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**Mathematics of Pesticide Adsorption in a Porous Medium:
Convective–Dispersive Transport with steady state water flow**

In

Two Dimensions

By

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**A Thesis submitted in partial fulfillment of the requirement for the
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Abstract

The transport of solutes through porous media where chemicals undergo adsorption or change process on the surface of the porous materials has been a subject of research over years. Usage of pesticides has resulted in production of diverse quantity and quality for the market and disposal of excess material has also become an acute problem. The concept of adsorption is essential in determining the movement pattern of pesticides in soil in order to assess the effect of migrating chemical, from their disposal sites, on the quality of ground water. In the study of movement of pesticides in the soil, the mathematical models so far developed only consider axial movement. The contribution of radial movement to the overall location of solutes in the porous media seems to have been disregarded by researchers in this field. The objective of this study is to close this gap by developing a mathematical model to determine the combined radial and axial movement of pesticides due to Convective – Dispersive transport of pesticides with steady – state water flow in a porous media.

The methodology will involve determining the comprehensive dispersion equation accounting for both axial and radial movement of solutes in the porous media and finding the solution of the governing equation using finite difference methods. The solution of this equation will be applied to the data from experiments carried out on adsorption and movement of selected pesticides at high concentration by soil department, University of Florida, Gainesville U.S.A. We will confine our study to single – Region Flow and Transport.

CHAPTER 1

1.0 INTRODUCTION

1.1 Background to the problem

The effect of pesticides and other related contaminants of ground water have created concern to users and specialists. Contamination of ground water is caused by the transport of solutes through porous media. This process involves adsorption or change process on the surfaces of porous material.

Given the high cost of farming and the danger posed by pests on agricultural products, usage of pesticide is part and parcel of effective farming practice. This usage of pesticides has resulted in production of diverse quality for the market and the disposal of excess material is an acute problem.

Possible procedures of disposing pesticides include: incineration, encapsulation, isolation in ground caves and mines, chemical stabilization, land spread and land filling. Of all these methods, disposal by landfills and land spreading appear to be more economical [12]. The disheartening fact is that these hazardous chemical disposals do not provide a guarantee that the disposed material will not migrate from the disposal site to the ground water. We therefore require versatile comprehension of various processes that influence the persistence, retention and leaching of these hazardous chemicals in the soil so that the right chemicals with less migration potential can be recommended for use without jeopardizing life. Organic pesticides are preferred to inorganic pesticides because most organics have high degradation potential thus leading to their being considered less dangerous as compared to inorganic pesticides, which can stay in the soil environment for a very long time.

Our focus will be based on adsorption of pesticides and other solutes while moving through a porous medium.

The concept of adsorption is essential in determining the movement patterns of pesticides in the soil because it helps in assessment of the effect of migrating chemicals on the quality of the ground water environment.

Purity of ground water has become of increased concern given the diminishing availability of safe usable water.

Ground water pollution may be defined as artificially induced degradation of natural ground water quality.

Pollution can impair the use of water and create hazard to public health through toxicity or spread of disease [6]

Ground water pollution may go undetected for years, while remediation is difficult and costly. Any attempt to evaluate ground water pollution requires an understanding of particular aquifer system, its discharge and pollution pathways [14]

1.2 Statement of the problem

Given that no known study of convective-dispersive transport with steady state water flow gives us two dimensions equation for assessing pesticides movement in a porous media, we have to find a mathematical formula to help in determining this movement.

1.3 Objective of study

All known equations that describe movement of solutes through porous media, only takes into account the movement in axial direction. Figure 1 below shows that, when we use the existing equations we will conclude that there is no pollution caused by dumping of pesticides in a pit located some distance from the borehole site. In this situation the dumping site has an impervious rock under it (i.e. acquiclude layer). Use of equation (1) due to Van Genuchten [16] below in the prediction of pesticide effect on the borehole will not be possible.

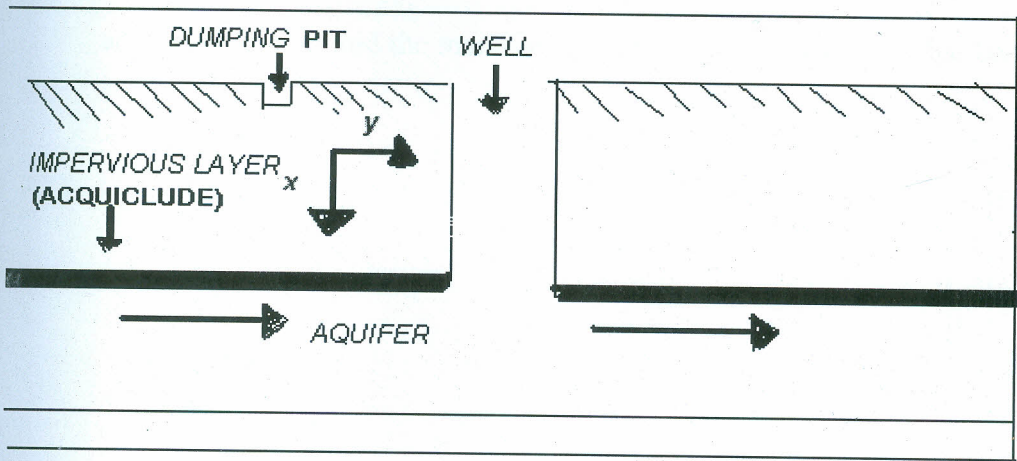


Figure 1 X-section of the rock strata

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \quad (1.0)$$

in which C is the concentration of solute, D is the dispersivity constant, V is the pore water velocity, ρ is the bulky density of the soil, S is amount sorbed by solid phase, θ is volumetric water content and t is time.

Seemingly it is possible to assume that the pesticides in dumping pit have no effect on the borehole. However, this is untrue. It is therefore necessary to develop an appropriate model to fill this gap.

1.4 Significance of the study

Most studies carried out on adsorption of chemical solutes in soils or porous media only take into account axial movement disregarding horizontal movement of these solutes. In this study we have taken care of both horizontal and axial movement of chemical solute in the subsurface environment thus coming up with comprehensive model describing the movement of these solutes.

The study is essential to:

- i. The users – so that they can determine the appropriate dumping site for given pesticides safeguarding the borehole or well.
- ii. The manufacturers – so that they can manufacture pesticides with low migration potential from the dumping site.
- iii. The researchers - so that they can be able to further carry out more studies so that they can provide sound advise to the user and the manufacturer and expand the knowledge base.

CHAPTER 2

2.0 LITERATURE REVIEW.

Taylor [5], in 1953 in his dispersion paper considers the diffusion of solute in a section through which poiseuille flow passes (i.e. laminar flow). If the mean velocity is U and the tube has radius a , the velocity V is described by

$$V = 2U\left(1 - \frac{r^2}{a^2}\right), \quad (2.0)$$

where r is the radial coordinate, a is the diameter of the tube.

Also the concentration C satisfies the equation

$$\frac{\partial C}{\partial t} + 2U\left(1 - \frac{r^2}{a^2}\right)\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial t} + \frac{\partial^2 C}{\partial x^2}, \quad (2.1)$$

where x is the longitudinal measurement along the tube and t is time.

Taylor [5], in 1956 showed that when Peclet number which is denoted P_e and defined by $P_e = \frac{aU}{D}$ is large (Peclet number is one of parameters used in assessing dispersivity), the effect of diffusion term in equation (2.1) is to disperse the mean solute concentration diffusively D^* about the position of its centre of mass $Ut = x$ with dispersion coefficient

$$D^* = \frac{a^2 U}{48D}. \quad (2.2)$$

Aris [5] later improved the above equation to

$$D_T = \frac{a^2 U}{48D_L} + D_L, \quad (2.3)$$

where D_T is the total dispersion coefficient, $D = D^* + D_L$, D^* is the molecular diffusion constant and D_L is the longitudinal dispersion constant which is valid for $\frac{U_a}{D_L} \geq 1$. The dispersion mechanism is due to the radial variation of velocity profile, which disperses the solute even if the diffusion is small.

The tortuosity (lack of straight forwardness) of the flow paths and the possibility of the adsorption on the solids surface cause D^* to be less than D and the ratios of the $\frac{D^*}{D}$ between 0.001 and 0.5 are commonly observed [5]. In porous media, remixing at pore junction causes dependence of D_L on flow velocity to the less quadratic and relation of the form

$$D_L = \alpha_L V^m, \quad (2.4)$$

where $1 < m < 1.2$ and α_L is a constant of Dispersivity.

Mixing at junctions also causes transverse dispersion to occur with the dispersion coefficient D_T (In transverse direction) that measures to be less than D_L by a factor of order 10, when $Pe \gg 1$ [20]

the Peclet number shows little variation with the increase in Reynolds number in liquids and is of order of unity [20]

The Reynolds number is given by

$$Re = \frac{U_c d \rho}{\mu}, \quad (2.5)$$

where U_c is critical velocity, d is diameter of particle, ρ is density of the fluid and μ is the viscosity of the fluid (Reynolds number is another parameter used in assessment of fluid flow).

Darcy [14], in 1856 described flow of water through homogenous layers in saturated soil as

$$q = \frac{Q}{At} = -K \frac{\partial H}{\partial z}, \quad (2.6)$$

where q is the flux density (LT^{-1}), Q is the volume of water (L^3) passing through a cross section area A (L^2) per unit time, $H(L)$ is the hydraulic head and is the sum of the gravitational head $z(L)$ and pressure head $h(L)$ and K is the hydraulic conductivity (LT^{-1}), which represents the ability of the soil to conduct water and is considered to be constant under saturated conditions. Equation (2.6) applies to non- steady state, unsaturated flow as in [15]

$$q = -k(h) \frac{\partial H}{\partial z}, \quad (2.7)$$

where K is a function of h (L), the pressure head.

Van Genuchten et al [26] developed a partial differential equation generally assumed to describe the movement of pesticides and other adsorbed solutes through soils under steady state water flow condition as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \quad (2.8)$$

Later Van Genuchten and Alves [27] came up with an equation for one dimensional, miscible displacement of an absorptive and degradable chemical species

$$\frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] - V \frac{\partial C}{\partial x} - R \frac{\partial C}{\partial t} = \mu C - \gamma, \quad (2.9)$$

where R is the retardation factor, μ is the decay constant and γ is zero order production rate.

Basically the equation applies to degradable organic pesticides and not un-degradable inorganic pesticides.

Langmuir [4], in 1915 came up with a model, which is also called ideal localized monolayer model, which was based on the assumptions below:

- i. The molecules are adsorbed on definite site
- ii. Each site can accommodate only one molecule
- iii. The area of each site is fixed quantity determine solely by the geometry of the surface.
- iv. The adsorption energy is the same at all site
- v. The adsorbed molecules cannot migrate across the surface or interact with neighbouring molecules

The equation gave

$$S = \frac{X_m b C_e}{1 + b C_e}, \quad (2.10)$$

$S = \frac{x}{m}$ is the amount of solute adsorbed x per unit weight of adsorbent m , C_e is equilibrium concentration of the solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface, also called Monolayer capacity, b is a constant related to the heat of adsorption Q $\left[b \propto \exp\left(-\frac{\Delta H}{RT}\right) \right]$ [4].

Freundlich [20], in 1926 came up with adsorption equation, which is widely used as a mathematical description of adsorption in aqueous system

$$S = S_e + S_k + S_{ir} , \quad (2.11)$$

where S_e is adsorption governed by instantaneous equilibrium reactions, S_k is adsorption governed by hysteretic kinetic reaction, S_{ir} is adsorption subject to irreversible retention.

- i. The Langmuir adsorption equation.

The instantaneous equilibrium reaction between the amount of chemical in solution and that sorbed by the solid phase is generally represent by one of the following three adsorption isotherms

The simplest chemical reaction model is the linear adsorption equation

$$S_e = K_d C , \quad (2.12)$$

where K_d is referred to as the distribution coefficient (slope of the adsorption isotherm)

- ii. Equation (2.13) is a special case of the Freundlich equation

$$S_e = K_d C^N , \quad (2.13)$$

where N is a fitting parameter.

- iii. The Lagmuir adsorption equation,

$$S_e = \frac{aC}{1+bc} , \quad (2.14)$$

where a and b are curve fitting parameters.

CHAPTER 3

3.0

BASIC CONCEPTS

3.1 Adsorption

Adsorption is a natural process by which fluids are attracted and then held at the surface of solid caused by surface tension. In any solid or liquid, atoms at the surface are subject to unbalanced forces of attraction normal to the surface. These forces are merely an extension of acting forces within the body of the material. A molecule in the centre of a liquid drop is attracted from all sides. While at the surface the attractive acting between adjacent molecules result in a net attraction in the bulky phase in the direction normal to the surface. Because of the unbalanced attraction at the surface there is a tendency of these molecules to be pulled from the surface into interior and for the surface to shrink to the smallest area that can enclose the liquid [18]. Adsorption is promoted by charged clay mineral, hydrous oxide coating on surfaces and organic matter functional groups with variable charges. Additionally, some solutes may co-precipitate, volatilize or degrade [32]

The adsorption process may be classified as physical or chemical.

3.1.1 Physical adsorption

Physical adsorption on solids is attributed to the forces of interaction between the solid surface and the adsorbent molecules that are similar to Van der Waals forces between the molecules. As these non-bonded molecules approach each other more closely, these attractive forces vanish and strong repulsive forces emerges, which cause a sharp rise in energy content of molecules making it less stable. These forces that include the electron and the nuclei of a system are electrostatic in origin and are termed as dispersive forces. The dispersive forces exist in all types of matter and always act as attractive force between an adjacent atom and molecule no matter how dissimilar. They are always present despite the nature of the other adsorbate-adsorbent potential [1]

The nature of the dispersive forces was first recognized in the 1930 by London Van der Waals [3]. Using Quantum mechanical calculation it was postulated that electron motion in an atom or molecule would lead to dipole oscillating dipole movement. At any instance, the lack of symmetry of the electron distribution about the

nuclei imparts a transient dipole moment to an atom or molecule that would average to zero over a long time interval. When in close proximity to a solid surface each instantaneous dipole of an approaching molecule induces an approximately oriented dipole moment in a surface molecule. These forces are known as dispersion forces because of this relationship. The dipole dispersion interaction energy, E , can be determined by

$$E = -\frac{C}{r^2}, \quad (3.0)$$

where C is a constant and r is the distance of separation between the interacting molecules.

In addition to dipole-dipole interactions other possible dispersion contributing to physical adsorption includes dipole-Quadrupole and Quadrupole interaction. If these are included, the total dispersion energy is given by

$$E = -\frac{C}{r^6} - \frac{C_1}{r^8} - \frac{C_2}{r^{10}} \quad (3.1)$$

where C_1 is a constant of dipole - Quadrupole interaction, C_2 is a constant of Quadrupole interactions

The overall interaction is expressed as

$$E = -\frac{C}{r^6} + \frac{B}{r^{12}} \quad (3.2)$$

where B is a repulsive interaction constant.

3.1.2 Chemical adsorption

This is characterized mainly by large interaction potentials that lead to high heats of adsorption approaching the value of chemical bonds. It involves transfer of electrons and formation of true chemical bonding between the adsorbate and the solid surface [4]. The high temperature associated with chemisorption is usually associated with activation energy released in chemical bonding. In chemisorption the adsorbed molecules remain in situ. (i.e. site specific)

3.1.3 Factors affecting adsorption

Nature of the adsorbent:

- i. Surface area and pore structure. - Adsorption of a solid adsorbent is directly proportional to the specific surface area and pore size distribution.

The more the surface area is accessible to the sorbate the higher the adsorption.

- ii. Particle size – The lower the particle diameter the higher the adsorption. But for very highly porous adsorbents most surface area reside in internal pore structure; therefore the adsorptive capacity is independent of the particle size. [35]
- iii. Chemistry of the surface – The presence of specific functional groups on the surface of adsorbent affects the adsorption process.

Nature of the adsorbate:

- i. In general, a higher solubility indicate a strong solute – solvent interaction or affinity – the extend of adsorption is expected to be low due to the necessity of breaking the solute solvent bond before adsorption occur.
- ii. The molecular weight and size of the adsorbate molecule also affect the adsorptive capacity [30]. The adsorptive capacity increases with an increase in mole weight.

Effect of temperature

- i. Since the process of adsorption is spontaneous, it is accompanied by decrease in entropy due to loss of degrees of freedom of the solute in passing from the dissolved state to the adsorbate state [34] The adsorption process is always exothermic therefore an increase in temperature will result in a reduction of equilibrium adsorptive capacity and otherwise for lower temperature.

3.2 Adsorption from liquids

The presentation of the amount of solute adsorbate per unit adsorbent as a function of the equilibrium concentration in bulky solution at a constant temperature is termed as the adsorption isotherm.

One of the most popular adsorption isotherm equations that is used for liquids was described as

$$S = KC_e^N, \quad (3.3)$$

where $S = \frac{x}{m}$, is adsorbed solid and C_e is the solute equilibrium constant.

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the substance and the

exponential distribution of sites and their energies.

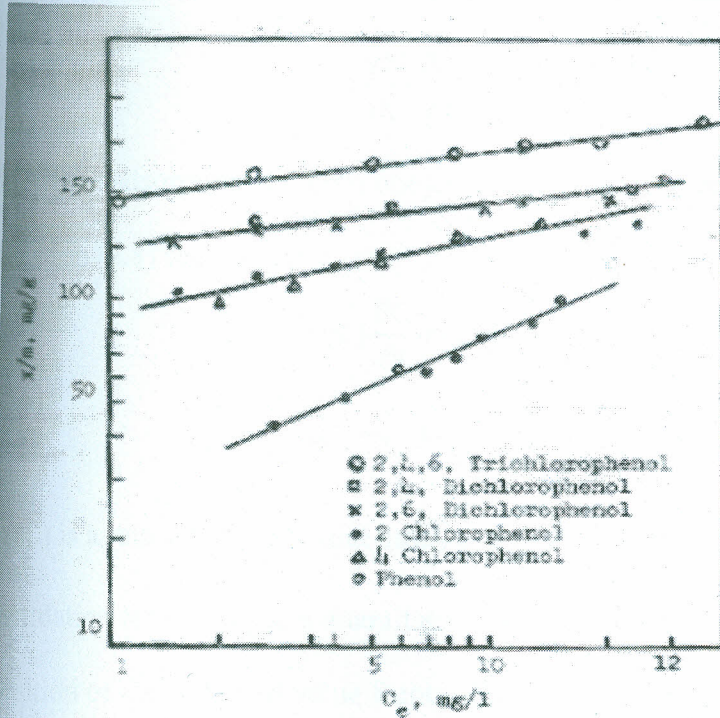


Fig 2: Logarithmic form of Freundlich adsorption isotherms for phenolic compound on activated carbon

For linearization of the data in equation (3.3) can be expressed as

$$\log S = \log K + N \log C$$

and plotting $\log S$ against C enables one to find N and K (see figure 2).

Steep slopes indicate high adsorptive capacity at equilibrium concentration that rapidly diminishes at lower concentration. Relatively flat slopes i.e. $N \ll 1$, indicate that the adsorptive capacity is only slightly reduced at lower equilibrium concentration.

3.3 Solution of one dimension equation

The partial differential equation assumed to describe the movement of pesticides and other solutes through soils under steady water flow condition is equation (2.8).

We shall solve the equation using numerical method in order to compare our subsequent results with two-dimensional equation which we intend to derive and solve.

In our study we shall use numerical methods to solve equation (2.8). The limitation of the equation is that it is in one dimension. We are going to develop a model for solving this equation numerically.

From equation (3.3), $S = KC^N$, since S is a function of another variable C

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C} \frac{\partial C}{\partial t} = NK C^{N-1} \frac{\partial C}{\partial t}. \quad (3.5)$$

When the adsorption isotherm obeys the Freundlich equation, the convective-dispersive solute transport model equation (2.8) reduces to:

$$R(C) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}, \quad (3.6)$$

$$\text{where } R(C) = \left(1 + \frac{\rho N K_d C^{N-1}}{\theta}\right) \quad (3.7)$$

$R(C)$ is a retardation term and index of pesticide mobility, K_d is the Freundlich [26] adsorption constant. The retardation term $R(C)$ is a quantitative index of pesticides' mobility in that its value is equal to the ratio of the position of the adsorbed value fronts. The value of the adsorption coefficient K in the equation (3.5) for non-adsorbed solutes is equal to zero hence $R(C) = 1$. For adsorbed solutes, $R(C)$ is greater than unity since the value of K is larger than zero. The larger values of $R(C)$ indicate reduced pesticides mobility in soils. It may be noted from equation (3.7) that for the case of non linear adsorption isotherms ($N < 1$), the retardation term varies inversely with solution concentration C . For nonlinear isotherm ($N = 1$), $R(C)$ is independent of pesticide solution concentration. Thus the shape of the equilibrium adsorption isotherm directly influences the mobility of pesticide and other adsorbed solutes through the soil.

Consider equation (3.6), when rearranged

$$D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - R(C) \frac{\partial C}{\partial t} = 0 \quad (3.8)$$

When a physical system depends on more than one variable, a general description of its behavior often leads to a equation containing partial differentials. Equation (3.6) is our partial differential equation and we solve it using finite difference method. The calculus of finite differences will enable solve this differential equation numerically.

by calculating the values of the function at discrete (finite) points.

The finite difference method is ideal for solving non linear equations. We replace the differential with its finite difference equivalent. We shall establish grids based on dimensions we are to consider. We use the (i, j) notation that is used to designate the pivot point for two-dimensional space (x, y) direction and (i, j) being the counters in the (x, y) directions. The partial derivative of C with respect to x implies that t is kept constant and vice versa.

Where n is an arbitrary Rx (O,T) boundary condition, where $R = a \leq x \leq b$ and $0 \leq t \leq T$.

The initial condition is that the concentration of pesticide at all positions in the soil at time zero is constant and equal to C_i . That is $C(x,0) = C_i$ for $x > 0$.

Boundary conditions: two conditions are necessary:

- i. In the first case the concentration of the pesticides at the position $x = 0$ is specified for a period of time, the concentration at the surface is zero. That is

$$C(0,t) = C_0 \text{ for } 0 < t \leq t_0$$

$$C(0,t) = 0 \text{ for } t > t_0$$

- ii. In the second case, the concentration of the pesticides in the solution entering the soil system at position $x = 0$ is specified for a period time. Following that time, the concentration at the surface is zero.

Mathematically this is written as,

$$-D \frac{dC}{dx} + VC \Big|_{x=0} = \begin{cases} VC_0, \text{ for } 0 < t \leq t_0. \\ 0, \text{ for } t > 0. \end{cases}$$

Assumptions

- i. The pore water velocity is constant in time and space. This condition can be met for a uniform soil if the flux density of water velocity and volumetric water content are constant for all positions all the times.
- ii. The spread of solute is dominated by hydraulic dispersion rather than diffusion.
- iii. The hydrodynamic dispersion can be approximated as the product of the dispersivity and pore water velocity.
- iv. The adsorption process is instantaneous and reversible and the adsorption isotherm can be described by

the model i.e the concentration of pesticide absorbed on the soil solids is proportional to the concentration in the solution,[14]

When we approximate the differential $\frac{\partial C}{\partial x}$ using central differences, we find

$$h = \Delta x$$

We now consider equation (3.8). The coefficient R(C), is a function of a dependent variable C, therefore the equation is quasilinear. For a properly posed initial value problem and its finite difference equation to satisfy the consistency condition, stability is necessary and sufficient condition for convergence.

Using forward difference,

taking $k = \Delta t$,

$$\frac{\partial C}{\partial x} = \frac{1}{h}(C_{i+1}^n - C_i^n), \quad (3.9)$$

$$\frac{\partial C}{\partial t} = \frac{1}{k}(C_i^{n+1} - C_i^n), \quad (3.10)$$

$$\frac{R(C_i^n)}{k} \{C_i^{n+1} - C_i^n\} = \frac{D}{h^2} \{(C_{i+1}^n - 2C_i^n + C_{i-1}^n)\} - \frac{V}{h}(C_{i+1}^n - C_i^n). \quad (3.11)$$

From equation (3.8)

$$C_i^{n+1} = \left(\frac{kD}{R(C_i^n)h^2} - \frac{kV}{R(C_i^n)h}\right)C_{i+1}^n + \left(1 + \frac{kV}{R(C_i^n)h} - \frac{2kD}{R(C_i^n)h^2}\right)C_i^n + \frac{kD}{R(C_i^n)h^2}C_{i-1}^n \quad (3.12)$$

Explicit methods similar to the one used in solving our equation above are computationally easier to solve, however, since our equation will become more complex when we introduce the second dimension to the above equation, we shall use implicit techniques because they are unconditionally stable while explicit techniques are conditionally stable. Now consider equation (3.8). We utilize the grid of figure 3 at half point in the n-direction ($i, n + 1/2$). Instead of expressing in terms of forward difference around (i, n) as it was done in the explicit computation, we express $\frac{\partial C}{\partial t}$, in terms of forward differences around the half point,

$$\frac{\partial C}{\partial t} \Big|_{i, n + \frac{1}{2}} = \frac{1}{k}(C_i^{n+1} - C_i^n) \quad (3.13)$$

The first and second order partial derivatives are expressed at the half point as a weighted average of the central differences at points $(i, n+1)$ and (i, n) as under:

$$\begin{aligned} \left. \frac{\partial C}{\partial x} \right|_{i, n + \frac{1}{2}} &= p \partial C_i^{n+1} + (1-p) \partial C_i^n, \\ &= \frac{1}{2h} \left[p C_{i+1}^{n+1} - p C_{i-1}^{n+1} + C_{i+1}^n - C_{i-1}^n - p C_{i+1}^n + p C_{i-1}^n \right]. \\ \left. \frac{\partial^2 C}{\partial x^2} \right|_{i, n + \frac{1}{2}} &= p \partial^2 C_i^{n+1} + (1-p) \partial^2 C_i^n, \\ &= p \left[\frac{1}{h^2} (C_{i+1}^{n+1} - 2C_i^{n+1} + C_{i-1}^{n+1}) \right] + (1-p) \left[\frac{1}{h^2} (C_{i+1}^n - C_i^n + C_{i-1}^n) \right]. \end{aligned}$$

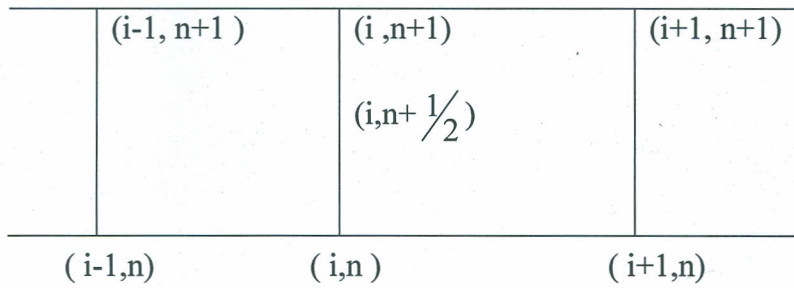


Figure 3: Display of nodal points.

Where p is in the range of, $0 \leq p \leq 1$.

Inserting the above expressions in equation (3.8) yields:

$$\begin{aligned} \frac{R(C_i^n)}{k} (C_i^{n+1} - C_i^n) &= \frac{D}{h^2} \left[p (C_{i+1}^{n+1} - 2C_i^{n+1} + C_{i-1}^{n+1}) + (1-p) (C_{i+1}^n - 2C_i^n + C_{i-1}^n) \right] \\ &\quad - \frac{V}{2h} \left[p (C_{i+1}^{n+1} - C_{i-1}^{n+1} - C_{i+1}^n + C_{i-1}^n) + (C_{i+1}^n - C_{i-1}^n) \right]. \end{aligned}$$

Using Schmidt method [12] i.e. $p=0$ we find:

$$C_i^{n+1} = \frac{k}{R(C_i^n)h} \left(\frac{D}{h} - \frac{V}{2} \right) C_{i+1}^n + \left(1 + \frac{2kD}{R(C_i^n)h^2} \right) C_i^n + \frac{k}{R(C_i^n)h} \left(\frac{D}{h} + \frac{V}{2} \right) C_{i-1}^n, \quad (3.14)$$

which is unconditionally stable. When $p=1$, the system is fully implicit.

CHAPTER 4

4.0 DERIVATION OF CONVECTIVE-DISPERSIVE SOLUTE TRANSPORT EQUATION WITH STEADY STATE WATER FLOW CONDITION

Average pore water velocity $V(\text{LT}^{-1}) = \frac{q}{\theta}$,

i.e. $q = -K \frac{\partial H}{\partial z}$, is the flux density, (from equation 2.6), $\theta = \frac{V_w}{V_s}$, in which V_w is volume of water in the porous media and V_s is volume of solids is used instead.

In this study we are going to use the concept of dispersion through a cylindrically packed soil vessel to derive our equation.

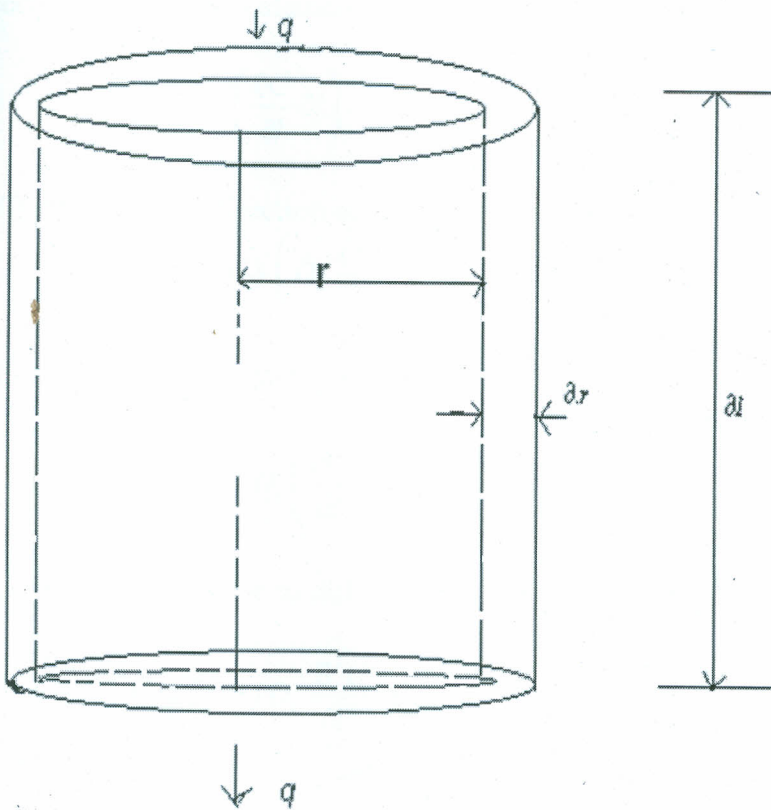


Figure 4: Derivation of the equation.

At very low flow rate, the dispersion is different in longitudinal and radial directions. The Dispersion coefficients denoted by D_L for longitudinal and D_R for radial

$$D(\theta, V) = D_{diff} + D_{dis}, \quad (4.0)$$

where D_{diff} (L^2T^{-1}) is molecular diffusion coefficient, D_{dis} (L^2T^{-1}) is the hydrodynamic dispersion and is the mixing or spreading of the solute during transport due to differences in velocities within a pore and between pores. The volumetric water content denoted by θ which we can assume to be the voidage for saturated soils.

The element height is denoted by ∂l . Inner radius is r and outer radius is $r + \partial r$, C is the concentration of the material to be dispersed and is a function of axial position l , radial position r , time t and dispersion coefficients D_R and D_L radial and axial respectively.

The rate of entry of reference material due to flow in axial direction is $q(2\pi r \partial r C)$. The corresponding efflux rate is

$$q(2\pi r \partial r) \left(C + \frac{\partial C}{\partial l} \partial l \right). \quad (4.1)$$

The net accumulation rate in element due to flow in axial direction is :

$$-q(2\pi r \partial r) \left(\frac{\partial C}{\partial l} \partial l \right). \quad (4.2)$$

Rate of diffusion in axial direction across inlet boundary is:

$$-(2\pi r \partial r \theta) \left(D_L \frac{\partial C}{\partial l} \right). \quad (4.3)$$

The corresponding rate at outlet boundary is:

$$(2\pi r \partial r \theta) D_L \left(\frac{\partial C}{\partial l} + \frac{\partial^2 C}{\partial l^2} \partial l \right). \quad (4.4)$$

The net accumulation rate due to diffusion from boundaries in axial direction is:

$$(2\pi r \partial r \theta) D_L \frac{\partial^2 C}{\partial l^2} \partial l. \quad (4.5)$$

Diffusion in radial direction at r is:

$$-(2\pi r \partial r \theta) \partial l D_R \frac{\partial C}{\partial r}. \quad (4.6)$$

The corresponding rate at radius $r + \partial r$ is

$$[2\pi(r + \partial r)\theta] \partial l \cdot D_R \left[\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \partial r \right]. \quad (4.7)$$

The net accumulation rate due to diffusion from boundaries is:

$$-[2\pi r \partial r \theta] \partial l \cdot D_R \frac{\partial C}{\partial r} + [2\pi(r + \partial r) \partial l(\theta)] D_R \left(\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \partial r \right). \quad (4.8)$$

If we ignore the last term, it becomes:

$$2\pi \theta D_R \partial l \left[\partial r \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \right]. \quad (4.9)$$

For a representative elementary volume of soil, the total amount of a given chemical species X (ML⁻³) is represented by the sum of the amount retained by the soil matrix and the amount present in the soil.

$$X = \rho_b S + \theta C, \quad (4.9)$$

where, ρ_b is the bulky density, and S is the amount of solute adsorbed,
and

$$\frac{\partial X}{\partial t} = \rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t}. \quad (4.10)$$

Now the total accumulation rate is:

$$\begin{aligned} & (2\pi r \partial r \partial l) \frac{\partial X}{\partial t} \\ &= (2\pi r \partial r \partial l) \left(\rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} \right). \end{aligned} \quad (4.11)$$

Thus from equations (4.0) through to (4.11), we have:

$$\left(\rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} \right) 2\pi r \partial r \partial l = -q(2\pi r \partial r) \frac{\partial C}{\partial l} \partial l + (2\pi r \partial r \theta) D_L \left(\frac{\partial^2 C}{\partial l^2} \partial l \right) + 2\pi \partial l D_R \left[\partial r \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \right], \quad (4.12)$$

and on dividing through by $(2\pi r \partial r) \partial l \theta$, we find

$$\left(\frac{\rho}{\theta} \frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} \right) = D_L \frac{\partial^2 C}{\partial l^2} + \frac{1}{r} D_R \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) - \frac{q}{\theta} \frac{\partial C}{\partial l} \quad (4.13)$$

Taking $l=x$ and $r=y$ our equation comes to

$$\frac{\rho}{\theta} \frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + \frac{1}{y} D_y \frac{\partial}{\partial y} \left(y \frac{\partial C}{\partial y} \right) - \frac{q}{\theta} \frac{\partial C}{\partial x} \quad (4.14)$$

But $\frac{q}{\theta} = V_x$ (pore water velocity), therefore equation (4.8) comes to

$$\left(\frac{\rho}{\theta} \frac{\partial S}{\partial C} * \frac{\partial C}{\partial t} + \frac{\partial C}{\partial t} \right) = D_x \frac{\partial^2 C}{\partial x^2} + \frac{1}{y} D_y \frac{\partial}{\partial y} \left(y \frac{\partial C}{\partial y} \right) - V_x \frac{\partial C}{\partial x} \quad (4.15)$$

From the Freundlich equation, equation (3.4), we have

$$S = KC^N, \quad \frac{\partial S}{\partial C} = KNC^{N-1}, \quad \frac{\partial S}{\partial t} = \frac{\partial S}{\partial C} \frac{\partial C}{\partial t}, = KNC^{N-1} \frac{\partial C}{\partial t} \quad (4.16)$$

Putting equation (4.16) in (4.15)

$$R(C) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} + \frac{1}{y} D_y \frac{\partial}{\partial y} \left(y \frac{\partial C}{\partial y} \right) \quad (4.17)$$

where, $R(C) = \left(1 + \frac{\rho}{\theta} KNC^{N-1} \right)$.

Equation (4.17) is our model equation describing two-dimensional movement of solute in the soil or porous media.

CHAPTER 5

5.0 FINITE DIFFERENCES SCHEME TO THE TWO DIMENSION EQUATION

The partial differential we have derived describing the movement of pesticides and other solute through the soils under steady flow condition similar to the one dimensional of Van Genuchten (1974)'s one-dimension equation is

$$R(C) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} + \frac{D_y}{y} \frac{\partial C}{\partial y} + D_y \frac{\partial^2 C}{\partial y^2} \quad (5.0)$$

The partial derivatives of C with respect to x, implies y and t are kept constant and vice versa.

i.e.

$$\left. \frac{\partial C}{\partial x} \right|_{i,j,n} \equiv \left. \frac{dC}{dx} \right|_{i,j,n} \quad , \quad (5.1)$$

$$\left. \frac{\partial C}{\partial y} \right|_{i,j,n} \equiv \left. \frac{dC}{dy} \right|_{i,j,n} \quad ,$$

and,

$$\left. \frac{\partial C}{\partial t} \right|_{i,j,n} \equiv \left. \frac{dC}{dt} \right|_{i,j,n} \quad . \quad (5.2)$$

The initial condition; the concentration of pesticides at positions in the at time zero is constant,

and equal to C_{i, j}, i.e. C(x,y,0) = C_{i,j} for x,y>0

Boundary conditions: two conditions are necessary.

- i. In the first case the concentration of pesticides at position x=0 and y=0 is specified for a period of time.
- ii. Following that time, the concentration at the surface is zero i.e.

$$C(0,0,t) = C_0 \quad \text{for } 0 < t \leq t_0 \quad (5.3)$$

and

$$C(0,0,t) = 0 \quad \text{for } t > t_0$$

- iii. In the second case, the concentration of pesticides in the solution entering the soil system at position $x=0$ and $y=0$ is specified for a period of time. Following that time the concentration at the surface is zero.

$$-\left(D_x \frac{\partial C}{\partial x} + D_y \frac{\partial C}{\partial y}\right) + VC \Big|_{\substack{x=0 \\ y=0}} = \begin{cases} VC_0 & \text{for } 0 < t \leq t_0 \\ 0 & \text{for } t > 0 \end{cases} \quad (5.4)$$

Assumptions:

From our analysis in one dimension equation, we noted that when the coefficient is a function of dependent variables, the equation is quasilinear. We even used finite difference approximations to solve the one-dimensional equation describing the movement of pesticides in the porous media with respect to time.

We later used implicit method to find a numerical solution, which was dependably stable. In this analysis we are going to solve our two-dimensional partial differential equation using implicit methods to ensure our result are unconditionally stable. Starting with equation (5.0), i.e.

$$R(C) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} + \frac{D_y}{y} \frac{\partial C}{\partial y} + D_y \frac{\partial^2 C}{\partial y^2}$$

The problem with seeking solutions to the above equation is complicated by the presence of complex geometry.

Solution by analytical means is complex, so we have to use numerical techniques to find the solution.

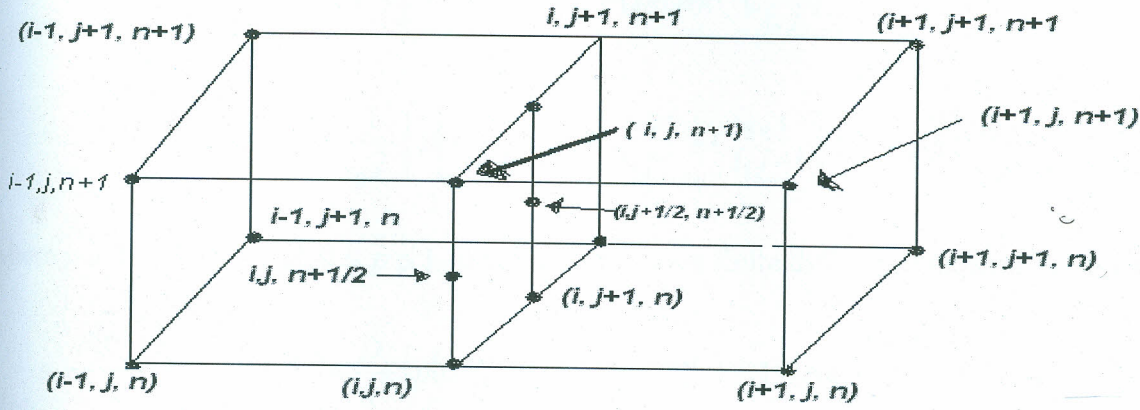


Figure 5: Two-dimensional nodal points

We utilize the grid of figure 5 in which the half a point in n -direction $(i, j, n + \frac{1}{2})$ is shown as K. Instead of expressing $\frac{\partial C}{\partial t}$ in terms of forward difference around (i, j, n) , we express it in terms of central differences around the half point.

$$\left. \frac{\partial C}{\partial t} \right|_{i,j,n+\frac{1}{2}} = \frac{1}{k} (C_{i,j}^{n+1} - C_i^n) \quad (5.5)$$

These first and second order partial derivatives are expressed at the half point as weighted averages of the central differences at points $(I, j, n+1)$ and (I, j, n)

Let $\Delta x=h$, $\Delta y=q$, $\Delta t=k$, then

$$\begin{aligned} \left. \frac{\partial C}{\partial x} \right|_{i,j,n+\frac{1}{2}} &= p \partial C_{i,j}^{n+1} + (1-p) \partial C_{i,j}^n \\ &= \frac{1}{2h} (p C_{i+1,j}^{n+1} - p C_{i-1,j}^{n+1} + C_{i+1,j}^n - p C_{i+1,j}^n + p C_{i-1,j}^n). \end{aligned} \quad (5.6)$$

$$\left. \frac{\partial C}{\partial y} \right|_{i,j,n+\frac{1}{2}} = \frac{1}{2q} (p C_{i,j+1}^{n+1} - p C_{i,j-1}^{n+1} + C_{i,j+1}^n - C_{i,j-1}^n - C_{i,j+1}^n + p C_{i,j-1}^n). \quad (5.7)$$

Also,

$$\begin{aligned} \left. \frac{\partial^2 C}{\partial x^2} \right|_{i,j,n+\frac{1}{2}} &= p \partial^2 C_{i,j}^{n+1} + (1-p) \partial^2 C_{i,j}^n, \\ &= \frac{1}{h^2} \{ p (C_{i+1,j}^{n+1} - 2C_{i,j}^{n+1} - 2C_{i,j}^{n+1} + C_{i-1,j}^{n+1}) + (1-p) [C_{i+1,j}^n - 2C_{i,j}^n + C_{i-1,j}^n] \}. \end{aligned} \quad (5.8)$$

$$\begin{aligned} \frac{\partial^2 C}{\partial y^2} \Big|_{i,j,n+\frac{1}{2}} &= p \partial^2 C_{i,j}^{n+1} + (1-p) \partial^2 C_{i,j}^n, \\ &= \frac{1}{q^2} \left\{ p \left[C_{i,j+1}^{n+1} - 2C_{i,j}^{n+1} + C_{i,j-1}^{n+1} \right] + (1-p) \left[C_{i,j+1}^n - 2C_{i,j}^n + C_{i,j}^n \right] \right\}, \end{aligned} \quad (5.9)$$

where p is in the range of $0 \leq p \leq 1$. Inserting the above finite difference expression in equation (5.0) we obtain:

$$\begin{aligned} \frac{R(C_{i,j}^n)}{k} (C_{i,j}^{n+1} - C_{i,j}^n) &= \frac{D_x}{h^2} \left[p(C_{i+1,j}^{n+1} - 2C_{i,j}^{n+1} + C_{i-1,j}^{n+1}) + (1-p)(C_{i+1,j}^n - 2C_{i,j}^n + C_{i-1,j}^n) \right] \\ &\quad - \frac{V_x}{2h} (pC_{i+1,j}^{n+1} - pC_{i-1,j}^{n+1} + C_{i+1,j}^n - C_{i-1,j}^n - pC_{i+1,j}^n + pC_{i-1,j}^n) \\ &\quad + \frac{D_y}{y} \left[\frac{1}{2q} (pC_{i,j+1}^{n+1} - pC_{i,j-1}^{n+1} + C_{i,j+1}^n - C_{i,j-1}^n - pC_{i,j+1}^n + pC_{i,j-1}^n) \right] \\ &\quad + \frac{D_y}{q^2} \left[P(C_{i,j+1}^{n+1} - 2C_{i,j}^{n+1} + C_{i,j-1}^{n+1}) + (1-P)(C_{i,j+1}^n - 2C_{i,j}^n + C_{i,j-1}^n) \right]. \end{aligned} \quad (5.10)$$

Again using Schmidt method i.e. $p = 0$ our equation reduces to

$$\begin{aligned} R(C_{i,j}^n)(C_{i,j}^{n+1} - C_{i,j}^n) &= \frac{D_x}{h^2} (C_{i+1,j}^n - 2C_{i,j}^n + C_{i-1,j}^n) - \frac{V_x}{2h} (C_{i+1,j}^n - C_{i-1,j}^n) + \frac{D_y}{2yq} (C_{i,j+1}^n - C_{i,j-1}^n) \\ &\quad + \frac{D_y}{q^2} (C_{i,j+1}^n - 2C_{i,j}^n + C_{i,j-1}^n), \end{aligned}$$

it eventually gives us

$$\begin{aligned} C_{i,j}^{n+1} &= \left[\frac{k}{R(C_{i,j}^n)} \left(\frac{D_x}{h} - \frac{V_x}{2} \right) \right] C_{i+1,j}^n + \left[1 - \frac{2kD_x}{R(C_{i,j}^n)h^2} - \frac{2kD_y}{R(C_{i,j}^n)q^2} \right] C_{i,j}^n + \\ &\left[\frac{k}{R(C_{i,j}^n)h} \left(\frac{D_x}{h} + \frac{V_x}{2} \right) \right] C_{i-1,j+1}^n + \left[\frac{kD_y}{R(C_{i,j}^n)q} \left(\frac{1}{q} + \frac{1}{2y_j} \right) \right] C_{i,j+1}^n + \left[\frac{kD_y}{R(C_{i,j}^n)q} \left(\frac{1}{q} - \frac{1}{2y_j} \right) \right] C_{i,j-1}^n. \end{aligned} \quad (5.11)$$

$n = 0, 1, 2, \dots, N$
 $i = j = 1, 2, \dots, M$

N and M are the largest value of i, j and n

When $\Delta x = \Delta y = h$ equation (5.11) becomes

$$\begin{aligned} C_{i,j}^{n+1} &= \left[\frac{k}{R(C_{i,j}^n)h} \left(\frac{D_x}{h} - \frac{V_x}{2} \right) \right] C_{i+1,j}^n + \left[1 - \frac{2kD_x}{R(C_{i,j}^n)h^2} - \frac{2kD_y}{R(C_{i,j}^n)h^2} \right] C_{i,j}^n + \left[\frac{k}{R(C_{i,j}^n)h} \left(\frac{D_x}{h} + \frac{V_x}{2} \right) \right] C_{i-1,j}^n \\ &\quad + \left[\frac{kD_y}{R(C_{i,j}^n)h} \left(\frac{1}{h} + \frac{1}{2y_i} \right) \right] C_{i,j+1}^n + \left[\frac{kD_y}{R(C_{i,j}^n)h} \left(\frac{1}{h} - \frac{1}{2y_i} \right) \right] C_{i,j-1}^n \end{aligned} \quad (5.12)$$

Let:

$$\begin{aligned}
\mathbf{A} &= \left[\frac{k}{R(C_{i,j}^n)h} \left(\frac{D_x}{h} - \frac{V_x}{2} \right) \right], & \mathbf{B} &= \left[1 - \frac{2kD_x}{R(C_{i,j}^n)h^2} - \frac{2kD_y}{R(C_{i,j}^n)h^2} \right], \\
\mathbf{C} &= \left[\frac{k}{R(C_{i,j}^n)h} \left(\frac{D_x}{h} + \frac{V_x}{2} \right) \right], & \mathbf{D} &= \left[\frac{kD_y}{R(C_{i,j}^n)h} \left(\frac{1}{h} + \frac{1}{2y_i} \right) \right], \\
\mathbf{E} &= \left[\frac{kD_y}{R(C_{i,j}^n)h} \left(\frac{1}{h} - \frac{1}{2y_i} \right) \right].
\end{aligned} \tag{5.13}$$

Equation (5.11) can also be expressed as:

$$C_{i,j}^{n+1} = AC_{i+1,j}^n + BC_{i,j}^n + CC_{i-1,j}^n + DC_{i,j+1}^n + EC_{i,j-1}^n. \tag{5.14}$$

This is a finite difference scheme to equation (5.0).

CHAPTER 6

6.0 METHODOLOGY OF CALCULATING TRUNCATION ERRORS.

Writing $C_{i,j}^n$ for the value of exact solution and $C(x, y, t)$ as the true value, we know that $C_{i,j}^n$ and $c_{i,j}^n$ satisfy the respective equation

$$R(C_{i,j}^n)h[C_{i,j}^{n+1} - C_{i,j}^n] = k\left[\frac{D_x}{h} - \frac{V_x}{2}\right]C_{i+1,j}^{n+1} - \frac{2k}{h}[D_x + D_y]C_{i,j}^n + k\left[\frac{D_x}{h} + \frac{V_x}{2}\right]C_{i-1,j}^n + kD_y\left[\frac{1}{h} + \frac{1}{2y_j}\right]C_{i,j+1}^n + kD_y\left[\frac{1}{h} - \frac{1}{2y_j}\right]C_{i,j-1}^n, \quad (6.0)$$

$$R(c_{i,j}^n)h[c_{i,j}^{n+1} - c_{i,j}^n] = k\left[\frac{D_x}{h} - \frac{V_x}{2}\right]c_{i+1,j}^n - \frac{2k}{h}c_{i,j}^n + k\left[\frac{D_x}{h} + \frac{V_x}{2}\right]c_{i-1,j}^n + kD_y\left[\frac{1}{h} + \frac{1}{2y_j}\right]c_{i,j+1}^n + kD_y\left[\frac{1}{h} - \frac{1}{2y_j}\right]c_{i,j-1}^n + \Delta t T_{i,j}^n, \quad (6.1)$$

where $T_{i,j}^n$ is the truncation error.

It is not practical to simply subtract these equations to obtain $e_{i,j}^n$, given the coefficients of $R(\bullet)$ are different.

We can first write.

$$R(c_{i,j}^n) = R(C_{i,j}^n) + (c_{i,j}^n - C_{i,j}^n) \quad (6.2)$$

$$= R(C_{i,j}^n) - e_{i,j}^n q_{i,j}^n \quad (6.3)$$

$$\text{Where, } q_{i,j}^n = \frac{\partial R}{\partial C}(\eta) \quad (6.4)$$

And η is some number between $C_{i,j}^n$ and $c_{i,j}^n$

We can now subtract equation (6.0) from (6.1) and obtain

$$R(C_{i,j}^n)h(e_{i,j}^{n+1} - e_{i,j}^n) + he_{i,j}^n q_{i,j}^n [c_{i,j}^{n+1} - C_{i,j}^n] = k\left[\frac{D_x}{h} - \frac{V_x}{2}\right]e_{i,j}^n - \frac{2k}{h}[D_x + D_y]e_{i,j}^n + k\left[\frac{D_x}{h} + \frac{V_x}{2}\right]e_{i-1,j}^n + kD_y\left[\frac{1}{h} + \frac{1}{2y_j}\right]e_{i,j+1}^n + kD_y\left[\frac{1}{h} - \frac{1}{2y_j}\right]e_{i,j-1}^n - \Delta t T_{i,j}^n, \quad (6.5)$$

$$e_{i,j}^{n+1} = \frac{k}{R(C_{i,j}^n)h}\left[\frac{D_x}{h} - \frac{D_x}{2}\right]e_{i+1,j}^n + \left[1 - \frac{2k}{R(C_{i,j}^n)h^2}(D_x + D_y)\right]e_{i,j}^n + \frac{k}{R(C_{i,j}^n)h}\left[\frac{D_x}{h} + \frac{V_x}{2}\right]e_{i-1,j}^n$$

$$+ \frac{kD_y}{R(C_{i,j}^n)h} \left[\frac{1}{h} + \frac{1}{2y_j} \right] e_{i,j+1}^n + \frac{kD_y}{R(C_{i,j}^n)h} \left[\frac{1}{h} - \frac{1}{2y_j} \right] e_{i,j-1}^n - \frac{e_{i,j}^n \bar{q}_{i,j}^n}{R(C_{i,j}^n)} (c_{i,j}^n - C_{i,j}^n) - \Delta t T. \quad (6.6)$$

The coefficient of $e_{i+1,j}^n, e_{i,j}^n, e_{i-1,j}^n, e_{i,j+1}^n, e_{i,j-1}^n$ arising from the three terms are non negative provided

$$1 - \frac{2k}{\text{Max}.R(C_{i,j}^n)h^2} [D_x + D_y] \geq 0, \\ \text{and} \\ 2k[D_x + D_y] \leq h^2 \text{Max}.R(C_{i,j}^n). \quad (6.7)$$

This is our new stability condition, and condition for the approximate to satisfy a maximum principle.

Generally it will need to be checked (and Δt adjusted) at each time step.

However, assuming that we can use a constant step Δt which satisfy for all i, j and n and that we have bounds

$$|C_{i,j}^{n+1} - C_{i,j}^n| \leq M_t \Delta t |q_{i,j}^n| \leq k, \quad (6.8)$$

we can write ,

$$E^{n+1} \leq [1 + kM_t (\Delta x)^2] E^n + \Delta t T. \quad (6.9)$$

In our previous notation:

$$(1 + kM_t (\Delta x)^2)^n \leq e^{kM_t n (\Delta x)^2} < e^{KM_t x^2} \quad (6.91)$$

This allows a global error bound obtained in terms of T.

CHAPTER 7 CALCULATIONS

7.0

To support the model equations, our data extracted from the study carried out on soils in U.S.A i.e. Webster silty clay loam (molisol) from Iowa, Cecil sandy loam (ultisol) from Georgia, and Eutis fine sand (Entisol) from Florida. These soils were selected on the basis of their taxonomic and textural representation of major U.S.A soils. Surface samples taken from depth range of 0 – 30 cm depth of each soil were dried and passed through a 2 mm sieve prior to storage and use. The information taken from the detailed account is the relevant to our mathematical model and not to give irrelevant information that will make our work to become amorphous. Selected physical and chemical properties of these soils pertinent to this study are listed.

TABLE 1: Physical and chemical properties of soil used in this study

Particle size fraction (%)

Soil	Sand	Silt	Clay	PH (1.1 paste)
Webster	18.4	45.3	7.3	6.5
Cecil	65.8	19.5	14.7	4.8
Eustis	93.8	3.0	3.2	4.1

We can use the locally available soil samples if the relevant properties have been experimentally determined

Pesticides:

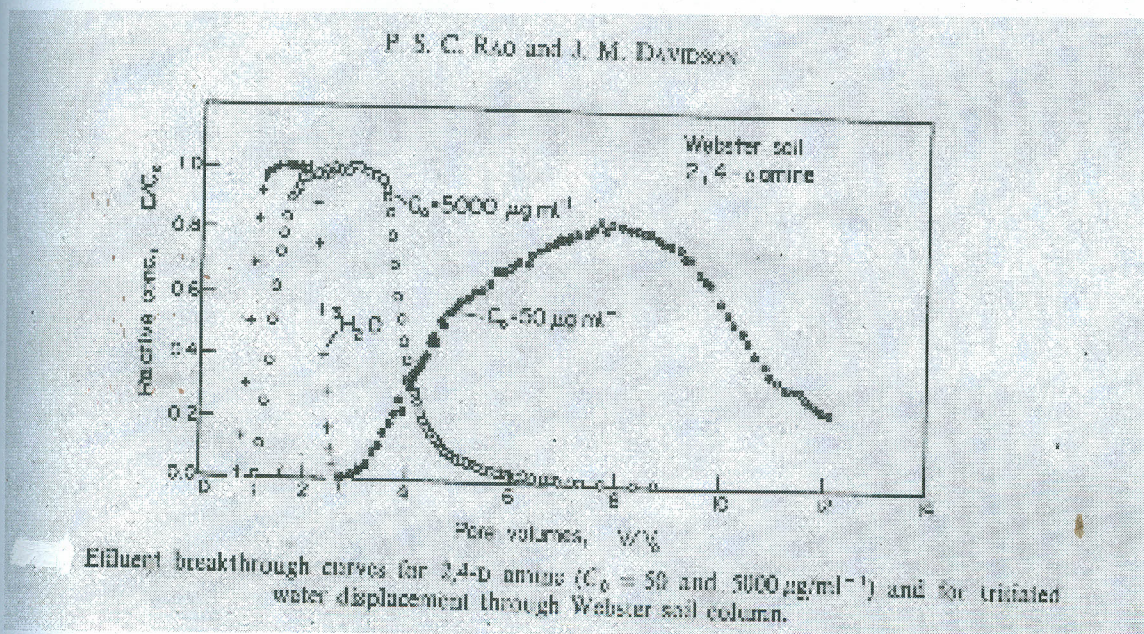
Four pesticides used in this study were 2, 4-d [2,4 Dichlorophenoxyacetic acid], atrazine [2- chloro- 4 – ethylamino – 6 – Isopylamino – 5 – triazine], terbacil [3-tert – butly – 5 – chloro – 6 – Methyluracil], and methyl parathion [0 – 0 – dimethly – 0 – p – nitrophenly phosphorothioate]

Column Displacement experiments (Relevant information)

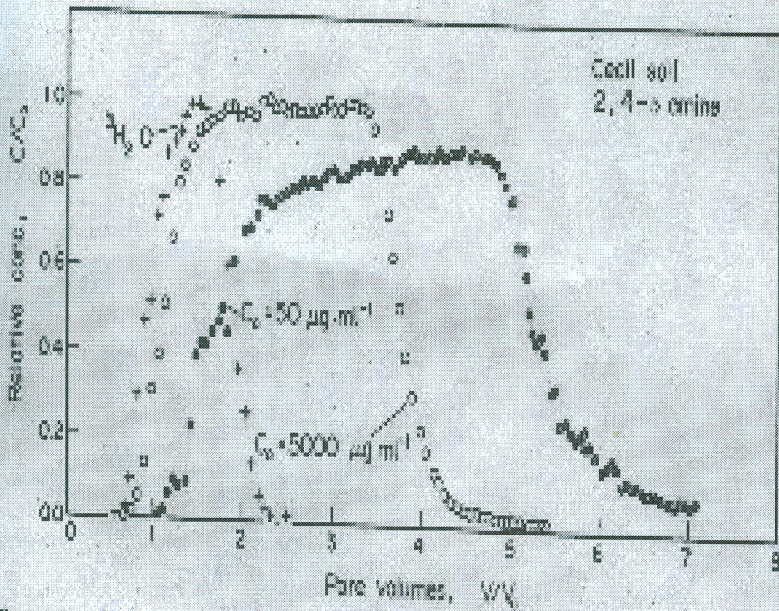
- Pesticides movement through saturated columns of Webster, cecil and Eutis soils was studied using miscible displacement technique [Davidson et al 1968 [18]
- Air dried soils were packed in small increments into glass cylinders (15 cm long: 45 cm squared cross sectional area)
- Medium porosity fitted glass end plates served to retain the soil in column.
- A known volume of pesticide solution at a desired concentration was introduced into soil at a constant flux using a constant volume peristaltic pump.
- The column experiments consisted of displacing 2, 4 – damine solution at two concentrations (i.e. 50 and 500 μgMI^{-1}) through the columns of cecil, Eutis and webster's soil and 5 to 50 μgMI^{-1} of atrazine through Eustis soil.
- All displacements were performed at a Darcy flux of approximately 0.22 cm/h to ensure equilibrium condition of pesticide adsorption during flow.
- The volume of water held in the soil column V_0 was gravimetrically determined at the end of each displacement by extruding the soil from glass cylinders and over drying

- The number of pore volume $\left(\frac{V}{V_0}\right)$ was calculated by dividing the cumulative outflow volume (V) by the total water volume V_0 in the soil column. Effluent pesticide concentration is expressed as relative effluent and input concentration $\left(\frac{C}{C_0}\right)$ where C and C_0 are, respectively. Plots of $\frac{C}{C_0}$ vs $\frac{V}{V_0}$ referred to as breakthrough curves (or BTC)

BTC. 4 Numbers Graphs

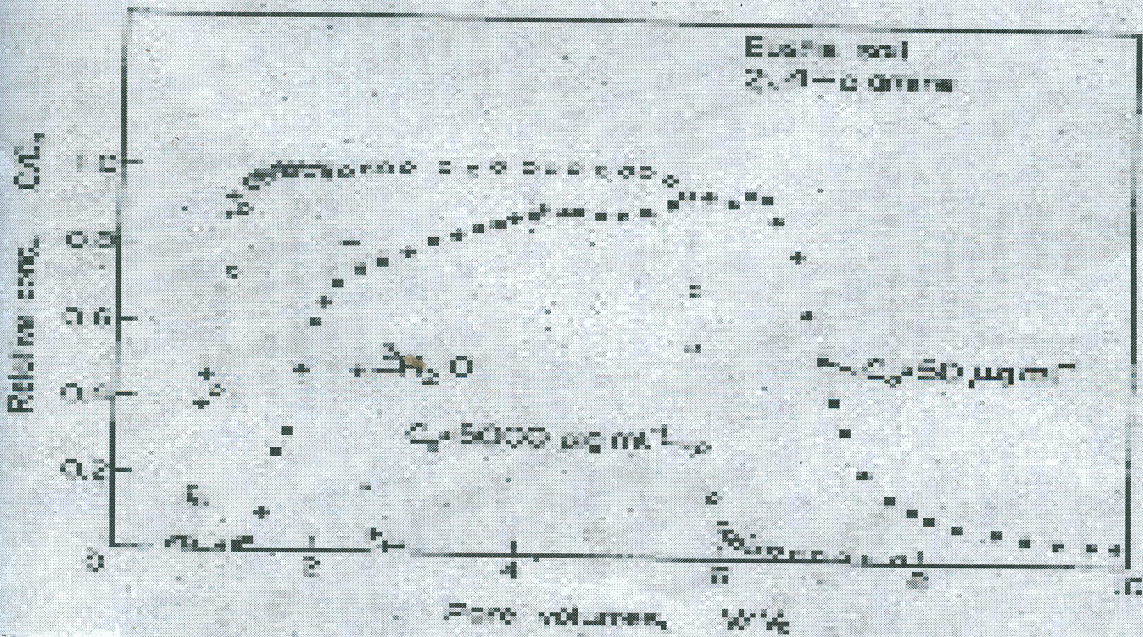


Graph 1



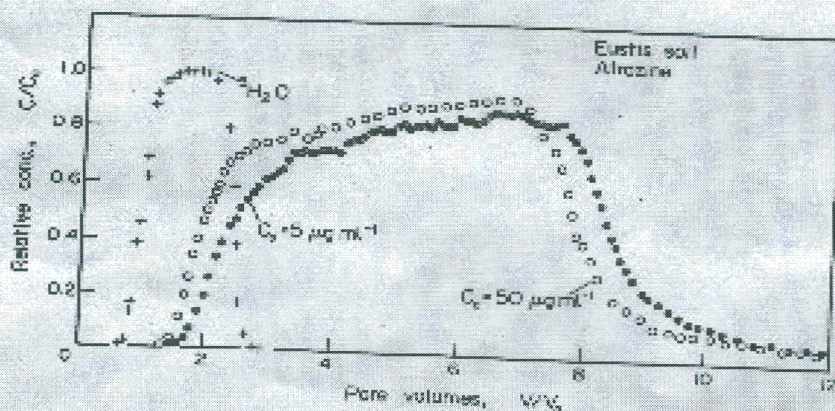
Effluent breakthrough curves for 2,4-D amine ($C_0 = 50$ and $5000 \mu g \cdot ml^{-1}$) and for tritiated water displacement through Cecil soil column.

Graph 2



Effluent breakthrough curves for 2,4-D amine ($C_0 = 50$ and $5000 \mu g \cdot ml^{-1}$) and for tritiated water displacement through Ezatis soil column.

Graph 3



Effluent breakthrough curves for atrazine ($C_0 = 5$ and $50 \mu\text{g ml}^{-1}$) and for distilled water displacement through Eustis soil column.

Graph 4

TABLE 2: Shows Freundlich constants calculated from equilibrium adsorption isotherm for various soil pesticide combination.

Pesticide	Soil	Kd	N
2,4 - d amine	Webster	4.62	0.70
	Cecil	0.65	0.83
	Eustis	0.76	0.76
Atrazine	Webster	6.03	0.73
	Cecil	0.89	1.04
	Eustis	0.62	0.79
Terbacil	Webster	2.46	0.88
	Cecil	0.38	0.99
	Eustis	0.12	0.88
Methly Parathion	Webster	13.39	0.75
	Cecil	3.95	0.85
	Eustis	2.72	0.86

In this analysis we will use 2, 4 - D amine on webster soil to quality our mathematical model.

Data extracted and calculated.

Generally at low rates of flow the effect of molecular diffusion predominate and cell mixing contributes relatively

to dispersion. But in liquids, molecular diffusion is insignificant at Reynold number upto unity [31]

Whatever the mechanism, however, the rate of dispersion can conveniently be described by dispersion coefficient

The dispersion rate in longitudinal and radial direction is represented by D_L and D_R respectively used in representing the behavior in two directions. The process is normally linear, with rates of dispersion proportional to the products of the corresponding coefficients and concentration gradients.

$$\text{Reynold number} = \frac{U_c d \rho}{\mu}$$

$$\text{Peclet number} = \frac{U_c d}{e D_{L \text{ or } D_R}}$$

$$\text{Schmidt number} = \frac{\mu}{\rho D_{L \text{ or } D_R}}$$

With liquids, Schmidt number is variable and is generally about three orders of magnitude greater than gases [31]

From the results in the literature pertaining longitudinal dispersion in liquids [31], it is shown that over a range of Reynolds number studied ($10^2 < Re_c < 10^3$) Peclet number show little variation and is of order of unity.

Given the sieve size used in experiment is of size 2 mm, our particle diameter is 2 mm. Void ration for such size of packing is =0.402.

- Taking our cylindrical vessel to be full ,

$$\text{Total volume} = 15 \times 45 = 675 \text{ cm}^3$$

$$\frac{V_V}{V_S} = 0.402 \quad \text{where } V_V - \text{volume of voids}$$

V_S - volume of solids

$$V_T = V_V + V_S$$

$$\frac{V_T - V_S}{V_S} = 0.402$$

$$V_T = (1.402)V_S$$

$$V_S = 482 \text{ cm}^3$$

- Given that the soil is saturated 100% volume of water in the soil =675 - 482

$$=193 \text{ cm}^3$$

- Darcy's flux = 0.22 cm/hr,

$$V = \frac{Q}{\theta} = \frac{0.22}{0.402} = 0.547 \text{ cm/hr}$$

where V is the pore water velocity.

- From our earlier literature, pecllet number in liquids is approximately equals to unity despite the varying Reynolds no

$$Pe = \frac{Ucd}{eD_L} = \frac{0.547(0.2)}{D_L}$$

$$D_L = 0.547 \times 0.2 = 0.11 \text{ cm}^2 / \text{hr}$$

- Based on the same concept

$$D_R = 0.11 \text{ cm}^2 / \text{hr}$$

- From the break through curve [18] Webster soil; results with 2-4- Δ amine pesticide

$$\frac{V}{V_0} = 1.05 \quad \text{for } 5000 \mu\text{gml}^{-1}$$

$$\frac{V}{V_0} = 2.75 \quad \text{for } 50 \mu\text{gml}^{-1}$$

where V is the amount of solution gone through the cylinder without pesticides i.e there was no detectable amount of pesticide in this solution meaning that the pesticide had been adsorbed completely.

Using V we can determine the amount of time taken for the adsorption to take place leaving no traces of pesticides.

$$V_0 = 193 \text{ cm}^3$$

- For pesticide concentration of $5000 \mu\text{gml}^{-1}$,

$$V = 1.05 \times 193 = 203 \text{ cm}^3$$

$$t = \frac{203}{45 \times 0.22} = 20.50 \text{ hrs}$$

$$X - \text{Section area} = 45 \text{ cm}^2$$

$$Q = 0.22 \text{ cm/hr.}$$

- For $50 \mu\text{gml}^{-1}$

$$V = 2.75 \times 193 = 530.75 \text{ cm}^3$$

$$t = 53.6 \text{ hrs.}$$

where t is the time taken for adsorption process to go on through the cylinder

Without any concentration going beyond the porous end.

$$X = 15 \text{ cm}$$

$$y = 15 \text{ cm}$$

$$D_x = D_y = h = 0.3 \text{ cm}$$

$$k = \Delta t_{(5000 \mu\text{gml}^{-1})} = 0.41 \text{ hrs}$$

$$k = \Delta t_{(50 \mu\text{gml}^{-1})} = 1.072 \text{ hrs}$$

$$\rho_b = \frac{V_s G + V_0 \gamma_w}{V_T}$$

γ_w - specific gravity of water.

G - specific gravity of soil = 2.68

$$= \frac{482 \times 2.68 + 193 \times 1}{675}$$

$$= 2.2 \text{ gcm}^3$$

From equation A, B, C, D and E we can determine the coefficients and subsequently $C_{i,j}^n$

$$R(C_{i,j}^n) = \left[1 + \frac{P_b}{\theta} KN (C_{i,j}^n)^{N-1} \right]$$

$$= \left[1 + 17.7 (C_{i,j}^n)^{-0.3} \right]$$

$$N = 0.7$$

$$\theta = 0.402$$

$$K = 4.62$$

For $5000 \mu\text{gml}^{-1}$ pesticide coefficients,

$$A = \frac{0.12733}{R(C_{i,j}^n)},$$

$$B = 1 - \frac{2.0004}{R(C_{i,j}^n)},$$

$$C = \frac{0.8749}{R(C_{i,j}^n)},$$

$$D = \frac{0.15033}{R(C_{i,j}^n)} \left(\frac{1}{h} + \frac{0.5}{y_j} \right),$$

$$E = \frac{0.15033}{R(C_{i,j}^n)} \left(\frac{1}{h} - \frac{0.5}{y_j} \right),$$

$$\Delta t = k = 0.41 \text{ hrs}$$

$$\Delta x = \Delta y = h = 0.30 \text{ cm}$$

For $50 \mu\text{gml}^{-1}$ pesticide concentration

$$A = \frac{0.33292}{R(C_{i,j}^n)},$$

$$B = 1 - \frac{5.2489}{R(C_{i,j}^n)},$$

$$C = \frac{2.2875}{R(C_{i,j}^n)},$$

$$D = \frac{0.39307}{R(C_{i,j}^n)} \left(\frac{1}{h} + \frac{0.5}{y_j} \right),$$

$$E = \frac{0.39307}{R(C_{i,j}^n)} \left(\frac{1}{h} - \frac{0.5}{y_j} \right).$$

The general formula for determining concentration with time is

$$C_{I,J}^{n+1} = AC_{i+1,j}^n + BC_{i,j}^n + CC_{i-1,j}^n + DC_{i,j+1}^n + EC_{i,j-1}^n.$$

$$\Delta t = k = 1.072 \text{ hrs}$$

$$\Delta x = \Delta y = h = 0.30 \text{ cm}$$

From the equation 5.0, we get the coefficients for one dimension equation analysis.

$$A = \frac{k}{R(C_i^n)} \left(\frac{D}{h} - \frac{V}{2} \right),$$

$$B = \left(1 - \frac{2kD}{R(C_i^n)h^2} \right),$$

$$C = \frac{k}{R(C_i^n)h} \left(\frac{D}{h} + \frac{V}{2} \right),$$

$$C_i^{n+1} = AC_{i+1}^n + BC_i^n + CC_{i-1}^n.$$

ONE DIMENSIONAL ANALYSIS

$\mu\text{gml}^{-1} (C_i^n)$

$R(C_i^n)$

Sno.	x	t/hrs	h/cm	Dt/k/hrs	Pesticide Concentration	
1	0.00	0	0	0	50	
2	0.30	1.072	0.3	1.072	49	6.5070
3	0.60	2.144	0.3	1.072	48	6.5412
4	0.90	3.216	0.3	1.072	47	6.5412
5	1.20	4.288	0.3	1.072	46	6.5763
6	1.50	5.36	0.3	1.072	45	6.6124
7	1.80	6.432	0.3	1.072	44	6.6495
8	2.10	7.504	0.3	1.072	43	6.6877
9	2.40	8.576	0.3	1.072	42	6.7271
10	2.70	9.648	0.3	1.072	41	6.7676
11	3.00	10.72	0.3	1.072	40	6.8095
12	3.30	11.792	0.3	1.072	39	6.8527
13	3.60	12.864	0.3	1.072	38	6.8973

14	3.90	13.936	0.3	1.072	37	6.9434
15	4.20	15.008	0.3	1.072	36	6.9912
16	4.50	16.08	0.3	1.072	35	7.0406
17	4.80	17.152	0.3	1.072	34	7.0919
18	5.10	18.224	0.3	1.072	33	7.1451
19	5.40	19.296	0.3	1.072	32	7.2004
20	5.70	20.368	0.3	1.072	31	7.2579
21	6.00	21.44	0.3	1.072	30	7.3178
22	6.30	22.512	0.3	1.072	29	7.3802
23	6.60	23.584	0.3	1.072	28	7.4455
24	6.90	24.656	0.3	1.072	27	7.5137
25	7.20	25.728	0.3	1.072	26	7.5851
26	7.50	26.8	0.3	1.072	25	7.6601
27	7.80	27.872	0.3	1.072	24	7.7389
28	8.10	28.944	0.3	1.072	23	7.8220
29	8.40	30.016	0.3	1.072	22	7.9096
30	8.70	31.088	0.3	1.072	21	8.0080
31	9.00	32.16	0.3	1.072	20	8.2055
32	9.30	33.232	0.3	1.072	19	8.3172
33	9.60	34.304	0.3	1.072	18	8.4369
34	9.90	35.376	0.3	1.072	17	8.5655
35	10.20	36.448	0.3	1.072	16	8.7044
36	10.50	37.52	0.3	1.072	15	8.8550
37	10.80	38.592	0.3	1.072	14	9.0193
38	11.10	39.664	0.3	1.072	13	9.1996
39	11.40	40.736	0.3	1.072	12	9.3988
40	11.70	41.808	0.3	1.072	11	9.6210
41	12.00	42.88	0.3	1.072	10	9.8710
42	12.30	43.952	0.3	1.072	9	10.1589
43	12.60	45.024	0.3	1.072	8	10.4852
44	12.90	46.096	0.3	1.072	7	10.8729
45	13.20	47.168	0.3	1.072	6	11.3402
46	13.50	48.24	0.3	1.072	5	11.9215
47	13.80	49.312	0.3	1.072	4	12.6777
48	14.10	50.384	0.3	1.072	3	13.7363
50	14.70	52.528	0.3	1.072	1	18.7000
51	15.00	53.6	0.3	1.072	0	1.0000

CONCENTRATION AND COEFFICIENT OF ONE DIMENSIONAL ANALYSIS

Sno.	A	B	C	C_i^{n+1}
1	0	0	0	
2	0.05112	0.597295	0.35155	49.300
3	0.05089	0.5994	0.34971	48.299
4	0.05062	0.60154	0.34784	47.297
5	0.05035	0.60371	0.34594	46.296
6	0.05006	0.60593	0.3440	45.294
7	0.04978	0.6082	0.34200	44.291
8	0.04949	0.61047	0.3400	43.291
9	0.04919	0.612802	0.3380	42.288
10	0.04889	0.615185	0.33603	41.291
11	0.04857	0.61761	0.33381	40.284
12	0.04827	0.62008	0.33282	39.330
13	0.04795	0.62261	0.32945	38.282
14	0.04976	0.6252	0.32720	37.357
15	0.04727	0.62782	0.32490	36.277
16	0.04694	0.63051	0.32255	35.275
17	0.04659	0.63326	0.3202	34.274
18	0.046233	0.63608	0.31769	33.272
19	0.045867	0.638959	0.31517	32.269
20	0.045492	0.64191	0.31259	31.267
21	0.04511	0.644966	0.30995	30.266
22	0.04471	0.64806	0.30723	29.262
23	0.04431	0.65125	0.30444	28.260
24	0.043889	0.654533	0.30158	27.252
25	0.043459	0.657916	0.29862	26.255
26	0.043016	0.6614	0.29558	25.253
27	0.042560	0.664996	0.292444	24.248
28	0.042088	0.66871	0.28921	23.247
29	0.041600	0.67255	0.28585	22.244
30	0.041095	0.67653	0.28238	21.241
31	0.04057	0.68065	0.27878	20.238
32	0.040025	0.68494	0.27503	19.235
33	0.039458	0.68947	0.27113	18.233
34	0.038865	0.69408	0.26706	17.228
35	0.038245	0.69896	0.26279	16.225
36	0.03759	0.70408	0.25833	15.221
37	0.03691	0.70947	0.25362	14.217
38	0.036186	0.71516	0.24865	13.213
39	0.03542	0.7212	0.24338	12.208
40	0.03460	0.72763	0.23776	11.203
41	0.03373	0.73454	0.23174	10.198
42	0.03277	0.74206	0.22517	9.192
43	0.03175	0.75005	0.21817	8.187
44	0.030618	0.75899	0.21039	7.180
45	0.029356	0.76893	0.20172	6.172
46	0.02792	0.7802	0.19188	5.164
47	0.62626	0.79331	0.18043	4.154
48	0.02425	0.80915	0.16660	3.142
49	0.021649	0.82959	0.14876	2.127
50	0.017802	0.85987	0.12233	1.105

ONE
DIMENSIONAL
ANALYSIS

$$\mu\text{gml}^{-1} (C_i^n)$$

Sno.	x	t/hrs	h/cm	Dt/k/hrs	Pesticide Concentration	$R(C_i^n)$
1	0.00	0	0	0	5000	
2	0.30	0.41	0.3	0.41	4900	2.3833
3	0.60	0.82	0.3	0.41	4800	2.3919
4	0.90	1.23	0.3	0.41	4700	2.4007
5	1.20	1.64	0.3	0.41	4600	2.4098
6	1.50	2.05	0.3	0.41	4500	2.4191
7	1.80	2.46	0.3	0.41	4400	2.4287
8	2.10	2.87	0.3	0.41	4300	2.4386
9	2.40	3.28	0.3	0.41	4200	2.4488
10	2.70	3.68	0.3	0.41	4100	2.4593
11	3.00	4.10	0.3	0.41	4000	2.4701
12	3.30	4.51	0.3	0.41	3900	2.4813
13	3.60	4.92	0.3	0.41	3800	2.4929
14	3.90	5.33	0.3	0.41	3700	2.5049
15	4.20	5.74	0.3	0.41	3600	2.5173
16	4.50	6.15	0.3	0.41	3500	2.5302
17	4.80	6.56	0.3	0.41	3400	2.5436
18	5.10	6.97	0.3	0.41	3300	2.5575
19	5.40	7.38	0.3	0.41	3200	2.5719
20	5.70	7.79	0.3	0.41	3100	2.5869
21	6.00	8.2	0.3	0.41	3000	2.6026
22	6.30	8.61	0.3	0.41	2900	2.6190
23	6.60	9.02	0.3	0.41	2800	2.6362
24	6.90	9.43	0.3	0.41	2700	2.6541
25	7.20	9.84	0.3	0.41	2600	2.6729
26	7.50	10.25	0.3	0.41	2500	2.6927
27	7.80	10.66	0.3	0.41	2400	2.7136
28	8.10	11.07	0.3	0.41	2300	2.7353
29	8.40	11.48	0.3	0.41	2200	2.7589
30	8.70	11.89	0.3	0.41	2100	2.7836
31	9.00	12.30	0.3	0.41	2000	2.8099
32	9.30	12.71	0.3	0.41	1900	2.838
33	9.60	13.12	0.3	0.41	1800	2.8681
34	9.90	13.53	0.3	0.41	1700	2.9004
35	10.20	13.94	0.3	0.41	1600	2.9353
36	10.50	14.35	0.3	0.41	1500	2.9731
37	10.80	14.76	0.3	0.41	1400	3.014
38	11.10	15.17	0.3	0.41	1300	3.0596
39	11.40	15.58	0.3	0.41	1200	3.1097
40	11.70	15.99	0.3	0.41	1100	3.1655
41	12.00	16.40	0.3	0.41	1000	3.2283
42	12.30	16.81	0.3	0.41	900	3.2999
43	12.60	17.22	0.3	0.41	800	3.3826

44	12.90	17.63	0.3	0.41	700	3.48
45	13.20	18.04	0.3	0.41	600	3.5973
46	13.50	18.45	0.3	0.41	500	3.7434
47	13.80	18.86	0.3	0.41	400	3.9333
48	14.10	19.27	0.3	0.41	300	4.1977
49	14.10	19.68	0.3	0.41	200	4.6113
50	14.70	20.09	0.3	0.41	100	5.446
51	15.00	20.50	0.3	0.41	0	1.0000

CONCENTRATION AND COEFFICIENT OF ONE DIMENSIONAL ANALYSIS

Sno.	A	B	C	C_i^{n+1}
1				
2	0.053413	0.57949	0.36710	4931.38
3	0.05322	0.58100	0.36578	4831.26
4	0.053026	0.58254	0.36444	4731.17
5	0.052826	0.58411	0.363059	4631.00
6	0.052623	0.58571	0.363059	4530.89
7	0.05242	0.58735	0.36023	4430.76
8	0.052202	0.58903	0.35877	4330.67
9	0.051985	0.59074	0.357277	4230.54
10	0.051763	0.592486	0.355772	4130.40
11	0.051564	0.594267	0.354196	4030.37
12	0.051304	0.596099	0.352597	3930.13
13	0.051065	0.597978	0.350957	3829.99
14	0.050820	0.599904	0.349275	3729.84
15	0.0505701	0.601875	0.347555	3629.70
16	0.050312	0.603905	0.34578	3529.54
17	0.050047	0.60599	0.34396	3429.81
18	0.049775	0.608133	0.34209	3329.23
19	0.49497	0.610327	0.34018	3229.08
20	0.049209	0.612587	0.33820	3129.76
21	0.049209	0.614924	0.336164	3028.73
22	0.048606	0.617335	0.334055	2928.55
23	0.04829	61983	0.33188	2828.36
24	0.047964	0.62052	0.331276	2727.68
25	0.04763	0.625051	0.32732	2627.97
26	0.04728	0.627809	0.32492	2527.79
27	0.046912	0.63068	0.32241	2427.56
28	0.04654	0.63361	0.319855	2427.34
29	0.04614	0.63674	0.31712	2227.10
30	0.04573	0.63996	0.3143	2126.85
31	0.0453	0.64333	0.31136	2026.59
32	0.04486	0.64686	0.3083	1926.34
33	0.04438	0.6506	0.30505	1826.11
34	0.04389	0.65446	0.30165	1725.77
35	0.04337	0.65856	0.29806	1625.46
36	0.04282	0.66291	0.29427	1525.15
37	0.04224	0.66749	0.29028	1424.82
38	0.041607	0.67244	0.28595	1324.43

39	0.040936	0.67772	0.28135	1224.04
40	0.040215	0.683399	0.276386	1123.62
41	0.03943	0.68956	0.27101	1023.16
42	0.038577	0.69629	0.26513	922.65
43	0.03763	0.70372	0.25865	822.10
44	0.03658	0.7120	0.25141	721.47
45	0.03539	0.7214	0.24321	620.78
46	0.034006	0.7322	0.23372	519.93
47	0.030326	0.7452	0.22243	419.00
48	0.030326	0.76125	0.20842	317.81
49	0.027606	0.78266	0.18973	216.21
50	0.23375	0.815975	0.16065	113.72
51				0.00

TWO DIMENSIONAL ANALYSIS

Sno.	$x_i = y_j$	t/hrs	h/cm	$k = \Delta t$	$\mu\text{gml}^{-1}(C^{n_i, j})$	$R(C^{n_i, j})$
					Pesticide concentration	
1	0	0	0	0	50	
2	0.30	1.072	0.3	1.072	49	6.507
3	0.60	2.144	0.3	1.072	48	6.5412
4	0.90	3.216	0.3	1.072	47	6.5763
5	1.20	4.288	0.3	1.072	46	6.6124
6	1.50	5.360	0.3	1.072	45	6.6495
7	1.80	6.432	0.3	1.072	44	6.6877
8	2.10	7.504	0.3	1.072	43	6.7271
9	2.40	8.576	0.3	1.072	42	6.7676
10	2.70	9.648	0.3	1.072	41	6.8095
11	3.00	10.720	0.3	1.072	40	6.8527
12	3.30	11.792	0.3	1.072	39	6.8973
13	3.60	12.864	0.3	1.072	38	6.9434
14	3.90	13.936	0.3	1.072	37	6.9912
15	4.20	15.008	0.3	1.072	36	7.0406
16	4.50	16.080	0.3	1.072	35	7.0919
17	4.80	17.152	0.3	1.072	34	7.1451
18	5.10	18.224	0.3	1.072	33	7.2004
19	5.40	19.296	0.3	1.072	32	7.2579
20	5.70	20.368	0.3	1.072	31	7.3178
21	6.00	21.440	0.3	1.072	30	7.3802
22	6.30	22.512	0.3	1.072	29	7.4455
23	6.60	23.584	0.3	1.072	28	7.5137
24	6.90	24.656	0.3	1.072	27	7.5851
25	7.20	25.728	0.3	1.072	26	7.6601
26	7.50	26.800	0.3	1.072	25	7.7389
27	7.80	27.872	0.3	1.072	24	7.8220
28	8.10	28.944	0.3	1.072	23	7.9096
29	8.40	30.016	0.3	1.072	22	8.0024
30	8.70	31.088	0.3	1.072	21	8.1008
31	9.00	32.160	0.3	1.072	20	8.2055
32	9.30	33.232	0.3	1.072	19	8.3172
33	9.60	34.304	0.3	1.072	18	8.4369
34	9.90	35.376	0.3	1.072	17	8.5655
35	10.20	36.448	0.3	1.072	16	8.7044
36	10.50	37.52	0.3	1.072	15	8.8550
37	10.80	38.592	0.3	1.072	14	9.0193
38	11.10	39.664	0.3	1.072	13	9.1996
39	11.40	40.736	0.3	1.072	12	9.3988
40	11.70	41.808	0.3	1.072	11	9.6210
41	12.00	42.88	0.3	1.072	10	9.8710
42	12.30	43.952	0.3	1.072	9	10.1589
43	12.60	45.024	0.3	1.072	8	10.4852
44	12.90	46.096	0.3	1.072	7	10.8729
45	13.20	47.168	0.3	1.072	6	11.3402
46	13.50	48.24	0.3	1.072	5	11.9215
47	13.80	49.312	0.3	1.072	4	12.6777

48	14.10	50.384	0.3	1.072	3	13.7303
49	14.10	51.456	0.3	1.072	2	15.3769
50	14.70	52.528	0.3	1.072	1	18.7000
51	15.00	53.60	0.3	1.072	0	1.0000

$$2(1.072)(0.22) \leq 0.3^2(18.7)$$

$$0.47168 \leq 1.683$$

CONCENTRATION AND COEFFICIENT OF TWO DIMENSIONAL ANAL

$C_{i,j}^{n+1}$
 $\mu\text{g/ml}$

Sno.	A	B	C	D	E	
1						50
2	0.051163	0.19335	0.35155	0.30204	0.10068	49.04
3	0.05090	0.197563	0.34971	0.2504	0.15023	48.14
4	0.05062	0.20185	0.34794	0.23244	0.16603	47.21
5	0.05035	0.2062	0.34594	0.22292	0.17338	46.19
6	0.05007	0.21063	0.34401	0.21675	0.17734	45.20
7	0.04981	0.215141	0.342046	0.210981	0.17981	44.06
8	0.04949	0.21974	0.34004	0.20868	0.180857	43.22
9	0.04919	0.22441	0.33801	0.205704	0.181504	42.22
10	0.048891	0.22918	0.33593	0.20310	0.181723	41.20
11	0.048582	0.23417	0.33381	0.20076	0.18164	40.22
12	0.048268	0.238992	0.331651	0.198598	0.181329	39.22
13	0.047948	0.244045	0.32945	0.195555	0.180840	38.18
14	0.04762	0.249213	0.327197	0.19420	0.180204	37.20
15	0.04729	0.254481	0.32490	0.192743	0.179451	36.22
16	0.046944	0.259874	0.32255	0.1909091	0.17859	35.22
17	0.046594	0.26539	0.32015	0.18911	0.17765	34.23
18	0.046236	0.27103	0.31770	0.18732	0.17661	33.22
19	0.045870	0.2768	0.315179	0.18554	0.17551	32.22
20	0.045495	0.28272	0.312595	0.183597	0.17434	31.22
21	0.04511	0.28879	0.309951	0.181972	0.1731	30.22
22	0.044714	0.295024	0.30723	0.180167	0.171787	29.22
23	0.04431	0.301423	0.304444	0.178342	0.170416	28.22
24	0.0438913	0.307999	0.301578	0.17493	0.168983	27.18
25	0.043462	0.314774	0.298625	0.17461	0.167483	26.26
26	0.043019	0.321751	0.295585	0.172691	0.1659187	25.22
27	0.042562	0.32956	0.292444	0.170727	0.1642849	24.22
28	0.042091	0.3363887	0.289206	0.168719	0.16251	23.21
29	0.0416025	0.3340843	0.2858517	0.166654	0.1608063	22.22
30	0.04109717	0.352052	0.2823795	0.16453	0.1589526	21.21
31	0.0405728	0.360319	0.278776	0.1623387	0.156758	20.21
32	0.0400279	0.36891	0.27503	0.160074	0.15499	19.21
33	0.03946	0.377864	0.27113	0.157725	0.15287	18.21
34	0.038868	0.038868	0.26706	0.15528	0.1506487	17.21
35	0.038247	0.396983	0.262798	0.152739	0.148312	16.21
36	0.037597	0.40724	0.25833	0.15008	0.145852	15.20
37	0.036912	0.418037	0.2536623	0.147288	0.143252	14.20
38	0.0361887	0.42944	0.248653	0.144348	0.140499	13.20
39	0.036099	0.441535	0.243382	0.141239	0.13757	12.20
40	0.034604	0.454433	0.237761	0.137931	0.134439	11.19
41	0.0337271	0.468250	0.231739	0.134395	0.131076	10.19
42	0.032771	0.48332	0.225172	0.130547	0.12740	9.18
43	0.031751	0.49940	0.218165	0.126448	0.12347	8.18
44	0.030619	0.517250	0.210385	0.121906	0.11910	7.17
45	0.0293575	0.537142	0.201716	0.116852	0.114226	6.17
46	0.027926	0.559711	0.191880	0.111126	0.108684	5.16
47	0.0262603	0.585973	0.180435	0.104473	0.102226	4.15
48	0.024247	0.617714	0.166602	0.096442	0.04411	3.14
49	0.021651	0.658650	0.148762	0.086095	0.084320	2.12
50	0.017803	0.71931	0.122326	0.070781	0.069351	1.10
51						0.00

TWO DIMENSIONAL ANALYSIS

Sno.	$x_i = y_j$	t/hrs	h/cm	$k = \Delta t$	$\mu\text{gml}^{-1}(C^n_{i,j})$	$R(C^n_{i,j})$
					Pesticide concentration	
1	0.00	0.00	0	0	5000	
2	0.30	0.41	0.3	0.41	4900	2.3833
3	0.60	0.82	0.3	0.41	4800	2.3919
4	0.90	1.23	0.3	0.41	4700	2.4007
5	1.20	1.64	0.3	0.41	4600	2.4098
6	1.50	2.05	0.3	0.41	4500	2.4191
7	1.80	2.46	0.3	0.41	4400	2.4287
8	2.10	2.87	0.3	0.41	4300	2.4386
9	2.40	3.28	0.3	0.41	4200	2.4488
10	2.70	3.69	0.3	0.41	4100	2.4593
11	3.00	4.10	0.3	0.41	4000	2.4701
12	3.30	4.51	0.3	0.41	3900	2.4813
13	3.60	4.92	0.3	0.41	3800	2.4929
14	3.90	5.33	0.3	0.41	3700	2.5049
15	4.20	5.74	0.3	0.41	3600	2.5173
16	4.50	6.15	0.3	0.41	3500	2.5302
17	4.80	6.56	0.3	0.41	3400	2.5436
18	5.10	6.97	0.3	0.41	3300	2.5575
19	5.40	7.38	0.3	0.41	3200	2.5719
20	5.70	7.79	0.3	0.41	3100	2.5869
21	6.00	8.20	0.3	0.41	3000	2.6026
22	6.30	8.61	0.3	0.41	2900	2.6190
23	6.60	9.02	0.3	0.41	2800	2.6362
24	6.90	9.43	0.3	0.41	2700	2.6541
25	7.20	9.84	0.3	0.41	2600	2.6729
26	7.50	10.25	0.3	0.41	2500	2.6927
27	7.80	10.66	0.3	0.41	2400	2.7136
28	8.10	11.07	0.3	0.41	2300	2.7356
29	8.40	11.48	0.3	0.41	2200	2.7589
30	8.70	11.89	0.3	0.41	2100	2.7836
31	9.00	12.30	0.3	0.41	2000	2.8099
32	9.30	12.71	0.3	0.41	1900	2.838
33	9.60	13.12	0.3	0.41	1800	2.8681
34	9.90	132.53	0.3	0.41	1700	2.9004
35	10.20	13.94	0.3	0.41	1600	2.9353
36	10.50	14.35	0.3	0.41	1500	2.9731
37	10.80	14.76	0.3	0.41	1400	3.014
38	11.10	15.17	0.3	0.41	1300	3.0596
39	11.40	15.58	0.3	0.41	1200	3.1097
40	11.70	15.99	0.3	0.41	1100	3.1655
41	12.00	16.40	0.3	0.41	1000	3.2283
42	12.30	16.81	0.3	0.41	900	3.2999
43	12.60	17.22	0.3	0.41	800	3.3826

44	12.90	17.63	0.3	0.41	700	3.4800
45	13.20	18.04	0.3	0.41	600	3.5973
46	13.50	18.45	0.3	0.41	500	3.7434
47	13.80	18.86	0.3	0.41	400	3.9333
48	14.10	19.27	0.3	0.41	300	4.1977
49	14.10	19.68	0.3	0.41	200	4.6113
50	14.70	20.09	0.3	0.41	100	5.4460
51	15.00	20.50	0.3	0.41	0	1

$$2 k [Dx + Dy] \leq h^2 MaxR (C_{i,j}^n)$$

$$MaxR (C_{i,j}) = 5.446$$

$$Dx = Dy = 0.11 \text{ cm}^2 / \text{hr}$$

$$2 (0.41) (0.11 + 0.11) \leq (0.3)^2 (5.446)$$

$$0.1804 \leq 0.49014$$

CONCENTRATION AND COEFFICIENT OF TWO DIMENSIONAL ANALYSIS

$$C_{i,j}^{n+1} / \mu\text{gml}^{-1}$$

Sno.	A	B	C	D	E	
1						5000
2	0.0534	0.15898	0.3671	0.3154	0.1051	4910
3	0.0532	0.16201	0.3658	0.2619	0.1571	4821
4	0.0530	0.1651	0.3644	0.2435	0.17394	4748
5	0.0524	0.16823	0.3631	0.2339	0.1819	4626
6	0.05264	0.1716	0.3617	0.2279	0.1864	4528
7	0.05242	0.1747	0.3602	0.2235	0.18913	4427
8	0.05221	0.1781	0.3588	0.2202	0.1908	4328
9	0.05199	0.1815	0.3573	0.2174	0.1918	4228
10	0.05178	0.18497	0.35575	0.2151	0.1924	4128
11	0.05155	0.18853	0.354196	0.21301	0.19272	4028
12	0.05132	0.192198	0.352597	0.21113	0.19277	3928
13	0.051077	0.19596	0.35096	0.209386	0.192635	3828
14	0.050832	0.199808	0.34928	0.20774	0.192354	3728
15	0.050582	0.20375	0.34755	0.20617	0.191953	3628
16	0.050324	0.20781	0.34578	0.20425	0.19145	3527
17	0.050059	0.21198	0.34396	0.20316	0.190847	3428
18	0.049786	0.216266	0.34209	0.201696	0.190171	3328
19	0.049508	0.220654	0.340176	0.200249	0.189424	3228
20	0.049221	0.225173	0.338204	0.198804	0.188609	3128
21	0.048924	0.23000	0.336164	0.197352	0.187725	3028
22	0.048618	0.2346697	0.33406	0.195888	0.186777	2927
23	0.048301	0.239663	0.331880	0.19440	0.185764	2828
24	0.047975	0.24479	0.329641	0.19291	0.18469	2727
25	0.047637	0.250103	0.32732	0.19138	0.18357	2627
26	0.047287	0.255617	0.32492	0.189818	0.182374	2527
27	0.046923	0.26135	0.32241	0.188214	0.181111	2427
28	0.0465455	0.26729	0.31982	0.186570	0.179785	2327
29	0.0461525	0.273479	0.317119	0.184874	0.178387	2226
30	0.045743	0.27993	0.314305	0.183122	0.176915	2126
31	0.0453148	0.286665	0.311363	0.181306	0.175356	2026
32	0.044866	0.293728	0.308284	0.179416	0.173720	1926
33	0.044395	0.30114	0.30505	0.17745	0.171985	1826
34	0.043901	0.30893	0.30165	0.175387	0.170152	1725
35	0.043379	0.31714	0.29806	0.173226	0.168205	1625
36	0.042827	0.32582	0.294272	0.170952	0.166137	1525
37	0.042246	0.33497	0.290279	0.168567	0.163948	1424
38	0.041617	0.344882	0.28595	0.165993	0.161566	1324
39	0.040946	0.35544	0.281345	0.16326	0.15902	1224
40	0.040224	0.366798	0.276386	0.1603299	0.156271	1123
41	0.039442	0.3791159	0.27101	0.157161	0.15328	1023
42	0.038586	0.392587	0.265129	0.153705	0.15000	922
43	0.037643	0.40744	0.25865	0.149904	0.146377	822
44	0.036589	0.424023	0.251408	0.1456686	0.1423199	721
45	0.035396	0.442804	0.243210	0.140882	0.137716	621
46	0.034015	0.4645509	0.233712	0.1353496	0.132375	520
47	0.032372	0.490402	0.22243	0.128784	0.126015	419
48	0.030333	0.5225	0.208424	0.1206448	0.118105	318
49	0.027613	0.56533	0.18973	0.1097998	0.107536	214

50	0.0233805	0.63195	0.16065	0.092951	0.091074	114
51						0

CHAPTER 8

CONCLUSION

- 1) Our calculations are in agreement with equation (6.7) i.e.

$$2K(D_x + D_y) \leq h^2 \text{MaxR} \left(C_{i,j}^n \right)$$

- 2) The lower the concentration of adsorbate the lower the adsorption which is qualified by the retardation factor which increases with lowering of the concentration i.e. it is inversely proportional to the concentration.
- 3) Explicit method used in one dimensional case produce negative coefficient thus confirming the instability of the method despite the, algebraic addition results but all implicit methods used in one or two dimension cases produce positive coefficients thus confirming the stability of implicit method.

RECOMMENDATIONS:

- 1) More studies need to be carried out on solving the two dimensional equation using analytical methods by introducing linearization factors [26]
- 2) We require a similar experimental study to be carried out on our locally available soils samples.

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