A MATHEMATICAL MODEL FOR DETERMINING DIFFUSION OF NITRATE CONTAMINANT IN UNDERGROUND WATER

BY

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Declaration

Declaration by the candidate

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Dedication

To my wife Honorine Murorunkwere, my sons Yan Bethel Ninkuru, Jan Caleb Ninziza and Evan Lahairoi Hezagira, my late father, my mother, my brothers and sisters and in-laws, my uncles and aunts

You have always offered me good pieces of advice .

Your love and support have been there for my rescue all the way in my life.

I hereby offer my gratitude to you.

Abstract

All living things, including human beings, need water to survive and to flourish. Unfortunately, many people in the world don't have access to clean and safe water. Groundwater is a valuable source of drinking water in many societies through wells. However, throughout the world, aquifers are being contaminated by chemicals from many sources. The diffusion process of nitrate highly contaminates underground water and there is no known mathematical model to evaluate it's effect. This study formulated a mathematical model for determining diffusion of nitrate contaminant in underground water. The mathematical model was used to determine the concentration of nitrate as an agricultural chemical contaminant in the ground at a given time and point using the definition of the model given by Velten. The analytical and numerical solutions of the diffusion equation characterizing the flow of chemicals in the ground were used to determine the concentration of nitrate. The numerical solutions of the model were implemented using MATLAB software and the analytical solutions were found using Fourier transform method. The results of the model were validated using the data of concentration of nitrate chemicals in water collected from eleven wells and tested using UV-Vis analysis. The tested water samples were collected from the wells around Moi University main Campus in Kesses Sub County. From the model formulated, one can easily predict the concentration of nitrate at given time and point in the soil using the diffusion equation and its solutions. The analytical solution of the model equation proved that nitrate contaminant is normally distributed. The numerical simulation with MATLAB showed that the concentration keeps reducing at the disposal area as it spreads in all directions unless the source of contamination is permanent. In this case, the concentration will always remain high at the disposal point. The laboratory analysis to check for the concentration levels of Nitrate showed that some of the samples were polluted by nitrate since the results were between $6.71 mg/l$ and $55.95 mg/l$. This is because the maximum allowed concentration level of nitrate is $10 mg/l$. The findings of this research can be used to advise farmers to build their wells at least a distance of $100 m$ from the source of contamination. These findings can also be used by policy makers and chemical manufacturers to inform and advise the population on the side effect of the chemicals. The formulated model is also applicable to underground water flow and its contamination as well as other mathematical modeling.

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Last but not least, I thank my Lord and Savior Jesus Christ who has been the source of my strength and inspiration through out my life.

List of Acronyms and Abbreviations

BC: Before Christ

CAS: Chemical Abstracts Service

CREAMS: Chemicals, Runoff and Erosion from Agriculture Management Systems

DDT: Dichlorodiphenyltrichloroethane

FT: Fourier Transform

IC: Initial Conditions

IUPAC: International Union of Pure and Applied Chemistry

IVP: Initial-Value Problem

LMP: Last Menstruation Period

MCL: Maximum Concentration Level

NAWQA: National Water Quality Assessment

NOC: N-nitroso Compounds

ODE: Ordinary Differential Equation

RMS: Root Mean Squared

USA: United States of America

USGS: United States Geological Survey

UV-Vis: Ultraviolet-Visible Spectrophotometry

Chapter 1

Introduction

1.1 Background information

The sources and causes of groundwater contamination are so many, and are as diverse as human activities as depicted in (Figure:1.1). As the number of potential contamination sources is growing, attempts to classify them have also been increasing. Scientists and organisations in the field of groundwater contamination have often followed their own categorization of sources of ground water contamination. A large number of classification of sources of contamination methods have been developed and subclassifications have also been prepared as discussed by (Harvey & Linquiti, 1989). Through these activities, chemicals and other disposed wastes may come in contact with groundwater making it contaminated. The majority of sources of groundwater contamination are from human activities, but contamination may also have a natural origin such as animal and plant decomposition. Groundwater composition is not the same everywhere, indeed groundwater vary in chemical composition, some contains elements that can be considered as nutritive or substances essential to human, animal and plants life and others contain natural substances that can be harmful to human health and the ecosystem.

Agriculture is one of the human activities that contribute to groundwater contamination. The use of fertilizers and pesticides, the storage and disposal of manure, stockpiling of materials, and a large number of other activities carry the risk that underground water may be contaminated. Although the activities are carried out at the land surface, infiltrating rain water, water used in irrigation and spray take contaminants down to the groundwater. Particularly, the diffusion of applied fertilizers, pesticides, and manure in farms contribute to serious contamination of large parts of water system (Zaporozec et al., 2002).

Fertilizers and other products used in agriculture are applied on the surface of the soil, from then, diffusion and other processes start spreading chemical constituents in the surrounding area. As the contaminants from these fertilizers and other products are spread in all directions, some of them move downwards to underground water which make it contaminated. As many people especially in developing countries are not able to treat water that they are using in their homes, the contaminant which is in the bore hole water find their way to the human body.

Using the equations governing the movement of water in underground such as diffusion equation, scientists have formulated mathematical models which can be used to predict the quantity of contaminant which can be found in ground water taking into consideration some variables such as: where the disposal area is located from the bore hole, properties of the soil and time between the disposal time and the water collection time.

A contaminant diffusing in the soil from the disposal area reaches underground water after some time and contaminate it. As the diffusion is a continuous process, the concentration of the contaminant varies; with high concentration at the source and low concentration at a distance from the source. If the source of contaminant is permanent, the concentration of the contaminant eventually affect a larger area before reaching a steady state. In this study, Mathematical determination of groundwater contamination due to agricultural activities, was done using mathematical equations developed in Sections 1.2 of this study.

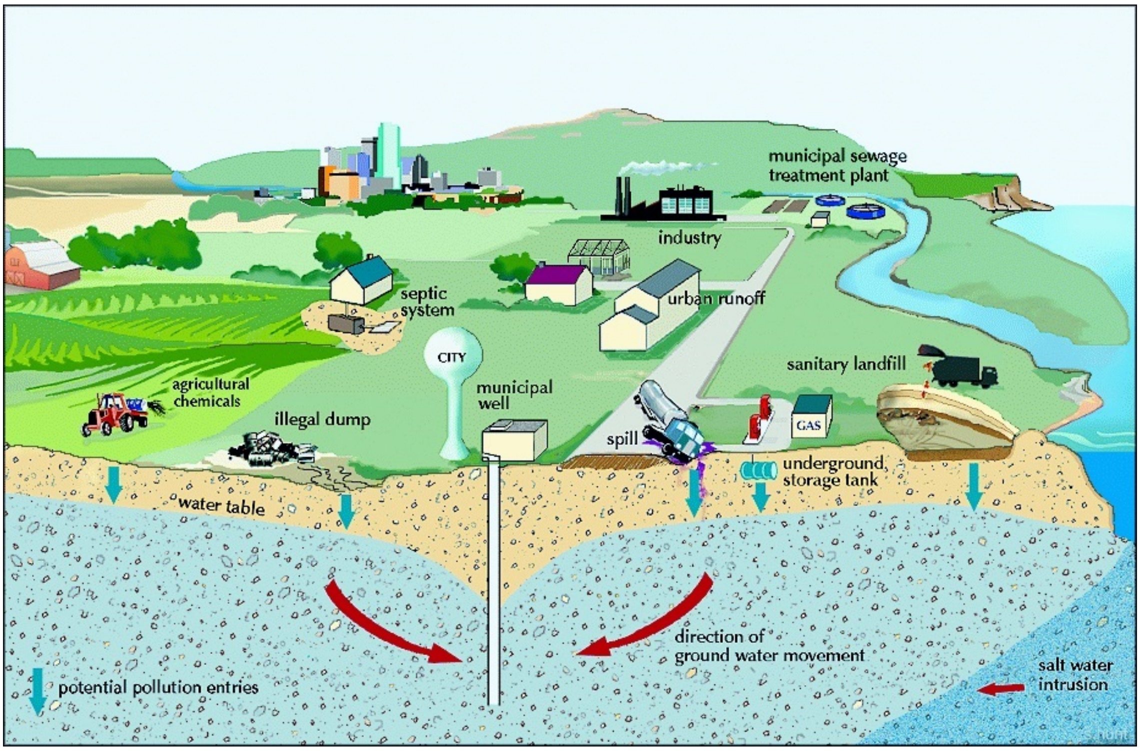

Figure 1.1. Illustration of water contamination

Source: (Zaporozec et al., 2002)

1.2 Diffusion

The diffusion equation can be derived using the definitions of concentration, flux, mass balance, control budget and Fick's law as found in the work by (Cushman-Roisin, 2012). The diffusion equation can also be derived using other methods such as the ones used in the book by (Crank, 1975). The diffusion equation may have source or decay, in such a case, the diffusion equation is said to be with reactions but if not, then it is without reactions.

1.2.1 Governing equations

The diffusion equation with reactions in one dimensional space is given by the equation (1.1)

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) - Kc + s \tag{1.1}$$

where,

c represent the concentration of a contaminant as a function of time and space. The variables x and t are respectively spatial and temporal variables;

D is the diffusion coefficient which may vary with the local turbulence intensity but, for simplicity, consider the case where D is a constant. In that case, the equation (1.1) becomes

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - Kc + s \tag{1.2}$$

and its analytical solution can be found.

K indicates the rate at which a targeted chemical is decaying and s represent the source.

The equation (1.1) reduces to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1.3}$$

when there is no source and decay.

1.3 Statement of the problem

Agrochemicals are among the most commonly reported contaminants and their presence in underground water is a very serious problem to human life as discussed by (Pavlis, Cummins, & McDonnell, 2010). Agrochemicals can contaminate underground water by diffusion (Zaporozec et al., 2002). Nitrate contaminant is one of the reported harmful chemicals, but there is no known mathematical model which have been developed to simulate underground water contamination by diffusing nitrate. The mathematical model developed determines the concentration of a diffusing chemical at any given time and point to avoid the construction of wells in a contaminated zone.

1.4 Objectives of the study

1.4.1 Main Objective

The main objective of this study was to develop and analyze a mathematical model for determining the concentration of nitrate as a component of agricultural chemical contaminants in underground water at a given time and point.

1.4.2 Specific Objectives

The specific objectives of the study were to:

(i) Formulate the model characterizing the flow of nitrate in the soil.

(ii) Apply the analytical solution of the mathematical model to describe the concentration of the chemical at given time and point.

(iii) Simulate the numerical solution of the mathematical model to show concentration profile in the study area.

(iv) Validate the model results by testing the concentration of chemicals in wells and comparing with numerical simulation results.

1.5 Justification

As it has been proved that many diseases are caused by agrochemicals, this study advised agrochemicals manufacturers to reduce the contamination of their products on human beings and environment. Since Kesses Sub County has a lot of agricultural activities and the locals use underground water for consumption and irrigation it was, therefore, prudent to check on the levels of contamination of underground water.

This work provided farmers with knowledge and tools to enable them to minimize the risk of underground water contamination. A mathematical model understandable by non-specialized scientific community such as farmers and other potential users has been provided as a tool to be used in determining the level of contamination of their wells resulting from use of chemicals on land.

On the other hand, policy makers are advised to make sure that all agrochemicals manufacturers are taking into consideration the adverse effects of their products on human beings and environment. Policy makers are, therefore, asked to provide knowledge and tools, to help farmers and the whole population to remain safe from agrochemicals contamination.

Chapter 2

Literature Review

2.1 Mathematical Modeling of the effects of agro-chemicals

2.1.1 Location and contamination of water

The hydrological cycle describes the continuous movement of water above, on, and below the surface of the Earth. The water on the Earth's surface (surface water) occurs as streams, lakes, and wetlands, as well as bays and oceans. Surface water also includes the solid forms of water (snow and ice). The water below the surface of the Earth primarily is ground water, but it also includes soil water. The interaction of ground water and surface water has been shown to be a significant concern in many of the issues related to water supply, water quality, and degradation of aquatic environments. For example, contaminated aquifers that discharge to streams can result in long-term contamination of surface water; conversely, streams can be a major source of contamination to aquifers. Surface water is commonly hydraulically connected to ground water, but the interactions are difficult to observe and measure and , therefore, have been ignored in water-management considerations and policies (Theis, 1935).

Human beings need ample clean water to quench their thirst, irrigate agricultural fields, and sustain all life forms in the environment. Clean water must be in our homes, communities, businesses, industries, and in nature. People need clean water today and will need it tomorrow. Humans rely on clean water in almost every aspect of their lives. This they do through drinking, bathing, cooking, swimming, fishing, and boating. Unfortunately, there is no guarantee that clean water, relied on so heavily, will always be available. The supply of clean water on the earth is limited, and it is being threatened by water pollution (Vigil, 2003).

The looming water crisis is becoming a major issue on the world agenda in the twenty-first century. The World Water Council presented the world water vision during the Second World water forum and ministerial Conference at The Hague in March 2000 (Cosgrove & Rijsberman, 2014). The Vision reported that 1.2 billion people or one fifth of the world population do not have access to safe drinking water, while half of the world population lack adequate sanitation. The Vision document further states that rapidly growing cities, burgeoning industries, and rapid rise in the use of chemicals in agriculture have undermined the quality of many rivers, lakes, and aquifers. It also emphasizes that the impacts of agriculture on water quality are less visible over time but at least as dangerous (as industrial), because many of the fertilizers, pesticides, and herbicides used to improve agricultural productivity slowly accumulate in groundwater aquifers and natural ecosystems (Zaporozec et al., 2002).

2.1.2 Effects of nitrate encountered in water

Contamination of drinking water by nitrate is a growing problem in many agricultural areas. Ingested nitrate can lead to the endogenous formation of N-nitroso compounds (NOC), which are potent animal carcinogens. Population-based case-control studies in Iowa and Nebraska evaluated community-supplied drinking water nitrate levels and cancers of the stomach, esophagus, bladder, brain, colon, rectum, pancreas, and kidney. Increased risks of colon, kidney, and stomach cancer were observed among those with higher ingestion of water nitrate and higher meat intake compared with low intakes of both. So far, the study found that women with higher average nitrate levels in public water supplies had increased risks of thyroid, ovarian, and bladder cancers. The population using private wells have considerably higher exposure to nitrate because private wells are not regulated and they are often located in agricultural areas. Using a geographical information system-based model that incorporates land use, soil characteristics, nitrogen inputs, and other factors, private well nitrate levels for the Agricultural Health Study cohort estimated and evaluated cancer risk among the applicators and their spouses. (Ward, 2015)

The problem of nitrate arises also from two medical conditions that have been linked to nitrate: *methaemoglobinaemia* (blue-baby syndrome) in infants, and *stomach cancer* in adults. Both are serious conditions and so there is a need of examining possible links carefully. However, it must be noted that these conditions are not caused by nitrate but by the nitrite which can be reduced. Nitrate itself is harmless and is most notable from a medical standpoint as a treatment for phosphatic kidney stones (Hester & Harrison, 1996).

Methaemoglobinaemia: The blue-baby syndrome can occur when an infant less than about one year old ingests too much nitrate. Microbes in the stomach convert the nitrate to nitrite and when this reaches the blood-stream it reacts with the haemoglobin, the molecule that transports oxygen around the body. Normal oxyhaemoglobin, which contains iron in the iron(II) state, becomes methaemoglobin in which the iron is in the iron(III) state and hence greatly lessen the capacity of the blood to carry oxygen which causes what might be described as chemical suffocation. Very young children are susceptible because foetal haemoglobin, which has a greater affinity for nitrite than normal haemoglobin, persists in the blood-stream for a while, and because their stomachs are not sufficiently acidic to inhibit the microbes that convert nitrate to nitrite.

Stomach Cancer: Of all the cancers, that of the stomach causes the second largest number of deaths. Only lung cancer kills more men, and only breast cancer kills more women. Stomach cancer is a painful and debilitating way to die, and the link to nitrate in water that has been suggested is a serious matter. There are good theoretical reasons for proposing such a link. Nitrite produced from nitrate could react in the stomach with a secondary amine coming from the breakdown of meat or other protein to produce an N-nitroso compound.

2.1.3 Use of Chemicals in Agriculture

Agricultural production relies heavily on manmade chemicals used as fertilizers and pesticides to regulate plant growth. Pesticides, herbicides and insecticides are released intentionally into the environment to control insects, weeds, plant diseases and other pests that affect crop or animal production, as well as to control insects that spread human diseases. Pesticides have a well-established role in agriculture and public health. The benefits of their use in terms of economic returns and of improved human health and well-being have led to the rapid world-wide adoption of this chemical technology. However, their use in advanced countries is often regulated and monitored because of potential problems associated with their injudicious use. Unfortunately, many developing countries lack the experience and expertise necessary to solve such problems (Plimmer, 1984).

The growing concerns about chemical use on farms have raised significant policy questions in USA at the national and state levels about the external costs associated with farming and the sustainability of agriculture. From an agricultural policy perspective, these concerns are difficult to balance against the economic needs of agriculture. Leaders of the farm community, the environmental community, and policymakers are exploring new ways of balancing the needs of farmers with those of the non-farm public. This balance is obviously a delicate one due to the economic, social, environmental, and political dimensions of the agricultural chemical issue (Adelaja, Sullivan, Hailu, Govindasamy, et al., 2010).

More generally, in terms of net input composition changes, lowering risk from pesticide use involves more materials and less land use, greater capital and labor intensity (perhaps though additional monitoring, or more careful application), and a potential shift from crop to animal commodity production. The costs incurred by agricultural producers to make such adjustments have increased over time, vary widely by region, and is higher in case of leaching as compared to runoff (Morrison Paul, Ball, Felthoven, Nehring, et al., 2000).

2.1.4 Evolution of the use of Agrochemicals

Agriculture must provide food supplies if population growth is to be sustained; conversely population growth requires changes in the way agriculture is carried on, prompting the expansion of the area under cultivation and intensive use of land already in cultivation (Grigg, 1987). The historical background of pesticides use in agriculture is dated back to the beginning of agriculture itself and it became more pronounced with time due to increased pest population paralleled with decreasing soil fertility. However, the use of modern pesticides in agriculture and public health is dated back to the 19^{th} century. The first generation of pesticides involved the use of highly toxic compounds, arsenic (calcium arsenate and lead arsenate) and a fumigant hydrogen cyanide in 1860's for the control of such pests like fungi, insects and bacteria. Other compounds included Bordeaux mixture (copper sulphate, lime and water) and sulphur. Their use was abandoned because of their toxicity and ineffectiveness. The second generation involved the use of synthetic organic compounds. The first important synthetic organic pesticide was dichlorodiphenyltrichloroethane (DDT) first synthesized by a German scientist Ziedler in 1873 and its insecticidal effect discovered by a Swiss chemist Paul M$\ddot{u}$ller in 1939. In its early days DDT was hailed as a miracle because of its broad-spectrum activity, persistence, insolubility, inexpensive and ease to apply (Zacharia, 2011). But, its sides effects were later discovered and DDT is now prohibited.

Since the 1940s, pesticide use has expanded because of the development of the synthetic organic compounds. The synthetic organic pesticides (i.e., man-made, carbon-containing chemicals) include the chemical groups; chlorinated hydrocarbons, organophosphates, carbamates, pyrethroids, phenoxy herbicides and a number of other chemical classes. Groups with similar chemical structure tend to be similar in their mode of action, fate in the environment and pest control properties, but not necessarily in their level of toxicity. Though pesticides may have different chemical structures, they can have similar modes of actions. Their activity tends to be highly specific, and they are often harmless to non target species (Hashmi & Khan, 2011).

2.1.5 Danger of Agrochemicals on human health

The quantities of pesticides that do not reach the target organism are of concern because of their potential impact on man and his environment (Plimmer, 1984). For example, the leading cause of infant mortality in the United States is birth defects, accounting for 20.1% of all infant deaths. There is a growing body of evidence that agrichemical exposures may contribute to birth defects. It has been shown that during the period from 1996 to 2002 women in the United States with LMPs in April-July (i.e. the time of conception) were significantly more likely to have a live birth with a birth defect than in other months. The report further demonstrates, using NAWQA surface water samples that concentrations of atrazine, nitrates and other pesticides also were higher in the months of April-July. The correlation between birth defects, pesticides and nitrates was statistically significant (Winchester, Huskins, & Ying, 2009). The same situation of birth defects have been observed in a study done in South Africa (Heeren, Tyler, & Mandeya, 2002). However, farm chemicals also have adverse effects on the farm and non-farm public. These adverse effects (or negative externalities) have generated significant public angst and debate in recent years, especially at the urban fringe where farmers are in close proximity to their non-farm neighbors (Adelaja et al., 2010). Pesticides may enter man's diet in many ways, but it is not only man that is at risk. There is also considerable concern for the environment. Natural resources such as soil and water must be considered. Non-target species must be protected from the adverse effects of pesticide residues. It is, therefore, important to detect pesticides and measure their quantities in food, crops, water, soils, air, animals, fish, and other components of the environment (Plimmer, 1984). The use of agricultural chemicals in attempting suicide has recently manifest itself as a problem in the field of emergency medical and psychiatric care in regions where agriculture is the primary industry in Japan. This is not only a Japanese phenomenon, but has also been observed in the United States, Sri Lanka, India, Jordan and Finland. Since the way chemicals are contaminating underground water may be different in different contexts determined by such parameters as soil properties and weather conditions, there is lack of enough knowledge on underground water contamination by chemicals used in agriculture in different places. Similarly, many people lack the knowledge of side effects of the use of chemicals to increase the agricultural production even though the political class have been making same fanatic effort to sensitize them on the same. Hence, the need of mathematical models to indicate how agrochemicals are contaminating water which may lead to undesirable effects on human health.

2.1.6 Effects of Agrochemicals on water Pollution

Groundwater pollution due to pesticides is a worldwide problem. According to the USGS, at least 143 different pesticides and 21 transformation products have been found in ground water, including pesticides from every major chemical class. During one survey in India, 58% of drinking water samples drawn from various hand pumps and wells around Bhopal were contaminated with Organo Chlorine pesticides. Once ground water is polluted with toxic chemicals, it may take many years for the contamination to dissipate or be cleaned up. Cleanup may also be very costly and complex, if not impossible (Aktar, Sengupta, & Chowdhury, 2009).

Chemicals used in agriculture have found their way into drinking water causing health complications. In fact, many chemicals have not had these side effects but once they are in contact with ground water they are converted into dangerous chemical form. Nitrate fertilizer is largely blamed for these fears.

Use of fertilizers would obviously increase food production to meet demand of expanding population but this only father aggravate the situation. Therefore the use of chemicals in agriculture presents global alarm and in particular where environmental degradation is rampant and unfortunately least groundwater contamination resulting from application of agricultural chemicals especially the fertilizer (Sunitha, Reddy, & Reddy, 2012).

Food safety and drinking water quality appear to dominate the current debate over agricultural chemical use, although other environmental considerations certainly are not discounted. With regard to food safety, pesticides used on fruits and vegetables appear to be of primary concern. This is because pesticide application rates are often higher on fruit and vegetable crops than on major crops such as corn, soybeans, and wheat, and because pesticide use is much closer in time to consumption of these products (Taylor, Penson Jr, Smith, Knutson, et al., 1991).

In the soil, fertilizers are converted to nitrate through nitrification by microorganisms and that nitrate can reach ground water. Even in ideal conditions, Plants use 50% of nitrogenous fertilizers applied to soil, 2-20% lost by evaporation, 15-25% react with organic compounds in the clay soil and the remaining 2-10% dissolves on the surface and ground water. The majority of nitrogenous fertilizers aren't absorbed products and they interfere with both underground and surface water (Savci, 2012).

2.1.7 Agrochemicals Modeling

Beginning with DDT in the late 1960's several established pesticides with effective weed or insect control were banned from the market because of undesirable environmental characteristics. Unfortunately, these undesirable characteristics (such as excessive mobility, persistence, or volatility) were determined or observed only after the chemical had been widely used. Because a certain amount of mobility and persistence is essential for proper management and performance of a pesticide, its pollution potential can only be minimized subject to its effectiveness for weed or insect control. For this reason, it is clear that environmental screening tests are needed at the time of development of the chemical when screening for toxicity is being performed. It is equally clear that this screening procedure cannot involve excessive experimentation, because of the massive numbers of chemicals involved. Instead, what it needed is a model that is able to make predictions of behavior of one chemical relative to another from a standard set of easily obtainable chemical benchmark properties (Jury, Spencer, & Farmer, 1983).

Ideally, the result of this screening procedure would be a classification of large numbers of chemicals into a smaller number of groups whose members display similar behavior. From these groups could be selected prototypes for more extensive experimentation under natural conditions.

Pesticide simulation models are not new. (Lindstrom, Boersma, & Gardiner, 1968) proposed a mathematical model for describing leaching of pesticides through soil columns. (Oddson, Letey, & Weeks, 1970) and (Davidson & McDougal, 1973) reported a theoretical leaching model for use with chemicals whose solid-liquid adsorption was linear, but for which the liquid and solid phases were not in equilibrium.

Leistra, in a series of papers (Leistra, 1973),(Leistra, 1978), (Leistra, 1979), has developed simulation models for both liquid and vapor phase movement as a function of time for variable boundary conditions. (Knisel et al., 1980) has assembled (with the aid of a number of authors) a model (CREAMS) for evaluating the amounts of pesticide in surface runoff.

This research formulated a model which can be used to calculate the concentration of any chemical at any place and time. As the environmental conditions such as soil properties, climatic factors are influencing the results (Murray, Lynn, & Malling, 1998), the validity of our model was tested in Uasin Gishu County, Kesses Sub County, in Eldoret, Kenya but the model can be applied in any different place.

2.2 Fourier Transform and the diffusion equation

2.2.1 Fourier Transform

The Fourier transformation is used as a mathematical or physical tool to transform the differential problem into algebraic problem that can be solved easily (Bracewell, 1965). The Fourier transform is among the most widely used tools for transforming data sequences and functions ($single\ or\ multi-dimensional$) from what is referred to as the time domain to the frequency domain (Shatkay, 1995).

The Fourier Transform operate by decomposing or separating a wave form or function into sinusoids of different frequencies which sum to the original wave form. The Fourier transform identifies or distinguishes the different frequency sinusoids and their respective amplitude as reported (Hoffman, 2004).

2.2.2 The diffusion equation

The process of diffusion is described by a partial differential equation known as diffusion equation. The diffusion equation is a parabolic equation, which was formulated for the first time by Jean Baptiste Fourier (Fourier, 1972) in 1807. The diffusion equation has been used to describe the conduction of heat in solids over the past two centuries. It has been proved that it is a powerful tool to be used to analyze the motion of particles by diffusion and to solve an enormous array of diffusion-type problems found in physical, biological, earth and social sciences. The diffusion equation is not the result of the research by Fourier alone, he was inspired by other researchers such as Fahrenheit, Abb Nollet, Bernouilli, black, clawford, Lavoisier , Laplace and Biot in their researches done between the year 1704 and 1807 as it can be found in the paper by (Narasimhan, 1999). Electrical, chemical diffusion and fluid flow in porous material experimentalists derived benefits of the diffusion equation by interpreting the results of their experiments by analogy to the diffusion phenomenon. Other researches such as in statistical mechanics and probability theory established relations with the heat conduction equation by recognizing the similarities between the mathematical behavior of their systems and mathematical solutions of the diffusion equation.

The Fourier Transform method is used in this work to evaluate the analytical solution of the diffusion equation.

2.2.3 Solutions of the diffusion equation

This section is mainly concerned with the aspect of the solutions of the diffusion equation. Solutions of the diffusion equation by different authors are explored and some of them are presented as solutions of heat equation. Most of these solutions are well developed by (Crank, 1975).

Evolution of diffusion equation solutions

Joseph Fourier is the first person to extend the diffusion of heat mathematically in his work entitled “The analytical theory of heat” originally written in French and translated in English in 1955 (Grattan-Guinness, 2005). In the work by (Grattan-Guinness, 2005), it is also written that Fourier never stated what motivated him to mathematicise heat diffusion. Fourier wrote many articles trying to mathematicise the diffusion process. At a certain stage Fourier consulted the Swiss physicist Pierre Prevost who was in accordance with Fourier’s work contrary to Laplace and Lagrange who were disappointed by Fourier’s work. So many other scientist has criticized Fourier’s work either positively or negatively. In spite of the objection by Lagrange and Laplace on the propagation of heat in solids, Fourier’s memoir and some additional work got a prize from the institute Lagrange and Laplace being in the committee.

Fick’s contribution

Fick was inspired by the work by Graham on the diffusion of salts in water. Based on the previous publications by Fourier and Ohm, Fick didn’t support Graham’s work. Fick say that according to the previous publications by Fourier and Ohm, “the transfer of salt and water happening in a unit of time, between two elements of space with filled differently concentrated solutions of the same salt, must be caeteris paribus, directly proportional to the difference of concentration, and inversely proportional to the distance of the elements from one another” (Fick, 1995). Fick supported Fourier's work on diffusion and said that several methods can be used to confirm by experimentation the diffusion equation and did it using some methods. The paper by (Philibert, 2006) show that many other authors contributed in the improvement of the research on diffusion in different domain and brought a lot in science.

2.3 Numerical solution

2.3.1 Numerical Solution Procedure

So many numerical methods have been developed up to now. These numerical techniques through computer algorithms are derived from equations that govern the model. A numerical model is obtained by transforming a mathematical (for example differential) formulation for continuous variables into discrete form. The discrete variables (for example hydraulic head in flow models, concentration, or pressure in transport models) of the model are determined at given points called nodes in a descretized model domain, determined by a grid (Allaire, 2007).

This requires the discretization procedure of the model domain. The discrete equations are defined in such manner that they apply to the discrete parts of the aquifer. The computer coding, are written using a well known numerical method theory and solve as many equations as they are for each discrete part of the aquifer. Points obtained by discretization belong to the same domain and what is finally obtained by solving the equation of our model is the concentration of a given chemical at any point of the grid (Turgay, Jamal, & Gregory, 2001). In general, (Hildebrand, 1987) say that "the ultimate aim of the field of numerical analysis is to provide convenient methods for obtaining useful solutions to mathematical problems and for extracting useful information from available solutions which are not expressed in tractable form".

2.3.2 Domain Discretization and numerical coding

To approximate numerically a single or a set of continuous partial differential equations, the discretization of these equations in both space and time is required. A predetermined mesh is most often used to achieve spatial discretization which fills the entire domain over which the governing equations apply. For computational contaminant transport applications, this domain corresponds to the entire contaminated field. Thus, the existence of a mesh determines the locations in the field at which the contaminant quantities are evaluated. A mesh is, therefore, an artificial geometric construction which facilitates the spatial discretization of the governing equations to be solved. Structured and unstructured mesh techniques techniques are the two most commonly adopted meshing strategies. Structured meshes are the method of choice for relatively simple geometries in which the grid simultaneously conforms to all geometry boundaries. In block-structured techniques, the domain is decomposed into a small number of topologically simpler domains, and each domain is meshed independently with a structured grid (Peyret, 1996).

Numerical coding consist in the process of translating the discretized mathematical problem into a computer program using a well developed and known numerical method. Numerical coding provide different ways to create a program that implement any Mathematical method chosen to be used.

The discretization of the governing equations into discrete components that can be implemented using computer codes is to cater for the variation of the concentration properties of the domain making it possible for an equation to be solved corresponding to each **block** in the discretized domain. The concentration at different points of the domain are generated by solving the diffusion equation which is a Partial Differential equation (PDE).

2.3.3 Numerical solutions of the diffusion equation

The diffusion equation characterizing heat flow and many other physical phenomenons have been solved numerically in different context by many authors such as (Gockenbach, 2005), (Ohtani, JUNG, Kobayashi, & Nishihara, 1975). The diffusion equation solution show how the heat or a contaminant can move from one place to many other points with time as it reduces in quantity at the starting point (Halpern, Wilson, & Turcotte, 2002).

2.4 Water analysis

Water analysis have been a concern for many year. The first edition of Standard Methods for the examination of water and waste water was published in 1905 under the title “Standard Methods of water analysis”. From then, the methods have been improved up to “Standard Methods for the Examination of Water and Waste water” published in 1999 which has been used in this study.

The details for laboratory analysis procedure which is used in this work can be found in (Association, Association, Federation, & Federation, 1999).

Chapter 3

Methodology

In this chapter the methods used to achieve the objectives listed in chapter one Section 1.4 are described.

3.1 A model as a set of mathematical statements

3.1.1 Introduction

Scientists and engineers give different definitions to the model according to their interests. The definition by (Velten, 2009) which is more general is adopted in this study. From definition 3.1.1 to the definition 3.1.4, the author was improving his definition for more understanding and completeness.

Definition 3.1.1 *A mathematical model is a set of mathematical statements*

$$M = \{\Sigma_1, \Sigma_2, ..., \Sigma_n\}. \tag{3.1}$$

The attempt of the definition above is not complete since it is related to the word "mathematical" of "mathematical model" only, without any reference to goals. Following the philosophy of the terms model, simulation, and system, let us improve the definition and define the model as:

Definition 3.1.2 *A mathematical model is a triplet (S, Q, M) where S is a system, Q is a question relating to S, and M is a set of mathematical statements in equation (3.1) which can be used to answer Q.*

3.1.2 State Variables and System Parameters

The main objective of the modeling procedure is to reduce the complexity of the original system. The power of the mathematical modeling procedure resides in reducing the dimensions of the problem. In other words, the reduction of the information content of complex systems in terms of reduced systems is one of the main benefits of mathematical models.

A reduced system can be defined in the following two steps:

Definition 3.1.3 *Let* (S, Q, M) *be a mathematical model. Mathematical quantities* $S_1, S_2, ..., S_n$ *which describe the state of the system* S *in terms of* M *and which are required to answer* Q *are called the* ***state variables*** *of* (S, Q, M).

Definition 3.1.4 *Let* $S_1, S_2, ..., S_n$ *be the state variables of a mathematical model* (S, Q, M). *Let* $p_1, p_2, ..., p_m$ *be mathematical quantities (numbers, variables, functions) which describe properties of the system* S *in terms of* M*, and which are needed to compute the state variables. Then* $S_r = \{p_1, p_2, ..., p_m\}$ *is* ***the reduced system*** *and* $p_1, p_2, ..., p_m$ *are the* ***system parameters*** *of* (S, Q, M).

From the definitions above, it is understood that the state variables are there to describe the system properties which are of interest and the system parameters are there to describe the system properties needed to obtain the state variables mathematically. Although there is finally a need of state variables to answer Q, the information needed to answer Q is already in the system parameters, that is, in the reduced system S_r. Using S_r, this information is expressed in terms of the state variables by means of mathematical operations, and this is then the final basis to answer Q.

3.2 The use of Fourier Transform

The analytical solution of the diffusion equation can be generated using Fourier Transform technique. This technique is used following the steps described in (Bernatz, 2010), (Haberman, 2012) and (Carslaw & Jaeger, 1959).

3.3 Solving the diffusion equation with pdepe MATLAB function

The numerical solutions of the diffusion equation are generated using pdepe MATLAB tool. The pdepe MATLAB tool have been used in other works such as (Yudianto & Xie, 2010) and (Pochiraju & Tandon, 2006). The MATLAB PDEs solver pdepe is given a PDE to be solved in the form of equation (3.2)

$$c(x,t,u,\frac{\partial u}{\partial x})\frac{\partial u}{\partial t} = x^{-m}\frac{\partial}{\partial x}\left(x^m f(x,t,u,\frac{\partial u}{\partial x})\right) + s(x,t,u,\frac{\partial u}{\partial x}), \tag{3.2}$$

where c is coefficient, u is the function to be solved, $m = 0, 1, 2$ if coordinates are cartesian, cylindrical or spherical respectively, f is the flux term and s is the source term.

3.4 Laboratory measurement of the chemical concentration

The quantity of nitrate contained in the samples collected from eleven wells was analyzed using UV-VIS spectrophotometer machine following the procedure describe by (Association et al., 1999).

Chapter 4

Results and discussion

In this chapter, results are presented using the methods developed in the previous chapter.

4.1 Formulation of the mathematical model

4.1.1 Introduction

The aim of this model was to help the population to predict, calculate and regulate the contamination of their wells. It's very important to know how human activities such as agricultural activities, waste deposit and others are contaminating underground water and wells. That is what the model of the present study was formulated to achieve.

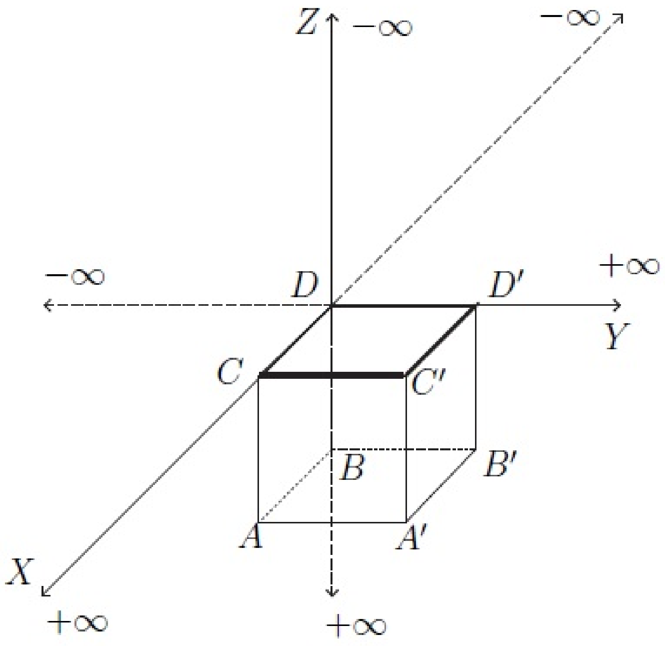

Figure 4.1. Model domain representation

The Figure 4.1 represent the domain of study. The chemical or any other contaminant is assumed to be disposed at a point on the the surface represented by the rectangle $CC'D'D$ and the chemical is moving by diffusion in all directions on the underground. The diffusion equation was solved with the assumption that it is from one point, a certain area or different areas but in any of these cases, a section of the rectangle $CC'D'D$ remain the area of disposal. The concentration of any diffusing substance depends on the distance from the disposal point and the point of sample collection. This work consider the case where diffusivity coefficient D is constant and equal in all directions and the concentration depends only on the distance from the source and time of observation.

4.1.2 Mathematical model formulation

In this section, the definitions provided in Section 3.1 are used to attain the first specific objective of the present study. According to the definition 3.1.2, a mathematical model is formulated by specifying the elements of the triplet (S, Q, M). The present mathematical model responds to the following question represented by (Q) in the triplet (S, Q, M):

What is the concentration of a particular chemical at given time and point in the underground water when the chemical diffuse from the disposal point ?

What the system S represents in the present model and the set of mathematical statements represented by M in the triplet (S, Q, M) have also to be given.

The system S is the soil where the chemical diffusion and water contamination take place.

The underground water contamination which is examined in this thesis through wells is also part of the system S. The system S is described by the different sources of contamination as observed in Figure 1.1. For the model of the present study, the system S was considered as a farm which is partly cultivated and partly residential area. The state variables $S_i,\ i = 1, 2, 3, ..., n$ are the portions of the farm which are cultivated. Fertilizers are then applied on some spaces S_i of the system S as the cultivated farms are not joined. The system parameters p_i are the same for some state variables and different for others.

The third element in the triplet (S, Q, M) to be determined for the model to be completely formulated is the set of mathematical statement M.

The set of mathematical statements M is then given by the diffusion equation and its solutions in different context. The diffusion equation characterize properly the contamination of ground water by disposed chemical since chemicals do not need any transporting material to move from one place to another in the underground.

The solution of the diffusion equation in different context can be found in (Cushman-Roisin, 2012).

4.2 Analytical solution of Diffusion equation

4.2.1 Solution of the diffusion equation and Gaussian function

The analytical solution of the diffusion equation (1.3) is generated by Fourier Transform technique. The fundamental solution of the diffusion equation discussed in many works such as (Farlow, 1993) and (Haberman, 1983) is

$$\begin{aligned} c(x,t) &= \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{+\infty} \delta(\xi) e^{-\frac{(x-\xi)^2}{4Dt}} d\xi \\ &= c_0 \frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{4\pi Dt}} \end{aligned} \tag{4.1}$$

The mathematical quantities D, t, x, c_0 and s where D is diffusivity, t is time, x is the location, c_0 is the initial concentration of the chemical in the soil and s the source are the system parameters which can be used to find the contribution of the different sources of contamination S_i called state variables. The values $D_1 = p_1$ and $t_1 = p_2$,... can be used to calculate the concentration brought by the source S_1, at time t_1 with diffusivity D_1 and other characteristics of the specific source of contamination in the system S. The quantities $D,\ t,\ ,x$ and c_0 are used to determine the concentration c of the chemical derived from the diffusion equation. This work consider the case where the diffusivity D is constant but naturally the diffusivity depends on the type of the soil.

The comparison between the fundamental solution of the diffusion equation in equation (4.1) and Gaussian function given by equation (4.2) below reveals that the fundamental solution of the one dimensional diffusion equation is also Gaussian of the form

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}}, \tag{4.2}$$

where μ is the mean and σ the standard deviation (Hogg & Craig, 1995).

The solutions of the diffusion equation in different context can be found in (Cushman-Roisin, 2012). These solutions of the diffusion equation in different contexts are related to the fundamental solution.

4.2.2 Discussion of the solution based on Gaussian function and the laboratory analysis results

As discussed by (Haberman, 1983), the concentration of the contaminant is high and located in a small space shortly after the release of the contaminant. As time goes, the contaminant reduces in concentration at the starting or disposal point and increase the contaminated area. From the laboratory results of the collected data, the concentration is high in the wells located near the disposal point and keep reducing as the distance from the disposal point and time increase.

4.3 Numerical solution of reaction-diffusion equations

This section is devoted to the generation of results of a simple reaction systems in 1-dimensional domain. These results are generated using MATLAB PDEs solver pdepe. The simulation of results started with a simple diffusion process and expanded the model including steady state and reaction term. In this cases, the source of contaminant is permanent, that is why the concentration at the starting point doesn't reduce as the contamination affect other points. When the source of contamination is not continuous, the quantity of the contaminant reduce at the starting point as it spreads to other points in the domain. The units of measurement in different cases are chosen according to the international system of units. The two last summands of the right of equation (1.1) reduces to s which takes different values in different contexts according to the fact that a reaction can generate a targeted chemical or reduce it or keep it constant. The reaction can't produce and reduce the quantity of a targeted chemical at the same time.

4.3.1 Case I: Diffusion process without reaction

This case consider the diffusion equation and solve it for one species $c(x,t)$ with diffusion coefficient $D = 1$ on a 1-dimensional domain of length $L = 1$ according to

$$\text{PDE}: \qquad \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{4.3}$$

$$\begin{aligned} \text{BC}: \qquad c(0,t) &= 1; \quad 0 < t < 1, \\ \frac{\partial c(L,t)}{\partial x} &= 0; \quad 0 < t < 1, \end{aligned} \tag{4.4}$$

$$\text{IC}: \quad c(x,0) = 0; \quad 0 < x \leq 1 \tag{4.5}$$

and $s = 0$ and the initial concentration equal to 0.

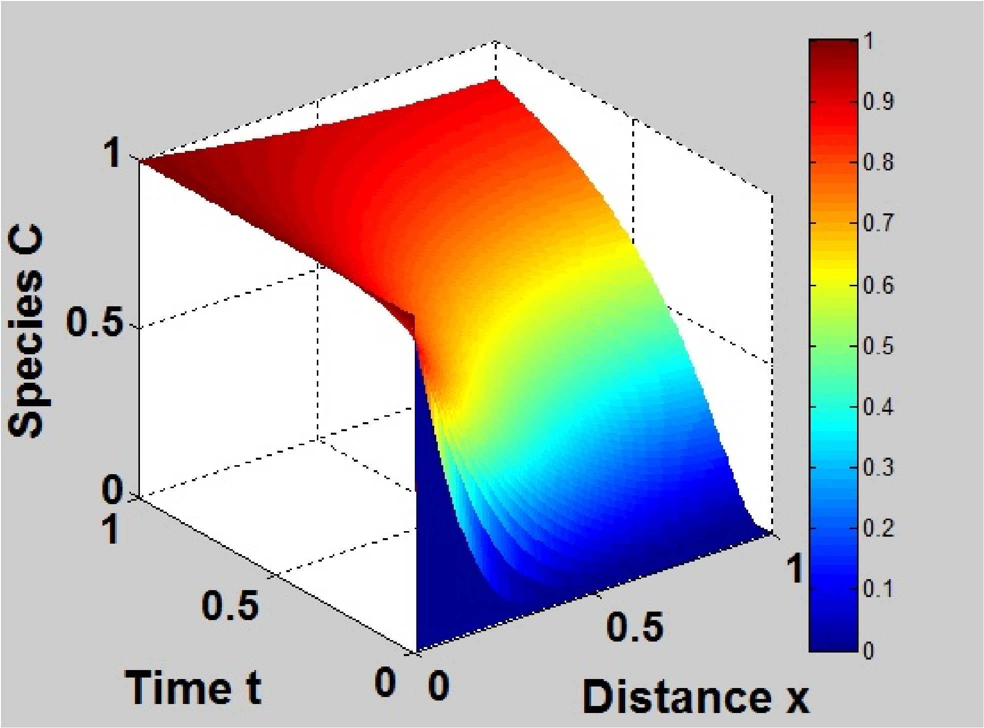

Figure 4.2. Surface representation of the concentration variation with respect to time in one dimension

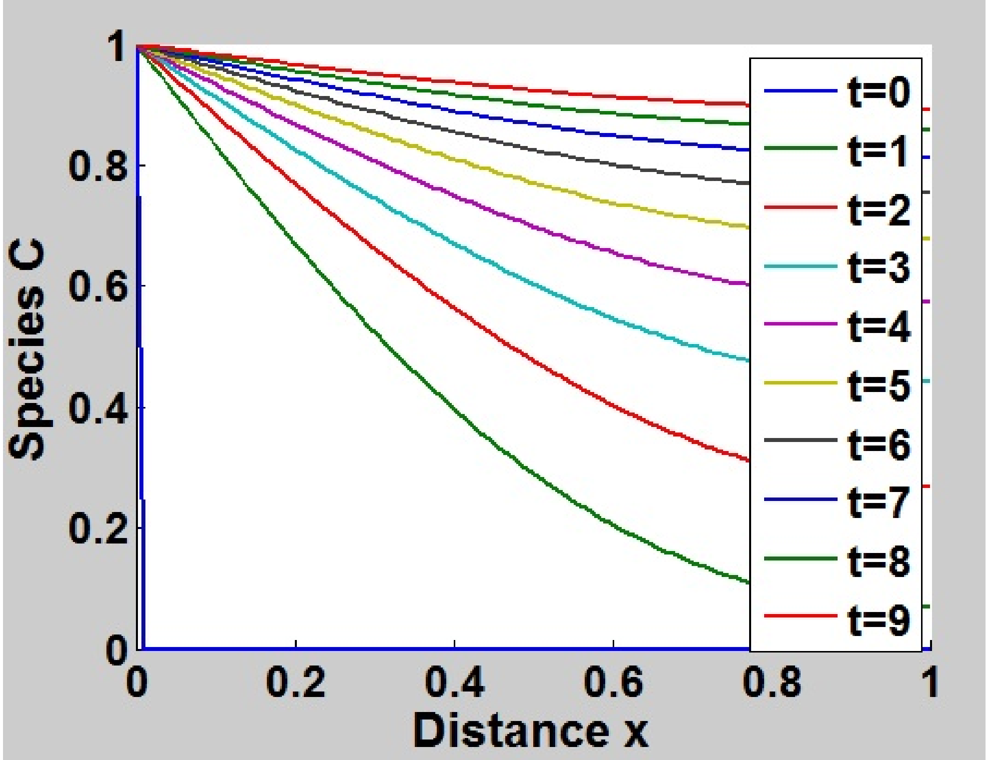

Figure 4.3. Curves representing concentration variation with respect to time

This results can be well discussed using the results in two dimension represented by the following Figure 4.4.

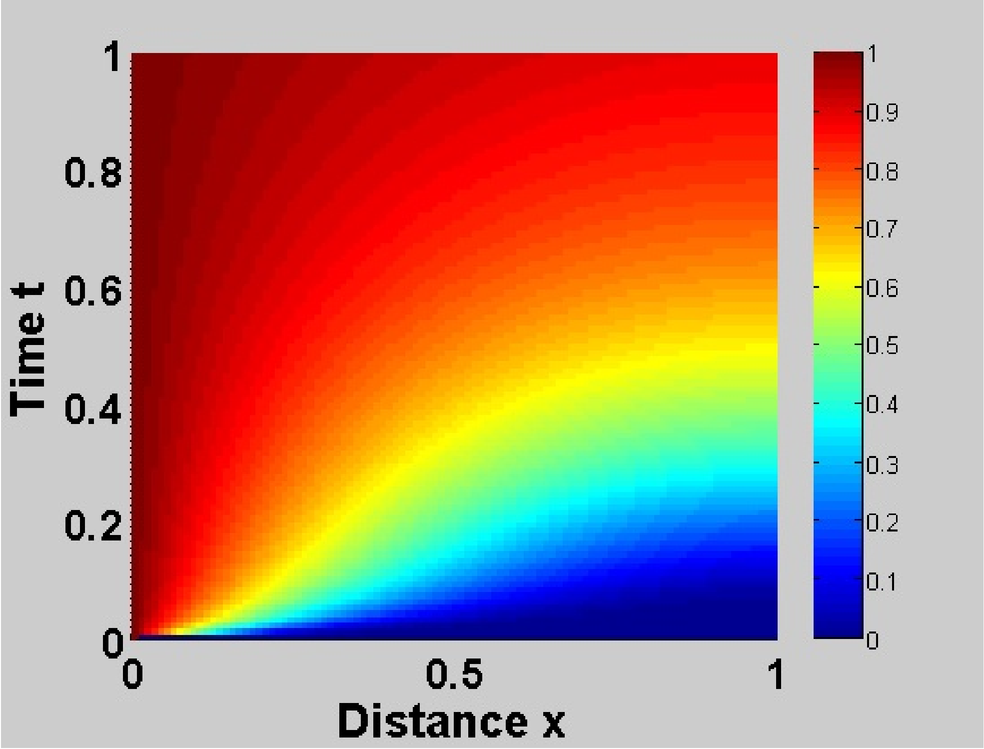

Figure 4.4. Variation of concentration with time in two dimension

As it can be observed on Figure 4.4, at time t very close to 0, this is just after the disposal of the contaminant, the concentration is high at the points which are very close to the disposal point $x = 0$ and there is no contamination at all at the point $x = 1$ located at a distance equal to 1 from the disposal point. As time goes up from zero to one, the contaminated area increases as it can be observed on the Figure 4.4. At time $t = 1$, the concentration is almost the same at all points in the domain even at the point $x = 1$ which was not contaminated at time $t = 0$. This evolution of the concentration of the contaminant in the domain observed in the Figure 4.4 shows very well that the contaminant diffuse and increase the contaminated area with time.

4.3.2 Case II: Diffusion equation at steady state without reaction

This case consider the diffusion equation which have reached the steady state and solve it for one species $c(x, t)$. Since in the case of steady state problem $\frac{\partial c}{\partial t} = 0$, then $D\frac{\partial^2 c}{\partial x^2} = 0$. This means that there is no transfer of material from one place to another in the domain. Considering a 1-dimensional domain of length 10 on the axis indicating the concentration of the species, 1 on distance axis, $L = 1$ and $s = 0$ according to

$$\text{PDE}: \qquad \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} = 0, \tag{4.6}$$

$$\begin{aligned} \text{BC}: \quad & c(0,t) = 1; \quad 0 < t < 1, \\ & \frac{\partial c(L,t)}{\partial x} = 0; \quad 0 < t < 1, \end{aligned} \tag{4.7}$$

$$\text{IC}: \quad c(x,0) = c_0 = 6; \quad 0 < x \leq 1, \tag{4.8}$$

The initial concentration c_0 is taken to be 6 at all points of the domain and remains the same as the evolution of the concentration reaches the steady state.

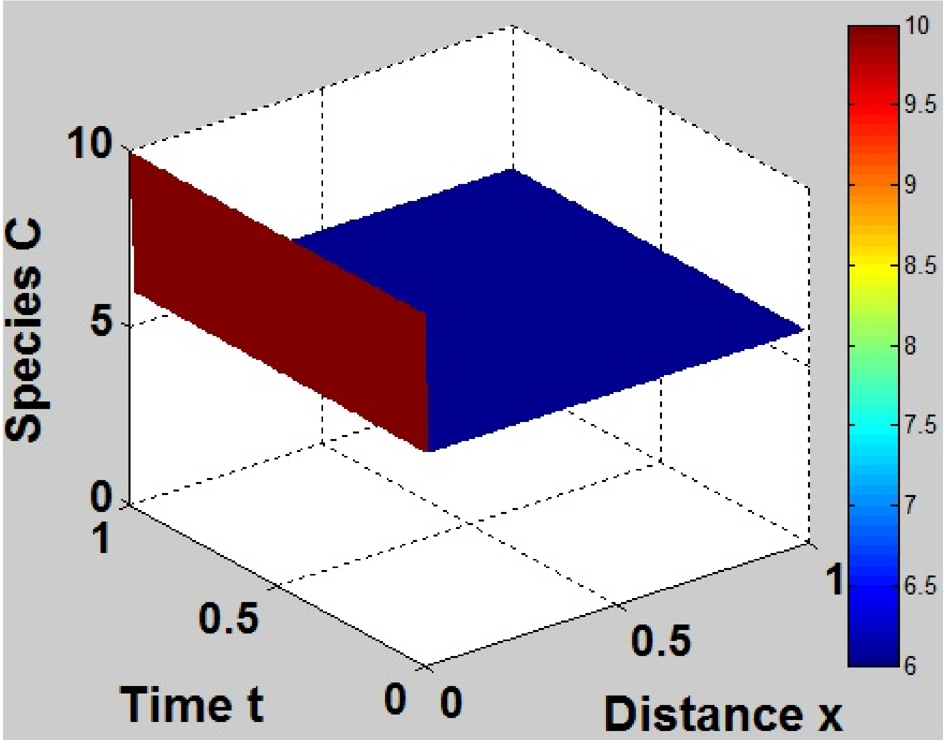

Figure 4.5. Surface representation of the concentration at steady state

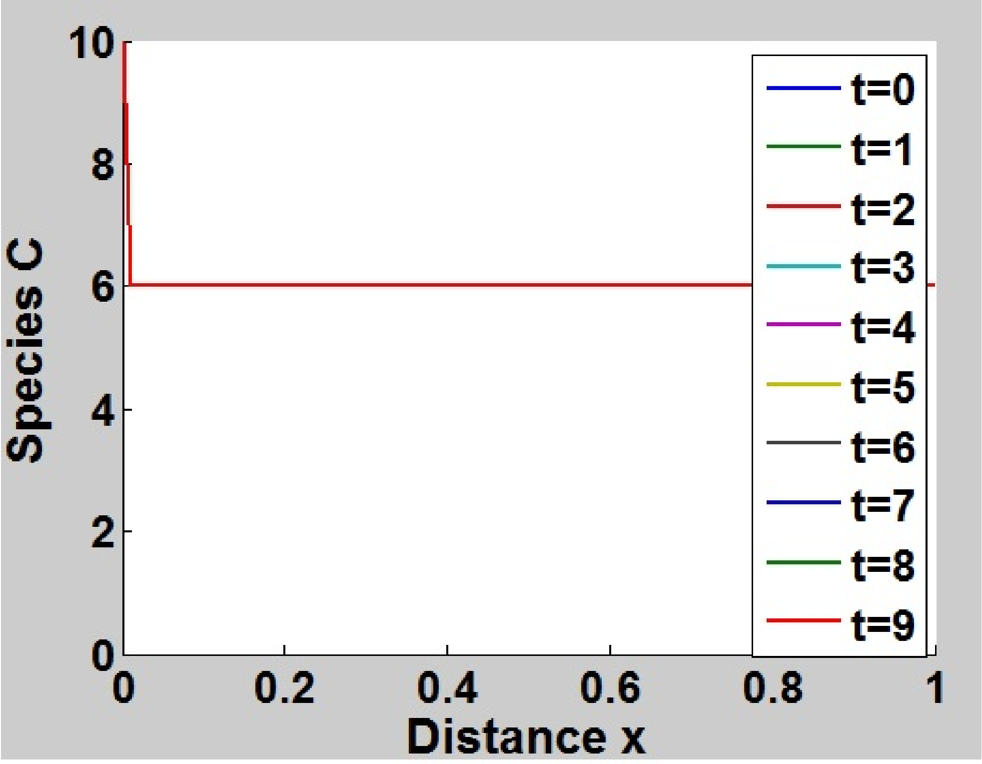

Figure 4.6. Curves representing concentration at steady state

Figure 4.6, show that all the concentration curves from time $t = 0$ to time $t = 9$ coincide. The graphs are the same since the concentration is the same and constant throughout the simulation time. It means that the simulation start when the contaminated area has reached the steady state and the diffusion stop since the diffusion take place from the area which is highly contaminated to the area with low level of contamination.

4.3.3 Case III: Diffusion equation with decay

This is the case where the diffusion equation has a decay term and was solved for one species $c(x,t)$. The diffusion coefficient $D = 1$ is used and the source s in the equation (3.2) is equal to -2. Then, there is reduction of the species in the domain as time goes. Considering a 1-dimensional domain of length $L = 1$, we have

$$\text{PDE}: \qquad \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + s, \tag{4.9}$$

$$\begin{aligned} \text{BC}: \qquad c(0,t) &= 1; \quad 0 < t < 1, \\ \frac{\partial c(L,t)}{\partial x} &= 0; \quad 0 < t < 1, \end{aligned} \tag{4.10}$$

$$\text{IC}: \quad c(x,0) = 1; \quad 0 < x \leq 1, \tag{4.11}$$

$s = -2$ and initial concentration equal to 1.

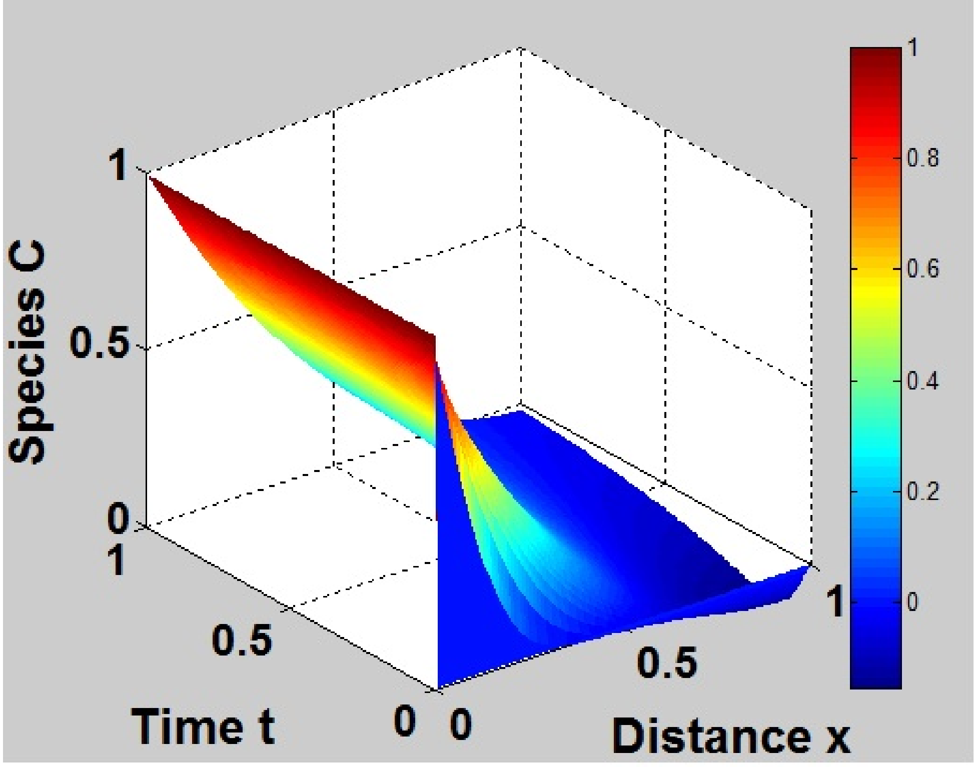

Figure 4.7. Surface representation of the evolution of the concentration when there is a decay

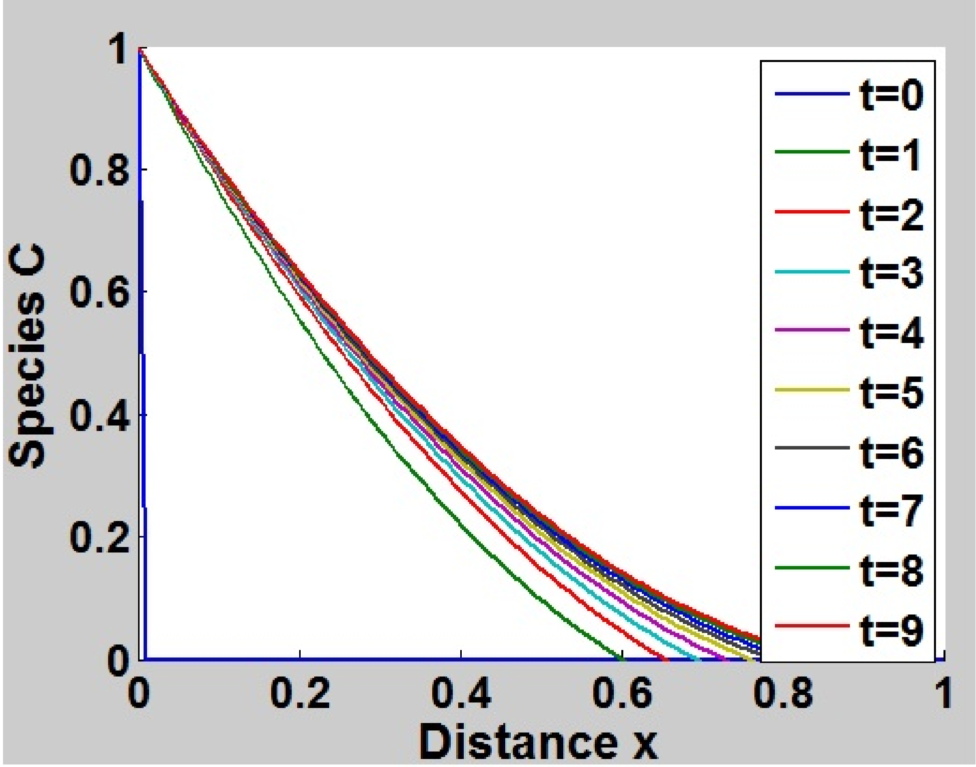

Figure 4.8. Curves representing the evolution of the concentration with decay

From Figure 4.8, it is seen that graphs are very close since the concentration of the contaminant is not increasing much. This is due to the decay factor which make the quantity of the contaminant to reduce continuously. In other words, the contaminant is applied on the domain of contamination and the decay process is removing it at the same time, which make the area almost free of contamination increment and the area remain with almost the same quantity of contaminant as the initial quantity all the time.

4.3.4 Case IV: Diffusion equation with point source

Here, the diffusion equation (1.2) which has a source term was solved for one species $c(x,t)$. For simplicity, the diffusion coefficient is fixed at $D = 1$ and the source term s at 2 but any other values can be taken without loose of generality. The difference between Case III and IV is the fact that the term s is negative for decay and positive for the source. Then, this is the case where the quantity of species keeps increasing with time in the domain.

A 1-dimensional domain of length 1 and the initial concentration $c_0 = 1$ were considered and hence we obtained the following results

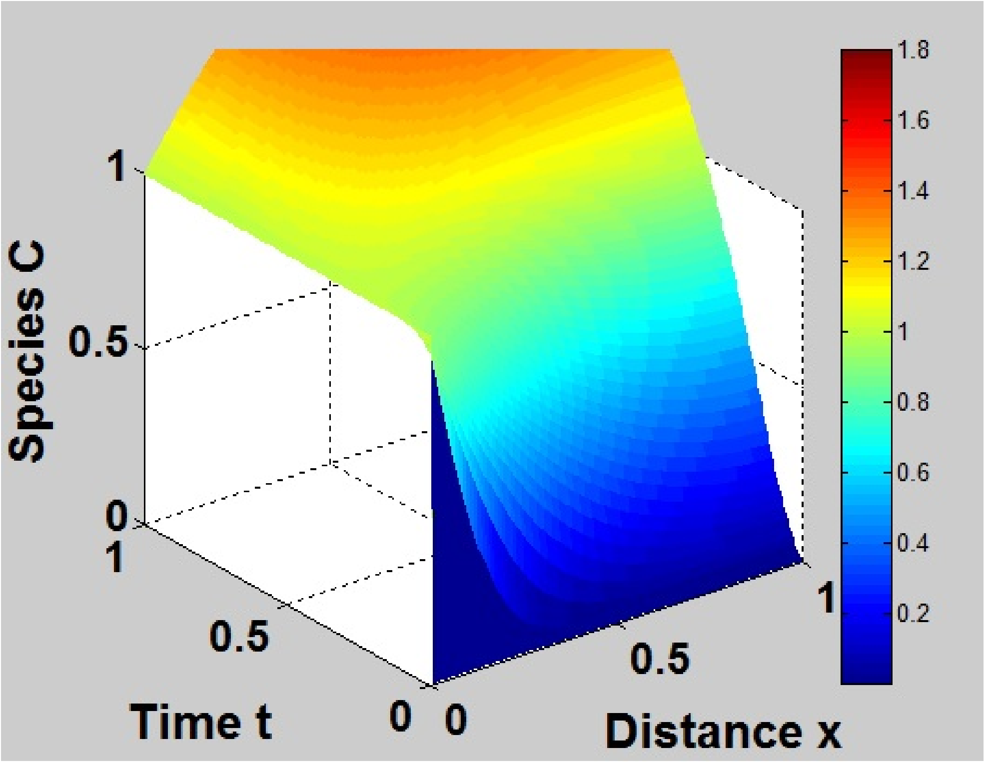

Figure 4.9. Surface representation of the concentration when it keeps increasing with time

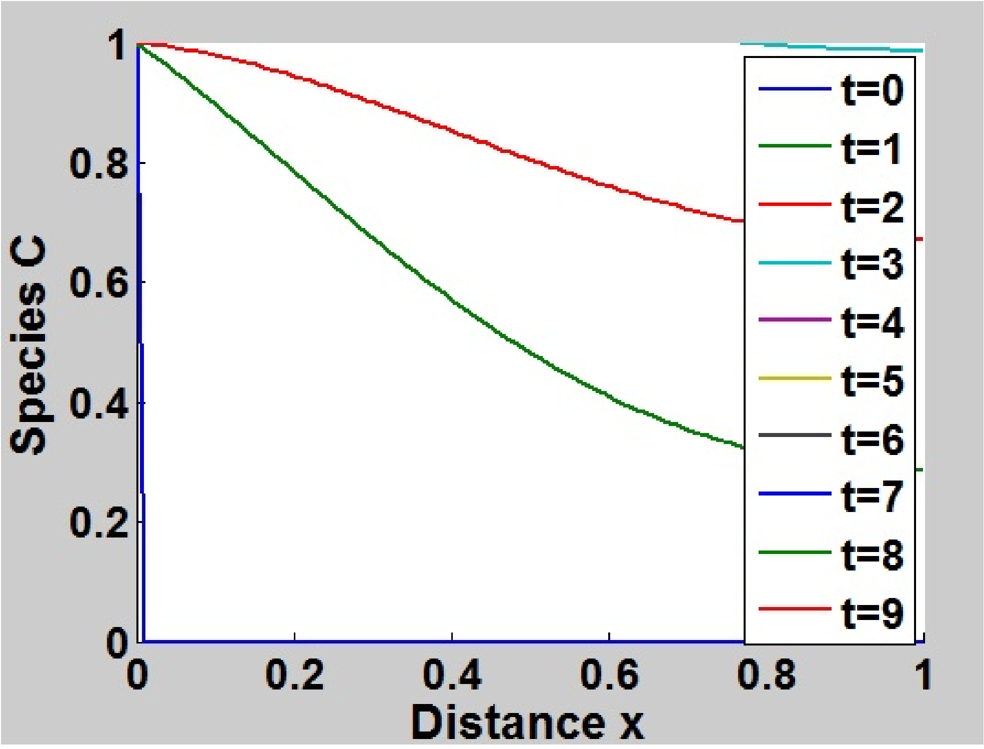

Figure 4.10. Curves representing concentration when it keeps increasing with time

It is clear that the Figures 4.9 and 4.10 do not appear in full. The reason is that the concentration of the species keeps increasing with time because of the source. At certain time the concentration is greater than one which is the maximum concentration to contain in the graph since the axis representing the concentration of the species is from zero to one. We generate Figures 4.11 and 4.12 bellow by extending the axes of the Figures 4.9 and 4.10. By increasing the the size of the axes indicating the concentration of the chemical at different points as in Figure 4.12, the graphs indicating the evolution of the concentration of the chemical at the all nine different times can be observed.

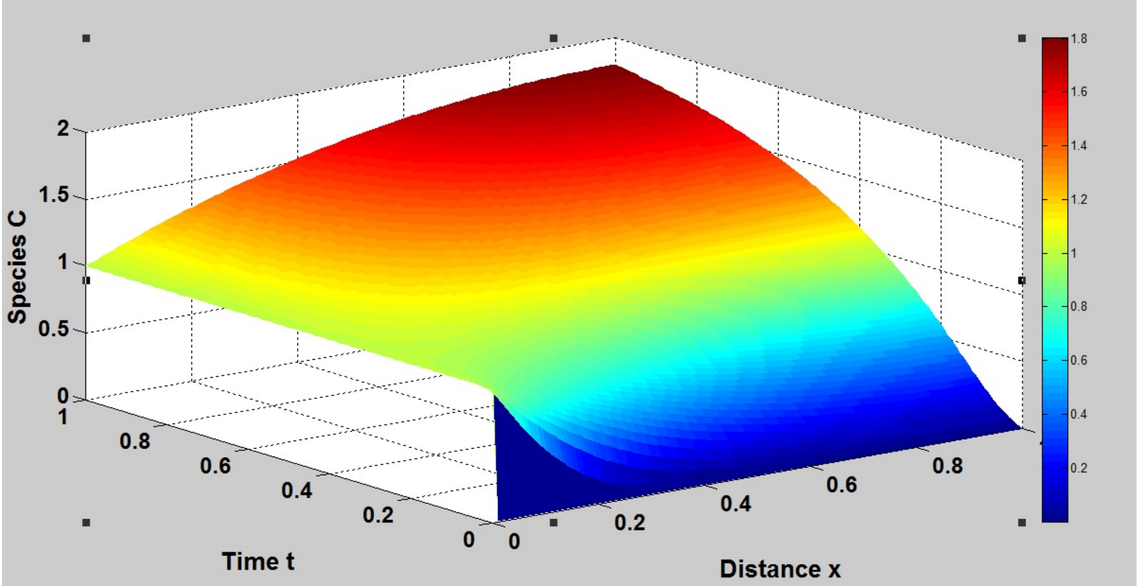

Figure 4.11. Surface representation of the concentration when it keeps increasing with time with extended axis

In the four cases discussed above, the contaminant is disposed at the point $x = 0$ at time $t = 0$. The highest concentration is found at the point $x = 0$ at time $t = 0$ before the contaminant starts diffusing. As time goes, the contaminant keep extending the area of contamination except in case II. The Case II is a particular case, as the concentration is the same at all points in the domain and the diffusion stops. The contaminant remains at the disposal point and the concentration remains

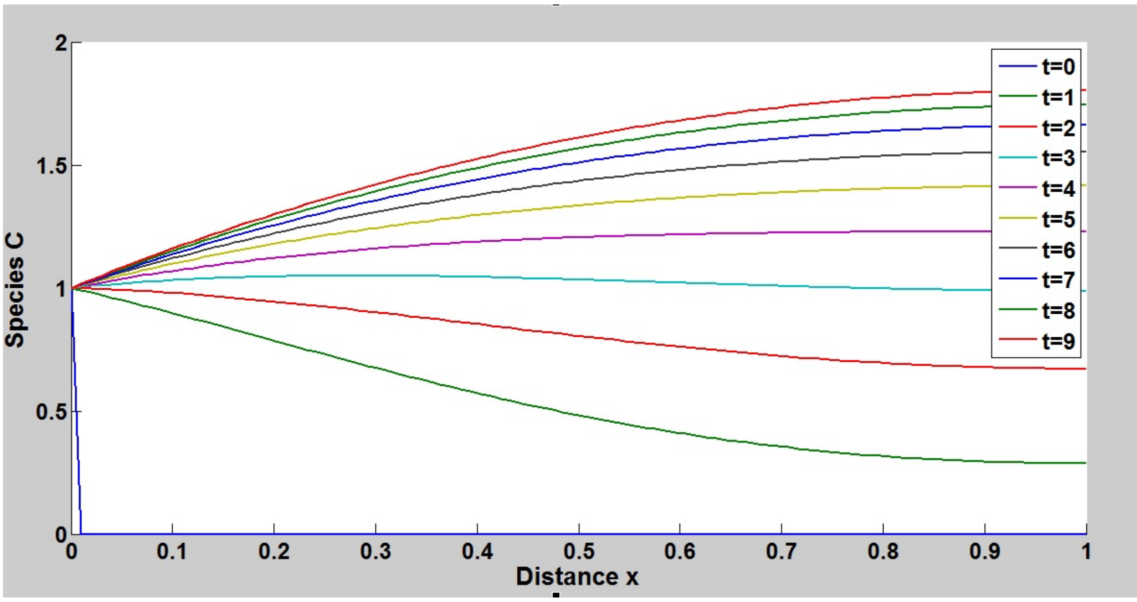

Figure 4.12. Curves representing concentration when it keeps increasing with time with increased Y-axis

the same as time goes. This means that the disposed chemical is not diffusing away.

4.3.5 Case V: Extension of the contaminant localized in an area at the beginning

This is the situation where the contaminant is disposed at one side of the domain. The contaminant is then spreading from the initial area where the contaminant was disposed at the beginning of the investigation. It is assumed that the contaminant is localized on the side of positive values of x as it is observed in Figure 4.13. The quantity of the contaminant on the side of negative values of x keep increasing with time and reducing on the side of positive values of x. This means that the contaminant which is first localized on the side of positive values of x keeps moving to the negative side of x values which make the side of negatives values of x contaminated.

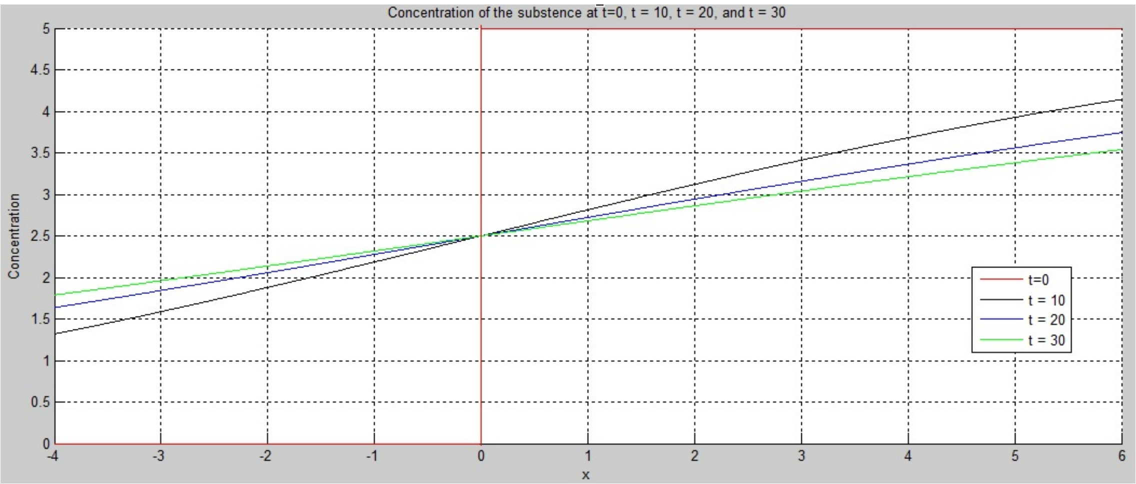

Figure 4.13. Graphs representing the evolution of the concentration when it keeps moving from the high contaminated area to the low contaminated one

4.4 Validation of the model of the present study

The Laboratory analysis results helped to confirm that nitrate from farming activities and other human activities are contaminating underground water. From the comparison of the simulated results and Laboratory analysis results, it was concluded that the diffusion equation results determined by analytical and numerical methods make sense. The Section 4.3 assume different situations by considering different values of the terms in the diffusion equation.

4.4.1 Field description

This study was conducted in the area around Moi University main Campus in Eldoret-Kenya (Figure 4.14). Moi University main Campus location is, 35km south east of Eldoret town, around 350km north west of Kenya's capital, Nairobi. The University is located in a rural setting, on land that was originally a wattle tree's plantation at the southern border of Eldoret Municipality (Kibet Bii & Wanyama, 2001). The area of study is selected based on geographical conditions which make the population of the area depend on underground water. Proximity to villages with higher agricultural production of maize and wheat. Farming in that area is done in a modern way using tractors during cultivation, planting and harvesting time. This study confirmed the effect of manure, pesticides, and other chemicals used in agriculture on underground water which is the source of water used by families in the area.

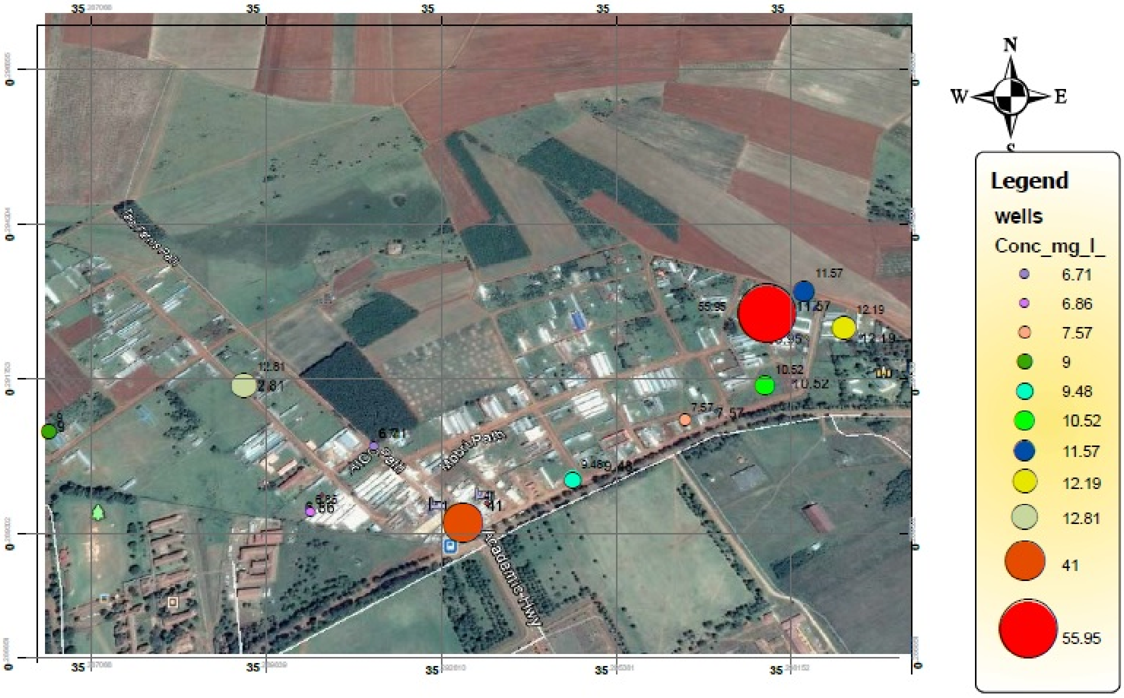

Figure 4.14. Map of the study area with eleven points locating investigated wells

4.4.2 Sampling

Water from eleven wells were collected from private hostels except two of them which were collected from a business center and private rentals. The sampling was done purposefully depending on the distance from the wells. Sampling is covered the study area as it can be observed in Figure 4.14. Water samples were collected in the morning because samples must be analyzed the same day after sampling to avoid errors in the results. All the wells where samples were collected from are well covered and water was pumped manually from the well except on the well numbered $1 - 2$ and the well numbered $1 - 7$ where water was taken from the well using a container attached on a rope.

4.4.3 Standards and absorbance

The following table report the volumes of the standard and the absorbance values given by UV-Vis.

Table 4.1

Concentration of standards and their absorbance

Different volumes of the used standards in ml for each	Absorbance
2	0.082
4	0.096
6	0.147
8	0.182
10	0.254

4.4.4 Calibration curve for KNO_3

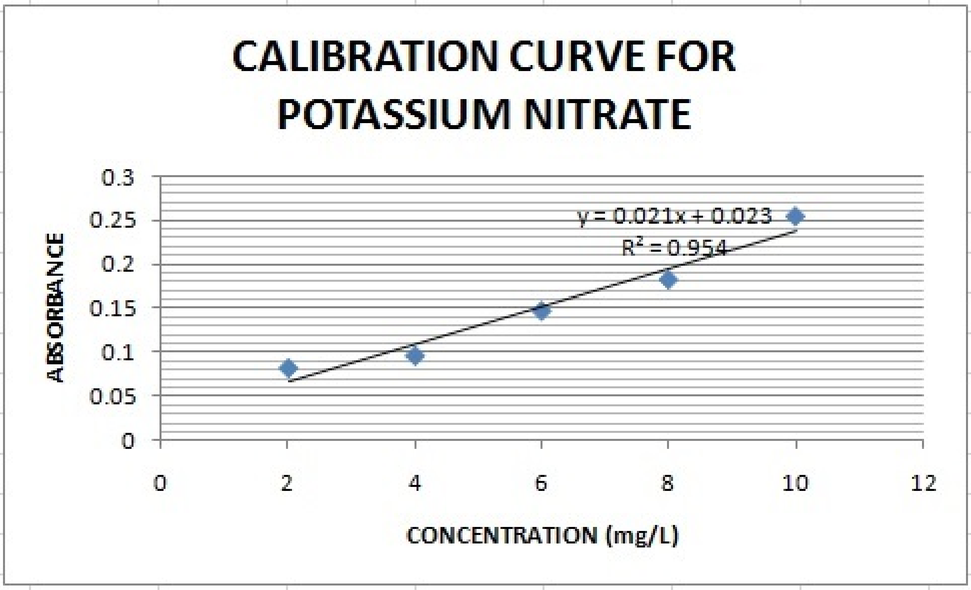

Figure 4.15. Calibration curve for KNO_3

The calibration curve is a linear equation which help us to calculate the concentration of nitrate in our samples.

Now, using the equation

$$y = 0.021x + 0.023 \tag{4.12}$$

of the calibration curve interpreted in Section 4.4.5 and the values given by the UV-Vis spectrophotometer, concentration of our samples were calculated.

4.4.5 Concentration of nitrates in different samples

The values given by the spectrophotometer represent y value in the equation (4.12) and x values are the concentrations of the samples reported in the table below.

Table 4.2

Concentration of nitrate in water samples

Sample code	**y values**	**concentrations of the samples(mg/l)**
1-1	0.279	12.19
1-2	0.266	11.57
1-3	1.98	55.95
1-4	0.244	10.52
1-5	0.182	7.57
1-6	0.222	9.48
1-7	0.884	41.00
1-8	0.164	6.71
1-9	0.167	6.86
1-10	0.292	12.81
1-11	0.212	9.00

The values of concentrations are not increasing or decreasing in any order as observed in the table above. The big farm which was expected to contaminate the wells is located at $60m$ from the the sample $1 - 1$ and at $30m$ from the farm $1 - 2$. Unexpectedly, the concentrations of nitrate are not the highest in the two wells which are most close to the biggest farm.

Reading in the Table: 4.2, the highest concentration of nitrate is found in the sample $1-3$. The observation around the well where the sample $1-3$ was collected from, reveals that there was a cowshed at $10m$ from the well as shown by the Figure: 4.16.

Figure 4.16. Cows dung in the fence near the well for sample 1-3

From the results of sample $1-3$ and the observation of the area where it was collected from, it showed that animal dung may have contributed to the increase in nitrate concentration in the well.

By analyzing the results in the Table: 4.2, it is seen that the concentration values are decreasing systematically with the distance from the biggest farm except at the wells where samples $1-3$, $1-6$, $1-7$, $1-10$ and $1-11$ are collected from. As explained for the sample $1-3$, even these other samples which are giving unexpected results are located near other contributors in nitrate concentration increment.

For instance, near the well where the sample $1-6$ was collected from, there were two dumping sites shown by photos in Figure 4.17 and Figure 4.18. Then, the results given by the sample $1-6$ and the observation of the area around the well where this sample was collected from, permit us to conclude that dumpings are contributing in the contamination of the wells.

The sample $1-7$ is located near a very big and permanent dumping site which has been there for a long time as it can be observed in Figure 4.19.

Figure 4.17. A functional dumping ground near the well for sample 1-6

Figure 4.18. Abandoned dumping site near the well for sample 1-6

Figure 4.19. Permanent dumping site near the well for sample 1-7

The sample $1-10$ is located in a plot where there are cows in the neighboring plot as it can be observed in Figure 4.20.

Figure 4.20. Cows in a neighboring plot for sample 1-10

4.4.6 Study area with data and contours

The Figure 4.21 shows the variation of concentration of contaminants in the study area. The Figure 4.21 was generated by MATLAB and show the variation of the concentrations according to the distribution of initial values of the concentration at the simulation time.

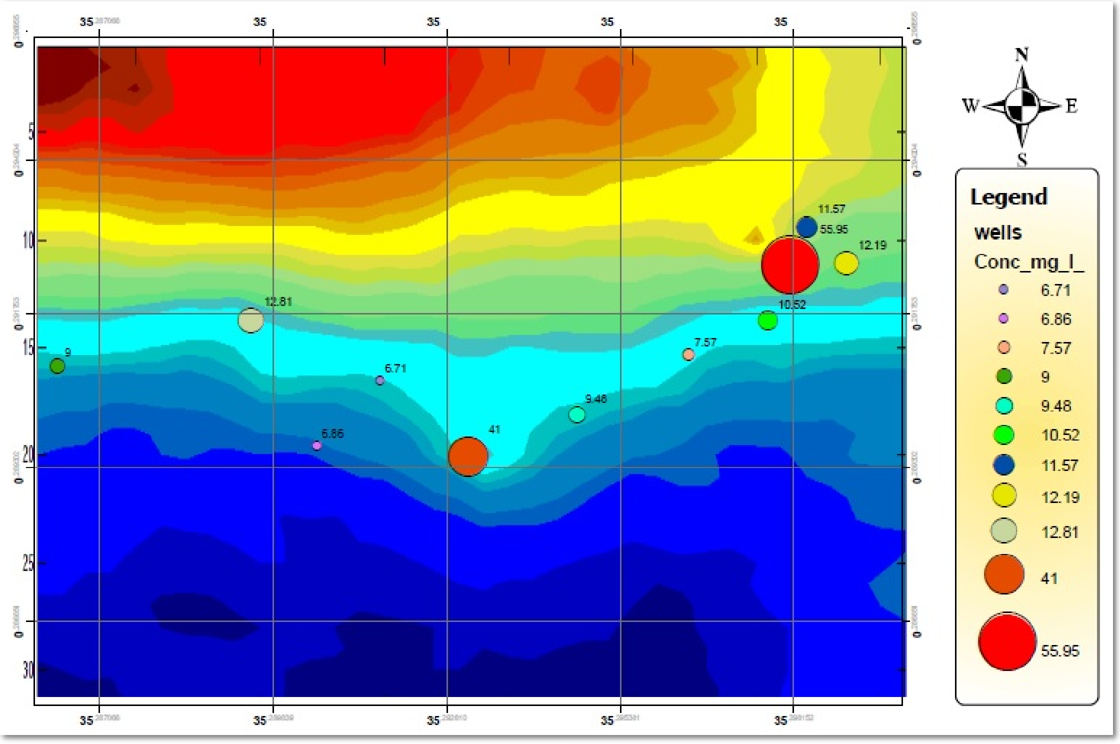

Figure 4.21. Study area with data and contours

4.4.7 Study area with data and line contours

The Figure 4.22 represent the same variation of concentration at different points on the study area except that the variation of the concentration in different areas is represented by concentration contour lines.

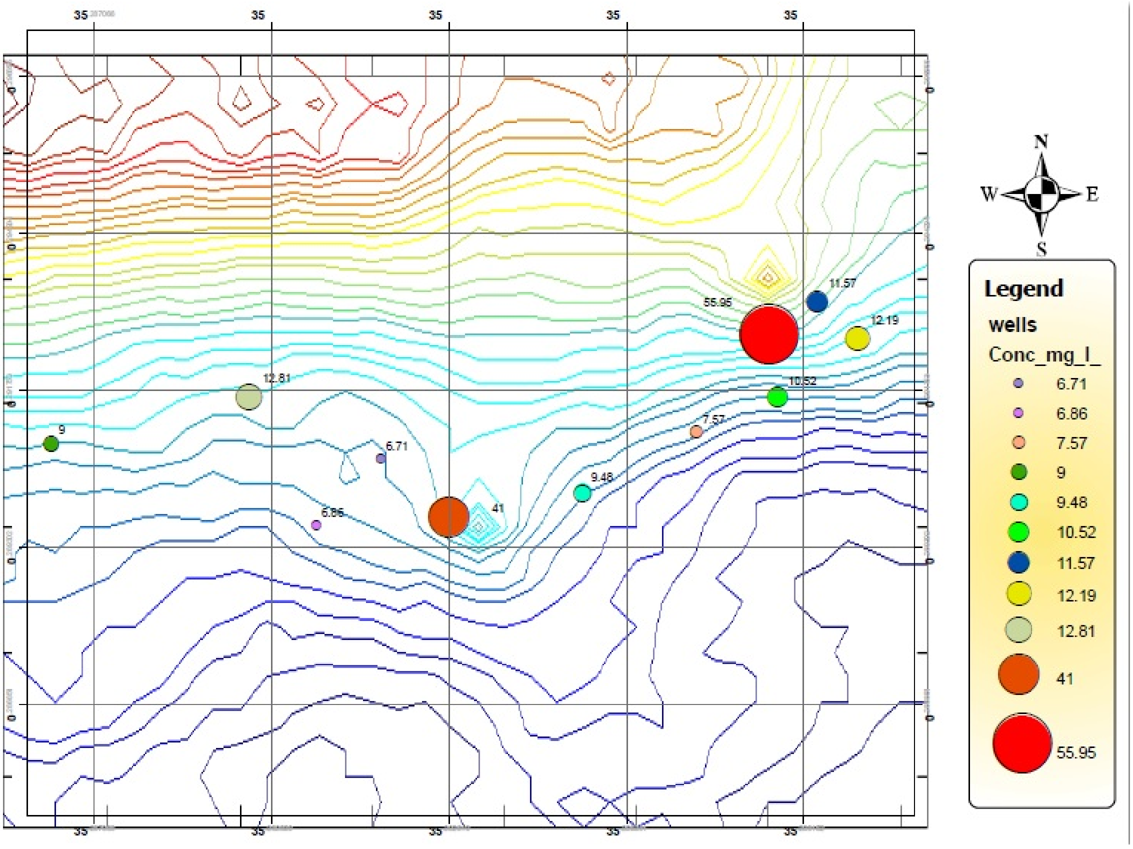

Figure 4.22. Study are with data and contours

4.4.8 Band of collected data

The observation of the Figure 4.23 shows that all our samples were collected in the same band. According to the variation of the concentration represented by Figures 4.21 and 4.22, the variation of the concentration in different wells should be small. The unexpected variation of concentration in consecutive wells as observed in the Figure 4.24 is due to the high concentrated sources located near the wells. The most contaminated well with 55.95 mg/l is located at 10m from the cowshed and the well located at around 100m from the cowshed has only 11.57 mg/l. This difference in concentration is due to the decay of nitrate as it diffuses through the soil.

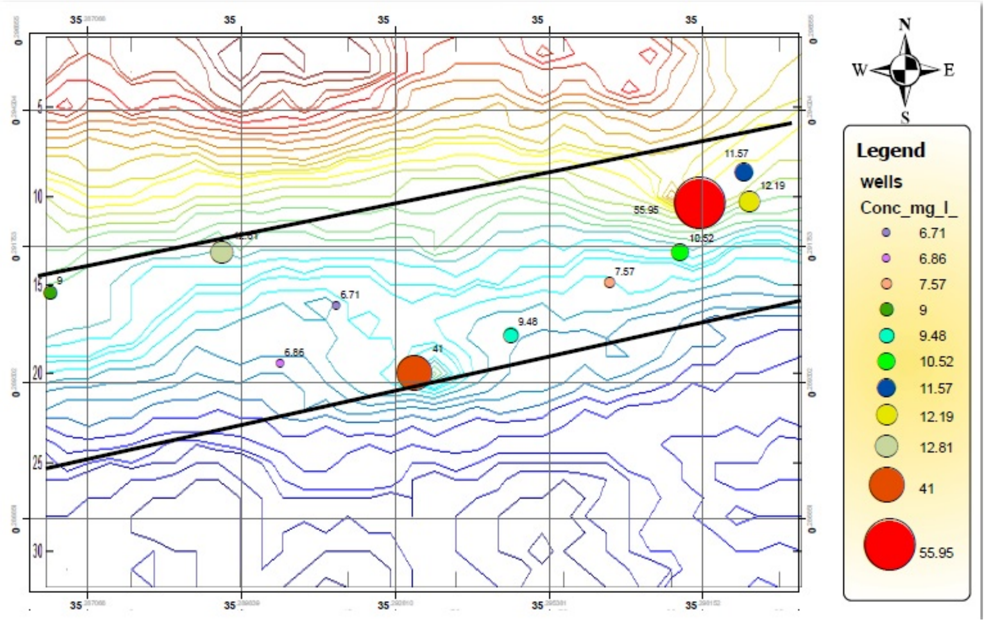

Figure 4.23. Band of collected results

4.4.9 Graphic representation of the variation of concentrations

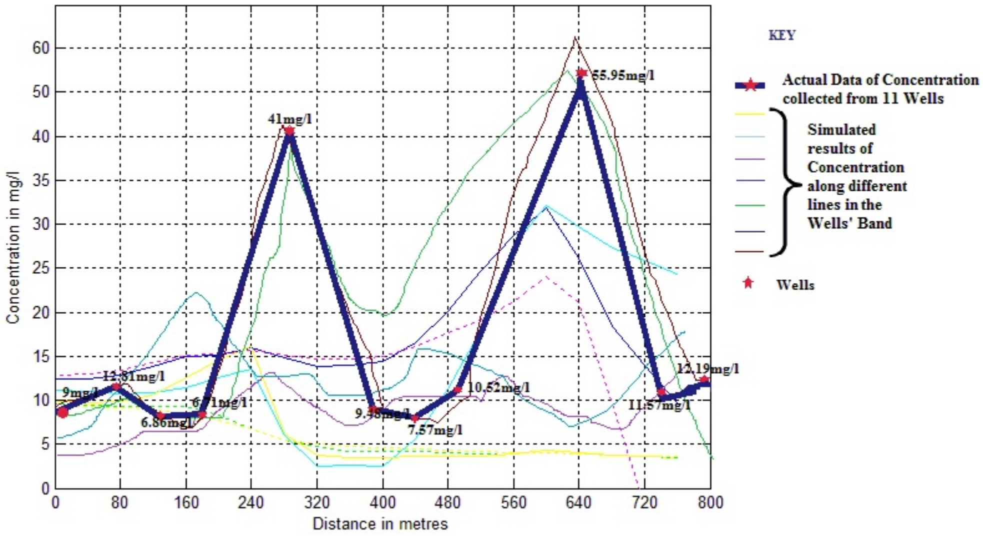

Figure 4.24. Variation of concentrations

The graph in Figure 4.24 shows that the concentration is not changing with distance. As discussed in previous sections, concentrations are changing depending on the sources of contamination as the source of contamination is not unique. So, a well located near a source of contamination is more contaminated by that source of contamination more than another source of contamination which is located far away from the well. According to the analytical solution of the diffusion equation which is Gaussian, the concentration should be reducing from the well located near the source of contamination compared to the well located far away from the source of contamination. Figure 4.24 shows that the variation of the concentration represented by different graphs in the figure and located in the band in Figure 4.23 are not very different, that is, the graphs are also located in the same band.

From the result of the research by (Jasa, Skipton, Varner, & Hay, 1996), the tested wells were not all contaminated since the Maximum Concentration Level (MCL) of nitrate is 10 milligrams per litter (mg/l).

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The model formulated by this study produced good results since the simulated results, the laboratory analysis and the analytical solutions are similar. This study solved the diffusion equation which governs the movement of contaminants from the area of disposal to groundwater. The analytical solution of the diffusion equation discussed in Section 4.2 showed that the evolution of the contamination by a diffusing contaminant obeys the Gaussian function. This means that the contaminant is normally distributed in the area of application.

The results generated by the codes in Cases I, II, III, IV and V in Section 4.3 confirmed the result of the analytic solution of the diffusion equation. The numerical solutions showing the evolution of the contamination process were found in different context in a given domain with given boundary and initial conditions in the domain. The laboratory analysis provided evidence of existence of nitrate in the groundwater with the same variation as the simulated results and this validates our mathematical model. The laboratory analysis results showed that the wells located near the source of contamination are highly contaminated which are similar to the analytical and numerical results of the diffusion equation. The concentration of nitrate in five out of eleven tested wells were bellow the M.C.L which is 10mg/l which means that other six tested wells are highly contaminated.

The work done in this thesis was based on finding a mathematical model for determining the concentration of a specific agricultural chemical contaminating underground water by diffusion with a particular focus on nitrate as groundwater contaminant, but, this model can be used for any diffusing contaminant.

5.1.1 Model formulated by the present study

The model of the present study was formulated according to the definition of the model by (Velten, 2009). The model was formulated by giving the components of the triplet (S, Q, M) in the definition 3.1.4 which are:

- The system S: the soil where the chemical diffusion and water contamination take place,
- The question Q to be answered by the model is: What is the concentration of a particular chemical at given time and point in the underground water when the chemical diffuse from the disposal point?
- The set of mathematical statements M to be used to respond to the question Q is: the diffusion equation and its solutions in different context,

in the present model.

5.2 Recommendations

5.2.1 Recommendations for Future Work

This thesis described how a contaminant diffuse from the disposal point to other points. The research formulated a mathematical model to predict contaminant transport and its distribution in the area surrounding the disposal point. Much work still remains to be done but this recommendations give some of them and these can be the subject of further research.

Soil and contaminant properties

The present study focused on nitrate but all contaminants do not behave the same way. Studies using the formulated model focusing on different chemicals are needed in order to understand how to avoid their side effects. To improve the model of the present study, since the literature show that chemicals used in agriculture can change properties and generate different types of chemicals, studies analyzing how chemicals are changing properties and generating other chemicals with time is necessary. The time taken by different chemicals while moving in soil is different from one soil to another, by this, researchers are advised to determine the diffusion coefficient of different chemicals in different types of soil.

Modification of transport properties

Using the model formulated by this study, the concentration of a given chemical can be calculated or predicted at any time and distance after the disposal. From this result, researchers can improve the formulated model by putting their efforts in changing the properties of the contaminant, so that it can move fast or slowly according to the observations and what is to be reduced. This can be done taking into consideration the fatal quantity (M.C.L) of a chemical. The determination of the M.C.L of different contaminants is also an interesting topic for future research since chemicals are so many and some of their properties are not well known.

Effect of natural organic matter and domestic wastes

The nitrate chemical discussed in this thesis can be generated by agrochemical fertilizers, domestic wastes, decompositions of plants and animals,etc..This thesis would like to recommend future researchers to put their efforts in quantification of nitrate generated by different plants, animals and other types of wastes. This can improve the formulated model by supplying the initial concentration to be used in different cases. This recommendation is made because after harvesting, the debris of some plants are collected in the compost for future use as manure. When they decompose, they produce a certain quantity of nitrate and other contaminants probably, which must be assessed and regulated. The domestic wastes are also used to prepare manure for agricultural use. For that purpose, the domestic wastes are also collected in a hole sometimes for a long period and their decomposition keeps contaminating the underground water.

5.2.2 Recommendations for agrochemicals users, governments and manufacturers

Recommendations for agrochemicals users

From this research, users of agrochemicals especially nitrogen fertilizers which produce nitrate during their decomposition are advised to build their wells far from the farm and other sources of contamination such as dumping and places where animals like cows stay permanently. According to the results obtained by laboratory analysis of our samples, the sample taken at a distance of 100m from the source of contamination present a very big difference in nitrate concentration from the sample which is taken at 10m from the source of contamination. Then, agrochemicals users, cattle keepers and the population near waste collection places are advised to build their wells at 100m at least from the source of contamination.

Recommendations for government toward manufacturers

Many people open their companies looking for money and do not take much care of the side effects of their activities. This thesis, would like to advise governments which are suppose to take care of the investors and consumers to control the quality of the products which are sold to their populations. The manufacturers should sponsor or pay researchers to conduct studies on the side effect of their products in different contexts and at different places as the quality of the soil and the climate can influence the reaction of the chemical. The governments should control the indications given by manufacturers to users since manufacturers may just want to popularize their products by telling users that their products can help them to increase the production without telling them how they should avoid the side effects of the products. Governments should employ their own experts to analyze the effect of the chemicals on the human being health before allowing the manufacturers to sell their products for use. The recommendations made in this section are formulated based on the information collected from some farmers using underground water but not reported in this work.

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Appendix A

Matlab Programs

A.1 Main function

```
function Diffusion
 % This is the main function. Within this function the meshes are defined,
 % PDEPE is called and the results are plotted
 clear; close all;

 %% Parameters
 P(1) = 1; %Diffusion coefficient D
 P(2) = 1; %c0
 L = 1; %Length of domain
 maxt = 1; %Max. simulation time
 m = 0; %Parameter corresponding to the symmetry of the problem (see help)
 t = linspace(0,maxt,100); %tspan
 x = linspace(0,L,100); %xmesh

 %%
 % Call of PDEPE. It needs the following arguments
 % m: see above
 % DiffusionPDEfun: Function containg the PDEs
 % DiffusionICfun: Function containing the ICs for t = 0 at all x
```

```
% DiffusionBCfun: Function containing the BCs for x = 0 and x = L

% x: xmesh and t: tspan

% PDEPE returns the solution as multidimensional array of size

% xmesh x tspan x (# of variables)

sol = pdepe(m,@DiffusionPDEfun,@DiffusionICfun,@DiffusionBCfun,x,t,[],P);

u = sol;


%% Plotting

% 3-D surface plot

figure(1)

surf(x,t,u,'edgecolor','none');

xlabel('Distance x','fontsize',20,'fontweight','b','fontname','arial')

ylabel('Time t','fontsize',20,'fontweight','b','fontname','arial')

zlabel('Species u','fontsize',20,'fontweight','b','fontname','arial')

axis([0 L 0 maxt 0 P(2)])

set(gcf(), 'Renderer', 'painters')

set(gca,'FontSize',18,'fontweight','b','fontname','arial')


% 2-D line plot

figure(2)

hold all

for n = linspace(1,length(t),10)

plot(x,sol(n,:),'LineWidth',2)
```

```
 end
 xlabel('Distance x','fontsize',20,'fontweight','b','fontname','arial')
 ylabel('Species u','fontsize',20,'fontweight','b','fontname','arial')
 axis([0 L 0 P(2)])
 set(gca,'FontSize',18,'fontweight','b','fontname','arial')
```

A.1.1 Function defining the boundary conditions

```
function [pl,ql,pr,qr] = DiffusionBCfun(xl,ul,xr,ur,t,P)
 % Boundary conditions for x = 0 and x = L;

 % Extract parameters
 c0 = P(2);

 % BCs: No flux boundary at the right boundary and constant concentration on
 % the left boundary
 pl = ul-c0; ql = 0; pr = 0; qr = 1;
```

A.1.2 Diffusion initial conditions function

```
function u0 = DiffusionICfun(x,P)
 % Initial conditions for t = 0; can be a funciton of x
 u0 = 0;
```

A.1.3 Function defining the variables used by pdepe solver

```
function [c,f,s] = DiffusionPDEfun(x,t,u,dudx,P)

 % Function defining the PDE


 % Extract parameters

 D = P(1);

 % PDE

 c = 1;

 f = D.*dudx;

 s = 0;
```

A.2 Matlab code generating the contours

function [P,V]=Contours(Grid,K,q)

```
Nx=Grid.Nx; Ny=Grid.Ny; Nz=Grid.Nz;

N=Nx*Ny*Nz;

hx=Grid.hx; hy=Grid.hy; hz=Grid.hz;

L = K.^(-1);

tx = 2*hy*hz/hx; TX = zeros(Nx+1,Ny,Nz);

ty = 2*hx*hz/hy; TY = zeros(Nx,Ny+1,Nz);

tz = 2*hx*hy/hz; TZ = zeros(Nx,Ny,Nz+1);

TX(2:Nx,:,:) = tx./(L(1,1:Nx-1,:,:)+L(1,2:Nx,:,:));

TY(:,2:Ny,:) = ty./(L (2,:,1: Ny-1,:)+L(2,:,2:Ny,:));

TZ (:,:,2: Nz) = tz./(L (3,:,:,1: Nz-1)+L(3,:,:,2:Nz));
```

```
% Assemble TPFA discretization matrix.

x1 = reshape(TX(1:Nx,:,:),N,1);

x2 = reshape(TX(2:Nx+1,:,:),N,1);

y1 = reshape(TY(:,1:Ny,:),N,1);

y2 = reshape(TY(:,2:Ny+1,:),N,1);

z1 = reshape(TZ(:,:,1:Nz),N,1);

z2 = reshape(TZ(:,:,2:Nz+1),N,1);

DiagVecs = [-z2,-y2,-x2,x1+x2+y1+y2+z1+z2,-x1,-y1,-z1];

DiagIndx = [-Nx*Ny,-Nx,-1,0,1,Nx,Nx*Ny];

A = spdiags(DiagVecs,DiagIndx,N,N);

%A(1,1) = A(1,1)+sum(Grid.K(:,1,1,1));

A(1,1) = A(1,1)+sum(Grid.K(:,10,10,1));

% Solve linear system and extract interface fluxes.

u = A\q;

P = reshape(u,Nx,Ny,Nz);

V.x = zeros(Nx+1,Ny,Nz);

V.y = zeros(Nx,Ny+1,Nz);

V.z = zeros(Nx,Ny,Nz+1);

V.x(2:Nx,:,:) = (P(1:Nx-1,:,:)-P(2:Nx,:,:)).*TX(2:Nx,:,:);

V.y(:,2:Ny,:) = (P(:,1:Ny-1,:)-P(:,2:Ny,:)).*TY(:,2:Ny,:);

V.z (:,:,2:Nz) = (P(:,:,1:Nz-1)-P(:,:,2:Nz)).*TZ(:,:,2:Nz);
```

A.3 Matlab code generating different graphs in the band

```
function Cross_Section

clear all,

c = 20;

Grid.Nx=c; Grid.hx=1/Grid.Nx;

Grid.Ny=c; Grid.hy=1/Grid.Ny;

Grid.Nz=1; Grid.hz=1/Grid.Nz;

data = randn(3,Grid.Nx,Grid.Ny);

Grid.K = exp(7*smooth3(smooth3(data,'gaussian',3),'gaussian',3));

N=Grid.Nx*Grid.Ny*Grid.Nz;

q=zeros(N,1);%Initialize q to have zeros

q([1:N])=[xlsread('data00.xls')];% Set the initial elements of q as per data0.xls

%P=hydrology(Grid,Grid.K,q);

P=Contours(Grid,Grid.K,q);

figure

plot(P(1,:),'r');hold on

plot(P(2,:),'b');hold on

plot(P(3,:),'c');hold on

plot(P(4,:),'k');hold on

plot(P(7,:),'g');hold on

plot(P(10,:),'y');hold on

plot(P(11,:),'r:');hold on
```

```
plot(P(13,:),'m:');hold on

plot(P(14,:),'c:');hold on

plot(P(17,:),'m');hold on

plot(P(19,:),'g:');hold on

plot(P(20,:),'y:');hold on

%mesh(P);

%surf(P);grid off

%contourf(P,11);
```