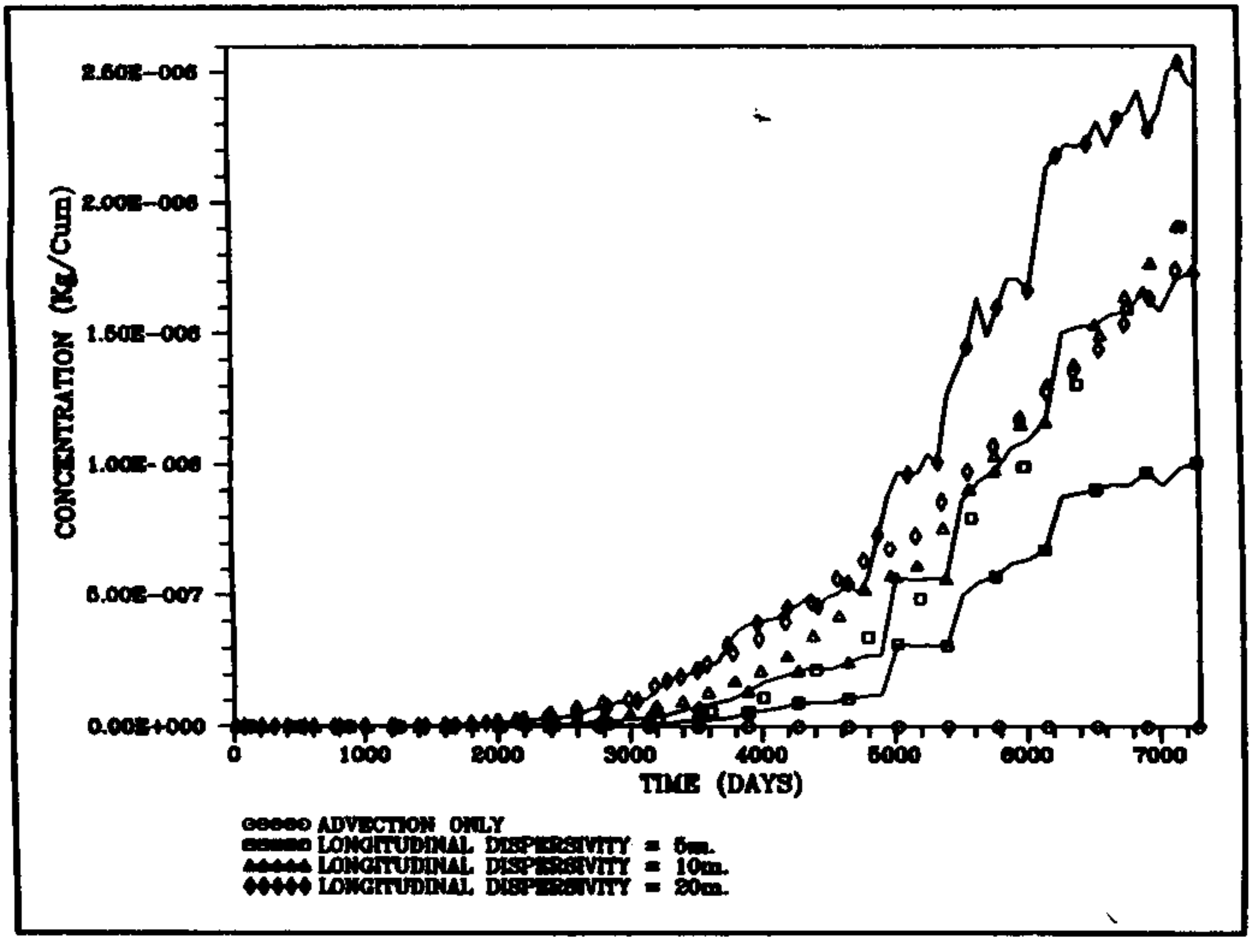


Figure 35: Breakthrough curves at cell (18,39) for the first layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ α_T/α_L = 0.5 and α_V/α_L = 0.5).

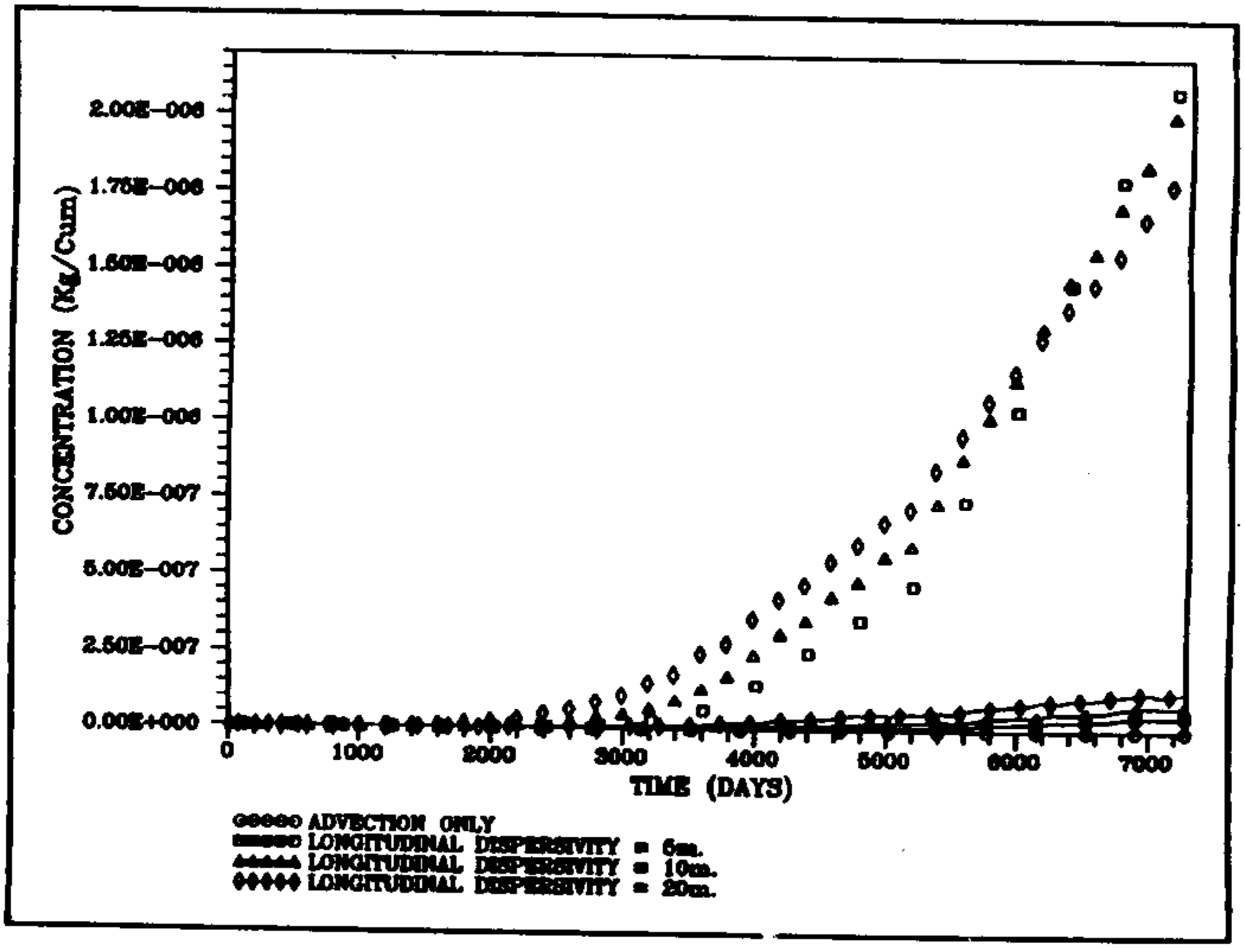


Figure 36: Breakthrough curves at cell (18,39) for the second layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ $\alpha_T/\alpha_L = 0.5$ and $\alpha_T/\alpha_L = 0.5$).

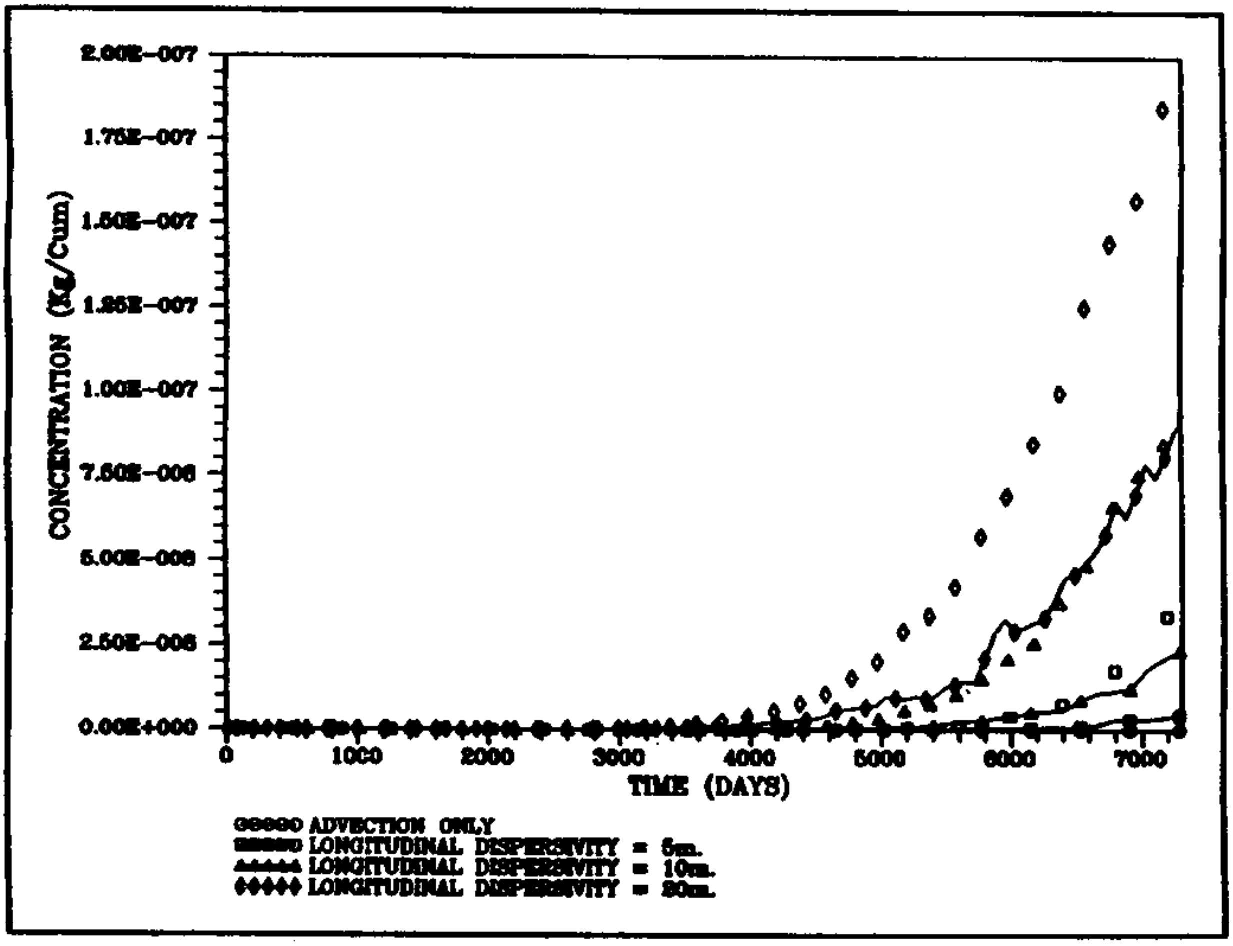


Figure 37: Breakthrough curves at cell (14,43) for the first layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ $\alpha_T/\alpha_L = 0.5$ and $\alpha_V/\alpha_L = 0.5$).

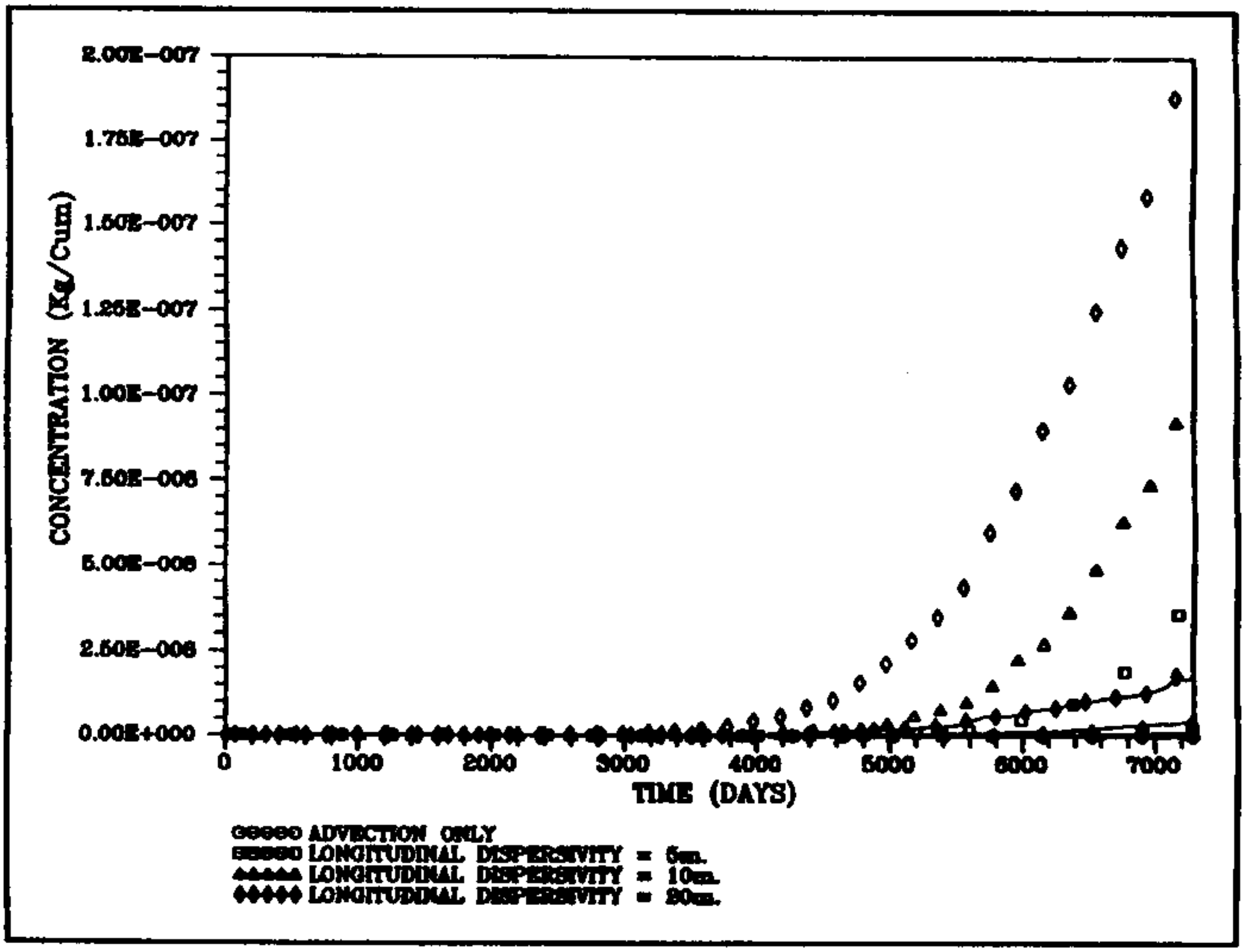


Figure 38: Breakthrough curves at cell (14,43) for the second layer with advection and with different values of dispersivities (line with symbols ⇒ with longitudinal dispersivity; only corresponding symbols ⇒ α_T/α_L = 0.5 and α_V/α_L = 0.5).

6.0 CONCLUDING REMARKS

i. One-dimensional analytical solution and results of numerical model comprehend well.

ii. Visualising a two or three-dimensional transport problem as one-dimensional will lead to errors due to transverse dispersion.

iii. Spreading of constituents in a transport problem increases with increasing dispersivity.

iv. The effect of transverse dispersivity becomes prominent as distance increases from the source.

v. Close to the source, the advective phenomena dominates the transport of pollutants, and its influence decreases with increase in distance from the source in the direction of groundwater flow.

vi. When the distance from the source increases, dominancy of dispersive transport over the advective transport shifts t[illegible]ak of concentration profile.

vii. Combined effect of longitudinal and transverse dispersivity reduces the concentration further in comparison to the longitudinal dispersivity alone.

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ANNEXURE. A-1

```
$DEBUG
      OPEN (UNIT=1, FILE=’INPUT.DAT’,STATUS=’OLD’)
      OPEN (UNIT=2, FILE=’ERFC1.DAT’,STATUS=’UNKNOWN’)
      READ(1,*) ALFAL,VEL,TIME,R,DIST,C,DIST1
C     ALFAL = Longitudinal Dispersivity [L].
C     VEL = Groundwater seepage velocity [L/T].
C     TIME = Simulation time [T].
C     R = Retardation factor [].
C     DIST = Starting value of distance [L].
C     C = Number of columns.
C     DIST1 = Cell width along rows [L].
      DENOM=1./(2.*SQRT(ALFAL*VEL*TIME/R))
      X=(DIST-(VEL*TIME/R))*DENOM
      WRITE(2,*)X,DIST
      DO 10 I=1,C
      DIST=(I*DIST1)-(DIST1*0.5)
      X=(DIST-(VEL*TIME/R))*DENOM
      WRITE(2,*)X,DIST
10    CONTINUE
      RETURN
      END
```

```
$DEBUG
      DIMENSION AX(500)
      OPEN(UNIT=1,FILE=’ERFC1.DAT’,STATUS=’OLD’)
      OPEN(UNIT=2,FILE=’ERFC2.DAT’,STATUS=’UNKNOWN’)
      PRINT*,’NUMBER OF COLUMNS’
      READ(*,*)C
      DO 10 I=1,C+1
      READ(1,*) AX(I),Y
      X=AX(I)
      XINDEX=X
      X1=X
      IF(X)4,5,5
4     X1=-X
5     CONTINUE
      IF(X1-15.)1,2,2
1     CONTINUE
      T=1.0/(1.0+0.3275911*X1)
      ERFX=1.0-(0.25482959*T-0.28449673*T**2+1.42141374*T**3-1.
     1       45315202*T**4+1.06140542*T**5)*EXP(-X1**2)
      GOTO 3
2     ERFX=1.
3     CONTINUE
      IF(XINDEX)6,7,7
6     ERFX=-ERFX
7     CONTINUE
      ERFC=1.-ERFX
C     CONGR=C/Co=0.5*erfc
      CONGR=0.5*ERFC
      WRITE(2,*)Y,CONGR
10    CONTINUE
      RETURN
      END
```

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