

**MATHEMATICAL MODELING OF PESTICIDE ADSORPTION IN A POROUS
MEDIUM; CONVECTION-DISPERSION TRANSPORT WITH STEADY STATE
WATER FLOW IN THREE DIMENSIONS**

BY

ADAMS, SETH HARRISON WETOYI

**A THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN APPLIED MATHEMATICS**

SCHOOL OF MATHEMATICS, STATISTICS AND ACTUARIAL SCIENCE

**MASENO UNIVERSITY
S.G. S. LIBRARY**

MASENO UNIVERSITY

© 2019

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 since it helps in assessing the effect of migrating chemical from their disposal sites on the quality of groundwater. Most studies done on the movement of pesticides in the ground environment in terms of mathematical models have so far been simulated and emphasis given to axial movement and in a few cases both axial and radial movements. Soil processes have a 3D (three dimensional) character; modeling therefore in principle, should employ three dimensions. It should also be noted that the appropriate number of dimensions is closely related to the required accuracy of the research question. The 1D (one dimension) and 2D (two dimension) approaches are limited since they are not capable of giving dependable regional influence of pesticides movement in the porous media and groundwater. They give only theoretical results which are devoid of the reality in the field due to lumping of parameters. In this study, 3D formula is derived so that it can enhance our capacity to analyze the realistic regional impact of adsorption of pesticides in a porous media and groundwater in the field condition since there is no lumping of parameters. In most cases we are supposed to adopt an existing equation and use it to solve the problem of research but given the many equations, it is wise to derive from the first principle in order to be sure of applicability of the equation to the research problem. The objective of this study is to develop a mathematical model which can be used to determine the combined 3D movement of pesticides with steady - state water flow in a porous media. The methodology involves determining the comprehensive dispersion equation accounting for 3D movement of solutes in the porous media and finding the solution of the governing equation using unconditionally stable finite difference 3D equation. The experimental results based on 1D are applied to 3D based on the dispersion constant being the same longitudinally and laterally at low flow rate in the porous media as informed by Reynold's number being less than 2300 for laminar flows. The equation is applied on the experiment done on adsorption of pesticide through a porous media. The results are applied to the equation and solved up to ten steps in order to test equation's suitability.

MASENO UNIVERSITY
S.G. S. LIBRARY

Chapter 1

Introduction

1.1 Mathematical Background

There are great challenges associated with farming due to increase of pests on both animals and plants. This has created room for manufacturers to cash in on this high demand of pesticides thus leading to increase in quantity and different quality of these pesticides in our markets. The disposal of the surplus and waste pesticide materials has become an acute challenge. The practiced disposal options are incineration, encapsulation, isolation in underground caves and mines, chemical stabilization, land spreading and land filling. Safe disposal of pesticides has an Economic implication, the most economical methods of disposals of pesticides is by landfills and land spread [24]. The contamination of ground water by migration of inorganic and organic pesticides from dumping sites has become an issue of increased concern in years. 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 groundwater environment [3]. Chemicals degrade ground water quality when they migrate from their disposal sites to the aquifers. The study of migration of pesticides from their disposal sites to the underground aquifer has to be understood well so that we can come up with effective ways of protecting groundwater resources from pollution. Predictions of the fate of ground-water contaminants can then be made in order to assess the effect of these chemicals on local water resources and to evaluate the effectiveness of remedial actions.

Two physical processes that govern the movement of ground water solutes are:

1. Advection, which describes the transport of solutes by bulky motion of flowing water in the ground due to pressure and gravitational energy [21].

2. Hydrodynamic dispersion, which describes the spread of solutes along and transverse to the direction of flow resulting from both mechanical mixing and molecular diffusion [16].

This mixing depends on molecular diffusion, geometry of the pores, and distribution of soil water velocity which equally depends on water in the medium. If the velocity of water is zero, the process of mixing occurs purely as a result of diffusion only.

Chemical reaction, including those mediated by micro-organisms or caused by interaction with aquifer material or other materials may also affect the concentration of solute.

These processes are described quantitatively by a derived 3-dimension partial differential equation referred to as "advective-dispersive solute transport equation" in this study. This equation yields the concentration as a function of time and distance from the contaminant source in 3D, i.e. x, y and z directions. This equation is applied to a particular ground water contaminant problem, data is required detailing the ground water velocity, coefficients of hydrodynamic dispersion, rate of chemical reactions, initial concentrations of solutes in the damping site, configuration of solute source and boundaries of pesticides movements in the ground flow system. Quantitative characterization of 3D material microstructure is essential for understanding relationships between microstructure and material properties.

In the ground flow system having irregular geometry and non-uniform media properties, numerical techniques are used to approximate solutions to the solute equation. The 3D analysis will provide details relevant to providing the details of study [25].

Porous media are made up of pore space and a solid matrix. The pore spaces are typically connected, which allows transport processes such as fluid flow, mass transfer, and heat transfer to take place inside. Transport in porous media is an important part of many engineering processes such as chromatography, reactor design, environmental remediation, petroleum recovery, catalysis, ion exchange etc. The structure of porous media is usually complex, so it is customary to model porous media by ignoring the micro mechanical details within the pores and instead to work with the volume-averaged laws that treat a porous medium as a macroscopically uniform continuum. At this scale, porous media are described by parameters such as permeability, and dispersion coefficients [8].

In most cases of practical interest, analytic solutions of the mathematical models are not possible, the mathematical models are transformed into numerical models, which, in turn, are solved by specially designed computer programs. Advantages of numerical approaches are; they can easily deal with variability in the flow transport parameters and there is flex-

ibility in representing parameters that facilitate modeling of layers or other more complex geometries in two and three dimensions [8].

Disadvantages of numerical approaches are; when doing numeric for a PDE that has unknown properties numeric are elusive, bug-prone, and sometimes just plainly wrong. In solving Ordinary Differential Equations, some methods are stable (backward Euler), some methods are unstable (forward Euler) and some have less global errors than others.

A modeling task can be subdivided into several steps:

- Preprocessing (transformation of data into a format appropriate for the numerical algorithm, including grid generation)
- Numerical calculation (direct modeling)
- Calibration (inverse modeling)
- Post-processing

Today's software packages or codes assist in all of these modeling steps [16, 28]

1.2 Basic Concepts

1.2.1 Steady Flow and Unsteady Flow

Steady-state flow refers to the condition where the fluid properties at a point in the system do not change over time. Time dependent flows are unsteady (also called transient)

1.2.2 Mass Balance

The conservation of mass principle gives the total amount of mass entering a control volume equal to the total mass leaving it,

$$\sum m_i = \sum m_e \quad (1.2.1)$$

where, i=inlet and e=exit. Now, let m_{cv} be mass of the control volume, then $\frac{\partial m_{cv}}{\partial t} = 0$, for steady flow.

1.2.3 Energy balance

Also, for energy balance for a process

$$E_{in} = E_{out} \quad (1.2.2)$$

$\frac{\partial E_{system}}{\partial t} = 0$, for steady flow E_{system} is energy in the control volume for a steady flow process, the total energy content of a control volume remains constant.

The total energy E of a simple compressible system consists of three parts; Internal energy U , Kinetic Energy $K.E.$ and Potential Energy $P.E.$ i.e. $E=U+KE+PE$

For Unit mass,

$$e = u + ke + pe = u + \frac{v^2}{2} + gz, \quad (1.2.3)$$

where, e =total energy per unit mass, u =internal energy, v =velocity of the system, gz =unit gravitational potential energy, g -is the acceleration due to gravity.

For a general steady-flow process, the energy balance can be written as,

$$Q_{in} + W_{in} + \sum m_{in} \left[h_{in} + \frac{v_i^2}{2} + gz_{in} \right] = Q_{out} + W_{out} + \sum m_e \left[h_e + \frac{v_e^2}{2} + gz_e \right] \quad (1.2.4)$$

From a closed thermodynamic system, the first law may be stated as:

$$\partial Q = \partial W + \partial U$$

or equivalently

$$\partial U = \partial Q - \partial W,$$

where ∂Q -is the quantity of energy added by heating the process, ∂W -Energy lost due to work, ∂U -is the change in internal energy.

$$\partial Q - \partial W = \sum m_e \left[h_e + \frac{v_e^2}{2} + gz_e \right] - \sum m_i \left[h_i + \frac{v_i^2}{2} + gz_i \right] \quad (1.2.5)$$

where W -Is work due to expansion=Pressure multiplied by volume and Q -Is internal energy

1.2.4 Peclets Number in mass transfer

Peclet Number,

$$P_e = \frac{uL}{D_m} \quad (1.2.6)$$

where, u -average velocity, L -characteristic length, D_m -molecular diffusion coefficient

The longitudinal dispersion coefficient, D_L , is lower than D_m for $Pe < 1$, where $D_L \sim P_e^{\alpha_L}$ with, $\alpha_L \sim 1.2$ for experiments on bead packs, sand packs and homogeneous stones.

For mechanical dispersion regime with $D_m \sim P_e$ the transverse dispersion coefficient, D_T , however is lower than D_L and typical scale approximately linearly with P_e [14]

For longitudinal dispersion in the absence of advection (Low Pe) molecular diffusion is the only mechanism for fluid mixing. This diffusion is restricted as the porous matrix acts as a barrier to molecules, thus reducing the mean free path of molecules which result in the ratio $\frac{D_L}{D_m}$ being smaller than unity [24]. The first effect of advection on dispersion are observed at $P_e = 0.1$.

At $P_e = 10$, advection starts to have a much-pronounced contribution on mixing but diffusion effect are still present. The best fit of the results $D_L \sim P_e^{\alpha_L}$ in the regime $10 < P_e < 400$, is with power law coefficient, $\alpha_L = 1.2$, where α_L -Longitudinal dispersivity[14]. The magnitude of transverse dispersion is much smaller than longitudinal dispersion and the power law coefficient to fit $D_T \sim P_e^{\alpha_T}$ is $\alpha_T = 0.94 < \alpha_L$ indicating a weaker transverse α_T dispersion dependent on P_e than longitudinal dispersion [24]. α_T -Transverse dispersivity.

D_L or D_T (L^2T^{-1}), $\frac{D_L}{D_m} \sim P_e$, $\frac{D_T}{D_m} \sim P_e$ for all $Pe \gg 1$

1.2.5 Mechanical Dispersion

The process where ground water velocity increases, the fluid mixing rate caused by difference of velocity in individual soil pore is a phenomenon is called mechanical or convective dispersion.

The mechanical dispersion account for: [4].

1. Micro scale spreading because of the parabolic velocity distribution in single pores.
2. Variability in velocities between different pores, and
3. The tortuosity, branching and interfingering of pore channels.

Hydrodynamic dispersion coefficient, D in a porous medium is the sum of mechanical dispersion coefficient D_m and molecular diffusion coefficient D_d expressed as; $D = D_m + D_d$. Molecular Diffusion Coefficient in the soil is given by; $D_d = D_{*d} \cdot \tau$ where, D_{*d} -is diffusion coefficient in water and τ -is tortuosity of porous medium is given by, $\tau = \left(\frac{L}{L_c}\right)^2 < 1$, L -is the straight line distance of a diffusing particle, L_c -is the real distance covered by diffusing particle moving through pores among solid particles of the soil.

Here the longitudinal dispersion is a result of differences in travel time along flowlines, which split at grain boundaries (or large obstacles), whereas transversal dispersion applies to dispersion perpendicular to that direction and is caused by variations in the microscopic velocity within each flow channel and from one channel to another. Vertical transverse dispersion is usually smaller than horizontal transverse dispersion. Microscopically there is no mixing; however, if the average concentration of a given volume of fluid is considered an apparent dilution or spreading is present. The mechanical dispersion in a variable aperture fracture is caused by Taylor dispersion, which results from velocity variations across the fracture aperture, and macro/geometric dispersion, which is caused by velocity variations in the planar of the fracture because of aperture variability [8]. Since Taylor dispersion is proportional to v^2 and macro dispersion is linear proportional to v , where v is the mean flux [LT^{-1}], mechanical dispersion will be negligible at Peclet numbers $\ll 1$. Dispersion takes effect at many scales, from pore-scale to larger scale. Variability in groundwater velocities may increase at larger scales for two reasons – either new, infrequently spaced, pore elements with higher-than-average velocities may be countered as scale is increased, as in fractured media, or there may be continuous variations in ensemble means from place to place, as in cases where Darcian permeability is inhomogeneous.

In 1D transport models, the approximations are mostly related with the averaging of radial porosity, velocity profiles, and dispersion coefficients. In 2D models, the approximation includes decoupling of flow fields from those of concentrations by assuming prescribed velocity profiles, which are radial or symmetric. As a consequence, these models cannot describe, in particular, the effects of flow or circulation within the voids between the particles or those of the stagnant zones around the particles or in the vicinity of the walls of the adsorber, on the concentration profiles. Similarly, the spatial variation in bed-porosity and dispersion coefficient in 2D models is incorporated via various empirical correlations reported in the literature. There is another limitation of the existing 1D or 2D models for packed beds having small d/d_p ratio in predicting concentration profiles within the voids. In principle, if the non-dimensional groups in different sets of equations for the conservation of species

and momentum and the corresponding non-dimensional boundary conditions are identical, the non-dimensional solutions should also be the same, although actual solutions for the velocity and concentration profiles will be different due to scaling effect. The situation, however, becomes rather non-trivial in packed beds due to different packing arrangements possible for the same d/d_p ratio, in which case overall bed-porosity may be the same but the local porosity vary from one arrangement to the other. As a consequence, the concentration profiles are different. This is one of the reasons why the existing literature correlations may not be realistic for calculating effective Pe for packed beds having low d/d_p ratio (<10), since concentration profiles will be significantly influenced by the packing arrangements. In such a case it would be more realistic to solve full 3D profiles without using any existing correlations, [8].

Langmuir [17] in 1915 came up with a model, which is also called ideal localized monolayer model, which was based on the following assumptions:

- (i) Adsorption takes place only at specific localized sites on the surface and saturation coverage correspond to complete occupancy of these sites,
- (ii) Each site can accommodate one and only one molecule or atom,
- (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, and
- (v) The adsorbed molecules cannot migrate across the surface or interact with neighboring molecules.

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

- i The simplest chemical reaction model is the linear adsorption equation

$$S_e = K_d C \quad (1.2.7)$$

where K_d is referred to as the distribution coefficient (slope of the adsorption isotherm), C is the concentration of solute in the solution.

ii Equation (1.2.7) is a special case of the Freundlich equation

$$S_e = K_d C^N \quad (1.2.8)$$

where N is a fitting parameter.

iii The Lagmuir adsorption equation,

$$S_e = \frac{aC}{1 + bC} \quad (1.2.9)$$

where a and b are curve fitting parameters.

1.2.6 Water flow

Darcy's Law: in 1856 Darcy [9] found that the rate of flow Q (volume/unit time) is

- i Proportional to the cross-sectional area A of the soil under consideration;
- ii Proportional to the difference in total head $\Delta h = (h_1 - h_2)$, over the length L over which fluid flow takes place, and
- iii Inversely proportional to that length L . The ratio $\Delta h/L$ is known as hydraulic gradient
i. Thus, Darcy's law is

$$v = \frac{Q}{A} = -k \left(\frac{h_1 - h_2}{L} \right) = -k \cdot i \quad (1.2.10)$$

where the ratio Q/A is the 'effective' or Darcy velocity v . This phenomenological or experimentally derived law can be generalized for an isotropic 3D porous medium as $\mathbf{v} = -k \nabla h$, where \mathbf{v} is the effective velocity vector with components v_x , v_y and v_z corresponding to the Cartesian x , y and z coordinates, and ∇h is the hydraulic gradient with components $i_x = \frac{\partial h}{\partial x}$, $i_y = \frac{\partial h}{\partial y}$ and $i_z = \frac{\partial h}{\partial z}$. The 'total head' h arises from the pressure potential p/γ_w , the elevation z , and the kinetic energy $\frac{v^2}{2g}$, where z is the elevation head with respect to some fixed reference datum, p is pressure, γ_w is the unit weight of the fluid (usually water) and g is the acceleration due to gravity. However, for a porous medium, the fluid velocity is usually low and changes in the piezometric head are much larger than the fraction of kinetic energy; so, the later contribution is usually neglected, leading to $h \approx p/\gamma_w + z$. This leads to the equation below which is reformulated in terms of elevation z and fluid pressure [30]:

$$v = -k \left(\frac{\nabla p}{\gamma_w} + \nabla z \right) = -\frac{k}{\rho_w g} (\nabla p + \rho_w g \nabla z) = -\frac{K}{\eta} (\nabla p + \rho_w g \nabla z) \quad (1.2.11)$$

∇p -Pressure gradient operator for 3D. ∇z Hydraulic head gradient operator for 3D

where ρ_w is the fluid density, η , is the fluid dynamics viscosity, and K is the intrinsic permeability of the granular medium linked to the hydraulic conductivity k as $K = \frac{k \cdot \eta}{(\rho \cdot g)}$.

A mass balance must be performed, and used along with Darcy's law, to arrive at the transient groundwater flow equation. This balance is analogous to the energy balance used in heat transfer to arrive at the heat equation. It is simply a statement of accounting, that for a given control volume, aside from sources or sinks, mass cannot be created or destroyed. The conservation of mass states that for a given increment of time (Δt) the difference between the mass flowing in across the boundaries, the mass flowing out across the boundaries, and the sources within the volume, is the change in storage.

$$\frac{\Delta M_{stor}}{\Delta t} = \frac{M_{in}}{\Delta t} - \frac{M_{out}}{\Delta t} - \frac{M_{gen}}{\Delta t} \quad (1.2.12)$$

Although Darcy's law (an expression of conservation of momentum) was determined experimentally by Darcy, it has since been derived from the Navier-Stokes equations via homogenization. It is analogous to Fourier's law in the field of heat conduction, Ohm's law in the field of electrical networks, or Fick's law in diffusion theory [3]. One application of Darcy's law is to water flow through an aquifer. Darcy's laws along with the equation of conservation of mass are equivalent to the groundwater flow equation, one of the basic relationships of hydrogeology. Darcy's law is also used to describe oil, water, and gas flows through petroleum reservoirs.

The original expression of Darcy's equation and a schematic is included below [9].

$$v = k \frac{h_1 - h_2}{l} = k \frac{\Delta h}{l}$$

where, u =flow velocity in cm/second, Δh =difference in manometer level, cm (water equivalent), l =total length of sand pack, cm. and k =Constant of permeability,

Q-discharge; 1 and 2 are corresponding inlet and outlet respectively in the equation below. Darcy's law [18] is a simple proportional relationship between the instantaneous discharge rate through a porous medium, the viscosity of the fluid and the pressure drop over a given distance.

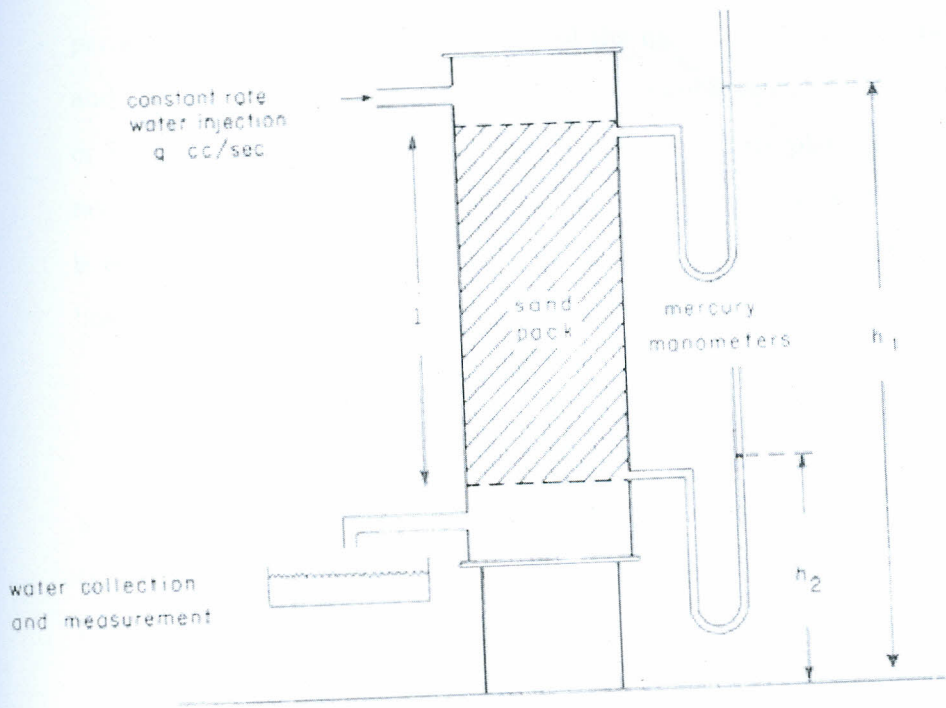


Figure 1 Schematic of Darcy's Experimental

$$Q = \frac{-\kappa A (P_2 - P_1)}{\mu L} \quad (1.2.13)$$

where P_1 is the atmospheric pressure at h_1 and P_2 is the atmospheric pressure at h_2 . The total discharge, Q (units of volume per time, e.g., m³/s) is equal to the product of the permeability (κ units of area, e.g. m²) of the medium, the cross-sectional area (A) to flow, and the pressure drop, all divided by the dynamic viscosity μ (in SI units e.g. kg/(ms) or Pas), and the length L the pressure drop is taking place over. The negative sign is needed because fluids flow from high pressure to low pressure. So if the change in pressure is negative (in the x -direction) then the flow will be positive (in the x -direction). Dividing both sides of the equation by the area and using more general notation leads to

$$q = \frac{-\kappa}{\mu} \nabla P = \frac{Q}{A} \quad (1.2.14)$$

where q is the flux (discharge per unit area, with units of length per time, m/s) and ∇P is the pressure gradient vector. This value of flux, often referred to as the Darcy flux, is not the velocity which the water travelling through the pores is experiencing [5]. The pore velocity (v) is related to the Darcy flux (q) by the porosity (Φ). The flux is divided by porosity to account for the fact that only a fraction of the total formation volume is available for flow. The pore velocity is, $v = \frac{q}{\Phi}$ where, Φ is porosity

In 3D dimensions

In three dimensions, gravity must be accounted for, as the flow is not affected by the vertical pressure drop caused by gravity when assuming hydrostatic conditions. The solution is to subtract the gravitational pressure drop from the existing pressure drop in order to express the resulting flow.

$$\vec{q} = \frac{-\kappa}{\mu} (\nabla P - \rho g \hat{e}_z) \quad (1.2.15)$$

where the flux \mathbf{q} is a vector quantity, $k(L^2T^{-1})$ is a tensor of permeability, ∇ is the gradient operator in 3D, g is the acceleration due to gravity, \hat{e}_z is the unit vector in the vertical direction, pointing downwards and ρ is the density.

Effects of anisotropy in three dimensions are addressed using a symmetric second-order tensor of permeability: [19]

$$K = \begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & K_{yz} \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix}$$

where the magnitudes of permeability in the x , y , and z component directions are specified. Since this is a symmetric matrix, there are *at most* six unique values. If the permeability is isotropic (equal magnitude in all directions), then the diagonal values are equal, $S_p [-]$

In general, for a given porous medium K_x , K_y and K_z do not need to be the same, in which case, the medium is called anisotropic. On the other hand, if $K_x = K_y = K_z$ the medium is called isotropic.

In general, x , y , z can have any orientation, but it is common to set z vertical and x and y horizontal. In three dimensions, all fluxes (Q , q , v) are vector quantities (3 components), as is the hydraulic gradient $l = [l_x : l_y : l_z]$, ($l_x = \frac{\partial h}{\partial x}$, $l_y = \frac{\partial h}{\partial y}$, $l_z = \frac{\partial h}{\partial z}$). The hydraulic head is still a scalar (1 component), while the hydraulic conductivity is a tensor quantity (9 components)

The most general 3D Darcy's law is written as: [18]

$q = -KI$, I is the gradient head

Or more explicitly,

$$\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = - \begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & K_{yz} \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix} \begin{pmatrix} \partial h / \partial x \\ \partial h / \partial y \\ \partial h / \partial z \end{pmatrix} \quad (1.2.6.2)$$

We can easily verify that previous 3D Darcy's law (with 3 principal components: $(K_x; K_y; K_z)$) is just a reduced form of the above equation when K is a diagonal tensor (under the condition that the coordinate axes are aligned with the principal axes of K).

1.2.7 Assumptions

Darcy's law [11] is a simple mathematical statement which neatly summarizes several familiar properties that groundwater flowing in aquifers exhibit, including:

- If there is no pressure gradient over a distance, no flow occurs (this is hydrostatic conditions),

- If there is a pressure gradient, flow will occur from high pressure towards low pressure (opposite the direction of increasing gradient - hence the negative sign in Darcy's law),
- The greater the pressure gradient (through the same formation material), the greater the discharge rate, and the discharge rate of fluid will often be different — through different formation materials (or even through the same material, in a different direction) — even if the same pressure gradient exists in both cases.

A graphical illustration of the use of the steady-state groundwater flow equation (based on Darcy's law and the conservation of mass) is in the construction of flow nets, to quantify the amount of groundwater flowing under a dam. Flow nets are commonly used in the design of earth dams.

Darcy's law is only valid for slow, viscous flow; fortunately, most groundwater flow cases fall in this category. Typically, any flow with a Reynolds number less than one is clearly laminar, and it would be valid to apply Darcy's law. Experimental tests have shown that for flow regimes with values of Reynolds number up to 10 may still be Darcian. Reynolds number (a dimensionless parameter) for porous media flow is typically expressed as

$$Re = \frac{\rho v d_{30}}{\mu} \quad (1.2.16)$$

where ρ is the density of the fluid (units of mass per volume), v is the specific discharge (not the pore velocity — with units of length per time), d_{30} is a representative grain diameter for the porous medium (often taken as the 30% passing size from a grain size analysis using sieves), and μ is the dynamic viscosity of the fluid.

1.2.8 Solute transport

Solute-spreading mechanisms Three physically based mechanisms have been proposed to explain spreading of solutes as they travel through the soil with the moving liquid phase: travel-time variations within the population of stream tubes, the analogy with molecular diffusion, and Levy processes. Sorption and transformation processes can be equally well implemented in models based on any of these three spreading mechanisms. Other concepts have emerged, such as the mobile-immobile solute transport model [12] for an overview of early work, but these are typically based on one of the three fundamental spreading mechanisms. For instance, some formulations of the mobile-immobile flow model assume the liquid phase in a soil to be partitioned in a mobile domain where flow occurs, and an

immobile domain in which the soil solution is stagnant. Usually, the Convection Dispersion Equation (CDE) is valid in the mobile domain, and diffusion is assumed in the immobile domain. A fourth mechanism has a less obvious physical connotation but merits attention because of its extraordinary generality: solute spreading by a Continuous-Time Random-Walk process (CTRW). CTRW describes solute movement in terms of the probability of a random displacement with a random travel time. It is distinct from random-walk models in which particle paths follow stream lines perturbed by random excursions [11]. This mechanism too can be implemented in derived modeling concepts, as was demonstrated by Dentz and Berkowitz [11] who included CTRW in a mobile-immobile model.

Brief information listed below can explain the basics.

Travel time variation within the population of stream of tubes:

This modeling concept views a soil volume as a population of stream tubes with randomly distributed travel times. The travel-time probability density function (pdf) is often assumed to be lognormal [11], resulting in the Convective Lognormal Transfer function model (CLT). In Stochastic-Convective Movement, solutes do not move with respect to the water which carries them: a solute particle never leaves the stream tube into which it entered at the inlet boundary of the soil volume, and at all times its velocity is equal to that of the water surrounding it. During stochastic-convective solute transport the degree of solute spreading in non-layered soils is proportional to the distance traveled, and the standard deviation of the travel time increases linearly with the travel distance [11]. For steady-state flow, the standard deviation of the travel distance increases linearly with time. Because solute particles are assumed not to leave their stream tubes, the SCM can only model the longitudinal spreading within the entire soil volume and cannot handle non-uniform solute applications at the inlet boundary.

Analogy with molecular diffusion:

The solute transport concept implemented in most solute transport models is the Convection-Dispersion Equation (CDE), which assumes a macroscopic uniform flow in which solutes are spread by a dispersive flux that is analogous to diffusion (i.e., proportional to the concentration gradient) and hence obeys Fick's law. The CDE reads:

$$\frac{\partial \theta C_l^r}{\partial t} = \nabla (\theta D \nabla c_l^r) - \nabla \left(\vec{J}_w C_l^r \right) \quad (1.2.17)$$

Here, $D(L^2T^{-1})$ is a tensor consisting of effective dispersion coefficients. \vec{J}_w is the vec-

tor of water flux densities (LT^{-1}) in the principal directions, c is the solute concentration (ML^{-3}), subscript l indicates the concentration relates to dissolved rather than sorbed solutes, and superscript r indicates a resident concentration. The water flux densities in \vec{J}_w are macroscopic, in the sense that local variations need not be explicitly accounted for. Instead, the effect these local variations in \vec{J}_w have on solute spreading is reflected in the values of the elements of \mathbf{D} . For soils this means that soil layers are usually assumed to be uniform, resulting in essentially parallel, vertical flow lines for many applications. The tensor \mathbf{D} is often simplified, with a scalar longitudinal dispersion coefficient D_L on the diagonal element corresponding to the axis parallel to the main flow direction, lateral D_R dispersion coefficients (L^2T^{-1}) on the remaining diagonal elements corresponding to the axes perpendicular to the main flow direction, and all off-diagonal elements equal to zero. According to the Stochastic-Convective Motion (SCM), solutes remain within the flow tube in which they entered at the soil surface. The Convection Dispersion Equation (CDE) assumes solutes continuously change flow tubes through Brownian motion. The Fractional Advection-Dispersion Equation (FADE) allows for periods of Brownian motion interspersed with periods during which solute particles do not leave their flow vessel.

The element of mechanical dispersion tensor \mathbf{D}_m , for our study, can be expressed in terms of longitudinal, α_l , and traverse dispersivities, α_t , the magnitude of velocity vector, \mathbf{V} , and the magnitude of its components \mathbf{v}_x , \mathbf{v}_y and \mathbf{v}_z , [5] as,

$$\begin{aligned}
 D_{m_{xx}} &= \left[\frac{\alpha_l v_x^2 + \alpha_t (v_y^2 + v_z^2)}{V} \right] \\
 D_{m_{yy}} &= \left[\frac{\alpha_l v_y^2 + \alpha_t (v_x^2 + v_z^2)}{V} \right] \\
 D_{m_{xy}} = D_{m_{yx}} &= \left[\frac{(\alpha_l - \alpha_t) v_x v_y}{V} \right] \\
 D_{m_{yz}} = D_{m_{zy}} &= \left[\frac{(\alpha_l - \alpha_t) v_y v_z}{V} \right] \\
 D_{m_{xz}} = D_{m_{zx}} &= \left[\frac{(\alpha_l - \alpha_t) v_x v_z}{V} \right] \\
 D_{m_{zz}} &= \left[\frac{\alpha_l v_z^2 + \alpha_t (v_x^2 + v_y^2)}{V} \right]
 \end{aligned}
 \tag{1.2.18}$$

If a coordinate system is chosen, such that the direction of the average groundwater

velocity is aligned with the x-direction ($V=v_x$ and $v_y=v_z=0$), the off-diagonal terms in the dispersion tensor (1.2.8.2) will equal zero, and the mechanical dispersion tensor can be simplified to,

$$\begin{aligned} D_{m_x} &= D_{m_{xx}} = \alpha_l V \\ D_{m_y} &= D_{m_{yy}} = \alpha_l V \\ D_{m_z} &= D_{m_{zz}} = \alpha_l V \end{aligned} \tag{1.2.19}$$

From a geological point of view, the subsurface is divided into aquifers and aquitards. The three-dimension equation problem of equation holds in aquifers. But in aquitards, there is no horizontal flow because the permeability is zero. Since the intrinsic permeability in the horizontal direction of Darcy's law are:

$$k_{zz} = k_{xy} = k_{xz} = k_{yx} = k_{yy} = k_{yz} = 0$$

Hence the transport equation for geological aquitards becomes

$$\theta \frac{\partial C}{\partial t} = \nabla \cdot (\theta D \nabla C) - \frac{\partial q_x C}{\partial x} + q_{so} C_s \tag{1.2.20}$$

$$\text{with } D = \begin{bmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{bmatrix} \tag{1.2.21}$$

and $D_{xx} = \alpha_L q_x$, $D_{yy} = \alpha_T q_x$, $D_{zz} = \alpha_T q_x$

The effective dispersion coefficient tensor \mathbf{D} , referred in this context is hydrodynamic dispersion coefficient. Hydrodynamic dispersion consists of mechanical dispersion and molecular diffusion. Hydrodynamic dispersion is the flux of solute. Solute flux, \mathbf{J} , is given by Fick's first Law as

$$\mathbf{J} = -\theta \mathbf{D} \cdot \mathbf{C} \tag{1.2.22}$$

()

In a flow system having uniform flow aligned with the x-axis, the coefficients of the hydro-

dynamic dispersion tensor, D_x, D_y and D_z are given by

$$D_x = D_{m_x} + D_d$$

$$D_y = D_{m_y} + D_d$$

$$D_z = D_{m_z} + D_d$$

(1.2.23)

D_{m_x}, D_{m_y} , and D_{m_z} are corresponding mechanical dispersion coefficients in x, y and z directions

In low flow, the dispersion due to diffusion is very low. It also depends on the scale flow being considered [3].

1.2.9 Levy Process

: The fractional advection-dispersion equation (FADE) represents the intermediate stages between the SCM and the CDE and includes the CDE as a special case. While the development of the SCM was triggered by the inability of the CDE to reproduce field-scale solute leaching it was found that assuming no dispersion at all was too strict. For flow processes in other fields of physics, Fokker-Planck equations have been developed that use fractional derivatives to account for non-Brownian movements with long-range spatial dependence (memory effect) or high velocity variability [8]. In its simplest form (one dimensional uniform flow, symmetric dispersion, uniform, conservative tracer), the fractional advection-dispersion equation is [7]

A three-dimensional (3D) analysis of transport and macrodispersion at the macrodispersion experiment (MADE) site [8] using the Fractional Advection-Dispersion Equation (FADE) developed [8] shows that the Levy dispersion process is scale dependent. Levy dispersion may be superior to Gaussian dispersion on a sufficiently small scale; on larger scales, both theories are likely to suffer from the fact that because of depositional structures most flow fields display an evolving, nonstationary structure. Motion in such fields is advection dominated, displays a lot of memory and therefore is not modeled well by Markov random processes which underlie the derivation of both the Gaussian and Levy advection dispersion equations [6, 27]. To improve plume simulation of an advection-dominated transport process, one would have to bring in more advective irregularity while simultaneously decreasing the Levy

dispersion coefficient. Therefore, on a 3-D basis, first-order Levy dispersion has limitations similar to Gaussian dispersion. However, this and related theories, such as the continuous time random walk (CTRW) formalism, are in the early stages of development and thus may be fruitful areas for further. While a three-dimensional theory of fractional (Levy) dispersion was been developed recently [7], most hydrological applications to date have been one-dimensional. These applications have been intriguing and promising, but transport in heterogeneous porous media is inherently 3D, and a 1D application may obscure much of the physical process that is actually occurring, especially if a 3D concentration distribution is averaged to produce a 1D distribution.

1.2.10 Implied additional environmental parameters

Hydrodynamic dispersion: -

Hydrodynamic dispersivity (α_L, α_T) is an empirical factor which quantifies how much contaminants stray away from the path of the groundwater which is carrying it. Some of the contaminants will be "behind" or "ahead" the mean groundwater, giving rise to a longitudinal dispersivity (α_L), and some will be "to the sides of" the pure advective groundwater flow, leading to a transverse dispersivity (α_T). Dispersion in groundwater is due to the fact that each water "particle", passing beyond a soil particle, must choose where to go, whether left or right or up or down, so that the water "particles" (and their solute) are gradually spread in all directions around the mean path. This is the "microscopic" mechanism, on the scale of soil particles. More important, on long distances, can be the macroscopic inhomogeneity's of the aquifer, which can have regions of larger or smaller permeability, so that some water can find a preferential path in one direction, some other in a different direction, so that the contaminant can be spread in a completely irregular way, like in a (three-dimensional) delta of a river. Dispersivity is actually a factor which represents our lack of information about the system we are simulating. There are many small details about the aquifer which are being averaged when using a macroscopic approach (e.g., tiny beds of gravel and clay in sand aquifers), they manifest themselves as an apparent dispersivity. Because of this, α is often claimed to be dependent on the length scale of the problem — the dispersivity found for transport through 1 m of aquifer is different than that for transport through 1 cm of the same aquifer material

Diffusion :-

This is a fundamental physical phenomenon by which Einstein explained Brownian motion, which describes the random thermal movement of molecules and small particles in gases and liquids. It is an important phenomenon for small distances (it is essential for the achievement of thermodynamic equilibria), but, as the time necessary to cover a distance by diffusion is proportional to the square of the distance itself, it is ineffective for spreading a solute over macroscopic distances. The diffusion coefficient, D , is typically quite small, and its effect can often be considered negligible (unless groundwater flow velocities are extremely low, as they are in clay aquitards). In our case we say diffusion results from the random collision of solute molecules and produce a flux of solute particles from areas of higher to lower solute concentration. [2] It is important not to confuse diffusion with dispersion, as the former is a physical phenomenon and the latter is an empirical factor which is cast into a similar form as diffusion, because we already know how to solve that problem. We will be examining the effect of three-dimensional approach of this factor in our analysis.

The retardation factor:-

This is another very important feature that makes the motion of the contaminant to deviate from the average groundwater motion. It is analogous to the retardation factor of chromatography. Unlike diffusion and dispersion, which simply spread the contaminant, the retardation factor changes its global average velocity, so that it can be much slower than that of water. This is due to a chemico-physical effect: the adsorption to the soil, which holds the contaminant back and does not allow it to progress until the quantity corresponding to the chemical adsorption equilibrium has been adsorbed. This effect is particularly important for less soluble contaminants, which thus can move even hundreds or thousands of times slower than water. The effect of this phenomenon is that only more soluble species can cover long distances. The retardation factor depends on the chemical nature of both the contaminant and the porous media.

Hydraulic conductivity (K) and transmissivity (T) :-

These are indirect porous media properties (they cannot be measured directly). T is the K integrated over the vertical thickness (b) of the porous media ($T=Kb$ when K is constant over the entire thickness). These properties are measures of a porous media ability to transmit water. Intrinsic permeability (κ) is a secondary medium property which does not depend on the viscosity and density of the fluid (K and T are specific to water); it is used more in the petroleum industry. Porosity does not directly affect the distribution of hydraulic head in a porous media, but it has a very strong effect on the migration of dissolved contaminants,

since it affects groundwater flow velocities through an inversely proportional relationship.

Water content (θ) is also a directly measurable property; it is the fraction of the total rock which is filled with liquid water. This is also a fraction between 0 and 1, but it must also be less than or equal to the total porosity.

The water content is very important in vadose zone hydrology, where the hydraulic conductivity is a strongly nonlinear function of water content; this complicates the solution of the unsaturated groundwater flow equation. Water content has no dimensional variable effect associated with it.

Tortuosity :-

This is one of the most meaningful 3D parameters of pore structure which express the degree of complexity of the sinuous pore path. Tortuosity can easily be related to conductivity of the porous medium since it provides an indication of increased resistance to flow due to pore system's greater path length ie an increased path length results in less connection or reduced hydraulic conductivity [31]. The shape factor coefficient, S_n , of the porous media is computed from morphological characteristics of pores,

$$S_n = \left[\frac{S_p}{N^2 \times \tau_p} \right] \quad (1.2.24)$$

where S_p is pore sphericity, τ_p pore path tortuosity, N is the number of pores,

$$S_p = \frac{\pi^{\frac{1}{3}} (6V_p)^{\frac{2}{3}}}{A_p} \quad (1.2.25)$$

V_p , A_p are pore volume and surface area respectively.

$$\Phi_a = \sum_i V_i / V_{img} \quad (\text{air fill porosity}) \quad (1.2.26)$$

$V_i [L^3]$ is the volume of the i^{th} pore (empty pore)

V_{img} - Volume of picat sub sample

$$\tau_p = \frac{\Phi_a A_p}{\pi R_p^2} \quad (1.2.27)$$

where R_p -radius factor.

The investigation of the shape, geographic pore properties, % porosity and hydraulic radius

of pores, tortuosity are determined by use of 3D high resolution computed tomography imagery. It is not possible in 2D case.

1.2.11 Interactive Volume Modeling

Interactive Volume Modeling (IVM) was developed to meet basic requirements of 3D problems, such as modeling, visualization and analysis. The use of visualization techniques and volume calculations provide some useful capabilities such as the ability to calculate the volume of material within specific property range and to be able to visualize where the volume of material occurs in 3D space.

IVM creates a uniform, regularly spaced 3D grid model with a calculation property value at each node. This grid model is then used to generate series of user defined surfaces equal values, which are called "iso surfaces". GOCAD is a computer aided design for geological applications. [10].

1.3 Statement of the problem

The main challenge to address that necessitated the design of this model is how to control the effect of migrating of dumped pesticides from their disposal sites to the ground water environment through understanding of the movement pattern from their disposal sites. With diminishing surface water resources and increasing demand with population increase, control of ground water pollution is inevitable.

To address this migration, many solutions for Advection-Dispersive equations are now available for a large number of initial and boundary conditions for 1D transport, but very few for 3D [29].

To accurately determine the flow of these migrating chemicals in the ground environment, 1D and 2D dimensional equations are limited because they work with lumped parameters to factor in missed dimension(s). The emphasis on use of 1D and 2D was due to complexities and costs associated with solving 3D equations.

Soil processes have a 3D character. Modelling therefore in principle should employ 3D. The target of any research question is to get the highest degree of accuracy possible. The number of dimensions is closely related to the required accuracy of a research question thus

making 3D modelling most ideal for practical purposes when it comes to solving this research problem. The strength with 3D flow models is that they provide detailed analysis of typical multidimensional flow.

This model is a good contribution to research. users and manufacturers.

1.4 Objectives of the study

General objective

The objective of this study is to model movement of pesticides in 3D by the advection-dispersive partial differential equation under a steady state water flow in a porous media.

Specific objective:

- i Derive 3D equation of advection-dispersion of pesticides adsorption in porous medium from the first principle.
- ii Solve the derived equation.
- ii Test the solution by applying it to experimental data so as to prove its validity.

1.5 Significance of the study

In this study we take care of 3D movement of chemical solute in the subsurface environment, thus giving us a comprehensive model describing the movement of these solutes. This study is essential to;

The users of pesticides: -

It helps them know how to safeguard water sources by identifying safe dumping sites away from water resources and determining the right pesticides for utilization in protecting their crop and animals from pests.

Manufacturer of pesticides: -

It helps them avoid manufacturing dangerous pesticides with high migration potential and low solubility in water in order to facilitate adsorption.

The researchers of pesticides: -

For 3D flow study, the researchers can be able to further carry out more studies in order to provide sound advice to the user and the manufacturer and expand knowledge. The lumped parameters as in the case of 1D and 2D are no more thus giving us detailed parameters associated with 3D.

Chapter 2

Literature Review

Modeling of water flow and pollutant transport in a porous media by Marcin K Widomiski et al, [23], is fairly modern with computer approach, but not specific to pesticide flow in a porous media. In that study, the authors intended to provide systematic information and examples of use of the numerical models to describe waste water flow transport of pollutants in sewer systems. Van Genuchten et al, [30] developed a partial differential equation generally assumed to describe the movement of pesticides and other adsorbed solutes through a porous soil media under a steady state water flow condition

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \quad (2.0.1)$$

where, C-Solute concentration, D-Coefficient of dispersion, v-Velocity, θ -porosity, ρ -density, S -Total amount of solute, t-time, and x-is the displacement in axial direction. This equation, if we have a confine aquifer, cannot be used to calculate the underground flow of pesticides to the aquifer. Should some drill a borehole some distance from a dumping site, the aquifer will be contaminated by the flow of pesticide in a lateral direction. Later Van Genuchten and Alives [28], came up with an equation for one-dimension miscible displacement and degradable chemical species (transport equation in 1D).

$$\frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] - v \frac{\partial C}{\partial x} - R \frac{\partial C}{\partial t} = \mu C - \gamma, \quad (2.0.2)$$

where, D is the coefficient of dispersion, C is the concentration. R is the retardation factor, x is the displacement in the longitudinal axis, μ is the decay constant, γ is the zero-order production rate and t is time. Basically, as stated the equation applies to degradable organic pesticides and not inorganic pesticides. Ed Perfect and Michael C. Sukop [13] reviewed a model of dispersion of nonreactive solute in saturated porous media. They explicitly stated that dispersion can occur as a result of diffusion, inter facial instability, mechanical mixing,

molecular size effect, and/or turbulence. Their focus was on combined effect of diffusion and mechanical mixing. From their review, velocity-based models such as convective-dispersion equations are widely used at present however they lack the power due to inversely estimated parameters. Geometrical dispersion models have been neglected in the past because of difficulties of parametrizing in the complex structure that occur in the natural porous media. The recent advances in fracture geometry, percolation and network theory may reduce these difficulties. The spread of solute in a porous medium during a saturated flow is important physio-chemical process, attributing to combination of diffusion and dispersive mechanism. Their focus was on pore geometry model for chemical transport. Taylor 1953 [29] derived the convective-diffusion equation

$$\frac{\partial C}{\partial t} + 2U\left(1 - \frac{y^2}{r^2}\right)\frac{\partial C}{\partial x} = D\left(\frac{\partial^2 C}{\partial y^2} + \frac{1}{y}\frac{\partial C}{\partial y} + \frac{\partial^2 C}{\partial x^2}\right) \quad (2.0.3)$$

The Discrete pore model equation is the Taylor's equation. Let

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial y^2} + \frac{1}{y}\frac{\partial C}{\partial y} + \frac{\partial^2 C}{\partial x^2}\right) - 2U\left(1 - \frac{y^2}{r^2}\right)\frac{\partial C}{\partial x} \quad (2.0.4)$$

where, r is the radius of the pipe while x and y are displacement due to movements of pesticides in axial and radial directions. $v(y) = 2U\left(1 - \frac{y^2}{r^2}\right)$ as indicated in Hagen-Poiseuille equation of laminar flows, U is average velocity. D is dispersion coefficient and is assumed to be independent and r is the radius of the tube. This is effectively two dimensions' equation. While numerical techniques have been employed in the equation above, there are few analytical solutions available. They go further to create conditions that enables the equation to be examined with geometrical factors incorporated. This review is in line with our thesis because it deals with nonreactive adsorptive materials but their primary consideration is the influence of the geometry on adsorption. The program *SWMS-3D* Code for Simulating water flow and solute transport in three dimensions [31], numerically solves Richards's equation for saturated-unsaturated water flow and convective dispersive equation for solute transport. The mixed form of Richards's equation in 3D is given by

$$\frac{\partial \theta(h_p)}{\partial t} = -\nabla \hat{J} = \nabla [K(h) \nabla (h_p + z)] \quad (2.0.5)$$

where

$$\hat{J} = \frac{\partial F}{\partial U} + \frac{\partial G}{\partial U} + \frac{\partial H}{\partial U},$$

$$U = (h, q_x, q_y, q_z)^T$$

$$q_x = h_p u, \quad q_y = h_p v, \quad q_z = h_p w$$

$$F = \left(q_x, \frac{q_x^2}{h} + \frac{1}{2}gh^2, \frac{q_x q_y}{h}, \frac{q_x q_z}{h} \right), G = \left(q_y, \frac{q_x q_y}{h}, \frac{q_y^2}{h} + \frac{1}{2}gh^2, \frac{q_y q_z}{h} \right)$$

$$H = \left(q_z, \frac{q_x q_z}{h}, \frac{q_y q_z}{h}, \frac{q_z^2}{h} + \frac{1}{2}gh^2 \right) [45]$$

where $\theta (L^3/L^3)$ is the volumetric water content in the soil, $z (L)$ is the vertical coordinate in reference to certain datum, $h_p (L)$ is the water column pressure at the point with elevation z and $\hat{K} (L/T)$ is the hydraulic conductivity tensor. This program may be used to analyze water and solute movement in unsaturated, partially saturate or fully saturated porous media. Here they use Galerkin-type linear finite element schemes. This program involves flow in all the three direction therefore not suitable for our analysis. Analytical solution for solute transport in three dimensions in semi-infinite porous media is presented in [14] and it presents several solutions for three dimensional solute transports in semi-infinite porous media with unidirectional flow first type (or flux) boundary conditions at inlet location of the medium. They use analytical method to solve the 3D problem [4] (Transport equation in 3D)

$$R \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - \mu C + \lambda$$

$$t)0 \quad .0 \angle x \angle \infty, \quad -\infty \angle y \angle \infty, \quad -\infty \angle z \angle \infty$$

(2.0.6)

here, μ is the general first order rate coefficient of decay (T^{-1}), λ is the generalized zero order rate coefficient for production ($ML^{-1}T^{-1}$). The equation is ideal for our work but the decay and zero order coefficients make the equation unsuitable for our case study. Adams [1] developed a two-dimensional equation describing the movement of pesticides in a porous medium under steady state flow condition. This study was based on the potential breakdown of the 1D equation due to existence of an impermeable layer (aquiclude) and development of a borehole away from the damping pit.

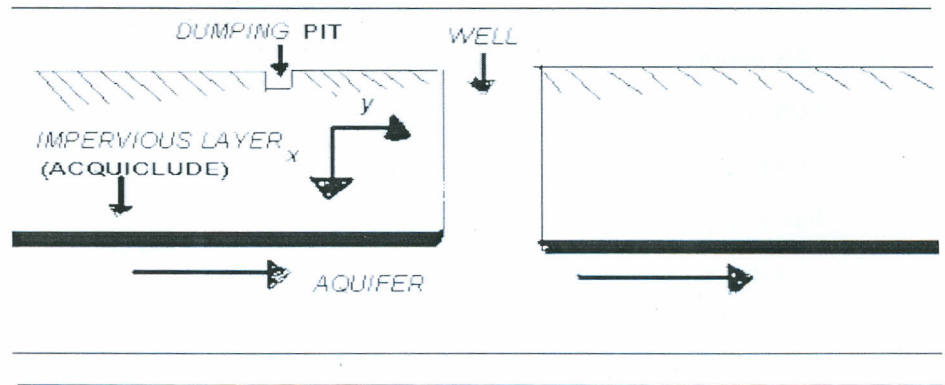


Figure 2: Sketch showing, the movement of pesticides in two dimensions

$$R(C) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} + \frac{1}{y} D_y \frac{\partial}{\partial y} \left(y \frac{\partial C}{\partial y} \right) \quad (2.0.7)$$

The above equation was developed from the first principle and proved suitable for the two-dimension flow.

Implicit numerical methods are stable in one-dimension problem but do not guarantee stability in multidimensional. Crank and Nicolson Method is a finite difference method used in solving partial differential equations and it is an implicit method which is unconditionally stable, accurate and deal with time matching problems by taking simple explicit and implicit methods. It prevents numerical challenges encountered by fully implicit schemes and shortens computing times by a factor of 2 [27]. It also does not encounter numerical problems such as negative distribution function or crash during matrix inversion that are seen in other implicit numerical methods. However, its matrix is too complicated to solve. Douglas and Gunn modified Crank and Nicolson Method. They jointly developed a general ADI scheme that is unconditionally stable and retains second order accuracy when applied to 3D problems with varied implicit and explicit steps. This method gives a tridiagonal matrix algorithm (TDMA) which is a simplified Gaussian elimination method [19].

These details are essential in analysis of many environmental studies related to irrigation and drainage strategies (efficient water use), transport of nutrients and pesticides movements towards groundwater and surface water system (pollution), surface water management of agricultural areas and natural areas (agronomic and ecological interest).

In this study, we derive a 3D convective dispersive equation describing movement of pesticides in underground porous media and solve the equation using an efficient Alternating Direction Implicit method by Peaceman and Rachford [32], and Douglas and Gunn [28] developed from a variation on the Crank Nicolson approximation.

Finally, we have used results of an experiment carried out in Soil Science Department, university of Florida, United States, to apply the formula developed to test its functionality. It is not practical to get all these details investigated with the samples locally because the instruments used are not common.

Chapter 3

Research Methodology

3.1 Introduction

Research Methodology consists of differential equations developed from analyzing ground-water flow (or solute transport in groundwater). The equation is derived from first principles governing molecular diffusion and hydrodynamic dispersion. Finally, the results are analyzed to confirm the suitability of this equation compared with the ones which are commonly used.

3.2 Derivation of convective-dispersive solute transport three-dimension equation with steady state water flow condition

From a control volume, we have the Mass conservation law $\sum M_{in} = \sum M_{out}$.

The speed of water in porous media is determined by considering the average pore water velocity $v(LT^{-1}) = \frac{q}{\theta}$ with $q = -k \frac{\partial H}{\partial l}$ (Darcy's law), the flux density, and $\theta = \frac{v_w}{v_s}$ in which v_w is the volume of water in the porous media and v_s is the volume of solids, k is the permeability, ∂H -the change in hydraulic head and ∂l -elemental distance travelled in longitudinal direction.

In this study we use the concept of dispersion through a cubically packed soil vessel with internal dimensions x , y , and z to derive our equation.

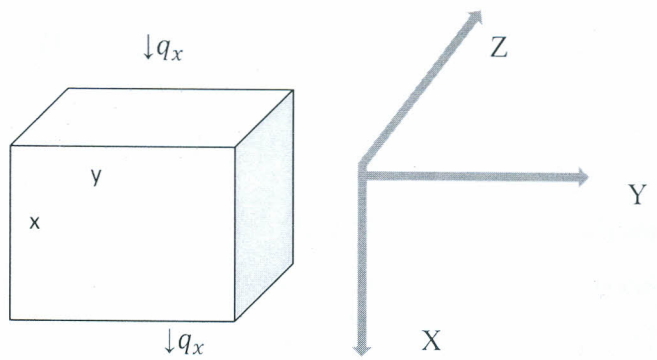


Figure 3: Cubically packed soil sample sketch used for deriving the 3D equation of adsorption of pesticides through a porous media.

At very low flow rate, the dispersion is different in the three directions. The dispersion coefficients are denoted by D_x , D_y , and D_z for x, y and z directions respectively. Sum dispersion coefficient D is given by;

$$D = D_m + D_d$$

$$D_{IJK} = D_{m_{IJK}} + D_{d_{IJK}} [4]$$

where $D_m (L^2T^{-1})$ is molecular diffusion coefficient and $D_d (L^2T^{-1})$ is the hydrodynamic dispersion and is the mixing spreading of the solute during transport due to differences in velocities within the pores and between the pores. The volumetric water content denoted by θ can be assumed to be a void ratio for saturated soils. The elemental height is denoted by ∂l . The measurements are denoted by x , y and z for x, y and z-axis of the cube respectively. C is the concentration of the material to be dispersed and is a function of axial position x , radial positions y and z , time t and dispersion coefficients D_R and D_L radial and axial respectively. The elemental displacement in X axis is ∂x , in Y axis is ∂y and in Z axis is ∂z . The rate of entry of reference adsorption material due to flow in axial direction from the flow in the sample sketch Fig 3,

$$q_l (y \partial y) C \tag{3.2.1}$$

The corresponding efflux rate,

$$q_l y \partial y \left(C + \frac{\partial C}{\partial l} \partial l \right) \tag{3.2.2}$$

The net accumulation rate in element due to axial flow,

$$-q_l y \partial y \frac{\partial C}{\partial l} \partial l \tag{3.2.3}$$

Rate of diffusion in axial direction across inlet boundary,

$$-y \partial y \theta D_x \frac{\partial C}{\partial l} \tag{3.2.4}$$

Corresponding rate at outlet boundary,

$$-y \partial y \theta D_x \left[\frac{\partial C}{\partial l} + \frac{\partial^2 C}{\partial l^2} \partial l \right] \tag{3.2.5}$$

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

$$y \partial y \theta D_l \frac{\partial^2 C}{\partial l^2} \partial l \tag{3.2.6}$$

Diffusion at inlet y and z direction

$$-z\theta\partial_z D_y \frac{\partial C}{\partial y} - y\theta\partial_y D_z \frac{\partial C}{\partial z} \quad (3.2.7)$$

The corresponding rate at y and z outlet is,

$$-z\theta\partial_z D_y \left[\frac{\partial C}{\partial y} + \frac{\partial^2 C}{\partial y^2} \partial y \right] - y\theta\partial_y D_z \left[\frac{\partial C}{\partial z} + \frac{\partial^2 C}{\partial z^2} \partial z \right] \quad (3.2.8)$$

The net accumulation rate due to diffusion from boundaries in axial directions y and z

$$y\partial_y\theta D_z \frac{\partial^2 C}{\partial z^2} \partial z + z\partial_z\theta D_y \frac{\partial^2 C}{\partial y^2} \partial y \quad (3.2.9)$$

For a representative 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, when the adsorption isotherm obeys the Freundlich equation the matrix and the amount present in the soil.

$$X = \rho_b S + \theta C \quad (3.2.10)$$

where, ρ_b is bulky density and S is the solute adsorbed and θC is the solute in the solution. Differentiating with respect to t , we get

$$\frac{\partial X}{\partial t} = \rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} \quad (3.2.11)$$

Now the total accumulation rate is

$$\partial x \partial y \partial z \frac{\partial X}{\partial t} = \partial x \partial y \partial z \left(\rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} \right) \quad (3.2.12)$$

From equations (3.2.3), (3.2.6), (3.2.9), and (3.2.12), we have the following combined equation by the conservation of mass law,

$$\partial x \partial y \partial z \left(\rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} \right) = y \partial_y \partial x \theta D_x \frac{\partial^2 C}{\partial x^2} - q_x y \partial_y \partial x \frac{\partial C}{\partial x} + y \partial_y \partial z D_z \frac{\partial^2 C}{\partial z^2} + z \partial_z \partial y \theta D_y \frac{\partial^2 C}{\partial y^2}$$

For a cube, $x=y=z$ and $x = \partial l = \partial x = \partial y = \partial z$

Thus, the above equation gives us,

$$\rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t} = D_x \theta \frac{\partial^2 C}{\partial x^2} - q_x \frac{\partial C}{\partial x} + D_y \theta \frac{\partial^2 C}{\partial y^2} + D_z \theta \frac{\partial^2 C}{\partial z^2} \quad (3.2.13)$$

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 per equation (1.2.7)

$$S = KC^N, \quad (3.2.14)$$

(Freundlich eqn relates a S and C)

where $S = x/m$, is adsorbed solid and C is the solute equilibrium constant.

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C} \frac{\partial C}{\partial t} = NK C^{N-1} \frac{\partial C}{\partial t}. \quad (3.2.15)$$

From equation (3.2.11) and (3.2.15) we get,

$$\frac{\partial X}{\partial t} = \rho_b \frac{\partial S}{\partial t} + \theta \frac{\partial C}{\partial t}$$

and

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

Thus, we have

$$\left(\rho_b NK C^{N-1} \frac{\partial C}{\partial t} + \theta \frac{\partial C}{\partial t} \right) = \theta D_x \frac{\partial^2 C}{\partial x^2} - q_x \frac{\partial C}{\partial x} + D_z \theta \frac{\partial^2 C}{\partial z^2} + \theta D_y \frac{\partial^2 C}{\partial y^2} \quad (3.2.16)$$

where $R(C) = (1 + \frac{\rho_b NK C^{N-1}}{\theta})$

Taking, $(LT - 1) = \frac{q}{\theta}$, the Advection-Diffusion equation from equation (3.2.13) is,

$$R(C) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \quad (3.2.17)$$

Therefore equation (3.2.17) is our model equation.

3.3 Problem formulation by finite difference

For isotropic porous media, the adsorption of solute is governed by equation (4.3.4).

This equation is the second order equation quasilinear partial differential equation. The first step is to establish a finite difference method solution of the equation is to discretize the continuous domain of its grids with finite number of grid points.

At time step n , the concentration of the solute $C(x, y, z, t)$ at grid point (i, j, k) can be replaced by $C(i\Delta x, j\Delta y, k\Delta z, n\Delta t)$ which is denoted by $C_{i,j,k}^n$.

The initial conditions for solving the model equations is that the concentration of pesticide at all positions in the soil at time zero is constant and equal to $C_{i,j,k}$. That is $C(x, 0, 0) = C_i$ for $x > 0$, $C(0, y, 0) = C_j$ for $y > 0$ and $C(0, 0, z) = C_k$ for $z > 0$

For boundary conditions, two conditions are necessary:

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

$$C(0, 0, t) = C_0$$

for $0 < t \leq t_0$

$$C(0, 0, t) = 0$$

for $t > t_0$

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

$$\left\{ VC_0, \text{ for, } 0 < t \leq t_0, \quad -D_x \frac{dC}{dx} + D_y \frac{\partial C}{\partial y} + D_z \frac{\partial C}{\partial z} + VC \Big|_{x=0} = 0, \text{ for, } t > 0 \right\}$$

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]

3.4 Alternate Direct Implicit Method (ADI)

The implicit method is also known as the Backward in Time Central in Space (BTCS) scheme and is unconditionally stable. Although it has great advantage, the drawback is that a tridiagonal system must be solved for each time step. The ADI method is what is used to solve the model equation. Below is a sketch of nonhomogeneous discretization

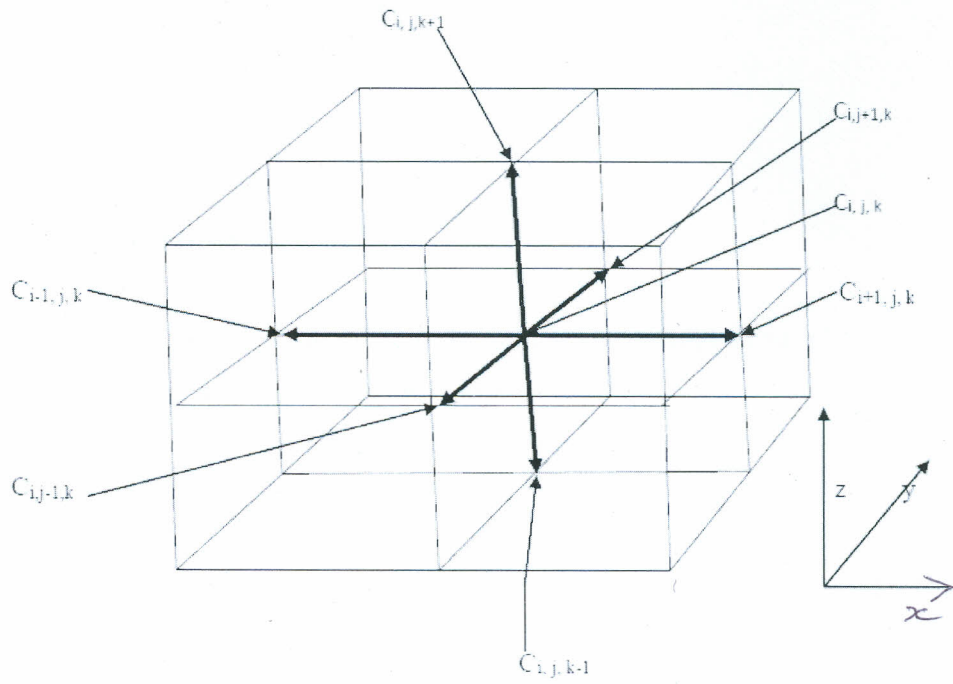


Figure 4: Sketch showing non-homogeneous discretization

Alternate Direct Implicit Method (ADI) is a Difference Method for solving Parabolic and Partial difference equations.

In this study we will deal with two methods

In this study we will deal with two methods

1. Crank-Nicolson Method,
2. Douglas-Gunn Method

3.4.1 Crank-Nicolson Method

Crank-Nicolson [26] dealt with the time marching problem by taking the average of simple explicit and implicit methods. For our equation (4.3.4) we have

$$\begin{aligned}
 R(C) & \frac{(C^{n+1} - C^n)}{\Delta t} \\
 & = D_x \frac{\partial_x^2 (C^{n+1} + C^n)}{2(\Delta x)^2} - v_x \frac{\partial_x (C^{n+1} + C^n)}{4(\Delta x)} \\
 & + D_y \frac{\partial_y^2 (C^{n+1} + C^n)}{2(\Delta y)^2} + D_z \frac{\partial_z^2 (C^{n+1} + C^n)}{2(\Delta z)^2}
 \end{aligned}$$

where, ∂_x -central difference in x direction, ∂_y - central difference in y direction and ∂_z - central difference in z direction.

Rearranging the Crank-Nicolson equation;

$$\begin{aligned}
 R(C_{i,j,k}^n) & \frac{(C_{i,j,k}^{n+1} - C_{i,j,k}^n)}{\Delta t} = \\
 D_x & \left(\frac{(C_{i+1,j,k}^{n+1} - 2C_{i,j,k}^{n+1} + C_{i-1,j,k}^{n+1})}{2(\Delta x)^2} \right) + D_x \left(\frac{(C_{i+1,j,k}^n - 2C_{i,j,k}^n + C_{i-1,j,k}^n)}{2(\Delta x)^2} \right) \\
 & - v_x \frac{(C_{i+1,j,k}^{n+1} - C_{i-1,j,k}^{n+1})}{4\Delta x} - v_x \frac{(C_{i+1,j,k}^n - C_{i-1,j,k}^n)}{4\Delta x} \\
 + D_y & \left(\frac{(C_{i,j+1,k}^{n+1} - 2C_{i,j,k}^{n+1} + C_{i,j-1,k}^{n+1})}{2(\Delta y)^2} \right) + D_y \left(\frac{(C_{i,j+1,k}^n - 2C_{i,j,k}^n + C_{i,j-1,k}^n)}{2(\Delta y)^2} \right) \\
 + D_z & \frac{(C_{i,j,k+1}^{n+1} - 2C_{i,j,k}^{n+1} + C_{i,j,k-1}^{n+1})}{2(\Delta z)^2} + D_z \left(\frac{(C_{i,j,k+1}^n - 2C_{i,j,k}^n + C_{i,j,k-1}^n)}{2(\Delta z)^2} \right) \quad (3.4.1)
 \end{aligned}$$

where $r_x = \frac{\Delta t}{(\Delta x)^2}$, $r_y = \frac{\Delta t}{(\Delta y)^2}$, $r_z = \frac{\Delta t}{(\Delta z)^2}$, $m_x = \frac{\Delta t}{\Delta x}$. and $i = 1, 2, \dots, I - 1$, $j = 1, 2, \dots, J - 1$, and $k = 1, 2, \dots, K - 1$.

The equation (3.0.0.20) above yields;

$$\begin{aligned}
& - \left(\frac{V_x m_{x_i}}{4R(C_{i,j,k}^n)} + \frac{D_x r_{x_i}}{2R(C_{i,j,k}^n)} \right) C_{i-1,j,k}^{n+1} - \frac{D_y r_{y_j}}{2R(C_{i,j,k}^n)} C_{i,j-1,k}^{n+1} - \frac{D_z r_{z_k}}{2R(C_{i,j,k}^n)} C_{i,j,k-1}^{n+1} \\
& + \left(1 + \frac{D_x r_{x_i}}{R(C_{i,j,k}^n)} + \frac{D_y r_{y_j}}{R(C_{i,j,k}^n)} + \frac{D_z r_{z_k}}{R(C_{i,j,k}^n)} \right) C_{i,j,k}^{n+1} - \left(\frac{D_x r_{x_i}}{2R(C_{i,j,k}^n)} - \frac{V_x m_{x_i}}{4R(C_{i,j,k}^n)} \right) C_{i+1,j,k}^{n+1} \\
& \quad - \frac{D_y r_{y_j}}{2R(C_{i,j,k}^n)} C_{i,j+1,k}^{n+1} - \frac{D_z r_{z_k}}{2R(C_{i,j,k}^n)} C_{i,j,k+1}^{n+1} \\
& = \left(\frac{D_x r_x}{2R(C_{i,j,k}^n)} + \frac{V_x m_x}{4R(C_{i,j,k}^n)} \right) C_{i-1,j,k}^n + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j-1,k}^n + \frac{D_z r_z}{2R(C_{i,j,k}^n)} C_{i,j,k-1}^n \\
& + \left(1 - \frac{D_x r_x}{R(C_{i,j,k}^n)} - \frac{D_y r_y}{R(C_{i,j,k}^n)} - \frac{D_z r_z}{R(C_{i,j,k}^n)} \right) C_{i,j,k}^n + \left(\frac{D_x r_x}{2R(C_{i,j,k}^n)} - \frac{V_x m_x}{4R(C_{i,j,k}^n)} \right) C_{i+1,j,k}^n \\
& \quad + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j+1,k}^n + \frac{D_z r_z}{2R(C_{i,j,k}^n)} C_{i,j,k+1}^n \tag{3.4.2}
\end{aligned}$$

The matrix generated by Crank-Nicolson Method has the best accuracy and unconditionally stable but its main disadvantage is that the matrix generated is expensive (or complicated) to solve.

Peaceman -Rachford and Douglas - Gunn [32] developed a variation of the Crank & Nicolson approximation which is known as the ADI Method. Douglas - Gunn scheme is more relevant for our calculation following the earlier discussion in the literature Review.

3.4.2 Douglas - Gunn Method

This numerical method is an alternative solution method which instead of solving 3D problem solves a succession of three one dimensional problems.

The breakdown of the method is explained diagrammatically as shown below [28].

Douglas - Gunn [32] modified the Crank- Nicolson method and developed a general ADI scheme that is unconditionally stable and retains second order accuracy when applied to 3D problems. This approach exploits the understanding that Implicit numerical methods are stable in one-dimension problem but do not guarantee stability in multi-dimensional

STEP 1: X Implicit

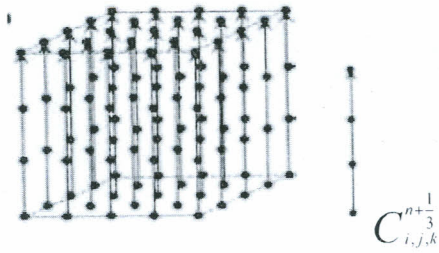


Figure 5: Explicit in (Y,Z)

STEP 2: Y Implicit

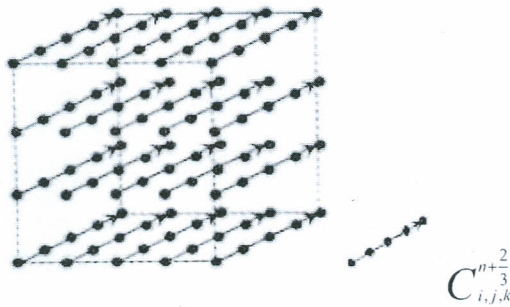


Figure 6: Explicit in (X,Z)

STEP 3: Z Implicit

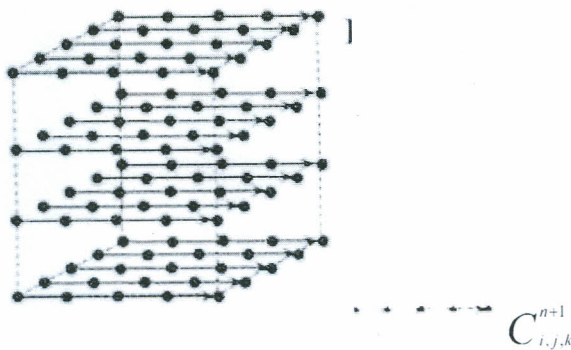


Figure 7: Explicit in (X,Y)

problems. The incorporation of Thomas algorithm is based on the fact that the inversions of matrices produced by explicit numerical methods are easier to solve compared to those of implicit numerical methods but require smaller time intervals. That is why the ADI method is preferred over other numerical methods.

Chapter 4

Model Equation Solution

Based on Douglas - Gumm approach we rewrite our equation as follows;

$$\begin{aligned}
 R(C) (C^{n+1} - C^n) &= D_x r_x \left(\partial_x^2 \left(\frac{C^{n+1} + C^n}{2} \right) - \frac{v_x m_x}{4} (\partial_x (C^{n+1} + C^n)) \right) \\
 &\quad + \frac{D_y r_y}{2} \partial_y^2 (C^{n+1} + C^n) + \frac{D_z r_z}{2} \partial_z^2 (C^{n+1} + C^n)
 \end{aligned}
 \tag{4.0.1}$$

Instead of directly solving the equation at time step n, we solve the same equation at three sub-time steps [32];

$$\begin{aligned}
 \text{Step 1:- } R(C) \left(C^{n+\frac{1}{3}} - C^n \right) &= \frac{D_x r_{x_i}}{2} \partial_x^2 \left(C^{n+\frac{1}{3}} + C^n \right) - \frac{v_x m_x}{4} \partial_x \left(C^{n+\frac{1}{3}} + C^n \right) \\
 &\quad + D_y r_y \partial_y^2 C^n + D_z r_z \partial_z^2 C^n
 \end{aligned}
 \tag{4.0.2}$$

$$\begin{aligned}
 \text{Step 2:- } R(C) \left(C^{n+\frac{2}{3}} - C^n \right) &= \frac{D_x r_{x_i}}{2} \partial_x^2 \left(C^{n+\frac{1}{3}} + C^n \right) - \frac{v_x m_x}{4} \partial_x \left(C^{n+\frac{1}{3}} + C^n \right) \\
 &\quad + \frac{D_y r_y}{2} \partial_y^2 \left(C^{n+\frac{2}{3}} + C^n \right) + D_z r_z \partial_z^2 (C^n)
 \end{aligned}
 \tag{4.0.3}$$

$$\begin{aligned}
 \text{Step 3:- } R(C) (C^{n+1} - C^n) &= \frac{D_x r_{x_i}}{2} \partial_x^2 \left(C^{n+\frac{1}{3}} + C^n \right) - \frac{v_x m_x}{4} \partial_x \left(C^{n+\frac{1}{3}} + C^n \right) \\
 &\quad + \frac{D_y r_{y_j}}{2} \partial_y^2 \left(C^{n+\frac{2}{3}} + C^n \right) + \frac{D_z r_{z_k}}{2} \partial_z^2 (C^{n+1} + C^n)
 \end{aligned}
 \tag{4.0.4}$$

Expanding the equation in the steps above we have

Step 1

$$\begin{aligned}
 R(C_{i,j,k}^n) (C_{i,j,k}^{n+\frac{1}{3}} - C_{i,j,k}^n) &= \frac{D_x r_{x_i}}{2} \left[(C_{i+1,j,k}^{n+\frac{1}{3}} - 2C_{i,j,k}^{n+\frac{1}{3}} + C_{i-1,j,k}^{n+\frac{1}{3}}) + (C_{i+1,j,k}^n - 2C_{i,j,k}^n + C_{i-1,j,k}^n) \right] \\
 &\quad - \frac{V_x m_x}{4} \left[(C_{i+1,j,k}^{n+\frac{1}{3}} - C_{i-1,j,k}^{n+\frac{1}{3}}) + (C_{i+1,j,k}^n - C_{i-1,j,k}^n) \right] \\
 &\quad + [D_y r_y (C_{i,j+1,k}^n - 2C_{i,j,k}^n + C_{i,j-1,k}^n) + D_z r_z (C_{i,j,k+1}^n - 2C_{i,j,k}^n + C_{i,j,k-1}^n)]
 \end{aligned} \tag{4.0.5}$$

Step 2

$$\begin{aligned}
 R(C_{i,j,k}^n) (C_{i,j,k}^{n+\frac{2}{3}} - C_{i,j,k}^n) &= \frac{D_x r_x}{2} \left[(C_{i+1,j,k}^{n+\frac{1}{3}} - 2C_{i,j,k}^{n+\frac{1}{3}} + C_{i-1,j,k}^{n+\frac{1}{3}}) + (C_{i+1,j,k}^n - 2C_{i,j,k}^n + C_{i-1,j,k}^n) \right] \\
 &\quad - \frac{V_x m_x}{4} \left[(C_{i+1,j,k}^{n+\frac{1}{3}} - C_{i-1,j,k}^{n+\frac{1}{3}}) + (C_{i+1,j,k}^n - C_{i-1,j,k}^n) \right] \\
 &\quad + \frac{D_y r_y}{2} \left[(C_{i,j+1,k}^{n+\frac{2}{3}} - 2C_{i,j,k}^{n+\frac{2}{3}} + C_{i,j-1,k}^{n+\frac{2}{3}}) + (C_{i,j+1,k}^n - 2C_{i,j,k}^n + C_{i,j-1,k}^n) \right] \\
 &\quad + D_z r_z [C_{i,j,k+1}^n - 2C_{i,j,k}^n + C_{i,j,k-1}^n]
 \end{aligned} \tag{4.0.6}$$

Step 3

$$\begin{aligned}
 R(C_{i,j,k}^n) (C_{i,j,k}^{n+1} - C_{i,j,k}^n) &= \frac{D_x r_x}{2} \left[(C_{i+1,j,k}^{n+\frac{1}{3}} - 2C_{i,j,k}^{n+\frac{1}{3}} + C_{i-1,j,k}^{n+\frac{1}{3}}) + (C_{i+1,j,k}^n - 2C_{i,j,k}^n + C_{i-1,j,k}^n) \right] \\
 &\quad - \frac{V_x m_x}{4} \left[(C_{i+1,j,k}^{n+\frac{1}{3}} - C_{i-1,j,k}^{n+\frac{1}{3}}) + (C_{i+1,j,k}^n - C_{i-1,j,k}^n) \right] \\
 &\quad + \frac{D_y r_y}{2} \left[(C_{i,j+1,k}^{n+\frac{2}{3}} - 2C_{i,j,k}^{n+\frac{2}{3}} + C_{i,j-1,k}^{n+\frac{2}{3}}) + (C_{i,j+1,k}^n - 2C_{i,j,k}^n + C_{i,j-1,k}^n) \right] \\
 &\quad + \frac{D_z r_z}{2} [(C_{i,j,k+1}^{n+1} - 2C_{i,j,k}^{n+1} + C_{i,j,k-1}^{n+1}) + (C_{i,j,k+1}^n - 2C_{i,j,k}^n + C_{i,j,k-1}^n)]
 \end{aligned} \tag{4.0.7}$$

Rearranging the equation gives us the equation which provides the matrix of solving the model equation;

Stage 1; Implicit in x direction, explicit in (y, z) directions

$$\begin{aligned}
& - \left(\frac{v_x m_x}{4R(C^n_{i,j,k})} + \frac{D_x r_x}{2R(C^n_{i,j,k})} \right) C_{i-1,j,k}^{n+\frac{1}{3}} + \left(1 + \frac{D_x r_x}{R(C^n_{i,j,k})} \right) C_{i,j,k}^{n+\frac{1}{3}} + \left(\frac{v_x m_x}{4R(C^n_{i,j,k})} - \frac{D_x r_x}{2R(C^n_{i,j,k})} \right) C_{i+1,j,k}^{n+\frac{1}{3}} \\
& = \left(\frac{D_x r_x}{2R(C^n_{i,j,k})} + \frac{v_x m_x}{4R(C^n_{i,j,k})} \right) C_{i-1,j,k}^n + \frac{D_y r_y}{R(C^n_{i,j,k})} C_{i,j-1,k}^n + \frac{D_z r_z}{R(C^n_{i,j,k})} C_{i,j,k-1}^n \\
& + \left(1 - \frac{D_x r_x}{R(C^n_{i,j,k})} - \frac{2D_y r_y}{R(C^n_{i,j,k})} - \frac{2D_z r_z}{R(C^n_{i,j,k})} \right) C_{i,j,k}^n + \left(\frac{D_x r_x}{2R(C^n_{i,j,k})} - \frac{v_x m_x}{4R(C^n_{i,j,k})} \right) C_{i+1,j,k}^n \\
& + \frac{D_y r_y}{R(C^n_{i,j,k})} C_{i,j+1,k}^n + \frac{D_z r_z}{R(C^n_{i,j,k})} C_{i,j,k+1}^n
\end{aligned} \tag{4.0.8}$$

Let, $A'_i = \frac{D_x r_x}{R(C^n_{i,j,k})}$, $B'_i = \frac{v_x m_x}{R(C^n_{i,j,k})}$, $C'_j = \frac{D_y r_y}{R(C^n_{i,j,k})}$ and $D'_k = \frac{D_z r_z}{R(C^n_{i,j,k})}$.

$$a_i C_{i-1,j,k}^{n+\frac{1}{3}} + b_i C_{i,j,k}^{n+\frac{1}{3}} + c_i C_{i+1,j,k}^{n+\frac{1}{3}} = d_i$$

Its matrix is, where $a_1 = 0$ and $c_n = 0$

$$\tag{4.0.9}$$

$$\begin{bmatrix}
b_1 & c_1 & & & & & & 0 \\
a_2 & b_2 & c_2 & & & & & \\
& a_3 & b_3 & c_3 & & & & \\
& & - & - & - & & & \\
& & & - & - & - & & \\
& & & & - & - & - & \\
& & & & & - & - & - \\
& & & & & & - & - & - \\
& & & & & & & - & - & - \\
& & & & & & & & - & - & - \\
& & & & & & & & & - & - & - \\
& & & & & & & & & & - & - & - \\
& & & & & & & & & & & - & - & - \\
& & & & & & & & & & & & - & - & - \\
& & & & & & & & & & & & & - & - & - \\
& & & & & & & & & & & & & & - & - & - \\
& & & & & & & & & & & & & & & - & - & - \\
0 & & & & & & & & & & & & & & & & a_n & b_n
\end{bmatrix}
\begin{bmatrix}
C_{1,j,k}^{\frac{4}{3}} \\
C_{2,j,k}^{\frac{7}{3}} \\
C_{3,j,k}^{\frac{10}{3}} \\
- \\
- \\
- \\
- \\
- \\
- \\
C_{n-1,j,k}^{n-\frac{2}{3}} \\
C_{n,j,k}^{n+\frac{1}{3}}
\end{bmatrix}
=
\begin{bmatrix}
d_1 \\
d_2 \\
d_3 \\
- \\
- \\
- \\
- \\
- \\
- \\
d_{n-1} \\
d_n
\end{bmatrix}$$

where,

$$\begin{aligned}
& a_i = - \left(\frac{1}{4} B'_i + \frac{1}{2} A'_i \right), \quad b_i = (1 + A'_i), \quad c_i = \left(\frac{1}{4} B'_i - \frac{1}{2} A'_i \right), \quad \text{and} \quad d_i = \left(\frac{1}{2} A'_i + \frac{1}{4} B'_i \right) C_{i-1,j,k}^n + \\
& C'_j C_{i,j-1,k}^n + D'_k C_{i,j,k-1}^n + \left(1 - A'_i - 2C'_j - 2D'_k \right) C_{i,j,k}^n + \left(\frac{1}{2} A'_i - \frac{1}{4} B'_i \right) C_{i+1,j,k}^n \\
& + C'_j C_{i,j+1,k}^n + D'_k C_{i,j,k+1}^n
\end{aligned}$$

Stage 2; Implicit in y direction, explicit in (x, z) directions

$$\begin{aligned}
 & -\frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j-1,k}^{n+\frac{2}{3}} + \left(1 + \frac{D_y r_y}{R(C_{i,j,k}^n)}\right) C_{i,j,k}^{n+\frac{2}{3}} - \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j+1,k}^{n+\frac{2}{3}} = \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i-1,j,k}^{n+\frac{1}{3}} \\
 & + \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i-1,j,k}^n + \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i-1,j,k}^n + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j-1,k}^n + \frac{D_z r_z}{R(C_{i,j,k}^n)} C_{i,j,k-1}^n \\
 & + \left(C_{i,j,k}^n - \frac{D_x r_x}{R(C_{i,j,k}^n)} C_{i,j,k}^{n+\frac{1}{3}} - \frac{D_x r_x}{R(C_{i,j,k}^n)} C_{i,j,k}^n - \frac{D_y r_y}{R(C_{i,j,k}^n)} C_{i,j,k}^n - \frac{2D_z r_z}{R(C_{i,j,k}^n)} C_{i,j,k}^n\right) \\
 & + \left(\frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i+1,j,k}^{n+\frac{1}{3}} + \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i+1,j,k}^n - \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i+1,j,k}^{n+\frac{1}{3}} - \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i+1,j,k}^n + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j+1,k}^n\right. \\
 & \qquad \qquad \qquad \left. + \frac{D_z r_z}{R(C_{i,j,k}^n)} C_{i,j,k+1}^n\right)
 \end{aligned} \tag{4.0.10}$$

Let

$$a_j C_{i,j-1,k}^{n+\frac{2}{3}} + b_j C_{i,j,k}^{n+\frac{2}{3}} + c_j C_{i,j+1,k}^{n+\frac{2}{3}} = d_j \tag{4.0.11}$$

where $a_j = 0$ and $c_n = 0$

$$\begin{bmatrix} b_1 & c_1 & & & & & & & & 0 \\ a_2 & b_2 & c_2 & & & & & & & \\ & a_3 & b_3 & c_3 & & & & & & \\ & & - & - & - & & & & & \\ & & & - & - & - & & & & \\ & & & & - & - & - & & & \\ & & & & & - & - & - & & \\ & & & & & & - & - & - & \\ & & & & & & & - & - & c_{n-1} \\ 0 & & & & & & & & & a_n & b_n \end{bmatrix} \begin{bmatrix} C_{i,1,k}^{\frac{5}{3}} \\ C_{i,2,j}^{\frac{8}{3}} \\ C_{i,3,k}^{\frac{11}{3}} \\ - \\ - \\ - \\ - \\ - \\ C_{i,n-1,k}^{n-\frac{1}{3}} \\ C_{i,n,k}^{n+\frac{2}{3}} \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ - \\ - \\ - \\ - \\ d_{n-1} \\ d_n \end{bmatrix}$$

$$a_j = -\frac{C'_j}{2}, b_j = (1 + C'_j), c_j = -\frac{C'_j}{2}$$

$$\begin{aligned}
 d_j = & \frac{1}{2} A'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{4} B'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{2} A'_i C_{i-1,j,k}^n + \frac{1}{4} B'_i C_{i-1,j,k}^n + \frac{C'_j}{2} C_{i,j-1,k}^n + D'_k C_{i,j,k-1}^n \\
 & + \left(C_{i,j,k}^n - A'_i C_{i,j,k}^{n+\frac{1}{3}} - A'_i C_{i,j,k}^n - C'_j C_{i,j,k}^n - 2D'_k C_{i,j,k}^n\right)
 \end{aligned}$$

$$+ \left(\begin{array}{c} \frac{1}{2} A'_i C_{i+1,j,k}^{n+\frac{1}{3}} + \frac{1}{2} A'_i C_{i+1,j,k}^n - \frac{1}{4} B'_i C_{i+1,j,k}^{n+\frac{1}{3}} - \frac{1}{4} B'_i C_{i+1,j,k}^n + \frac{C'_j}{2} C_{i,j+1,k}^m \\ + D'_k C_{i,j,k+1}^n \end{array} \right)$$

Step 3; Implicit in z direction, explicit in (x, y) direction

$$\begin{aligned} & -\frac{D_z r_z}{2R(C_{i,j,k}^n)} C_{i,j,k-1}^{m+1} + \left(1 + \frac{D_z r_z}{R(C_{i,j,k}^n)} \right) C_{i,j,k}^{m+1} - \frac{D_z r_z}{2R(C_{i,j,k}^n)} C_{i,j,k+1}^{m+1} \\ & = \left(\begin{array}{c} \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i-1,j,k}^m + \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i-1,j,k}^n + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j-1,k}^{n+\frac{2}{3}} \\ + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j-1,k}^n + \frac{D_z r_z}{2R(C_{i,j,k}^n)} C_{i,j,k-1}^n \end{array} \right) \\ & + \left(C_{i,j,k}^n - \frac{D_x r_x}{R(C_{i,j,k}^n)} C_{i,j,k}^{n+\frac{1}{3}} - \frac{D_x r_x}{R(C_{i,j,k}^n)} C_{i,j,k}^n - \frac{D_y r_y}{R(C_{i,j,k}^n)} C_{i,j,k}^{n+\frac{2}{3}} - \frac{D_y r_y}{R(C_{i,j,k}^n)} C_{i,j,k}^n - \frac{D_z r_z}{R(C_{i,j,k}^n)} C_{i,j,k}^n \right) \\ & + \left(\begin{array}{c} \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i+1,j,k}^{n+\frac{1}{3}} + \frac{D_x r_x}{2R(C_{i,j,k}^n)} C_{i+1,j,k}^n - \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i+1,j,k}^{n+\frac{1}{3}} - \frac{v_x m_x}{4R(C_{i,j,k}^n)} C_{i+1,j,k}^n + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j+1,k}^{n+\frac{2}{3}} \\ + \frac{D_y r_y}{2R(C_{i,j,k}^n)} C_{i,j+1,k}^n + \frac{D_z r_z}{2R(C_{i,j,k}^n)} C_{i,j,k+1}^n \end{array} \right) \end{aligned} \quad (4.0.12)$$

$$a_k C_{i,j,k-1}^{n+1} + b_k C_{i,j,k}^{n+1} + c_k C_{i,j,k+1}^{n+1} = d_k$$

(4.0.13)

Matrix is, where $a_k = 0$ and $c_n = 0$

$$\begin{bmatrix} b_1 & c_1 & & & & & & & & & 0 \\ a_2 & b_2 & c_2 & & & & & & & & \\ & a_3 & b_3 & c_3 & & & & & & & \\ & & - & - & - & & & & & & \\ & & & - & - & - & & & & & \\ & & & & - & - & - & & & & \\ & & & & & - & - & - & & & \\ & & & & & & - & - & - & & \\ & & & & & & & - & - & c_{n-1} & \\ 0 & & & & & & & & & a_n & b_n \end{bmatrix} \begin{bmatrix} C_{i,j,1}^2 \\ C_{i,j,3}^3 \\ C_{i,j,k}^4 \\ - \\ - \\ - \\ - \\ - \\ C_{i,j,n-1}^n \\ C_{i,j,n}^{n+1} \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ - \\ - \\ - \\ - \\ - \\ d_{n-1} \\ d_n \end{bmatrix}$$

$$a_k = -\frac{D'_k}{2}, b_k = (1 + D'_k), c = -\frac{D'_k}{2}$$

$$d_k = \left(\frac{1}{2}A'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{4}B'_i C_{i-1,j,k}^n + \frac{1}{4}B'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{2}A'_i C_{i-1,j,k}^n + \frac{C'_j}{2} C_{i,j-1,k}^{n+\frac{2}{3}} + \frac{C'_j}{2} C_{i,j-1,k}^n + \frac{D'_k}{2} C_{i,j,k-1}^n \right) \\ + \left(C_{i,j,k}^n - A'_i C_{i,j,k}^{n+\frac{1}{3}} - A'_i C_{i,j,k}^n - C'_j C_{i,j,k}^{n+\frac{2}{3}} - C C_{i,j,k}^n - D'_k C_{i,j,k}^n \right) \\ + \left(\frac{1}{2}A'_i C_{i+1,j,k}^{n+\frac{1}{3}} + \frac{1}{2}A'_i C_{i+1,j,k}^n - \frac{1}{4}B'_i C_{i+1,j,k}^{n+\frac{1}{3}} - \frac{1}{4}B'_i C_{i+1,j,k}^n + \frac{C'_j}{2} C_{i,j+1,k}^{n+\frac{2}{3}} \right) \\ + \left(\frac{C'_j}{2} C_{i,j+1,k}^n + \frac{D'_k}{2} C_{i,j,k+1}^n \right)$$

The above is the solution to the model equation, which are equations (4.0.8), (4.0.10) and (4.0.12).

$$\text{Let } A'_i = \frac{D_{x_i} r_x}{R(C_{i,j,k}^n)}, \quad B'_i = \frac{V_{x_i} m_x}{R(C_{i,j,k}^n)}, \quad C'_j = \frac{D_{y_j} r_y}{R(C_{i,j,k}^n)} \text{ and } D'_k = \frac{D_{z_k} r_z}{R(C_{i,j,k}^n)}$$

$I=1,2,\dots,I, j=1,2,\dots,J$ and $k=1,2,\dots,K$

In each of the three steps, we have $I + 1$ equations for each of (j, k) , $J + 1$ equations for each of (i, k) and $K + 1$ for each of (i, j) value. We also have three unknown values in variables in each step.

In all the three cases, the tridiagonal matrix can be solved by use of Thomas algorithm.

In numerical algebra, the triadiagonal matrix (TDMA), which is simplified form of Gaussian elimination can be used to solve numerical equations like this. The triadiagonal system of one dimension for n unknown may be written as;

$$a_i C_{i-1,j,k}^{n+\frac{1}{3}} + b_i C_{i,j,k}^{n+\frac{1}{3}} + c_i C_{i+1,j,k}^{n+\frac{1}{3}} = d_i$$

$$a_j C_{i,j-1,k}^{n+\frac{2}{3}} + b_j C_{i,j,k}^{n+\frac{2}{3}} + c_j C_{i,j+1,k}^{n+\frac{2}{3}} = d_j$$

$$a_k C_{i,j,k-1}^{n+1} + b_k C_{i,j,k}^{n+1} + c_k C_{i,j,k+1}^{n+1} = d_k$$

(4.0.14)

where $a_1 = 0$ and $c_n = 0$

This algorithm is only applicable to matrixes that are diagonally dominant, as illustrated

below;

$$\begin{bmatrix}
 b_1 & c_1 & & & & & & & & & & 0 \\
 a_2 & b_2 & c_2 & & & & & & & & & \\
 & a_3 & b_3 & c_3 & & & & & & & & \\
 & & - & - & - & & & & & & & \\
 & & & - & - & - & & & & & & \\
 & & & & - & - & - & & & & & \\
 & & & & & - & - & - & & & & \\
 & & & & & & - & - & - & & & \\
 & & & & & & & - & - & c_{n-1} & & \\
 0 & & & & & & & & & a_n & b_n & \\
 \end{bmatrix}
 \begin{bmatrix}
 C_{1,j,k} \\
 C_{2,j,k} \\
 C_{3,j,k} \\
 - \\
 - \\
 - \\
 - \\
 - \\
 C_{n-1,j,k} \\
 C_{n,j,k}
 \end{bmatrix}
 =
 \begin{bmatrix}
 d_1 \\
 d_2 \\
 d_3 \\
 - \\
 - \\
 - \\
 - \\
 - \\
 d_{n-1} \\
 d_n
 \end{bmatrix}$$

(4.0.15)

The same matrix is developed for (j, k)

The first step consists of modifying the coefficients as follows, denoting the new modified coefficients with primes

$$c'_i = \begin{cases} \frac{c_i}{b_i}; i = 1 \\ \frac{c_i}{b_i - c'_{i-1} a_i}; i = 2, 3, \dots, n-1 \end{cases}$$

(4.0.16)

$$d'_i = \begin{cases} \frac{d_i}{b_i}; i = 1 \\ \frac{d_i - d_{i-1} a_i}{b_i - c'_{i-1} a_i}; i = 2, 3, \dots, n-1 \end{cases}$$

(4.0.17)

This is a forward sweep. The solution is obtained by back substitution;

$$C_n = d'_n$$

$$C_i = d'_i - c'_i x_{i+1}; i = n-1, n-2, \dots, 1$$

(4.0.18)

This will be the method that will be applied in finding the solution of the model equation.

4.1 Confirmation of stability using Von Neumann Method

Fourier method is preferred to other methods because of its power and flexibility in analysis, it has facilitated an incredibly diverse range of applications to modern science and engineering.

Douglas and Gunn derived an ADI scheme based on "approximating factoring" that is unconditionally stable and retains second order accuracy when applied to three dimensions' schemes.

A development of the scheme that highlights the approximate factorization point of view is best carried out making use of a *delta* form of the equation. A delta form expresses the unknown quantity as the change from a known value of the variable of interest. Here we use a time delta and define,

$$C_{i,j,k}^{n+1} = C_{i,j,k}^n + \Delta C_{i,j,k}. \quad (4.1.1)$$

In this analysis, the discrete Fourier transform is used

$$\text{Take } C_{i,j,k}^n = \sum_{ijk} \hat{C}_{i,j,k}^n e^{\kappa\theta_x i} e^{\kappa\theta_y j} e^{\kappa\theta_z k}, \quad (4.1.2)$$

$\kappa = \sqrt{-1}$, $\hat{C}_{i,j,k}^n$ is a discretized concentration, $\theta_x = 2\pi\omega_x x_i$, $\theta_y = 2\pi\omega_y y_j$, and $\theta_z = 2\pi\omega_z z_k$.

$i = 0, 1, \dots, I - 1$, $j = 0, 1, \dots, J - 1$, and $k = 0, 1, \dots, K - 1$,

$-\pi \leq \theta_x, \theta_y, \theta_z \leq \pi$, and $\omega = (\omega_x, \omega_y, \omega_z)$

Using the discretization and Fourier transform for equations (4.3.3) and (4.0.17) we get following,

Stage 1

$$\left(1 - \frac{1}{2}A'_i\partial_x^2 + \frac{1}{4}B'_i\partial_x\right) C^{n+\frac{1}{3}} = \left(1 + \frac{1}{2}A'_i\partial_x^2 - \frac{1}{4}B'_i\partial_x + C'_j\partial_y^2 + D'_k\partial_z^2\right) C^n \quad (4.1.3)$$

Equation (4.1.3) becomes;

$$\begin{aligned}
 & C_{i,j,k}^{n+\frac{1}{3}} - \frac{1}{2}A'_i \left(C_{i+1,j,k}^{n+\frac{1}{3}} - 2C_{i,j,k}^{n+\frac{1}{3}} + C_{i-1,j,k}^{n+\frac{1}{3}} \right) + \frac{B'_i}{4} \left(C_{i+1,j,k}^{n+\frac{1}{3}} - C_{i-1,j,k}^{n+\frac{1}{3}} \right) \\
 &= \left[\begin{array}{l} C_{i,j,k}^n + \frac{1}{2}A'_i \left(C_{i+1,j,k}^n - 2C_{i,j,k}^n + C_{i-1,j,k}^n \right) \\ -\frac{B'_i}{4} \left(C_{i+1,j,k}^n - C_{i-1,j,k}^n \right) \\ +C'_j \left(C_{i,j+1,k}^n - 2C_{i,j,k}^n + C_{i,j-1,k}^n \right) \\ +D'_k \left(C_{i,j,k+1}^n - 2C_{i,j,k}^n + C_{i,j,k}^n \right) \end{array} \right]
 \end{aligned}
 \tag{4.1.4}$$

Using equation (4.1.2), we find the following expression;

$$\begin{aligned}
 & \left[1 - A'_i \left(\frac{e^{\kappa\theta_x} + e^{-\kappa\theta_x}}{2} - 1 \right) + \frac{1}{2}B'_i\kappa \left(\frac{e^{\kappa\theta_x} - e^{-\kappa\theta_x}}{2\kappa} \right) \right] \hat{C}_{i,j,k}^{n+\frac{1}{3}} = \\
 & \left[\begin{array}{l} 1 + A'_i \left(\frac{e^{\kappa\theta_x} + e^{-\kappa\theta_x}}{2} - 1 \right) - \frac{1}{2}B'_i\kappa \left(\frac{e^{\kappa\theta_x} - e^{-\kappa\theta_x}}{2\kappa} \right) \\ 2C'_j \left(\frac{e^{\kappa\theta_y} + e^{-\kappa\theta_y}}{2} - 1 \right) + 2D'_k \left(\frac{e^{\kappa\theta_z} + e^{-\kappa\theta_z}}{2} - 1 \right) \end{array} \right] \hat{C}_{i,j,k}^n
 \end{aligned}
 \tag{4.1.5}$$

From basic trigonometry, $\text{Sin}\theta = \frac{e^{\kappa\theta} - e^{-\kappa\theta}}{2\kappa}$ and $\text{Cos}\theta = \frac{e^{\kappa\theta} + e^{-\kappa\theta}}{2}$. Therefore;

$$\text{Cos}\theta = \text{Cos}^2\frac{\theta}{2} - \text{Sin}^2\frac{\theta}{2}, \quad \text{Sin}^2\frac{\theta}{2} + \text{Cos}^2\frac{\theta}{2} = 1 \quad \text{and} \quad \text{Sin}\theta = 2\text{Sin}\frac{\theta}{2}\text{Cos}\frac{\theta}{2},$$

Therefore,

$$\left[1 + 2A'_i\text{Sin}^2\frac{\theta_x}{2} + B'_i\kappa\text{Sin}\frac{\theta_x}{2}\text{Cos}\frac{\theta_x}{2} \right] \hat{C}_{i,j,k}^{n+\frac{1}{3}} = \left[\begin{array}{l} 1 - 2A'_i\text{Sin}^2\frac{\theta_x}{2} - B'_i\kappa\text{Sin}\frac{\theta_x}{2}\text{Cos}\frac{\theta_x}{2} \\ -4C'_j\text{Sin}\frac{\theta_y}{2} - 4D'_k\text{Sin}\frac{\theta_z}{2} \end{array} \right] \hat{C}_{i,j,k}^n
 \tag{4.1.6}$$

The amplification factor $\xi^{\frac{1}{3}}$ is given as;

$$\left[1 + 2A'_i\text{Sin}^2\frac{\theta_x}{2} + B'_i\kappa\text{Sin}\frac{\theta_x}{2}\text{Cos}\frac{\theta_x}{2} \right] \xi^{\frac{1}{3}} = \left[1 - 2A'_i\text{Sin}^2\frac{\theta_x}{2} - \kappa B'_i\text{Sin}\frac{\theta_x}{2}\text{Cos}\frac{\theta_x}{2} - 4C'_j\text{Sin}^2\frac{\theta_y}{2} - 4D'_k\text{Sin}^2\frac{\theta_z}{2} \right]
 \tag{4.1.7}$$

where $\theta_x = \theta_y = \theta_z = \theta = m\pi; m \in I, J, K$, and let $\xi^{\frac{1}{3}} = G_x$, let $\text{sin}\frac{\theta_x}{2} = s_x$, $\text{cos}\frac{\theta_x}{2} = c_x$,

$$\sin \frac{\theta_y}{2} = s_y, \text{ and } \sin \frac{\theta_z}{2} = s_z$$

$$\xi^{\frac{1}{3}} = \frac{(1 - 2A'_i s_x^2 - B'_i \kappa s_x c_x - 4C'_j s_y^2 - 4D'_k s_z^2)}{(1 + 2A'_i s_x^2 + B'_i \kappa s_x c_x)}$$

Using conjugate to eliminate the complex denominator.

$$\xi^{\frac{1}{3}} = \frac{(1 - 2A'_i s_x^2 - B'_i \kappa s_x c_x - 4C'_j s_y^2 - 4D'_k s_z^2) ((1 + 2A'_i s_x^2) - (B'_i \kappa s_x c_x))}{((1 + 2A'_i s_x^2)^2 + (B'_i \kappa s_x c_x)^2)}$$

For cases where , $A'_i = C'_j = D'_k = A'$ and $\theta_x = \theta_y = \theta_z = \theta$

$$\xi^{\frac{1}{3}} = \frac{(1 - 10A' s^2 - B'_i \kappa s c) ((1 + 2A' s^2) - (B'_i \kappa s c))}{((1 + 2A' s^2)^2 + (B'_i \kappa s c)^2)}$$

$$G_x = \left[\frac{|(1 - 8A' s^2 - 20(A')^2 s^4 + (B'_i \kappa s c)^2)^2 + (12AB'_i s^3 c + 2B'_i \kappa s c)^2|}{((1 + 2A' s^2)^2 + (B'_i \kappa s c)^2)} \right] \leq 1$$

(4.1.8)

Stage 2

$$\begin{aligned} C^{n+\frac{2}{3}} - \frac{1}{2} C'_j \partial_y^2 C^{n+\frac{2}{3}} &= C^n + \frac{1}{2} A'_i \partial_x^2 C^{n+\frac{1}{3}} - \frac{1}{4} B'_i \partial_x C^{n+\frac{1}{3}} + \frac{1}{2} A'_i \partial_x^2 C^n - \frac{1}{4} B'_i \partial_x C^n \\ &+ \frac{1}{2} C'_j \partial_y^2 C^n + D'_k \partial_z^2 (C^n) \end{aligned}$$

(4.1.9)

Following the same process as in stage 1

$$\begin{aligned} \left(1 + 2C'_j \sin^2 \frac{\theta_y}{2}\right) \hat{C}_{i,j,k}^{n+\frac{2}{3}} &= \left[1 - 2A'_i \sin^2 \frac{\theta_x}{2} - 2C'_j \sin^2 \frac{\theta_y}{2} - 4D'_k \sin^2 \frac{\theta_z}{2} - B'_i \kappa \sin \frac{\theta_x}{2} \cos \frac{\theta_x}{2}\right] \hat{C}_{i,j,k}^n \\ &- \left[2A'_i \sin^2 \frac{\theta_x}{2} + B'_i \kappa \sin \frac{\theta_x}{2} \cos \frac{\theta_x}{2}\right] \hat{C}_{i,j,k}^{n+\frac{1}{3}} \end{aligned}$$

quad

(4.1.10)

$$\hat{C}_{i,j,k}^{n+\frac{1}{3}} = \left[\frac{1 - 2A'_i \text{Sin}^2 \frac{\theta_x}{2} - 4C'_j \text{Sin}^2 \frac{\theta_y}{2} - 4D'_k \text{Sin}^2 \frac{\theta_z}{2} - \kappa B'_i \text{Sin} \frac{\theta_x}{2} \text{Cos} \frac{\theta_x}{2}}{1 + 2A'_i \text{Sin}^2 \frac{\theta_x}{2} + \kappa B'_i \text{Sin} \frac{\theta_x}{2} \text{Cos} \frac{\theta_x}{2}} \right] \hat{C}_{i,j,k}^n$$

Making the denominator real numbers by multiplying denominator and nominator with conjugator of denominator gives us;

$$\hat{C}_{i,j,k}^{n+\frac{1}{3}} = \left[\frac{|(1 - 8A's^2 - 20(A')^2 s^4 + (B'_i sc)^2) + \kappa(12AB'_i s^3 c + 2B'_i sc)|}{((1 + 2A's^2)^2 + (B'_i sc)^2)} \right]$$

which gives us,

$$\hat{C}_{i,j,k}^{n+\frac{2}{3}} = \frac{\left[\begin{array}{c} (1 - 6A's^2 - 12A'^2 s^4 + 8A'^3 s^6 - 10A'B'^2_i s^4 c^2 + B'^2_i s^2 c^2) \\ -\kappa(B'_i sc - 16A'B'^2_i s^4 c^2 - 16A'^2 B'_i s^5 c) \end{array} \right] \hat{C}_{i,j,k}^n}{((1 + 2A's^2)((1 + 2As^2)^2 + (B'_i sc)^2))}$$

(4.1.11)

where $\theta_x = \theta_y = \theta_z = \theta = m\pi$; $m \in I, J, K$, and let $\xi^{\frac{2}{3}}$

(4.1.12)

Stage 3

$$\begin{aligned} R(C) (C^{m+1} - C^m) &= \frac{D_x r_x}{2} \partial_x^2 (C^{n+\frac{1}{3}} + C^n) - \frac{v_x m_x}{4} \partial_x (C^{n+\frac{1}{3}} + C^n) \\ &+ \frac{D_y r_y}{2} \partial_y^2 (C^{n+\frac{2}{3}} + C^n) + \frac{D_z r_z}{2} \partial_z^2 (C^{n+1} + C^n) \end{aligned}$$

(4.1.13)

Following the process in Stage 2;

$$\hat{C}_{i,j,k}^{n+1} = \left[\frac{\left(\begin{array}{c} (1 - 4A's^2 - 24A'^2 s^4 - 16A'^3 s^6 - 18A'B'^2_i s^2 c^2 + B'^2_i s^2 c^2 + 16A'^4 s^8 - 20A'^2 B'^2_i s^4 c^2) \\ -\kappa(B'_i sc - 16A'B'^2_i s^4 c^2 - 16A'^2 B'_i s^5 c^2 + 2A'B'_i s^3 c - 32A'^2 B'^2_i s^6 c^2 - 32A'^3 B'_i s^7 c) \end{array} \right)}{\left((1 + 2A's^2)^2 \left((1 + 2A's^2)^2 + (B'_i sc)^2 \right) \right)} \right] \hat{C}_{i,j,k}^n$$

Amplification factor

$$\xi_{i,j,k}^{n+1} = \left[\frac{\begin{aligned} & \left(1 - 4A's^2 - 24A'^2s^4 - 16A'^3s^6 - 18A'B'_i{}^2s^2c^2 + B'_i{}^2s^2c^2 + 16A'^4s^8 - 20A'^2B'_i{}^2s^4c^2 \right) \\ & - \kappa \left(B'_isc - 16A'B'_i{}^2s^4c^2 - 16A'^2B'_i{}^2s^5c^2 + 2A'B'_is^3c - 32A'^2B'_i{}^2s^6c^2 - 32A'^3B'_is^7c \right) \end{aligned}}{\left((1 + 2A's^2)^2 \left((1 + 2A's^2)^2 + (B'_isc)^2 \right) \right)} \right] \quad (4.1.15)$$

$$G_z = \left[\frac{\begin{aligned} & \left| \left(1 - 4A's^2 - 24A'^2s^4 - 16A'^3s^6 - 18A'B'_i{}^2s^2c^2 + B'_i{}^2s^2c^2 + 16A'^4s^8 - 20A'^2B'_i{}^2s^4c^2 \right)^2 \right. \\ & \left. + \left(B'_isc - 16A'B'_i{}^2s^4c^2 - 16A'^2B'_i{}^2s^5c^2 + 2A'B'_is^3c - 32A'^2B'_i{}^2s^6c^2 - 32A'^3B'_is^7c \right)^2 \right| \end{aligned}}{\left((1 + 2A's^2)^2 \left((1 + 2A's^2)^2 + (B'_isc)^2 \right) \right)} \right] \leq 1 \quad (4.1.16)$$

From the details above, the numerator is diminishing and denominator increasing therefore the theorem is right.

4.2 Determination of time step using stability criteria

4.3 Fourier or Von Neumann Stability analysis

Using Fourier transform,

$$C_{i,j,k}^n = \sum \hat{C}_{i,j,k}^n e^{\kappa\theta_x i} e^{\kappa\theta_y j} e^{\kappa\theta_z k} \text{ and let } \Delta x = \Delta y = \Delta z = h \quad (4.3.1)$$

and let $\Delta x = \Delta y = \Delta z = h$

(4.3.2)

$$C_{i,j,k}^{n+1} = C_{i,j,k}^n + \Delta C_{i,j,k}.$$

(4.3.3)

Fitting this in the model equation ;

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

(4.3.4)

Using equation (4.3.1),

Fourier transforms give;

$$R(\hat{C}_{i,j,k}^n) \frac{\partial \hat{C}_{x,y,z}}{\partial t} = \hat{C}_{i,j,k}^n \left(\frac{2D_x (\text{Cos}\theta_x - 1)}{h^2} - \frac{V_x \kappa \text{Sin}\theta_x}{2h} + \frac{2D_y (\text{Cos}\theta_y - 1)}{h^2} + \frac{2D_z (\text{Cos}\theta_z - 1)}{h^2} \right)$$

(4.2.1.3)

Define;

From equation

$$R(\hat{C}_{i,j,k}) \Delta \hat{C}(\theta_x, \theta_y, \theta_z) = \Delta t \hat{C}_{i,j,k}^n \left(-\frac{4D_x \text{Sin}^2 \frac{\theta_x}{2}}{h^2} - \frac{4D_y \text{Sin}^2 \frac{\theta_y}{2}}{h^2} - \frac{4D_z \text{Sin}^2 \frac{\theta_z}{2}}{h^2} - \frac{V_x \kappa \text{Sin}\theta_x}{2h} \right)$$

(4.3.5)

A particular time stepping scheme will be stable provided \hat{C} lies in its stability region.

Suppose that the stability region is contained in an ellipse:

$$\text{Stability Region: A: } \left(\frac{x}{\alpha_0} \right)^2 + \left(\frac{y}{\beta_0} \right)^2 \leq 1 \quad (4.2.1.4)$$

If real and imaginary parts \hat{C} are;

$$\hat{C} = \Re(\hat{C}) + i\Im(\hat{C})$$

(4.3.6)

then the scheme is stable provided,

$$\left(\frac{\Re(\hat{C})}{\alpha_0}\right)^2 + \left(\frac{\Im(\hat{C})}{\beta_0}\right)^2 \leq 1$$

which implies that:

$$\left[\left(\frac{-4\Delta t}{\alpha_0 h^2}\right)^2 \left(D_x \sin^2 \frac{\theta_x}{2} + D_y \sin^2 \frac{\theta_y}{2} + D_z \sin^2 \frac{\theta_z}{2}\right)^2 + \left(\frac{-\Delta t}{\beta_0 h}\right)^2 \left(\frac{1}{2} v_x \sin \theta_x\right)^2\right] \leq 1$$

(4.2.1.6)

which can be a sufficient condition, using $\theta_x = \theta_y = \theta_z = \theta = \frac{\pi}{2}$

Maximum value of a sine function is realized at $\frac{\pi}{2}$

$$\left[\left(\frac{-4\Delta t}{\alpha_0 h^2}\right)^2 \left(\frac{D_x}{2} + \frac{D_y}{2} + \frac{D_z}{2}\right)^2 + \left(\frac{-\Delta t}{\beta_0 h}\right)^2 \frac{1}{4} v_x^2\right] \leq 1$$

Implying that;

$$\Delta t \leq \left[\left[\left(\frac{-4}{\alpha_0 h^2}\right)^2 \left(\frac{D_x}{2} + \frac{D_y}{2} + \frac{D_z}{2}\right)^2 + \left(\frac{-v_x}{2\beta_0 h}\right)^2 \right]^{-1} \right]$$

(4.3.7)

α_0 and β_0 are constants which can be assumed to be equal to 1.

4.4 Determination of fractional step using stability in Multispace dimensions

Model Equation (4.3.4) is

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

Based on Discret Fourier Transformation and its inverse

$$C_{i,j,k} = \sum_{w=-N/2}^{N/2-1} C_w e^{2\pi i \omega (x_i + y_j + z_k)}$$

$$\hat{C}_w = \frac{1}{N} \sum_{ijk=0}^{N-1} C_{i,j,k} e^{-2\pi i \omega (x_i + y_j + z_k)h}$$

$$0 \leq x, y, z \leq 1$$

$$C(x, y, z, 0) = C_0(x, y, z)$$

C and C₀ 1Period

Discretization in space,

$$R(C) \frac{dC}{dt} = \left[2D_{x_i} D_{+x} D_{-x} C_{i,j,k} - 2v_{x_i} D_{+x} C_{i,j,k} + D_{y_j} D_{+y} D_{-y} C_{i,j,k} + D_{z_k} D_{+z} D_{-z} C_{i,j,k} \right] \quad (4.3.0.2)$$

$$i = 0, 1, 2, \dots, N - 1$$

$$j = 0, 1, 2, \dots, N - 1$$

$$k = 0, 1, 2, \dots, N - 1$$

$$\theta_x = 2\pi\omega_x x_i$$

$$\theta_y = 2\pi\omega_y y_j$$

$$\theta_z = 2\pi\omega_z z_k$$

$$R(\hat{C}_w) \frac{d\hat{C}_w}{dt} = \Delta t \left(- \left(\frac{4D_x \text{Sin}^2 \frac{\theta_x}{2}}{h_x^2} \right) - \left(\frac{4D_y \text{Sin}^2 \frac{\theta_y}{2}}{h_y^2} \right) - \left(\frac{4D_z \text{Sin}^2 \frac{\theta_z}{2}}{h_z^2} \right) - \left(\frac{v_x k \text{Sin} \frac{\theta_x}{2} \text{Cos} \frac{\theta_x}{2}}{2h} \right) \right)$$

(4.4.1)

$$h = \partial x = \partial y = \partial z$$

And the scheme will be stable for

$$Q(\theta_x, \theta_y, \theta_z) = \Delta t \left(- \left(\frac{4D_x \text{Sin}^2 \frac{\theta_x}{2}}{h_x^2} \right) - \left(\frac{4D_y \text{Sin}^2 \frac{\theta_y}{2}}{h_y^2} \right) - \left(\frac{4D_z \text{Sin}^2 \frac{\theta_z}{2}}{h_z^2} \right) - \left(\frac{v_x k \text{Sin} \frac{\theta_x}{2} \text{Cos} \frac{\theta_x}{2}}{2h} \right) \right)$$

(4.3.0.4)

For maximum value $\theta = \frac{\pi}{2} = \theta_x = \theta_y = \theta_z$,

$$|(Q)^2| = \left| \left[\left(\frac{-4\Delta t}{h} \right)^2 \left(\frac{D_x}{2h_x^2} + \frac{D_y}{2h_y^2} + \frac{D_z}{2h_z^2} \right)^2 + \left(\frac{v_x}{h} \right)^2 \right] \right|$$

(4.4.2)

$$\Delta t = |(Q)^2| \left| \left[(-4)^2 \left(\frac{D_x}{2h_x^2} + \frac{D_y}{2h_y^2} + \frac{D_z}{2h_z^2} \right)^2 + \left(\frac{v_x}{h_x} \right)^2 \right]^{-1} \right|$$

(4.4.3)

For Forward Euler time step, we require,

$|1 + Q| \leq 1$ Or since $Q \in \Re$ we need $-2 \leq Q \leq 0$

Chapter 5

Findings, Discussions and Results

5.1 Applications and Results

5.1.1 Experiment on adsorption and movement of selected at high concentration in soils

These experimental findings were used when analyzing 2D equations of Pesticides flow in the porous media under steady flow state [1, 24]. The experiment was designed for one dimension but was applied to two dimensions for low flow water in a porous media considering the theoretical parameters that govern process.

There is no documented experiment of this nature carried out in Kenya.

All the data availed here (both calculated and extracted from experimental results) is for facilitating analysis of the output through application and not meant for comparison of the output.

This analysis contains more information for purposes of giving a background of the experiment but eventually it will focus on one sample 2, 4 - D amine on Webster soil to qualify our mathematical model.

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 relevant to our mathematical model and not to give irrelevant information that will make our work to become amorphous. Experiment was carried out at Selected physical and chemical properties of these soils pertinent to this study are listed.

Table 5.1: Physical and chemical properties of soil used in this study

Particle size fraction (%) [24]

Soil	Sand	Silt	Clay	PH (1.1 paste)
Webster	18.4	45.3	38.3	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)

1. Pesticides movement through saturated columns of Webster, cecil and Eutis soils was studied using miscible displacement technique [24].
2. Air dried soils were packed in small increments into glass cylinders (15 cm long: .45 cm squared cross sectional area)
3. Medium porosity fitted glass end plates served to retain the soil in column.
4. A known volume of pesticide solution at a desired concentration was introduced into soil at a constant flux using a constant volume peristaltic pump.
5. The column experiments consisted of displacing 2, 4 - damine solution at two concentrations (i.e. 50 and 5000 μgMl^{-1}) through the columns of cecil. Eutis and webster's soil and 5 to 50 μgMl^{-1} of atrazine through Eustis soil.
6. All displacements were performed at a Darcy flux of approximately 0.22 cm/h to ensure equilibrium condition of pesticide adsorption during flow.

Table 5.2: Freundlich constants

7. The volume of water held in the soil column V_o was gravimetrically determined at the end of each displacement by extruding the soil from glass cylinders and over drying
8. The number of pore volume $\left(\frac{V}{V_o}\right)$ was calculated by dividing the cumulative outflow volume (V) by the total water volume V_o I the soil column. Effluent pesticide concentration is expressed at relative effluent and input concentration $\left(\frac{C}{C_o}\right)$ where C and C_o are, relatively. Plots of $\frac{C}{C_o}$ vs $\frac{V}{V_o}$ referred to as break through curves (or BTC)

BTC. 1 Number Graph [24]

The table below shows Freundlich constants calculated from equilibrium adsorption isotherm for various soil pesticide combination. [24]

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 qualify our mathematical model.

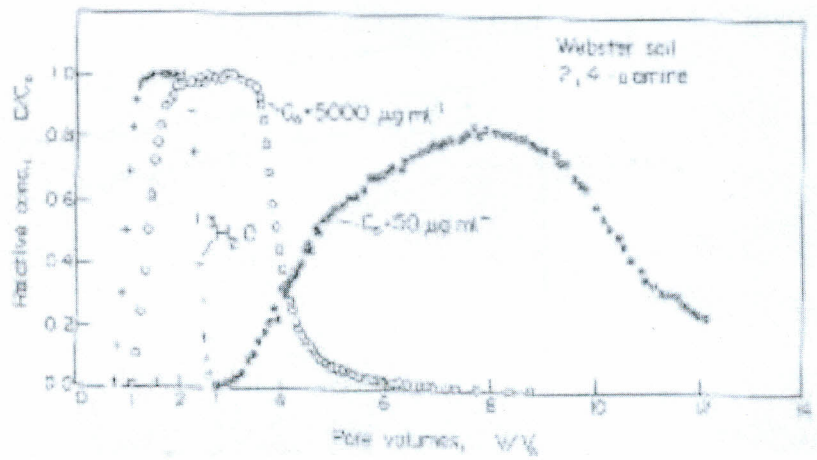


Figure 8: Sketch showing Effluent Breakthrough curves for 2,4-D amine two concentrations titiated water displacement through Webster soil column

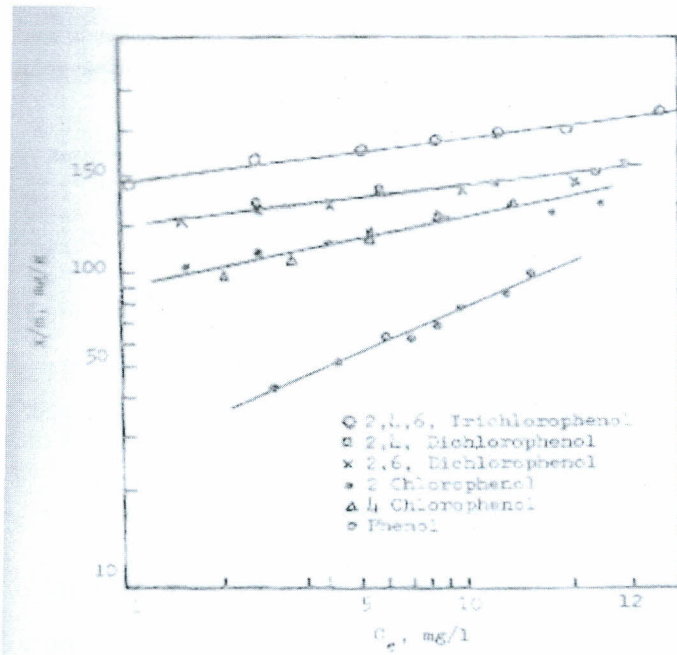


Figure 9: Logarithmic form of Freundlich adsorption isotherms for phenolic compound on activated carbon

5.1.2 Information extracted and calculated

Generally, at low rates of flow the effect of molecular diffusion predominates and cell mixing contributes relatively to dispersion. But in liquids, molecular diffusion is insignificant at Reynold number up to unity [31]. Whatever the mechanism, however, the rate of dispersion can conveniently be described by dispersion coefficient. The dispersion rate in three directions is represented by D_x , D_y and D_z respectively used in representing the behavior in three directions. The process is normally linear, with rates of dispersion proportional to the products of the corresponding coefficients and concentration gradients.

From Basic Concepts, for very low values of Reynold number like our case ($Re < 1$) the two dispersion coefficients are approximately the same and equal to molecular coefficients.

From the Column Displacement experiments (From summary of Relevant information) [24]

Given the sieve size used in experiment is of size 2 mm, our particle diameter is 2 mm.

From Table 5.1, Webster soil contains 18.4% sand, 38.3% Clay and 45.3% silt. From soil mechanics literature, Average bulk densities of,

$$\text{Sand} - \rho_{sand} = 1.6 \text{ g/cm}^3,$$

$$\text{Clay} - \rho_{clay} = 1.2 \text{ g/cm}^3$$

$$\text{Silt} - \rho_{silt} = 1.3 \text{ g/cm}^3$$

Total volume of soil is 45 cm^2 cross section area of the sample X 15cm the height of the sample, $V_T = 675 \text{ cm}^3$.

Pro by mass of each soil is using the % content from table 5.1,

$$\text{Mass} = \% \text{ content X volume of sample X density.}$$

$$M_{sand} = 198.72 \text{ g.}$$

$$M_{clay} = 310.23 \text{ g, and}$$

$$M_{silt} = 397.51 \text{ g}$$

Bulk density of our sample, $\rho_b = \frac{Mass}{Volume} = 1.343 \text{ g/cm}^3$, $\theta =$ Void ratio, $\theta = 1 - \frac{\rho_b}{\rho_s}$, from soil mechanics literature, ρ_s - particle density = 2.65 g/cm^3 and $\theta = 0.507$.

1. Taking our cylindrical vessel (In this sample we use the cylindrical vessel for purposes of getting the basic parameters but our sample is cubical) to be full,

$$V_T = V_V + V_S$$

where, V_v is volume of voids, V_S is volume of solids.

$$\frac{V_T - V_S}{V_S} = 0.507$$

$$V_T = (1.507) V_S$$

$$V_S = 447.91 \text{ cm}^3$$

1. Given that the soil is saturated 100% volume of water in the soil $V_v = (675 - 447.91) \text{ cm}^3 = 227.09 \text{ cm}^3$

1. Darcy's flux = 0.22 cm/hr . (From details of column displacement statement number 6).

$$v = \frac{Q}{\theta} = \frac{0.22}{0.507} = 0.434 \text{ cm/hr}$$

where v is the pore water velocity.

1. Reynolds number, $Re = \frac{vd\rho}{\mu} = \frac{0.434 \times 0.2 \times 0.9975}{335.556} = 2.58 \times 10^{-4} \leq 2300$ laminar flow.

where, v - flow velocity in cm/hr , d - is the diameter of the of particle of the soil sample in cm , ρ - is the density of water in g/cm^3 and μ - is viscosity of water in g/cmhr .

1. From our earlier literature, peclt number in liquids is approximately equals to unity despite the varying Reynolds number

$$Pe = \frac{vd}{D_L} = \frac{0.434(??)}{D_L} = 1, v \text{ and } d \text{ remain as in } Re.$$

$$D_L = D_x = 0.434 \times 0.2 = 0.0868 \text{ cm}^2/\text{hr}.$$

1. Based on the same concept at low flow rate the radial dispersion coefficient is the same as the longitudinal dispersion coefficient.

$$D_y = D_z = 0.0868 \text{ cm}^2 / \text{hr}.$$

2. From the break through curve [33] Webster soil; results with 2-4-D amine pesticide

$$V_V = V_0 = 227.09 \text{ cm}^3$$

$$\frac{V}{V_0} = 6.5 \text{ for } 5000 \mu\text{gml}^{-1}$$

$$V = 1476.1 \text{ cm}^3$$

where, V is the volume that passed through the sample, concentration recorded zero trace of pesticide.

For $5000 \mu\text{gml}^{-1}$. Time taken for V to go through the sample,

$$t = \frac{1476.1}{45 \times 0.434} = 75 \text{ hr}$$

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

Without any concentration going beyond the porous end, for purposes of this analysis.

$x = \frac{V}{A} = \frac{1476.1}{45} = 34 \text{ cm}$ - This is the length of travel of the adsorption water that eliminated the pesticide from the sample. For three dimensions, we assume the process of adsorption moved the same distance, $x = 34 \text{ cm}$, $y = 34 \text{ cm}$, $z = 34 \text{ cm}$.

From equation, (3.2.16)

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

$$= \left[1 + \frac{1.343 \times 4.62 \times 0.7}{0.507} (C_{i,j,k}^n \times 10^{-6})^{-0.3} \right],$$

$$= 1 + 540.5154 (C_{i,j,k}^n)^{-0.3}, \text{ (this converts micrograms automatically to Grams).}$$

From table 5.2, $N = 0.7$, $K = 4.62$, $\theta = 0.507$ (Calculated).

And for very low flow, the hydrodynamic dispersion coefficient is the same,

$$D_x = D_y = D_z = D.$$

From equation (4.3.4),

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

relevant parameters are available,

1. Hydrodynamic dispersion coefficient is the same for 3D for flows with laminar flow with Reynolds number less than 2300,

$$\text{Reynold number } Re = 2.58 \times 10^{-4} \leq 2300$$

@23 degrees Celsius,

2. The dispersion coefficient D in laminar flows is the same in all dimensions,
3. The properties of the soil sample remain the same in 3D, i.e., Reynolds number, Peclet number, porosity, void ration, grain distribution and Permeability.

5.2 Courant-Friedrich-Levy Condition

This is a necessary condition for convergence while solving certain partial differential equations numerically in mathematics. We use it to determine the time step and fractional steps.

$$CFL = \frac{v \Delta t}{\Delta x} \leq 1$$

$$\frac{0.434 \Delta t}{h} \leq 1$$

For the purpose of this calculations, $\Delta t = 1hr$, and $h = 0.40cm$.

Below find list of parameters for calculations of Pesticides flow in a porous media

SAMPLE 1

Table 5.3: List of parameters for calculations of Pesticides

	$C_{0,0,0} =$ $5000\mu gml^{-1}$
$m_x =$ $\Delta t / \Delta x$	2.5
$r_x =$ $\Delta t / \Delta x^2$	6.25
$r_y =$ $\Delta t / \Delta y^2$	6.25
$r_z =$ $\Delta t / \Delta z^2$	6.25

$$C_{0,0,0}(5000\mu mg l^{-1})$$

Let $A'_i = \frac{D_{x_i} r_x}{R(C_{i,j,k}^n)}$, $B'_i = \frac{v_{x_i} m_x}{R(C_{i,j,k}^n)}$, $C'_j = \frac{D_{y_j} r_y}{R(C_{i,j,k}^n)}$ and $D'_k = \frac{D_{z_k} r_z}{R(C_{i,j,k}^n)}$.

Stage 1; Implicit in x direction, explicit in (y, z) directions, equation, (4.0.8),

$$\begin{aligned} & - \left(\frac{1}{4} B'_i + \frac{1}{2} A'_i \right) C_{i-1,j,k}^{n+\frac{1}{3}} + (1 + A'_i) C_{i,j,k}^{n+\frac{1}{3}} + \left(\frac{1}{4} B'_i - \frac{1}{2} A'_i \right) C_{i+1,j,k}^{n+\frac{1}{3}} \\ & = \left(\frac{1}{2} A'_i + \frac{1}{4} B'_i \right) C_{i-1,j,k}^n + C'_j C_{i,j-1,k}^n + D'_k C_{i,j,k-1}^n \\ & + (1 - A'_i - 2C'_j - 2D'_k) C_{i,j,k}^n + \left(\frac{1}{2} A'_i - \frac{1}{4} B'_i \right) C_{i+1,j,k}^n \end{aligned}$$

+ $C'_j C_{i,j+1,k}^n + D'_k C_{i,j,k+1}^n$. This is in the form of equation (4.0.9)

$$a_{I,j,k} C_{i-1,j,k}^{n+\frac{1}{3}} + b_{I,j,k} C_{i,j,k}^{n+\frac{1}{3}} + c_{I,j,k} C_{i+1,j,k}^{n+\frac{1}{3}} = d_{I,j,k}$$

$$a_{I,j,k} C_{i-1,j,k}^{n+\frac{1}{3}} + b_{I,j,k} C_{i,j,k}^{n+\frac{1}{3}} + c_{I,j,k} C_{i+1,j,k}^{n+\frac{1}{3}} = d_{I,j,k}$$

Stage 2; Implicit in y direction, explicit in (x, z) directions, equation, (4.0.10),

$$\begin{aligned} & - \frac{C'_j}{2} C_{i,j-1,k}^{n+\frac{2}{3}} + (1 + C'_j) C_{i,j,k}^{n+\frac{2}{3}} - \frac{C'_j}{2} C_{i,j+1,k}^{n+\frac{2}{3}} = \frac{1}{2} A'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{4} B'_i C_{i-1,j,k}^{n+\frac{1}{3}} \\ & + \frac{1}{2} A'_i C_{i-1,j,k}^n + \frac{1}{4} B'_i C_{i-1,j,k}^n + \frac{C'_j}{2} C_{i,j-1,k}^n + D'_k C_{i,j,k-1}^n \\ & + \left(C_{i,j,k}^n - A'_i C_{i,j,k}^{n+\frac{1}{3}} - A'_i C_{i,j,k}^n - C'_j C_{i,j,k}^n - 2D'_k C_{i,j,k}^n \right) \end{aligned}$$

$$+ \left(\begin{array}{c} \frac{1}{2}A'_i C_{i+1,j,k}^{n+\frac{1}{3}} + \frac{1}{2}A'_i C_{i+1,j,k}^n - \frac{1}{4}B'_i C_{i+1,j,k}^{n+\frac{1}{3}} - \frac{1}{4}B'_i C_{i+1,j,k}^n + \frac{C'_j}{2} C_{i,j+1,k}^n \\ + D'_k C_{i,j,k+1}^n \end{array} \right)$$

This translates to the form of equation, (4.0.11),

$$a_{i,j,k} C_{i,j-1,k}^{n+\frac{2}{3}} + b_{i,j,k} C_{i,j,k}^{n+\frac{2}{3}} + c_{i,j,k} C_{i,j+1,k}^{n+\frac{2}{3}} = d_{i,j,k}.$$

Step 3; Implicit in z direction, explicit in (x, y) direction, equation; (4.0.12),

$$\begin{aligned} & -\frac{D'_k}{2} C_{i,j,k-1}^{n+1} + (1 + D'_k) C_{i,j,k}^{n+1} - \frac{D'_k}{2} C_{i,j,k+1}^{n+1} \\ & = \left(\begin{array}{c} \frac{1}{2}A'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{4}B'_i C_{i-1,j,k}^n + \frac{1}{4}B'_i C_{i-1,j,k}^{n+\frac{1}{3}} + \frac{1}{2}A'_i C_{i-1,j,k}^n + \frac{C'_j}{2} C_{i,j-1,k}^{n+\frac{2}{3}} \\ + \frac{C'_j}{2} C_{i,j-1,k}^n + \frac{D'_k}{2} C_{i,j,k-1}^n \end{array} \right) \\ & + \left(C_{i,j,k}^n - A'_i C_{i,j,k}^{n+\frac{1}{3}} - A'_i C_{i,j,k}^n - C'_j C_{i,j,k}^{n+\frac{2}{3}} - C C_{i,j,k}^n - D'_k C_{i,j,k}^n \right) \\ & + \left(\begin{array}{c} \frac{1}{2}A'_i C_{i+1,j,k}^{n+\frac{1}{3}} + \frac{1}{2}A'_i C_{i+1,j,k}^n - \frac{1}{4}B'_i C_{i+1,j,k}^{n+\frac{1}{3}} - \frac{1}{4}B'_i C_{i+1,j,k}^n + \frac{C'_j}{2} C_{i,j+1,k}^{n+\frac{2}{3}} \\ + \frac{C'_j}{2} C_{i,j+1,k}^n + \frac{D'_k}{2} C_{i,j,k+1}^n \end{array} \right) \end{aligned}$$

This translates to, equation,

$$a_{i,j,K} C_{i,j,k-1}^{n+1} + b_{i,j,K} C_{i,j,k}^{n+1} + c_{i,j,K} C_{i,j,k+1}^{n+1} = d_{i,j,K}.$$

(5.2.1)

Table 5.4: Second list of calculation Parameter for ten steps

	$b_{I,j,k}$	$c_{I,j,k}$	$d_{I,j,k}\mu g$	$a_{i,J,k}$	$b_{i,J,k}$	$c_{i,J,k}$	$d_{i,J,k}\mu g$	$a_{i,j,K}$	$b_{i,j,K}$	$c_{i,j,K}$	$d_{i,j,K}$
0	1.01262	-	4933.288	0	1.01262	-	4933.42	0	1.01262	-	4935.
		0.000025				0.00631				0.00631	
-	1.01257	-	4866.713	-	1.01257	-	4866.89	-	1.01257	-	4867.
0.012545		0.000025		0.006285		0.006285		0.00629		0.00629	
-	1.01252	-	4799.8355	-	1.01252	-	4801.03	-	1.01252	-	4801.
0.012495		0.000003		0.00626		0.00626		0.00626		0.00626	
-	1.01242	0.000000	4732.7575	-	1.01242	-	4733.67	-	1.01242	-	4734.
0.01242				0.00621		0.00621		0.00621		0.00621	
-	1.01237	0.000000	4664.011	-	1.01237	-	4666.67	-	1.01237	-	4667.
0.012368				0.000619		0.00619		0.00619		0.00619	
-	1.01232	0.000000	4598.9408	-	1.01231	-	4599.66	-	1.01231	-	4599.
0.012313				0.006155		0.006155		0.00616		0.00616	
-	1.01226	0.000000	4531.8217	-	1.01226	-	4533.01	-	1.01226	-	4533.
0.01226				0.00613		0.00613		0.00613		0.00613	
-	1.01221	0.000000	4464.818	-	1.01221	-	4465.32	-	1.01221	-	4466.
0.012209				0.006105		0.006105		0.00611		0.00611	
-	1.01215	0.000000	4397.836	-	1.01215	-	4398.29	-	1.01215	-	4399.
0.012153				0.006075		0.006075		0.00608		0.00608	
-	1.0121	0.0000	4330.811	-	1.01209	-	4331.58	-	1.01209	-	4333.
0.01210				0.006045		0.006045		0.00605		0.00605	

From equation (4.3.3) to (4.0.18)

$$c' = \begin{cases} \frac{c_i}{b_i}; i = 1 \\ \frac{c_i}{b_i - c'_{i-1}a_i}; i = 2, 3, \dots, n-1 \end{cases}$$

$$d'_i = \begin{cases} \frac{d_i}{b_i}; i = 1 \\ \frac{d_i - d_{i-1}a_i}{b_i - c'_{i-1}a_i}; i = 2, 3, \dots, n-1 \end{cases}$$

This is a forward sweep. The solution is obtained by back substitution;

$$x_n = d'_n$$

$$x_i = d'_i - c'_i x_{i+1}; i = n-1, n-2, \dots, 1$$

Table 5.5: Output of flow of ten steps in 3D

x_i, y_j, z_k	$t_{i,j,k}$	$d'_{i,j,k}$	NO	t/Hrs.	$C_{i,j,k}^n$ In μgml^{-1}	Retardation constant $R(C_{i,j,k}^n)$	$C_{i-1,j,k}^{n+\frac{1}{3}}$, $C_{i,j-1,k}^{n+\frac{2}{3}}$, $C_{i,j,k-1}^{n+1}/$ μgml^{-1}
0		-	0	0	5000	42.9872	
0.4	0	4871.806	1	1	4933	43.1575	4871.806
	-	4871.936					4902.265
	0.006231	4874.337					4904.665
	-						
	0.006231						
0.8	0	4867.42092	2	2	4866	43.3308	4867.4209
	-	4837.280					4867.084
	0.006207						4867.214
	-	4837.528					
	0.006212						
1.2	0	4800.637	3	3	4799	43.5072	4800.637
	-	4771.9344					4801.572
	0.006183	4771.947					4801.219
	-						
	0.006183						
1.6	0	4733.581	4	4	4732	43.6869	4733.581
	-	4704.870					4733.495
	0.006134	4705.677					4734.299
	-						
	0.006134						

x_i, y_j, z_k	$h_{i,j,k}$	$d'_{i,j,k}$	NO	t/Hrs.	$C_{i,j,k}^n$ In μgml^{-1}	Retardation constant $R(C_{i,j,k}^n)$	$C_{i-1,j,k}^{n+\frac{1}{3}}$ $C_{i,j-1,k}^{n+\frac{2}{3}}$ $C_{i,j,k-1}^{n+1}$ μgml^{-1}
0		-	0	0	5000	42.9872	
2.0	0	4664.83935	5	5	4665	43.8700	4664.8393 4665.1058
	-	4638.766					4666.127
	0.006115						
	-	4638.707					
	0.006115						
2.4	0	4599.70056	6	6	4598	44.0564	4599.7005 4599.578
	-	4572.017					4599.667
	0.006080	4572.078					
	-						
	0.006080						
2.8	0	4532.6407	7	7	4531	44.2464	4532.640 4532.765
	-	4506.128					4533.600
	0.006056	4506.562					
	-						
	0.006056						
3.2	0	4465.62078	8	8	4464	44.4401	4465.6207 4465.162
	-	4438.634					4464.66
	0.006031	4438.014					
	-						
	0.006036						
3.6	0	4398.5119	9	9	4397	44.6376	4398.511 4398.451
	-	4372.452					4399.93
	0.006002	4373.519					
	-						
	0.00601						
4.0	0	4330.891	10	10	4334	44.8391	4330.891 4331.581
	-	4306.260					4333.264
	0.005973	4307.911					
	-						
	0.005978						

5.3 Discussion

1. The equation derived for calculation of flow of pesticides in a porous media is ideal for estimation of the movement of solute in the subsurface environment in 3D for steady state flow. The other parameters not considered are decay, chemical reactions with the solute in ground environment and biological decomposition of organic pesticides. These are ideal fodder for further advancement of the equation. Unsaturated flows are not considered in this derivation.
2. Solving the equation using Crank-Nicolson method gives the best accuracy and it is unconditionally stable, however, the matrix generated by this method is expensive to solve thus making it unsuitable for use. Douglas-and Gunn method is ideal for use in solving this equation because it generates a matrix which is easily solved by Thomas algorithm as can be seen in the thesis analysis of the matrix above.
3. Manual computation of this matrix is cumbersome. There is need for programming data so that computer generates results fast and effectively.
4. The applications and results are based on an experiment carried out in United State of America on adsorption and movements of selected pesticides at high concentration in Soils, [33]. This experiment was run for 1D flow, however, in our study we used these parameters to apply to our 3D equation because at low flow rate the radial dispersion coefficient is the same as longitudinal dispersion coefficient. With the available values of dispersion coefficient of both radial and longitudinal, 3D outputs are assured.
5. Examining the ten steps of calculating flow of pesticides in x, y, and z direction as shown in the last table 5, the values of flow of pesticides in all the three dimensions are almost the same when the flow is laminar. It's evident from the results that the application to 3D was realistic. For turbulent flow we would have different dispersive constant thus yield conspicuous variation in both radial and longitudinal flows of pesticides.

Chapter 6

Conclusion and Recommendations

6.1 Conclusion

The theoretical output figures prove that the equations are correct representation of anticipated flow pattern of the pesticide in the porous media. The flow figures show progressive reduction of the adsorbent as the path distance increases up to insignificant quantity. It is evident that from the calculations, the amount of pesticides flow in all three directions is always the same when the flow is laminar. With the declining quantities of the adsorbent with time and distance, the suitability of the equation is confirmed. Finally, it can be indicated here that the equation is suitable for all pesticides flow and adsorption in porous media under steady state flow condition as long as all parameters governing the flow are determined.

6.2 Recommendations

More experiments of adsorption are required for 3D to provide comparative analysis and output so as to establish the suitability of this method on different samples. It is worth noting that the output can be further fine-tuned through computer programming of the equation for calculation. This is likely to give conspicuous flow of information of adsorption of pesticides in a porous media. More experiments may give different results if we increased the flow to almost turbulent level. Migration of pesticides experience different rainfalls at the disposal point thus necessitating varied examinations. Further analysis is necessary for different dispersion constants because the migration from the disposal sites doesn't always depend on laminar flow. At times we have storms which trigger turbulent flow therefore that creating varied dispersion constants.

References

- [1] Adams S.H. W. (2008), Convective- Dispersive transport of Pesticides in a Porous media by steady state water flow in two dimensions. (MSc Thesis).
- [2] Anderson, D.A, Tannehill, J.C., and Pletcher, R.H. (1984), Computational *Fluid Mechanics and Heat Transfer*, McGraw-Hill, New York.
- [3] Bailey G.W. & White J.L. (1970), Factors influencing adsorption, desorption and movement of pesticides in the soil. *Residue Rev.* 32, 29-92.
- [4] Bear, J. (1979). *Hydraulics of Ground Water*, McGraw Hill Inc. 567, New York.
- [5] Belcher, R. C. and Paradis, A. (1992). 'A mapping approach to three-dimensional Modeling', In Turner A.K. [ed], *Three-Dimensional Modeling with Geoscientific Information Systems*, Kluwer Academic Publisher, Dodrecht, The Netherlands.
- [6] Benson. D., Wheatcraft. S. and Meerschaet, M.. (2000) *The fractional order governing equation of Levy motion*, Water Resource Research 36, 1413-1424.
- [7] Benson, D., Schumer, R., Meerschaert, M., and Wheatcraft, S., (2001) Fractional dispersion, Levy motions, and MADE Tracer tests. *Transport in porous media* 42, 211-240.
- [8] Biswal B., Hilfer R. (1999), Microstructure analysis of reconstructed porous media, *Physical* A266307-311.
- [9] Brown G.O., Henry Darcy and the making of the law, (2002); Department of Biosystems and Agriculture Engineering; Oklahoma University, still water, Oklahoma, USA.
- [10] Ceary, R. W., and M.J. Unga, (1978), Groundwater Pollution and hydrology; Mathematical Models and Computer programs, Res. Rep 78-WR-15, Water Resource, Program, Depart. Of Civil Engineering, *Princeton Univ. Princeton*, N.J.
- [11] Dentz, M. and B. Berkowitz (2003). Transport behavior of a passive solute in continuous time random walks and multirate mass transfer, *Water Resources Research.* 39(5), 1111, doi:10.1029/2001WR001163, 2003.
- [12] Dullein, F.A.L., (1979) *Porous media fluid flow transport and pore structure*, 2nd Edition, Academic Press, New York.

- [13] Ed Perfect and Michael C. Sukop (2001). Models relating to solute Dispersion to pore space Geometry in saturated media. Soil Science Society America WI 53711, USA. Physical and Chemical processes of water and solute transport/retentions in the soil, SSSA *special Publication* No 56.
- [14] Feike J. Leij, Marcel G. Schaap, and Martinus Th. Van Genuchten, (1998), Neural Network Analysis for Hierarchical Prediction of Soil hydraulic Properties, *Soil Science Society of America JOURNAL*, Volume 62.
- [15] Godunov S.K. (1959). A finite difference method for computation of discontinuous solution of the equation of fluid mechanics. *Mat. Sb.*,47, pp.357-393
- [16] Maier R. S., D. M. Kroll, R. S. Bernard, S.E. Howington, J. F. Peters, (2003), Hydrodynamic dispersion in confined packed beds: Physics of fluids: Volume 15. *Trans. Institute. Chem. Eng. 47, London.*
- [17] Leszek C., Mielczyslaw R. B., Ewa K-C, (2000), Some generalization of Langmuir isotherms. *Internet Journal of Chemistry [ISSN:1099-8292], University of Mining and Metallurgy, Faculty of Fuels and Energy, al. Mickiewicza 30, 30-059 Crawcow, Poland.*
- [18] Liakopoulos A.C. Dr. Eng. (1965), Darcy's Coefficient of permeability as a symmetrical tensor of second rank. *Hydrological Science Journal*. ISSN:0020-6024.
- [19] Kolgan N.E. (1975). Finite-difference schemes for computation of three-dimensional solution of gas dynamics and calculation of a flow over a body under an angle of attack. *Uchenye Zapiski TsaGI [Sci. Notes of Central Inst. of Aerodynamics]*. 6, No. 2, pp. 1-6 (in Russia)
- [20] J. Douglas Jr. and J. E. Gunn (1964), A general formulation of an alternating direction method-Part 1. Parabolic and hyperbolic problems, *Numerische Mathematik*, Vol. 6 pp. 428-453.
- [21] Javandel I. C. Doughty, and C.F. Tsang, (1984). Ground water transport: Handbook of Mathematical models. *American Geographical Union. Washington D.C.* 228p.
- [22] Jury. W. A. (1982) Simulation of solute transport using a transfer function model. *Wat. Resour. Res.* 18
- [23] Marcin K. Widomski, Dariusz Kowalski, Malgorzata Iwanek, Grzegorz Lagod, (2013), Modeling of Water Flow and Pollutants Transport in Porous Media. Mognografie-Politechnika Lubelska, Publisher: Lublin University of Technology, Poland. www.biblioteka.pollub.pl
- [24] P. S. C. Rao and J. M. Davidson (1978), Adsorption and movement of selected pesticides at high concentration in the soil. Soil Science Department, University of Florida, Gainesville, FL 32611, USA.

- [25] Quiber J. A (1984), A new three-dimensional modeling technique for studying porous media, j colloid. Interface Sci 98 pp 84-102.
- [26] R. B. E. Serife and K. Ibrahim (2018), On the l2 *Stability of Crank-Nicolson Differential Scheme for Time Fractional Heat Equations*, Department of Mathematics, Faith University, TR-34500, Intanbul, Turkey.
- [27] Ramon Van Handel (2009), The stability of conditional Markov processes and Markov chains in radom environment. The Annals of Probability, 2009. Vol. 37, No 5, 1876-1925.DOI: 10.1214/08-AOP448. Institute of Mathematical Statistics.
- [28] Simunek, Huang K and Van Genuchten M. Th. (1995), The SWMS 3D Code for *Simulating water flow and solute in 3D variable saturated Media*, Version 1.0, Research Report No. 139, 168 pages report, U. S. SALINITY LABORATORY, AGRICULTURAL RESEARCH, U. S. DEPARTMENT OF AGRICULTURE, RIVERSIDE, CALIFORNIA.
- [29] Vlasis G M, Scotiris E. P. (2007), Mass transfer, Lecture 7: Dispersion, *Particle Technology laboratory, Department of Mechanical Process Engineering, ETH Zurich, CH 8092, Switzerland.*
- [30] Van Genuchten M. Th., Davidson J.M. and Wierenga, P.J. (1974). An Evaluation of kinetic and equilibrium equation for predicting pesticide movement through porous media. *Soi. Sci. Soc. AM, Journal vol. 38. issue1, page 29.*
- [31] Voullienme-C. Daniel, Murillo J., and Pilar Garcia-Navarro, (2012), Numerical simulation of groundwater-surface interaction by external coupling of 3D Richards equation and full 2D shallow water equation. XIX International Conference on Water Resources, CMWR2012, *University of Illinoise at Urban-Campaign.*
- [32] Yuan Wang-Ting and Charlie-Ping Chen, (2002), 3-D Thermal-ADI: A Linear-Time Clip Level Transient Thermal Simulator, IEEE TRANSACTION ON COMPUTER-AIDED DESIGN OF INTEGRATED CIRCUITS AND SYSTEMS, VOL. 21.