MOELLING REACTIVE POLLUTANT TRANSPORT IN GROUND WATER: THE CASE OF TWO SPECIES

HANS TAH, MBAH

Student Number: 201047609

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Supervisor: Prof. Abdon Atangana

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Declaration

I hereby declare that this dissertation ''Modelling the Transport of Reactive Pollutans in groundwater: The Case of two Species'', is of my own work. The dissertation was carried out at the institute of Groundwater Studies at the University of the Free State, Bloemfontein, under the supervision of Professor Abdon Atangana. I earnestly declare that, to the best of my knowledge, no part of this dissertation was previously submitted for the requirement of a degree, diploma or any other tittle of recognition at any institution. All sources used for this compilation have been fully acknowledged in the reference list.

With that said, I cede copyright of this dissertation in favour of the University of the Free State.

Full name: Hans Tah, MBAH

Student number: 2010047609

Date: June 2019

Dedication

First and foremost, I want to thank the God of heaven, the creator of all mankind for giving me the strength and good health to   pursue with my masters degree through to this end.

To Prof. A. Atangana, I humbly express my deep appreciation for accepting me under his benevolent supervision and mentorship as a masters student. Most especially, I want to thank him for teaching me the value of time, given its abundance in nature, yet in limited access. His spiritual and academic leadership transformed my masters studies into a complete learning experience, not common in the classroom setting. And to his lovely wife Dr. Ernestine Atangana and their two sons, Melchizedeck and Diophnatene, I am forever greatfull for their selfless support and encouragemnent during this period.

Finally and most importantly, this work would not have been possible without the love, support and motivation from my family. To Gladys and Fredrick my mom and dad, Blanche and Dolly my siblings, I dedicate this humble work of mine with with great hope that you accept it warmness in your hearts.

Abstract

The locations of a significant number of industrial facilities, landfills and almost all mineral ore bodies are characterised by high in situ stresses and fractures and fissures act as flow paths for fluids underground. Regional scale fracture systems that transport pollution from spatially isolated source locations can cause mixing of chemical pollutants from different source origins due to fracture-fracture flux across two or more intersecting fractures, hence reactive transport. Alerts of groundwater contamination in response to multicomponent pollution transport have been investigated using a mathematical model of the hydrodynamic response of incompressible fluids such as groundwater flow. Fundamental to the model is the conservation of mass associated with the applied source strength and the concentration velocity field redistributions after source has released pollution, assuming the formation is homogenous. Solute distribution depends on the formation porosity and generally, fluids travel faster in fractures than in sedimentary formations. Different variations of the deterministic advection dispersion equation have been employed to predict coupled transport/reactive processes by substitution of a reaction term (retardation factor, etc..) which accounts for the changing concentration of the solid face components through time due to chemical reaction. However, fractured aquifers are inherently heterogeneous due to interconnecting fractures. The results in a non-homogenous mathematical formulation which difficult to solve analytically. As a result, most research endeavours have tended to depend on numerical solutions, increasingly made possible through advanced computational power. Even though it is questionable to what extend numerical models of groundwater reactive transport can be useful in making accurate quantitative predictions, it is still possible for a reactive model to predict the outcome of a particular chemical representation in an aquifer. Nevertheless, the linear, non-homogenous advection dispersion equation can still be solved analytical using the Green's function method.

In this thesis, we show how the advection-dispersion transport equation can be extended to account for geochemical reaction processes in a heterogeneous media. For the hypothetical case study, the system was made of a homogenous and a non-homogenous sub-component. The study's methodological approach involved coupling of the homogenous transport phase with the non-homogenous system. The solution of the homogenous equation is obtained using Laplace transform and the exact solution of the new non-homogenous equation is obtained analytically using Laplace transform and the Green's Function method. Both sub-models were solved numerically using the Crank-Nicolson discretization scheme and their stability conditions also established. For the proposed fracture flow system, the linear non-homogenous model was able to approximate the contribution

of reactive transport processes in the system. Chemical reactions can attenuate the spread of a contaminant plume due to processes such as sorption and precipitation. The model presented in this thesis was able to predict fate of each species within the system. Mass transfer during and after the reaction resulted in the depletion of one source with respect to another, which the model showed positive results in capturing. The thesis concludes with a chapter on chemical equilibria which is the basis of kinetic modelling and the understanding of the progress of chemical reactions.

LIST OF GREEK NOTATIONS

α	Alpha
λ	Lambda
τ	Tau
δ	Zeta
∂	Partial differential
$\mathcal{L}$	Laplace
ρ	rho
μ	Mu
Σ	Sigma
Δ	Delta
k_c	Equilibrium constant
G	Exergeration factor
ε	Epsilon
σ	Sigma

ABBREVIATIONS AND NOTATIONS

eq.	Equation
ADE	Advection-dispersion equation
D	Dispersion Coefficient
v	Seepage velocity
R	Retardation factor
t	Time
exp	Exponent
1-D	One-dimensional
f	Function
ϵ	Element of
C	Concentration
cos	Cosine
sin	Sine

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Chapter one: Introduction

General motivation

Over thousands of years, humans development and adaptation have been closely linked to the extraction of oil, metals and most importantly water resources for survival. While this trend has helped to drive modern industrialisation and the generation of significant rents for resource rich nations and the global economy, observations and empirical studies since the 20th century increasingly points towards a legacy of toxic solute contamination and an increasingly poor water quality. An increasing population growth rate, the demand for geo-environmental resources are rising and so are stresses on the environment. Today, contamination of ground water coupled with the threatening impact of climate change, is threatening livelihoods globally. Recent years of groundwater investigations in industrialized countries have seen a shift from ground water supply to mitigating ground water quality (CHERRY et al., 1975).

Generally, groundwater is a preferred fresh water source over surface water sources as it is naturally better protected from pollution, less subject to seasonal and perennial fluctuations, more evenly spread across vast regions and generally of better quality (Ebrahim, 2013). Ground water provides one of the largest reserves of total water resources in some countries such as Tunisia, Belgium, Netherlands, Germany and morocco where it constitutes 95%, 83% and 75% of the total water resources respectively (Zektser and Lorne, 2004). Of all reservoirs within the hydrological cycle, the ground water system represents only 0.76% of all water while providing 30.1% of all fresh water supplies on Earth (Maidment, 1993). In South Africa, ground water provides the water supply to more than 300 towns and 65% of the population (DWAF, 2002) even though it contributes only about 13% of the total volume of water consumed even in the country. Two-thirds of the country is characterised by a semi-desert to desert climate and largely dependent on groundwater. Although irrigation is the largest user if groundwater, excessive pupping of ground water associated with overexploitation of ground mineral resources is increasing the impact of human activities on aquifers in South Africa and many parts of the world. Directly measurable impact include a decline in ground water levels and deterioration of groundwater quality.

In most regions around the world, especially Africa, mining has been the main driver of environmental degradation due to its role in the contamination and competition for surface and groundwater (Economic Commission For Africa, 2011). Soil and ground water become contaminated when toxic industrial emissions fall as precipitation and enter ground water systems through the vadoose zone (Figure. 1.). This often degrades soils, aquifers (leakage and recharge) and streams (surface and sub-surface runoff and leakage). Other sources include improperly lined industrial landfills, mining tailings and chemicals spilled during

transportation. Most heavy metals don't degrade like carbon-based materials, making soil decontamination difficult and very costly. Ground water contamination is also caused by the discharge of affluent, which contains toxic chemicals used for the processing of mineral ores such as cyanide, organic chemicals and leached heavy metal oxides (including lead and zinc oxides). In most cases, the affluent, which is mostly acidic, infiltrates into water bodies, posing dangers to the community and aquatic life. Industrial waste often contains heavy metals that pollute urban soil and cropland. Lead is the most common toxin found, according to the United States Drug Agency.
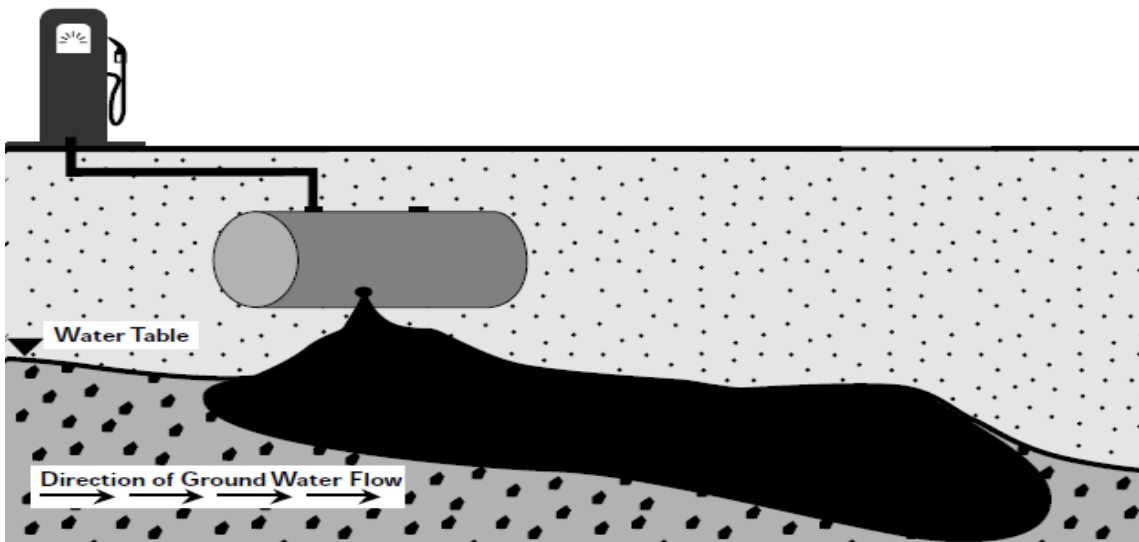
Figure 1: Pollution transport in groundwater

Public debates are becoming more practical and there is a general heightened awareness of the challenges associated with ground water contamination. It is against this bearing that scientists, researchers and engineers are spending significant research time to understand the hydro-environmental and ecological dynamics associated with different pollution sources. The increase in public attention towards issues of water pollution can be asserted to a number of factors including

- Increased awareness of the potential health risks in connection with polluted ground water, e.g. South Africa between 1993 to 2007, there were outbreaks of diarrhoea and typhoid in Delmas, Mpumalanga Province (Nealer, 2009).

- Many factors impact negatively on water resources however, the activity with the greatest impact of all on water and the environment is mining. As a world leader in this sector with abundant mineral resources, mining accounts for a significant portion of the South African economy as well as the world's production and reserves (GDAEC, 2008). The Crocodile River in Limpopo has been polluted by Acid Mine Drainage (AMD) and radioactive sludge from the West Ran mines (FarmiTracker, 2010).

Aside from the surface factor associated with ground water contamination, the impact of climate change and global warming is an increasing concern to the health of our aquifers and groundwater systems. Elevated groundwater temperatures during the past decade with predictions of future intensification have been linked to rapid climate warming (Figura, 2011). For permafrost regions, the release of sequestered carbon due to thawing possess is an emerging concern (Solomon, 2007). Subsurface biochemical processes are vulnerable to climate change-induced temperature increases and so is groundwater quality. Diffuse groundwater discharge mechanisms tend to reduce diel and seasonal temperature fluctuation in streams while discrete discharge can create in- stream thermal anomalies that provide cold water thermal refugia for aquatic species during summer when groundwater is generally cooler than surface water (Breau, 2011) (Hayashi, 2001). As a result, temperature increases induced by climate change are threatening the survival of lotic systems (Mayer, 2012.). The thermal future of shallow aquifers bears an uncertain risk given the complexities involved with attempting to quantify the thermal responses of streams and rivers to climate change.

Contaminated ground water does not only threaten public health and the environment, but can also be very costly to clean up. The sources of ground water contamination are many and as diverse as the human activities that cause them (Figure 1.1). Different sites are contaminated to a varying degrees and the management of these sites is a great concern considering the environmental and ecological risks. The gravity of ground water contamination is partly dependent on the waste and leachate characteristics, including volume, composition, time rate of release of contaminants, concentration of the various constituents, size of source and density of leachate among other site-specific details.

Effects of groundwater contamination

Groundwater contamination is a threat to plant and animal life due to the decrease in the quality of water. A degraded water quality is associated with low oxygen content, which is required to support all forms of life. Other impacts include degraded surface systems, high clean-up costs and potential health issues. In some cases, the severity of loss in water quality has led to a complete abandonment of groundwater as a source of water for domestic and irrigation use. In California alone, 4000 wells have been abandoned since 1984 due to saltwater intrusion Figure 2. Generally speaking, all industries associated with water such as fishing, ore washing and irrigation would be negatively impacted by groundwater pollution
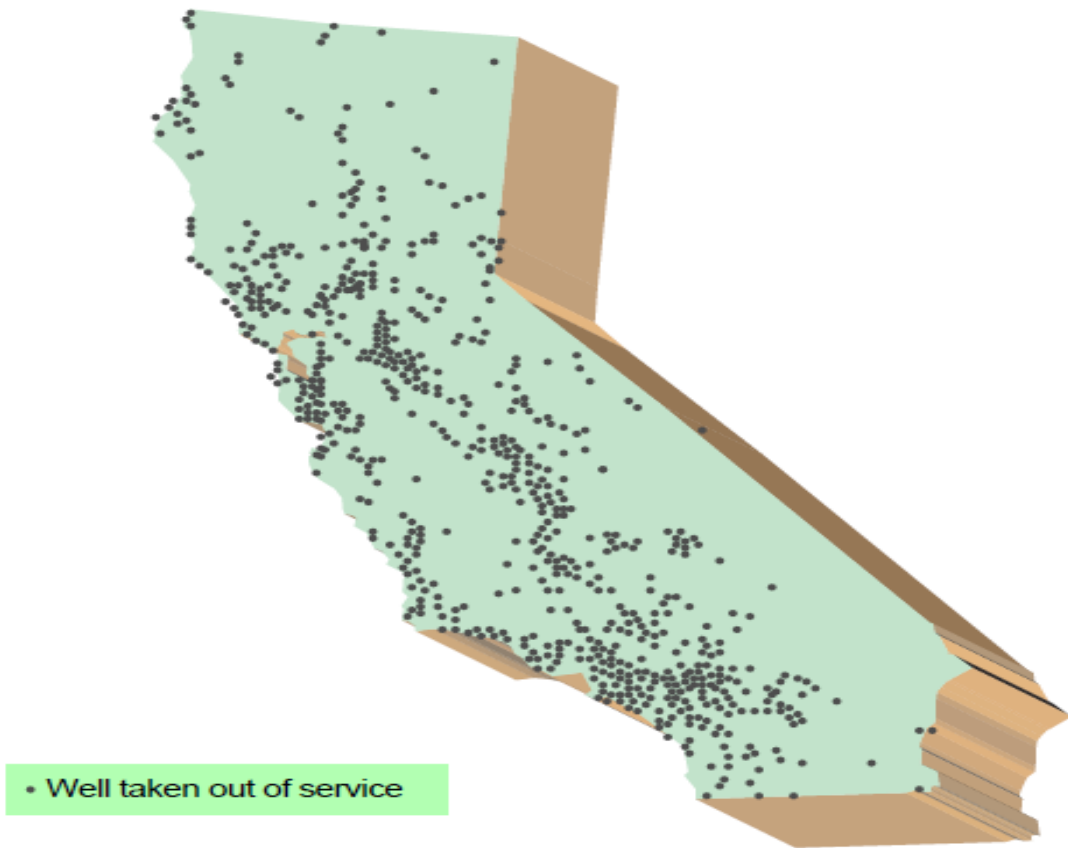
Figure 2: Four thousand decomisioned wells since 1984 due to groundwater contamination (Bowman, 2001), (California Department of Health Services.)

Potential health problems associated with groundwater pollution.

Rural communities are often highly dependent on groundwater sources even though most are unable to pay for the expensive clean up technologies in case of pollution threats. The spread of diseases such as hepatitis, cholera and typhoid fever has been linked to polluted groundwater and poor water sanitation. Nitrate induces illness called Methemoglobinemia (Blue baby syndrome) is a consequence of polluted groundwater. In most cases, the contamination can go on for long periods without any alarm until birth defects starts being reported. Ground water contamination from Benzene is known to cause cancer and other related diseases. Table 2. displays a list of potential harmful compounds of most household products.

Table 1: *: Potential harmful components of common household products*

Product	Toxic constituents
Lubricants	Phenols
Hydraulic fluid	Fluorocarbons
Battery electrolytes (Used in vehicles and electronics)	Acid
Kerosene	Fossil fuel (HC)
Refrigerator fluid	Trichloro-ethane
Jewellery processing	Cyanide
Chlorine for pool treatment	Hypochloride
Coolant systems (Organic)	Glycol
Car engine transmission fluid	Xylene
Dyes	Heavy metals
Sodium chlorite (Salt)	Sodium pollution
Jet fuel	Fossil fuel (HC)
Vanish paint	Toluene
Cleaning detergents	Heavy metals
Printer ink	Phenols
Polish for metals	Naphtha
Disinfectant	Xylenol
Laqua liner	Hydrocarbons
Damaged tar	Xylene
Grease remover	Chlorinated hydrocarbons

Using models to solve groundwater problems

Groundwater is the most important fresh water source, supplying water for agriculture and industrial use, while more than two billion people depend on it for domestic consumption faster rate than it is being recharged through rain infiltration. Uncertainties also exist as to how much pumping and drawing down of this resource is being done before there is a devastating effect on the environment and socio-economic systems, which we have already observed and continue to increasingly predict. Defining the quantity and quality of water supplied from an aquifer.

Decisions as determining the annual sustainable yield, locating wells for pumping and artificial recharge as well as identifying controlling conditions at aquifer boundaries need to be made. Remediation approaches are site specific and dependant of the type of pollutant. In addition to existing ground water quality issues (over pumping), public attention has lately focused on groundwater contamination by hazardous industrial waste, leachate from landfills, by oil spills and radioactive waste in repositories located in deep geological formations. It can be seen from above that management of groundwater would not be effective by just achieving supply goals, nor violating specified quality standards. For this to happen, the planner needs a tool that will provide information about the response of the system in order to compare alternative modes of action, a model.

Generally, natural systems are complicated (have numerous parts) and complex (densely interconnected parts) to be described in their entirety. A model is a simplification of reality (contains only those features that are of primary importance to the modeller's purpose) and can be represented graphically, mathematically, physically or verbally for use in investigating certain phenomena or to predict future behaviour of processes. A good groundwater model is a valuable tool for manging the resource, and environmental issues arising from its flow can be simulated using groundwater models (Anderson and Woessner, 1992). A model that can quantify heads in time, within a heterogeneous hydrogeological system would be considered as robust (Anderson M. , 2015). These models have the potential to make important contribution in the sustainable management and utilisation of the groundwater resource. Groundwater models can be subdivided into two categories; Groundwater flow models, those that can solve the head distribution in time over a domain while predicting the hydrological changes due to activities such as surface water developmental projects (irrigation with groundwater and abstraction) while solute transport models on the other hand are those that can calculate the solute concentration distribution within an aquifer (Poeter & Hill, 1997). Solute transport is influenced by dispersion, advection and chemical reaction. Transport models can be conservative, where chemical species are non-reactant, or reactive if there is chemical reactions between the species in solution.

Hydro-geological models

A hydrogeologic model can be defined as a conceptual and mathematical construct used for quantitative and qualitative analyses of subsurface flow and transport at a site in a way that serves the purpose for which they model was built (USNRC, 2003). They are necessary to both describe and predict water quality conditions. A Geohydrological model consists of site description, backed by a set of regional and site data. A mathematical framework then incorporates the description and the data using boundary condition used to evaluate system behaviour and performance. These models typically solve for head or pressure distribution, solute concentration, fluid and solid flux velocity, solute travel time and other associated performance measures. In fact, considering the alarming impact of climate change, a true solution to groundwater quality and quantity supply is one of the challenges that requires both a holistic approach and a regional response. Generally, hydrogeologic models can be divided in four; Physical model, conceptual model, mathetamatical(analytical or numerical) model. Below is a summary of each type and how they each interelate.

Physical models

A physical model is a laboratory based experimentally to describe groundwater flow and transport processes; an example is the ''SandBod Model'' (Figure. 2) which represents a smaller scale of the natural porous domain. Physical models are used to collect information necessary for updating existing datasets and benchmark examples. Additionally, they can be used to study contamination movement in groundwater under different site and field conditions. (Hoopes & Harleman, 1967).
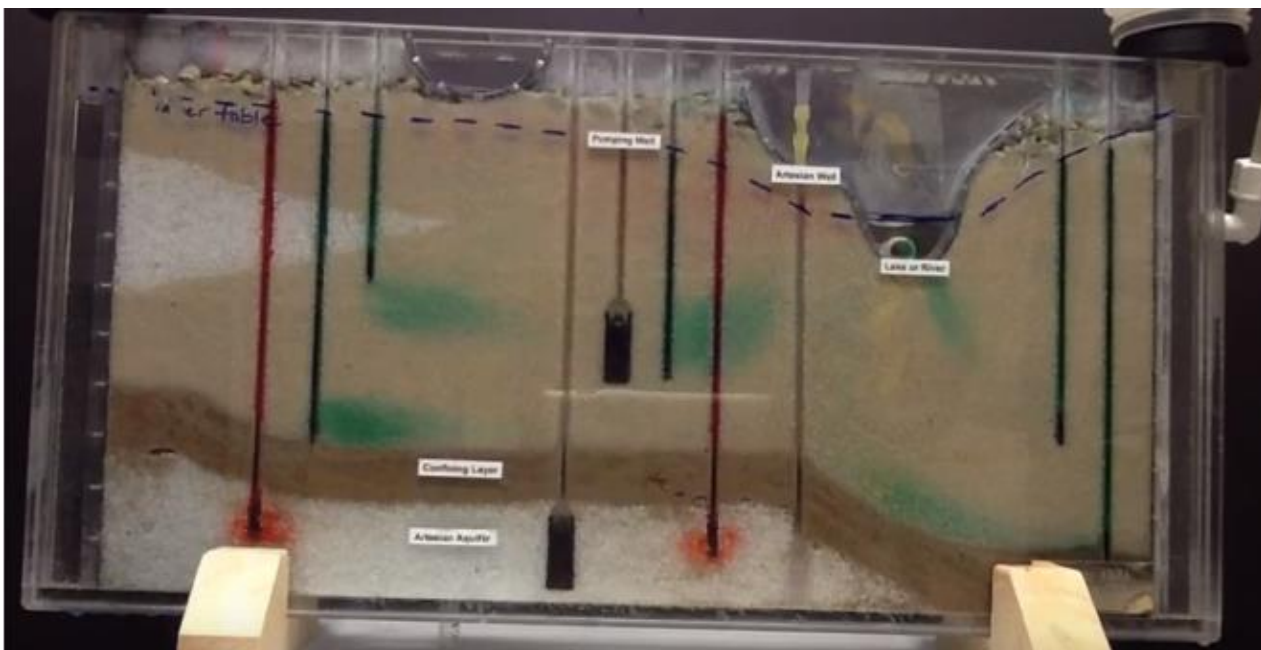
Figure 3: Sandbox groundwater model, (Masarik, 2013)

Conceptual models

A conceptual model incorporates all descriptive aspects of the model, which maybe both qualitative and quantitative. According to Paul Roman, Alfred A. Brooks, and Lorenzo de la Torre in Physics Today (1998), ''physical (and hydrogeologic) reality exists objectively but is not directly accessible to us. It uses sensory impressions and experiences to reveal itself to us (thought observation and experiment) in signatures or bits''. To In order to assimilate the pieces of site and regional information gathered, observations are described, contemplated upon, correlated, connected, systematized, interpreted and integrated into a body knowledge or mental construct called the conceptual model. According to (Anderson and Wessner, 1992), a conceptual model is a pictoral reprepresentation of the groundwater flow system, often presented as block diagrams or cross sections (figure. 2). Building a conceptual model is the most important step of the modelling process. It is the foundation of the mathematical model, and strongly ditermines which computer codes are to be used. Its development includes mapping and identification of hydrostratigraphic units and natural systems boundaries, assemply of field data including water balance data, data needed to assign values to aquifer parameters and significant hydrologic stresses. Field visits are required to maintain cognaissance of the reality.
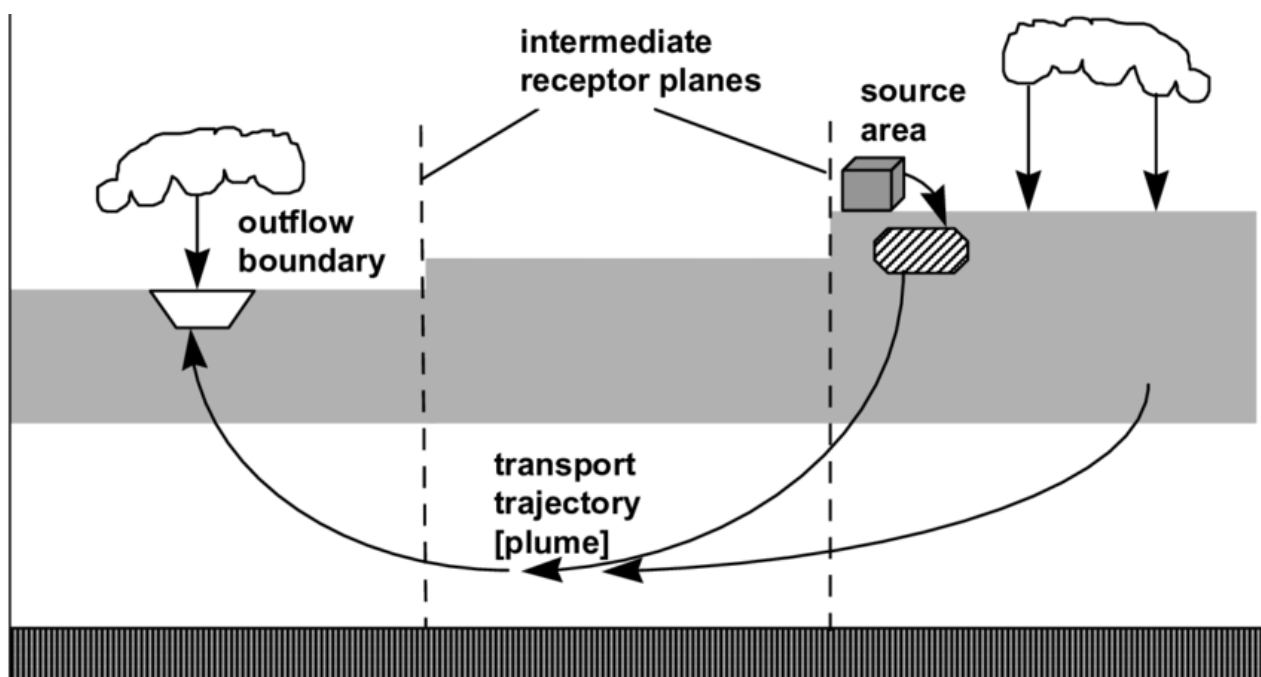
Figure 4: A simple conceptual model for the transport of mobile pollutants (Hofstee, 2004)

Mathematical models

A mathematical model is the conceptual model formulated in the form of mathematical equations suitable for systems evaluation. They represent all the physio-chemical processes relevant to flow and transport at the site within a given range of space-time scales subject to well-defined forcing source as pollutant sources and boundary conditions. Scale definition includes specifying its spatial, temporal dimensions. A

mathematical model should be able to lend its self to computation for later presentation (numerical or graphical) and analysis (deterministic and statistical) of the results. Figure 3 succinctly describes a mathematical hydrogeologic model. Mathematical models help formulate the conceptual models of site hydrogeology and flow/transport dynamics in mathematical language.

Mathematical model of groundwater transport
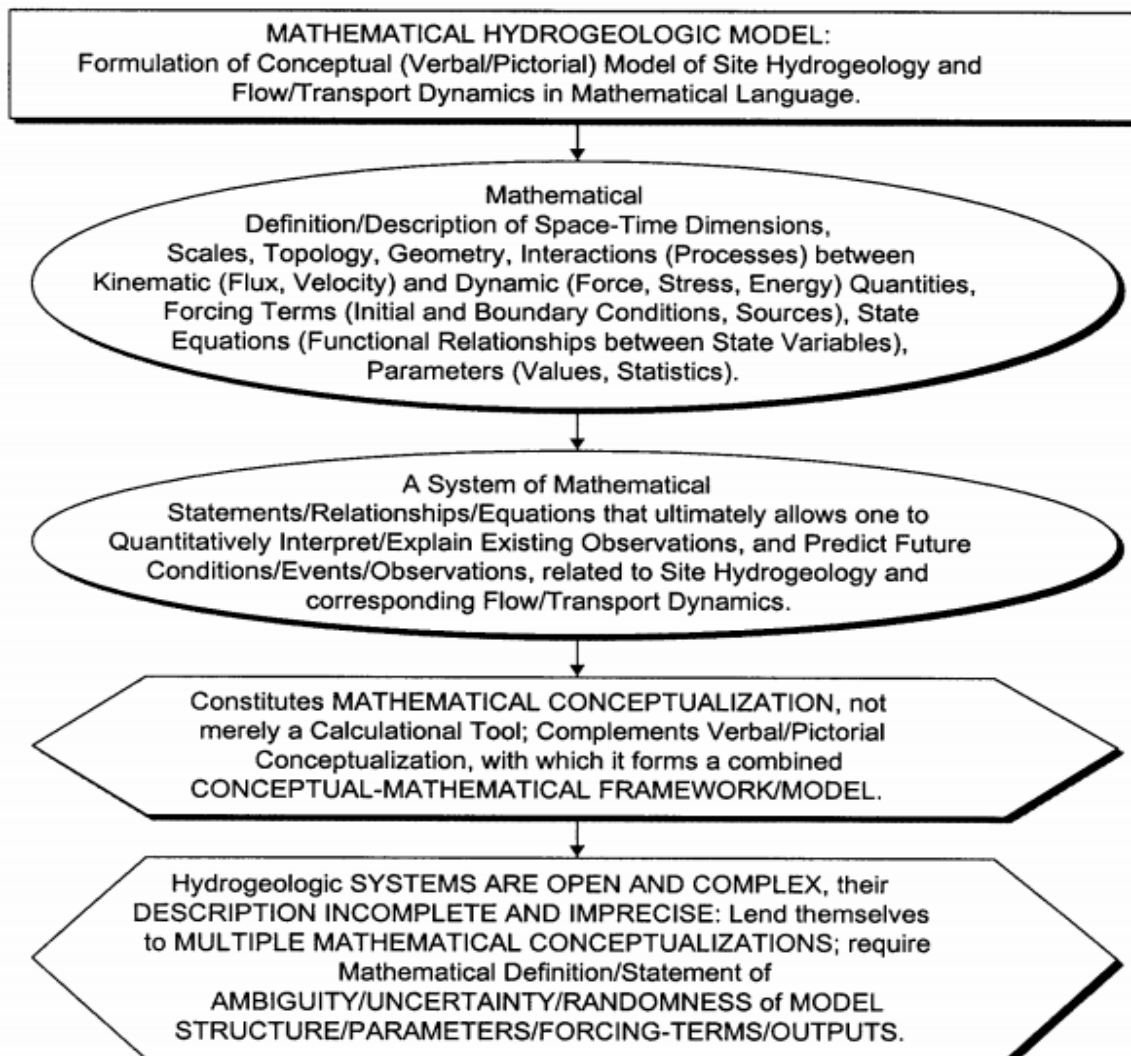
Figure 5: Mathematical formulation of hypothesis

The need to model reactive groundwater transport with different species.

Waste disposal (domestic, municipal and industrial) is a common global practice and together with urbanisation and some agricultural practices constitute a contamination thread of health and environmental concerns (Robertson, 1991) (VALIELA, 1997). There has been a positive correlation between the increase in uses of the groundwater resources and the growing awareness amongst groundwater stakeholders of the need to protect the environment and groundwater. While the use of mathematical modelling for groundwater pollution studies has been developed and recognised as an efficient tool for describing and

simulating pollutant behaviour in aquifers since the early nineteen fifties, the limitations and challenges involved with its applications to practical problems has been challenged by to factors such as the scale effect and heterogeneities of geological formations, data scarcity and issues of well posness of the mathematical problem. The standard groundwater transport equation is an important tool in groundwater management. Adequate understanding and description of the physical meaning of its parameters will produce results that both correspond with the observed phenomena as well as reduce remediation cost. It is thus required of models, the capability to capture different levels of complexities influencing transport of dissolved solutes in groundwater.

In a real life scenario, an aquifer is likely to receive pollution from more than one source, adding to the already existing heterogeneities that inherently constitute the formation. Source identification procedures have been developed through the years and there exist a large body of literature dealing with the solution of pollution source identification issues (Juliana, 2001). While these methods are indispensable as a groundwater management tool, the extent of their practicality is limited due to the fact that the number of pollution sources maybe an unknown just as their location and release histories, all of which are required for characterising the pollution sources. One way to approach this situation is by considering the effect of mixing contaminant plumes of different source location which brings us to the concept reactive transport. Reactive transport modelling in the subsurface is a highly complex involving physical, chemical and biological processes as well as interactions between solutes and geological media. For example, most heavy metals such as chromium, arsenic, copper, nickel, selenium, uranium and zin, their most stable oxidation state is usually the most toxic which typically occurs in near surface conditions (Duruibe, 2007). Also, the chemical reduction of certain metal is known to reduce their mobility which is of great significance in determining the remediation approach (Violante, 2010). On the other hand, groundwater pollution caused by organic compounds tends to occur under anaerobic conditions which have to be considered in any attempt to describe subsurface chemical interaction in groundwater.

From here we can attest that in order to meet modelling objectives, we need to be able to comprehensively describe factors influencing pollutant spread within the study domain. Hazard assessments of the risks arising from the groundwater pollution will be inadequate without the capacity to predict the behaviours of chemical contaminants in flowing ground water. Toxic contaminants transported in groundwater are most often undergoing chemical reactions resulting in mass transfer between the different phases and species. This research is divided into six chapters. Chapter two includes all relevant literarures reviews neccesory to set the stage, chapter three contains the analytical solutions of the of the homogenous and non-homogenouse subcomponents obtained by Laplace and Greens function methods respectively. Chapter four covers the numerical discritisation scheme used along with the stability analysis for the model. Chapter five

introduces the basic concepts of chemical kinetic equilibria relevant to contaminantion migration in groundwater and finally, chapter six presents the discussions and conclusions. Stated below are the general and main objectives.

The general objectives

- Build a reactive transport model than can capture the reactive contributions of chemical species from diverse sources interacting due to formation heterogeity (fractures).

The main Objectives

- Obtain the exact solution of the homogenouse model sub-component using Laplace transform.
- Obtain the the exact solution of the non-homogenous model using the Greens function method.
- Discretise and establish stability condition of the numerical scheme.

Chapter 2: Literature review

Introduction

Solute species being transported through the subsurface can be reactive or non-reactive (conservative). A reactive chemical species migrating through groundwater could take part in chemical and microbiological processes which could transform and retard the species. Such reactions in a geochemical environment are generally termed reactive processes.

(Hagen, 1839) and (Poiseuille, 1840) were the first scientists to mathematically describe groundwater flow, using equations of viscous flow through capillary tubes. In 1956, Henry Darcy derived the well-known ''Darcy equation'' which can simulate water flow through porous media. Darcy's law to this day has been used as a reference for obtaining better numerical and experimental simulations used in solving groundwater related problems one of which is groundwater contamination. Once groundwater is contaminated, cleaning it can be a complex process. Models are used to predict future response of the system to different stresses including pollution. According to (Anderson and Woessner, 1992) the modelling process has three main objectives

- Predicating the behaviour of certain events that may expose the system

- Gaining an overview of the dominant parameters which can be helpful if more data is acquired.

- Formulating the regulatory guidelines for area of study by generating the appropriate geological conditions (porous or fracture) for flow analysis.

While groundwater pollution continues to be a growing threat to public and environmental health, chemically reactive pollutant species in solution can naturally attenuate a spreading pollution plume (Haji-Djafari S, Antommaria, and Crouse, 1979). Chemical attenuation in inorganic solutes is mostly influenced by adsorption, precipitation, oxidation and hydrolysis while attenuation of organic pollutants mostly happens through adsorption or microbial mediated breakdown processes. The behaviour of organic compounds under anaerobic conditions is of importance since such conditions generally prevail in contaminated groundwater. A measure of how well a process is understood determines the relative success in attempting to model it. Genuine and quantifiable predictions of contaminant distribution are only possible through appropriate formulation of the processes that influence their migration (HOMAS, 1984). In the saturated zone, advection, mechanical dispersion, molecular diffusion and molecular/chemical mass transfer all can control solute transport in groundwater. Failure to understand dispersion in porous and fractured media at a level required to construct a reliable mathematical model would be a big setback.

Not all toxic metals (heavy metals, transition metals, metalloids, radionuclides and radionuclides and other organic species) are mobile in the saturated zone. Mobility of these constituents depends on the pH and hydro-geochemical conditions, the ionic strength, the redox conditions, the mineralogy, the solid-phase surface area and the complexing capacity. Even though reactive transport models are increasingly used in simulating multi source pollution transport in groundwater, the capabilities to prediction attenuation increasingly being challenged by the complexities associated with chemical processes within dynamic groundwater systems. Furthermore, mixing and continuous redistribution of dissolved species caused by molecular diffusion and mechanical dispersion contributes to the difficulties in developing reliable methods for predicting the chemical behaviour of contaminants in the saturated zone. To predict the behaviour of contaminants in groundwater the contributing effect of each influencer must be adequately represented in a model or group of models, conservative or reactive. This chapter opens with a general presentation of the different type of geo-hydrological models. It then considers the different sources and types of groundwater contaminants while commenting on those of acute concern. Emphasis is on the processes that cause pollution transport and chemical mass transfer, in a manner which these processes are presented in models.

Types and sources of groundwater contamination

Measures are often put in place to protect surface water storage reservoirs used for domestic purposes including warning signs and indication of no trespass by humans. On the contrary, groundwater reservoirs hardly fully benefit from such foresight and thus are often less protected. Development on land typically carries on without considering the underlying aquifers and their recharge zones.

Types of groundwater contaminants.

The types of contaminants found in groundwater are as plentiful as its different uses, both organic and inorganic. Organic compounds and other pathogens can enter where surface makes its way into groundwater (Winter, 1998). Common pollutants found in groundwater include synthetic organic chemical, radionuclides, hydrocarbons, inorganic cations, inorganic and anions. Contaminants can be classified based on the following five properties (METZGER, 2005);

- Persistence: Some groundwater contaminants tend to not breakdown easily and thus persist in the environment for long periods of time. Polychlorinated Biphenyl (PBC) is an example of a persistent contaminant in the environment.

- Adsorption: How tightly will a compound attached to soil particles. The lower the bond, the less likely will leaching occur.

- Solubility: The dissolving capacity of a substance in a solvent. The higher the solubility of a compound, the easier it will dissolve in water and get to the water table. Methyl Tertiary Butyl Ether (MTBE) is an example of a contaminant with high water solubility.

- Volatility: The more volatile a compound is, the more likely it will go into gaseous form upon exposure to the atmosphere.

- Molecular size: The smaller the molecule, the more likely it can travel in porous media.

Sources of groundwater contamination

Sources of groundwater contamination are widespread. Groundwater may be contaminated by contaminants reaching the water table from surface activities such as oil spills or from sub-surface sources, above the water table such as leaking underground nuclear waste storage facilities, existing wells and contaminated recharged water. Contaminants can enter an aquifer through different means including; Infiltration of surface water through soil, sediment and rock, direct flow from surface water (fractured rock formations), direct flow through contaminated wells, cross contamination from other aquifers through improperly built well casings (Phipps, 2002).

There exist over 30 different potential sources of groundwater contamination listed by the American Office of technological Assessment (OPA, 1984), categorized into six classes (Tale 2.0).

Point source contamination refers to those originating from a specific location such as a buried underground storage tank. None point contamination on the other hand comes from an influx of pollutants over a large area, typically caused by agricultural chemical inputs.

Naturally occurring contaminants

Some naturally occurring substances tend to accumulate in high concentrations, exceeding standard necessary for domestic use. These compounds accumulate when water percolating through soil picks up and transports naturally occurring mineral salts and organic compounds. These substances enter groundwater dissolved in solution or as particulate matter (organic). The concentration of dissolved minerals tends to increase with downwards migration. Some common groundwater contaminants include hydrogen sulphides are products of decomposing organic matter. Radon, a radioactive gas is a product of uranium decomposition found in most crustal rocks. Other examples include chromium (III, IV and V) and arsenic.

Anthropogenic pollutants

Anthropogenic pollutants are those that result from human mediated activities. Of concern to water quality are potential threats that can be divided as agricultural, septic tanks, underground storage tanks, landfills,

mines, urban runoff and industrial operations. Common examples of anthropogenic pollutants include nitrates, salt and salinity, seawater intrusion and arsenic. Also, lateral migration caused by excessive pumping and vertical and vertical seepage of salt water into other fresh water aquifers are processes that can potentially degrade water quality.

Solute transport processes in ground water

In this section, we will present the different processes that influence the transport of dissolved solutes in groundwater. These processes are responsible for the spatial and temporal changes in concentrations of the different solutes in solution even though that can be important for the natural attenuation of migrating plumes in groundwater. As already mentioned in chapter 1, chemical reactions may occur between some components of the pollutant which may influence the fate of the contaminants such as a decrease in the mass of dissolved pollutants. Modelling groundwater contamination makes use of the different transport processes such as advection, diffusion and dispersion to simulate the response of an aquifer or system of aquifers to future and current pollution stresses of concern to the quality of water and integrity of the groundwater system. To do this, we will first briefly outline some of the properties that influence the flow of groundwater in an aquifer.

Groundwater properties

Subsurface water is composed of both a horizontal and vertical component. Horizontally, the rate and direction of flow is determined by a host of parameters characterising a porous media and the water. The vertical distribution of groundwater constitutes of two parts; the saturated and unsaturated zone. These are two layers separated by the water table or the phreatic surface.

Porosity

The porosity of a medium is the ratio of volume of open voids (pores) to the total volume of the rock. It can be stated mathematically as;

$$\theta = \frac{V_p}{V_m} \qquad (2.1)$$

Where θ is the porosity of the medium

V_p Is the volume of pores $[L^3]$

V_m Is the total volume of the material, inclusive of the solid and non-solid components $[L^3]$

Porosity occurs as primary (mainly depositional) or secondary (fracture, solution and diagenetic) porosity in the saturated zone beneath the water table is a direct measure of the amount of water stored per unit volume. It is a fraction scale with the maximum value at 1 and minimum at 0. It typically ranges from 0.01 in granites to above 0.5 in clay (Wikipedia, 2018).

Fractures usually do not contain much volume however, by joining pre-existing pore's, they can significantly increase porosity in what is referred to as fracture porosity. In some rare cases, none petroleum reservoir rocks such as granite can become reservoir rocks with sufficient fracturing and fracture interconnection.

Hydraulic conductivity, transmissivity and intrinsic permeability

Hydraulic conductivity, K $[L.T^{-1}]$ is a formation property that describes the ease of with which water can move through the pore spaces of fractures. It is influenced by the intrinsic permeability of the material and the degree of saturation of the formation rock. Hydraulic conductivity can be proportional to porosity; For example, if we consider two similar sandy aquifers, the one with a higher porosity will always have a higher hydraulic conductivity due to the presence of open voids for water to flow through. Generally, gravel and a sandy aquifer will have a higher porosity and so will be the ease of extracting water from them because of their high transmissivity. However, the porosity/hydraulic conductivity relation has another side mainly because there exist no direct proportionality between the porosity and hydraulic head but rather an inferred proportionality. E.g. clays, due to their small throat radii are known for their very low hydraulic conductivity yet they have very high porosities (owing to their mineral structures). As a result, clays tend to hold more water per volume of bulk material but do not release water rapidly and therefore have low hydraulic conductivity.

Transmissivity is a measure of how much water an aquifer can transmit horizontally. It depends on the aquifer's hydraulic conductivity, K and on the saturated thickness of the aquifer b;

$$T = K_s \times b \qquad\qquad (2.2)$$

Where T

Common transmissivity values for aquifers would be $10^{-4}\ m.s^{-1}$ in sandy aquifers, $10^{-6}\ m.s^{-1}$ for silt and $10^{-7}\ m.s^{-1}$ for clays (Bedient et al, 1999).

Permeability measures the ability of an aquifer to transmit fluid s through it. The intrinsic permeability K $[L^2]$ of a material is that of the medium only, independent of fluid properties. It is related to hydraulic conductivity K by;

$$K = k\left(\frac{\rho \mathrm{g}}{\mu}\right)$$
$$(2.3)$$

Where

Where

μ is the dynamic viscosity $[M.L^{-1}.T^{-1}]$

ρ is the fluid density and $[M.L^{-2}]$

g is the gravitational constant $L.T^{-2}$

Storage coefficient

The storage coefficient S is defined as the volume of water an aquifer can release or take up into storage per unit surface area, per unit change in the hydraulic head. For confined aquifers, S is in the range of 0.00005 to 0.005 which shows that large pressure changes produce very small changes in the storage volume of the aquifer. In an unconfined aquifer the storage coefficient lies between 0.025 to 0.07 (Bedient *et al.*, 1999).

Groundwater flow

Henry Darcy was the first person to study groundwater flow by experimentation (Fetter, 1998). His results established that for flow through porous media, the flow rate has a proportionality with the unit cross sectional area and the loss in head and inversely proportional to the distance covered.

$$Q = -KA\frac{dl}{dh}$$
$$(2.4)$$

Where

Q is the volumetric discharge of water $[L^3.T^{-1}]$

K is the hydraulic conductivity $[L.T^{-1}]$

A is the cross sectional area $[L^2]$

$\frac{dh}{dl}$ is the gradient of the hydraulic head $[L.L^{-1}]$

Contaminant transport processes in saturated media

In groundwater, the main processes that influence contaminant transport include advection, diffusion and dispersion.

Contaminant transport by advection

Advection can be seen as the mechanical transport of solutes in bulk groundwater flux through matrix pores. The concentration of contaminant in groundwater and volume of flowing groundwater both determine the contaminant mass flux being transported. For one dimensional flow, volume of water equals the product of the average linear velocity (normal to cross sectional area in porous media) and the effective porosity. This volume of water flowing $F[MT^{-1}L^{-2}]$ can be calculated using the equation;

$$F_x = V_x n_e C \tag{2.5}$$

Where,

V_x is average linear velocity in the along the x-axis LT^{-1}

n_e is the effective porosity

C is the solute concentration ML^{-3}

The average linear velocity V_x is the water flux rate flux rate of water across the unit cross sectional area of a porous medium

$$V_x = \frac{K}{n_e}\frac{dh}{dl} \tag{2.6}$$

Where K is the hydraulic conductivity $[L.T^{-1}]$

Where K is the hydraulic conductivity $[L.T^{-1}]$

$\frac{dh}{dl}$ is the hydraulic gradient $[L.L^{-1}]$

It can be seen from above that, the average linear velocity equals the ratio of Darcy velocity and effective porosity.

Contaminant transport by diffusion (molecular diffusion)

Diffusion is a processed controlled by the difference in the concentration gradients between two points. In groundwater, solutes will move from points of higher concentration to those of lower concentration weather it is stationary or flowing (Figure 4.a). The fluid mass being diffused follows Fick's first law given in one dimension as;

$$F = -D_d\frac{dC}{dx} \tag{2.7}$$

Where F is the mass flu of solute per unit area $[M.T^{-1}.L^{-2}]$

D_d is the diffusion coefficient $[M. L^{-3}]$. This value is different for each pollutant and can be dependent on temperature amongst other factor.

$\frac{dC}{dx}$ is the concentration gradient $[M. T^{-3}. L^{-1}]$

For a time varying concentration, the Fickian law applied, given as;

$$\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2}$$ (2.8)

Where $\frac{\partial C}{\partial t}$ is changing concentration with respect to time $[M. L^{-3}. T^{-1}]$.

It is also logical to consider that diffusion cannot proceed in porous media as fast as in water due to obstructions by mineral grains. In response to this, a parameter D^* $[M. L^{-3}. T^{-1}]$ called effective diffusion coefficient has been introduced.

$$D^* = \omega D_d$$ (2.9)

Where ω is the tortuosity coefficient. It accounts for the shape of the path of flow in porous media.

Dispersion processes

In porous media, dispersion describes the spreading of discrete volumes of pollutant as it flows through the subsurface. Inject a spot of dye in a porous medium through which groundwater is flowing and notice the spot increase in size as it is transported down gradient. Dispersion is important in groundwater pollutant transport studies because contaminants can arrive at the discharge point earlier than the arrival times calculated from the average groundwater velocity vectors. Dispersion compartmentalises transport velocities in the pollutant plume resulting in some parts of the plume moving faster than the average groundwater velocity. Dispersion is scale dependent and be caused by microscopic and macroscopic effects. Mechanical and hydrodynamic dispersion are caused by microscopic influences, specifically the variation of velocities on a microscale from average groundwater velocities (Figure 5a). Miscroscopic dispersion causes the spread of electrolytes which can be explained by the continued branching and subdivision of the capillary pores around the individual grains comprising the matrix. Macroscopic dispersion on the other hand is caused by the presence of large heterogeneities within the sub-surface host environment. A typical example demonstrated by Skibitzike and Robinson (1963) used lenses composed of high permeability material trapped in a low permeability matrix caused a spreading dye plume through a tank of porous media as shown in figure 5b.

It is generally recognized that the spreading of contaminant by dispersive transport is dependent not only on microscopic dispersion, but also on the influence of subsurface heterogeneities (Anderson, 1979) .
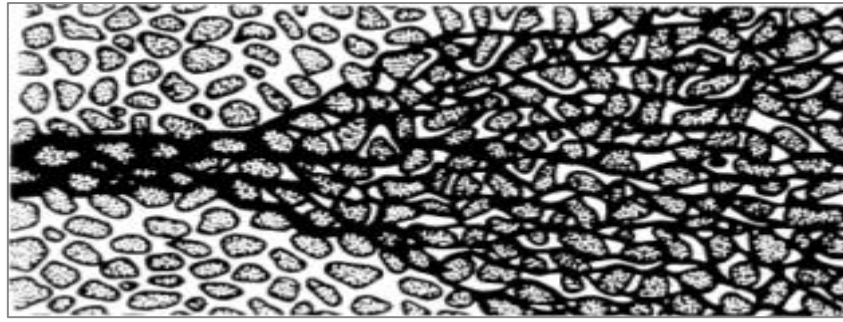
Figure 6: Microscopic dispersion (adapted from Freeze and Cherry, 1979).
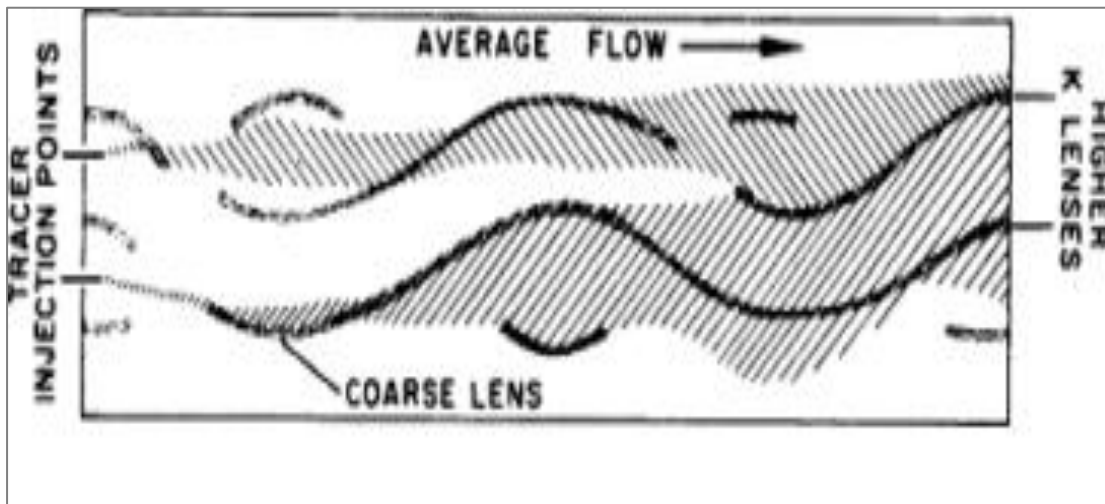
Figure 7: Macroscopic dispersion (adapted from Skibitzkie and Robinson, 1963).

2.1.1.1. *Mechanical dispersion*

In a porous media, groundwater velocity along the longitudinal x-direction will cause longitidunal dispersion along the horizontal plane. (figure 4b) or spreading parallel to the x-axis and transverse dispersion parallel to the y and the z axes. This is called Mechanical dispersion (changing groundwater flow velocity) and causes mixing and the spread of contaminant over great volumes of the aquifer.

The coefficient of longitudinal mechanical dispersion can be stated as = $\alpha_L \bar{v}$.
Where;
α Is dynamic dispersion in the principal direction of flow $[L]$ and
$\bar{v}$ The advective velocity (average linear velocity) of the ground water in the principal direction of flow$[L.T^{-1}]$.

In the same manner,
The Coefficient of transverse mechanical dispersion = $\alpha_T \bar{v}$.

Where

α Is the dynamic dispersivity in the transverse direction $[L]$ and

$\bar{v}$ Is the advective velocity (average linear velocity) of the ground water in the principal direction of flow, $[L.T^{-1}]$.
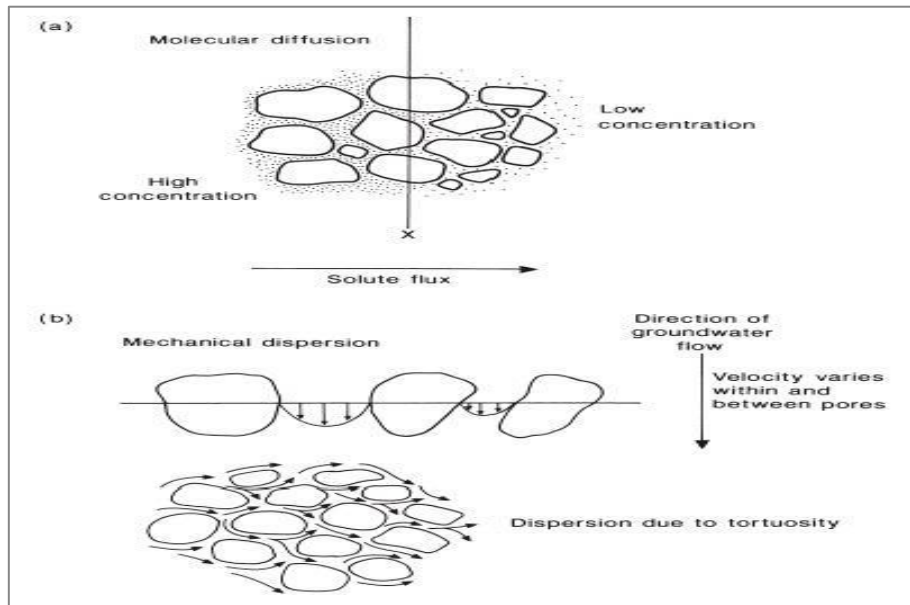
Figure 8: Schematic diagram showing the processes in molecular diffusion and mechanical dispersion.

Hydrodynamic dispersion

This is the combination of molecular diffusion and mechanical dispersion in flowing groundwater. It can be defined as follows;

$$D_L = \alpha_L v + D^*$$

$$D_T = \alpha_T v + D^* \qquad\qquad (2.10)$$

Where

D_L Is the longitudinal hydrodynamic dispersion coefficient $[L^2.T^{-1}]$

D_T Is the transverse hydrodynamic dispersion coefficient $[L^2.T^{-1}]$

α_L is the longitudinal dynamic dispersivity $[L]$

α_T is the transverse dynamic dispersivity $[L]$

Dispersion in fractured media

Dispersion The above discussions have been mainly on dispersion in porous media. The application of dispersion in fractured rock is of considerable importance given that some fractured rocks formations such as shales, granite and salt tend to be commonly used as repositories of hazardous nuclear waste. Clay which is susceptible to fracturing has become a favourite candidate for dumping municipal and industrial low level radioactive waste. Dispersion in fractured rock has been researched by many modellers including (Grisak, 1980) and (Tang, 1981). It generally assumed that dispersion and advection take place on in the fracture network while molecular diffusion from fracture to matrix is possible.

In fractured media, mechanical mixing occurs at fracture intersections due to velocity variation on rough fracture surfaces. The presence of different fracture sets can also induce velocity variation. Given that fractures can localise mass and high a concentrate on gradient, diffusion between fractures and matrix can be very significant in the spread of contaminant.
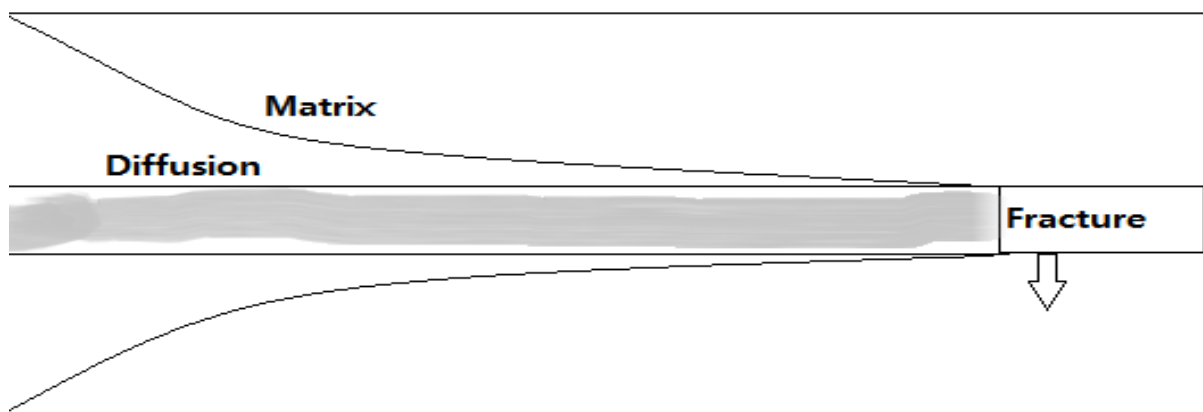
Dispersivity

DisperFigure 9: Diagram of Fractured media showing relationship between transport and matrix : of porous materials. It generally assumes a maximum value in the flow durection lower by one-thirtieth to one-fiftieth in the perpendicular or transverse direction (Figure 6.). Transport by dispersion usually follows a log normal distribution whose mean position represents transport at the advective velocity of water.
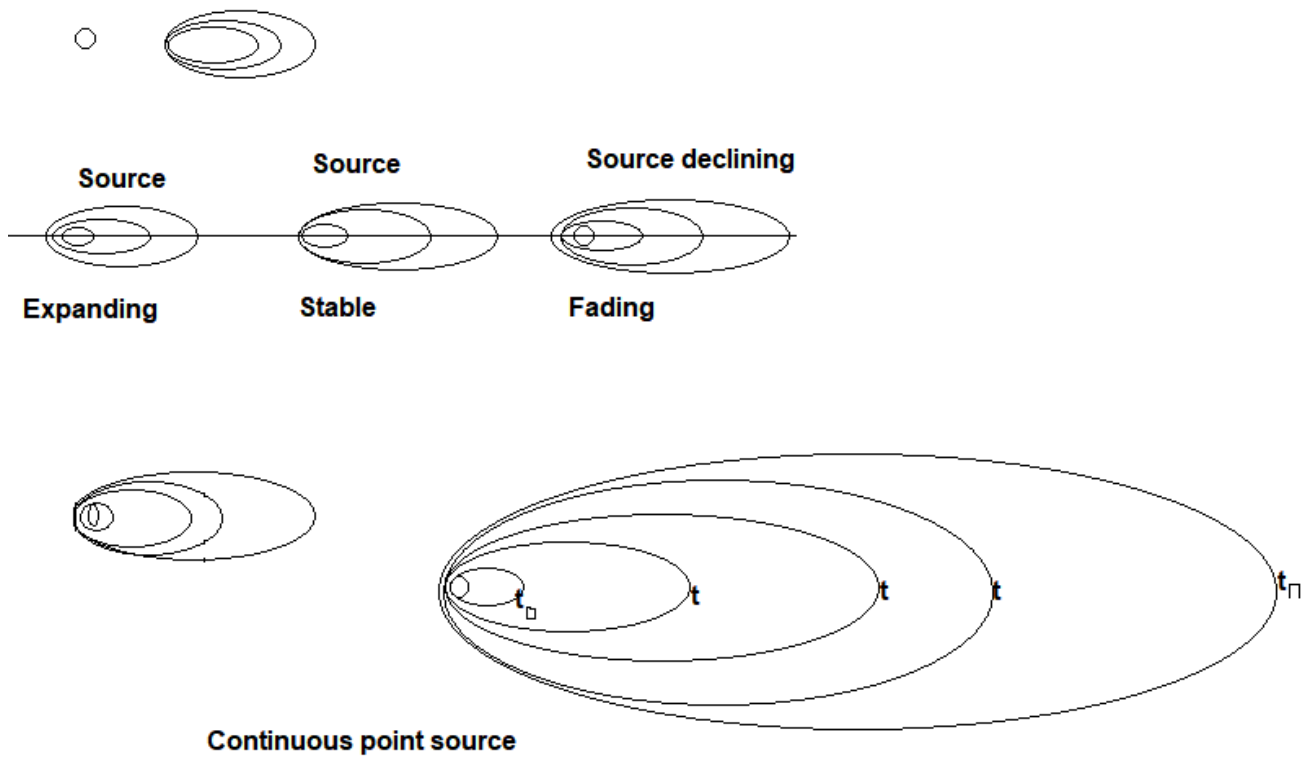
Figure 10: Diagram showing the effect of longitudinal dispersion on pollution plume

Equations of mass transfer

The advection dispersion model is derivation is based on the law of mass conservation of solute flux into and out of a small representative elementary volume of a porous medium. Its application is based on the assumptions of steady-state flow and the validity of Darcy's law. More so, the medium has to homogenous and isotropic. In flowing groundwater, the solute is transported both by advection and by hydrodynamic dispersion. In dimension, the Solute transport is given by

$$Transport\ by\ afdvection = v_x n_e C dA \qquad (2.11)$$

$$Transport\ by\ dispersion = n_e D_x \frac{\partial C}{\partial x} dA \qquad (2.12)$$

Where v_x is the average linear velocity in the x direction $[L.T^{-1}]$

n_e Is the effective porosity (Dimensionless)

D_x Is the hydrodynamic dispersion coefficient in the x direction $[L^2.T^{-1}]$

By considering the assumptions above, the total mass transfer in the $x-direction$ over a given unit cross sectional area.

$$\frac{F_x}{dA} = v_x n_e C - n_e D_x \frac{\partial C}{\partial x} \tag{2.13}$$

And can be generally written as;

$$F_x = v_x n_e C - n_e D_x \frac{\partial C}{\partial x} \tag{2.14}$$

The negative sign indicates that dispersion controlled flux follows the direction of decreasing concentration gradient. That is, from areas of higher to those of lower concentration. By conservation of mass, the flux of solute entering the representative elementary volume and the flux leaving it must be equal. Hence,

The difference between flux of solute entering and leaving the representative volume is

$$-\left(\frac{dF_x}{dx} + \frac{dF_y}{dy} + \frac{dF_z}{dz}\right) dxdydz \tag{2.15}$$

The rate of mass change (concentration) in the representative elementary volume is

$$n_e \frac{\partial C}{\partial x} dxdydz \tag{2.16}$$

By law of mass conservation, the change in mass most equals the measured difference from the representative elementary volume.

$$-\left(\frac{dF_x}{dx} + \frac{dF_y}{dy} + \frac{dF_z}{dz}\right) dxdydz = n_e \frac{\partial C}{\partial x} dxdydz \tag{2.17}$$

By substituting the values of F_x, F_y, and F_z for each direction x, y, z and cancellation of n_e from both sides, we can obtain the transport governing equations. For homogenous flow of groundwater in one-dimension given a isotropic medium,

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \tag{2.18}$$

While for two-dimensional flow with the flow direction along the x axes, the equation becomes

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} \tag{2.19}$$

Where D_L is dispersion coefficient along the principal flow direction $[L^2 . T^{-1}]$

Where D_T is the dispersion along the transverse direction $[L^2 . T^{-1}]$

Transport of reactive dissolved solutes

The transport and distribution of toxic chemicals in the subsurface is influenced by chemical reactions as a result of mass exchange between different existing phases (liquid phase, solid phase). As mentioned earlier, transport processes in ground water can serve in the natural attenuation of pollution plume. The chemical attenuation of inorganic contaminants happens through processes such adsorption, precipitation, oxidation or reduction while organic contaminants can be adsorbed or degraded by microbial processes. On the other hand, boichemical reactions that could influence the composition of groundwater include acid-base reactions, solution-precipitation reactions, oxidation-reduction reactions, ion pairing or complexation, microbiological processes and radioactive decay. Sorption processes such as adsorption and contaminant partitioning between aqueous and solid phases can attenuates or retard the transport of dissolved species in groundwater and remain of importance to the tracking of organic.

Attenuation due to sorption can be described by retardation equation below;

$$R_d = 1 + K_d \frac{(1-n)\rho s}{\theta} \tag{2.20}$$

Where R_d is known as the retardation factor,

K_d I the partitioning coefficient

ρs is the solid state mass density of the sorbing material and

θ is the moisture content.

Below the groundwater table, i.e. the saturated zone, θ equates to the porosity and the equation can thus be written as;

$$R_d = 1 + K_d \frac{\rho s}{n} \tag{2.21}$$

The retardation factor is dimensionless and is a measure of the attenuated transport of a reactive contaminant species compared relative to the advective transport of water. It can expressed as follows:

$$R_d = \frac{\bar{v}_w}{\bar{v}_c} = \frac{l_w}{l_c} = \frac{t_c}{t_w} \tag{2.22}$$

Where the subscripts w and c , represent water and dissolved contaminant species respectively.

v is the average linear velocity,

l is the distance travelled by water or the central mass of contaminant plume and

t is the arrival time of water or the mid-point of a contaminant break through curve.

Contaminant transport fate processes

The role played by advection and hydrodynamic dispersion is that of redistributing the dissolved contaminant throughout the geological formation without causing any change in its physical or chemical state. However, the some physical, chemical and biological processes can transform dissolved solutes into other forms such as change from liquid in the water to solid state in formation material.

Sorption

Involves the association of dissolved or gaseous substances with solid material (Bedient *et al.,* 1999). Sorption can be classified into adsorption and adsorption. Adsorption is the process by which a contaminant attaches itself to the surface of the solid particle while absorption simply refers to the association of the contaminant within a solid particle. Sorption can also be broken into two categories; Chemisorption, where the solid is incorporated on solid particle surface by a chemical reaction and cation exchange, where a cation attracted to a nearby negatively charged particle is stationed by electrostatic forces (Fetter, 1998). The opposite of sorption is desorption. This refers to the dissociation of the binding bonds and sorbed molecule leading to its return to the solution or gaseous phase.

Contaminant partitioning between the aqueous aqueous, solid or gaseous phase is determined by the partitioning coefficient. Localised chemical equilibrium during reactive transport exist between these two phases, pointing to the existence of a positive relationship between the volume of the sorbed species and the solute concentration present in the liquid phase. This is also called the partitioning coefficient (K_d) already discussed in section 2.4.5.

$$K_d = \frac{C^*}{C}$$
(2.23)

Where K_d is the partitioning coefficient $[L^3.M^{-1}]$

C^* Represents the solute mass sorbed $[M.M^{-1}]$

C Represents the solute concentration within the solution $[M.L^{-3}]$

Assuming that there is no biological reactions tacking place other than sorption and replacing C^* by K_dC, We can obtain a new advection dispersion equation stated below as:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{B_d}{\theta} \frac{\partial(K_dC)}{\partial t}$$
(2.24)

This same equation can be re-written as

$$\frac{\partial C}{\partial t}\left(1 + \frac{B_d}{\theta}K_d\right) = D_L\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} \qquad (2.25)$$

Where $\left(1 + \frac{B_d}{\theta}K_d\right)$ is the retardation factor.

Abiotic transformation

Transformation of the original composition or form of a species due to biological activity.

Hydrolysis

These reactions are responsible for the transfer of electrons amongst contaminant and the present chemical species. Reduction is the gain in electrons while oxidation is the loss of electrons. Biologically mediated oxidation-reduction reactions occur at a much faster rate than abiotic reaction due to the catalytic effect of some micro-organisms. It is for this reason that abiotic processes are usually neglected during transport calculations.

Oxidation-reduction

These reactions are responsible for the transfer of electrons amongst contaminant and the present chemical species. Reduction is the gain in electrons while oxidation is the loss of electrons. Biologically mediated oxidation-reduction reactions occur at a much faster rate than abiotic reaction due to the catalytic effect of some micro-organisms. It is for this reason that abiotic processes are usually neglected during transport calculations.

Elimination

Elimination reactions are common among specific contaminant groups such as halogens, ethane and propane. This happens through the release of a halogen group and a proton from nearby carbon atoms forming a carbon-carbon single bond.

Biodegradation

This is the process of complete conversion of a contaminant into its mineralised end products e.g. $CO_2.H_2O$ and salts by metabolic activity of living organisms. The process is fuelled by bacterial that are indigenous to the aquifer. Metabolic activity alters contaminants chemical form without causing mineralisation. This is called the process of biotransformation.

Chapter 3

Analytical solutions of reactive contaminant transport from a one-Dimensional finite source in a constant thickness aquifer.

Analysis of the Mathematical model.

For this purpose, we consider an initially pure and fractured aquifer, receiving pollution from two sources in reactive interaction with each other along zones of intense shear. We also assume that the aquifer is confined with no existing contaminant species and free from any geo-genic sources. The general geometry of the hypothetical scenario is shown in figure 3.1. The origin of the coordinate system is at the upper boundary and the positive Z-axis is downward. The bottom of the aquifer is lined by a no flow boundary $Z = d$. The water table which separates the vadose and saturated zones is also considered as a no flow boundary. We assume that the slope of the water table is negligible and it is parallel with the lower boundary. Steady state groundwater flow is along the x-axis.

Solute transport at equilibrium can be represented for the a one dimensional system as follows:

$$\begin{cases} \dfrac{\partial C_A}{\partial t} - D_x \dfrac{\partial C^2 C_A}{\partial x^2} + V \dfrac{\partial C_A}{\partial x} = K_1 C_A & (3.1A) \\[4mm] \dfrac{\partial C_B}{\partial t} - D_x \dfrac{\partial C^2 C_B}{\partial x^2} + V \dfrac{\partial C_B}{\partial x} = K_2 C_B - K_1 C_A & (3.1B) \end{cases}$$

With boundary conditions:

$$C(x, 0) = c_0 = 0 \tag{3.2}$$

Boundary conditions:

$$C(0, t) = c_1 \exp(-\gamma t) \; as \; t \to \infty \; and \; \frac{\partial C}{\partial x}(x, t) = 0 \tag{3.3}$$

And assuming that an initial pollution concentration of c_0 with boundary condition as prescribed by Dirichlet.

Where

C is the solute concentration (kg/m^3); time, t measured in (days); D_x I accounts for the coefficient of hydrodynamic dispersion in $x - direction \; m^2$/day; The groundwater flow velocity measured as v in (m/day); λ_1 is retardation constant $(1/day)$ and b is the aquifer's thickness m.
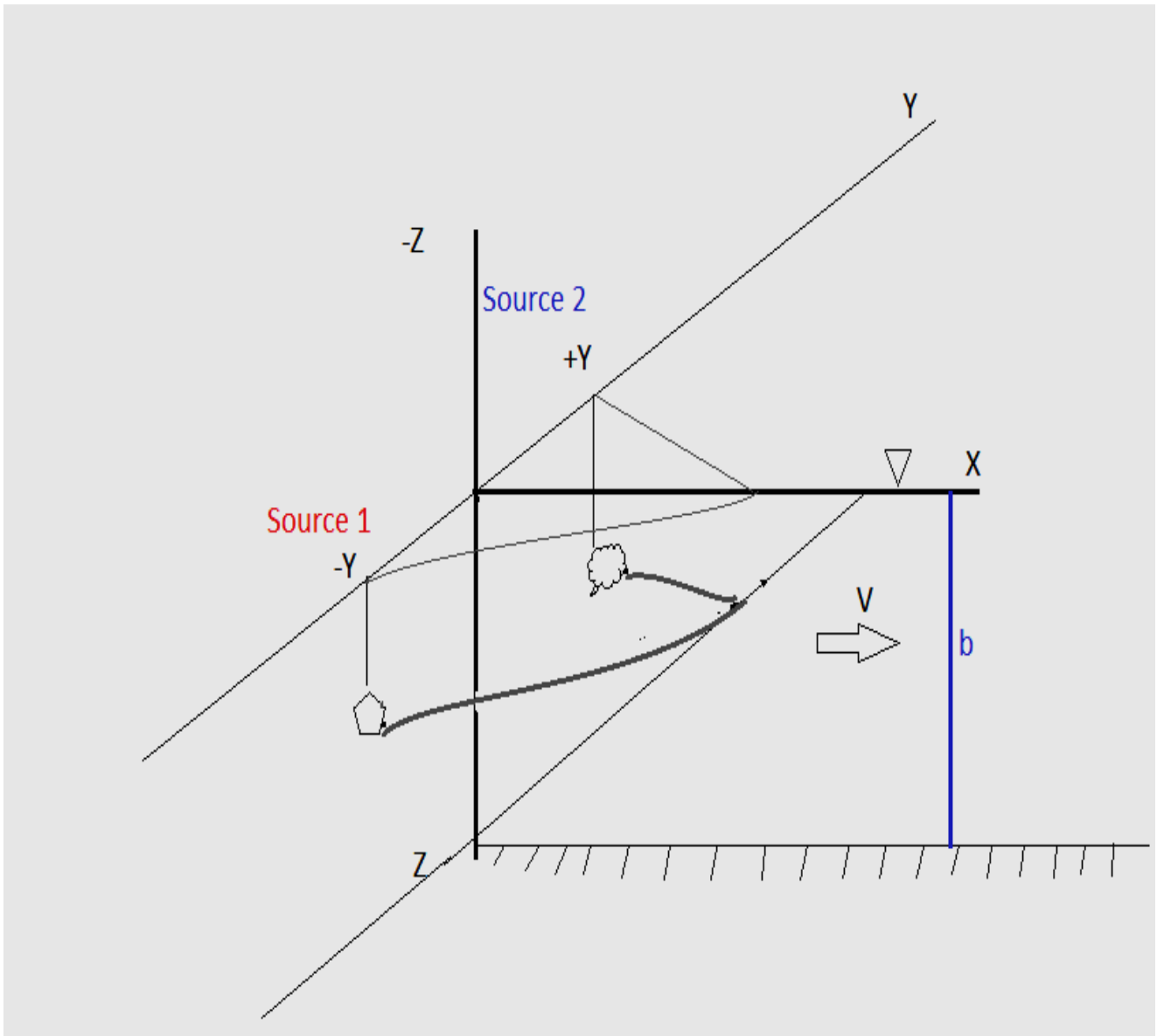
Figure 11: A schematic diagram of a two, one-dimensional source bodies within parallel non-penetrable boundaries. Both upper and lower boundaries are no flow zones.

Solution derived using La Place transform method.

Case 1:

The solution of the first equation can be obtained using the application of La Place transform on both sides, as follows.

$$\mathcal{L}\left(\frac{\partial C_A}{\partial t} - D\frac{\partial^2 C_A}{\partial x^2} + V\frac{\partial C_A}{\partial x} + K_1 C_A\right) = \mathcal{L}(0) \tag{3.4}$$

Where $\mathcal{L}$ is the Laplace transform operator; and results to

$$sC(x) - C(0) - D\frac{\partial^2 C_A}{\partial x^2} + V\frac{\partial C_A}{\partial x} + K_1\, C(x) = 0 \tag{3.5}$$

Equation (3.2) represents the La-Place transform variable with respect to the time. We can directly observe from that the partial differential equation becomes an ordinary non-homogenous differential equation of order 2 with the partial derivatives becoming total derivatives. Equation (3.2) breaks down to

$$DC'' + VC' + (s + K_1)C = c_0 \tag{3.6}$$

The homogenous solution associated to the above equation is given as

$$C_h(x) = A_1\,\exp(r_1, x) + A_2\,\exp(r_2, x) \tag{3.7}$$

Where A_1 and $= A_2$ are arbitrary constants, and

$$r_2 = \frac{V_r \pm \sqrt{V^2 - 4D_r\,(s + K_1)}}{2D_r} \tag{3.8}$$

The particular solution associated to the given equation is given by $\tag{3.9}$

$$C_q(x) = A_1 e^{(r_1, x)} + A_2 e^{(r_2, x)}$$

Where $A_1\,(x)$ and $A_2\,(x)$ are functions to satisfy the following system of equations

$$\begin{cases} A_1'(x)exp(r_1, x) + A_2'(x)exp(r_2, x) = 0 & \tag{3.10a} \\ r_1 A'(x)exp(r_1, x) + r_2 A_2'(x)exp(r_2, x) = g(x) & \tag{3.11b} \end{cases}$$

Hence the particular solution is given by

$$C_p(x) = \frac{c_0}{s + K_1} \tag{3.12}$$

Giving the general solution for the ordinary non-homogenous differential equation is given by

$$C(x) = A_1\,exp(r_1, x) + A_2\,exp(r_2, x) + \frac{c_0}{s + K_1} \tag{3.13}$$

We can obtain the coefficients $A_1\ and\ A_2$ using our boundary initial and boundary conditions in the Laplace space as follows;

$$\mathcal{L}\big(c(0, t)\big) = \frac{c_1}{\gamma + K_1} = c_1 exp\,(-\gamma t) \tag{3.14}$$

Applying the following boundary condition

$$\lim_{x \to \infty} c(x)^n \to 0$$

$$A_2 = 0 \tag{3.15}$$

Going forward, using the initial condition (3.14) gives;

$$A_1 = -\frac{c_0}{K_1 + s} + \frac{c_1}{\gamma + s}$$

But

$$c_0 = 0 \text{ so that}$$

$$A_1 = \frac{c_1}{\gamma + s} \tag{3.16}$$

The solution of the ordinary differential equation follows thus;

$$\frac{c_0}{K_1 + s} + exp\left(x \frac{V_r - \sqrt{V_r{}^2 - 4D_r\,(s + K_1)}}{2D_r} \right)\left[\frac{c_1}{K_1 + s} - \frac{c_0}{\gamma + s}\right] \tag{3.17}$$

$$= exp\left(x \frac{V_r - \sqrt{V_r{}^2 - 4D_r\,(s + K_1)}}{2D_r} \right) \text{ when } c_0 = 0.$$

We know that the solution of the hydrodynamic dispersion equation is given as

$$c(x, t) = \mathcal{L}^{-1}(c(x)) \tag{3.18}$$

Where $\mathcal{L}^{-1}$ is the inverse Laplace transform operator.

The first term of the sum is invertible and gives

$$\mathcal{L}^{-1}\left(\frac{c_0}{K_1 + s}\right) = c_0 exp(-K_1 t) \tag{3.19}$$

The inverse Laplace transform of the second term can be obtained by applying the convolution theorem since we have a product of two functions, namely;

$$exp\left(x \frac{V_r - \sqrt{V_r{}^2 - 4D_r\,(s + K_1)}}{2D_r} \right) \tag{3.20}$$

For the second expression, the inverse Laplace transform reads

$$\mathcal{L}^{-1}\left(exp\left(x \frac{V_r - \sqrt{V_r{}^2 - 4D_r\,(s + K_1)}}{2D_r} \right) \right) = \frac{x exp\left(-\frac{(-Vt + x)^2 - tK_1}{4D_r} \right)}{\sqrt[2]{(\pi|D_r)}t^{3/2}} \tag{3.21}$$

$$= f(t)$$

$$\mathcal{L}^{-1}\left\{\frac{c_1}{K_1+s} - \frac{c_0}{\gamma+s}\right\} = c_1 exp\,(-\gamma t) - c_0\,exp\,(-\gamma t) \quad (3.0$$

The Laplace of the second term of the sum can be expressed as

$$\int_0^t f(x)g(\varepsilon - t)d\varepsilon c \qquad (3.22)$$

Using the table of integral we find that the above integral yields to

$$\frac{c_1 exp\,(-\gamma t)}{2}\left\{exp\left(x\frac{V_r - u_r}{2D_r}\right)erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right)\right. \qquad (3.23)$$
$$\left. + exp\left(x\frac{V_r + u_r}{2D_r}\right)erfc\left(\frac{x + u_r t}{2\sqrt{D_r\,t}}\right)\right\}$$
$$- \frac{c_0 exp\,(-\gamma t)}{2}\left\{erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right)\right.$$
$$\left. + exp\left(x\frac{q_r}{2D_r}\right)erfc\left(\frac{x + u_r t}{2\sqrt{D_r\,t}}\right)\right\}$$

$$\frac{c_1 exp\,(-\gamma t)}{2}\left\{exp\left(x\frac{V_r - u_r}{2D_r}\right)erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right) + exp\left(x\frac{V_r + u_r}{2D_r}\right)erfc\left(\frac{x + u_r t}{2\sqrt{D_r\,t}}\right)\right\}$$
$$- \frac{c_0 exp\,(-\gamma t)}{2}\left\{erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right) + exp\left(x\frac{q_r}{2D_r}\right)erfc\left(\frac{x + u_r t}{2\sqrt{D_r\,t}}\right)\right\} \qquad (3.24)$$

Where

$$u_r = \sqrt{V_r{}^2 + 4D_r\,(K - \gamma)} \qquad (3.25)$$

And $erfc(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty exp(-v^2)\,dv$ is error function. Therefore the analytical solution of the hydrodynamic dispersion equation given the prescribed initial and boundary conditions is given as

$$c(x,t) = \frac{c_1 exp\,(-\gamma t)}{2}\left\{exp\left(x\frac{V_r - u_r}{2D_r}\right)erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right)\right. \qquad (3.26)$$
$$\left. + exp\left(x\frac{V_r + u_r}{2D_r}\right)erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right) + c_0 exp\,(-\gamma t)\right\}$$

This same analytical solution for the hydrodynamic dispersion equation for $c_0 = 0$ was presented (*clearly and Ungs*, 1978) stated in equation (3.2.9) below as;

$$c(x,t) = \frac{c_1 exp\,(-\gamma t)}{2}\left\{ exp\left(x\frac{V_r - u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right)\right.$$

$$\left. + exp\left(x\frac{V_r + u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right)\right\} \tag{3.27}$$

Solutions obtained using Green's function method

Equation $3.1B$ can be solved using the Method Green's function. A green's function is used in solving inhomogeneous linear differential equations by providing a split time representation of a systems response at a particular point (x', t), due to a field source point given at (x', τ) (Gringarten and Ramey, 1973). Eventhough the this method is advantageous in providing easy handling of various types no flow boundary and initial conditions, it has remained scarely utilized for solving groundwater pollution related problems.

$$\frac{\partial C_B}{\partial t} - D_x \frac{\partial C^2 C_B}{\partial x^2} + V \frac{\partial C_B}{\partial x} = K_2 C_B - K_1 C_A$$

Above mathematical model has a heterogeneous and a homogeneous part. The heterogeneous part can be solved using Green's function method. Green's function in this problem is defined as the concentration at (x, t) due to an instantaneous point source of strength unity generated at the point (x', τ) , the aquifer being initially kept at zero concentration and boundary surface being kept at zero concentration (Gringarten and Ramey, 1973). The Green's function of this problem can be obtained by solving the following differential equation with initial and boundary conditions.

Solution of the homogenous system

Solution for homogenous part provides the particular solution and can be presented below as follows;

The solution of the first equation can obtain using the application of La Place transform which gives;

$$sC(x) - C(0) - D\frac{\partial^2 C_A}{\partial x^2} + V\frac{\partial C_A}{\partial x} + K_1\,C(x) = 0 \tag{3.28}$$

Where $\mathcal{L}$ is the Laplace transform operator; and results to

$$sC(x) - C(0) - D\frac{\partial^2 C_B}{\partial x^2} + V\frac{\partial C_B}{\partial x} + K_1\,C(x) = 0 \tag{3.29}$$

$$C_B(x,t) = \frac{c_1 exp\,(-\gamma t)}{2}\left\{ exp\left(x\frac{V_r - u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right)\right.$$

$$\left. + exp\left(x\frac{V_r + u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r\,t}}\right) + c_0 exp\,(-\gamma t)\right\} \tag{3.30}$$

This same analytical solution for the hydrodynamic dispersion equation which is also the particular solution for $c_0 = 0$ was presented ($clearly\ and\ Ungs$, 1978) stated in equation (3.2.9) below as;

$$C_B(x,t) = \frac{c_1 \exp(-\gamma t)}{2} \left\{ \exp\left(x\frac{V_r - u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r t}}\right) \right.$$

$$\left. + \exp\left(x\frac{V_r + u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r t}}\right) \right\} \tag{3.31}$$

Solution of the heterogeneous part using Green's function

$$\frac{\partial C_B}{\partial t} - D_x \frac{\partial C^2 C_B}{\partial x^2} + V \frac{\partial C_B}{\partial x} = K_2 C_B - K_1 C_A \tag{3.32}$$

The solution for the homogenous part can be stated as

$$C_B(x,t) = \frac{c_1 \exp(-\gamma t)}{2} \left\{ \exp\left(x\frac{V_r - u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r t}}\right) \right.$$

$$\left. + \exp\left(x\frac{V_r + u_r}{2D_r}\right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r t}}\right) \right\} \tag{3.33}$$

Equation 3.1B is a non-homogenous thus requiring the application of Green function method.

$$\frac{\partial C_B}{\partial t} - D \frac{\partial^2 C_B}{\partial x^2} + V \frac{\partial C_B}{\partial x} = -K_1 C_A \tag{3.34}$$

Apply Laplace

$$s\tilde{C} - C(0) - D\frac{\partial^2 \tilde{C}_B}{\partial x^2} + V\frac{\partial \tilde{C}_B}{\partial x} = -\tilde{C}K_1 \tag{3.35}$$

$$D\frac{\partial^2 C_B}{\partial x^2} - V\frac{\partial C_B}{\partial x} + s\tilde{C} - \tilde{C}K_1 = 0 \tag{3.36}$$

$$D\frac{\partial^2 \tilde{C}_B}{\partial x^2} + V\frac{\partial \tilde{C}_B}{\partial x} - \tilde{C}(s + K_1) = 0$$

The Green's function method gives a solution to non-homogenous linear differential equations defined on a domain with boundary problems. In Green terms, this can be written as;

$$D\frac{\partial^2 G}{\partial x^2} + V\frac{\partial G}{\partial x} - G(s + K_1) = \sigma(0) \tag{3.37}$$

Applying Laplace transform to the Greens function to the;

$$\mathcal{L}\left(D\frac{\partial^2 G}{\partial x^2} + V\frac{\partial G}{\partial x} - G(s + K_1)\right) = \mathcal{L}(\sigma(0)) \tag{3.38}$$

$$D(p^2\tilde{G} - pG' - G(0)) + V\left(p\tilde{G} - G(0)\right) - \tilde{G}(s + K_1) = 1$$

$$Dp^2 \tilde{G} + Vp\tilde{G} + \tilde{G}(s + K_1) = 1$$

$$(Dp^2 + Vp + (s + K_1))\tilde{G} = 1$$

$$\tilde{G} = \frac{1}{(Dp^2 + Vp - (s + K_1))}$$

$$\tilde{G}(x, t) = \frac{1}{\frac{-V \pm \sqrt{V^2 + 4D(s + K_1)}}{2D}} \tag{3.39}$$

Where

$$p = \frac{-V \pm \sqrt{V^2 + 4D(s + K_1)}}{2D}; \quad p = \frac{-V - \sqrt{V^2 + 4D(s + K_1)}}{2D} \text{ Or } p = \frac{-V + \sqrt{V^2 + 4D(s + K_1)}}{2D}$$

If we consider

$$\frac{-V - \sqrt{V^2 + 4D(s + K_1)}}{2D} = \frac{-V - \sqrt{\Delta}}{2D} = \alpha_- \tag{3.40}$$

And

$$\frac{-V + \sqrt{V^2 + 4D(s + K_1)}}{2D} = \frac{-V + \sqrt{\Delta}}{2D} = \alpha_+ \tag{3.41}$$

The roots of the above equation can be written as

$$\tilde{G}(x, s) = \frac{1}{(p - \alpha_-)(p - \alpha_+)} \tag{3.42}$$

Equation 3.3.4 can be written in the form 4''

$$\frac{1}{(p - \alpha_-)} \cdot \frac{1}{(p - \alpha_+)} \tag{3.43}$$

The inverse of $\tilde{G}(p, s) = \mathcal{L}\tilde{G}(x, s) = \mathcal{L}\left(\frac{1}{(p-\alpha_-)} \cdot \frac{1}{(p-\alpha_+)}\right)$. Given the product of two functions, we use the convolution theory which states thus;

The inverse Laplace transform of a convolution is given by the product of the inverse of the individual functions. Here, the inverse Laplace of $\tilde{G}$ will be a product inverse of $\tilde{f}(p)$ and $\tilde{h}(p)$ and is given by

$$\mathcal{L}(f(a) \cdot g(b)) = \mathcal{L}f(a)\mathcal{L}(b) \tag{3.44}$$

The inverse functions of $\tilde{G}$ given as

$$\mathcal{L}^{-1}\left(\tilde{G}(x,s)\right) = \int_0^\tau e^{\alpha_-,\tau}\, e^{\alpha_+(t-\tau)}\, d\tau$$

(3.45)

Simplifying gives

(3.46)

$$\mathcal{L}^{-1}\left(\tilde{G}(x,\tau)\right) = \int_0^x e^{\alpha_-,\tau}\, e^{\alpha_+(x-\tau)}\, d\tau$$

$$G = e^x \int_0^x e^{(\alpha_--\alpha_+)x}\, d\tau$$

Change of variable.

Let $e^{(\alpha_--\alpha_+)x} = y,\ dy = (\alpha_- - \alpha_+)dx$

$$G = e^{x\alpha_+}\left[\frac{1}{\alpha_- - \alpha_+}\cdot e^{x(\alpha_--\alpha_+)}\right]$$

(3.47)

$$G = e^{x\alpha_+}\left[\frac{1}{\alpha_- - \alpha_+}\cdot e^{x(\alpha_--\alpha_+)}\right]\Bigg|_0^t$$

Substituting equations

$$G(t) = e^{x\alpha_+}\left[\frac{1}{\alpha_- - \alpha_+}\cdot e^{x(\alpha_--\alpha_+)} - \frac{1}{\alpha_- - \alpha_+}\right]$$

$$G(t) = e^{x\alpha_+}\left[\frac{1}{\alpha_- - \alpha_+}\cdot e^{x(\alpha_--\alpha_+)} - \frac{1}{\alpha_- - \alpha_+}\right]$$

(3.48)

Substitute

$$G(t,s) = e^{x\left(\frac{-V-\sqrt{\Delta}}{2V}\right)}\left[\frac{1}{\dfrac{-V-\sqrt{\Delta}}{2D} - \dfrac{-V+\sqrt{\Delta}}{2D}}\cdot e^{x\left(\frac{-V-\sqrt{\Delta}}{2V}-\frac{-V+\sqrt{\Delta}}{2V}\right)} \right.$$

$$\left. - \frac{1}{\dfrac{-V-\sqrt{\Delta}}{2D} - \dfrac{-V+\sqrt{\Delta}}{2D}}\right]$$

(3.49)

The above equation can be further simplified as

$$G(t,s) = e^{x\left(\frac{-V-\sqrt{\Delta}}{2D}\right)}\left[\frac{1}{\dfrac{-V-\sqrt{\Delta}}{2D} - \dfrac{-V+\sqrt{\Delta}}{2D}}\right] e^{x\left(\frac{-V-\sqrt{\Delta}}{2D}-\frac{-V+\sqrt{\Delta}}{2D}\right)} - 1$$

(3.50)

Substituting 3.3.2 and 3.3.3

$$G(t,s) = e^{x\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\left[\frac{1}{\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D} - \frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}}\right].$$ (3.51)

$$e^{x\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D} - \frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)} - 1$$

The exact solution in Laplace space can be written as

$$C(x,s) = C_1(x,s) + \int_0^x C(0,s).G(x-\tau,s)d\tau$$ (3.52)

Where $C(t,s)$ is the term for the exact solution; $C(0,s)$ is the particular solution given by equation 3.2.9; C (0, s) is the term for initial pollution source concentration for which case is 0; and $\int_0^t G(t-\tau,s)d\tau$ is the integral of equation.

The exaction solution can be thus written as;

$$C(t,s) = C_1(t,s) + \int_0^t C(0,s).G(t-\tau,s)d\tau$$

$$C(t,s) = \frac{c_1 exp\,(-\gamma t)}{2}\left\{exp\left(x\frac{V_r-u_r}{2D_r}\right)erfc\left(\frac{x-u_rt}{2\sqrt{D_r\,t}}\right) + \right.$$ (3.53)

$$exp\left(x\frac{V_r+u_r}{2D_r}\right)erfc\left(\frac{x-u_rt}{2\sqrt{D_r\,t}}\right)\right\} + C(0,s)\int_0^t G(t-\tau,s)d\tau$$

To obtain the $\int_0^t G(t-\tau,s)d\tau$, we can express in terms of equation3.3.8 and simplifying further gives,

$$G(x,s) = e^{x\alpha_+}\left[\frac{1}{\alpha_- - \alpha_+}.\left(e^{x(\alpha_--\alpha_+)}\right) - 1\right]$$ (3.54)

$$\int_0^x G(x-\tau,s)d\tau = \frac{1}{\alpha_--\alpha_+}\int_0^x e^{(x-\tau)\alpha_+}.e^{(x-\tau)(\alpha_--\alpha_+)} - e^{(x-\tau)\alpha_+}.d\tau$$

$$\int_0^x G(x-\tau,s)d\tau = \frac{1}{\alpha_- - \alpha_+}\int_0^x \left(e^{a_1(t-\tau)} - e^{a_2(t-\tau)}\right).d\tau$$ (3.55)

After integrating we obtain the following

$$\int_0^x G(t-\tau,s)d\tau = \frac{1}{\alpha_- - \alpha_+}\left(\frac{1}{a_-}e^{\alpha_-(x-\tau)} - \frac{1}{a_+}e^{\alpha_+(x-\tau)}\right)$$ (3.56)

Let $(t - \tau) = y$

$$G(x - \tau, s) = \frac{1}{\alpha_- - \alpha_+}\left(\frac{1}{a_-}e^{x\alpha_-} - \frac{1}{a_+}e^{yx}\right)\Big|_0^x \tag{3.57}$$

Substituting equation 3.3.8

$$G(x - \tau, s) =$$

$$\left[\left(\frac{1}{\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)-\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\left(\frac{1}{\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)}e^{x\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)-\right.$$

$$\left.\left.\frac{1}{\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}e^{x\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\right] - \left[\left(\frac{1}{\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)-\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\right] \tag{3.58}$$

This can further simplify to

The equation above is still in Laplace space. To bring it to the real space, we apply inverse Laplace transform as follows

$$\mathcal{L}^-\left(G(-\tau, s)\right) = \left[\left(\frac{1}{\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)-\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\left(\frac{1}{\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)}e^{t\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\right.$$

$$\left.\left.-\frac{1}{\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}e^{\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\right]$$

$$-\left[\left(\frac{1}{\left(\frac{-V-\sqrt{V^2+4D(s+K_1)}}{2D}\right)-\left(\frac{-V+\sqrt{V^2+4D(s+K_1)}}{2D}\right)}\right)\right] \tag{3.59}$$

$$G(x, s)$$

$$
= \left(\frac{D}{\sqrt{V^2 + 4D(s + K_1)}} \right) \frac{1}{\left(\frac{-V - \sqrt{V^2 + 4D(s + K_1)}}{2D} \right)} \cdot \left[\frac{x exp\left(-\frac{(-Vt + x)^2 - tK_1}{4D_r} \right)}{\sqrt[2]{(\pi|D_r)} t^{3/2}} \right]
$$

$$
- \frac{1}{\left(\frac{-V + \sqrt{V^2 + 4D(s + K_1)}}{2D} \right)} \cdot \frac{x exp\left(-\frac{(-Vt + x)^2 - tK_1}{4D_r} \right)}{\sqrt[2]{(\pi|D_r)} t^{3/2}}
$$

(3.62)

The exact solution to the linearized heterogeneous advection dispersion equation can be written as;

$$C(t, x)$$

$$
= \frac{c_1 exp\,(-\gamma t)}{2} \left\{ exp\left(x \frac{V_r - u_r}{2D_r} \right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r t}} \right) + exp\left(x \frac{V_r + u_r}{2D_r} \right) erfc\left(\frac{x - u_r t}{2\sqrt{D_r t}} \right) \right\}
$$

$$
+ \left[\left(\frac{1}{\left(\frac{-V - \sqrt{V^2 + 4D(s + K_1)}}{2D} \right) - \left(\frac{-V + \sqrt{V^2 + 4D(s + K_1)}}{2D} \right)} \right) \left(\frac{1}{\left(\frac{-V - \sqrt{V^2 + 4D(s + K_1)}}{2D} \right)} \frac{x exp\left(-\frac{(-Vt + x)^2 - tK_1}{4D_r} \right)}{\sqrt[2]{(\pi|D_r)} t^{3/2}} \right. \right.
$$

$$
\left. - \frac{1}{\left(\frac{-V + \sqrt{V^2 + 4D(s + K_1)}}{2D} \right)} \frac{x exp\left(-\frac{(-Vt + x)^2 - tK_1}{4D_r} \right)}{\sqrt[2]{(\pi|D_r)} t^{3/2}} \right) \right] - \left[\left(\frac{1}{\left(\frac{-V - \sqrt{V^2 + 4D(s + K_1)}}{2D} \right) - \left(\frac{-V + \sqrt{V^2 + 4D(s + K_1)}}{2D} \right)} \right) \right]
$$

(3.61)

Chapter 4: Numerical approximation

Introduction

In this chapter, the mathematical model is implemented into a numerical model capable of describing the transient evolution of mineral water systems as a well as the changing composition of the solution. The formulation, performance and accuracy of the reactive transport model are significantly influenced by the scale of the governing process (Barh, 1987).

Numerical techniques can be classified in to low order methods and global methods. The former includes finite difference (FD), Finite element (FE), and finite volume (FV) methods whereas the late constitutes spectral and pseudo spectral methods. In this example, we present a finite element discretisation method to approximate the partial differential equation. In numerical approximation, the approximate solution is represented by functional values at certain discrete points (grid points or mesh) for which calculations will be performed. This requires the transformation of the partial differential equations into a discrete approximation. To achieve this, a representative spatial discretization increment Δx and a representative time increment Δt are introduced. A control on the space time discretization is given by the Perlet and Courant criteria (MacQuarrie, 1990). The specific constrains will be determine the temporal and spatial discretization method used. The Peclet number compares the time scale for dispersion and diffusion with the time scale for advection and for a phase A, the Peclet number is given as;

$$P_e = \frac{v_A \Delta x}{D_A} \tag{4.0}$$

The courant number (Courant-Friedrichs-Lewy criterion), is defined as the adjective courant number, and determines the fractional distance travelled relative to the grid spacing due to advection in a single step in time. The advection courant number for a phase A is given by;

$$Cr_{a.A} = \frac{v_A \Delta t}{\Delta x} \tag{4.1}$$

Where the characteristic length for advection is defined by the spatial discretization interval Δx. Similarly, for a purely diffusive transport, the diffusive Courant number for a phase p can be expressed as

$$Cr_{D,A} = \frac{2D_A \Delta t}{\Delta x} \tag{4.2}$$

Which relates the time increment Δt to the time scale of macroscale diffusive transport. For Geochemical reactions, an equivalent courant number can be derived to relate the time scale for geochemical reactions to the time increment Δt.

$$Cr_r = \frac{\Delta t}{t_r} \tag{4.3}$$

The main aim of the chapter is solve the dynamic model given in the previous chapter using Crank-Nicolson finite-difference method. We also investigate an present the stability condition of the model.

4.2 Finite difference method

This method involves replacing differential equations by finite difference equations written in algebraic form whose solutions are a function of grid points. We can say that a finite difference solution basically involves three steps;

4.2.1 Discretization scheme equation

$$\frac{\partial C_A}{\partial t} - D\frac{\partial C^2 C_A}{\partial x^2} + V\frac{\partial C_A}{\partial x} = K_1 C_A \tag{4.4}$$

Where $V > 0$

Crank-Nicolson Scheme

The Crank-Nicolson scheme is an implicit scheme. Instead of considering mesh points for performing calculations, the discretization is made at the midpoint of between $the\ ith\ and\ (i+1)th$ levels.

The condition necessary for convergence of some PDE's solved by the method of finite differences is given by the Courant-Fredreich-Lewy number. For the Crank-Nicolson numerical scheme, a low CFL number (0.5) is required for numerical accuracy. This surfaces when the explicit time scheme is used for the numerical solution. The simulation tends to produce incorrect results if the time step is longer than that for a certain explicit time-marching computer.

Forward difference approximation in time

$$\frac{\partial C_A}{\partial t} = \left(\frac{C_{A,i}^{n+1} - C_{A,i}^n}{\Delta t} \right) \tag{4.5}$$

Central difference dispersion

$$D\frac{\partial^2 C_A}{\partial x^2} = D\left[\frac{\left(C_{A,i+1}^n - 2C_{A,i}^n + C_{Ai-1}^n\right)}{(\Delta x)^2} + \frac{\left(C_{A,i+1}^{n+1} - 2C_{A,i}^{n+1} + C_{A,i-1}^{n+1}\right)}{(\Delta x)^2} \right]$$

$$= \frac{D}{2(\Delta x)^2}\left[\left(C_{A,i+1}^n - 2C_{A,i}^n + C_{A,i-1}^n\right) + \left(C_{A,i+1}^{n+1} - 2C_{A,i}^{n+1} + C_{A,i-1}^{n+1}\right) \right] \tag{4.6}$$

Central difference Advection

$$V\frac{\partial C_A}{\partial x} = V\left[\frac{(C_{A,i+1}^{n+1} - C_{A,i-1}^{n+1})}{2(\Delta x)} + \frac{(C_{A,i+1}^{n} - C_{A,i-1}^{n})}{2(\Delta x)}\right] \tag{4.7}$$

$$= \frac{V}{2\Delta x}\left[(C_{A,i+1}^{n+1} - C_{A,i-1}^{n+1}) + (C_{A,i+1}^{n} - C_{A,i-1}^{n})\right] \tag{4.8}$$

Central difference Reaction constant

$$K_1 C_A = K\left[(C_{A,i}^{n+1} + C_{A,i}^{n})\right] \tag{4.9}$$

Hence, the finite difference approximation can be written thus;

$$\frac{C_{A,i}^{n+1} - C_{A,i}^{n}}{\Delta t} = \frac{D}{(\Delta x)^2}\left[(C_{A,i+1}^{n+1} - 2C_{A,i}^{n+1} + C_{A,i-1}^{n+1}) + (C_{A,i+1}^{n} - 2C_{A,i}^{n} + C_{A,i-1}^{n})\right]$$
$$- \frac{V}{\Delta x}\left[C_{A,i+1}^{n+1} - C_{A,i-1}^{n+1} + C_{A,i+1}^{n} - C_{A,i-1}^{n}\right] + K(C_{A,i}^{n+1} + C_{A,i}^{n}) \tag{4.10}$$

Where the following terms can be represented.

$$\frac{D\Delta t}{(\Delta x)^2} = \alpha, \text{ And}$$

$$\frac{V\Delta t}{\Delta x} = \beta$$

We expand and simplify with common terms

$$C_{A,i}^{n+1} = C_{A,i}^{n} + \frac{1}{2}\alpha C_{A,i+1}^{n} - \alpha C_{A,i}^{n} + \frac{1}{2}\alpha C_{A,i-1}^{n} - \frac{1}{2}\beta C_{A,i+1}^{n} + \frac{1}{2}\beta C_{A,i-1}^{n} + \frac{1}{2}K_1 C_{A,i}^{n}$$
$$+ \frac{1}{2}\alpha C_{A,i+1}^{n+1} - \alpha C_{A,i}^{n+1} + \frac{1}{2}\alpha_{A,i-1}^{n+1} - \frac{1}{2}\beta C_{A,i+1}^{n+1} + \frac{1}{2}\beta C_{A,i-1}^{n+1} + \frac{1}{2}K_1 C_{A,i}^{n+1} \tag{4.11}$$

$$C_{A,i}^{n+1} = C_{A,i}^{n} - \alpha C_{A,i}^{n} + \frac{1}{2}K_1 C_{A,i}^{n} + \frac{1}{2}\alpha C_{A,i+1}^{n} - \frac{1}{2}\beta C_{A,i+1}^{n} + \frac{1}{2}\alpha C_{A,i-1}^{n} + \frac{1}{2}\beta C_{A,i-1}^{n}$$
$$+ \frac{1}{2}\alpha C_{A,i+1}^{n+1} - \frac{1}{2}\beta C_{A,i+1}^{n+1} - \alpha C_{A,i}^{n+1} + \frac{1}{2}K_1 C_{A,i}^{n+1} + \frac{1}{2}\alpha_{A,i-1}^{n+1} + \frac{1}{2}\beta C_{A,i-1}^{n+1}$$

Open up the brackets

$$C_{A,i}^{n+1} = \left(1 - \alpha + \frac{1}{2}K_1\right)C_{A,i}^{n} + \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n} + \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n+1} - \left(\alpha - \frac{1}{2}K_1\right)C_{A,i}^{n+1}$$
$$+ \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n+1}$$

Collecting together like terms and opening up brackets.

$$C_{A,i}^{n+1} + \left(\alpha - \frac{1}{2}K_1\right)C_{A,i}^{n+1}$$

$$= \left(1 - \alpha + \frac{1}{2}K_1\right)C_{A,i}^{n} + \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n} \quad (4.12)$$

$$+ \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n+1} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n+1}$$

The final discretised equation can then be written as;

$$C_{A,i}^{n+1}\left(1 + \alpha - \frac{1}{2}K_1\right)$$

$$= \left(1 - \alpha + \frac{1}{2}K_1\right)C_{A,i}^{n} + \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n} \quad (4.13)$$

$$+ \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n+1} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n+1}$$

If we consider the following notation, the above equation can the broken down as;

$$\left(1 + \alpha - \frac{1}{2}K_1\right) = a$$

$$\left(1 - \alpha + \frac{1}{2}K_1\right) = b$$

$$\left(\frac{\alpha}{2} - \frac{\beta}{2}\right) = c$$

$$\left(\frac{\alpha}{2} + \frac{\beta}{2}\right) = d$$

$$aC_{A,i}^{n+1} = bC_{A,i}^{n} + cC_{A,i+1}^{n} + cC_{A,i+1}^{n+1} + dC_{A,i-1}^{n} + dC_{A,i-1}^{n+1} \quad (4.14)$$

Equation 2.2.4 becomes the first order Crank Nicolson finite difference approximation of the one dimensional advection-dispersion equation.

Discretization scheme for second equation

The second equation is stated thus;

$$\frac{\partial C_B}{\partial t} - D\frac{\partial C^2 C_B}{\partial x^2} + V\frac{\partial C_B}{\partial x} = K_2 C_B - K_1 C_A \quad (4.15)$$

From equation 2.2.1, 2.2.3 can be written as

$$C_{B,i}^{n+1} - C_{B,i}^n = \frac{1}{2}\left[\frac{D\Delta t}{(\Delta x)^2}\left(C_{B,i+1}^n - 2\,C_{B,i}^n + C_{B,i-1}^n\right) - \frac{V\Delta t}{\Delta x}\left(C_{B,i+1}^n - C_{B,i-1}^n\right) + K_2 C_{B,i}^n\right]$$

$$+ \frac{1}{2}\left[\frac{D\Delta t}{(\Delta x)^2}\left(C_{B,i+1}^{n+1} - 2\,C_{B,i}^{n+1} + C_{B,i-1}^{n+1}\right) - \frac{V\Delta t}{\Delta x}\left(C_{B,i+1}^{n+1} - C_{B,i-1}^{n+1}\right)\right] \tag{4.16}$$

$$+ K_2 C_{B,i}^{n+1}\Big] - K_1 C_A$$

Expand and simplify with common terms

$$C_{B,i}^{n+1} = C_{B,i}^n + \left[\frac{1}{2}\alpha C_{B,i+1}^n - \alpha C_{B,i}^n + \frac{1}{2}\alpha C_{B,i-1}^n - \frac{1}{2}\beta C_{B,i+1}^n + \frac{1}{2}\beta C_{B,i-1}^n + \frac{1}{2}K_2 C_{B,i}^n\right.$$

$$+ \left[\left(\frac{1}{2}\alpha C_{B,i+1}^{n+1} - \alpha\,C_{B,i}^{n+1} + \frac{1}{2}\alpha_{B,i-1}^{n+1} - \frac{1}{2}\beta C_{B,i+1}^{n+1} + \frac{1}{2}\beta C_{B,i-1}^{n+1}\right.\right. \tag{4.17}$$

$$\left.\left.+ \frac{1}{2}K_2 C_{B,i}^{n+1}\right)\right]\Big] - K_1 C_{A,i}^{n+1} - K_1 C_{A,i}^n$$

Open up the brackets and collecting like terms gives

$$C_{B,i}^{n+1} = C_{B,i}^n + \frac{1}{2}\alpha C_{B,i+1}^n - \alpha C_{B,i}^n + \frac{1}{2}\alpha C_{B,i-1}^n - \frac{1}{2}\beta C_{B,i+1}^n + \frac{1}{2}\beta C_{B,i-1}^n + \frac{1}{2}K_2 C_{B,i}^n \tag{4.18}$$

$$+ \frac{1}{2}\alpha C_{B,i+1}^{n+1} - \alpha\,C_{B,i}^{n+1} + \frac{1}{2}\alpha_{B,i-1}^{n+1} - \frac{1}{2}\beta C_{B,i+1}^{n+1} + \frac{1}{2}\beta C_{B,i-1}^{n+1} + \frac{1}{2}K_2 C_{B,i}^{n+1}$$

$$- K_1 C_{A,i}^{n+1} - K_1 C_{A,i}^n$$

The final discretised equation can then be written as;

$$C_{B,i}^{n+1}\left(1 + \alpha - \frac{1}{2}K_2\right)$$

$$= \left(1 - \alpha + \frac{1}{2}K_2\right)C_{B,i}^n + \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{B,i+1}^n + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{B,i-1}^n \tag{4.19}$$

$$+ \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{B,i+1}^{n+1} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{B,i-1}^{n+1} - K_1 C_{A,i}^{n+1} - K_1 C_{A,i}^n$$

If we consider the following constants below, the above equations can be broken down as;

$$\left(1 + \alpha - \frac{1}{2}K_2\right) = a$$

$$\left(1 - \alpha + \frac{1}{2}K_2\right) = b$$

$$\left(\frac{\alpha}{2} - \frac{\beta}{2}\right) = c$$

$$\left(\frac{\alpha}{2} + \frac{\beta}{2}\right) = d$$

$$aC_{B,i}^{n+1} = bC_{B,i}^n + cC_{B,i+1}^n + cC_{B,i+1}^{n+1} + dC_{B,i-1}^n + dC_{B,i-1}^{n+1} - \left(K_1 C_{A,i}^{n+1} + K_1 C_{A,i}^n\right) \qquad (4.20)$$

Stability analysis

The time-dependent advection dispersion equation is widely employed in many applications, for example financial mathematics and flow simulation (Chua, 1984) (McCArtin, 2003) just to name a few. Many authors have studied the stability of the Crank Nicolson method for numerical discretization of ODEs and PDEs see (Witek ML, 2008) and (Company R, 2009) however, none of these works has taken into account the cusp effect of two separate source particle tracks on the stability of the method.

In numerical analysis, calculations with a lesser magnification of approximation error are said to be numerically stable. A desired property, the stability of a model is pre-requisite to performing simulations. Obtaining a robust enough model, capable of reproducing results within a certain range is the goal here. The system is stable if and only if the solution of the numerical scheme remains bounded for a fixed time, as the step size turns to zero. A stable PDE is said to be converging (Lax equivalence theorem).

To prove our discretisation results on the stability of the crank Nicolson scheme of two particle tracks for the time-dependent coefficient hydro-dispersion equation we make use of the explicit approximation for the boundary conditions. We note that the use of explicit boundary conditions can reduce the stability of our scheme, rendering the Crank Nicolson method with explicit boundary conditions conditionally convergent while other methods such as the implicit Euler method with explicit boundary conditions is unconditionally stable (Oishi, 2015). Generally, the results for the explicit boundary conditions hold for time-dependent diffusion with advections provided. Given a systems with periodic boundary conditions, the variation of the error may be represented as a finite Fourier series given as;

$$\epsilon(x) = \sum_{M=1}^{M} A_m e^{ik_m x} \qquad (4.21)$$

Where $K_m = \frac{\pi m}{L}$ $m = 1, 2, \cdots M$ and $M = \frac{L}{\Delta x}$

We assume the error amplitude varies with time. The difference equation for error is linear, i.e., each term behaves as though it is the series its self. On this premise, we can comfortably formulate the error growth of a typical term.

$$\epsilon_m(x, t) = \sum_{m=1}^{M} C_{A,i}^n . e^{ik_m x}$$

(4.22)

Where α is a constant.

By substituting equation (2.22)into equation, (2.20) we are able to understand how error varies in time steps. If we consider the following notation, the above equations can the broken down as;

$$C_{A,i}^{n+1}\left(1 + \alpha - \frac{1}{2}K_1\right)$$
$$= \left(1 - \alpha + \frac{1}{2}K_1\right)C_{A,i}^n + \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^n + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^n$$
$$+ \left(\frac{\alpha}{2} - \frac{\beta}{2}\right)C_{A,i+1}^{n+1} + \left(\frac{\alpha}{2} + \frac{\beta}{2}\right)C_{A,i-1}^{n+1}$$

(4.23)

If we consider the following notation, the above equations can the Brocken down using;

$$\left(1 + \alpha - \frac{1}{2}K_1\right) = a$$

$$\left(1 - \alpha + \frac{1}{2}K_1\right) = b$$

$$\left(\frac{\alpha}{2} - \frac{\beta}{2}\right) = c$$

$$\left(\frac{\alpha}{2} + \frac{\beta}{2}\right) = d$$

$$aC_{A,i}^{n+1} = bC_{A,i}^n + cC_{A,i+1}^n + dC_{A,i-1}^n + cC_{A,i+1}^{n+1} + dC_{A,i-1}^{n+1}$$

(4.24)

First, we note the error terms expressed as

$$\epsilon_{A,i}^{n+1} = C_{n+1} . e^{ik_m x}$$
$$\epsilon_{A,i}^n = C_n . e^{ik_m x}$$
$$\epsilon_{i+1,A}^n = C_n . e^{ik_m(x+\Delta x)}$$
$$\epsilon_{i-1,A}^n = C_n . e^{ik_m(x-\Delta x)}$$
$$C_{A,i+1}^{n+1} = C_{n+1} . e^{ik_m(x+\Delta x)}$$
$$C_{A,i-1}^{n+1} = C_{n+1} . e^{ik_m(x-\Delta x)}$$

(4.25)

We insert the error term $C_{A,i}^n = e^{ik_m x}$ in to the finite difference scheme 2.2.4

$$aC_{n+1} \cdot e^{ik_m x} = bC_n \cdot e^{ik_m x} + cC_n \cdot e^{ik_m(x+\Delta x)} + dC_n \cdot e^{ik_m(x-\Delta x)} + cC_{n+1} \cdot e^{ik_m(x+\Delta x)}$$

$$+ \, dC_{n+1} \cdot e^{ik_m(x-\Delta x)} \tag{4.26}$$

We expand and simplify exponential powers

$$aC_{n+1} \cdot e^{ik_m x} = bC_n \cdot e^{ik_m x} + cC_n \cdot e^{ik_m x} e^{ik_m \Delta x} + dC_n \cdot e^{ik_m x} e^{-ik_m \Delta x)}$$

$$+ \, cC_{n+1} \cdot e^{ik_m x} e^{ik_m \Delta x} + dC_{n+1} \cdot e^{ik_m x} e^{-ik_m \Delta x} \tag{4.27}$$

Factor out the common terms $e^{ik_m x}$ to have;

$$aC_{n+1} = bC_n + \left(cC_n e^{ik_m \Delta x} + cC_{n+1} e^{ik_m \Delta x} \right) + \left(dC_n e^{-ik_m \Delta x)} + dC_{n+1} e^{-ik_m \Delta x} \right)$$

$$\tag{4.28}$$

$$aC_{n+1} = bC_n + c\left(C_n e^{ik_m \Delta x} + C_{n+1} e^{ik_m \Delta x} \right) + d\left(C_n e^{-ik_m \Delta x)} + C_{n+1} e^{-ik_m \Delta x} \right)$$

$$aC_{n+1} = bC_n + c(C_n + C_{n+1})e^{ik_m \Delta x} + d(C_n + C_{n+1})e^{-ik_m \Delta x)}$$

Using the identity

$$sin(k_{m\Delta x}) = \frac{1}{2}\left(e^{ik_m \Delta x} + e^{-ik_m \Delta x)} \right) \tag{4.29}$$

$$aC_{n+1} = bC_n + 2c(C_n + C_{n+1})sin(k_{m\Delta x})$$

$$C_{n+1} = \frac{b}{a}C_n + \frac{2c}{a}(C_n + C_{n+1})sin(k_{m\Delta x})$$

The system stability condition can be assed using method of the exaggeration factor.

The exaggeration factor G is given as

$$G = \frac{C_{n+1}}{C_n} \tag{4.30}$$

$$\frac{C_{n+1}}{C_n} = \frac{b}{a} + \frac{2c}{a}\left(1 + \frac{C_{n+1}}{C_n} \right)sin(k_{m\Delta x})$$

$$G = \frac{b}{a} + \frac{2c}{a}(1 + G)sin(k_{m\Delta x})$$

Expand and make G subject of the formula

$$G = \frac{b + 2csin(k_{m\Delta x})}{a - 2csin(k_{m\Delta x})} \tag{4.31}$$

$$\left| \frac{b + 2csin(k_{m\Delta x})}{a - 2csin(k_{m\Delta x})} \right| \leq 1$$

Hence, the system is stable when

$$\frac{\left|b + 2c\sin\left(k_{m\Delta x}\right)\right|}{\left|a - 2c\sin\left(k_{m\Delta x}\right)\right|} \leq 1 \qquad (4.32)$$

The system is stable when the when

$$|b + 2c\sin(k_m\Delta x)| \leq |a - 2c\sin(k_m\Delta x)| \qquad (4.33)$$

$$\left|a - 2c\sin\left(k_{m\Delta x}\right)\right| = \begin{cases} a - 2c\sin(k_m\Delta x) \ if \ a - 2c\sin(k_m\Delta x) > 0 \\ -a + 2c\sin(k_m\Delta x) if \ a - 2c\sin(k_m\Delta x) < 0 \end{cases}$$

Where

$$\left(1 + \alpha - \frac{1}{2}K_1\right) = a$$

$$\left(1 - \alpha + \frac{1}{2}K_1\right) = b$$

$$\left(\frac{\alpha}{2} - \frac{\beta}{2}\right) = c$$

Chapter 5:

Reactive Transport and Kinetic modelling

Introduction

The concept of reactive transport is one of theoretical interest and practical importance. There exist a multitude of geochemical processes including such diverse phenomena as the transport of toxic waste and radio nuclides, hydrothermal ore deposits and metamorphism which are all products of reactive transport. These systems have sometimes been described as open boi-geochemical reactors, involving interactions between the solid phases, migrating fluids, and microbes (Litchner, 1996). Modelling the transport of toxic chemicals coupled with the combined effect of chemical reactions can be achieved using the deterministic advection dispersion approach or the stochastic model approach however, the scope of this research is limited to the deterministic model.

A component undergoing solute transport in groundwater is subject different form of interactions with other material. This happens either through pore water or on mineral grain surfaces. Mineral reactions are of different types and the duration of each of these types plays a role in the geochemical evolution of groundwater. Groundwater composition in the presence of solid phases is controlled by the solid phase considering that some components might be retarded. Major changes in chemical composition of a plume migrating in groundwater occur with the development of a front of short distances. These chemical changes occur over relatively shorter distances relative to the scale of the model and groundwater velocity. These conditions coupled with the fast reaction rates results in an aqueous face that is under chemical equilibrium. On the other hand, fronts that develop over long distances are characterized by slower chemical reaction rates. It is in these instances that chemical kinetic reactions become important.

Chemical reactions can be differentiated by time for which it takes for the system to be in chemical equilibrium. Generally, fast reactions are under chemical equilibrium relative to the transport time scale. Some chemicals exhibits slower reaction rates and can be assumed conservative (non-reactive).

Generally, the mathematical formulation of reactive transport requires an in-depth understanding of the different chemical processes to be investigated. Rapid urbanization coupled with the rising demand for industry and agricultural activities has led to an increase of pollution instances by landfill leachate, industrial solvents, sewage leak and Acid Rock drain just to name a few (Figure. 11) In some cases, these sources eventually interact with each other and with the formation material (rock surfaces). The changing concentrations of reactants and the creation of new products only confounds the modelling challenge.

Hence the ability to understand the progress of chemical reactions remains critical if sound modelling results are the aim.

In the natural system (fractured or porous, and highly heterogeneous) varying hydraulic and physicochemical properties are the main transport controls. Conduits are generally crucial for groundwater flow and pollution transport. This is typically exemplified by karst and fractured formation where flow is predominantly turbulent flow as oppose to laminar flow observed in porous formations (Liedl, 2003). Pollution can be caused by a variety of anthropogenic and natural reasons and so are their many sources. Some natural processes include soil erosion, physicochemical weathering and mass wasting, seawater intrusion and volcanic eruption etc. On the other hand, anthropogenic causes which are the focus of this section include industrial, agricultural and different types of disposed waste materials. In one way or another pollutants reach the groundwater system through the hydraulic cycle. As water circulates through the hydraulic circle, pollutants are transferred through the soil into the aquifer horizon.

In response to the exponential growth of computer computational power, the ability to quantify reactive transport has greatly advanced. In this regards, a vast array of comprehensive reactive transport models have been developed and applied to the field of groundwater pollution. These models can be used either quantitatively or qualitatively where insight into a reactive process is needed. An important part of the modelling process is validation. Here the modeler substitutes real number values to represent a starting measure (concentration), the beginning of a though process that will eventually be accepted, rejected or require the modification of the original hypothesis.

Pollutant transport in groundwater is predominantly controlled by flow of groundwater. However, the rate of a reaction can be influenced by a variety of standard geochemical and biological processes such as complexation, acid-base reactions, oxidation reactions, precipitation and desorption processes. Aside of the classical chemistry process listed above, reactive transport can occur between distinct components originating from two separate sources that mix where two fractures converge. This can be typically observed in a karst or fractured rock aquifer.
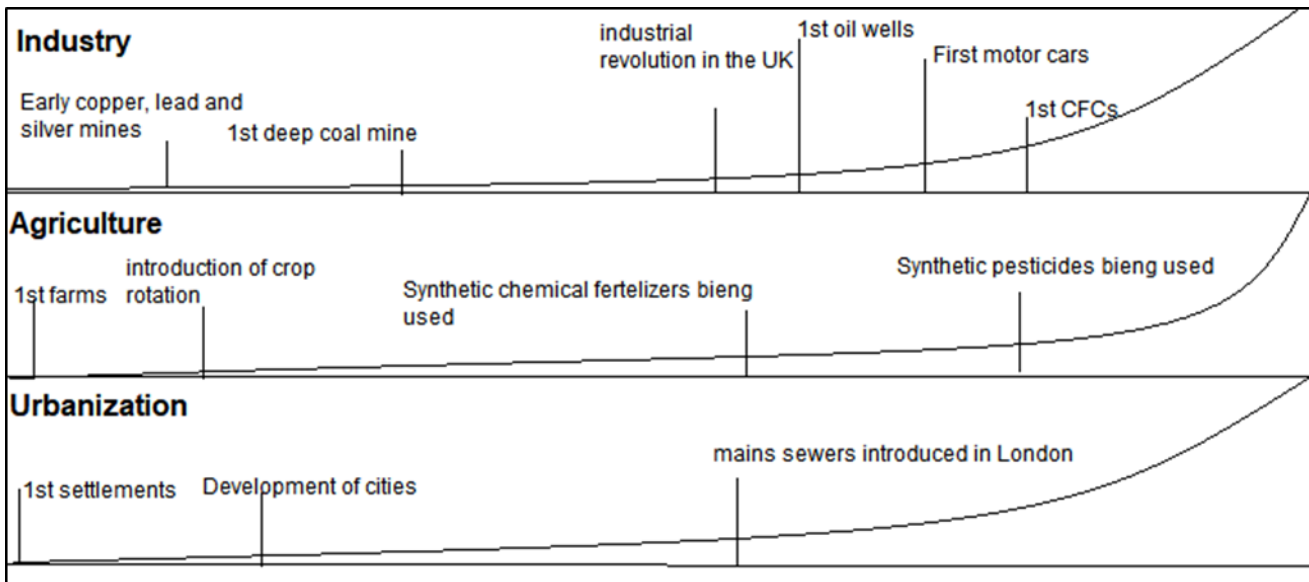
Figure 12: Schematic presentation of human activities and their impacts on groundwater. (Adapted from UNEP 2003).

In most experimental studies than not, conceptualizing subsurface heterogeneity and complexities has been achieved using geostatistical models as a substitute for the sedimentary and hard rock (crystalline and fractured) aquifer formations. These models usually assume hydraulic log conductivity as a stationary Random Space Function with a multi-Gaussian probability distribution (Rubin, 2003). This is possible if there is adequate geological data required to map out the location and characteristics of conduit networks within a fractured or karst aquifers to an adequate degree. Modelling software such as MUDFLOW and FEFLOW have been used for this purpose, by simulating the conduit networks at varying scales using techniques which include lines of drain cells and internal sinks (Quinn, 2000) as well as pathways of higher hydraulic conductivity (Lindgren, 2004).
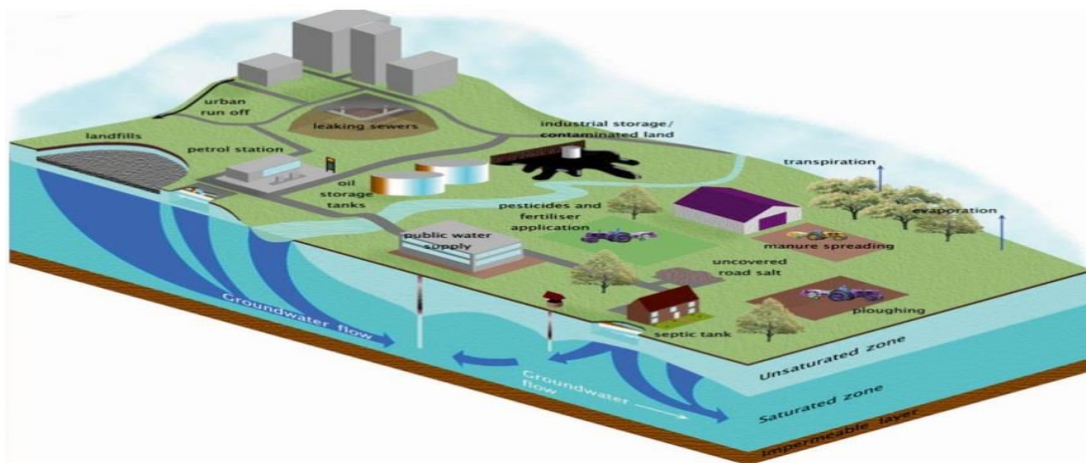

Figure 13: Schematic presentation showing different potential pollution sources in an urban setting

A description of fluid rock interaction requires knowledge of mineral surface area, a quantity that is hard to measure and may change with time (Linchter, 1996). Secondly, microbial systems which we now know to playing an important role in the evolving geochemical groundwater environment remain poorly understood.

Finally, a problem of fundamental importance is upscaling properties obtained from observations at the pore and molecular scales to the macro or continuum scale at which most reactive transport models are applicable. A main objective of this section is to quantitatively analyse the space and time distribution of a hypothetical pollutant resulting from the reaction between two chemical components transported in groundwater. Reactive transport models are more and more frequently applied to investigate the mechanisms involved in contaminant migration in aquifers, investigation that generally requires the modelling of the hydrochemistry of the said aquifer. Modelling studies that couple chemistry and transport in fractured aquifers are scarce. Especially, if we consider two point sources with the aims to use the model to investigate contaminant migration. The classical mass-balance approaches, quoted in chapter one, cannot capture the full complexity of chemical reactions occurring in an aquifer, from both thermodynamic and kinetic points of view. For the purpose of this study we consider the example of a 1-D model as already stated in the first section for use in modelling contaminant speciation and mobility using pH as the main parameter. This chapter opens with a discussion of some important aspects of groundwater geochemistry including water groundwater quality and chemical analysis of groundwater including flow chemistry and health implication of groundwater contamination

This chapter will be dedicated to kinetic modelling. Subsurface geochemical reactions typical carry on over long geological time spans, and this allows for the assumption of kinetic equilibria, which underpins the theory of kinetic modelling. The chapter will be restricted to describe the kinetic aspects of reactive transport modelling. Multispecies and single species reactive transport formulations generally assume the transport of the constituents to be independent of other system reactive processes. The chapter opens with a short literature review of modelling reactive transport and kinetics associated. Chemical processes that control the composition of groundwater are discussed. Chemical representation of groundwater quality by means of standard ternary graphs, including the potential health effects of groundwater contamination are also listed.

Kinetics

Chemical processes involve the transformation of matter from one form to another, which may often be assigned a first order reaction constant as a good approximation. Hence, with sufficient grasp of the chemistry in a given system, combinations of chemical reaction as well as the subsequent generation of products can be characterized by a set of reversible chemical reaction schemes that follow first order kinetics.

In most experimental studies than not, conceptualizing subsurface heterogeneity and complexities has been achieved using geostatistical models as a substitute for the sedimentary and hard rock (crystalline and

fractured) aquifer formations. These models usually assume hydraulic log conductivity as a stationary Random Space Function with a multi-Gaussian probability distribution (Rubin, 2003). This is possible if there is adequate geological data required to map out the location and characteristics of conduit networks within a fractured or karst aquifers to an adequate degree. Modelling software such as MUDFLOW and FEFLOW have been used for this purpose, by simulating the conduit networks at varying scales using techniques which include lines of drain cells and internal sinks (Quinn, 2000) as well as pathways of higher hydraulic conductivity (Lindgren, 2004).

There remain many challenges for an accurate or even semi-quantitative description of all chemical processes taking place in geochemical systems. However, powerful computing capabilities are making it possible to describe the evolution of a set chemical reactions happening with a system. Nevertheless, it is hardly ever the ambition of one single model to accurately capture all reaction and transport mechanisms responsible for the ever changing subsurface geochemical environment. A multitude of physical, geochemical and biological processes influence solute transport. The complex interaction between each of these processes limits the study of individual processes involved since they are both dependent on each other. Solute transport tends to commonly employ models that explain the physical processes of advection and dispersion while using the kinetic constant and partitioning coefficient to describe chemical speciation and sorption within the system. While these models can accurately capture the transport phenomena, they are unable to reveal the chemical products and layers of sophisticated geochemical processes often underlying some of the observed trends such as pH-dependent reactions. On the other hand, chemical equilibrium models can describe pH-dependent reactions but not transport. As stated by (Lagache, 1976) and (Berner, Scott and Jacques, 1980), for a given temperature range, most geochemical reactions such as hydrolysis and acid base reactions, etc., proceeds at a rate determined by the reaction kinetics of the system. In this light, the objective of the chapter is not to apply our parabolic advection dispersion reactive transport model, but rather to present the main concepts that underlie reactive transport from the a kinetic point of view. Yeh, (1989) applied the sequential iteration approach by dividing each time step into a reaction step and a transport step. During the reaction process, an equilibrium submodel is executed for each elementary representative volume (ERV). The results of the equilibrium submodel determines the solute mass in dissolved, precipitated, and sorbed form. Using this information, a transport step is then considered which the solute transport model physically transports the mobile phases of each solute. This process method neglects the coupling of transport and chemistry and as such the proceedure is itirated untill an acceptable level of convergence is attained

Chemical reactions and processes affecting water composition

From the surface, pollution begins its journey to water table, firstly by infiltration through the soil column (vadose) during which it is retarded due adsorption and degradation by organic components in the soil. When the seep arrives the water table, its response in the flowing groundwater can be predicted through a variety of transport processes, which include advection, molecular diffusion and hydrodynamic dispersion as already discussed. Coupled to the transport, the chemical alteration that take place between the reactive substances and the changing thermodynamics also plays a key role in describing the fate of reactive species. Some chemical constituents such as halogenated hydrocarbons tend to remain thermodynamically unstable with species such as CO_2 or CH_4. However, their degradation by natural attenuation can be a very slow process (tens to thousands of years) so that they tend to persist in groundwater.

Factors that affect water composition are controlled by the different solute and their sources, including gases, solution or precipitation reactions and rock interactions. Carbon dioxide is one of the most encountered chemical species in groundwater and its pure form is generally non-reactive. However in aqueous solution under given pressure and temperature conditions, it can react with water to produce carbonic acid. Carbonic acid intern dissociates to form $H+$ and carbonate ion which also dissociates into a proton $(H+)$ and carbonate$(-)$. In this example, the activity clearly depends on the concentration of hydrogen $(H+)$ ion, whose log activity is called pH. The activity of carbon dioxide in groundwater is dependent on the partial pressure of carbon dioxide in the system. In groundwater where partial pressure is higher, pH is generally low however the presence of calcite or other carbonate rich rocks in an aquifer system can buffer the pH by dissolution. This concept has been used to curb the health risks to human by preventing trace element mobility caused by droppingpH. The impact of chemicals on an aquifer's quality is complex. All reactions are coupled yet independent thus making it difficult to evaluates their combined effect.

Background

The ability to predict and describe the changing composition of natural groundwater with time and space typically requires reliable equations that describe the rates at which the different reaction systems proceed in aqueous solutions and solution compositions. While it is often easily possible to model the fate of a conservative (non-reacting pollutants) species, assuming the advection dispersion equation and homogeneity, modelling the outcome of reactive transport requires a bit more care. The accuracy of such an attempt doesn't not only require a thorough understanding of the resulting chemical hydrology, but also a robust appreciation of all the mechanistic (thermodynamics) processes underlying geochemical trends, not forgetting the complex computational requirements.

Geochemical reactions can be classified using two main class categories; Firstly, as a homogenous (one-phase) or heterogeneous (multiple phases) and secondly, they can be classified based on the rate of the forward reaction, i.e. fast or slow reactions. Knowledge of a system thermodynamics is used to describe the forward reaction direction as well as entropy and energy changes involved with the reaction. The forward reaction rate of a system is the resultant force between the driving force and the resistance against change. Fast reactions, also considered as local equilibrium reactions are thermodynamically reversible and the reactions rates are influenced by rate of transport of the reacting specie, often by means of molecular diffusion and advection. On the other hand, slow reactions are thermodynamically irreversible (can only proceed in one direction) and tend to depend on the area of the reacting surface. They are also called kinetic reactions.

Considering our hypothetical case of mixing two pollution point sources at given distance from the source, local kinetic equilibrium can be assumed since flow velocity is fast within the fracture, ensuring that at any meeting point, the resulting mixing will ensure the reaction rate proceeds fast. Coupling of the transport and a kinetic equilibrium model produces a set of algebraic and partial differential equations that can be solved using a computer. Yeh, (1989) applied the sequential iteration approach by dividing each time step into a reaction step and a transport step. During the reaction process, an equilibrium submodel is executed for each elementary representative volume (ERV). These results of the equilibrium submodel determines the solute mass in dissolved, precipitated, and sorbed form. This information allows for a transport step to be performed where the transport model phyiscally transports a mobile phasee of each solute present. This ititration process is generally repeated till an acceptable level of convergene is attained since coupling of transport and chemistry is not completed attained.

Key principles and methods

Given a closed systems, the kinetic relationships of the reactants with products can be easily derived. Most commonly encountered reactions are mono or bi-molecular. Monomolecular reactions involve internal change of a molecule while bimolecular involves the mass transfer processes between molecular species. By writing kinetic relationships as gradient equations, and applying the laws of mass action, one can actually model the fate if the system. The most simple example is an irreversible first order (monomolecular) decay or conversion reaction:

Simple kinetics

The simplest example is an irreversible first order (monomolecular) decay or conversion reaction:

$$A \xrightarrow{k} B$$

This mechanism results into a set of differential equations expressed as;

$$\frac{d[A]}{dt} = -K[A]$$

$$\frac{d[B]}{dt} = -K[B]$$

B is created out of the excess presence of A. Where K' is also called the pseudo order rate constant. I this case, the rate is considered to be independent of B and determined more by the concentration of A present.

$$\frac{d[B]}{dt} = -K[B] = K'$$

Given a second order reaction that is irreversible, representation can be as follows

$$2A \xrightarrow{k} B$$
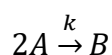
$$\frac{d[A]}{dt} = -2K[B]^2$$

$$\frac{d[B]}{dt} = K[A]^2$$

Subject to constant temperature and ph conditions, These differential equations are easily solved.

Complex kinetics

Considering a non-equilibrium system below;

$$A \rightleftharpoons B$$

Given K_1 and K_2.

The rate equation in differential form can be presented as

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

For a system of equations representing a set of reactive processes,

$$[A] = \frac{[A]_0}{k_1 + k_2}\left(k_2 + k_1 . exp^{-(k_1+k_2)t}\right)$$

$$[B] = \frac{[A]_0 k_1}{k_1 + k_2} \left(1 - exp^{-(k_1+k_2)t}\right)$$

After a time t, both forward and reverse reactions become equal. This can be written in the form of the equilibrium constant, $k_{d.equ}$.

$$k_{d.equ} = \frac{k_1}{k_1} = \frac{[B]}{[A]}$$

Calcite dissolution in groundwater can be modelled using the equilibrium constant relationship. Generally, the rate at which equilibrium is attained occurs faster than the rate of conversion of each specis to another. Figure 12 shows the
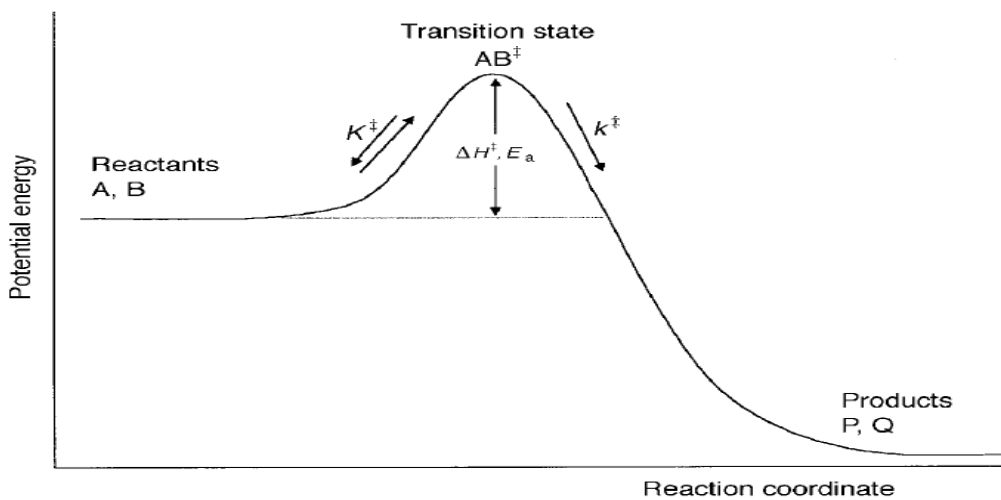

Figure 14: Potential energy variation curve during a chemical reaction (Adapted from Wagenigen 2015).

Discussion

The retardation factor will be used as the analytic parameter for the purpose of this discussion. The model approaches reactive transport by considering the possible case two spatially isolated source pollutants with a history of interaction, in space and time. Both sources, U1 and U2 pitch the groundwater horizon at 1000g/l along high velocity preferential trajectories, followed by an exponential decay in concentrations due to retardation. A third pick, captures the process linked to new mass contribution from U1 as a result mixing caused by aquifer heterogeneity. The new contributing quantity peaks at and quickly decays from 60 concentration units to 0 units. The model was also tested for a higher retardation coefficient value and the obtained results show a positive correlation with trends expected from kinetic modelling. Using a higher retardation factor can attenuate the transport process as shown by the last 8 set of images. This was a case of mixing at concentrations higher than described above, such that the new contributing quantity now peaks at 250 concentration units as opposed to 60.   After reacting, the resulting system continuous in a state of reactive transport, whose faith is entirely captured by the model. Unlike the routine approach of modelling by lumping reactive process into one parameter, this model does not only provides a tool for simulating the fate of reactive species in groundwater but also provides useful insight into the mass balance relationships associated with each participating species.
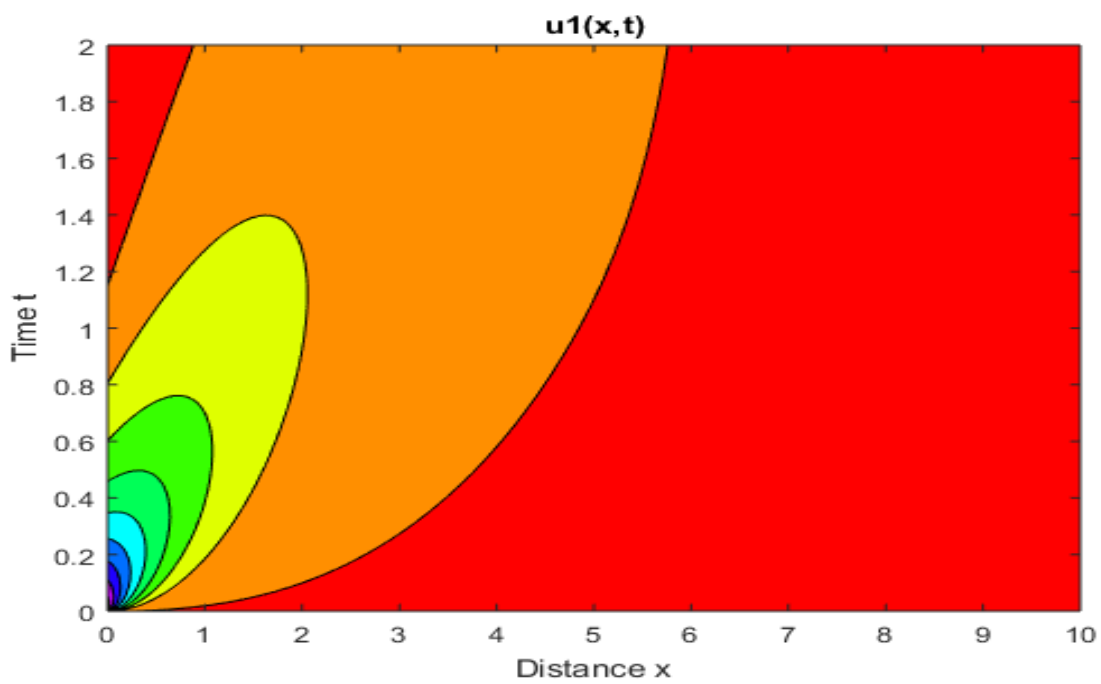
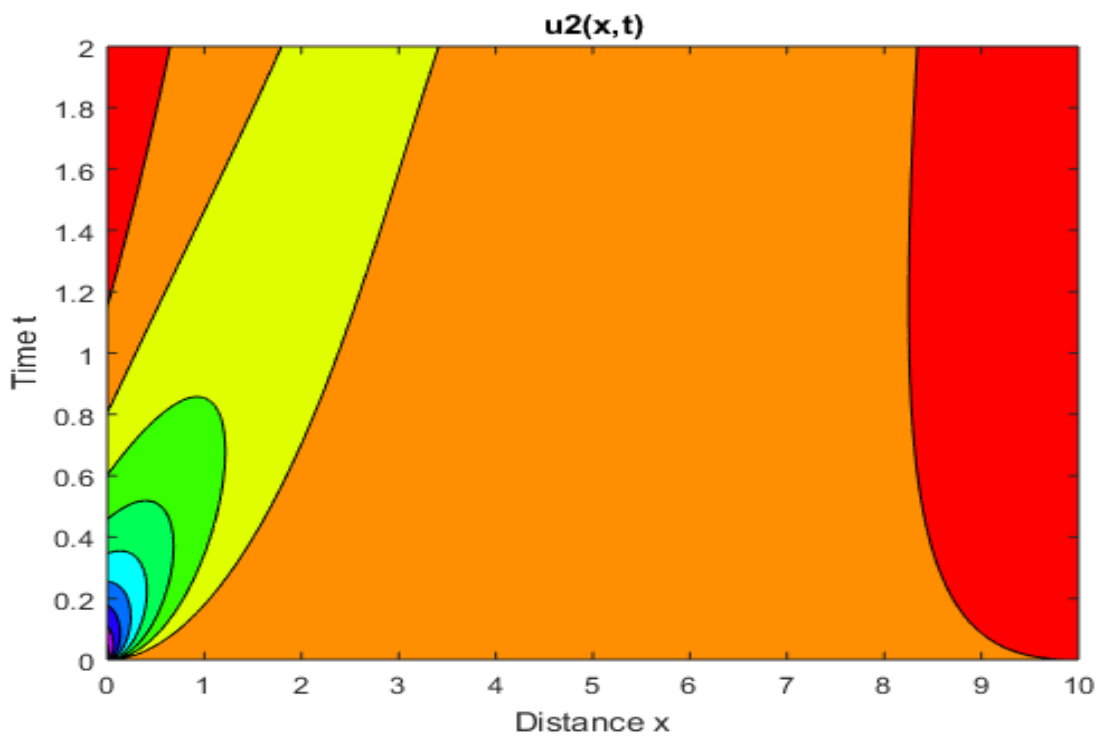**Figure 15:** Section showing pollutant migration from source (U-1) along the x-direction with respect to time

Figure 16: Section showing pollutant migration from source (U-2) along the x-axis with respect to time
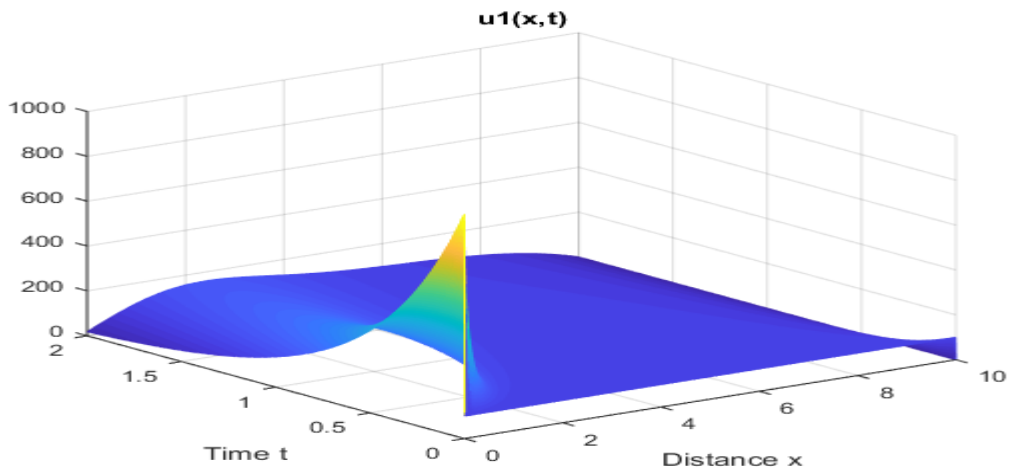
Figure 17: Surface showing U-1 concentration distribution along X-direction in [0,2] and t in [0,2], C(0,t) = C1exp(-t) = 1000exp(-t) C(x,0) = C0
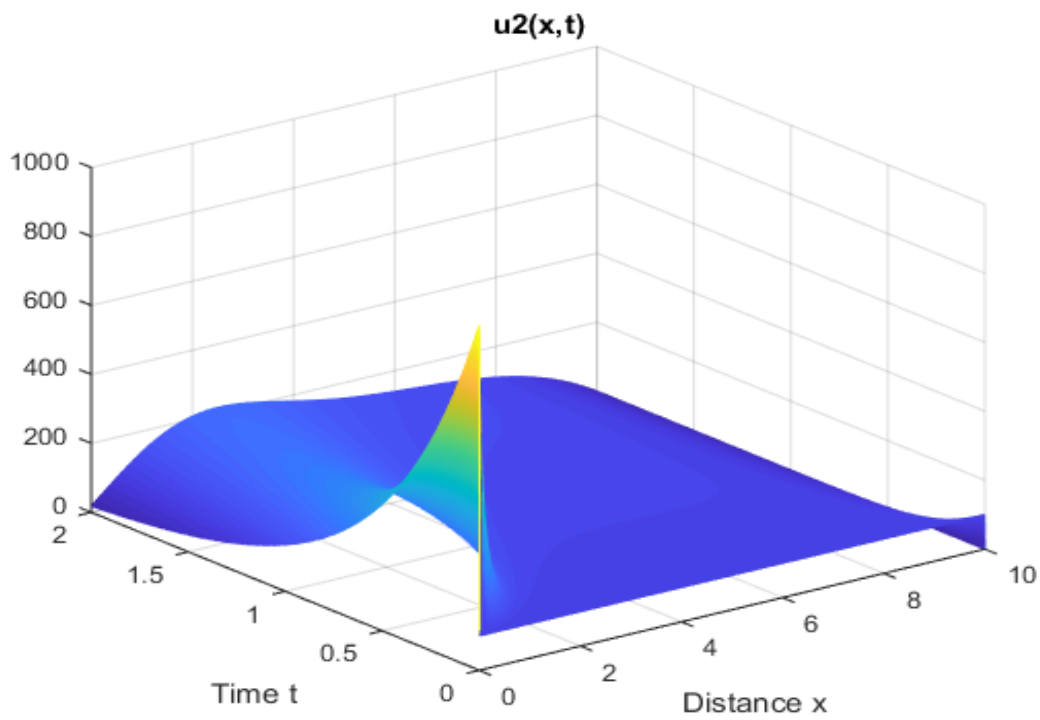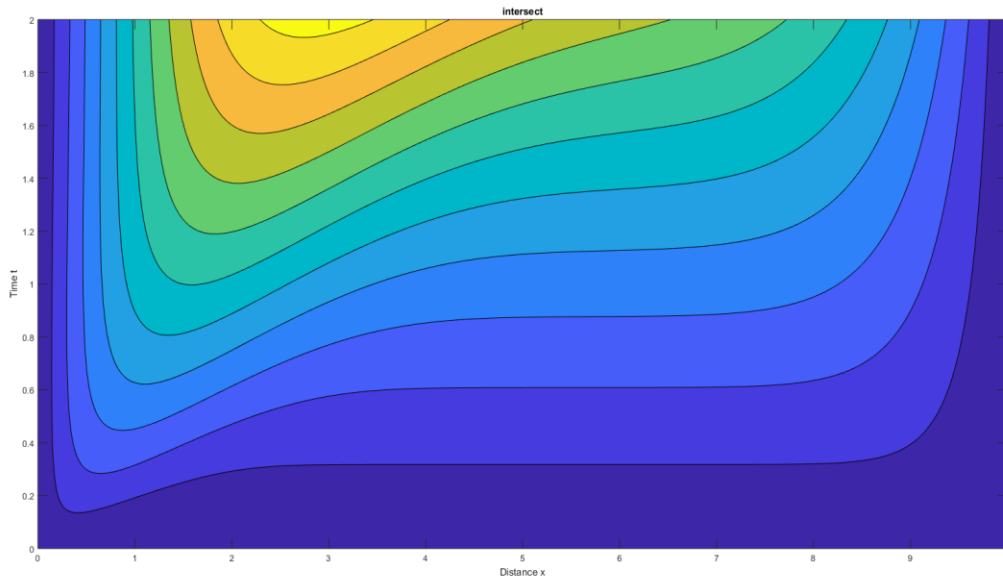

Figure 18: Surface showing U-2 concentration distribution along X-direction in [0,2] and t in [0,2], C(0,t) = C1exp(-t) = 1000exp(-t) C(x,0) = C0

Figure 19: Contour plot showing pollution spread along reactive fronts after mixing of the two sources (low retardation factor)
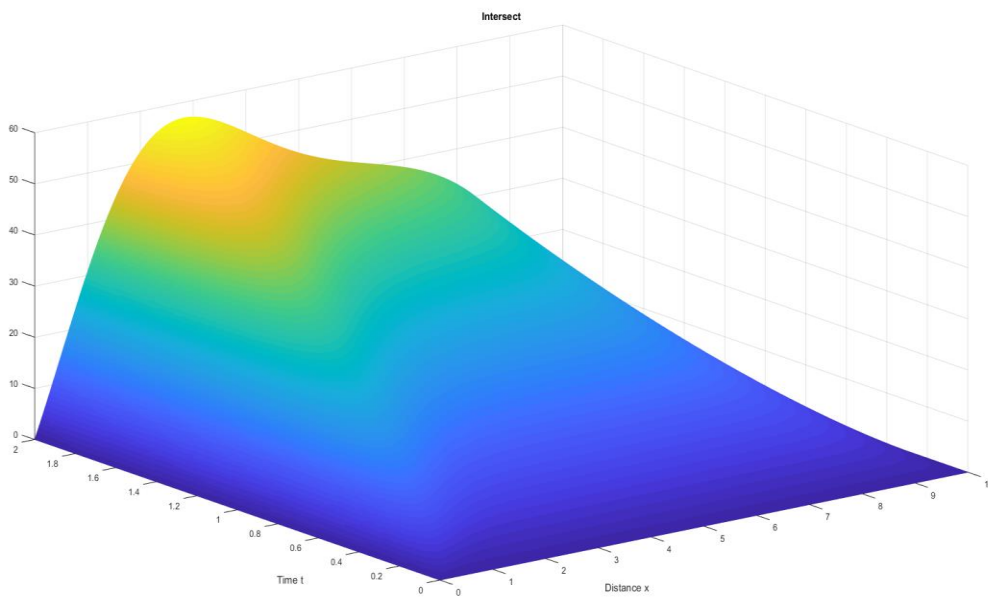

Figure 20: Surface showing concentration distribution for x in [0, 2] and t [0, 2], c (0, t) after mixing of two sources with low retardation factor.
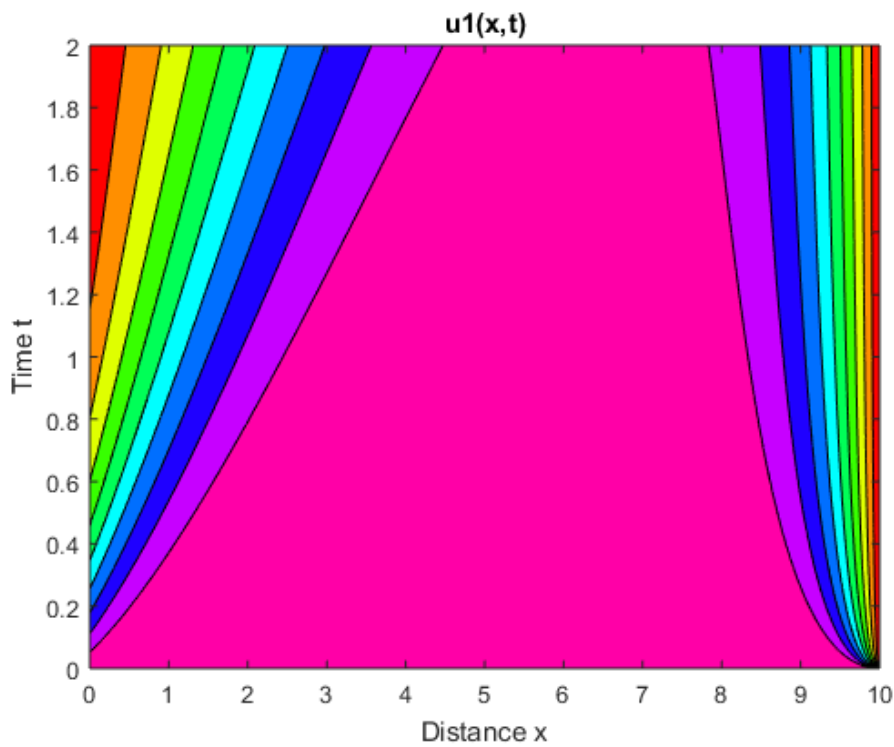
Figure 21: Contour map showing the transport of pollution from source, U-1 along a preferential
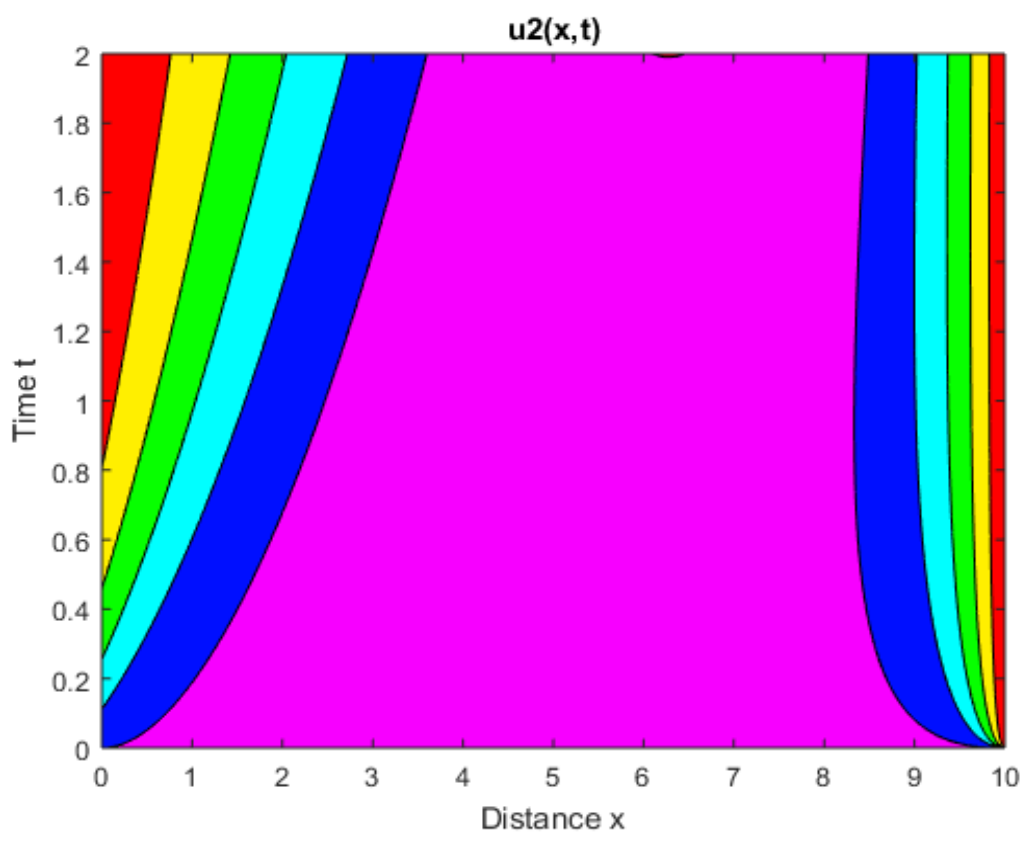

Figure 22: Contour map showing the transport of pollution from source, U-1 along a preferential path (low retardation factor)
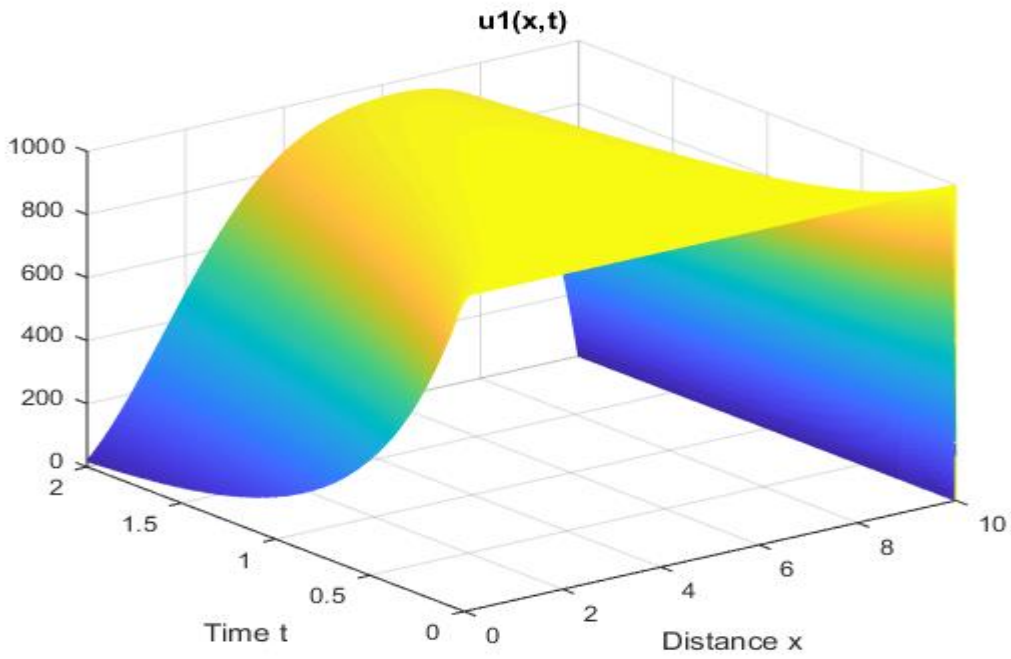
Figure 23: Surface showing U-1 concentration distribution along X-direction in [0,2] and t in [0,2], C(0,t) = C1exp(-t) = 1000exp(-t) C(x,0) = C0 (high retardation factor)
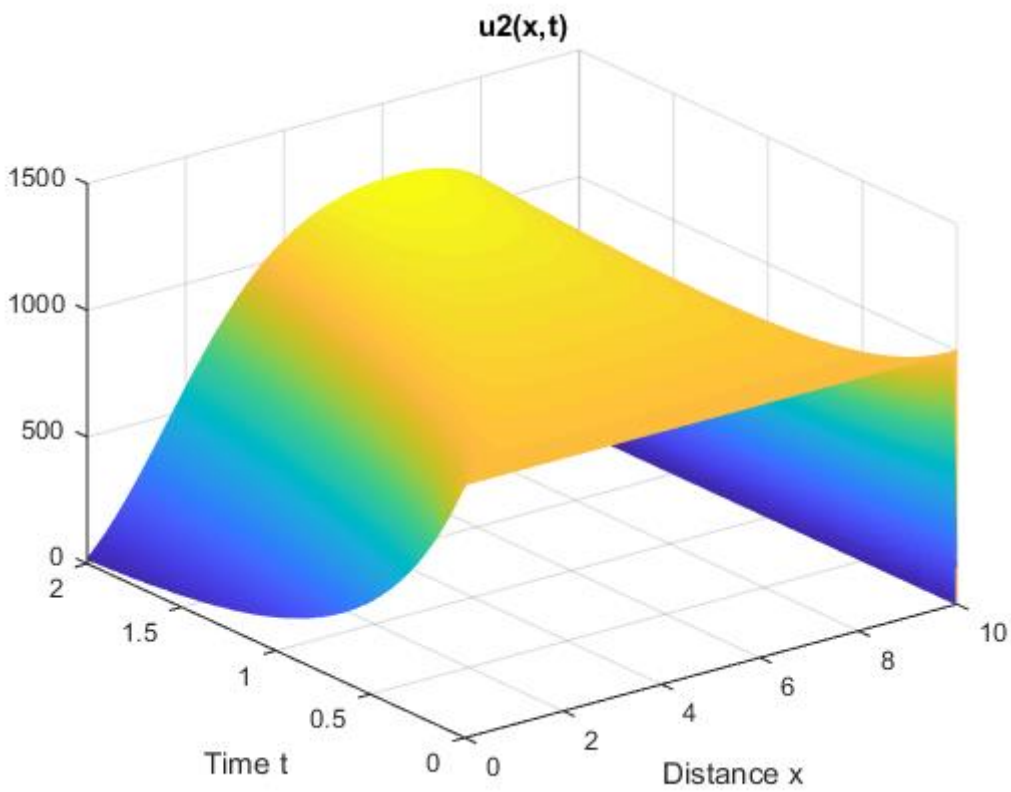

Figure 24: Surface showing U-2 concentration distribution along X-direction in [0,2] and t in [0,2], C(0,t) = C1exp(-t) = 1000exp(-t) C(x,0) = C0 (high retardation factor)
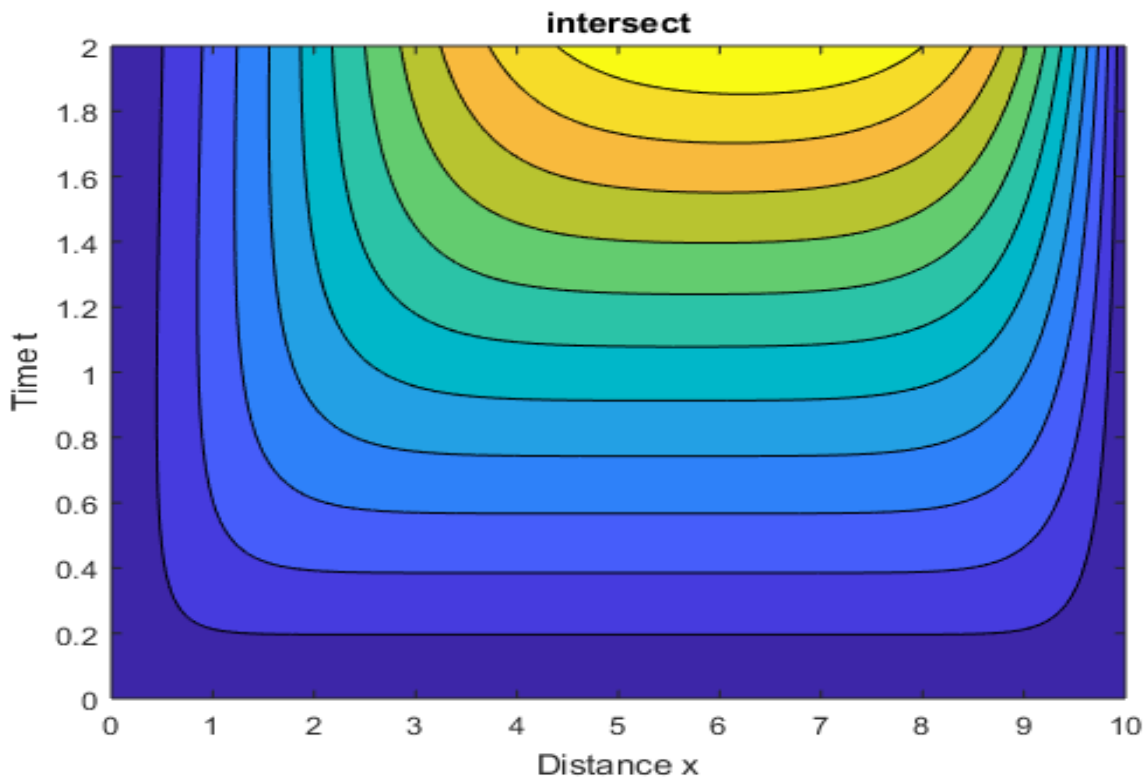
Figure 25: Contour plot showing pollution spread along reactive fronts after mixing of the two sources. (The case of a high retardation coefficient)
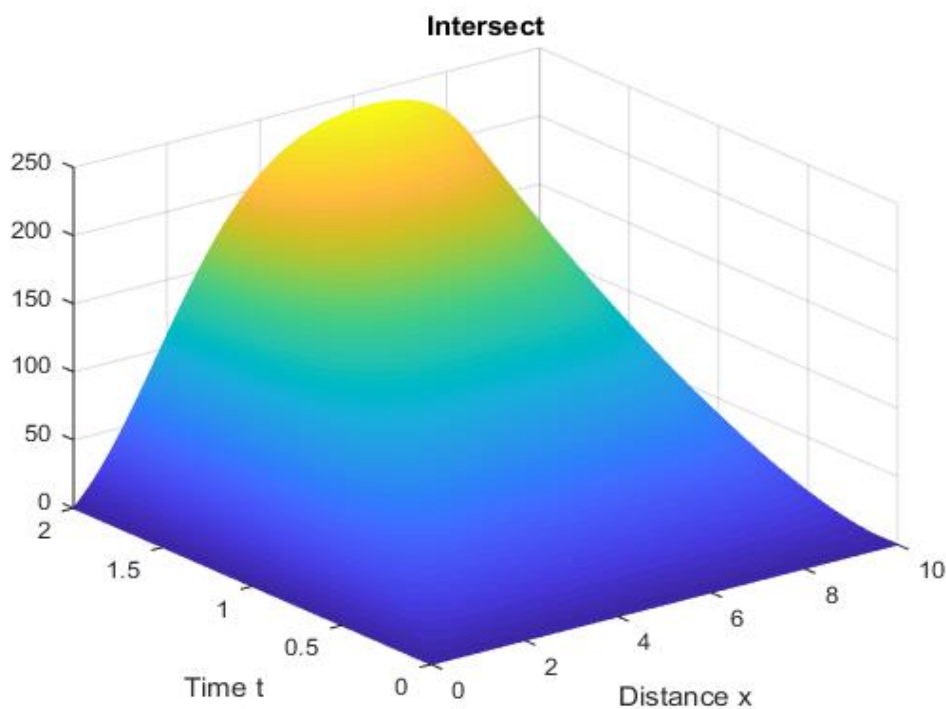

Figure 26: Surface plot showing concentration distribution after the mixing of U1 and U2 under the influence of a low retardation coefficient.
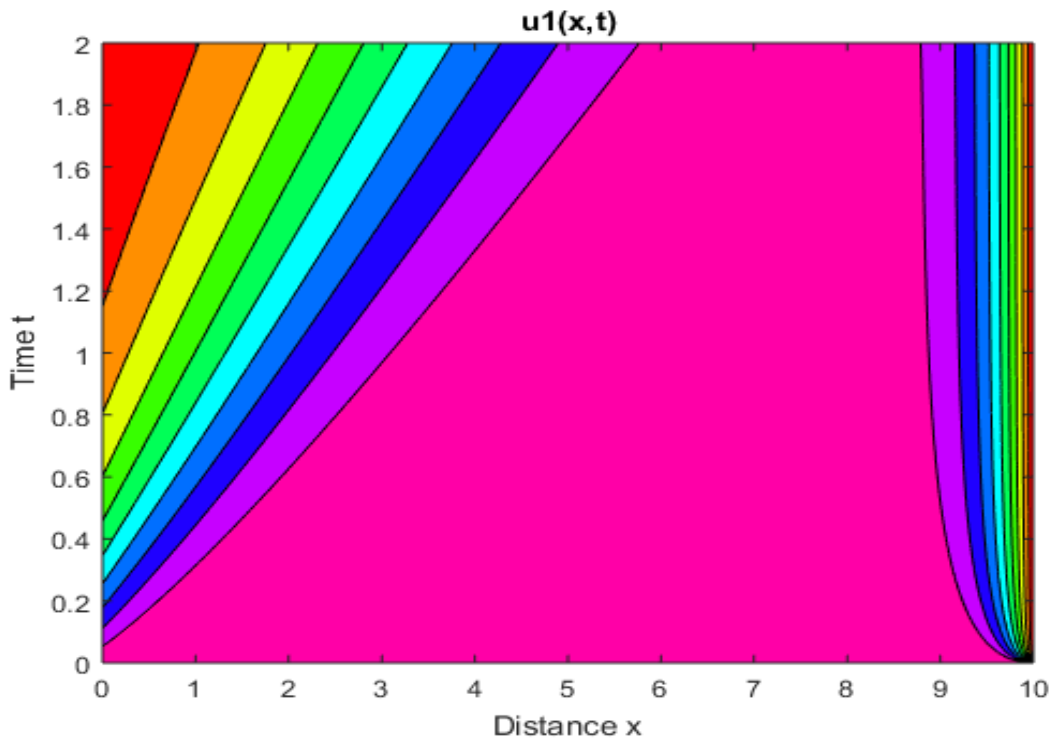
Figure 27: Contour plot showing U-1 source pollution migration along a preferential flow path influence by a low retardation factor.
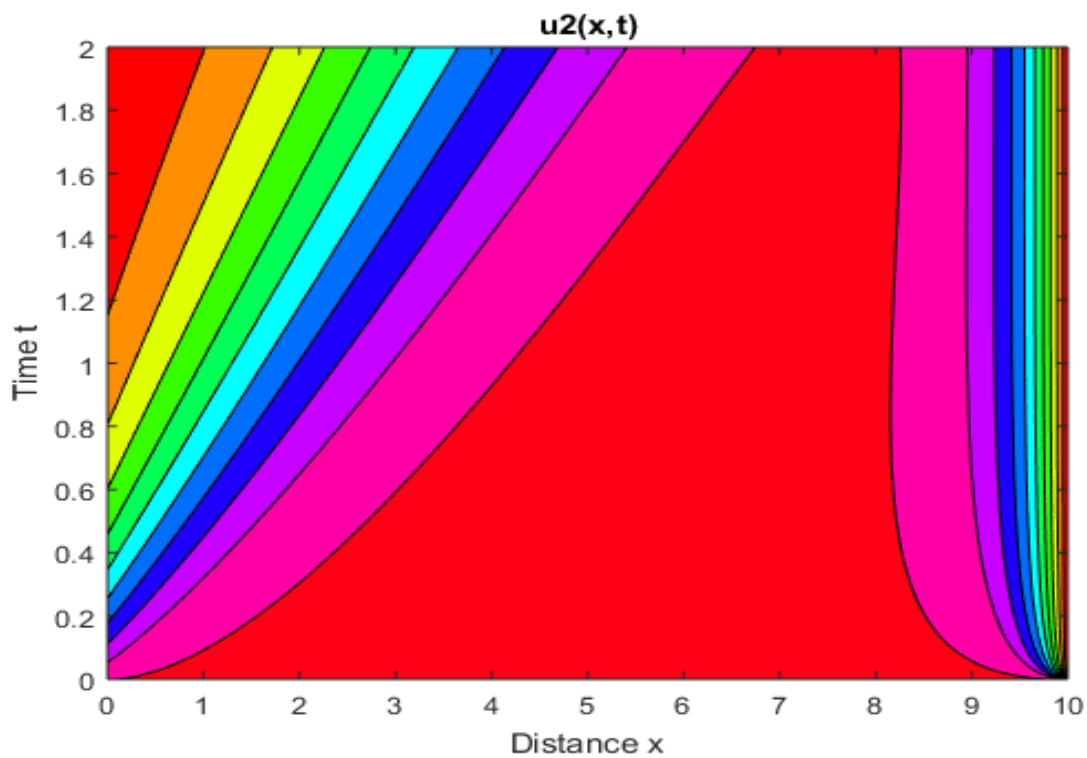
Figure 28: Contour plot showing U-2 source pollution migration along a preferential flow path influence by a low retardation factor.
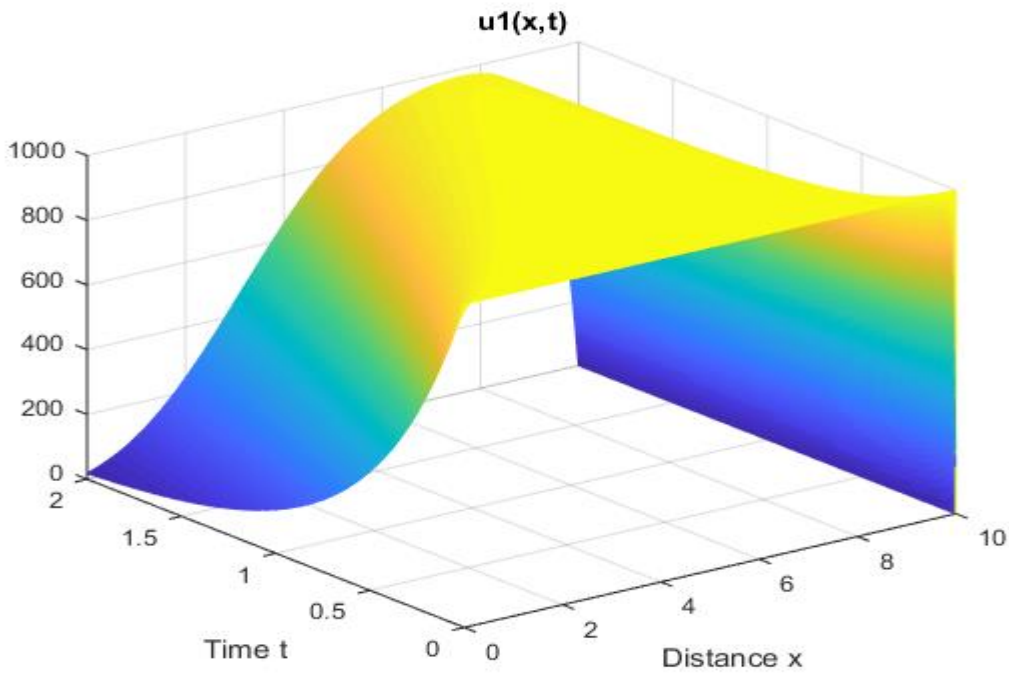
Figure 29: Surface showing U-1 concentration distribution along X-direction in [0,2] and t in [0,2], C(0,t) = C1exp(-t) = 1000exp(-t) C(x,0) = C0. (Very high retardation factor)

Figure 30: Surface showing U-2 concentration distribution along X-direction in [0,2] and t in [0,2], C(0,t) = C1exp(-t) = 1000exp(-t) C(x,0) = C0. (Very high retardation factor)

Figure 31: Contour plot showing pollution spread after intersection. (High retardation factor)

Figure 32: Surface showing the distribution of pollution after mixing. (Low retardation factor)

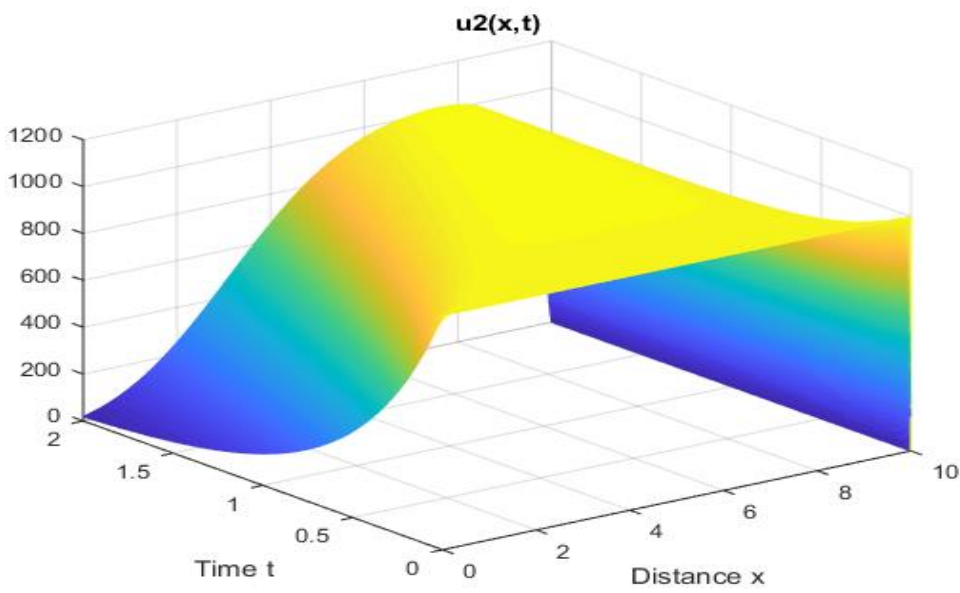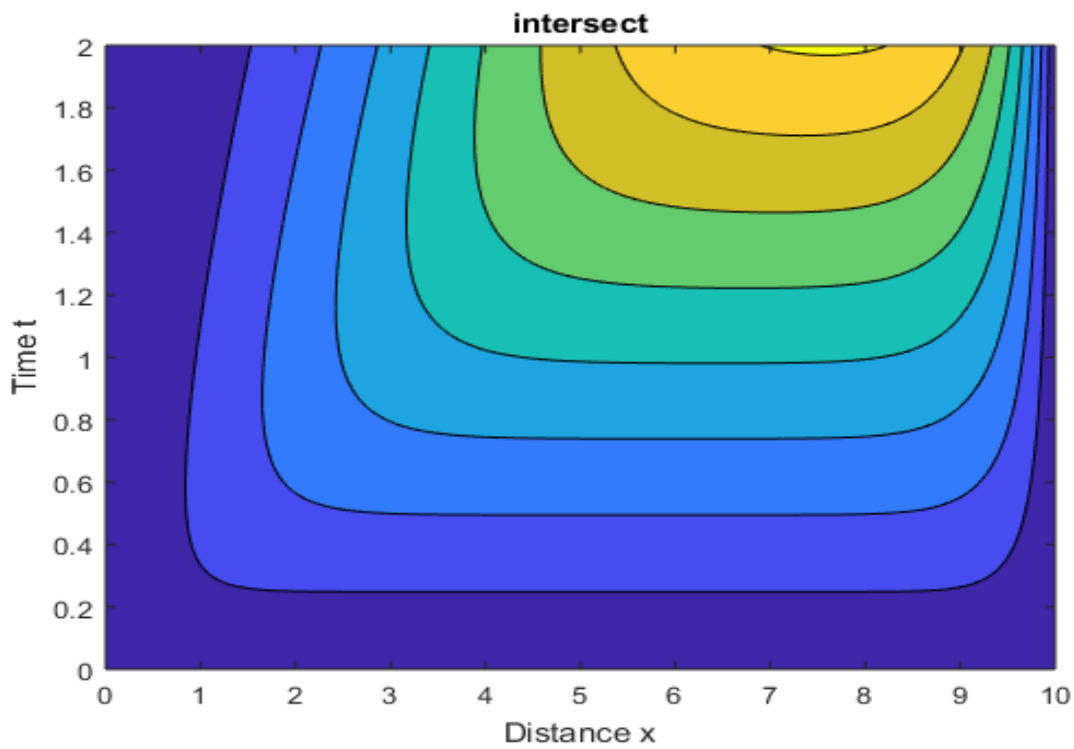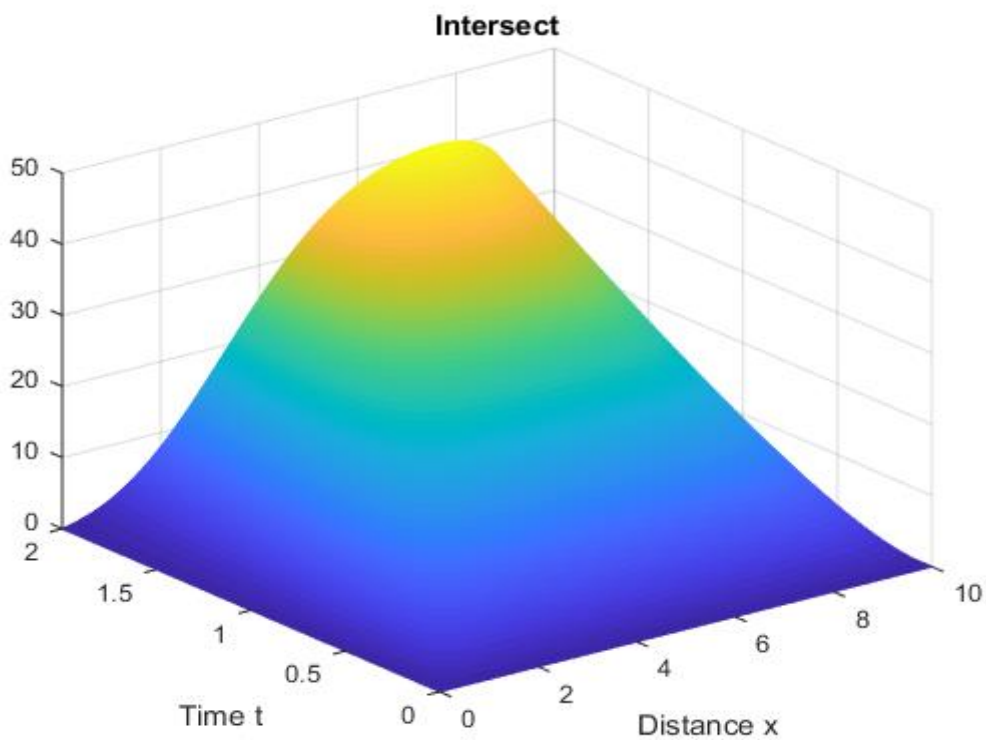# Conclusion

Fractured aquifers have the potential to deliver large quantities of fresh water to boreholes intersecting the fracture networks, even though they remain the most vunerable to an increasing chemical pollution thread. The basis of this thesis was to describe and to model the fate of reactive pollutants in fracture dominated groundwater transport. The hypothetical scenario in question involved the intersection of two fractures from a regional fault system, which can form due to structural deformation of the lithosphere, caused by changing regional stress fields over geoligic time. Each fracture represents a travel pathway transporting pollution through the subsurface.

The movement of water in fractures is predominantly controlled by advection, and dispersion to a lesser extend. Routinely, the transport and transformation of reactive contaminants in groundwater has been decribed using the classical advection dipersion model with the addditon of a reaction term (sink) to captures the nature of the chemial process taking place. In reactive transport research, most studies have focused on modelling classical chemcial proccesses involving mass tranfer (adsorbtion, precipitaion, molecular diffusion etc.) between different states of matter, from fracture to sorrounding rock matrix and vice-versa. In geological systems, these processses can continue for thousands and even millions of years, providing a valid bases to assume kinetic equilibrium. However, in fractured systems, homogeneity is a rare occurrence and the closest analog would be the case of a self similar fractured systesm for which the stocastic approach can best suit.

Two point sources are monitored for a process of contaminant transport by coupling of the linear homogenous and the linear non-homogenous source solutions. The exact solution of the linear system is obtained by using Laplace transform and the Green function method.

A Finite Element Method (FEM) numerical analysis was perfomred for both the homogenous and the non-homogenous models using the Crank Nicolson discritized scheme which is unconditionally stable. The stability of resultant descritized scheme is obtained using the exegration factor (G) method and the system is said to be stable for the above approximation method, given a set of initial conditions. Using the software Matlab numerical simulation were performed using different aquifer parameters. Numerical simulation an intersection with high concentration,when the velocity of water is high within the fractures and also when the decay rate is high. However,with low velocity and low decay rate one will expect less concentration at the   intersection   point

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