NUMERICAL MODELING OF HEAVY METALS IN RIVERINE SYSTEMS IN ELDORET, UASIN GISHU COUNTY, KENYA

MUNENE EMILY NAITORE, BSc.
I56/23509/2011

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science (Physics) in the School of Pure and Applied Sciences of Kenyatta University

MAY 2018

DECLARATION

This thesis is my original work and has not been presented for a degree in any other university or for any other award.

Signature.. Date................................

Emily Naitore Munene (I56/23509/2011)

Department of Physics

SUPERVISORS

We confirm that the work reported in this thesis was carried out by the candidate under our supervision.

Signature.. Date................................

Dr. Nadir O. Hashim

Department of Physics

Signature.. Date................................

Dr. Willis J. Ambusso

Department of Physics

DEDICATION

This work is dedicated to my dear parents Mr. and Mrs. Munene, my sisters and my husband Duncan and sons Jeremy and Munene. All your love and generosity are marked in my heart forever. To all I say God bless you.

ACKNOWLEDGEMENTS

I would like to honor my supervisors Dr. Nadir Hashim and Dr. W.J. Ambusso and express my sincere gratitude to them for their positive criticism, suggestions, and encouragement. I am grateful for their availability for consultation, even when they were pressed with other responsibilities. I also acknowledge the entire teaching and non-teaching staff of Physics Department, Kenyatta University. Thank you for your support in the course of this study.

To my colleagues (Stephen Kamau, Geoffrey kirui, Robert Magare, Josphat Kariuki, Mavyline Motari, Frt. James). Sharing academic knowledge through class discussions and personal consultations that made it possible for all of us to pass over from course work to research work. I acknowledge the assistance from Chemistry Department, Kenyatta University, for letting me use their facilities and for their technical assistance.

Many thanks also to the National Commission for Science, Technology and Innovation (NACOSTI), Kenya, for the financial support towards my MSc research.

Finally I greatly appreciate the moral support from my parents, my husband and my siblings for their love and support both spiritually and materially. God bless you abundantly.

All glory to God Almighty the creator of the heavens and earth. May all the praise, wisdom, thanks, power and strength be to him forever and ever, Amen.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS AND ABBREVIATIONS

ADE	Advection Dispersion Equation
ADZ	Aggregated Dead Zones
EMC	Eldoret Municipal Council
GIS	Geographic Information System
GoK	Government of Kenya
IFDM	Integrated Finite Difference Method
KNBS	Kenya National Bureau of Standards
PDE	Partial Differential Equations
RMSE	Root Mean Square Error
SPARROW	Spatial Referenced Regressions on watershed Attributes
UNEP	United Nations Environment Programme
WHO	World Health Organization

ABSTRACT

Heavy metals are gradually being added into water resources due to the rise in Municipal, industrial and agricultural activities. The fate of heavy metals being in water systems is mainly controlled by transport processes. Transportation of heavy metals by rivers can be both as metal in solution and adsorbed to suspended solids. A one dimension environmental model has been developed in this work to simulate the transport of heavy metals discharged into a riverine system. The model has been developed by solving a mass transport equation. The governing equation describing the mathematical model is discretized implicitly by integral finite difference method (IFDM). Heavy metal samples were collected along river Sosiani as it passes through Eldoret town. The concentration levels of copper, zinc and lead metals was analysed. The concentration values obtained from the heavy metal analysis were above WHO standards of 0.2mg/l and 0.05mg/l for copper and lead respectively for drinking water. The model developed in this study was validated for spatial variation of heavy metal concentration. The model considered multiple sources of pollutants. During validation, field parameters like flow rate and dispersion coefficient were varied so as to reduce the differences between simulated and measured values. There was close agreement between the measured and the simulated values. Correlation coefficients of 0.8879, 0.7907 and 0.8644 for zinc, copper and lead were respectively obtained. The results of the dissolved heavy metal concentrations agree well with the measured data. The results obtained in this study show that the model demonstrated good capabilities for describing spatial characteristics of heavy metals in riverine systems. It can be concluded that by using mass balance model it is possible to simulate heavy metal transport in surface waters for risk assessment purposes and is shown to be a useful management tool in monitoring water quality in the River Sosiani.

CHAPTER ONE

INTRODUCTION

1.1 Background

Concern and awareness of riverine contaminant problems particularly with regard to water pollution has been on the rise (Falconer and Lin, 2003). Increase in municipal, industrial and agricultural activities, contribute significantly to water pollution problems in natural water bodies causing significant negative effects on resources and the environment. There is need to control and prevent pollution of rivers since they make up the most main inland water resources. In order to manage these rivers effectively, reliable information on the quality of water is of essence.

In the study of water pollution problems, hydrodynamicists, hydrologists and environmental scientists widely use dispersion processes in rivers. Concentration change of any element due to dispersion phenomena is an important factor in evaluating the pollutant behavior in rivers (Kimwaga *et al.,* 2011).

A powerful and essential tool for the solution of problems associated with water resources is provided by numerical methods (Wood, 1983). Numerical models use the original Partial Differential Equations (PDE) form of Advection Dispersion Equations (ADE) and have specific initial and boundary conditions which depends on the type of the source releasing the pollutants. This enables the use of numerical model to simulate point and multiple kinds of release. With the use of models, it is possible to integrate all the temporal and spatial variables into the prediction of water quality. The important variables that must be properly understood are the pollutant travel time in a river, the pollutant dispersion rate, the change in peak concentrations and the patterns that result from the pollutant movement.

There is the extensive use of mathematical modeling in the management of water resources for hydrological purposes (Coulthard and Macklin, 2003). It is now a useful management tool for forecasting the effect of different management policies. An example is in evaluating the water quality of a water body after a new waste water treatment plant has been constructed, or assessing the impact of the growth in industries and increased discharges.

Models can be one, two or three dimensional. One dimensional is whereby series of computational elements extend downstream and describing the longitudinal gradients that are prevalent in streams. Two dimensional considers both the longitudinal and vertical flow variations and three dimensional the flow variations considered are longitudinal, vertical and lateral.

This research focuses on the development of a one dimensional model which solves the mass transport equation which governs the concentration of heavy metals in riverine systems. The transport equation which incorporated the sources and sinks and the adsorption terms, was solved so as to predict the concentration variation of heavy metals in rivers. The equation was discretized implicitly using integral finite difference method to generate mathematical algorithms that were solved. To solve the tri-diagonal system of equations, Thomas algorithm subroutine was used. The concentration distribution profiles generated were analyzed and predictions made.

These results were validated using data of heavy metal concentration collected from River Sosiani in Eldoret to demonstrate the usefulness of the model as a water quality assessment tool for the area of study.

1.2 Heavy metals and their toxicity

Heavy metals refer to a group of metaloids with a specific gravity of 5.0 or greater according to Alloway and Ayres (1993). These metals include lead, mercury, chromium, arsenic, calcium, copper and zinc among others. Their occurrence in the environment is natural, and when they are discharged into the environment, they are transported by air and water. Their concentrations at any given point depend on local geology and additional anthropogenic activities such as agriculture and mining (Wilson and Pyatt, 2007).

The origin of pollutants can be from either point or non-point sources which vary in both time and space (Hermond and Fechner, 1994). Point sources introduce pollutants at well-defined locations along the water course while non-point sources are distributed along the watercourse. Examples of point sources include discharges from factories and sewage treatment plants while those of non-point sources include agricultural run-off, mining waste and industrial activities. Sources can further be divided into continuous and instantaneous sources. Continuous sources introduce pollutants to the stream for an extended period of time. Instantaneous sources add pollutant mass to the stream over very short periods. An example is an accidental spill where contaminants enter a stream in a matter of minutes.

Pollution of natural water sources interferes with the normal use of public water supply, recreation, and water aesthetics and may cause serious health problems (Ochieng`, 2000). Many of the chemicals and substances that are found in water bodies may be naturally occurring. The key in determining chemicals natural component is their concentration. At high concentrations, these substances can have adverse effects on aquatic flora and fauna.

Low concentrations of heavy metals in living organisms are essential for enzymatic activities and many biological processes, but they become toxic at high concentration (Agbozu *et al.,* 2007). Some heavy metals such as mercury, silver, lead and nickel are highly toxic elements (Richardson and Niebor, 1980) and others such as iron, copper and zinc are necessary for plants and animals.

Heavy metals can enter an organism body through ingestion, inhalation, and absorption through the skin or mucous membranes. Once absorbed in the body, these heavy metals compete with other ions and bind to proteins, leading to impairing of enzymatic activity damaging many important organs within the body. The ability of heavy metals to accumulate in living tissues over time reaching toxic levels is a common feature and this leads to a phenomenon referred to as bioaccumulation. When the biological half-life of an element is long, there is a greater risk of chronic poisoning though the environmental levels of the toxin may not be high (Meador *et al.,* 1995). Even for the heavy metals that are necessary in the body, their concentration above the optimum levels may pose serious health concerns. Prolonged exposure of an organism to heavy metals can cause slow progress in physical, muscular and neurological degenerative process and lead to emergence of allergies and cancer (Khan *et al.*, 2009).

Signs of heavy metal poisoning are; mental confusion, muscles and joints pains, recurrent headaches, short-term memory loss, gastrointestinal upsets, food intolerances, poor vision and chronic fatigue, among others. Cadmium is one of the potential human carcinogens, causing lung cancer and damage. Lead toxicity leads to malfunctioning of several organs in the body including the kidneys, liver, reproductive system, hematopoietic system, endocrine system and central nervous system (ATSDR, 1999). Exposure to lead metal has developmental and neuro-behavioral effects on feotusses, infants and children and high blood pressure in adults. Zinc toxicity causes vomiting, dehydration, abdominal pains, dizziness and lack of muscular imbalance. High copper levels in organisms contributes to many health problems which include; anemia, mental incapacitation, arthritis/rheumatoid arthritis; elevated blood pressure, Nausea/vomiting, hyperactivity, self-withdrawal, autism, stuttering, postpartum psychosis, insomnia, liver inflammation and enlargement, heart problems and cystic fibrosis (Alluri *et al.*, 2007).

1.3 Heavy metals in surface water

The existence of heavy metals in aquatic ecosystems is as a result of two main sources of pollution: natural process and anthropogenic activities. The main source being anthropogenic activities. Heavy metals occur in water bodies in colloidal, particulate, and dissolved phases, even if the concentrations in dissolved part are usually low (Kennish, 1992). Metal suspensions may be found in oxides, hydroxides, silicates, or sulfides; or may also be adsorbed in the sediments by silica, clay or organic matter. The dissolved part is generally ions or unionized multi-metallic chelates or complexes. The solubility of heavy metals in water is mainly controlled by the pH of the water, the concentration and the type of ligands on which the adsorption of the metal can take place, the mineral components, oxidation state of the systems and the redox environment of the system (Connell and Miller, 1984).

Heavy metals do not degrade, volatilize or decay and therefore transport processes control their fate in natural waters (Novotny and Salomons 1995). The heavy metals behavior in the aquatic environment is intensely affected by adsorption on organic and inorganic particles (Duinker *et al*., 1982, Valenta *et al*., 1986). The fraction of the heavy metals that is dissolved may be transported by the processes of advection and dispersion in the water column (Wu *et al*., 2005). Sediment dynamics govern the transportation of the fraction of metals in particulate form with the sediments. Fine clay silt in the water column poses as a potential threat to aquatic life since the silt acts as a source for the organic chemical and heavy metals entering or leaving the column.

Heavy metals are gradually and progressively being added into the water sources. This is through anthropogenic activities and natural phenomena such as the seepage of mineral ores. Their concentration in the dissolved phase as well as that adsorbed to the sediments mainly depends on the concentration levels of the metal in the inflow water stream (Pintilie *et al*., 2007). There has risen a great concern of heavy metals presence in the environment because of their elevated release, nature of toxicity and adverse effect on human beings.

1.4 Mass transport in rivers

The transport of a material by advection and diffusion is dependent on the hydrological and hydrodynamic characteristics of the particular environment. Concentration of heavy metals transported in riverine systems is simulated by numerically solving a set of governing differential equations. These equations describe the advection and dispersion of the pollutant by the water.

Numerical algorithms are used in solving the differential equations whereby these algorithms must satisfy several conditions that are important in making useful water quality simulations. Convergence conditions must be met by numerical schemes which are used in solving the governing transport equations and model rightfully the conservation and dispersion properties of the equation (Byun *et al.*, 2000). The solution of a convergence numerical scheme approaches the true solution of the corresponding partial differential equation as the grid spacing and time-step size become infinitesimally small. By reducing the sizes of the grid spacing and time-step, a numerical solution of any desired accuracy within finite precision bounds can be provided by a convergence numerical scheme. In the development of this dispersion model, integral finite difference is the numerical scheme used. The partial differential equations describing heavy metal transport include terms representing derivatives of continuous variables. Finite-difference methods are based on the approximating derivatives by discrete linear changes over small discrete intervals of space or time. If the intervals are sufficiently small, then all the linear increments will represent a good approximation of the true curvilinear surface.

Discretization of the governing equations is in space and time dimensions, allows the reduction of partial differential equation to simultaneous solution of a set of algebraic equations (Konikow, 1996). The equations are implicitly discretized where there are several unknown variables. Finite difference equations have to be converted to computer programs using an appropriate computer language.

1.5 Statement of the Research Problem and Justification

Discharges from manufacturing processes and wastewater from centers of pollution over several decades in many rivers have led to environmental damage. The introduction routes and the spread of heavy metals in the environment however have not been fully assessed. Understanding how these pollutants disperse from the initial discharge point as a critical step in developing strategies to address environmental pollution is of interest. This study focuses on developing a one dimensional model to describe the transport of heavy metals in riverine systems. The study is concerned in giving a better understanding of numerical methods that are used in predicting heavy metal transport and fate for impressions on the water quality of the area.

1.6 Objectives of the research project

1.6.1 General objective

The general objective of this study is to use theoretical methods in developing a numerical model for the transport and prediction of heavy metal contamination in riverine systems.

1.6.2 Specific objectives

The specific objectives of this study are:

1. To assess and compare the concentration levels of heavy metals along river Sosiani as it passes through Eldoret town.
2. To formulate the equations governing the dispersion of heavy metals discharged into riverine systems using theoretical methods.
3. To develop a computer program for numerically solving the equations describing the dispersion of heavy metals in rivers
4. To simulate and predict the spatial and temporal characteristics of the spread of heavy metal concentration in time and space.
5. To use field data from Sosiani River to validate the dispersion model and identify the sources and sinks.

1.7 Significance of the research project

Significant increase of heavy metals in the ecosystem has fuelled a lot of research on their fate and transport. This has led to the use of numerical models in simulating heavy metal transport in riverine systems. Numerical models provide a valuable tool in prediction of the transport and fate of dissolved heavy metals in surface waters. There is still the infrequent use of computer-based tools in predicting the dispersal of heavy metals, even though they can be relied on in decision-making by the regulatory authorities, marine environment agencies and industry (Ng *et al.,* 1996). Computer use has provided an opportunity in understanding and assessing our water resources better through various schemes testing and through comprehensive numerical model simulations.

A one dimensional environmental model developed in this work attempts to determine the variation of heavy metal concentration with time and distance discharged into a riverine system and give a better understanding on the fate and transport of heavy metals in rivers. The model is applied to River Sosiani in Eldoret, which is feared that it is heavily contaminated with heavy metals due to continuous effluents from anthropogenic activities around the town.

Figure 1.1: A section of river Sosiani where sampling took place. The presence of pipes indicates that the river water is used by the residents either for irrigation or domestic use.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pollution in River Sosiani

River Sosiani cuts across Eldoret town in Uasin-Gishu County. It is an example of natural water bodies facing a challenge of environmental degradation (UNEP, 1988). The river is threatened by uncontrolled pollution and is choking with pollution and its water volume declining. A major challenge in Eldoret town is domestic and industrial wastes. According to Nyakaana (1996), the river passes through areas where agricultural activities such as grain growing and horticultural production are practiced. Therefore, Sosiani River is of value both economically and environmentally in the western region of Kenya.

Sosiani River is facing alarming levels of pollutants originating from both point and non-point sources mainly caused by anthropogenic activities such as urbanization, industrialization, agriculture, municipal sewage disposal, population pressure and settlements within the Uasin-Gishu area. At Kipkenyo dumpsite, the waste material is not segregated and all nature of waste including medical waste garbage, waste from hotels and salons among others are evident. Water levels in Sosiani river have reduced drastically and marine life has been killed by the polluters who have turned it into a dumping site. The most contaminators along river Sosiani are the car wash sheds and the Kipkenyo dump site (Cheserek *et al.,* 2012).

Assessment of water quality variation on human health in the river Sosiani catchment in Kenya was done by Ontumbi *et al.*(2015). The results showed that there was presence of feacal coliforms in the water samples collected in river Sosiani, hence the possibility of water contaminant problems. Waterborne diseases like typhoid, diarrhea and cholera cases were reported in the nearby health facilities.

Heavy Metals concentration and Nutrient Loads along river Sosiani in Kenya were also assessed (Amadi *et al.,* 2013). Investigation of pollution loads was done to obtain data on level and nature of contaminations. Water, soil and sediment samples were collected from five sites and analyzed. UV spectrophotometric screening and colorimetric methods were used to determine the nitrates. Ascorbic acid and Olsen methods were used to determine phosphates. Phosphates and nitrates concentration levels were below the recommended values of Kenya Bureau of Standards (KEBS) which are 10.0 ppm and 3.0 ppm respectively. This is shows that the anthropogenic activities in the area do not affect the water quality as far as nitrate and phosphate levels. Wet digestion method was used to analyze heavy metals and the obtained values were above the set limits. Values of zinc were above the set standards of WHO of 0.50 ppm for drinking water and this led to the conclusion that water from Sosiani River was not safe to use domestically.

Heavy metals in water and sediments and their bio-concentration in plants in river Sosiani were assessed by Jepkoech *et al.* in 2013. The results showed that the levels of heavy metal concentrations in plants and water samples were within the accepted limits and others were above the WHO standards. It was concluded that there was a need to control point sources along river Sosiani that could be contributing to high concentrations of heavy metals. There should be continuous monitoring of the river pollution and appropriate monitoring protocol should be established.

Surface water pollution in river Sosiani was carried out by Kangogo in 2009. Critical analysis and library synthesis study of the state-of-the-art knowledge in land use and its related impacts within the river was studied. The results showed that the water from river Sosiani was unfit for domestic use since pollutants like coliform counts, fertilizers, and heavy metals were recorded to exceed WHO recommended levels in natural waters. It was noted that there was no regular garbage collection in many informal settlements and proper industrial treating devices. There was also no viable waste management practices coupled with little enforcement of environmental protection laws. To check this alarming situation, immediate measures were needed and the study therefore proposed mitigation measures on the negative impacts of the human activity on the pollution of waters of the study area.

2.2 Modeling pollution in rivers

A hydrodynamic Model for river Sosiani was developed by Kudenyo in 2013 as a water management tool. The model simulated the flow in the catchment area was used to give an understanding of the hydrology and hydraulics of the river. To simulate the discharge from river Sosiani, MIKE 11 HD software was applied. ArcView 3.3 GIS software was used to delineate the catchment of the river from topographical map sheets after digitization. Physical survey was used to obtain the geometrical parameters of the river. The model was calibrated and validated using streamflow measured at the catchment outlet that was collected for three years. The Efficiency Index (EI) and Root Mean Square Error (RMSE) were obtained to evaluate the reliability of the module. The EI and RMSE obtained were 0.75 and 0.050 m^3/s, respectively. However, the model tended to overestimate and underestimate very high and very low flows. For future model calibration and validation, it was recommended that stations to monitor the flow be set up at the identified sites to collect more data. It was found that this model is useful for various watershed management purposes, including the development of the river's water quality model.

Marusic *et al.* (2012) developed a two dimensional mathematical model of hydrodynamics and dispersion of pollutants in order to determine the fluoride dispersion for a sector of river Prut, the Ungheni town in Eastern Europe. The fundamental equation of advection dispersion was used for mathematical modeling of pollutant transport and dispersion and applied to the turbulent flow regime. The numerical simulation of hydrodynamics was performed by solving the system of equations. The numerical simulation of fluoride dispersion was performed and used the resulting hydrodynamics to calculate a solution of the equations using the finite element method. The obtained model can be used for modeling any other sector of the Prut river and can be useful in predicting and preventing emergency situations.

A two-dimensional numerical model was developed by Kyung-Suk *et al.* in 2011 for simulating the field flows and the radioisotope concentration distributions injected into the river. To examine the characteristics of transporting a pollutant and estimating the coefficients of dispersion in a river system, a tracer experiment using radioisotope was carried out. To estimate the flow patterns and the phenomena of dispersion in the river, radioisotope 82Br was used in the form of aqueous ammonium bromide. Underwater glass-vial crusher was used to instantaneously inject the radioisotope into the flow as a point source. Based on the radioisotope measured data, moment method determined the dispersion coefficients. The experimental results were compared with the measured results. The calculated results and the trajectory model developed to estimate the unknown source position showed reasonable within error range.

Schwarz *et al*. (2006) developed a SPARROW model, which uses watershed modeling technique to relate to measurements for quality of water at the monitoring stations network to water shed attributes containing the stations. The model consists of a non-linear regression equation which describes the transport non-conservative pollutants from point and diffuses sources on land to rivers network. The model predicts pollutant about the key pollutant sources and properties of the watershed that control transport over spatial scales.

A numerical and an analytical model were developed by Ani *et al*. (2010) for predicting contaminant transport in the Romanian Somes river. The model aimed at developing an efficient software framework for applications buildings that can cope with pollutants of different potential. It is dedicated to modeling pollutant transport by use of both numerical methods for solving and implementing the analytical solution of the underlying PDE. The modeling results provide information on the evolution of time and space for pollutant concentration. The results from the comparison of the two models reveal their restrictions and incentives.

A numerical model for pollutant dispersion in rivers based on CFD techniques was developed in 2004 by Modenesi *et al*. There was a special need to develop a three dimensional model that was to be fast and significant improvement in its performance. The results showed that the model had the capability of giving detailed information on the diffusion of soluble inert particles in a river. The model when required also accounts for the loss of volatized substances. The experimental data used was obtained from the Atibaia river in the state of São Paulo in Brazil, where there is discharge of effluent from numerous industries. The results show a good agreement with the experimental data.

A one dimensional partial differential equation hydrodynamic model was designed by Duarte *et al.* (1999). The model incorporated the ADZ modeling technique. The method is relatively recent to modeling dispersion processes and it gives accurate predictions of the time travel and dispersion of rivers downstream. A pollutant dispersion model based on the advection dispersion equations was also described for non-stationary flowing open channels. The performance of the two mathematical models was applied in the basin of river Mondego found in the central region of Portugal for evaluating numerical techniques performance reproducing the observed dispersion behavior of the river. There was a good agreement between the numerical models and the measured data. There was good agreement of the hydrodynamic model results with experimental data, which allows water quality impact assessment of different discharges scenarios in rivers.

A model was also developed by Yvetta in 2002 to determine pollutant transport in natural channel, upper part of the Ondava river in Slovakia. The numerical model was based on the solutions of advection-diffusion equation and on the stream tubes conception. It included also computation of self-purification effect, simulation possibility of arbitrarily situated unsteady pollution sources, and the influence of “dead zones”. The input data of the model was the geometric characteristics of the cross-sections and the profiles of the velocity in locations selected for the computed part of stream. The model showed that it is possible to estimate or predict the pollution transformation from the simulation results.

2.3 Modeling heavy metal dispersion in rivers

Heavy metal and sediment transport two-dimensional river flow model for natural watercourses was developed by Horvat *et al.* (2015). Heavy metal transport model was developed by the enablement of the active-layer implementation for the sediment transport computation because the occurrence of heavy metals in dissolved and adsorbed phases. The model accounted for pollutant moving in dissolved phase, adsorbed on bed-load and on suspended sediment, deposited on river bed in the active-layer or adsorbed in deeper strata sediment. Field measurements from a section of river Danube were used in conducting Simulations for water flow, heavy metal and sediment transport. Comparison between the pollutant concentration measured and the simulated values showed some disagreements, though as indicated by the field survey, the model reproduced the same orders of magnitude. The simulation values showed good agreement with the field data. It can be concluded therefore that the model developed is certainly applicable for the simulations of heavy metal transport in natural water bodies.

An environmental model was developed by Njiru (2013) to simulate the temporal variation of lead concentration released into a river system. The transport equation which governs the dispersion of lead concentration was solved to develop the model. The equation was discretised explicitly using finite difference method. A computer program was developed using c++ programming language which divided the river into blocks. A close agreement between the field and simulated results was realised, where a correlation coefficient of 0.9124 was found. The data of lead concentration in Nairobi river was used to calibrate and certify the model as well as make its predictions.

A two dimensional model for describing transport and transformation of heavy metals in fluvial rivers was formulated by Sui (2009). Basic principles of hydraulics, environmental chemistry, transport of sediments mechanics and recent improvements along with simplified three test cases were considered. The equations reflected in the model are; water flow and transport of sediment governing equations, transport and transformation equations of heavy metal contaminants, and equations of diffusion and convection for kinetics of adsorption and desorption of concentrations of heavy metal particulates on bed sediments, suspended and bed loads. The model was applied in calculating the transport and transformation of heavy metals in a flow that is steady, uniform and equilibrium laden sediment. The simulated data from the model presented a close agreement with the measured data. The transport and transformation of heavy metals in flows with laden sediment with riverbeds rich in clay, not only has the generality of the common tracer contaminants, but also possesses the transport-transformation characteristics which are brought about by the motion of sediment as exhibited by numerical simulation and theoretical analysis.

A steady state model describing the fate and transport of trace metals in a shallow water system was developed by Young-Soo Lee (2000). Settling and re-suspension of solids were defined through empirical equations relating a net sediment transport rate to average stream velocity. Adsorption and desorption kinetics were simulated based on inverse relationships formulated between suspended solids and partition coefficients. The model was successfully calibrated to two independent water quality surveys and validation was indicated from analysis of a third survey. The results of the statistical evaluation and spatial plots depicting predicted and observed concentrations of trace elements along the river generated by the developed model showed the developed model was suitable for use in the waste load allocation process in shallow river systems.

There is rise in public concern globally in relating to environmental matters citing some of the quality of water and problems of pollution that have always been considered on regular basis by river water managers. A hydro-environmental model was developed by Falconer *et al*. (2003) to simulate the water quality and flow, sediment transport and the predictions of concentrations of heavy metals in riverine systems. The model emphasized on the impact of some major variables in two fundamental hydro-environmental processes. The processes contain the coliform bacteria decay and heavy partitioning. For the case of heavy metal partitioning; velocity, suspended sediment and distributions of heavy metal concentration were studied. Then the model was applied to the Mersey Basin in United Kingdom to examine the sorption and desorption of metals dissolved onto, and from the suspended sediments in the basin. The concentrations of the sediments suspended agreed well with the field values, although there was the peak level underestimation by the model for the concentration of suspended sediment.

A model for assessing water quality in estuaries was developed by Veselinka *et al.* (1998) to simulate the spatial distribution of heavy metals, under typical sediment suspension and hydrodynamic flow regimes. The model was linked to the hydrodynamic model, a salt transport model and a suspended sediment model which were constructed earlier. The observations made agree well with the simulated values for the heavy metal distributions, sediment suspension and estuary salinity. The profiles in the water column calculated for heavy metals in dissolved and sorbed form indicate maximum heavy metal accumulation in the turbidity zone. Concentrations tend to diminish near the sea due to polluted fluvial sediments mixing with unpolluted marine sediments. The study concluded that a small portion of heavy metals enters the sea.

Rona and Steef (2003) developed a large-scale GIS-based model for water quality. The model described heavy metal loads as an emission function from point and non-point, surface runoff, types of soils, land use and hydrogeology. The model results were compared with the experimental values for loads of heavy metal from Elbe Basin in Central Europe and showed reasonable agreement. The uncertainty analysis demonstrated that the model simulations reliability affected directly by the quality and distribution of the input data like soil data, land cover data, emission data and rainfall data. The analysis also indicated that the present suggested measures were not enough in achieving quantity reductions of loads of heavy metals in the basin.

Lack of river interaction description with the floodplains is another model shortcoming.

This study is aimed at assessing the concentration levels of zinc, lead and copper metals in the dissolved phase in river Sosiani giving an overview of the extent of heavy metal pollution in this river .This is because the area which this river passes has experienced growth in industries and urbanization in the last five years. The study also focuses in modeling the transport of the heavy metals concentration in riverine systems in one dimension. The governing transport equation will be discretised implicitly using integral finite difference method. Most of the described studies have used explicit scheme of discretization. The model will incorporate the hydraulic flow characteristics of rivers where the parameters will be a function of time since the flow is unsteady. Spatial and temporal variation of concentration of heavy metals will be emphasized in the study. The concentration levels of heavy metals in river Sosiani will be used to validate the developed model. The study will use the strengths of the above described studies, minimizing the shortfalls.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Introduction

A discussion of sample collection and analysis, the pollutant transport processes, the mathematical equations governing contaminant transport of pollutants in rivers and the discretization procedures and their implementation are presented in this section. Procedure code for implementing algorithm derived from numerical solution of the governing equations is discussed.

3.1.1 Sample collection and preparation

Sampling was done along river Sosiani. Water samples were collected from each of the seven stations using 0.5 L plastic bottles which had been cleaned earlier. The plastic bottles were rinsed with the river water, before collecting the samples. Without infiltration, the collected water samples were digested with 5 ml of nitric acid to $pH < 2$. The acid was added to acidify and preserve the water samples.

To prepare the samples for analysis, a sample from each sampling bottle was mixed thoroughly by shaking. A 50 ml of water sample was pipetted into a digestion flask. The sample was brought to boiling slowly on a hot plate controlling the temperature at 70^0 C evaporating it to about 15 ml, followed by addition of 3 ml concentrated nitric acid and 5 ml concentrated sulphuric acid while continuing heating until the solution cleared and brown fumes were no longer evident. The digested samples were cooled and filtered then topped to the mark with de-ionized water. Using Atomic Absorption Spectrophotometer the digest was analyzed for total copper, zinc and lead metals.

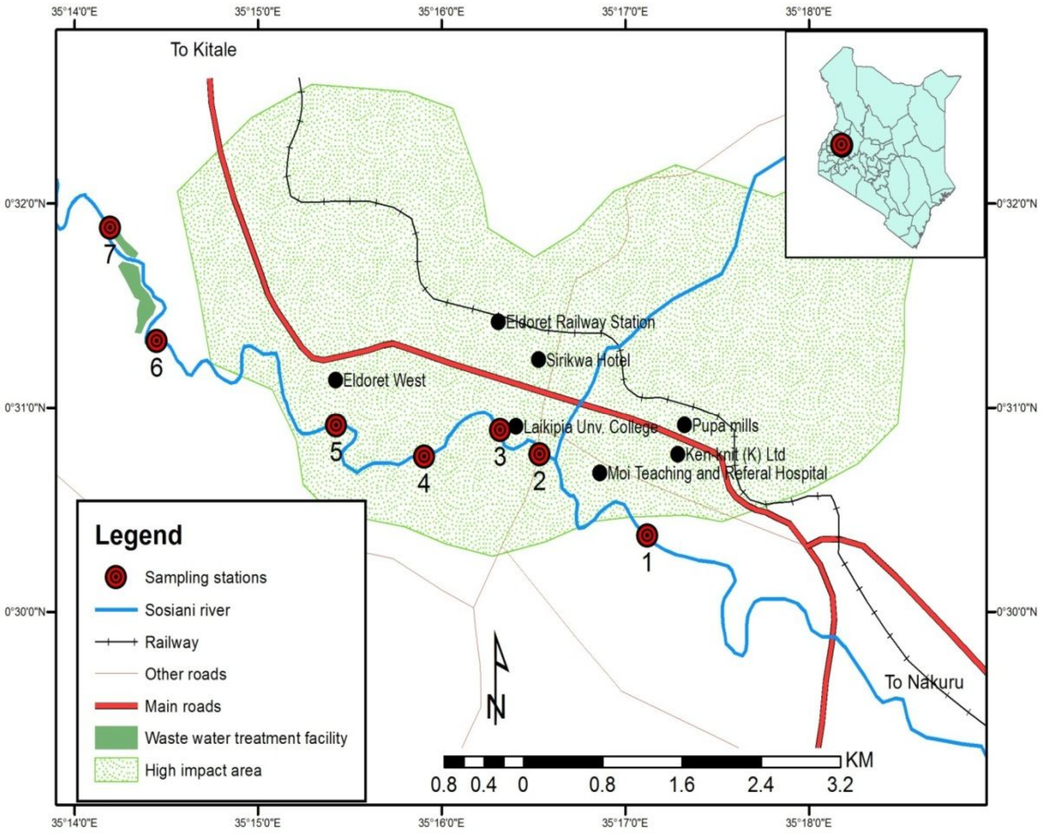

Figure 3.1: Location of the study area showing the seven sampling sites along Sosiani river. (1. MTRH, 2.Langas bridge, 3. Pioneer, 4.Kipkaren, 5. West Indies, 6.Kipkenyo dumpsite, 7.WWTF)

3.1.2 Sample Analysis

To analyze the concentration levels of the heavy metals in the water samples, the technique of atomic absorption spectrophotometry is used. The technique measures the quantity of energy the sample absorbs. An atomic absorption spectrophotometer possesses a light source; i.e a lamp, sample cell, monochromator, a detector and an output device. When a sample solution is aspirated into flame, the sample element is changed into atomic vapour of that element. Some atoms are thermally excited by the flame whereas most of them remain in the ground state. The light source i.e the hollow cathode lamp of that specific metal emits a radiation of a specific wavelength which is absorbed by the ground state atoms. Each element to be determined requires a different lamp. A specific wavelength which is absorbed by the sample is selected by a monochromator excluding other wavelengths. The wavelength of radiation given off by the lamp is similar as that of the absorbed by the atoms in the flame. The amount of energy adsorbed by the sample is measured in the form of light photons. A detector measures the light wavelengths transmitted by the sample, and compares the wavelengths with wavelengths that had passed through the sample originally. The light signal is converted into an electrical signal which is equivalent to the intensity of light by the detector. The resultant signal appears in the readout as energy absorption peaks at distinct wavelengths. A schematic diagram of an atomic absorption spectrophotometer is given in figure 3.2.

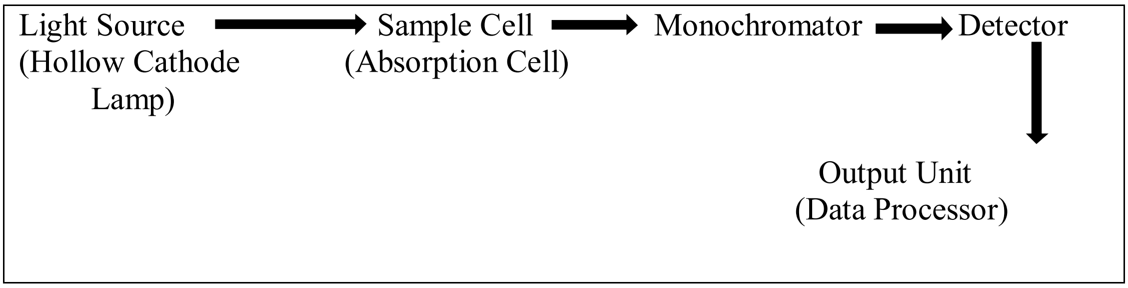

Figure 3.2: Schematic diagram of an atomic absorption spectrophotometer.

The energy necessary for an electron to leave an atom is known as ionization energy. This energy is specific to each chemical element. A characteristic spectral line is emitted by the atoms of a specific element. Due to the uniqueness in the configuration of electrons in the outer shell of an atom, we get wavelengths with distinct pattern for each atom at which it absorbs energy. This uniqueness enables the sample to be analysed qualitatively. Beer-Lambert law is used in the calculation of the mass of any element. This law states that the amount of energy absorbed in the sample is proportional to the concentration of the element in the sample and the path length (thickness of the sample solution). The law is usually written as:

$$A = a(\lambda) * b * c \qquad (3.1)$$

Where A is the absorption measured,

$a(\lambda)$ is a coefficient of the wavelength absorption,

b is the path length (solution thickness) and

c is the analyte concentration

More radiation is absorbed when the number of atoms in the vapour is high. A calibration curve which is obtained by use of known concentration standards, determines the concentration of the element in the sample. The amount absorbed by the standard is matched with the calibration curve enabling the calculation of the concentration of the said metal in the unknown sample.

3.2 Theory of surface water transport processes and equations.

The basic equations for fluid motion and transport consist of conservation equations for water mass, momentum and constituent mass form the basis for simulating changes in water body hydrodynamics, flow and volumes, velocities and water surface elevation or depths. In order to simulate the transport of water quality constituent, knowledge of fluid flows and volumes are necessary. These equations are advective-dispersive equations or the mass balance equations used in water quality simulation.

3.2.1 Physics of constituent transport process

Water quality changes in rivers are due to physical transport and exchange process. The basic principle of transport phenomena is about exchange of energy, mass or momentum between systems on fluid mechanics, heat and mass transfer. Transport phenomena describes the process that take a system of particles from a non-equilibrium state to an equilibrium state, from an equilibrium state to a non-equilibrium state, or from one non-equilibrium state to another.

The transport of a constituent is effected by two main processes namely advection and dispersion. They may be accompanied with chemical or physical processes such as adsorption and absorption. The adsorption and absorption rates are expressed as functions depending on concentrations of the analyzed substances within the phases participating in the transport. Advection is the movement of contaminants due to the river flow. Dispersion is the spreading and mixing of contaminants and includes combined effects of molecular diffusion, mechanical mixing and transverse and vertical shear mixing. Advective and diffusive processes can usually be considered independently. There is movement in the centre of the mass transported downstream in advection, while the concentration mass spreads out to a larger region which is less concentrated in diffusion. Molecular diffusion is a microscopic process which involves collisions of molecules. In surface water flow, mechanical mixing is associated with turbulence and the velocity gradients within planes perpendicular to the flow direction.

When the water flow is turbulent, as in rivers, one usually deals with quantities averaged over such time scales as to smoothen out eddy fluctuations. The procedure used is to express the instantaneous quantities (e.g. flow velocity) as the sum of an averaged quantity and a fluctuation with a zero mean value over the time scale considered. The fluctuation will contribute to the spreading. This process is termed as turbulent diffusion, and compared to molecular diffusion in river flows, it is of more importance. Advection is controlled by stream flow velocity. In one dimension, the advection equation in mass transport in rivers takes the form;

$$\frac{\partial c}{\partial t} = -u\frac{\partial c}{\partial x} \tag{3.2}$$

Where:

x = Streamwise distance

t= Time

u = velocity

c = Concentration of the constituent

Diffusion can be modeled by using Fick’s First Law. This law relates the flux of diffusion to the concentration assuming a steady state. It suggests that the particles move from high concentration region to a low concentration region, with a degree proportional to the gradient of concentration. If there is a difference in the concentration of a particular solute between one region of a solution and another, then there is a tendency for the substance to diffuse from where it is more concentrated to where it is less concentrated. This is because of the random collisions among particles which eventually will evenly distribute the solute throughout the volume of the solution. Fick’s first law is illustrated in figure 3.3.

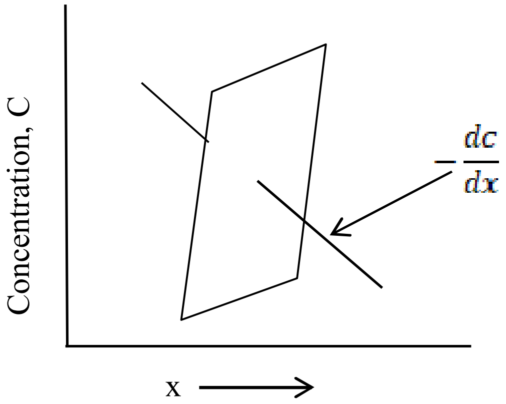

Figure 3.3: Schematic illustration of Fick's first law. The particle concentration gradient is the driving force of the diffusion.

In one spatial dimension, the law is given as:

$$J_x = -D\ (dc/dx) \tag{3.3}$$

Where:

J_x= mass flux in the x direction

D = the diffusion coefficient

dc/dx= the concentration gradient

The negative sign indicates that diffusion occurs in a direction opposite to that of increasing concentration. The diffusion coefficient is used to quantify the rate of the diffusive process. In a water body, the diffusion coefficient is low if little or no mixing or turbulence occurs. Otherwise if there is mechanical mixing present in a river flow, then the diffusion coefficient would be high. The relationship between dispersion and diffusion is that they will both mix a contaminant in a water body. However, whereas diffusion mixes contaminants in water due to random motions in the water over time dispersion mixes contaminants in water due to velocity differences in a given space (Chapra, 1997).

Fick's second law brings about the change of a contaminant with time caused by diffusion. It is a partial differential equation which in one dimension is:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{3.4}$$

3.2.2 Transport in riverine systems

A river is a natural stream of flowing water. Rivers are relatively long, shallow and narrow, and have obvious horizontal movement in the downstream direction (Hermond and Fechner-Levy, 1994). Gravity and friction are the two main forces working on the water in a river. Gravity makes the river to flow downstream and friction is experienced between the water with banks and river bottom and it opposes the motion of the river water. The effect of the two forces was not considered in this study. Friction affects the pressure and velocity of the river.

In general, the average river velocity systematically increases with the distance from the river bottom and sides, reaching a maximum near the centre of the river and usually below the water surface. Solute mass dissolved in the mid-channel near the surface water will travel downwards faster than the mass dissolved in water near the channel sides. The distribution of the solute mass elongates in the direction of the flow due to water moving slower near the banks, bottom and the surface.

Rivers often acts as a sink for pollutants released into the river. These pollutants include effluents from industries, dumpsites and wastewater treatment facilities that release heavy metals, pathogens and nutrients into the river. They are also sources of pollution in the watershed, subject to the year time or the river section.

3.2.3 Adsorption of pollutants

Adsorption can be defined as the process that occurs when molecules of a substance accumulate on the surface of an adsorbent, leading to the formation of a molecular layer. In this process, there is diffusion of molecules in a fluid to the surface of a solid, attaching with the solid surface or are held there by weak intermolecular forces. It is an important phenomenon in controlling the water quality in riverine systems and can define the fate and transport of the contaminants. Heavy metals are transported partly as metals in solution and partly as metals adsorbed to the suspended materials. This suspended material is attached to the bottom of the rivers and accumulates in the sediment. High organic matter content at the muddy river bottom contributes to the uptake of heavy metals in municipal rivers (Fumi and Shizuo, 1982). The adsorption interactions between heavy metals on suspended clay minerals have been studied by Gagnon *et al.* (1992) and it was concluded that lead metal has a higher affinity for clay minerals. Comparing the adsorption of metal ions by the sizes of the constituents, small sized elements like clay and silt adsorbs much better than the higher sized elements.

The kinetics of adsorption gives an explanation of the adsorption characteristics and mechanisms. The constant rate of adsorption using first order reaction kinetic is given as;

$$\frac{dc}{dt} = k(c_e - c_t) \tag{3.5}$$

Where k = coefficient of rate of adsorption for the first order adsorption,

c_t = the amount of heavy metal adsorbed at time t and

c_e = the amount of heavy metal adsorbed at saturation.

Adsorption is studied through isotherm which is the mount of adsorbate on the adsorbent as a function of its concentration at constant temperature.

Adsorption is a common technique used to remove metal ions from several industrial discharges (Gottipati and Mishra, 2012). The model over-predicts the pollutant concentration downstream of the release point, if the effects of adsorption are not taken into account.

3.2.4 Water quality modeling in rivers

Water quality models incorporate the equations for conservation of mass transport for water and transformation of materials in water. These equations deal with flow rates, volumes, depths and velocities of water. Transfer of energy, chemical and biological kinetics and chemical equilibrium expressions are included in the transport and transformation equations.

For calibration and verification of a model, there is a requirement of parameter values. These parameter values are also needed as model input in defining the initial and boundary conditions. Boundary conditions are specifications of flows and loads entering the riverine system. Initial conditions are required in order to define parameter values. These conditions are usually input data defined by the values of primary water quality parameters, flow, depth of the river include in the model.

The models give a description of the main water quality processes, and normally require the constituent and hydrological inputs. These water quality models include dispersion and advection transport which depends on the characteristics of the hydrology and hydrodynamics of the water body.

In order to reduce pollution of water which causes degradation downstream and upstream of rivers as well as estuarine and coastal areas, proper management of river basins is important. In most riverine systems, longitudinal flow dominates throughout the system hence a one dimension system.

The flow of a river depends on whether the flow changes with time and/or location or not. When the flow does not change with time then it is said to be a steady flow otherwise unsteady. Another river flow characteristic is that if the flow does not vary with location along the length of the channel, then the flow is said to be uniform flow, otherwise non-uniform. In uniform flow, the flow velocity, water volume and depth remain the same at each cross-section of the reach of the channel. Essentially flow is never concurrently unsteady and uniform, thus unsteady flow indicates non-uniform flow as well. However, the applications for the modeling are common for both steady and unsteady non-uniform and steady uniform flow.

3.2.5 Contaminant Transport equation

In surface waters, the most commonly used models fall under the classification of the equations of shallow water, in which the assumption is that the flow is shallow relative to the dimensions of the problem in consideration. The flow is considered as one-dimensional, where there is uniform velocity over across-section, the level of the water is horizontal across the section and the angle of cosine made by the bed and the horizontal is given as the unity since the average slope of the beds channel is too small. The density is also constant in time and in space.

The environmental model developed is based on partial differential equation which is one-dimensional and in surface waters describing non-stationary flow (ICIM, 1992). The model equation translates the laws of mass and momentum conservation mathematically. Equation 3.6 is a one-dimensional transport equation describing the concentration of an element as a function of location and time as water quality part;

$$\frac{\partial(VC)}{\partial t} = -\frac{\partial(QC)}{\partial x} + \frac{\partial}{\partial x}\left(AD_x\frac{\partial C}{\partial x}\right) \pm P \qquad (3.6)$$

Noting that Q = AU, then the equation above becomes;

$$\frac{\partial(VC)}{\partial t} = -\frac{\partial(AUC)}{\partial x} + \frac{\partial}{\partial x}\left(AD_x\frac{\partial C}{\partial x}\right) \pm P \qquad (3.7)$$

Where C= concentration, mg/l,

A= cross-sectional area of the river,

t= time,

x= streamwise distance,

U= mean longitudinal velocity of river flow, m/s,

D_x= dispersion coefficient, m^2/s,

V= Volume, m^3,

Q = flow rate, m^3/s

P = external sources and sinks, mg/s

The longitudinal dispersion coefficient (D_x) in riverine systems is dependent on several hydrodynamic factors including; width, depth, velocity and shear velocity.

Equation (3.7) is for a one-dimensional system, such as a long, narrow tube full of water, where significant variations in concentration may be assumed to occur only along the length of the tube.

Sources and sinks (P) of contaminants comprise of wasteloads, and the chemical and physical processes that change the amount of these wasteloads. In the equation above the value of P is positive for sources and negative for sinks.

Using product rule on the left hand side of equation 3.7 we have;

$$\frac{\partial (VC)}{\partial t} = V\frac{\partial C}{\partial t} + C\frac{\partial V}{\partial t}$$

Assuming a steady flow, $\frac{\partial Q}{\partial t} = \frac{\partial V}{\partial t} = 0$ then;

$$\frac{\partial(VC)}{\partial t} = V\frac{\partial C}{\partial t}$$

Then equation 3.7 becomes;

$$V\frac{\partial C}{\partial t} = -\frac{\partial(AUC)}{\partial x} + \frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) \pm P \qquad (3.8)$$

The first term in the right hand side of equation 3.8 is the advection term and the second term is the dispersion term. Taking into account the effect of adsorption, the equation above becomes;

$$V\frac{\partial C}{\partial t} = -\frac{\partial(AUC)}{\partial x} + \frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) \pm P - KC \qquad (3.9)$$

This will be used in discretized form in a computer code.

3.3 Numerical solution implementation

This section entails translating the mathematical equation into solving the real problem. This was attained by discretizing the governing equations and setting up the computer codes.

3.3.1 Discretizing the governing equations

In numerical coding, the continuous variable domain is replaced by a discrete variable. The partial differential equation governing pollutant transports in surface water flow was discretised using integrated finite difference method (IFDM). The differential equations that describe the movement of heavy metals include terms that represent derivatives of continuous variables.

Equation 3.9 is discretised for use in the computer program. It is expressed in the fully implicit form which produces non-diagonal matrices, where the algebraic equations cannot be solved in stand-alone fashion because each equation contains several unknowns. The unconditional stability of most implicit schemes and the usage of large time steps give the possibility of reaching the final time faster compared to the explicit scheme which is limited in stability. Compared to an explicit solution update, the cost per time step is large. Accuracy is subject to consideration when using small time steps in explicit schemes. If the interest is of a steady-state solution, then it is advisable to use local-time stepping with the unconditionally stable implicit scheme.

Implicit discretization solutions produces a system of algebraic equations with non-zero coefficients only on the main diagonal, the lower and the upper diagonal is called a tridiagonal system of equations. The type of system used in solving such a tridiagonal system of equations is Thomas algorithm which is a special type of Gaussian elimination. The solution of the tri-diagonal matrix can be obtained in O (n) operations. The form of the equation is;

$$F_j c_{j-1} + g_j c_i + h_j c_{j+1} = d_j \qquad j = 1, k, n$$

where f_1 and h_n are zero.

Considering a tridiagonal system of n equations with n unknown $c_1, c_2 \ldots\ldots\ldots c_n$ as given below;

$$\begin{bmatrix} g_1 & h_1 & & & 0 \\ f_2 & g_2 & h_2 & & \\ & f_3 & g_3 & \ddots & \\ & \ddots & \ddots & \ddots & h_{n-1} \\ 0 & & & f_n & g_n \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ d_n \end{bmatrix}$$

Zero elements are not saved in the memory and also the operation $0 - x.0 \rightarrow 0$ are not realised. This leads to using less computer memory and time saving.

The solution algorithm starts with k = 2, ……., n:

$$m = \frac{f_k}{g_{k-1}}$$

$$g'_k = g_k - mh_{k-1}$$

$$d'_k = d_k - md_{k-1}$$

Then: $c_n = \dfrac{d'_n}{g_n}$

The above equation involves only one unknown. It is solved in turns reducing the next last equation to one and to find all the other unknowns, we use backward substitution.

And finally for k = n-1, ….., 1:

$$c_k = \frac{d'_k - h_k c_{k+1}}{g_k}$$

On discretizing the advection and the dispersion terms equation (3.9) becomes;

$$\left[\frac{C_j^{n+1} - C_j^n}{\Delta t}\right] V = -\frac{AU}{2\Delta x}\left(C_{j+1}^{n+1} - C_{j-1}^{n+1}\right) + \frac{AD}{\Delta x^2}\left(C_{j+1}^{n+1} - 2C_j^n + C_{j-1}^{n+1}\right) - KC_j^{n+1} \qquad (3.10)$$

The concentration in the next time step as a result of advection becomes;

$$C_j^{n+1} \quad = \quad C_j^n \quad + \quad \frac{AU\Delta t}{2\Delta x V}\left(C_{j-1}^{n+1} - C_{j+1}^{n+1}\right) \qquad (3.11)$$

The concentration in the next time step as a result of dispersion becomes;

$$C_j^{n+1} \quad = \quad C_j^n \quad + \quad \frac{AD\Delta t}{\Delta x^2 V}\left(C_{j+1}^{n+1} - 2C_j^{n+1} + C_{j-1}^{n+1}\right) \qquad (3.12)$$

where C_j^{n+1} is the concentration in block j in the next time step,

C^n_j is the concentration in block j in the current time step,

Δt is the time step,

Δx is the space step,

A_x is the cross-section area of the river,

U is the longitudinal velocity of the river,

D_x is the longitudinal dispersion coefficient,

K is the adsorption coefficient,

C_{j+1}^{n+1} is the concentration in the next block in the next time step and

C_{j-1}^{n+1} is the concentration in the previous block in the next time step.

3.3.2 Numerical coding

The process of translating the discretised mathematical problem into a computer program was considered in this section. Coding is the implementation of the algorithms obtained from discretised solutions of the governing equations using a computer program. These modules were written in FORTRAN 77 programming language which is portable and simple to familiarize with.

The problem under study comprised of the input information, the mathematical algorithm and the output data. The input data consisted of information like the size and properties of the river, initial and boundary conditions on the concentration of heavy metals. The mathematical model involved the procedure for solving the resulting algorithm of the governing equations. Whereas the output data was as a result obtained after the execution of the computer program. The simulator structure is shown in figure 3.4.

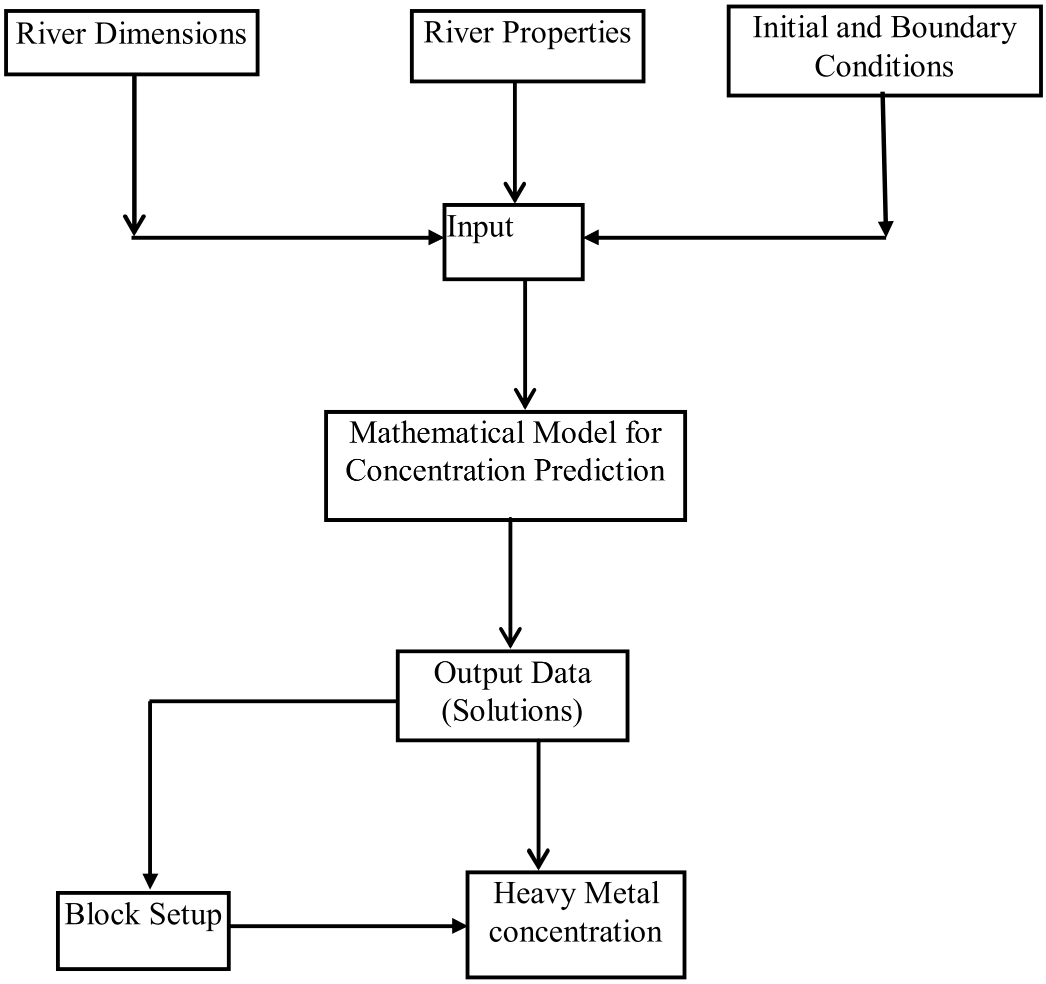

Figure 3.4: A chart showing the flow of information in the simulator.

Cartesian and node-centered grid design was used in this model. The number of blocks in the entire grid was arbitrary. In designing the grid river dimensions, dispersion coefficient, adsorption value, flow rate and concentrations were of *double precision* type and the number of blocks and time steps was of *real* type. This information was implemented as the input data in the program and was used to calculate other river section information. Simulation time steps along each block remained fixed throughout the grid. Velocity was taken constant over a cross-section.

In each side of the model grid, a gradient of zero heavy metal concentration was stated as boundary conditions except at the source zone. **Thomas_algorithm** subroutine was used to solve the tridiagonal matrices arising from the implicit discretization of the governing transport equation. The main function for the solution of the transport equation computes the concentration of the contaminant for each block volume during the entire simulation time. The algorithm of the program used to compute the solver function in this work is illustrated on figure 3.5.

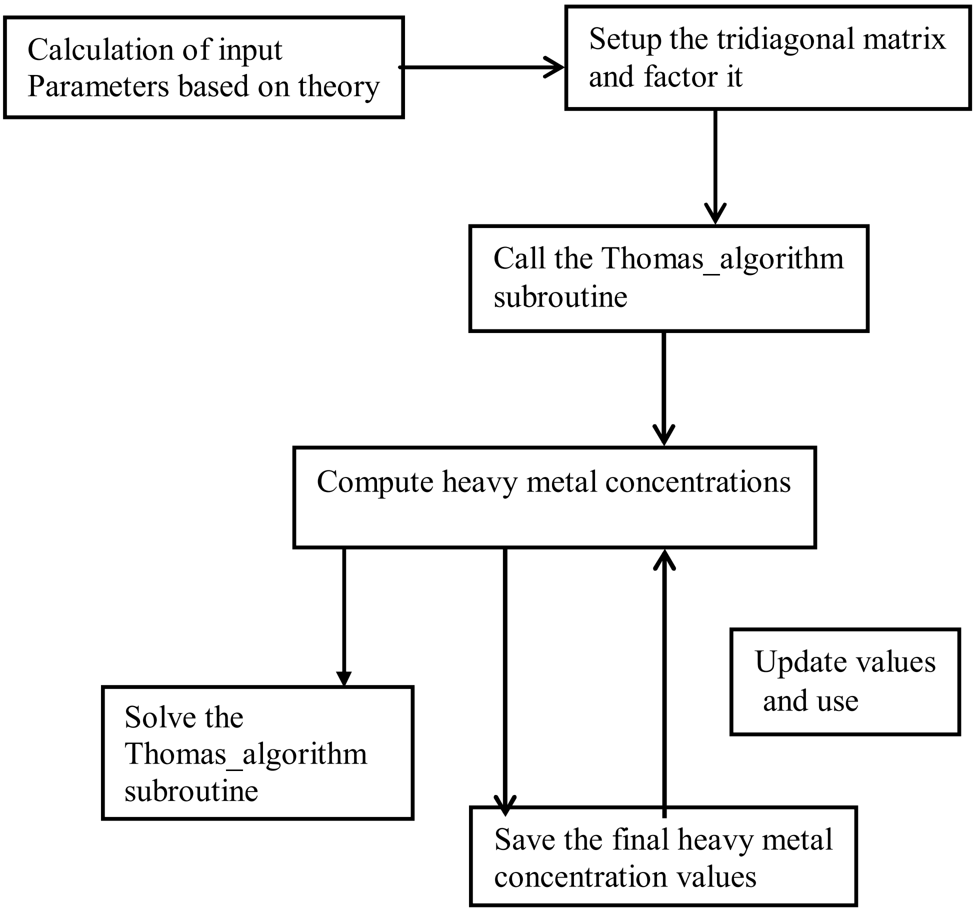

Figure 3.5: Algorithm block solver used in this work.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Introduction

The one dimensional model developed in this study was used to simulate the transport of heavy metals in rivers. This chapter is hereby presented by first looking at the generic tests and then the match of the simulated results with the field data. The generic tests were intended to check the performance of the simulator. The sensitivity of the simulator was studied by varying adsorption, dispersion and flow rate values.

4.2 Generic testing

4.2.1 Heavy metal concentration curves

Heavy metal transport through rivers depends on the advection and dispersion processes. Both are involved in the mass transport equation. Tests were done to investigate how each of these processes could affect the concentration of the heavy metals at any given time after its instantaneous injection at a point in the river. Each mechanism was observed by testing the processes and noting their effects. Later all the processes were combined so as to show the overall effect on the temporal and spatial heavy metal concentration.

Figure 4.1 shows the concentration breakthrough curves for advection transport only. It shows that the concentration available to the next neighboring point reduces with distance from injection point. This agreed with the principal of contaminant dilution due to transport mechanisms. As the heavy metal is passed to the neighborhood, its concentration level in the source point is reduced.

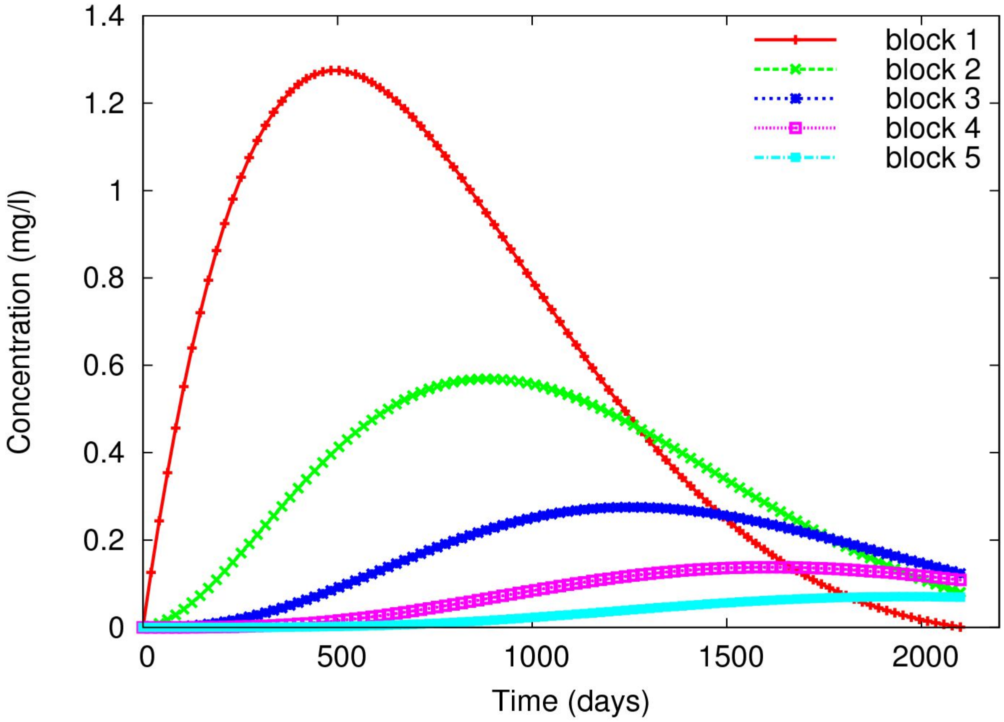

Figure 4.1: Breakthrough curve for the temporal variation of heavy metal concentrations due to advection process transport only for instantaneous injection case.

Figure 4.2 shows the effect of dispersion process in the transportation of heavy metals in rivers. There is an early time peak of concentration and an extended tail of low concentration exhibited by dispersion. When an initial volume of concentrate is added at a point, the volume of the flow increases, increasing the rate of dispersion. High dispersion means that the solute diffuses through the grid volume much faster, doing so little quickly leading to a higher concentration value before the solute is being transported out of the grid hence the early time concentration peak. The extended period of low tailing comes about because the role that dispersion plays is minimized after the incorporation of the process of mass transfer. There is a steep rise in the leading edge indicating increase in rapid mixing and there is a sharp fall in the tailing edge showing that the role played by dispersion has been minimized.

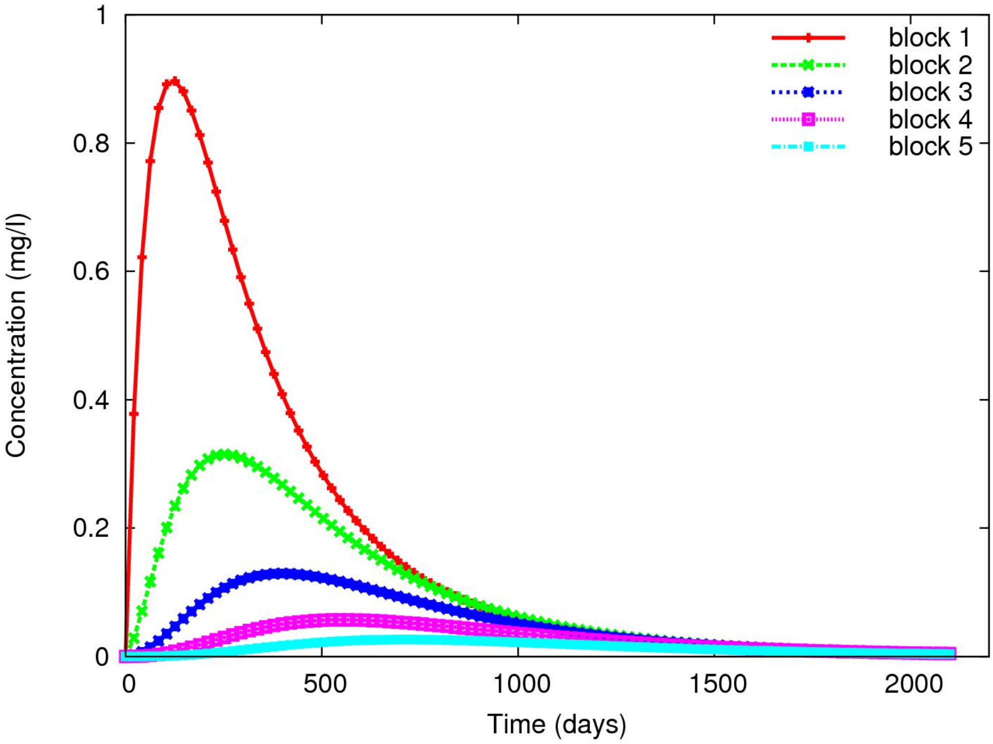

Figure 4.2: Breakthrough curve for the temporal variation of heavy metal concentrations due to dispersion process transport only for instantaneous injection case.

Advection and dispersion are compared under the same hydrodynamic conditions. Advection is realized to be the major pollutant movement mechanism while the effect of dispersion was minimal, since concentration levels were high during advection alone. Dispersion is usually a slow process compared to advection. This is illustrated in figure 4.3

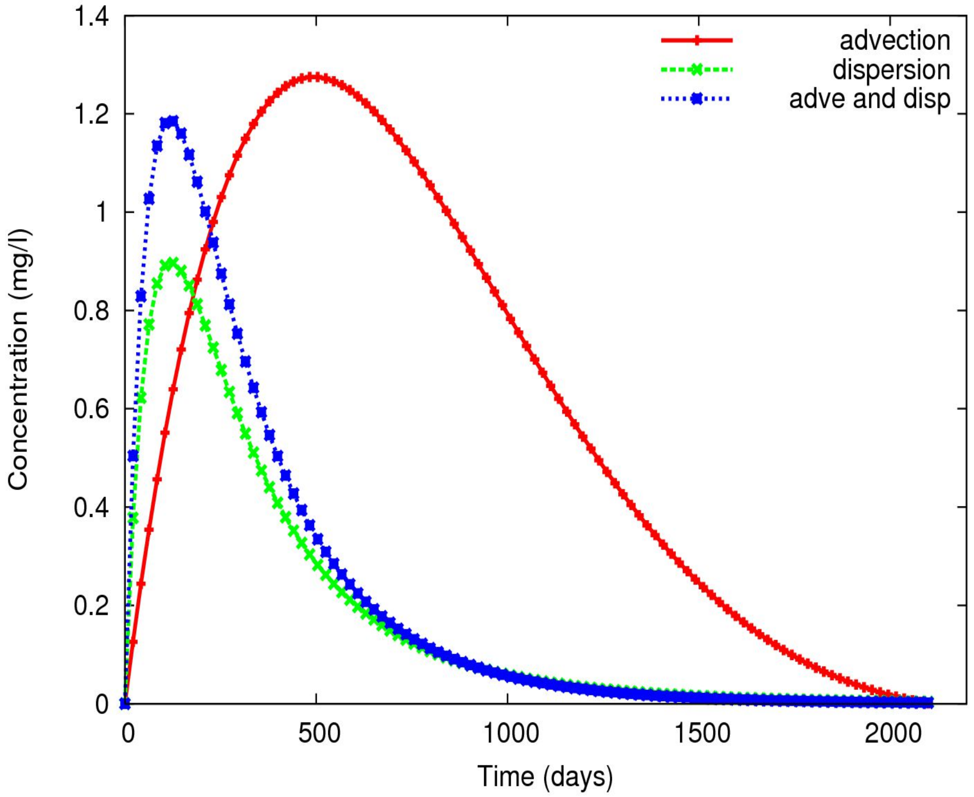

Figure 4.3: Comparison of advection and dispersion transport processes simulated in block 2.

Figure 4.4 shows the model results for constant continuous concentration injection source. It is observed that there is a tendency of the curves to attain an equilibrium value. This indicates that the amount of the contaminant entering the block equals the amount leaving the block. As the distance from the source increases the subsequent block concentrations decreases. This is because the subsequent blocks receive the contaminant through diffusion therefore reducing the overall block concentration .The above information can be used to estimate the effect of multiple spills.

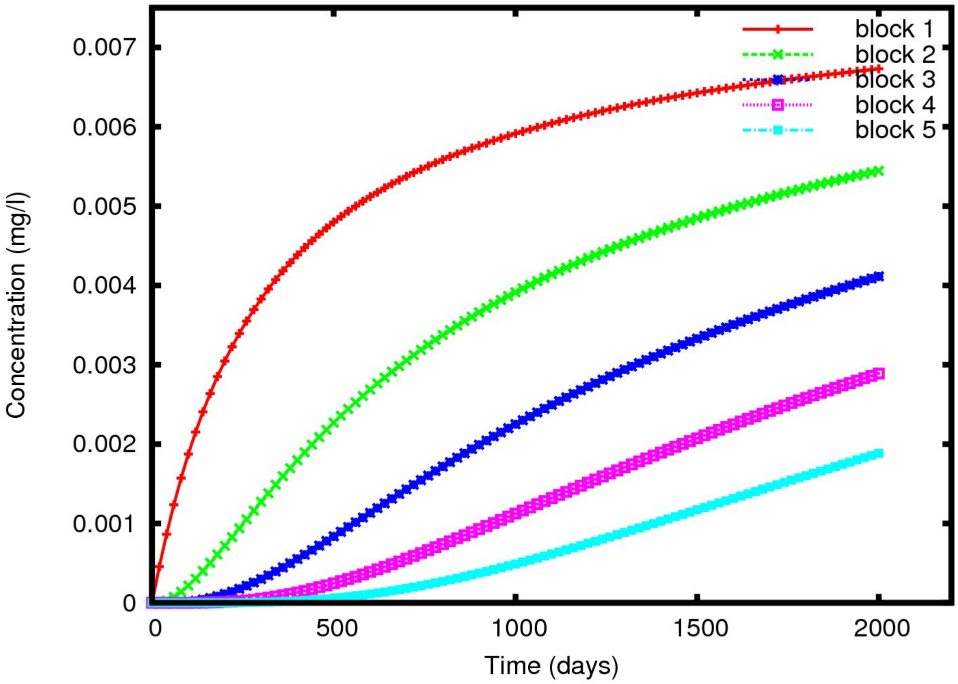

Figure 4.4: Temporal variation of heavy metal concentration for continuous injection case at a point source.

For spatial variation of contaminant concentration testing for fixed concentration at X=0, the results were reflected in figure 4.5. At T1 there is gradual/abrupt decrease of the contaminant concentration compared to subsequent time intervals. As an initial amount of contaminant is added at a point, the reach volume increases due to the inflow of the contaminant. As the velocity increases, the time it takes for the contaminant to be transported to the reach end decreases. At T5 the contaminant had time to diffuse as the fluid flow hence a slow descent.

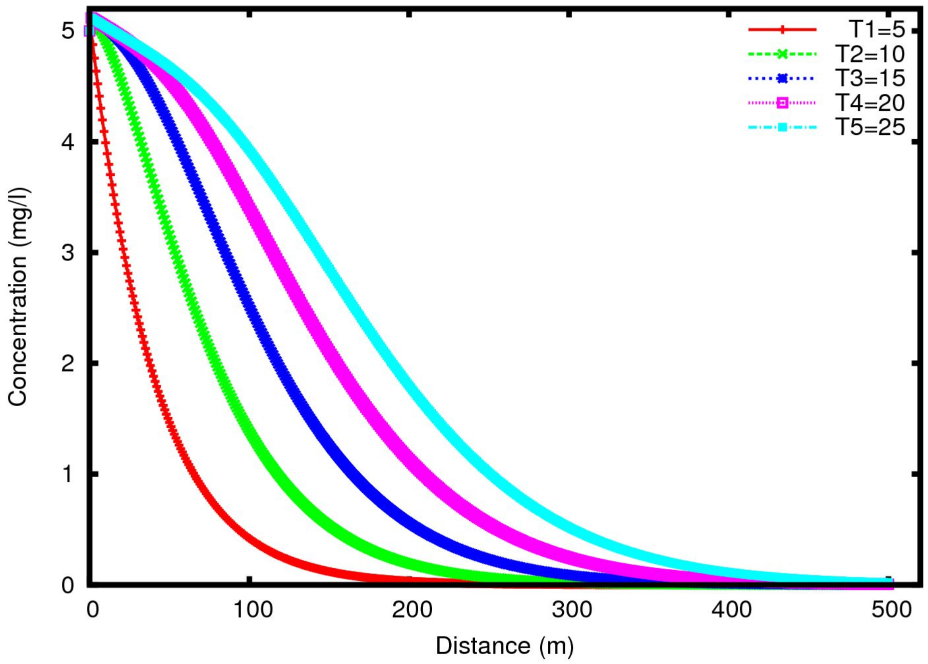

Figure 4.5: Spatial variation of heavy metal concentrations for fixed concentration at x=0.

4.2.2 Effect of varying field parameters

In this section, the effects of the field parameters affecting heavy metal concentration are examined. They are dispersion coefficient (D), flow rate (Q) and adsorption (K).

Longitudinal dispersion coefficient is a key parameter in determining the pollution concentration. The effects in varying the dispersion coefficient simulated in this work are shown in figure 4.6. They indicate that dispersion coefficient varies directly with the concentration peak values and peak arrival time. When the value of dispersion coefficient is low, the dispersion phenomenon is minimal and the transport out of the grid cell takes a relatively longer time. This is the reason for a weak peak when values of dispersion coefficient are small indicating that the solute is slowly given out.

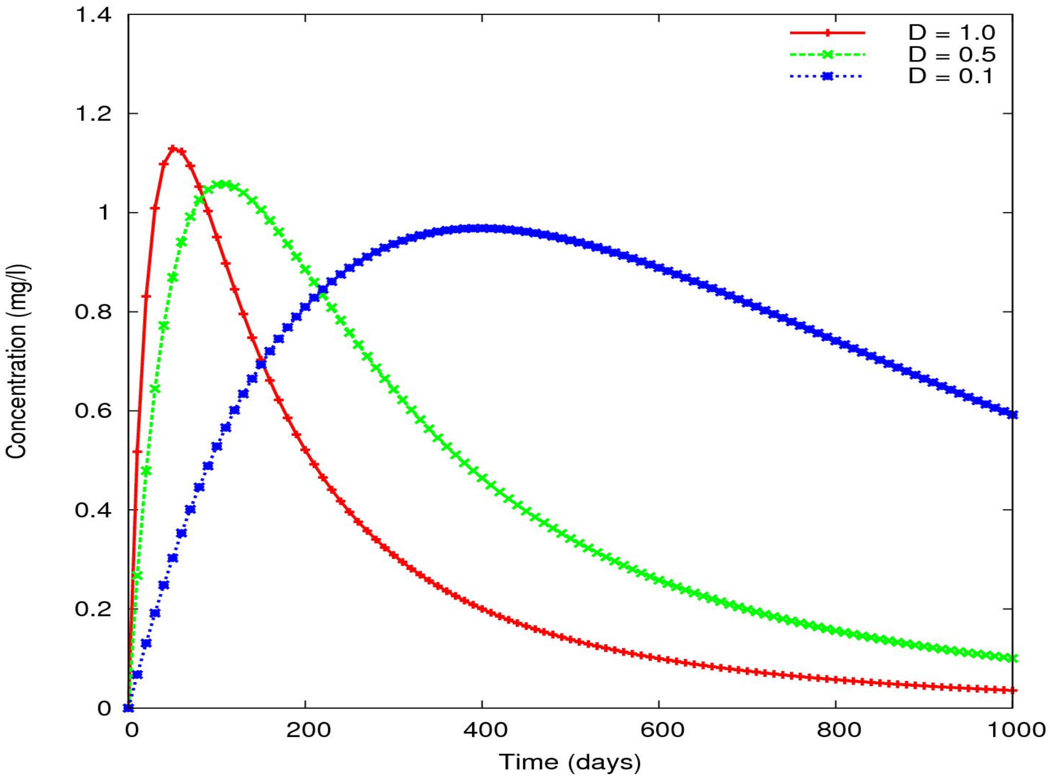

Figure 4.6: The effect of dispersion coefficient value on heavy metal concentrations simulated in block 2.

The amount of fluid that flows through a point at a particular time is known as flow rate. Figure 4.7 shows the effect of flow rate in block 2 simulated in this work. A large amount of water flow dilutes concentration of the contaminants that are released into the river. Increasing the flow rate gives rise to a shorter time for saturation and this affects the amount of the pollutant that can be degraded or produced in the section of a river thus often causing minimal water quality problems. High flow rate also leads to increase in the river mixing thus enhancing the capacity of the river to assimilate and brings about the reduction of the contaminant concentration gradient.

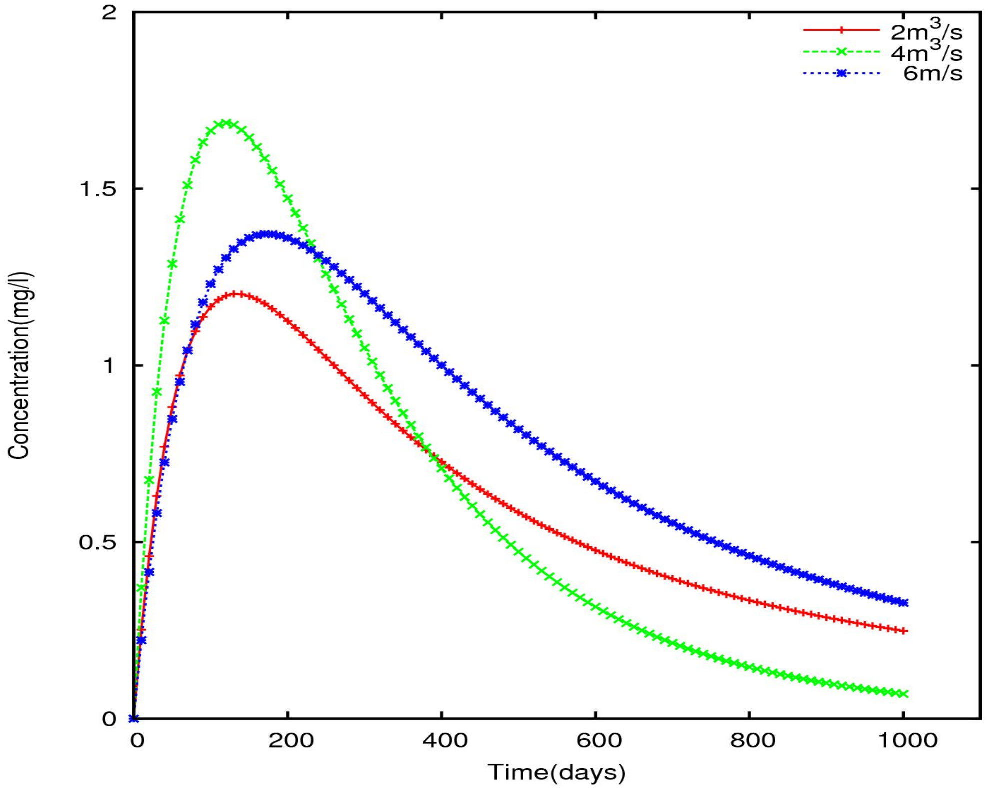

Figure 4.7: The influence of flow rate on heavy metal concentrations simulated in block 2.

Adsorption is the binding of ions or molecules of fluids onto a surface. It is a common phenomenon affecting chemical species present in a liquid. The chemical leaves the fluid phase and becomes attached to the solid surface. Figure 4.8 shows the effect of adsorption in block 2 simulated in this work. Adsorption value varies inversely with the concentration peak values and directly with the peak arrival time. Increase in adsorption means more solute molecules are attached to the river sediments hence a low concentration value of the dissolved heavy metal being transported. Adsorption is one of the ways of removing heavy metal contaminant from the surface waters.

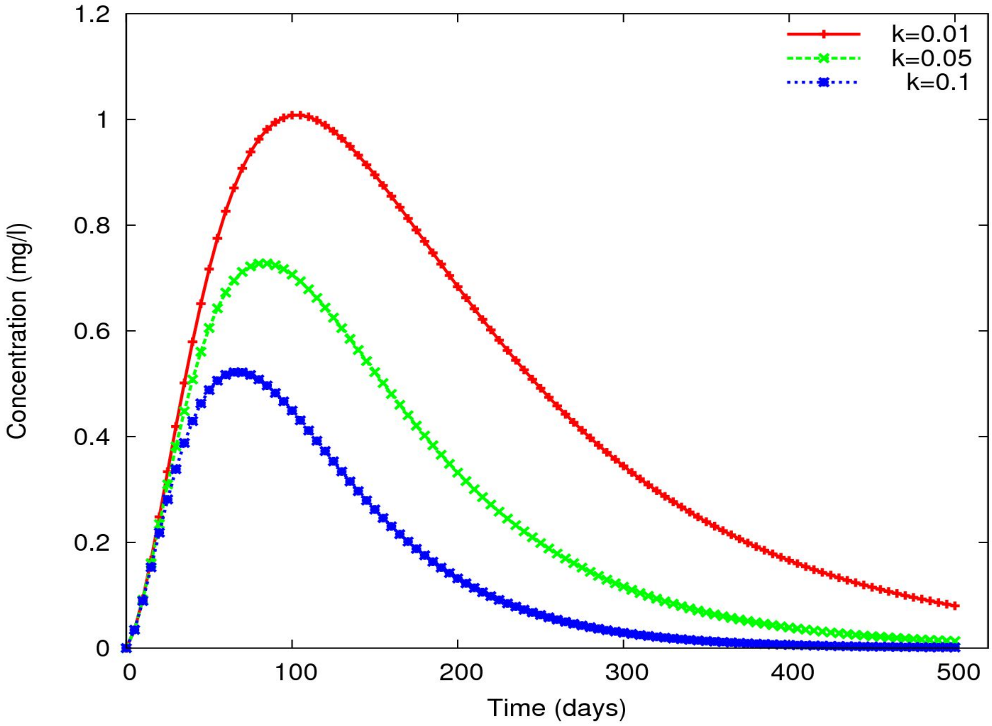

Figure 4.8: Effect of adsorption in block 2 simulated in this work.

4.3 Heavy metal Concentrations in Water Samples

The mean copper, zinc and lead concentrations water sampled from river Sosiani are summarized in Table 1.

Table 4.1: Total heavy metal concentrations in water samples (mg/L).

Sites	Zinc	Copper	Lead
1	0.43±0.06	0.32±0.04	0.1±0.01
2	0.48±003	0.28±0.03	0.23±0.02
3	0.46±0.02	0.35±0.03	0.08±0.02
4	0.42±0.02	0.30±0.01	0.06±0.01
5	0.35±0.02	0.27±0.02	0.07±0.01
6	0.39±0.02	0.3±0.05	0.09±0.03
7	0.32±0.02	0.22±0.02	0.12±0.01

4.4 Model Validation

The process of verifying that the system of the model represented performs in line with its designed objectives as expected is known as validation. The model developed in this study was validated for spatial variation of heavy metal concentration considering multiple sources of the pollutants. The initial heavy metal level of 2mg/l was set in the entire model domain. Field parameters were varied by trial and error using graphical considerations in each case of heavy metal concerned so as to reduce the differences between simulated and measured values. For example, the dispersion values for this kind of data marching for a specific metal were 1.0, 1.0 and 1.5 for lead, zinc and copper respectively. Also the flow rate values for lead, zinc and copper metals were 0.2, 0.4, and 0.2 respectively. The measured data was approximated to correspond to the grid cells in the grid system of the simulated data for each case.

Table 4.2: Comparison between the field and the simulated values for heavy metal Concentration.

Distance (x1000m)	Zinc		Lead		Copper	
	Simulated Mg\l	Measured Mg\l	Simulated Mg\l	Measured Mg\l	Simulated Mg\l	Measured Mg\l
0	0.43	0.43	0.14	0.10	0.35	0.32
1	0.49	0.48	0.21	0.23	0.27	0.28
2	0.49	0.46	0.14	0.08	0.38	0.35
3	0.47	0.42	0.088	0.06	0.34	0.30
4	0.38	0.35	0.07	0.07	0.24	0.27
5	0.37	0.39	0.09	0.09	0.31	0.30
6	0.37	0.32	0.11	0.12	0.27	0.22

The simulated data match the measured values as shown in the figures 4.9- 4.11.

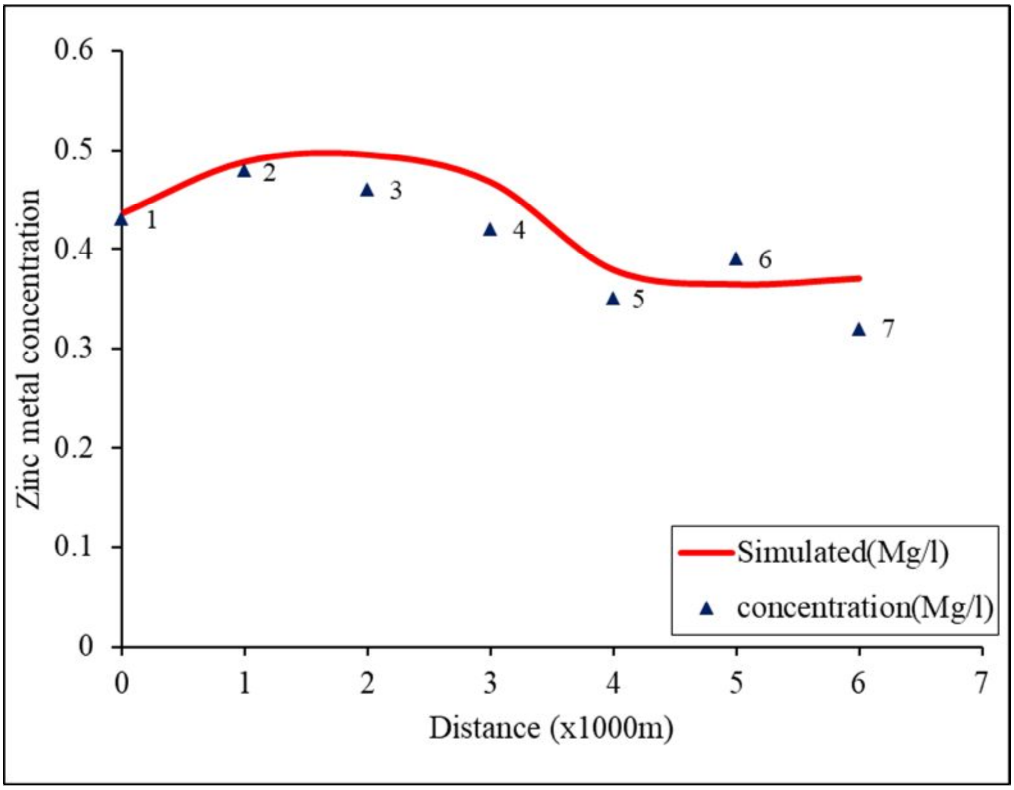

Figure 4.9: Match of field data and the simulated breakthrough curve for Zinc Concentration. (1. MTRH, 2. Langas bridge, 3. Pioneer, 4. Kipkaren, 5.West Indies, 6.Kipkenyo dumpsite, 7.WWTF)

There is increase in zinc concentration near Moi Teaching and Referral Hospital (MTRH) and the wastewater treatment facility (WWTF). High values of zinc near MTRH can be attributed to use of zinc related fertilizers from wheat and flower farms and anthropogenic activities upstream. Chemicals used in Timber treatment and preservation factories are discharged in the river increasing the zinc metal levels in the river. Most of these factories are located along the river and neighbor the hospital. At the WWFT zinc sources include effluents from industries and the urban areas and the leachates from Kipkenyo waste dumpsite along the river.

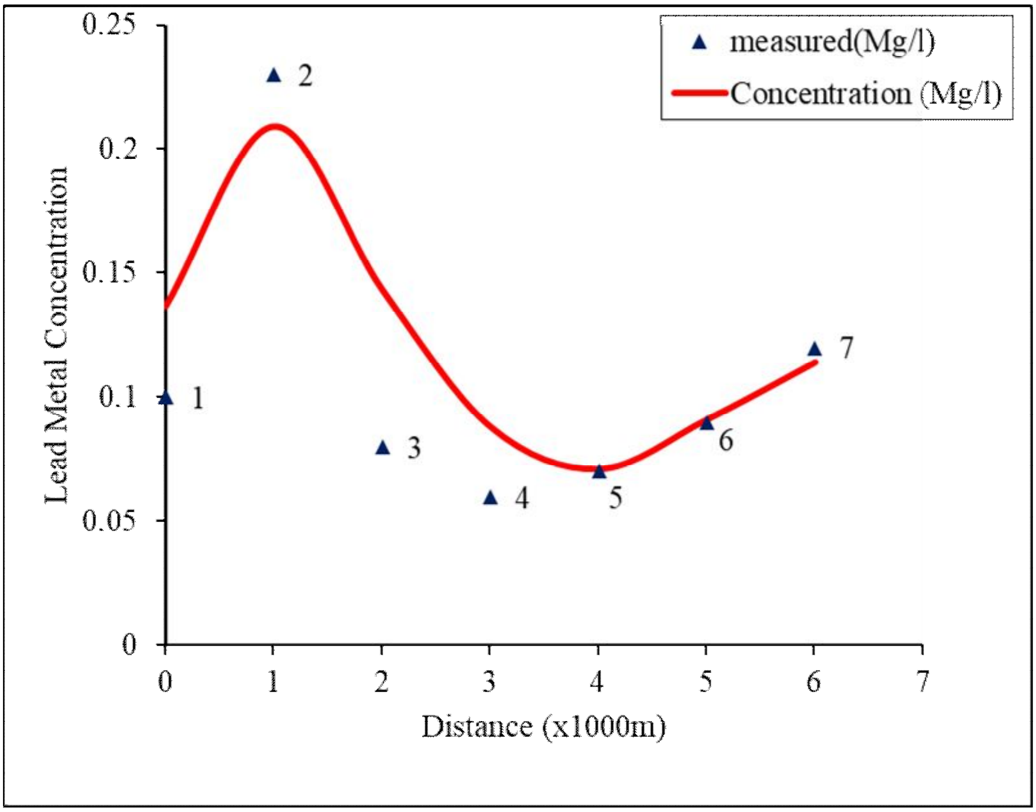

Figure 4.10: Match of field data and the simulated breakthrough curve for Lead Concentration. (1. MTRH, 2. Langas bridge, 3. Pioneer, 4. Kipkaren, 5.West Indies, 6.Kipkenyo dumpsite, 7.WWTF)

There is increase in lead metal concentration levels around Langas bridge and near the wastewater treatment facility in Huruma. These can be attributed to point and diffuse sources from industries and urban associated activities like car washes, garages, scrap metal bandas, electronics and battery recyclers. It can also be due to pollution from town effluents and vehicle emission. There is significant spatial variation of the lead concentration which can be attributed to high degree of adsorption exhibited by lead on clay soils.

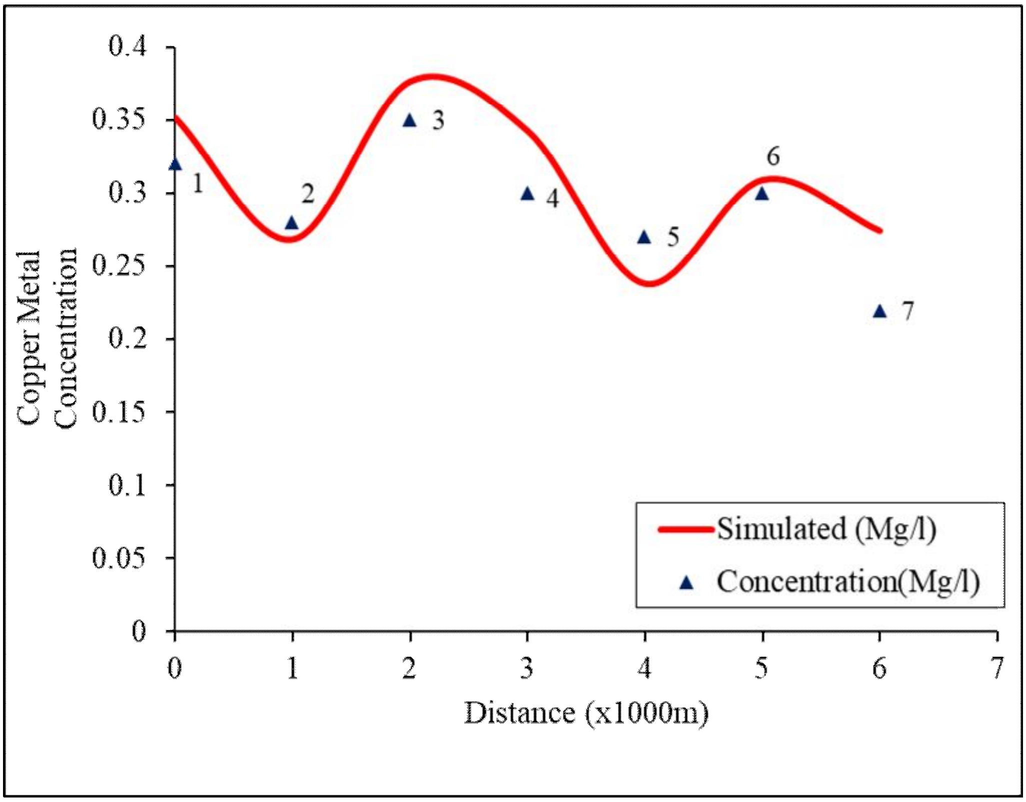

Figure 4.11: Match of field data and the simulated breakthrough curve for Copper Concentration. (1. MTRH, 2. Langas bridge, 3. Pioneer, 4. Kipkaren, 5.West Indies, 6.Kipkenyo dumpsite, 7.WWTF)

Copper metal concentration was high around Pioneer and near Kipkenyo dumpsite in Huruma. This suggests the probability of inputs of copper into the river from effluents from the textile industries, flower farms, timber treatment plants and from scrap metal operations. The low values at West Indies could be due to the dilution effects.

There is an increase of the three heavy metals near the wastewater treatment facility. This could be that in urban areas, the central collector of heavy metals is the sewer system and since heavy metals cannot be degraded in waste water treatment systems, hence the only means of loss from the urban sewer system is through the sewage sludge withdrawal. The simulated data agreed with the field data for the spatial metal concentration.

The field data was plotted against the simulated data as illustrated in figures 4.12-4.14. Correlation coefficients of 0.88789, 0.864395 and 0.79068 for zinc, copper and lead respectively were obtained.

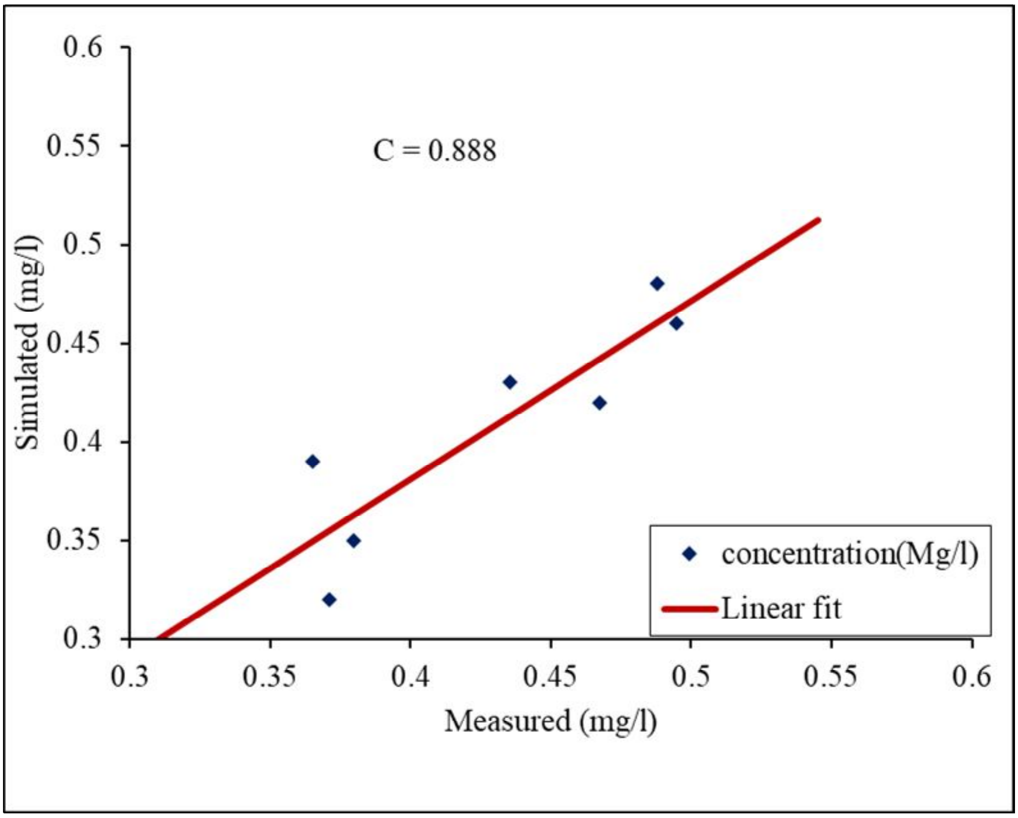

Figure 4.12: Correlation between simulated and measured values for zinc.

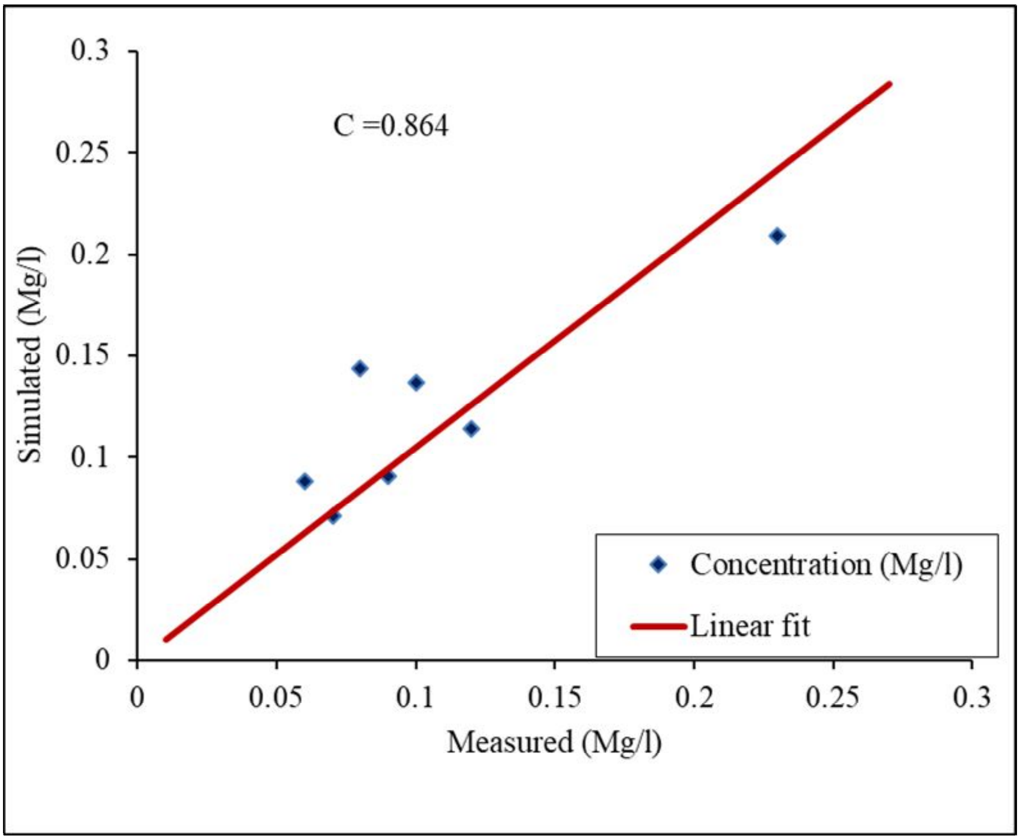

Figure 4.13: Correlation between simulated and measured values for Lead.

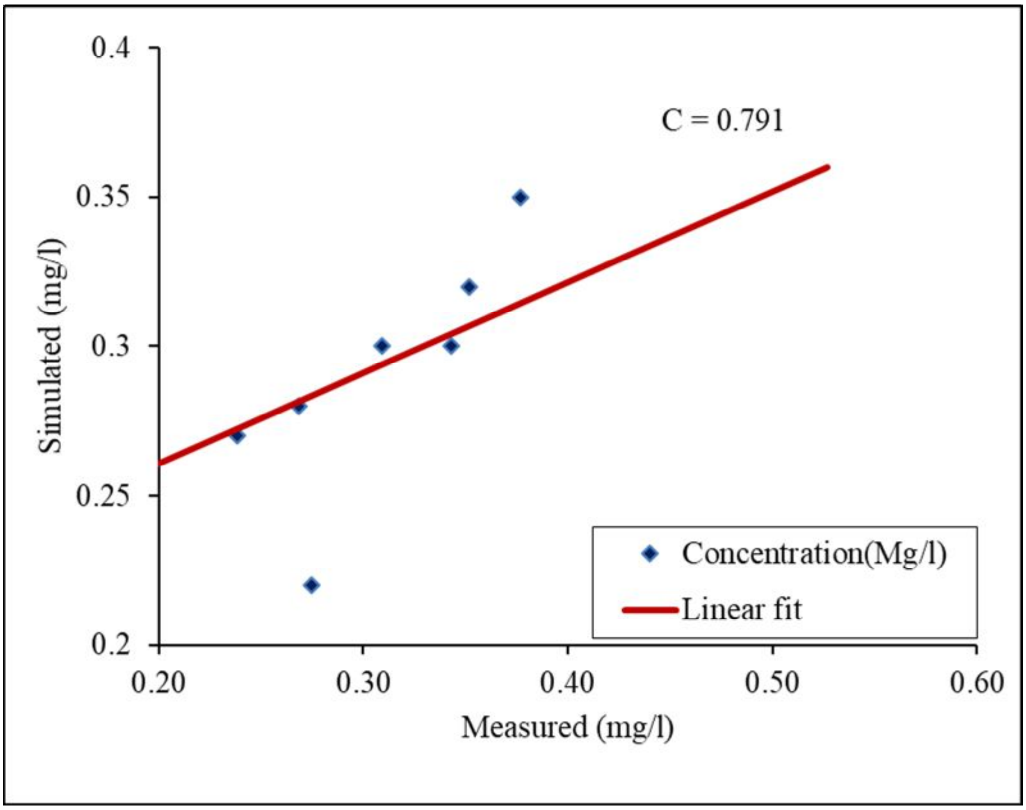

Figure 4.14: Correlation between simulated and measured values for Copper.

There is a stronger relationship of the simulated data to the measured data when the correlation value is closer to +1. As can be seen from figures 4.12-14, there is a good correlation between the measured values and the corresponding predicted values.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In heavy metal analysis results, the concentration of lead (0.23mg/l) and copper (0.35mg/l) at site 1 and 3 respectively were above the WHO standards recommended for domestic use i.e. 0.05mg/l for lead, 0.2mg/l for copper and 0.5mg/l for zinc. Hence the water from river Sosiani is not safe for use domestically as far as lead and copper levels are concerned.

The numerical model developed in this study was describing the transport heavy metals released in riverine systems. The two mechanisms of transport i.e. advection and dispersion at first were simulated differently and it was realized that advection was the major pollutant movement mechanism while the effect of dispersion was minimal. The simulator also indicated effect of various field parameters like dispersion coefficient, flow rate and adsorption values on concentration profiles which proved the success of the simulator. This was clearly indicated in the results obtained during generic testing. Several of these simulations for continuous and instantaneous injections of contaminant into the river were run to check the feasibility of the model. The curves for heavy metal concentration were affected by changes in adsorption values, dispersion coefficient and flow rate as seen from the effect of varying field parameters. These attested to the accurate solution of the governing equations and their coding in developing the simulator.

In the validation stage, flow rate and dispersion values were calibrated to obtain a match for simulated spatial concentration data and field data for heavy metal concentration. A close agreement was obtained between the simulated and field data indicating that the simulation can be used as a tool for describing spatial characteristics of heavy metal transport in riverine systems. Plots of simulated data against field data showed a linear relation where in all the three metals there was a strong positive relationship since their correlation coefficient is close to 1. Also there was the consideration of multiple sources in validating the model and this showed that the presented model can be used in practical situations when heavy metal pollutants are discharged into any river system from several point sources.

The numerical solution of the governing equation is the same as far as the explicit scheme employed by Njiru (2012) and the implicit scheme employed in this work is concerned.

5.2 Recommendations

To save river Sosiani from further pollution due to flow of heavy metals into the river, conservation measures are supposed to be taken. Farmers in the catchment should be educated on the use of pesticides, herbicides and fertilizers which contain the required heavy metals suitable for the crops. In order to remove heavy metals from industrial wastewater, processes like Chemical precipitation, Electrodialysis, Coagulation and flocculation, Ultrafiltration, Reverse osmosis and Adsorption (Dimple, 2014) can be used before the waste water is released in the river. To cater for the heavy metal leachates from Kipkenyo waste dumpsite, the county government should get another area which is far away from the river to put up a dumpsite. Contaminants like car washes, timber treatment and preservative industries are supposed to be relocated to other areas which are not near the river.

The simulator developed in this study can be modified to predict the spatial and temporal concentration levels of other surface water contaminants at the area of this study and areas elsewhere.

Implicit and explicit schemes employed in the numerical solution of the governing equation could be used to see how the two schemes compare in two or three dimensional modeling.

REFERENCES

Agbozu I.E, Ekweozor I.K.E, Opuene K. (2007). Survey of heavy metals in the catfish synodontis claria. *International Journal of Environmental Science and Technology*, 4(1): 94-97.

Agency for Toxic Substances and Disease Registry (ATSDR. Public Health Service. Atlanta: U.S. Department of Health and Human Services; (1999). Toxicological Profile for Lead.

Alloway, B.J. and Ayres, D.C. (1993). Chemical principles of environmental pollution. *Blackie Academic and Professional*, London. Pp140.

Alluri, H.K., Ronda, S.R., Settalluri, V.S. Bondili, V. S., Suryanarayana, V., Venkateshwar, P. (2007), Biosorption: Aneco-friendly alternative for heavy metal removal. *African Journal of Biotechnology*. 6 (25): 2924-2931.

Amadi E.K. (2013). Nutrient Loads and Heavy Metals assessment along Sosiani River, Kenya. *Journal of Chemistry and Material Research*. ISSN 2225- 0956 3(12).

Ani E. C., Kraslawski A, Cristea1 V.M, Agachi1 P. S. (2010).Dynamic Simulation of Somes River Pollution Using MATLAB and COMSOL Models. REV. CHIM. (Bucharest) 61(11).

Byun, D.W.; Young.J and Plein, J (2000) Numerical transport algorithms for the community multi scale air quality (emaq) chemical transport model in generalized coordinates. Atmospheric Modelling Division National Exposure Research Laboratory U.S. Environmental Protection Agency. Pp 7.

Chapra, S.C. (1997). Surface Water Quality Modeling. McGraw-Hill, Inc., New York, New York.

Cheserek G. J., Syagga P., Olima W.H.O., (2012) "Strategic planning for urban sustainable development: Challenges and opportunities facing selected towns in Western Kenya". Sustainable Futures, Kampala, Uganda.

Connell D.W., Miller G.J., (1984). *Chemistry and Ecotoxicology of Pollution*. John Wiley & Sons, New York.

Coulthard, T.J.; Macklin, M.G. (2003). Modeling long-term contamination in river systems from historical metal mining. *Geology*. 31: 451–454.

Dimple Lakherwal (2014). Adsorption of Heavy Metals: A Review. *International Journal of Environmental Research and Development.* ISSN 2249-3131 4(1): 41-48.

Duarte, A.A.L.S., Pinho J.L.S., Vieira, J.M.P., Boaventura, R.A.R.(1999) Comparison of Numerical Techniques Solving Longitudinal Dispersion Problems in the River Mondego. *Computational Methods in Engineering and Science.* 2: 1197-1206.

Duinker J.C.,Nolting R.F., and Michel D.,(1982). Effects of salinity, pH and redox conditions on the behavior of Cd, Zn, Ni, and Mn in the Scheldt estuary. *Thalassia Jugoslavica.* 18:191-202.

Falconer, R.A. & Lin, B. (2003). Hydro-environmental modelling of riverine basins using dynamic rate and partitioning coefficients. *International Journal of River Basin Management*. 1(1): 81-89.

Fumi Tada, Shizuo Suzuki (1982). Adsorption and desorption of heavy metals in bottom mud of urban rivers. *Water Research Journal*. 16 (10): 1489-1494.

Gagnon, C., Armac, M. & Brindle, J.R. (1992) Sorption interactions between trace metals (Cd and Ni) and Phenolic substances on suspended clay minerals. *Water Research Journal.* 26: 1067-1072.

Gottipati Ramakrishna and Mishra Susmita, (2012). Application of response surface methodology for optimization of Cr(III) and Cr(VI) adsorption on commercial activated carbons. *Research Journal of Chemical Sciences*. 2(2): 40-48.

Hermond H.F., Fechner-Levy, Elizabeth J. (1994), *Chemical Fate and transport in the environment.* Academic press, San Diego, California, 1- 136.

Horvat Z, Isic M, Spasojevic M. (2015). Two dimensional river flow and sediment transport model. *Environmental Fluid Mechanics*. 15(3): 595–625.

ICIM (1992), DUFLOW - A micro-computer package for the simulation of unsteady flow and water quality processes in one-dimensional channel systems, Bureau ICIM, Rijswijk, The Netherlands.

Jepkoech K, J., Simiyu M.G., Arusei M. R. (2013) Selected heavy metals in water and sediments and their bioconcentrations in plant (*polygonum pulchrum*) in Sosiani River, Uasin-Gishu county, Kenya. *Journal of Environmental Protection* 4: 796-802.

Kangogo D. (2009). Surface water pollution in Sosiani River, Uasin Gishu District. Unpublished B.Sc. Thesis University of Nairobi, Kenya.

Kennish, M. (1992). Ecology of estuaries: anthropogenic effects. CRC Press, Inc., Boca Raton, Florida, USA. 1: 494.

Khan S, Farooq R, Shahbaz S, Khan MA and Sadique M (2009). Health Risk Assessment of heavy metals for population via consumption of vegetables. *World applied sciences journal.* 6: 1602-1606.

Kimwaga R. J., Banaddaa N., Ayaaa F., Nhapi I., Walic U.G. and D.A. Mashaurid D.A. (2011). Modeling Diffusive Flux of Non-Point Source Pollutants in Lake Victoria: A Comparison Study of Fick's Law and the Fokker-Planck Law. *The Open Environmental Engineering Journal*. 4:105-111.

Konikow, L.F (1996). Use of numerical models to simulate ground water flow and transport. US Geological Survey, Reston, Virginia, USA. Pp77.

Kudenyo C.O., (2013). Development of a hydrodynamic model for River Sosiani. *Journal of environment and earth science.* ISSN 2224-3216 (paper) ISSN 2225-0948 (online) 3(9).

Kyung-Suk S., Ki-Chul K., Sung-Hee J. and Jung-Lyull., (2011). Numerical simulations for pollutant transport using radioisotope data in river system. *Progress in nuclear science and Technology*. 1: 372-375.

Meador, J.P., Stein, J.E., Reichert, W.L., Varanasi, U.,(1995). Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. *Reviews of Environmental Contamination and Toxicology.*143: 79–16.

Marusic, G., Sandu, I., Moraru, V., Filote, C., Ciufudean, C., Be'liu, V., Vasilache, V., Stefanescu, B., 'Evcenco, N., (2012). Floride dispersion modeling for River-Type systems. *Journal Meridian Ingineresc.* Technical University of Moldova. 4: 28-32.

Modenesi, K., Furlan, L.T., Tomaz, E., Guirardello, R., and Núnez, J.R. (2004). A CFD model for pollutant dispersion in rivers. *Brazilian Journal of Chemical Engineering.* ISSN 0104-6632 21(4): 557-568.

Ng B., Turner A., Tyler A.O., Falconer R.A., Millward G.E. (1996). Modelling contaminant geochemistry inestuaries. *Water Research,* 30: 63-74.

Novotny V and Salomons U (1995). *Diffuse sources of pollution by toxic metals and impact in receiving water in heavy metals*. Springer NY, London. Pp. 33-52.

Richardson D.H.S, Nieboer E (1980). The replacement of the nonde-script term heavy metals by a biologically and chemistry significant classification of metal ions. *Environmental Pollution Series* B 1:3–26.

Njiru N Sophy (2013). Application of mass transport model to study temporal variation of concentration of lead in a riverine system.' Unpublished M.Sc. Thesis Kenyatta University, Kenya.

Nyakaana J.B. (1996). Kenya's Development Policy: The Case of Eldoret. An Assessment of its Implementation and Impact. A PhD Thesis. Faculty of Environmental Studies. University of Amsterdam.

Ochieng` M. Ongocho (2000). Heavy metals: cadmium, copper, iron, lead, manganese and zinc in well water resources in Kisumu municipality. Kenyatta University Moi Library The TD 427.O25.

Ontumbi, G.M., Nyabero C., Catherine C.S. (2015). Assessment of water quality variation on human health in the river Sosiani catchment, Kenya. *International Journal of Innovation and Research in Education Sciences* 2(2): 2349-5219.

Pintilie S., Loredana B., Camelia B., Lucian V. P., Florina U., Maria G.(2007) Modelling and Simulation of Heavy Metal Transport in Water and Sediments. *Environmental Engineering and Management Journal.* 6(2): 153-161.

Rona v and Steef, P. (2003). Modeling point and diffuse metal emissions and loads in the river basin. *Hydrological process.* 17: 1307-1328. John Wiley and Sons.

Schwarz, G.E., Hoos, A.B., Alexander, R.B., and R.A. Smith, (2006). The SPARROW surface water-quality model: Theory, application, and user documentation, U.S. Geological Survey Techniques and Methods Report, Book 6, Chapter B3.

Sui L. H. (2009). Two dimensional numerical modeling of chemical transport-transformation in fluvial rivers; formulation of equations and physical interpretation. *Journal of Hydroinformatic*s. 11: 106-118.

UNEP/WHO/GEMS. (1988) *Global pollution and health*. Geneva Switzerland Pp. 1-70.

Valenta P., E.K. Duursma, A.G.A. Merks, H. Rutzel and H.W. Nurnberg, (1986). Distribution of Cd, Pd and Cu between the dissolved and particulate phase in the Eastern Scheldt and Western Scheldt estuary. *Science of Total Environment Journal*. 53: 41-76.

Veselinka Vuksanovic, Florimond De Smedt, Serge Van Meerbeeck & Didier Reyns. (1998). A time depdndent flow model for heavy metals in the Scheldt estuary. *Hydrobologia.* 366: 143-155.

Wilson, B. and Pyatt, F.B., (2007). Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey. UK. *Ecotoxicology and Environmental Safety*. 66: 224–231.

Wood W. L (1983). Introduction to numerical methods for water resources. Clavendon press oxford. Pp 1-27.

Wu, Y.; Falconer, R. A. & Lin, B. (2005) Modelling trace metal concentration distributions in estuarine waters. *Journal of Estuarine, Coastal and Shelf Science,* 64: 699-709.

Young-Soo Lee (2000). Fate and transport of trace metals in a small river system. *Environmental Engineering Research,* 5: 135-142. Korean Society of Environmental Engineers.

Yvetta Velísková (2002). Numerical prediction of pollutant dispersion in upper part of Ondava River. *Institute of Hydrology*. Slovak republic.

APPENDIX I

Simulated data for spatial zinc concentration levels

Block 7	Block 8	Block 9	Block 10	Block 11	Block 12	Block 13
0.0000	2.0000	0.0000	0.0000	0.0000	0.0000	0.0143
0.0000	2.0000	0.2000	0.0200	0.4002	0.0400	0.0321
0.0000	1.7900	0.3580	0.0537	0.7169	0.1075	0.0575
0.0003	1.4340	0.5735	0.1434	1.1520	0.2876	0.1292
0.0007	1.2830	0.6417	0.1925	1.2920	0.3866	0.1736
0.0024	1.0280	0.7196	0.2878	1.4610	0.5804	0.2742
0.0039	0.9208	0.7362	0.3312	1.5020	0.6697	0.3279
0.0092	0.7391	0.7374	0.4054	1.5270	0.8254	0.4371
0.0245	0.5350	0.6885	0.4812	1.4700	0.9943	0.5920
0.0321	0.4820	0.6644	0.4971	1.4370	1.0340	0.6387
0.0514	0.3949	0.6107	0.5164	1.3590	1.0890	0.7224
0.0632	0.3598	0.5825	0.5204	1.3170	1.1060	0.7589
0.0914	0.3042	0.5265	0.5191	1.2310	1.1230	0.8206
0.1441	0.2523	0.4492	0.4995	1.1030	1.1130	0.8851
0.1641	0.2422	0.4262	0.4897	1.0630	1.1030	0.8995
0.2072	0.2313	0.3856	0.4670	0.9851	1.0730	0.9185
0.2299	0.2300	0.3681	0.4548	0.9481	1.0550	0.9236
0.2771	0.2346	0.3390	0.4298	0.8782	1.0150	0.9257
0.3011	0.2401	0.3274	0.4174	0.8452	0.9929	0.9231
0.3731	0.2668	0.3042	0.3829	0.7539	0.9225	0.9035
0.4195	0.2911	0.2977	0.3633	0.6992	0.8738	0.8822
0.4417	0.3047	0.2969	0.3549	0.6736	0.8494	0.8697
0.4835	0.3339	0.2998	0.3409	0.6258	0.8011	0.8416
0.5029	0.3491	0.3032	0.3354	0.6036	0.7773	0.8264
0.5382	0.3801	0.3135	0.3276	0.5623	0.7310	0.7940
0.5540	0.3956	0.3202	0.3252	0.5433	0.7086	0.7772
0.5929	0.4405	0.3446	0.3239	0.4923	0.6448	0.7253
0.6117	0.4680	0.3635	0.3275	0.4634	0.6056	0.6905
0.6188	0.4807	0.3734	0.3304	0.4504	0.5870	0.6732
0.6289	0.5038	0.3936	0.3384	0.4273	0.5522	0.6392
0.6317	0.5141	0.4037	0.3432	0.4171	0.5359	0.6227
0.6334	0.5318	0.4234	0.3543	0.3995	0.5057	0.5907
0.6324	0.5392	0.4329	0.3604	0.3920	0.4918	0.5753
0.6265	0.5510	0.4507	0.3733	0.3795	0.4664	0.5460
0.6219	0.5553	0.4589	0.3800	0.3744	0.4592	0.5320
0.6096	0.5609	0.4737	0.3935	0.3665	0.4441	0.5058
0.6020	0.5622	0.4801	0.4002	0.3635	0.4149	0.4936
0.5745	0.5604	0.4956	0.4194	0.3584	0.4016	0.4604
0.5528	0.5546	0.5024	0.4308	0.3577	0.3945	0.4324
0.5411	0.5505	0.5047	0.4361	0.3581	0.3884	0.4243
0.5165	0.5400	0.5071	0.4453	0.3599	0.3830	0.4032
0.4772	0.5191	0.5053	0.4558	0.3648	0.3780	0.3825
0.4537	0.5110	0.5034	0.4583	0.3699	0.3726	0.3785

0.4401	0.5023	0.5008	0.4602	0.3741	0.3694	0.3750
0.4356	0.4878	0.4950	0.4676	0.3798	0.3651	0.3710

APPENDIX II

The Computer program

```
      program main
      implicit none
      integer nt,nx,j,n,nn
      parameter(nx=100)
      double precision T,X,u,dx,dt,k1,k2,x1,x2,t1,t2,C(100),Cnew(100),D
      double precision k,UW,SL,H,CA,V,UD
      real f(100),g(100),h(100)



! nx= number of spatial nodes
! nt= number of temporal nodes
! X= total simulation length
! T= total simulation time
! dx= spatial discretization step
! dt= temporal step size
! u= constant velocity
! D = longitudinal dispersion coefficient
! k = adsorption coefficient
! UW = upstream width
! SL = section length
! H = height


! initialize date
      UW = 1
      UD =1
      H = 1.
      u = 0.2D+00
      nt = 100.0D+00
      D =1.5D+00
      k =0.01
! set X values
      x1 = 0.0D+00
      x2 = 1000D+00
      dx = ( x2 - x1 ) / ( nx  )

! set T values
      t1 = 0.0D+00
      t2 = 1200.0D+00
      dt = ( t2 - t1 ) /  ( nt )

! parameter calculations
      CA = dx*UW
```

```
      V = dx*UW*UD
! initial condition

      t = 0.0D+00
      do j = 0, nx
         C(j) = 5.0D+00
      enddo
      k1 = CA*U*dt/2./dx/V
      k2 = CA*D*dt/dx/dx/V

c Setup the tridiagonal matrix and factor it
      k1 = CA*U*dt/2./dx/V
      k2 = CA*D*dt/dx/dx/V
       do 2 j = 1,nx-1
      f(j) = -k1-k2
      g(j) = 1 + 2*k2 + K
      h(j) = k1-k2
      C(j) = 0.
      C(1) = 5.
2      continue

      call tridag(f,g,h,C,n)
      print 8,t,C(1),C(2),C(3),C(4),C(5),C(6),C(7),C(8),C(9)
      print*

      do 3  n=1, nt
       t =  (n)*dt

       do 4 j = 1,nx
        Cnew(j) = C(j)- (k1-k2)*Cnew(j+1) - (2*k2 + k*dt/V)*Cnew(j)
     &  + (k1 + k2)* Cnew(j-1)

4       continue
       do 5 j = 1,nx
        C(j) = Cnew(j)
5       continue
      print 8,t,C(1),C(2),C(3),C(4),C(5),C(6),C(7),C(8),C(9)
      print *

3       continue

8      format (10(e12.4))
      stop
      end

      subroutine tridag (f,g,h,C,nn)
c solves a tridiagonal system using the Thomas Algorithm
c there are nn equations, in the tridiagonal form:
c f(i)*y(i-1) + g(i)*y(i) + h(i)*y(i+1) = d(i)
```

```
c here, f(1) and h(nn) are assumed 0, and ignored
c y is returned in C, g is altered

      integer nn,i,k
      real f(nn),g(nn),h(nn),d(nn),ym

      do 10 k = 2,nn
      ym = f(k)/g(k-1)
      g(k) = g(k) - ym*h(k-1)
      d(k) = d(k) - ym*d(k-1)
   10 continue
      d(nn) = d(nn)/g(nn)
      k = nn
      do 2 i =2,nn
      k = nn + 1 - i
      d(k)= (d(k) - h(k)*d(k+1))/g(k)
    2  continue
      return
  100 format(/3x,'diagonal element .eq. 0 in tridag at k = ',i2/)
      end
```