ASSESSMENT OF IMPACT OF RESERVOIR'S CONTAMINATED BOTTOM SEDIMENTS ON SURFACE WATER QUALITY BY SEDIMENT-WATER INTERACTION MODEL

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ABSTRACT

ASSESSMENT OF IMPACT OF RESERVOIR'S CONTAMINATED BOTTOM SEDIMENTS ON SURFACE WATER QUALITY BY SEDIMENT-WATER INTERACTION MODEL

In this study, an approach for the assessment of the life-long impact of submersed contaminated bottom sediments in projected reservoirs on surface water quality is presented. A sediment-water interaction model designed to simulate contaminants in the sediments and in the overlying water column is developed and the impact of contaminated bottom sediments on water quality is investigated under different scenarios.

One goal of this study is to investigate the contribution of contaminated soils underlying the reservoir compared to the contaminants transported by surface and groundwater influx. The proposed study predicts the long term impact of the selected site on water quality before the construction of the dam.

The sediment-water interaction model developed in this study consists of three main layers: water column which can be specified as well mixed or stratified according to the temperature profile in the vertical column, a mixed sediment layer and a deep sediments layer. In the model, mass balance equations for contaminants are solved for the water column and the mixed sediment layer.

This study further presents the projection of possible contamination in a reservoir based on the analysis of the soil samples collected from the reservoir bottom before the filling of the reservoir. Reverse modeling approach for the prediction of contaminant concentration in the water column originating from the bottom sediments is applied. Transfer of five heavy metals; Copper, Zinc, Chromium, Nickel, and Lead existing in bottom sediments of Çamlı Basin to the reservoir water is modeled.

ÖZET

BARAJ HAZNELERİNİN TABANINDA BULUNAN KİRLETİCİLERİN SU KALİTESİNE ETKİSİNİN ZEMİN- SU KOLONU ETKİLEŞİM MODELİYLE DEĞERLENDİRİLMESİ

Bu çalışmada, su temini amacıyla inşası planlanan barajların sular altında kalacak alanlarında zeminde bulunan kirleticilerin yüzeysel sulara baraj ömrü boyunca etkisinin değerlendirilmesi için bir yaklaşım sunulmuştur. Tabanda ve su kolonunda bulunan kirleticileri modelleyebilmek için zemin-su kolonu etkileşim modeli geliştirilmiş ve baraj haznesi zemininde halihazırda var kirleticilerin su kalitesine etkisi farklı senaryolar altında araştırılmıştır.

Bu çalışmayla hedeflenen göl alanında halihazırda var olan kirleticilerin, yeraltı suyu yoluyla ve yüzeysel sularla taşınan kirleticilerin oranına katkısını belirlemektir. Bu modelleme çalışması baraj havzası için seçilen yerin uzun vadede su kalitesini nasıl etkileyeceği hakkında baraj inşa edilmeden ön fikir verecektir.

Bu çalışmada geliştirilen zemin-su kolonu etkileşim modeli düşeyde üç ana katman içermektedir. Birinci katman, dikey sütundaki sıcaklık profiline göre iyi karışmış ya da tabakalaşmış şekilde de modellenebilen su sütunu tabakası, ikinci katman karışmış zemin tabakası, üçüncüsü ise derin tortu tabakasıdır. Modelde, kirleticiler için kütle denge denklemleri, su sütunu ve karışmış zemin tabakası için çözülmektedir.

Bu çalışmayla, baraj haznesi doldurulmadan önce haznenin dibinden alınan zemin örneklerini baz alan, haznede ileride oluşabilecek kirlilik modellenebilecektir. Su kolonunda tabandaki kirleticilerden kaynaklı kirletici konsantrasyonlarının tahmini için ters modelleme yaklaşımı uygulanmıştır. Bu yaklaşımla, Çamlı Havzasının zemininde halihazırda mevcut olan beş ağır metalin (bakır, çinko, krom, nikel ve kurşun) ölçülmüş değerleri kullanılarak göl suyuna transferi modellenmiştir.

To my Beloved Son

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CHAPTER 1

INTRODUCTION

Water is one of the most essential natural resources of life. The accessibility and quality of water have always played a vital part in setting the boundaries of people's homes and determining the quality of their lives. In other words, water can be defined as "life." It is the source of ecosystems, food and other aspects of life. All life forms need water to survive. Not only humans but also microorganisms, for instance, need water so that they can produce energy to continue their existence. Fresh water is also important for organisms that share the same habitat with humans which are the ecological fundamentals for a sustainable environment.

However, water must be considered as a finite source and it must be realized that water resources have limits and boundaries to its availability. For example, fresh water which was so plentiful on the planet is now turning into a scarce source. Conflicts about water have already evolved into "deprivation" rather than "desperation." (Tolba, et al. 2004)

Reasons of water scarcity, when examined, can vary from uncontrolled population increase to unexpected changes due to climate change and to failures for sustainable management of resources. It can be seen that all these reasons and others restrict the use of water. According to a research conducted by Stockholm International Water Instituted in 2008, 1.4 billion people live in "closed basins" which is a term signifying the regions where present water cannot satisfy the agricultural, industrial, municipal, and environmental demanding. The UN Food and Agricultural Organization (FAO) stated in 2007 that 1.2 billion people live in regions that experience water scarcity. FAO estimates that the quantity of water-scarce will reach to 1.8 billion people by 2025 (Gardner 2010).

Apart from the stated reasons, water scarcity can also be due to physical or economical problems. Physical water scarcity can be defined as insufficient water to meet the needs. On the other side, economic water scarcity occurs when water is available but inaccessible due to lack of investment or poor management techniques.

No matter what the situation is, it is a fact that need for fresh water connects nearly 7 billion people with each other. Some countries face rising shortages and drought while others deal with pollution and some diseases. Sometimes, some conflicts come about over distribution and flowing water or the scarcity of it causes deep divisions within and across the borders (Map room: Water Scarcity 2009).

In summary, growing scarcity of water is one of the leading problems challenging the human civilization in the 21st century. In order to cope with this situation, World Water model is developed and put into use to estimate global world water resources, using dynamic system approaches. This has shown that there is a strong relationship between the world water resources and forthcoming industrial development of the world and it has also shown that water scarcity which the world is facing today will turn out to be the most important problem on the universal level (Wurbs 1995).

In this issue, the importance of water management gains vitality. Water management includes the improvement, control, protection, and beneficial usage of rivers and reservoirs which make up of surface and ground water resources. Services obtained by the water management involves water supply for agricultural and industrial uses, waste-water treatments, protection and improvement of environmental sources, reduction of pollution, hydroelectric power generation, water sets, erosion and sedimentation control and controlling and reducing the number of flood events.

The measurement and complicity of problems analyzed with this model range greatly. For instance, one or several software packages may be enforced in the design of an urban storm water detention basin with a watershed area of less than one square kilometers. Other models may be used to make the operations of a major multiple-reservoir optimal, multiple-purpose such as flood control, water supply, hydropower, recreation system regulating the water resources of a river basin with a drainage area of a thousand square kilometers. At the local level, models may be practiced both by a consulting firm to prepare a permit application for enlargement of the wastewater treatment plant of a small municipality and by a state regulatory agency to assess the permit application. Likewise, on a larger geographic scale, models may be used to formulate and assess plans for solving regional or basin wide nonpoint source pollution problems. Models may also be used to estimate drawdown conditions to be expected as a small but growing community increases its groundwater pumpage or alternatively to evaluate the ground-water resources available from a large regional aquifer supplying water users placed in several cities (Wurbs 1995, Simonovic 2004).

However, this model has lived a shift in 1970s and 1980s in terms of its objections. Although, when first used, it concentrated on the water management, it has recently concentrated on protection of water quality and environmental resources just as the rest of the world (Simonovic 2004).

Not only availability but also quality of water has a vital role in determining the quality of people's lives. Although there has been plenty of fresh water on Earth, water has not always been available when and where it is needed and it is also not always of appropriate quality for all uses. Conventionally, water management in developed countries concentrated on expanding and leading the country' supplies of fresh water to meet the needs of the users. A number of large dams were built in and during the twentieth century to expand the supply of fresh water for stated time and places. However, this "building dams" time has already passed and now, in twenty first century, the limited water supply and established infrastructure require that demand be administrated more effectively under the boundaries of available sustainable supply. Water-use information can be used to assess the effects of population growth and efficiency of the alternative water management policies and regulations (Water Encyclopedia 2011).

No matter what, the quality of water still holds an important place. The reason for this issue to become alarming is humans. People currently distract and regulate more than half of globally readily fresh water run off for their own benefit including using dams or distractions on rivers. Moreover, ground water resources are becoming increasingly used for agricultural and urban aims at numbers which exceed the natural capability of these reserves to recharge themselves. As a consequence of human disturbance and misuse, water quality continues to decrease with the aid of the changes of natural conditions and from a variety of pollutants including pesticides, excessively-used nutrients, pathogenic organisms and the most ever-present item: sediment (Cooper, et al. 2001).

Sediment production affecting the water quality of streams is well documented. In general, landscape scale system of readily-used technology controls these sources and effects of it remain unfulfilled even though the necessity for such a detailed action obtains desired goals of water quality, wild life and land protection and maintenance is largely recognized. The achievement of these goals will help provide sustained environmental health and productivity in the agricultural area. This way, recommendations for controlling and reducing general watershed problems through form implementation of beneficial and effective technologies (Cooper, et al. 2001).

However, awareness of the necessity to protect freshwater seems finite. This is mostly the reason why people are not aware of the value of fresh water. On the other hand, appreciating it means insurance to its well-being. It is certain that if scientists are not able to put a value on ecosystem goods and services, politicians will assess it as a "zero value." For this situation, Kingsford states that water should no longer be free or cheap resource. If a realistic economical value is to be assessed, it will be a leading driver for society to change its attitude towards water and fresh water biodiversity (Biol. Rev. 2006). Leaving what is told about the issue, if it is to be given what should be done to obtain fresh water, then it must be noted that there are many ways to do it. As stated, fresh water is a term which signifies the naturally flowing water on the Earth's surface such as logs, rivers and streams. Techniques to obtain and conserve fresh water from these resources are called stream restoration or river reclamation.

When water quality is of concern, the transport of naturally appearing constituents, like nutrients, solids, and contaminants in a watershed are influenced by a mixture of interactions including meteorological conditions, land use, urban and rural watershed runoff, groundwater transport, surface water transport, and biological processes in the water column and sediment bed. Mathematical models designed to demonstrate the transport pathways and fate of contaminants in the aquatic environment can be used as powerful instruments in understanding, and differentiating, the relative significance of natural processes and human activities on trends in water quality and aquatic ecosystem resources. This study focuses on improving quality of water for future projected reservoirs by developing a sediment-water interaction model to be used as a tool for selection of the sites. In water supply reservoirs, water quality can deteriorate due to environmental contaminants including heavy metals, and for the remediation of the pollutants, understanding interaction of water column with bed sediments is the key.

This thesis includes seven chapters. Chapter 1 aims to present a brief introductory background to the research subject. Previous relevant studies are reviewed in Chapter 2. Mechanism of sediment transport is summarized in Chapter 3. The sediment-water interaction model (SWIM) is described in Chapter 4. In Chapter 5, SWIM model is compared to existing sediment water interaction models. Application of the SWIM Model for a projected dam, Çamlı Dam and Reservoir site is presented in Chapter 6. Finally, the main results and the conclusions of the study are summarized in Chapter 7.

CHAPTER 2

LITERATURE REVIEW

Water quality models are relatively new those have been gradually developed in the last 30 years. Wood (1980) developed the first water quality model in a study of slurry flow in a pipe network. In a generalization of this formulation, Males et al. (1985) used simultaneous equations to calculate the spatial distribution of variables those could be associated with links and nodes such as concentration, travel times, costs and other variables. By the mid- 1980s, water quality models were developed that incorporated the dynamic behavior of water networks (Grayman, et al. 1988). The usability of these models was greatly improved in the 1990s with the introduction of the public domain EPANET model (Rossman 2000). This led to the development of other Windows based commercial water distribution system models that are in use today. In more recent years, research and development has centered on modeling chemical reactions, integrating models with other systems such as geographic information systems, and application of optimization techniques to assist in model calibration, and system operation and design. Over these past 30 years, developments in water quality modeling can be categorized by time periods and important milestones. The 1980's was a period of preliminary development of steady state and dynamic models and initial field studies. In 1991, Environmental Protection Agency of USA (EPA) sponsored a technology transfer conference in Cincinnati that brought together specialists from around the world that had been involved in some manner in the area of water quality analysis. The conference established the stage and set the direction for the next 15 years. In fact, examination of the research agenda indicates that many of the topics identified then are still active areas of research and requirements today. The 1990's are described by the development of user friendly models, research on chlorine dynamics, improvement of models of storage facilities, and the beginning of microbial modeling. In the 21st century, concentration has been placed on water security modeling, modeling water age as a surrogate for water quality, use of models to develop water quality operations, expansion in modeling of processes and conversions, and a re-examination of some of the underlying hypothesis in water quality modeling. At this time, the field of water quality modeling is expanding in breadth, complexity, and general admission. Nevertheless, there are many fields where study is still needed before water quality modeling will become a routine tool that water utilities can use with confidence to make important design and operational resolutions (Grayman 2006).

In water quality systems, the transport pathways and fate of naturally appearing constituents, like nutrients, solids, and contaminants in a watershed are directed by a mixture of interactions of precipitation, land uses, urban and rural watershed runoff, groundwater transport, wastewater and storm water inputs, surface water transport, kinetic transformations and biological processes in the water column and sediment bed. Mathematical models can be utilized to understand the natural processes in water quality and aquatic ecosystem resources. Models can help support the development of management plans, such as remediation of contaminated sites, with quantitative evaluations and comparisons of the effectiveness of alternative plans.

Mathematical models are formed as a series of mass balance equations designed to quantitatively stand for the major processes and interactions stated by the conceptual model (i.e., hypotheses) that identify the transport and fate of pollutants, such as organic chemicals or heavy metals, in the aquatic environment. So as to clearly determine the impact of solids and pollutant inputs from watershed runoff, wastewater discharges and other external sources on transport and fate of the pollutant in the water column and sediment bed, the equations of a model are based on the preservation of mass to accurately account for all the inputs, transformations and outflows of the pollutant in the surface water system.

Surface water models differ in terms of the choices made for the definition of the open boundaries of the physical domain and the corresponding specification of terms in the model equations that explain pollutant loads, physical transport processes and kinetic interactions as either (a) externally acquired data that are input to the model or (b) internally presented data that are calculated by model formulations. For instance, a number of water quality models describe the wetted perimeter and water surface of a water body as the boundaries of the physical domain of the model. Source terms in the model represented by watershed runoff, atmospheric deposition, groundwater interactions and sediment-water exchange of constituents (e.g., nutrients, dissolved oxygen, contaminants) are then provided as externally supplied boundary conditions for input to the model.

As a result of the fact that water quality management issues have become gradually complex in the last ten years, the physical domain boundaries of models have reached beyond the water column of a water body to openly incorporate transport pathways and mass loading of pollutants that are either internally computed or linked with watershed runoff models, regional air quality models, groundwater models, hydrodynamic models, aquatic ecosystem models, sediment transport and contaminant bioaccumulation models (Thomann 1998, Di Toro 2001).

Along with the other ways for the specification of the open boundaries of the physical domain of a model, surface water models are further discerned by consideration of the spatial and temporal scales of resolution, state variables, kinetic interactions and biogeochemical processes. Collectively these exhibit the level of complexity of a model as: (a) a screening level model; (b) an intermediate level model or (c) an advanced or complex level model.

2.1. Screening Models

Screening-level water quality models are structured as highly simplified models to enact only a few selected pollutants as state variables, with restricted interactions and few key processes. These models are used to provide basic engineering estimates of the effect of pollutant loading on water quality conditions. Analyses using screening models can be carried out cheaply to identify watersheds, geographic areas or river reaches that could have major pollution sources and related water quality problems. EPA’s Water Quality Assessment Methodology (WQAM) is an example of a screening level tool that has been used for relatively simplified calculations of the transport and fate of conventional pollutants and toxic contaminants (Mills, et al. 1982).

2.2. Intermediate Models

Intermediate, or planning-level, models usually include a more sophisticated featuring of transport processes and pollutant loads that ascertain the fate of multiple pollutants, with consideration given to numerous processes and kinetic interactions. Intermediate models often describe a simplified, or “lumped”, representation of a state variable (e.g., organic carbon) with no explicit differentiation of either the dissolved and particulate forms or the labile and refractory forms of a constituent. Intermediate models also often describe the mass exchange of a constituent at the sediment-water interface as an externally designated empirical forcing function rather than an internally simulated process. Intermediate models have been developed as one-dimensional, two-dimensional and three-dimensional models, with time dependency of the model represented as either steady-state or time variable. Intermediate models are typically applied to support prioritization and targeting of specific watersheds or river reaches for regulatory control efforts for specific pollution sources, or for comparative evaluations and selection of alternative pollution control strategies to achieve water quality objectives. Examples of intermediate water quality models developed as steady state analytical formulations for assessments of the transport and fate of solids and contaminants in the water column and sediment bed include SMPTOX3 (Limno Tech 1993) and MICHRIV (USEPA 1984). Summaries of other intermediate-level formulations for contaminants are given in Dickson et al. (1982).

2.3. Advanced Models

Advanced models combine state-of-the-art scientific understanding of physical transport and many aquatic ecosystem processes and kinetic interactions of biological and chemical particles. Exchange of constituents across trophic levels and between the water column and sediment bed is often defined in sophisticated models to supply a total mass balance designation of the contaminants of concern. Advanced models, designed initially for research goals, are now being used for eloborate water quality management and ecological studies of large watersheds (e.g., Chesapeake Bay) and large rivers (e.g., Upper Mississippi River; Middle Hudson River). These models, associated with watershed runoff models hydrodynamic models and watershed runoff models, have been developed to resolve cases concerned with, sediment transport, contaminant fate, eutrophication and bioaccumulation.

Advanced Contaminant fate models involve CE-QUAL-ICM/TOXI, EFDC, and WASP5-TOXI5. The U.S. Army Corps of Engineers Waterways Experiment Station developed CE-QUAL-ICM/TOXI for eutrophication and contaminant fate studies of nutrient and toxicant loading to Chesapeake Bay (Cerco and Cole 1993). The contaminant fate model component of EFDC (Hamrick 1992, 1996, Tetra Tech 1999b) is structured in kinetic terms which are for contaminants similar in detail to the one used in CE-QUAL-ICM/TOXI, WASP5-TOXI5 (Ambrose, et al. 1993) and WASTOX (Connolly and Winfield 1984). The more advanced contaminant models like CEQUAL-ICM/TOXI and EFDC also include advanced sediment transport models (Tetra Tech, 1999a) with state-of-the-art particle resuspension and deposition formulations functionally equivalent to formulations designed for SEDZL, an advanced sediment transport model (Ziegler and Lick 1986, Ziegler, et al. 1990, Ziegler and Nesbit 1994, 1995).

The pathways and interactions of contaminants and solids are conducted by complex sophisticated processes, and in nearly all cases require an analysis using either an intermediate or advanced level of detail.

In this study, the new sediment water interaction model (SWIM) was developed for the assessment of the life-long impact of submersed contaminated bottom sediments in projected reservoirs on surface water quality. Equations of three different existing models were benefited from when developing the SWIM model. These models are Recovery Model by US Army Corps of Engineers (Ruiz, et al. 1998), TOXI5 by USEPA (Gualtieri, et al. 1999) and Analytic Model by Gualtieri (Gualtieri, et al. 1997). The Recovery Model developed by US Army Corps of Engineer is the water quality model which is for evaluating the effects of contaminated sediments on surface water. The second main model TOXI5 which is the part of WASP Model is dedicated to simulate the contaminant transport mechanism. This model has been used to understand the pesticides pollution. Unlike the TOXI5 Model, in Analytic Model, it is assumed that the system is a well mixed surface water and the resulting concentration are accessed by analytical solution both for steady state and time variable conditions. On the other hand, in both TOXI5 and Recovery Models analytical solutions are utilized to attain the concentration values.

CHAPTER 3

MECHANISM OF SEDIMENT TRANSPORT

Sediment transport mechanism is related to sediment and water particles. Understanding the physical properties of water and sediment particles is essential to the learning of the mechanism of sediment transport. Some basic properties of water and sediment transport are described below.

3.1. Physical Properties of Water

In sediment transport studies one of the most important points is the basic properties of water. Properties of water are described below.

3.1.1 Viscosity

Viscosity is the property of water that emerges from the cohesion and interaction between molecules and it provides resistance against deformation. Dynamic viscosity depends on the shear stress and velocity gradient.

As a result of the cohesion and interaction between molecules, resistance to deformation is observed. The property of viscosity determines the rate of this resistance to deformation. Newton's law of viscosity is based on the connection between shear stress, velocity gradient dynamic viscosity.

$$\tau = \mu \frac{du}{dy} \tag{3.1}$$

where,

τ =shear stress (M/L^2)

μ =dynamic viscosity (M / (LT))

$\frac{du}{dy}$ =velocity gradient

Kinematic viscosity is the ratio between dynamic viscosity and fluid density (Yang 1996).

$$\upsilon = \frac{\mu}{\rho} \tag{3.2}$$

where,

υ =kinematic viscosity (L^2/T)

3.1.2. Density

Density is the quantity of matter which is contained in a unit volume of the substance.

$$\rho = m / v \tag{3.3}$$

where,

m =mass (M)

V =volume (L^3)

3.1.3. Specific Weight

Specific weight is expressed as weight per unit volume. Specific weight can be defined as (Yang 1996):

$$\gamma = \rho g \tag{3.4}$$

where,

γ =specific weight ($M/L^2/T^2$)

ρ =density (M/L^3)

g =gravitational acceleration (L/T^2)

3.2. Physical Properties of Sediment

In order to understand the sediment transport mechanism settling velocity, particle size, shape and specific gravity are important.

3.2.1. Settling Velocity

Settling velocity (or the terminal fall velocity) is the most important property of sediment particle. Settling velocity is function of the volume, shape and density of the particle, viscosity and density of the fluid. If the properties of the particle and fluid are known, the settling velocity of sediment particle can be calculated. Settling velocity is related to relative flow conditions between the sediment particle and water during conditions of sediment entrainment, deposition and transportation. Settling velocity can be calculated from a balance between the particle submerged weight and the resulting force from fluid drag (Yang 1996). The general drag equation is:

$$F_D = C_D \rho A \frac{{v_s}^2}{2} \tag{3.5}$$

where,

F_D = drag force

C_D = drag coefficient

ρ = density of water

A = the projected area of particle

v_s = the settling velocity

The particle submerged weight for the spherical sediment particle is

$$W_s = \frac{4}{3} r^3 \pi (\rho_s - \rho) g \tag{3.6}$$

where,

W_s =submerged weight

r =radius of the particle

ρ_s and ρ = densities of sediment and water respectively.

The drag coefficient thus obtained is:

$$C_D = \frac{24}{\mathrm{Re}} \tag{3.7}$$

where,

Re= Reynolds number

If the Reynolds numbers less than 1.0 this equation is acceptable;

$$\mathrm{Re} = \frac{v_f d_s}{\upsilon} \tag{3.8}$$

where,

υ= water's kinematic viscosity

d_s =sediment diameter

From Equation 3.5 and Equation 3.7, Stokes (1851) equation can be obtained;

$$F_D = 3\pi d\rho v_f \upsilon \tag{3.9}$$

From the equality of Equation 3.6 and Equation 3.9, the settling velocity for a sediment particle can be obtained as below:

$$v_s = \frac{1}{18}\frac{\gamma_s - \gamma_w}{\gamma_w} g \frac{{d_s}^2}{\upsilon} \tag{3.10}$$

where,

γ_s and γ_w = specific weights of sediment and water respectively.

If the particle diameter less than or equal to 0.1 mm, this equation is acceptable.

3.2.2. Particle Size

Particle size which can be defined as the physical properties of the sediment particle is the most important parameter for the sediment transport mechanism. The sediment particle size can be determined by various methods such as sieve analysis, optical methods or visual accumulation tube analysis.

3.2.3. Shape

Particle shape is the second fundamental sediment property for natural sediments. Shape is defined as the geometric configuration and it is independent of the sediment particle size and particle composition. Corey (Schulz, et al. 1954) investigated several shape factors and defined the shape factor as:

$$Sp = \frac{c}{\sqrt{ab}} \tag{3.11}$$

where;
a=long diameter
b=intermediate diameter
c=short diameter

3.2.4. Particle Specific Gravity

The specific weight of the sediment to specific weight of water is known as particle specific gravity. It usually ranges numerically from 2.6 to 2.8 in natural solids. Quartz, which is the most common mineral has the specific gravity of 2.65. (US Army Corps of Engineers 2008).

3.3. Bulk Properties of Sediment

There are three important bulk properties which are specific weight, porosity and particle size distribution for the sediment. These properties are described below.

3.3.1. Specific Weight

Specific weight of sediment is described as weight per unit volume.

$$\gamma_d = (1 - p)\gamma_s \tag{3.12}$$

where,

γ_d = specific weight of deposited sediment

p =porosity

Specific weight varies with time depending on the composition of sediment mixture.

3.3.2. Porosity

Porosity is described as volume of voids to the total volume of sample and it depends on shape, particle size and degree of the compression.

$$p = \frac{V_v}{V_t} \tag{3.13}$$

where,

V_v =void volume

V_t =total volume of sample

3.3.3. Particle Size Distribution

Various sediment particles may have different size and shapes. Taking a number of samples and making a statistical analysis to describe the mean, distribution and the standard deviation of the sample is needed to determine the sediment properties (Yang 2003).

The variation in particle sizes in a sediment mixture is determined with a gradation curve, which is a cumulative size-frequency distribution curve showing particle size versus accumulated percent finer, by weight. It is common to refer to particle sizes according to their position on the gradation curve.

CHAPTER 4

ONE DIMENSIONAL SEDIMENT TRANSPORT MODEL (SWIM)

A new sediment-water interaction model developed based on existing sediment water interaction models proposed by Ruiz (1998) and Gualtieri (2001) is utilized to study the interaction between contaminant and aquatic environments. In water quality modeling for environmental contaminants including heavy metals, interaction of water column with bed sediments is a key process and for the understanding of the behavior of pollutants in lake and reservoirs and for improvising different strategies to remediate the pollutants, numerical models simulating the sediment-water interaction can be used. This chapter describes the basics of sediment-water interaction model (SWIM) and discusses the sensitivity of the model results to important parameters utilized within the model. Unlike the existing sediment-water column interaction models assuming that the system is idealized as a well-mixed surface water layer underlined by a stratified sediment column, our model can simulate stratified surface water underlined by a stratified sediment column which is the most common environment encountered in the nature. The calculations in SWIM were performed by utilizing Visual Basics Software. In one dimensional model, the system is idealized as stratified surface water layer underlined by a mixed sediment layer, underlined by two layers composed of both contaminated and clean deep sediment layers (Figure 4.1).

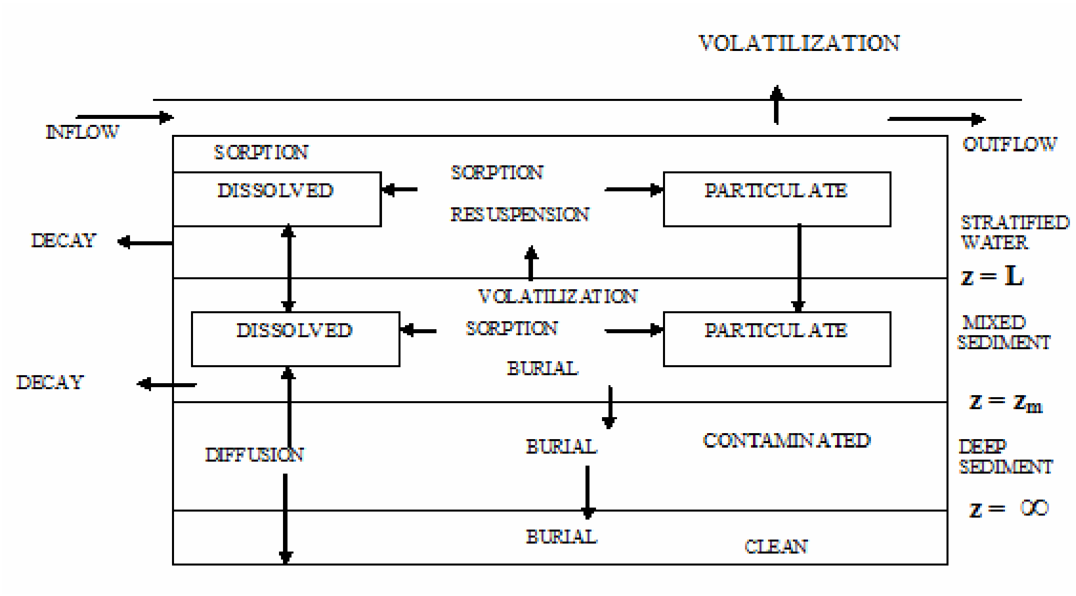

Figure 4.1. Theoretical representation of the sediment-water column interaction model

SWIM computes sediment and water contaminant concentrations and fluxes as a function of time. In the model, mass balance equations for contaminants are solved for the water column and for the mixed sediment layer. Mass balance for the solids is solved for mixed sediment layer considering settling, resuspension and burial processes between the layers. Definition of these processes can be summarized as: *Volatilization*, which is defined as vaporization of dissolved sample; *sorption* is when one substance takes up or holds another one; *diffusion* can be defined as movement of a fluid from an area of higher concentration to an area of lower concentration; *resuspension* is a renewed suspension of insoluble particles after they have been precipitated; *burial* is the accumulation of particles in the bottom; *settling* is lowering of particles by gravity; *partition* is the distribution of solute into parts. Advection-diffusion decay equations are used to model contaminant concentration in the deep sediments layer.

4.1. Calculation of Particle Velocities

4.1.1. Settling Velocity

Sediment characteristics significantly affect the behaviour of contaminants. Calculation of settling, resuspension and burial velocities thus have particular importance in modeling sediment water interaction. For calculating settling velocity, two different equations were selected and incorporated to the model:

a) Stokes Settling Velocity (Yang 2003)

$$V_s = \frac{8.64g}{18\mu}(\rho_p - \rho_w) * d^2 p \tag{4.1}$$

where;

V_s = Stoke's Settling Velocity, m/day

g = Gravitational acceleration, 9.81 m/sn^2

μ = Viscosity value for water, 0.01 poise (poise=g/cm^3-sn) at 20º

ρ_p = Density of particle, g/cm^3

ρ_w = Density of water, g/cm^3

d_p = Particle size, mm

It can be easily seen in equation 4.1, settling velocity value depends on kinematic viscosity and density of water those are function of water temperature. The kinematic viscosity and density of water can be calculated by using the equations 4.2 and 4.3 (McCutcheon, et al. 1994).

$$\mu = 1.79^2 * 10^{-6} / (1 + 0.0337 * T + 0.000221 * T^2) \tag{4.2}$$

$$\rho = 1000 * (1 - (T + 288.9414) / (508929.2 * (T + 68.12963)) * (T - 3.9863)^2) \tag{4.3}$$

where;

T= Temperature, ° C

b) Rubey's Formula (Yang 2003):

$$V_{ru} = F * [1000 * dg(\frac{\rho_s - \rho_w}{\rho_w})]^{1/2} \tag{4.4}$$

where;

V_{ru} = Settling velocity, m/s

$F = 0.79$ for particles greater than

For the calculation of the parameter F, formula 4.5 can be used which depends on the particle diameter:

$$F = \left[\frac{2}{3} + \frac{36 * \nu^2}{g * d^3(\rho_s / \rho_w - 1)}\right]^{1/2} - \left[[\frac{36 * \nu^2}{g * d^3(\rho_s / \rho_w - 1)}]^{1/2}\right] \tag{4.5}$$

4.1.2. Burial Velocity

In SWIM the burial velocity is calculated as a function of settling velocity (EPA 2010). The equation for calculation of the burial velocity is given below,

$$Vb = \alpha * Vs \tag{4.6}$$

where;

α =probability of deposition upon contact with bed

4.1.3. Resuspension Velocity

After calculating the settling and burial velocity values, resuspension velocity can be calculated by using the equation which depends on both velocities. The velocity equation provided in the literature was utilized for calculation of the resuspension velocity as given below (Chapra and Reckhow 1983).

$$0 = V_s A_w S_w - (V_r + V_b) A_m (1 - \varphi) \rho_p \tag{4.7}$$

where;

V_s = Settling velocity, m/year

A_w and A_m = Surface area of water and mixed sediment, respectively, m^2

V_r = Resuspension velocity of sediments, m/year

V_b =Burial Velocity of sediments, m/year

φ =Porosity

ρ_p = Density of particle, g/cm^3

4.2. Mass Balance Equations of SWIM

The mass balance equation for the sediments in the water column can be written as

$$\begin{aligned} V_w \frac{dC_w}{dt} &= Q * C_i - Q * C_w - k_w V_w C_w - V_s A_w F_{pw} C_w + V_r A_m C_m \\ &+ V_d A_m \left(F_{dp} C_m - F_{dw} C_w \right) + W \end{aligned} \tag{4.8}$$

where;

V_w = Volume of water body, m^3

C_w and C_m = Concentration of contaminant for both water and mixed layers, respectively, $\mu g/m^3$

C_i = Inflow concentration, $\mu g/m^3$

t = Time, year

Q = Flow rate, m^3/year

k_w = Decay rate constant of contaminant for water column, $year^{-1}$

k_v =Volatilization rate of contaminant, $year^{-1}$

V_s = Settling velocity of particle, m/year

A_w and A_m = Surface areas of water and mixed sediment layers, respectively, m^2

F_{pw} = Ratio of contaminant which is in the particulate form in water layer

V_r =Resuspension velocity of particle, m/year

V_d = Diffusion mass transfer coefficient at sediment-water interface, L/t

F_{dp} = Contaminant concentration rate in sediment pore water to contaminant concentration in total sediment

F_{dw} = Fraction of contaminant concentration in dissolved form

W = External loadings, M/t

The mass balance equation for mixed sediment layer can be written as,

$$\begin{aligned} V_m \frac{dC_m}{dt} &= -k_m V_m C_m + V_s A_w F_{pw} C_w - V_r A_m C_m - V_b A_m C_m \\ &+ V_d A_m \left(F_{dw} C_w - F_{dp} C_m\right) + V_d A_m \left(F_{dp} C_s 0 - F_{dp} C_m\right) \end{aligned} \tag{4.9}$$

where;

V_m = Volume of mixed layer, m^3

k_m = Decay rate constant of contaminant in mixed layer, $year^{-1}$

V_b = Burial velocity of particle, m/year

$C_s 0$ = Contaminant concentration at the top of the deep contaminated layer, mg/m^3

Mass balance equation for the mixed sediment layer has the initial condition which can be stated as $C_m = C_{m0}$.

The mass balance equation for both deep sediment and clean sediment layers can be formulized by using with one dimensional advection-diffusion-decay equations. In order to calculate contaminant concentration in deep sediment layer, mass balance equation is used as shown below;

$$\frac{\partial C_s}{\partial t} = \varphi F_{dp} D_s \frac{\partial^2 C_s}{\partial z^2} - V_b \frac{\partial C_s}{\partial z} - k_s C_s \tag{4.10}$$

where;

C_s = Contaminant concentration in deep sediment layer, g/m^3

D_s = Diffusion rate in sediment pore water, m^2/year

φ = Sediment porosity

z = Depth into sediment, m (At the top of the deep sediment z=0)

k_s = Decay rate constant of contaminants in deep sediment layer, year^{-1}

The initial and boundary condition which is related to mass balance equation for deep and clean sediments layer can be stated as;

- Initial Condition : At t=0 $C_s=C_{s0}$ (for the condition $L>z>z_m$ (between mixed and deep layers)
- Initial Condition: At t=0 $C_s=0$ ($\infty>z>L$) z_m (deep layer)

- Boundary Condition: At $z=z_m$, $J=J_{ms}$ (at deep layer)
- Boundary Condition: At $z=\infty$, $\frac{\partial Cs}{\partial z}=0$

4.3. Partition Coefficient

For the organic contaminants the partition coefficient value can be computed by using the equation (4.11) which is shown below:

$$K_d = 0.617 * f_{oc} * K_{ow} \tag{4.11}$$

where;

f_{oc} = Weight fraction of carbon in solid matter, g-orgC/g

K_{ow} = Octanol- water partition coefficient, (mg/m^3-octanol)(mg/m^3-water)

If the contaminant is named as A, the ratio of contaminant which is in the particulate form can be described as;

$$Fpw = \frac{\dfrac{A_{mass}(Particulate)}{V_{Total}}}{\dfrac{A_{mass}(Dissolved) + A_{mass}(Particulate)}{V_{Total}}}$$

And it can be computed by using equation (4.12).

$$Fpw = \frac{Kdw * Sw}{1 + Kdw * Sw} \tag{4.12}$$

If the ratio of contaminant which is in the dissolved form is defined by F_{dw} ;

$$Fdw = \frac{\dfrac{A_{mass}(Dissolved)}{V_{Total}}}{\dfrac{A_{mass}(Dissolved) + A_{mass}(Particulate)}{V_{Total}}}$$

And it can be computed by using equation (4.13)

$$Fdw = \frac{1}{1 + Kdw * Sw} \tag{4.13}$$

If the ratio of contaminant which is in the dissolved form in mixed sediment layer is defined by F_{dp};

$$Fdp = \frac{\dfrac{A_{Mass}}{V_{PoreWater}}}{\dfrac{A_{Mass}(Dissolved) + A_{Mass}(Particulate)}{V_{Total}}}$$

And it can be computed by using equation (4.14)

$$Fdp = \frac{1}{\varphi + Kds * (1 - \varphi)\rho p} \tag{4.14}$$

where;

K_{dw} and K_{ds} = Partition coefficient of contaminant in water and sediments, respectively, m^3/g

ρ = Density of sediment solids, g/m^3

S_w = Suspended solid concentration which is in water, g/m^3

In SWIM, for a stratified water column where water temperatures are not homogeneous throughout the column, water column is divided into layers and water densities are calculated as a function of temperature. Then, based on the calculated settling and resuspension velocities for the given stratified conditions, the mass balance equation for the sediments in the water column is solved to calculate projected contaminant concentration. In this manner, seasonality in a reservoir/lake system can be included in the projection. Calculated concentration in the water column corresponding to the given time is used for calculation of mass balance equation for the contaminant concentration in the mixed layer. For the deep layer, the initial and boundary conditions are defined based on the concentration of the mixed sediment layer corresponding to the given time step and then mass balance equation for deep sediment layer is solved to determine the projected contaminant concentration in the deep layer. Code developed for these processes is provided in Appendix A.

4.4. Discussion of Different Settling and Resuspension Velocities on Contaminant Concentration

SWIM Model is run by using the Dieldrin substance. Dieldrin is a kind of insecticide and its use was prohibited in 1987 by U.S. Environmental Protection Agency (EPA) due to its harmful effects in the environment and especially human health. Dieldrin can break down in soil and water, very slowly. Also, those who exposed for a long time can face headaches, dizziness, irritability, vomiting and uncontrolled muscle movements. Besides these, Dieldrin has also negative impact on the animals such as nervous system affects. Dieldrin measurements and its related parameters were available in the literature for the numerical model we utilized to compare our SWIM model.

In addition to this, the SWIM Model is run by using the parameters given in Table 4.1 to investigate the effect of different settling velocities (Rubey and Stoke’s) and the corresponding resuspension velocities.

Table 4.1. The values of parameters for SWIM Model for simulation of Dieldrin concentration

Parameters Used in SWIM Model		
Parameters	**Unit**	**SWIM**
Flow Rate into and out of the Water Body (Q)	m^3	$2*10^7$
Volume of Water Body (V_w)	m^3	$1*10^8$
Volume of Mixed Layer (V_m)	m^3	$1*10^7$
Area of Water (A_w)	m^2	$1*10^7$
Area of Mixed Layer (A_m)	m^2	$1*10^7$
Decay Rate Constant in Water (k_w)	1/year	0.22
Volatilization Rate of The Contaminant (k_v)	1/year	7.536
Decay Rate Constant in Deep Sediment Layer (k_s)	1/year	0
Inflow Concentration (C_i)	$\mu g/m^3$	1000
Contaminant Concentration in Water (C_w)	$\mu g/m^3$	1000
Initial Contaminant Concentration in Water (C_{w0})	$\mu g/m^3$	0
Contaminant Concentration in Mixed Layer (C_m)	$\mu g/m^3$	Depends on Concentration of Water Layer
Contaminant Concentration in Deep Sediment (C_s)	$\mu g/m^3$	Depends on Concentration of Mixed Layer
Contaminant Concentration at the top of the Deep Sediment ($C_{s(0)}$)	$\mu g/m^3$	Depends on Concentration of Mixed Layer
Suspended Solid Concentration in the Water (S_w)	$\mu g/m^3$	1000
Settling Velocity (V_s)	m/year	Calculated
Resuspension Velocity (V_r)	m/year	Calculated
Burial Velocity (V_b)	m/year	Calculated
Fraction of Contaminant in Particulate Form in the Water (F_{dw})	Dimensionless	0.606
Fraction of Contaminant in Dissolved Form in the Water (F_{pw})	Dimensionless	0.393
Porosity (Φ)	Dimensionless	0.7
Density of the Sediment Solids (ρ_p)	g/m^3	$2.65*10^6$
Density of Water (ρ_w)	g/m^3	$1*10^6$
Diffusive Mass Transfer Coefficient (V_d)	m/year	$1.4406*10^{-6}$

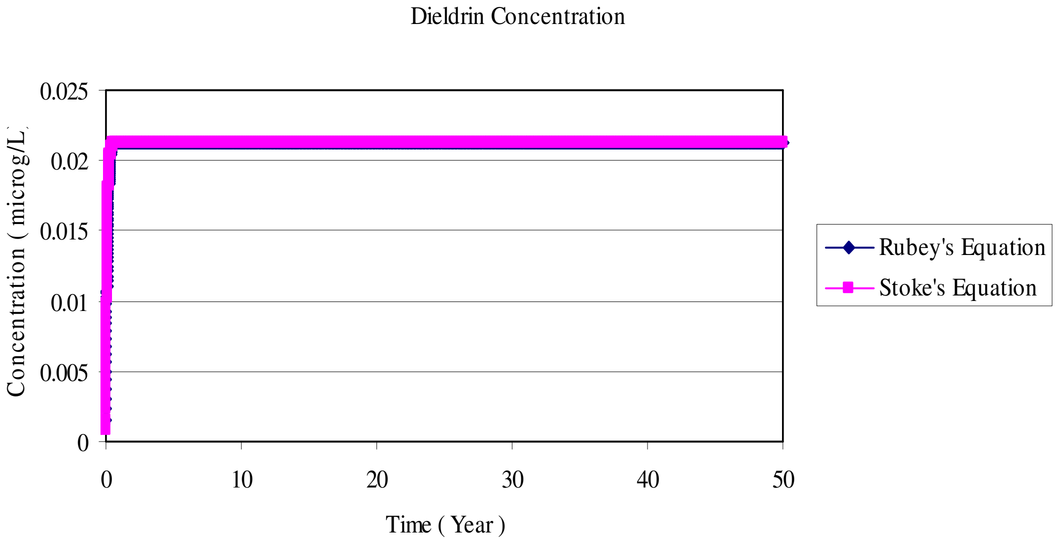

Figure 4.2. Dieldrin concentration depends on velocity formula

When both Stoke's and Rubey's Velocity equations are used, it is observed that same results are obtained for the particle diameter of $11.36*10^{-7}$ m .However particle size is an important parameter in calculating the settling velocities. Therefore, the effect of utilizing different particle size on settling velocity calculated using two different formulations were investigated. In the simulations SWIM Model is run using the parameters given in Table 4.1 As seen in Figure 4.3, velocities calculated using Rubey's and Stoke's equations are only same for the small particle sizes (less than 0.0002 mm) and greatly differ with respect to the formulation used for larger particles.

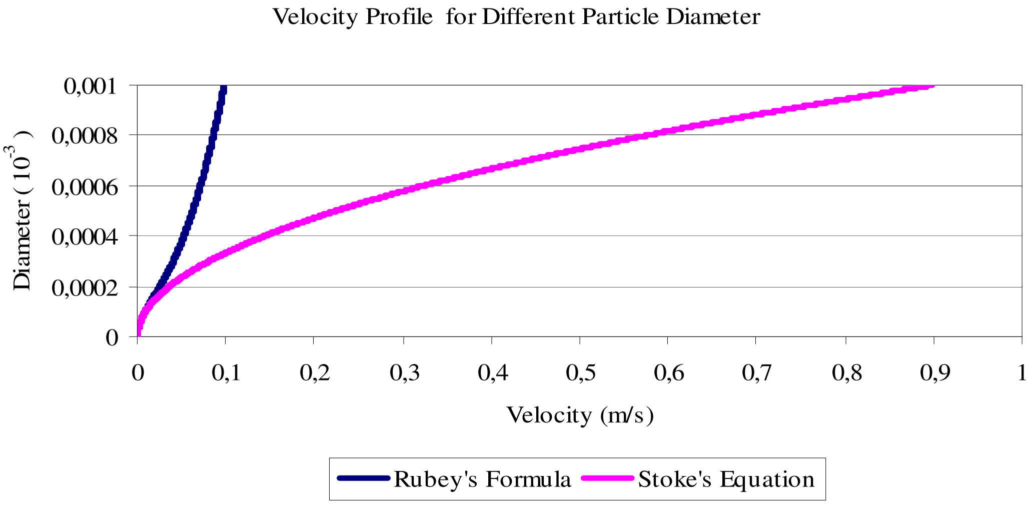

Figure 4.3. Settling velocities calculated as a function of particle size with respect to two different formulations

Likewise settling velocities depend greatly on particle size, the calculated contaminant concentrations depend on settling velocities. The SWIM Model is run using the parameters given in Table 4.1 to investigate the effect of using different settling and resuspension velocities on contaminant concentration for both water column and mixed sediment layer.

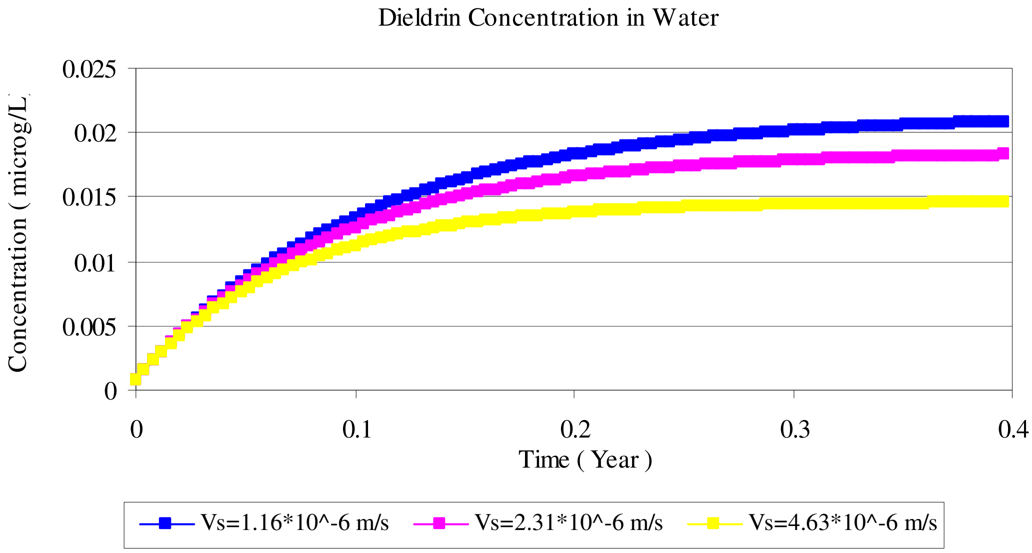

Figure 4.4 Simulated dieldrin concentration in water for the different settling velocity values

When settling velocity is set to a constant value as it is set in the other models and the simulated concentrations are compared to the values obtained by doubling of this constant value from 36.5 to 73 m/year, it is observed that simulated concentrations are decreased in the water layer by 14.3 % and increased in mixed layer and deep layer by 66.7 % and 72.7 % respectively. Results of the sensitivity analysis for different settling velocities are summarized in Table 4.2.

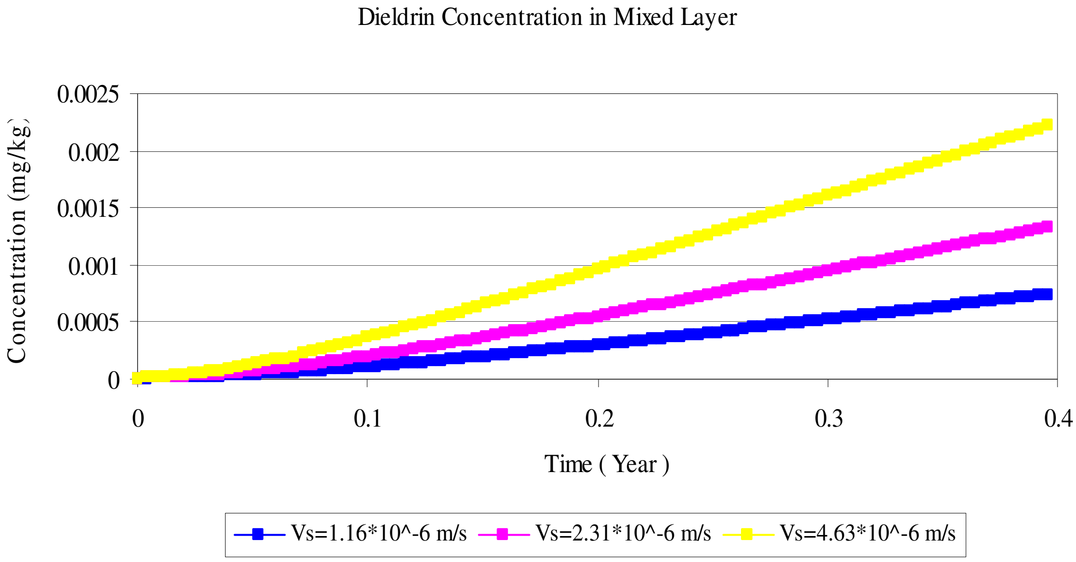

Figure 4.5. Simulated dieldrin concentration in the mixed layer for the different settling velocity values

It can be easily seen that in Figure 4.5 if the settling velocity value increases, unlike the water layer, concentration of contaminant increases in mixed layer during the period of simulation. Figures 4.6 and 4.7 show the effect of using different resuspension velocities in water column and mixed layer, respectively.

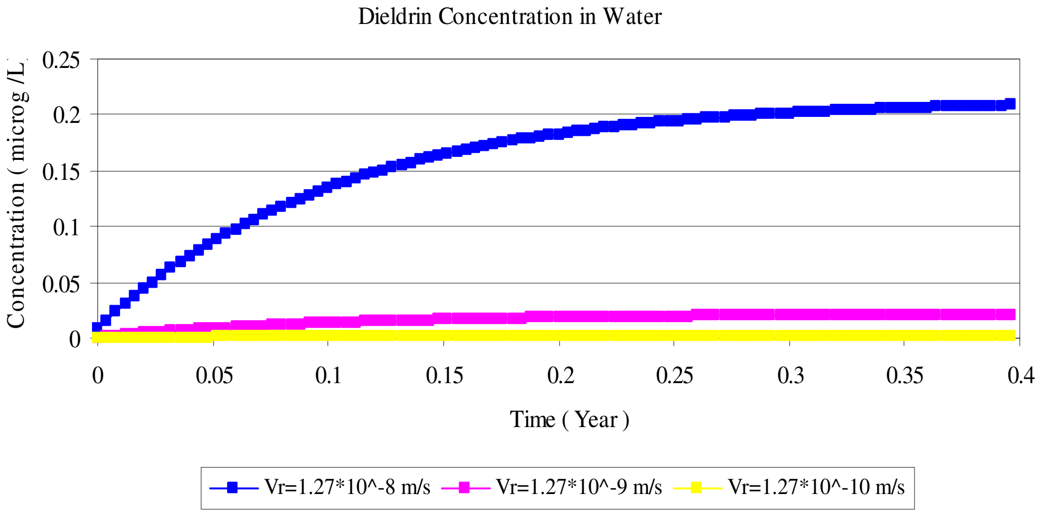

Figure 4.6. Simulated dieldrin concentration in water column for different resuspension velocities

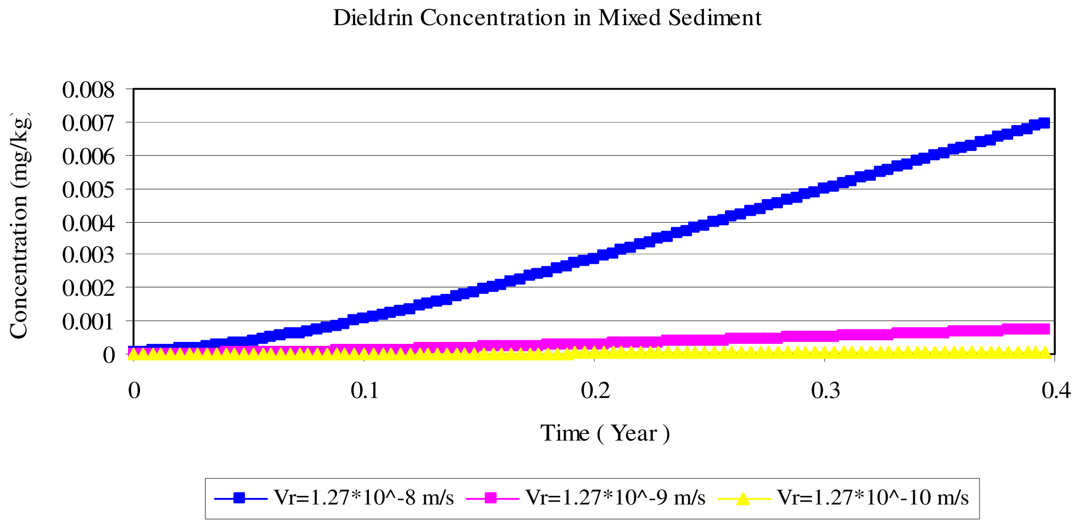

Figure 4.7. Simulated dieldrin concentration in mixed layer for different resuspension velocities

4.5. Comparison of Contaminant Concentration Results for Different Inflow Concentrations

Using the parameters provided in Table 4.1, effect of inflow concentration on projected contaminant concentration is investigated.

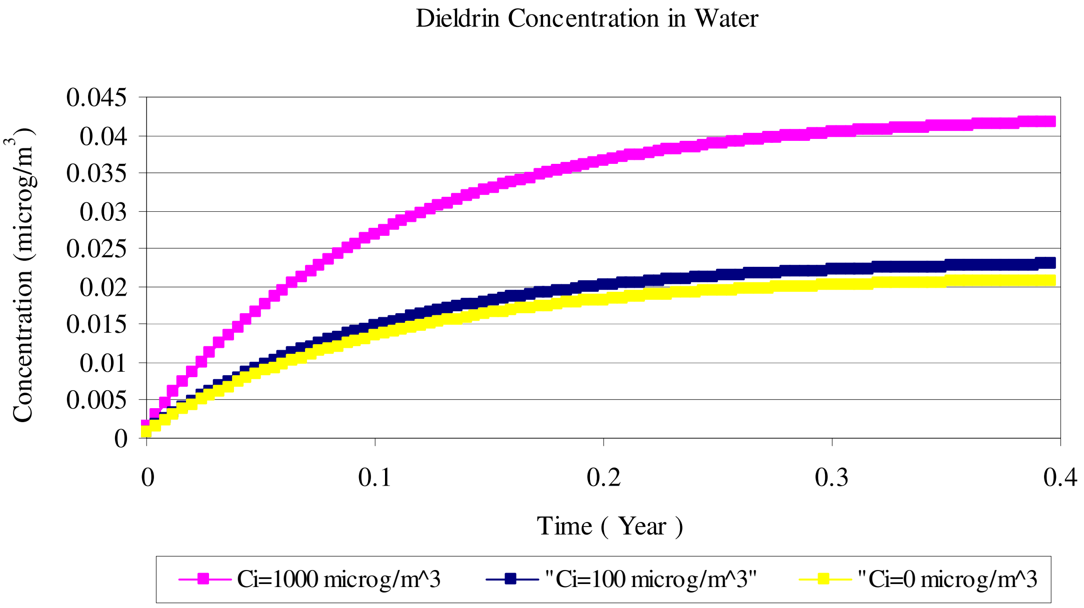

Figure 4.8. Simulated dieldrin concentration in water for different inflow concentrations

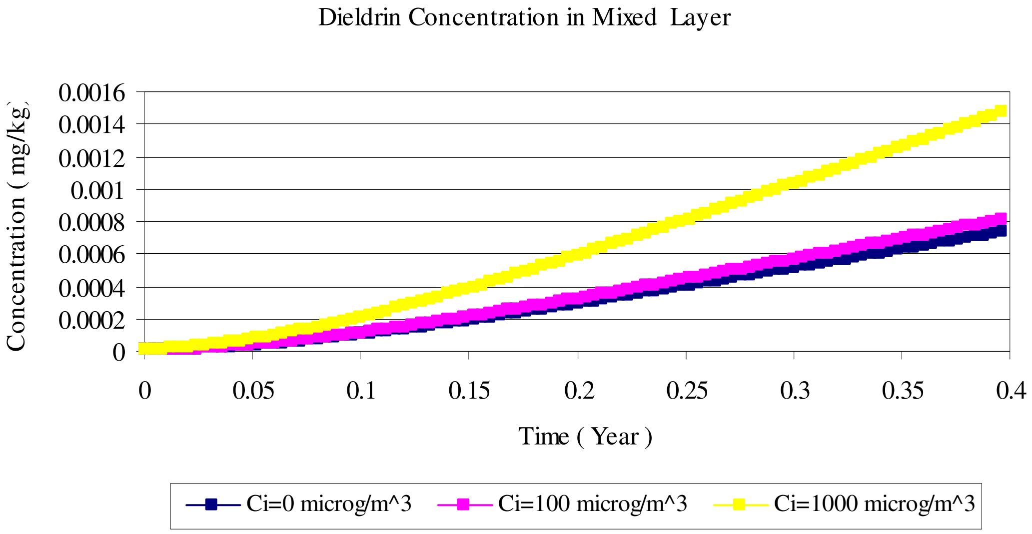

Figure 4.9. Simulated dieldrin concentration in mixed layer for different inflow concentrations

As shown in Figures 4.8 and 4.9, when the inflow concentration is doubled, the simulated concentrations are also doubled. Results of the sensitivity analysis are summarized in Table 4.2.

4.6. Comparison of Contaminant Concentration Results for Different Initial Concentrations

Using the parameters provided in Table 4.1, effect of initial contaminant concentration on projected contaminant concentration is investigated. As shown in Figures 4.10 and 4.11, when initial concentrations are increased from zero to 1000 microg/m^3, simulated concentration in the water layer remained same whereas in mixed layer and deep layers the values increased by up to 36 %. Results of the sensitivity analysis for different initial concentrations are summarized in Table 4.2.

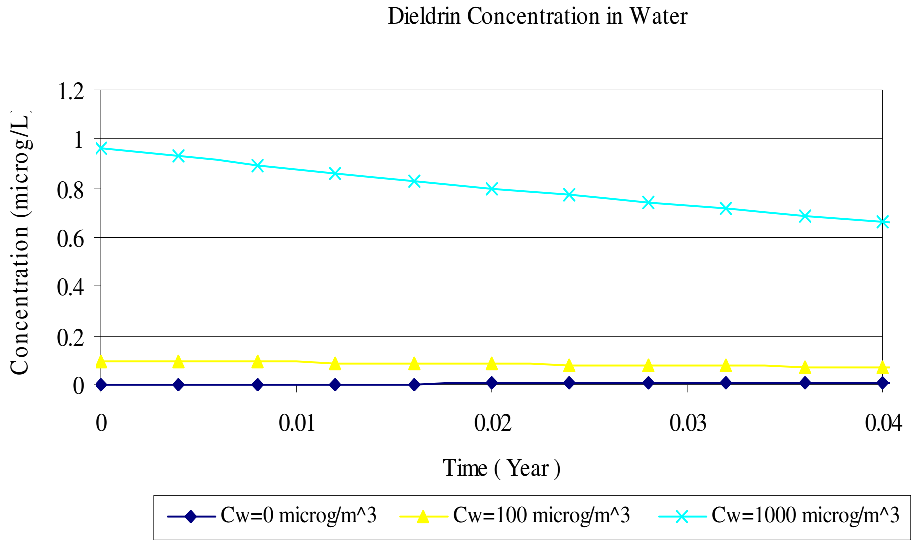

Figure 4.10. Simulated dieldrin concentration in water for different initial concentration values

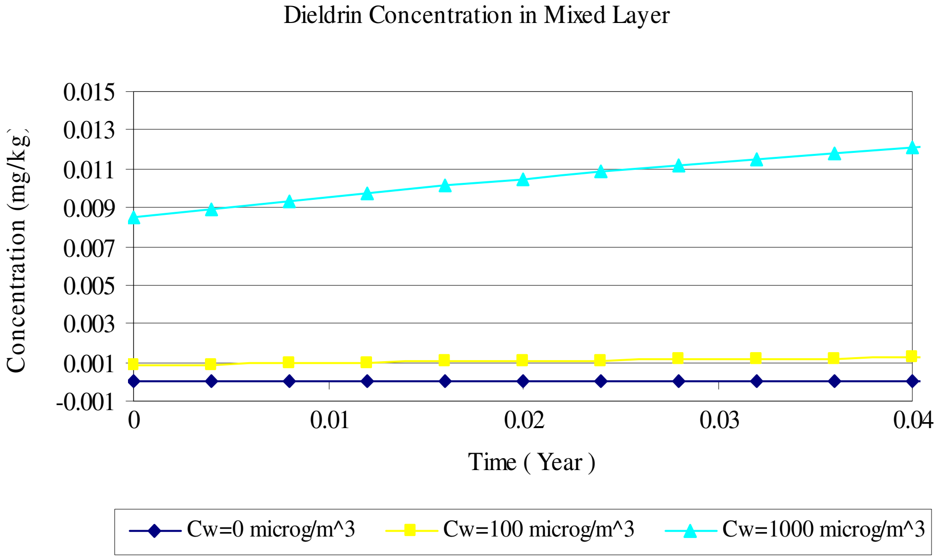

Figure 4.11. Simulated dieldrin concentration mixed layer for different initial concentration values

4.7. Comparison of Contaminant Concentration Results for Different Porosity Values

Using the parameters provided in Table 4.1 effect of porosity on projected contaminant concentration is investigated. As shown in Figures 4.12 and 4.13, projected contaminant concentration values increased in both water column and mixed sediment layer as the porosity increased. Results of the sensitivity analysis for porosity are summarized in Table 4.2.

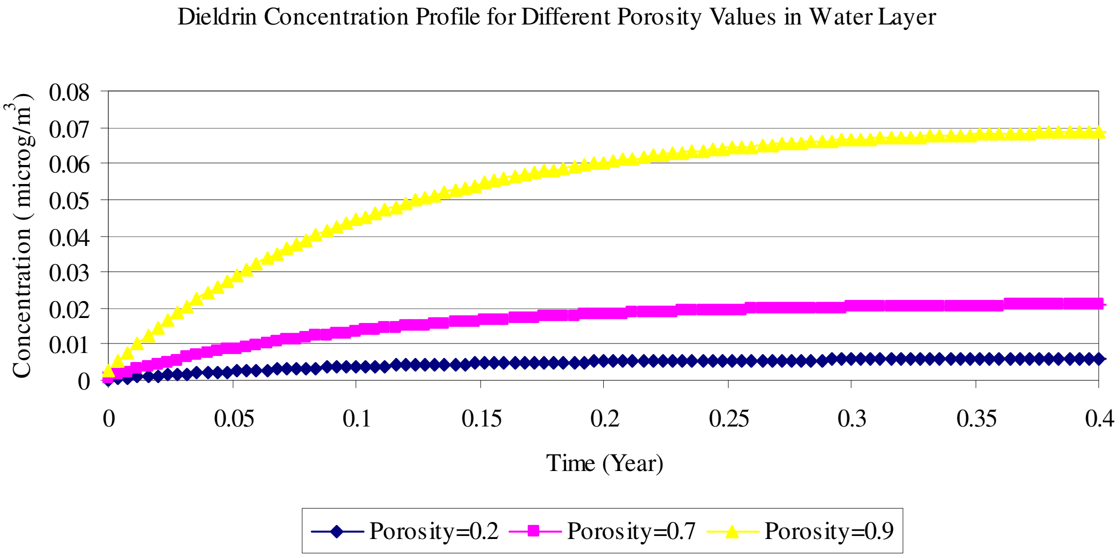

Figure 4.12. Simulated dieldrin concentration in water column for different porosity values

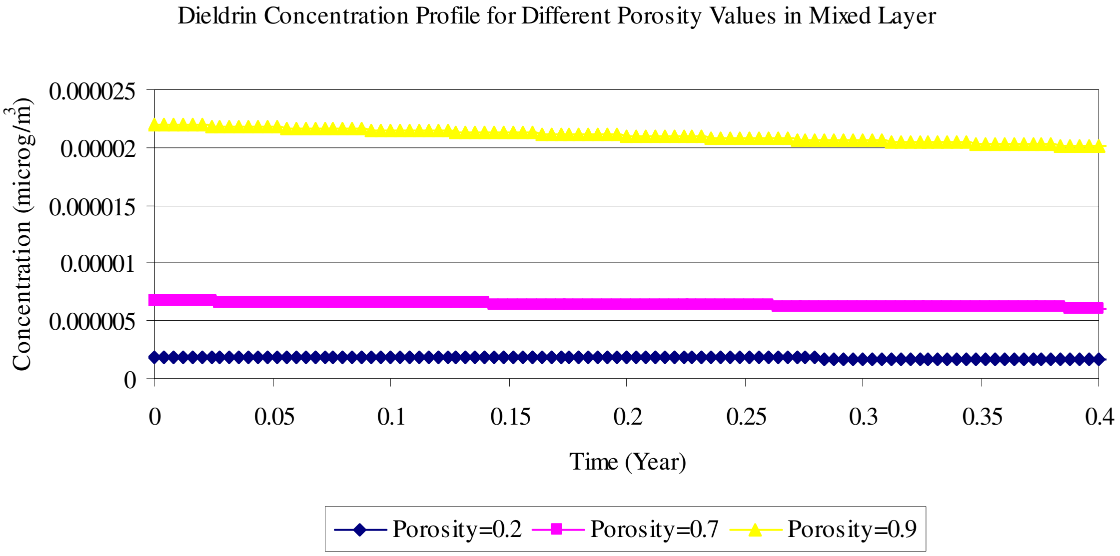

Figure 4.13. Simulated dieldrin concentration in mixed layer for different porosity values

Table 4.2. Results of the sensitivity analysis for settling velocity, initial andinflow concentrations and porosity.

Settling Velocity (m/year)		**Initial Concentration (microg/m^3)**		**Inflow Concentration (microg/m^3)**		**Porosity**	
V_{s1}	36.5	C_{i1}	0	C_{inf1}	1.0E+05	φ_{i1}	0.7
V_{s2}	73	C_{i2}	1000	C_{inf2}	1.0E+06	φ_{i2}	0.2
V_{s3}	54	C_{i3}	500	C_{inf3}	5.0E+05	φ_{i3}	0.5
C_{w1}	0.021	C_{w1}	0.021	C_{w1}	2.13	C_{w1}	0.021
C_{w2}	0.018	C_{w2}	0.021	C_{w2}	21.3	C_{w2}	0.005
C_{w3}	0.019	C_{w3}	0.021	C_{w3}	10.67	C_{w3}	0.0115
$\%_{1-2}$	14.3	$\%_{1-2}$	-	$\%_{1-2}$	900	$\%_{1-2}$	76.2
$\%_{1-3}$	9.5	$\%_{1-3}$	-	$\%_{1-3}$	49.9	$\%_{1-3}$	45.2
C_{m1}	0.009	C_{m1}	0.009	C_{m1}	0.89	C_{m1}	0.009
C_{m2}	0.015	C_{m2}	0.01	C_{m2}	8.91	C_{m2}	0.003
C_{m3}	0.012	C_{m3}	0.0096	C_{m3}	4.5	C_{m3}	0.005
$\%_{1-2}$	66.7	$\%_{1-2}$	11.1	$\%_{1-2}$	901	$\%_{1-2}$	66.7
$\%_{1-3}$	33.3	$\%_{1-3}$	6.7	$\%_{1-3}$	49.9	$\%_{1-3}$	44.4
C_{s1}	7095	C_{s1}	7095	C_{s1}	7.0E+05	C_{s1}	7095
C_{s2}	12254	C_{s2}	10386	C_{s2}	7.0E+06	C_{s2}	1418
C_{s3}	9733	C_{s3}	8741	C_{s3}	3.5E+06	C_{s3}	3698
$\%_{1-2}$	72.7	$\%_{1-2}$	36.3	$\%_{1-2}$	900	$\%_{1-2}$	80
$\%_{1-3}$	37.2	$\%_{1-3}$	23.2	$\%_{1-3}$	49.9	$\%_{1-3}$	47.8

4.8. Comparison of Contaminant Concentration Results for Mixed vs Stratified Water Column Conditions

Using the parameters provided in Table 4.1, effect of stratification on settling velocities and projected contaminant concentration is investigated. Projected contaminant concentration increase as the water temperature increases as can be seen in Figure 4.14. Concentration is significantly higher for the stratified water column conditions as compared with the mixed water suggesting that stratified conditions of the reservoir need to be accounted for in predicting contaminant concentrations. Simulated contaminant concentration values increased in all layers for the stratified water column conditions by 36.8 % for the water layer, 51.5 % for the mixed layer, 50.9 % for the deep layer, as compared to the mixed water column conditions (Figure 4.15). Table 4.3 summarizes the results of the sensitivity analysis.

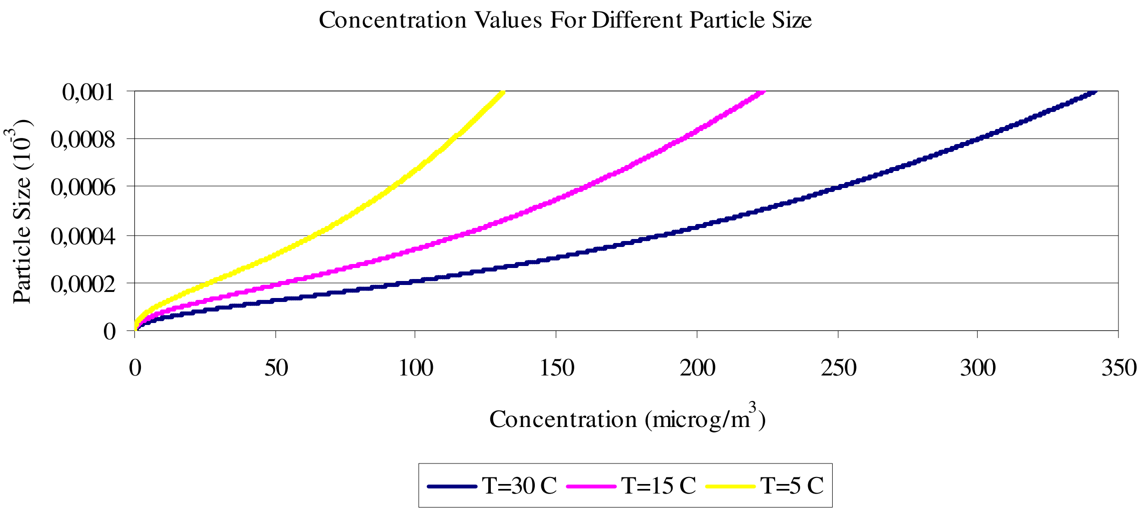

Figure 4.14. Dieldrin concentration calculated with Rubey's settling velocity formula for different particle size and for stratified condition

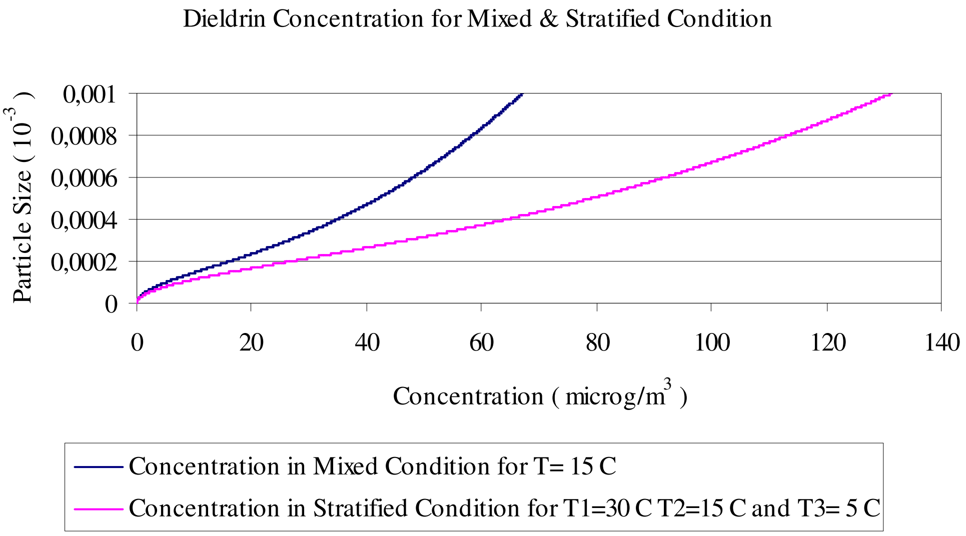

Figure 4.15. Comparison of simulated dieldrin concentration for mixed and stratified conditions calculated with Rubey's settling velocity formula

Table 4.3. Results of the sensitivity analysis for different water temperatures and stratification conditions

Mixed Water column		**Stratified Water Column**	
T_1 (°C)	15	Constant T (°C)	15
T_2 (°C)	30	Varying T (°C)	30,15,5
C_{w1}	0.019	C_{w1}	0.019
C_{w2}	0.025	C_{w2}	0.026
% change	31.6	% change	36.8
C_{m1}	6.40E-07	C_{m1}	6.40E-07
C_{m2}	9.10E-07	C_{m2}	9.70E-07
% change	42.2	% change	51.5
C_{s1}	1.3	C_{s1}	1.3
C_{s2}	1.847	C_{s2}	1.963
% change	42	% change	50.9

CHAPTER 5

COMPARISON OF SEDIMENT-WATER INTERACTION MODEL (SWIM) TO EXISTING MODELS

5.1. Analytical Model Proposed by Gualtieri (1997)

Mass balance equations depending on the steady-state condition provides the basis to the analytical model introduced by Gualtieri (1997). This model is used to investigate water quality in terms of the contaminant transformations between water column and mixed sediment layer. The theoretical scheme of the analytical model proposed by Gualtieri (1997) is provided as in the following figure:

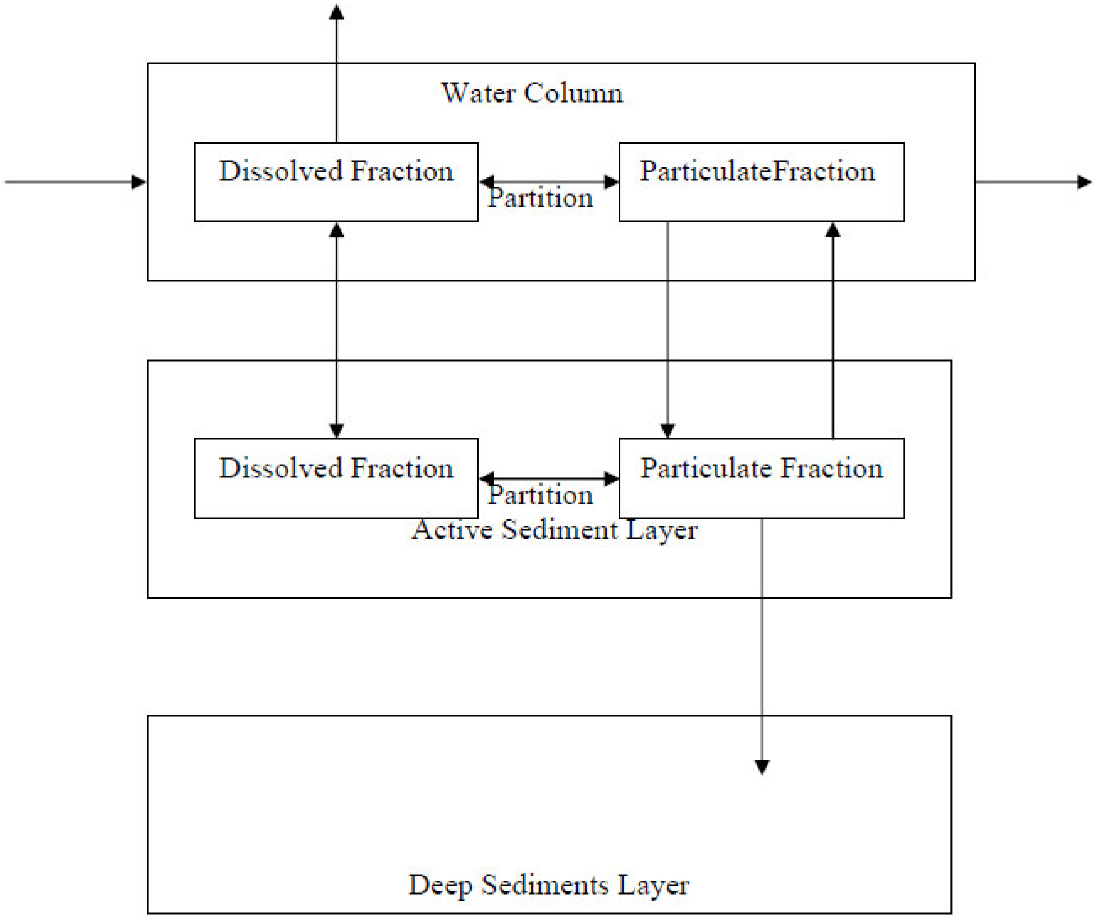

Figure 5.1. The theoretical scheme of analytical model proposed by Gualtieri (1997)

5.1.1. Mass Balance Equations

In the analytical model, the mass balance formula solved for the contaminant concentration in the water column and in the sediment layer is as follows;

$$V_{l\,ake}\frac{dC_{l\,ake}}{dt}=Q_{i\,n}*C_{in}-Q_{out}*C_{lake}-V_s*A*F_{p\_lake}*C_{lake}-V_{vol}*A*F_{d\_lake}*C_{lake}$$
$$+V_r*A*F_{p\_sed}*C_{sed}+V_{diff}*A*(F_{d\_sed}*C_{sed}-F_{d\_lake}*C_{lake})\tag{5.1}$$

and

$$V_{sed}\frac{dC_{sed}}{dt}=(V_s*A*F_{p\_lake})-(V_r*A*F_{p_{sed}}*C_{sed})-(V_b*A*F_{p\_sed}*C_{sed})$$
$$+V_{diff}*A*(F_{d\_lake}*C_{lake}-F_{d\_sed}*C_{sed})\tag{5.2}$$

where;

V_{lake} = volume of lake, m^3

V_{sed} = volume of sediment, m^3

A = Water Column and Active Sediments area, respectively, m^2

F_{d_lake} and F_{p_lake} = Dissolved fraction in the lake

F_{d_sed} and F_{p_sed} = Particulate fraction in the sediments

C_{lake} = Water column's contaminant concentration, (ML^3)

C_{sed} = Sediment's contaminant concentration, (ML^3)

In the model, the diffusion rate which occurs in water column is compared to settling and resuspension and negligible quantitatively. According to this assumption, the mass balance formula is written as ;

$$V_w=\frac{dC_w}{dt}=Q*C_i-Q*C_w-(V_s*A*F_{p\_lake}*C_w)\_(V_{vol}*A*F_{d\_lake}*C_w)$$
$$+(V_r*A*F_{d\_sed}*C_m)\tag{5.3}$$

and

$$V_{sed}\frac{dC_m}{dt} = V_s * A * F_{p\_lake} * C_w - (V_r * A * F_{p\_sed} * C_m) \\ -(V_b * A * F_{p\_sed} * C_m) \tag{5.4}$$

If the equations (5.3) and (5.4) are divided by area and simplified ; equations (5.5) and (5.6) are obtained which are provided below;

$$V_f * C_i - V_f * C_w - V_{vol} * F_{d\_lake} * C_w - V_s * F_{p\_lake} * C_w \\ + V_r * F_{p\_sed} * C_m = 0 \tag{5.5}$$

and

$$V_s * F_{p\_lake} * C_w - V_r * F_{p\_sed} * C_m \\ - V_b * F_{p\_sed} * C_m = 0 \tag{5.6}$$

where,

for steady state condition;

$Q_{in} = Q_{out} = Q$

$V_f = Q/A$

5.2. Toxi 5 Model proposed by Gualtieri 1999

TOXI 5 sediment-water column interaction model is the part of the water quality model (WASP5) developed by USEPA. TOXI5 model is developed to examine the fate of toxics. In recent years, TOXI5 Model has been utilized in order to determine the effects of contamination which are caused by pesticides, especially. The theoretical scheme of TOXI5 Model is shown below.

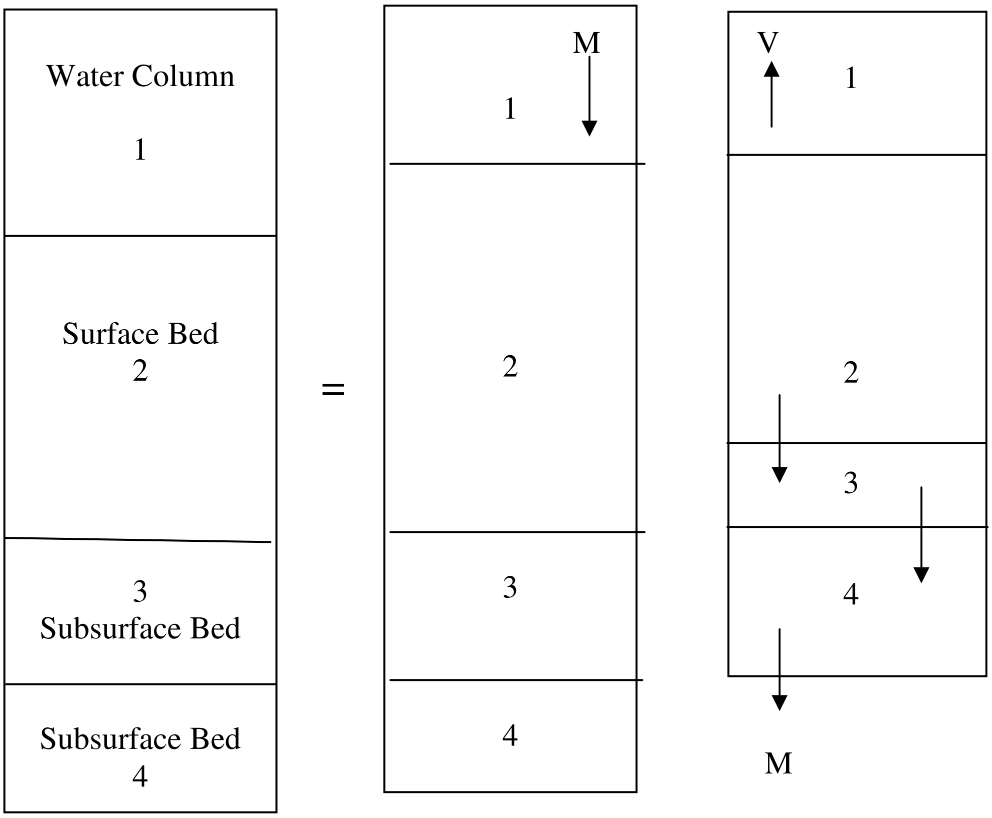

Figure 5.2. The theoretical scheme of analytical model

The mass balance formula for TOXI5 Model can be written as ;

$$\begin{aligned}\frac{\partial}{\partial t}(AC) &= \frac{\partial}{\partial X}\left(-U_x * A_c + E_x * A * \frac{\partial C}{\partial X}\right)\\ &+ A*(S_l + S_b) + A*S_k\end{aligned} \tag{5.7}$$

where;

A = Area, m^2

C = Component concentration, in water body, mg/L or g/m^3

U_x = Longitudinal advective velocity, m/day

E_x = Longitudinal diffusion coefficient, m^2/day

S_l = Direct and diffuse loading rate, g/m^3-day

S_b = Ratio of boundary loadings, g/m^3-day

S_k = Total kinetic transformation rate, (positive is source and negative is sink) g/m^3-day

This equation describes the three main categories of water quality processes. The first part is dominated as movement, the second part represents loading and the last part represents transformation.

5.2.1. Settling Velocity

The settling velocity value is calculated using Stoke's equation which depends on particle size;

$$V_s = \frac{8.64g}{18\mu}(\rho_p - \rho_w) * d^2 \tag{5.8}$$

where;

V_s = Stoke's Settling Velocity, m/day

g = Gravitational acceleration, 9,81 cm/sn^2

μ = Viscosity Value for water, 0.01 poise (poise=g/cm^3-sn) at 20º

ρ_p = Density of particle , g/cm^3

ρ_w = Density of water, 1.0 g/cm^3

d_p = Particle size mm

In order to calculate the ratio of sediment, equation (5.9) which is shown in below can be used ;

$$W_{bs} = Ai_j * (V_r * S_i - V_s * S_j) \tag{5.9}$$

where;

W_{bs} = Sediment's flow rate, g/day

S = Concentration of sediment, g/m^3

V_s = Settling Velocity, m/day

V_r = Resuspension velocity, m/day

A_{ij} = area, m^2

i = Benthic layer

j = Water layer

5.2.2. The Constant Bed Volume Option

The mass balance equation for the sediment which is in a stationary upper bed can be written as ;

$$d_i \frac{\partial S_i}{\partial t} = V_s * S_j - (V_r + V_b) * S_i \tag{5.10}$$

In this equation, it is assumed that the depth of the bed stands constant and the dispersive mixing is neglected.

where,

V_b = Burial (sedimentation) velocity of the upper bed (m/day)

S_i = Sediment concentration in the upper bed, g/m^3

S_j = Sediment concentration in the water , g/m^3

d_i =Depth of the upper bed, m

V_r = Resuspension velocity in the upper bed , m/day

V_s = Settling velocity in the upper bed , m/day

For the lower bed layer the equation (5.11) can be written as;

$$d_k \frac{\partial S_k}{\partial t} = V_b * S_i - V_{sk} * S_k \tag{5.11}$$

where;

S_k = Sediment concentration in the lower bed, g/m^3

V_{sk} = Burial velocity of the lower bed, m/day

d_k = Depth of the lower bed, m

The resulting mass balance equation for the upper bed can be written as;

$$Vs * Sj = (Vr + Vb) * Si \tag{5.12}$$

where;

V_s = Settling velocity in the water, m/day

S_j = Sediment concentration in the water, g/m^3

V_r = Resuspension velocity in the upper bed, m/day

V_b = Burial velocity in the upper bed, m/day

S_i = Sediment concentration in the upper bed, g/m^3

The resulting mass balance equation for the lower bed can be written as;

$$W_s * S_i = V_b * S_k \qquad (5.13)$$

where;

V_b =Burial velocity of the lower bed, m/day

S_k = Sediment concentration in the lower bed, g/m^3

5.3. Recovery Model by Ruiz (1998)

Recovery is the model which is developed by US Army Corps of Engineers to understand the interaction between sediment and water column. Recovery model can simulate several mechanisms including sorption, degradation, deposition, suspension, bioturbation and resuspension processes. The theoretical scheme of the Recovery Model is shown below:

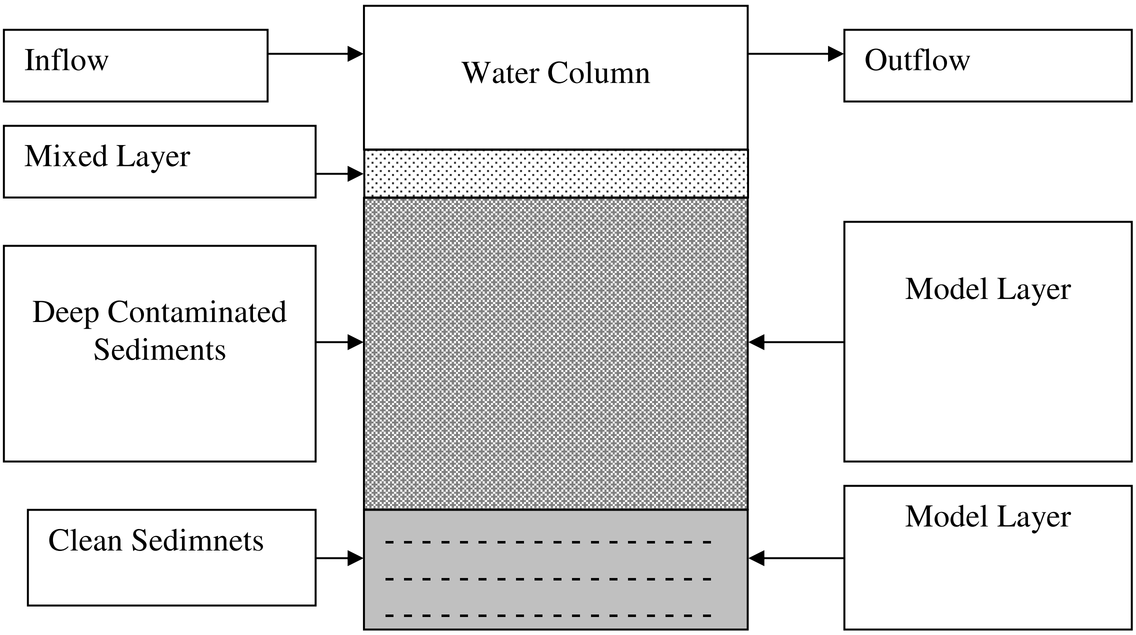

Figure 5.3. Theoretical scheme of the recovery model

5.3.1 Description of the Recovery Model

5.3.1.1 Mass Balance

The mass balance equations for the contaminant in the water column is shown as below:

$$
\begin{aligned}
V_w \frac{dC_w}{dt} &= QC_i - QC_w - k_w V_w C_w - V_s A_w F_{pw} C_w + V_r A_m C_m \\
&+ V_d A_m \left(F_{dp} C_m - F_{dw} C_w \right) + W
\end{aligned}
\tag{5.14}
$$

where;

V_w = Volume of water body, m^3

C_w and C_m = Concentration of contaminant for both water and mixed layers, respectively, µg/m^3

C_i = Inflow concentration, µg/m^3

t = Time, year

Q = Flow rate, m^3/year

k_w = Decay rate constant of contaminant for water column, year^{-1}

k_v =Volatilization rate of contaminant, year^{-1}

V_s = Settling velocity of particle, m/year

A_w and A_m = Surface areas of water and mixed sediment layers, respectively, m^2

F_{pw} = Ratio of contaminant which is in the particulate form in water layer

V_r =Resuspension velocity of particle, m/year

V_d = Diffusion mass transfer coefficient at sediment-water interface, L/t

F_{dp} = Contaminant concentration rate in sediment pore water to contaminant concentration in total sediment

F_{dw} = Fraction of contaminant concentration in dissolved form

W = External loadings, M/t

The mass balance equation for the mixed sediment layer can be written as;

$$\begin{aligned} V_m \frac{dC_m}{dt} &= -k_m V_m C_m + V_s A_w F_{pw} C_w - V_r A_m C_m - V_b A_m C_m \\ &+ V_d A_m \left(F_{dw} C_w - F_{dp} C_m\right) + V_d A_m \left(F_{dp} C_{s0} - F_{dp} C_m\right) \end{aligned} \tag{5.15}$$

where;

V_m = Volume of mixed layer, m^3

k_m = Decay rate constant of contaminant in mixed layer, year^{-1}

V_b = Burial velocity of particle, m/year

In the mass balance equation which is about mixed sediment layer the initial condition at t=0 is $C_m = C_{m0}$.

For the Recovery Model; both deep contaminant layer and clean sediment layer can be modeled using one-dimensional advection-diffusion-decay equation which can be written as;

$$\frac{\partial C_s}{\partial t} = \varphi F_{dp} D_s \frac{\partial^2 C_s}{\partial z^2} - V_b \frac{\partial C_s}{\partial z^2} - k_s C_s \tag{5.16}$$

where;

C_s = Contaminant concentration in deep sediments; mg/m^3

D_s = Diffusion rate in sediment pore water; m^2/year

Φ= Sediment porosity

Z= depth into sediment, m (At top of deep sediment z=0)

k_s = Decay rate constant of contaminant in deep sediment, year^{-1}

The initial and boundary condition which are related to mass balance equation for deep and clean sediments layer can be written as;

- Initial Condition : At t=0 $C_s=C_{s0}$ (for the condition $L>z>z_m$)
- Initial Condition: At t=0 $C_s=0$ ($\infty>z>L$)
- Boundary Condition: At $z=z_m$, $J=J_{ms}$
- Boundary Condition: At $z=\infty$, $\frac{\partial C_s}{\partial z} = 0$

where;

L = Distance (Which is from top of mixed layer to bottom of contaminant layer)

J = Contaminant's mass flux, g/(m^2-year)

J_{ms} = Contaminant's mass flux which is from mixed layer to sediment layer, g/(m^2-year)

5.3.1.2. Solids Budget

According to the mass balance equation for mixed sediment layer, the settling (V_s), resuspension velocit (V_r), and burial velocities (V_b) can be computed. The mass balance formula which is related to the velocity terms can be written as :

$$V_s A_w S_w - (V_r + V_b) A_m (1-\varphi)\rho_p = 0 \tag{5.17}$$

where;

ρ_p = density of particle, gm/m^3

In Recovery Model, when two of the three velocity terms are known, the third can be computed by using the equation (5.17).

In this study three different sediment-water column interaction models are compared and the differences and similarities between them are analyzed. In all models, mass balance equations for water column, mixed layer and deep layer are similar. In Recovery model, constant values for settling and burial velocities can be designated whereas velocities are calculated in analytical and TOXI5 models. In TOXI5 and analytical models, settling velocity values are calculated by using Stoke's settling velocity equation and the burial velocity value can be calculated based on the settling velocity. In the SWIM model developed during this study, settling velocity values are calculated by using both Stoke's and Rubey's formulations proposed for settling velocity and burial and resuspension velocities are calculated based on settling velocity from the velocity equation proposed by Boyer and Chapra (1994). In other models, the simulated system is composed a mixed water column, mixed sediment layer and deep sediment layer whereas in SWIM Model, water column can be divided into several layers to simulate stratified conditions in the water column.

5.4. Comparison of Projected Contaminant Concentration Simulated By Recovery and SWIM Models

The time series of concentration values are modeled for 10 years using SWIM Model and the results are compared to the results modeled by the Recovery Model. Contaminant concentrations modeled by the two models are presented for water, mixed and deep layers.

In order to investigate the effects of initial and inflow concentrations, temperature, and porosity on the simulated concentrations sensitivity analysis for these parameters are conducted and results are presented for both models. Root-mean-square error (RMSE), mean absolute error (MAE), mean relative error (MRE) analysis are utilized for the quantification of differences between the two model results. RMSE, MAE and MRE are calculated by Equations 5.18, 5.19, 5.20 respectively.

$$RMSE = \left[\sum_{n=1}^{N} \frac{\left(C_{est} - C_{m}\right)^{2}}{N} \right]^{1/2} \tag{5.18}$$

$$MAE = \frac{1}{N}\sum_{N=1}^{N}\left|C_{est} - C_{m}\right| \tag{5.19}$$

$$MRE = \frac{100}{N}\sum_{N=1}^{N}\frac{\left|C_{est} - C_{m}\right|}{C_{m}} \tag{5.20}$$

where;

C_{est} = the modeled concentration using SWIM model;

C_{m} = the modeled concentration using Recovery model;

N = the number of data points;

5.4.1. Water Layer

SWIM Model is run using the parameters given in Table 4.1 to calculate the projected contaminant (Dieldrin) concentration at the water column and the results are compared to the results of the Recovery model for the same conditions. Both the simulated concentrations by the Recovery Model and the simulated concentrations by the SWIM Model are shown in Figure 5.4.

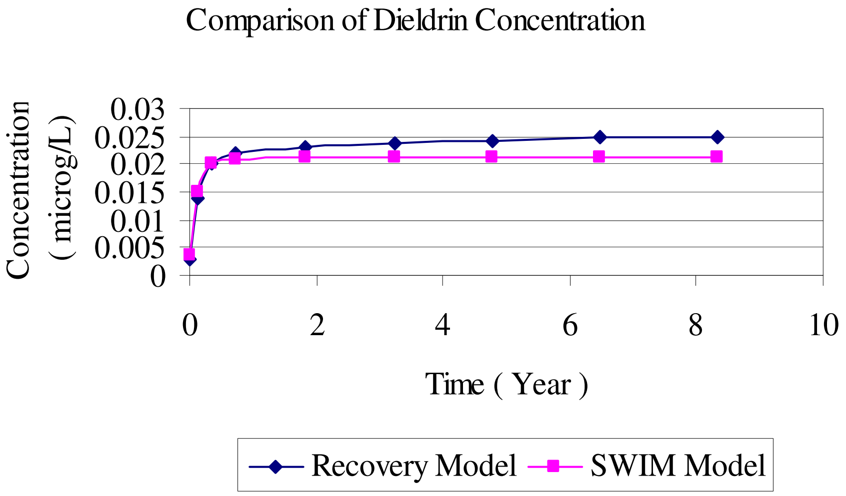

Figure 5.4. Dieldrin concentration in water column simulated by the Recovery and SWIM models

It can be seen from Figure 5.4, the projected sediment concentrations are consistent with the results of the Recovery. The computed error measures for this simulation are 0.0022 microg/L, 0.0018 microg/L, and 10.26% for RMSE, MAE and MRE respectively.

Following this analysis, both Recovery and SWIM models are run using different values for initial concentration value. Results of this simulation are shown in Figure 5.5.

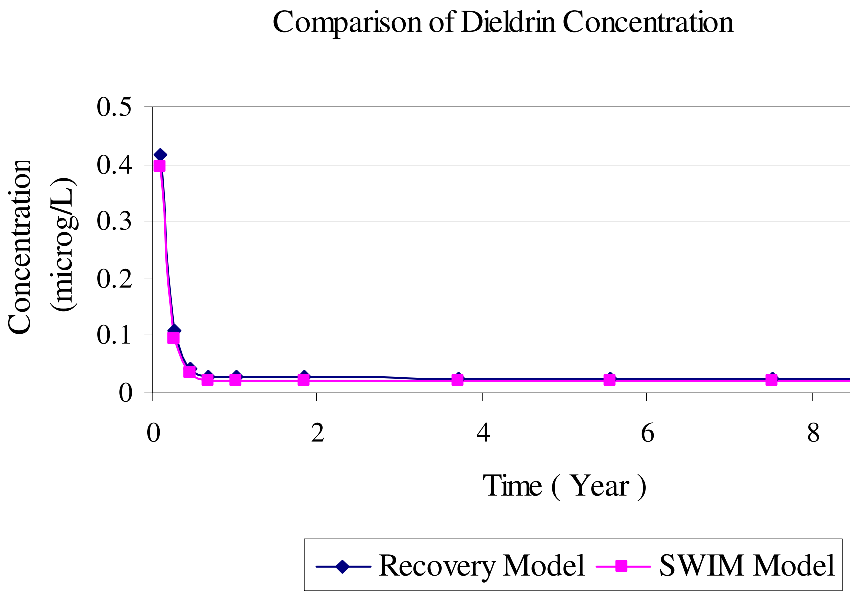

Figure 5.5. Dieldrin concentration in water column simulated by the Recovery and SWIM models for initial concentration of 1000 microg/m^3

It can be seen from Figure 5.5 , the projected sediment concentrations are consistent with the results of the Recovery. The computed error measures for simulation are 0.0012 microg/L, 0.0004 microg/L, and 1.48% for RMSE, MAE and MRE respectively.

After that, both Recovery and SWIM models are run using different values of inflow concentration. Results of this simulation are shown in Figure 5.6. The computed error measures for this simulation are 2.248 microg/L, 1.845 microg/L, and 8.98% for RMSE, MAE and MRE respectively.

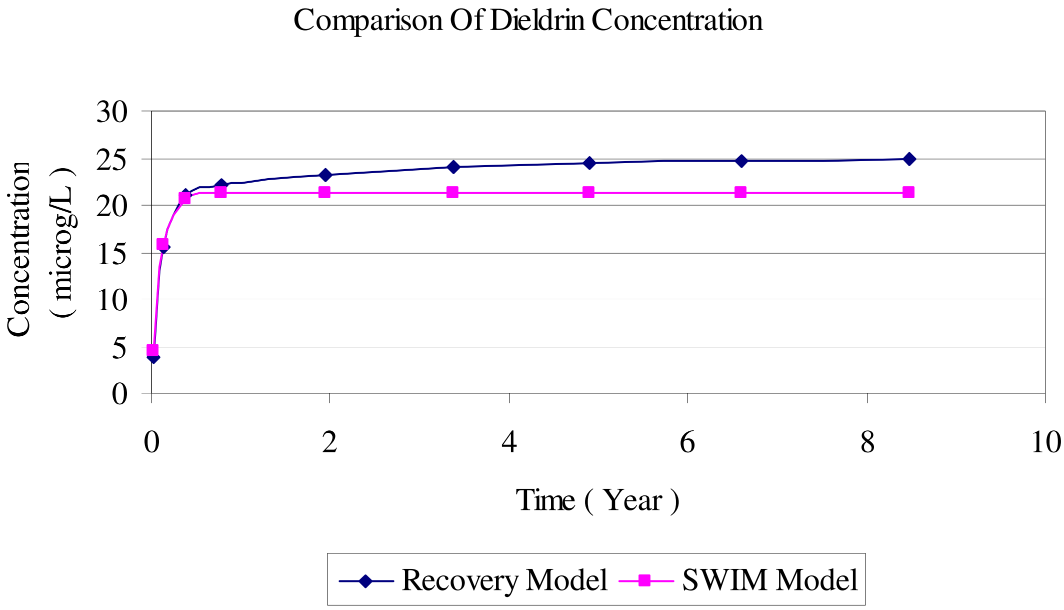

Figure5.6. Dieldrin concentration in water column simulated by the Recovery and SWIM models for the inflow concentration of 1*10^6 microg/m^3

5.4.2. Mixed Sediment Layer

SWIM Model is run using the parameters given in Table 4.1 to calculate the projected contaminant concentration at the mixed sediment layer and the results are compared to the results of the Recovery model for the same conditions. Both the simulated concentrations by the Recovery Model and simulated concentrations by the SWIM Model are shown in Figure 5.7. The computed error measures for this simulation are 8.69E-04 mg/kg, 0.00073 mg/kg, and 23.3 % for RMSE, MAE and MRE respectively.

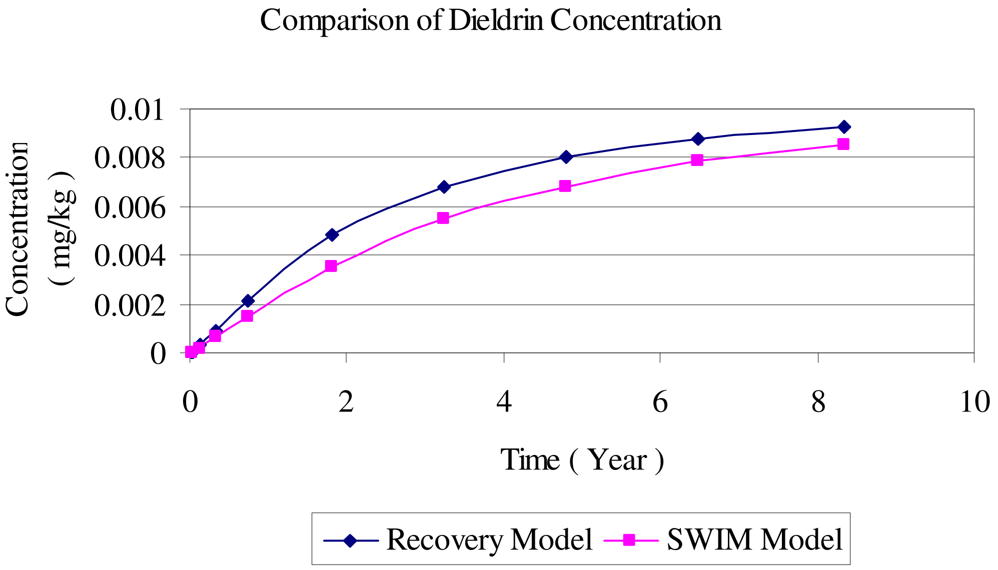

Figure 5.7. Simulated dieldrin concentration in the mixed layer in Recovery and SWIM models

After these calculations both Recovery and SWIM model are run using different values of initial concentration and results are presented in Figures 5.8. The computed error measures for this simulation are 1.3E-03 mg/kg, 0.0011 mg/kg, and 8.77 % for RMSE, MAE and MRE respectively.

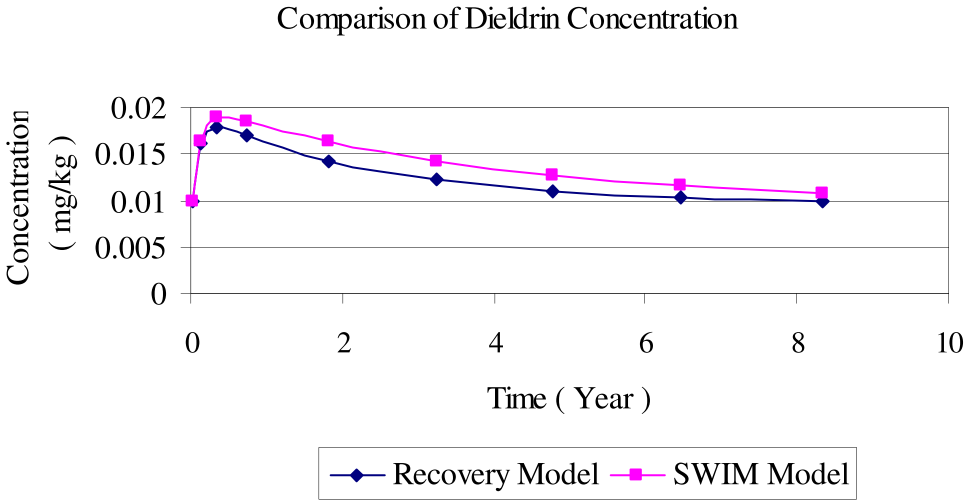

Figure 5.8. Dieldrin concentration in mixed layer simulated by the Recovery and SWIM models for initial concentration of 1000 microg/m^3

After that, both Recovery and SWIM model are run using different values of inflow concentration and results are presented in Figures 5.9 The computed error measures for this simulation are 0.84 mg/kg, 0.68 mg/kg, and 17.32 % for RMSE, MAE and MRE respectively.

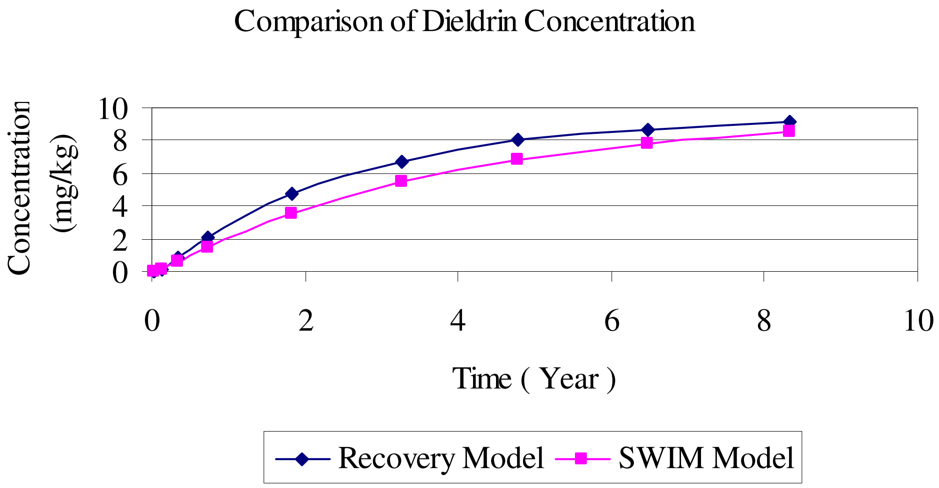

Figure 5.9. Dieldrin concentration in mixed sediment layer simulated by the Recovery and SWIM model for inflow concentration of $1*10^6$ microg/m^3

5.4.3. Deep Sediment Layer

SWIM Model is run using the parameters given in Table 4.1 to calculate the projected contaminant concentration at the deep sediment layer and the results are compared to the results of the Recovery model for the same conditions. Both the simulated concentrations the Recovery Model and simulated concentrations by the SWIM Model are shown in Figure 5.10 The computed error measures for this simulation are 180.3 microg/m^3, 143.6 microg/m^3, and 13.6 % for RMSE, MAE and MRE respectively.

After that, both Recovery and SWIM model are run using different values of inflow concentration and results are presented in Figures 5.11 The computed error measures for this simulation are $0.19*10^6$ microg/m^3, $0.144*10^6$ microg/m^3, and 43.44% for RMSE, MAE and MRE respectively. Finally, both Recovery and SWIM model are run using different values of initial concentration and results are presented in

Figures 5.12. The computed error measures for this simulation are 0.0028 microg/m^3, 0.0026 microg/m^3, and 35.18 % for RMSE, MAE and MRE respectively.

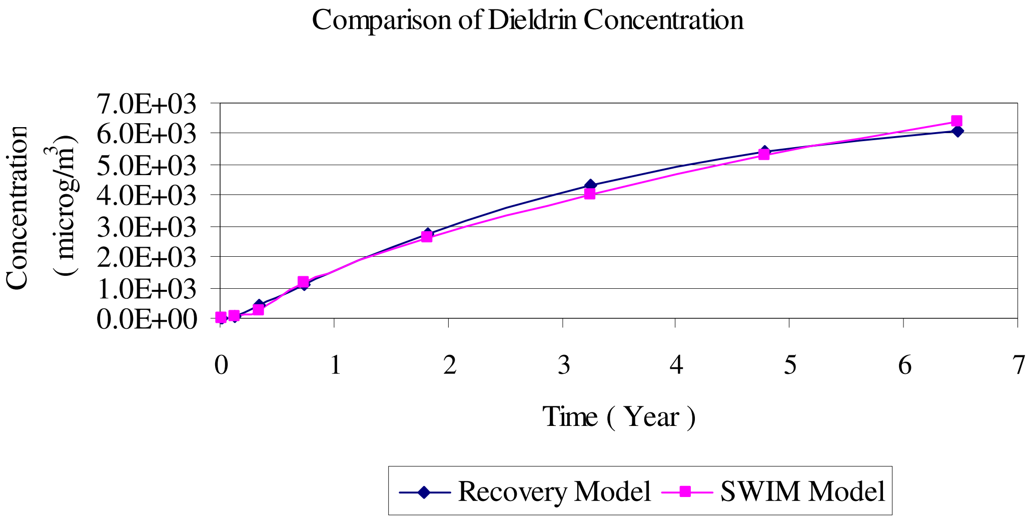

Figure 5.10. Dieldrin concentration in deep sediment layer simulated by the Recovery and SWIM models.

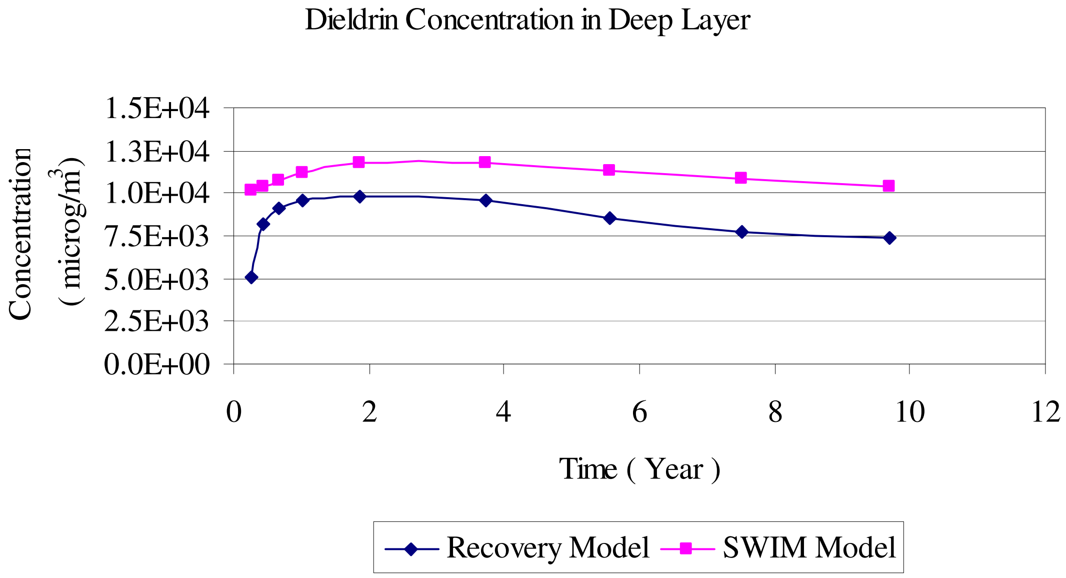

Figure 5.11. Dieldrin concentration in deep sediment layer simulated by the Recovery and SWIM models for initial concentration of 1000 microg/m^3

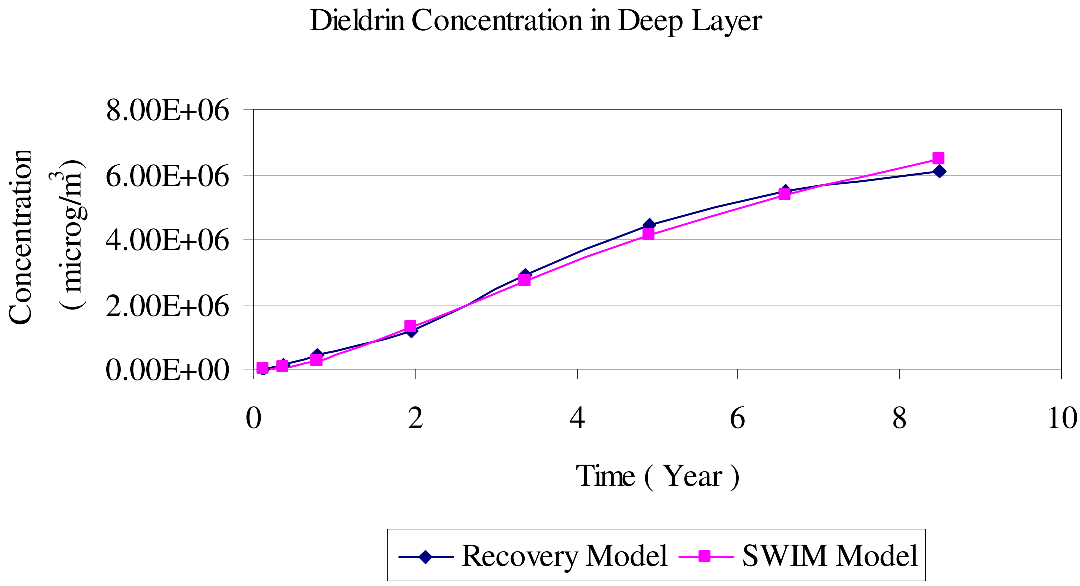

Figure 5.12 Dieldrin concentration in deep sediment layer simulated by the Recovery and SWIM model for inflow concentration of $1*10^6$ microg/m^3

5.5. DDE Simulations:

SWIM and Recovery Models are run using the parameters given in Table 5.1 for DDE (dichloro-diphenyldichloro-ethylene). The study by Ruiz et al. applied the Recovery model to analyze a fieldscale experiment in which a flooded limestone quarry was dosed with the insecticide, DDE. The quarry was treated with DDE at a concentration of 0.2 mg/m^3 to the epilimnion. The quarry was analyzed after the treatment, and the results showed that essentially all of the DDE was initially released in the epilimnion. The quarry was periodically sampled, and the results are used to validate the numerical model. Figure 5.13 and 5.14 shows the comparison of simulated DDE concentrations by the SWIM model and by the Recovery model with the observed DDE concentrations for water and mixed sediment layers respectively. Since no observed data were available for the deep sediment layer, Figure 5.15 shows only the comparison of SWIM and Recovery models since there are no field data available for deep sediment layer.

Table 5.1. The values of parameters for SWIM Model for simulation of DDE concentration

Parameters Used in SWIM Model for DDE		
Parameters	**Unit**	**SWIM**
Flow Rate into and out of the Water Body (Q)	m^3	200
Volume of Water Body (V_w)	m^3	1000
Volume of Mixed Layer (V_m)	m^3	100
Area of Water (A_w)	m^2	1000
Area of Mixed Layer (A_m)	m^2	1000
Decay Rate Constant in Water (k_w)	1/year	1.54*10-3
Volatilization Rate of The Contaminant (k_v)	1/year	5.89
Decay Rate Constant in Deep Sediment Layer (k_s)	1/year	1.54*10-3
Inflow Concentration (C_i)	µg/m^3	0
Contaminant Concentration in Water (C_w)	µg/m^3	3500
Initial Contaminant Concentration in Water (C_{w0})	µg/m^3	0
Contaminant Concentration in Mixed Layer (C_m)	µg/m^3	Depends on Concentration of Water Layer
Contaminant Concentration in Deep Sediment (C_s)	µg/m^3	Depends on Concentration of Mixed Layer
Contaminant Concentration at the top of the Deep Sediment ($C_{s(0)}$)	µg/m^3	Depends on Concentration of Mixed Layer
Suspended Solid Concentration in the Water (S_w)	µg/m^3	500
Settling Velocity (V_s)	m/year	Calculated
Resuspension Velocity (V_r)	m/year	Calculated
Burial Velocity (V_b)	m/year	Calculated
Fraction of Contaminant in Particulate Form in the Water (F_{dw})	Dimensionless	0.992
Fraction of Contaminant in Dissolved Form in the Water (F_{pw})	Dimensionless	0.00765
Porosity (ϕ)	Dimensionless	0.65
Density of the Sediment Solids (ρ_p)	g/m^3	$2.5*10^{6}$
Density of Water (ρ_w)	g/m^3	$1*10^{6}$
Diffusive Mass Transfer Coefficient (V_d)	m/year	$2.746*10^{-6}$

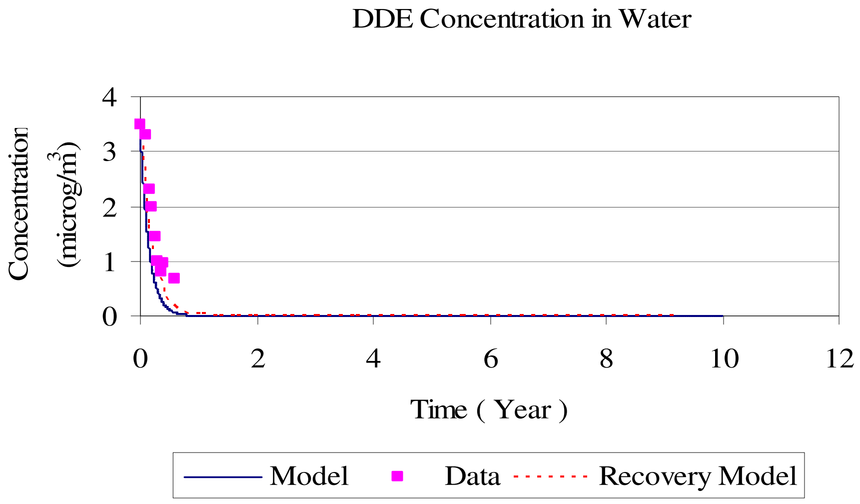

Figure 5.13. Comparison of simulated DDE concentrations for the water layer

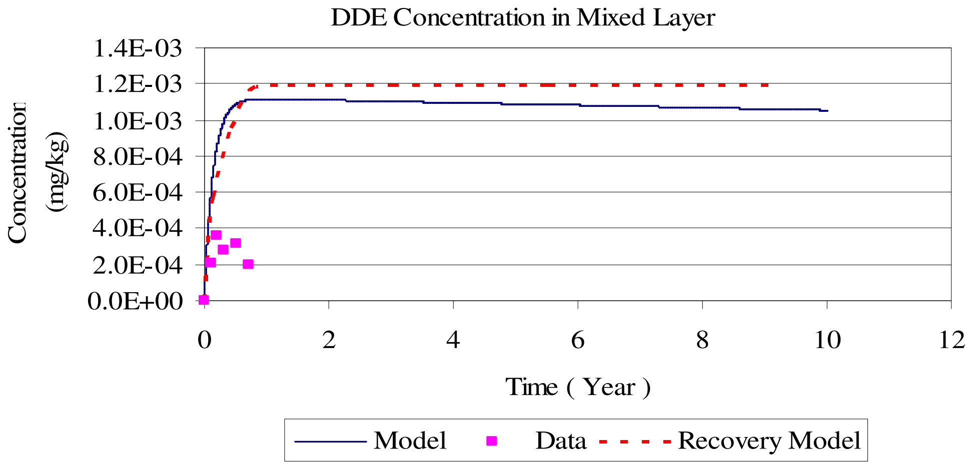

Figure 5.14. Comparison of simulated DDE concentrations for the mixed sediment layer

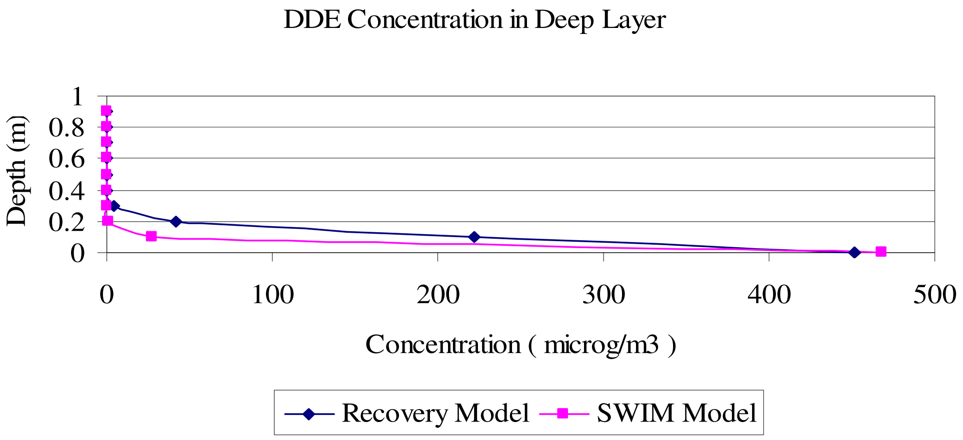

Figure 5.15. Comparison of simulated DDE concentrations for deep sediment layer

CHAPTER 6

APPLICATION OF THE SWIM MODEL TO ÇAMLI BASIN

In this thesis, the main objective is to assess the life long impact of submersed contaminated bottom sediments in projected reservoirs on surface water quality. In this respect, Çamlı Dam, the construction of which is being planned by İZSU was selected. Çamlı Dam is projected as a rockfill dam to supply drinking water to İzmir, which has a population of 3 million 796 thousand with a %1.5 annual grow rate, is the fastest growing city in West Anatolia. İzmir's average daily domestic water consumption increases day by day and the total daily water consumption in 2009 is 505.427 m^3. An average of 21.5 million m^3 fresh water is planned to be obtained from Çamlı Reservoir. From Güzelbahçe to İzmir city center, lots of settlements in İzmir will benefit from this new source of fresh wate. The main characteristics of Çamlı basin are given below (İZSU 2011) ;

Table 6.1 Characteristics of Çamlı Basin

Reservoir / Basin Property	**Value**
Drainage Basin Area	62 km^2
Average Amount of Water (Annual)	$22.54 * 10^6$ m^3
Height from the River Bed	75 m
Annual Available Domestic Water Supply	$21.50 * 10^6$ m^3
Height of the Dam	91 m
Embankment Type	Rock fill
Thalweg Elevation	85 m
Crest Level of the Dam	160 m
Minimum Operation Level of the Reservoir	105 m
Normal Operation Level of the Reservoir	156 m
Maximum Water Elevation of the Reservoir	157.66 m
Surface Area of the Reservoir (at normal water elevation)	0.854 km^2
Reservoir Volume at Minimum Water Surface Elevation	$1.28 * 10^6$ m^3
Reservoir Volume at Normal Water Surface Elevation	$23.98 * 10^6$ m^3
Reservoir Volume at Maximum Water Surface Elevation	$25.36 * 10^6$ m^3
Active Volume of the Reservoir	$22.71 * 10^6$ m^3

The SWIM model is then applied to Çamlı Reservoir to predict the long term impact of the contaminants attached to the site sediments on water quality. For this purpose, soil samples taken and analyzed before the construction of the dam were obtained from a graduate thesis (Mutlu, 2004). Map provided in Figure 6.1 shows the basin and the sampling locations. Heavy metal concentrations monitored at water samples are given in Table 6.2, concentrations monitored at sediment samples are given in Table 6.3. The maximum values of the concentrations monitored along the main river are selected and used as initial concentrations in the water column and as inflow concentrations in the SWIM Model. Contaminant concentrations of the deep layer are set to the values determined from the analysis of the sediment samples. Other parameters such as density of sediment solids, molecular diffusivity and decay rate are obtained from the literature.

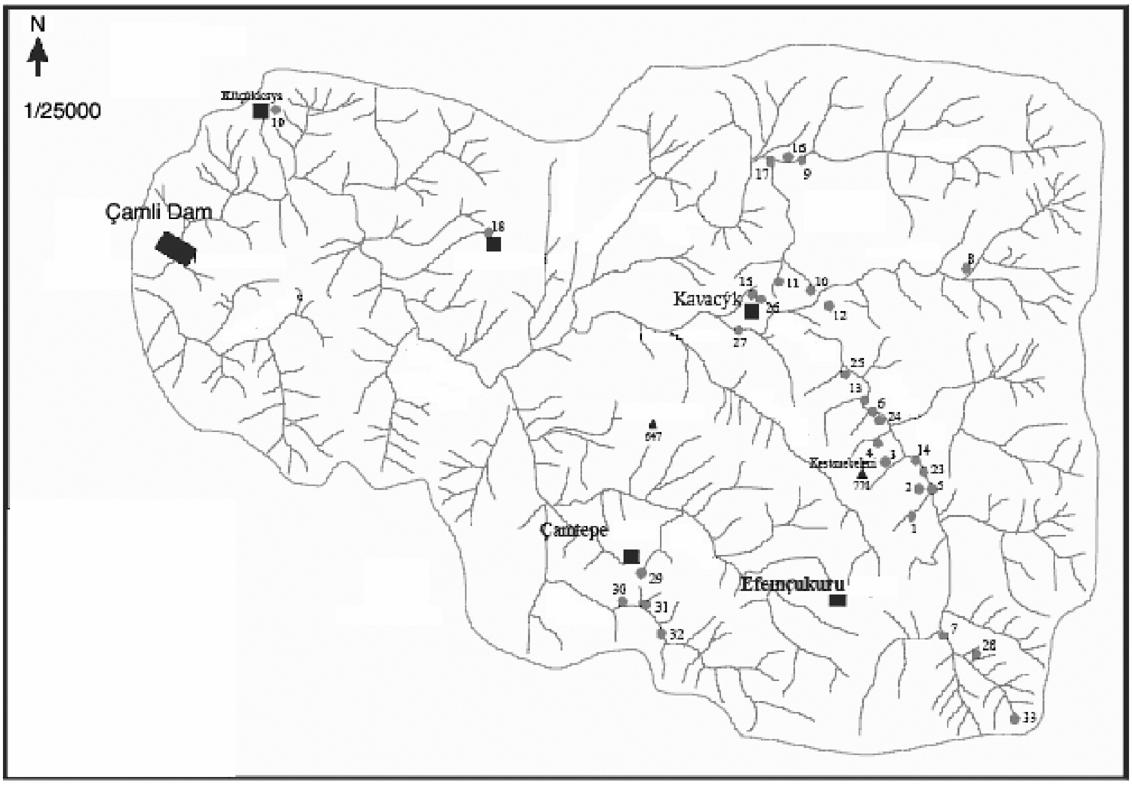

Figure 6.1. Çamlı Basin and the sampling locations within the basin

Table 6.2. Heavy metal concentrations observed at water samples (mg/L)

Element Sample No	Pb	Li	Cr	Zn	Cd	Cu	Co	Ni	Mn	Fe	Sb	Al	As
1	0.012	0.005	0.017	0.006	0.004	0.001	0.009	0.007	0.111	0.572	0.063	0.411	*
2	0.006	0.003	0.017	0.008	0.004	0.001	0.007	0.013	0.513	0.517	0.083	0.5	*
3	**0.506**	0.033	**0.089**	0.211	0.009	0.088	0.029	0.07	0.809	4.722	0.056	15.31	*
4	0.022	0.003	0.089	0.172	0.002	0.022	0.008	0.02	0.745	4.25	0.042	0.37	*
5	0.003	0.001	0.017	0.003	0.003	0.001	0.006	0.009	0.015	0.318	0.049	0.094	*
6	0.021	0.002	0.017	**0.01**	0.002	0.003	0.005	0.01	0.191	2.306	0.049	0.289	*
7	0.024	0.004	0.027	0.007	0.004	0.001	0.008	0.011	0.012	1.75	0.097	0.119	*
8	0.023	0.001	0.006	0.033	0.004	0.008	0.009	0.014	0.05	0.24	0.143	0.08	*
9	0.018	0.001	0.006	0.02	0.003	0.007	0.009	0.009	0.02	0.42	0.143	0.12	*
10	0.025	0.003	0.01	0.021	0.004	0.008	0.01	0.014	0.01	0.04	0.151	0.07	*
11	0.021	E	0.013	0.118	0.003	0.006	0.004	0.006	0.01	0.99	0.128	0.17	*
12	0.023	0.005	0.015	0.034	0.003	0.011	0.009	0.014	0.01	0.65	0.12	0.04	*
13	0.031	0.002	0.015	0.054	0.003	0.01	0.014	0.018	0.13	0.33	0.183	0.18	*
14	0.027	0.001	0.006	0.015	0.002	0.007	0.007	0.007	0.05	0.1	0.081	0.05	*
15	0.016	0.002	0.008	0.022	0.003	0.006	0.007	0.011	0.03	0.08	0.143	0.15	*
16	0.175	E	0.015	0.018	0.003	0.007	0.007	0.011	0.02	0.47	0.151	0.29	*
17	0.021	0.001	0.006	0.016	0.003	0.006	0.007	0.011	0.01	0.01	0.143	0.2	*
18	0.037	0.001	0.006	0.245	0.004	0.009	0.01	0.014	0.01	0.46	0.151	0.18	*
19	0.021	0.001	0.006	0.087	0.003	0.007	0.06	0.01	0.02	0.25	0.128	0.08	*
20	0.029	0.007	0.008	0.166	0.004	0.012	0.009	0.017	0.04	0.28	0.073	0.14	*
21	0.027	0.038	0.015	0.215	0.005	0.007	0.013	0.018	0.01	0.08	0.175	0.11	*
22	0.017	0.009	0.014	0.016	0.004	0.007	0.015	0.026	0.011	0.14	0.168	0.007	<.5
23	0.015	0.01	0.014	0.031	0.004	0.011	0.014	0.016	0.007	0.18	0.053	0.024	0.001
24	0.026	0.003	0.028	**0.233**	0.005	0.018	0.019	0.028	0.044	0.25	0.177	0.009	0.001
25	0.026	0.008	0.049	0.109	0.006	0.023	0.02	**0.049**	0.036	0.88	0.149	0.008	0.0067
26	0.024	0.006	0.042	0.03	0.005	0.017	0.017	0.028	0.171	1.44	0.177	0.022	0.0007
27	0.023	0.005	0.042	0.881	0.005	0.028	0.014	0.031	0.205	0.79	0.101	0.001	0.0028
28	0.03	*	0.045	0.092	0.003	0.045	0.017	0.018	0.019	1.41	0.197	*	*
29	0.007	*	0.036	0.125	0.002	0.004	0.013	0.013	0.025	0.11	0.146	*	*
30	0.026	*	0.054	0.271	0.003	0.007	0.02	0.026	0.025	0.41	0.197	*	*
31	0.02	*	0.045	0.011	0.002	0.003	0.017	0.022	0.019	0.54	0.206	*	*
32	0.015	*	0.036	0.01	0.002	0.001	0.014	0.017	0.005	0.18	0.154	*	*
33	0.015	*	0.045	0.008	0.001	0.002	0.014	0.013	0.005	0.18	0.129	*	*
EPA	0.02		0.1		0.005	1.3		0.1			0.006	0.05	0.01
WHO	0.05		0.05	5-15	0.01	1-1.5			0.1-0.5	0.3-1			0.01
TS 266	0.05		0.05	0.1-5	0.005	1.1-3		0.05	0.02-0.05	0.005-0.2	0.01		0.01

Table 6.3. Heavy metal concentrations observed at sediment samples

Sample No	**Dates**	**Cu (ppm)**	**Pb (ppm)**	**Zn (ppm)**	**Ni (ppm)**	**As (ppm)**	**Cd (ppm)**	**Sb (ppm)**	**Cr (ppm)**	**Hg (ppm)**	**Fe %**	**PI**
1	10.05.2004	**36.2**	167	171	106.5	38.7	0.3	0.5	59	0.03	4.3	8
2	10.05.2004	36	81.6	169	105.2	19.9	0.4	0.4	56.4	0.02	4.05	6
3	10.05.2004	37.9	65.5	155	97.8	25.4	0.3	0.3	54.8	0.06	3.94	6
4	10.05.2004	32.9	82.6	168	96.8	20.2	0.5	0.3	54.6	0.02	3.66	4
5	10.05.2004	57.2	**445.7**	**781**	**161**	75.4	2.2	0.4	**197.2**	0.03	4.98	17
6	10.05.2004	40	134.1	385	109.1	44.6	1	0.5	75.5	0.02	3.95	9
7	10.05.2004	42.3	235.6	380	156.2	54.3	1.1	0.5	151.3	0.03	4.38	12

Reverse modeling for the prediction of contaminant concentration in the water column originating from the bottom sediments is composed of two modules (See Appendix B). In the first module, heavy metal concentrations monitored in the dam site sediments are assumed as initial deep layer concentrations (C_{s0}) and mixed layer concentrations are calculated using the mass balance equation for the mixed sediment layer. Initial concentration of contaminant for mixed layer is assumed equal to the contaminant concentration in water (C_w) which is obtained from the measurements. Once the concentration in the mixed layer is calculated using the mass balance equation for the mixed layer, this value is set equal to the water column concentration at the boundary and the mass balance equation for the water column is utilized to calculate water column concentrations. In the second module, initial contaminant concentration in the column (C_w), inflow contaminant concentration (C_i) are considered together with the contaminant concentration due to the deep layer concentration calculated as described in the first module. Then the mass balance equation for the mixed sediment layer and advection-diffusion-decay equation for the deep sediment layer are solved. These processes are repeated for each time interval of 0.5 year with a time step of 0.05 year.

In this section, modeling of transfer of five heavy metals; Copper, Zinc, Chromium, Nickel, and Lead existing in bottom sediments of Çamlı Basin to the reservoir water is described. Table 6.4 summarizes the parameters and Table 6.5 summarizes the properties of the selected heavy metal concentrations used in the SWIM Model. As described above the transfer of metals to the water column is modeled. Chromium concentration in the water layer increased from 0.089 mg/L to 0.1 mg/l in ten years (Figure 6.2), in the mixed layer it reached to 0.112 mg/l (Figure 6.3) and in the deep layer it decreased from 197.2 mg/L to $3*10^{-4}$ mg/l (Figure 6.4).

Table 6.4. The values of parameters for SWIM Model for simulation of Heavy Metal Concentration

Parameters	**Unit**	**Value**
Flow Rate into and out of Water Body (Q)	m^3	$22.54*10^6$
Volume of Water Body (V_W)	m^3	$23.98*10^6$
Volume of Mixed Layer (V_m)	m^3	$854*10^3$
Surface Area of Water Column (A_w)	m^2	$854*10^3$
Surface Area of Mixed Layer (A_m)	m^2	$854*10^3$
Decay Rate Constant in Water (k_w)	1/year	Depends on type of heavy metal
Volatilization Rate of Contaminant (k_v)	1/year	0
Decay Rate Constant in Deep Sediment Layer (k_s)	1/year	Depends on type of heavy metal
Inflow Concentration (C_i)	$\mu g/m^3$	Given in Table 6.3
Contaminant Concentration in Water Column (C_w)	$\mu g/m^3$	Given in Table 6.3
Initial Contaminant Concentration in Water Column (C_{w0})	$\mu g/m^3$	Given in Table 6.3
Contaminant Concentration in Mixed Layer (C_m)	$\mu g/m^3$	Depends on Concentration of Water Layer
Contaminant Concentration in Deep Sediment Layer (C_s)	$\mu g/m^3$	Depends on Concentration of Mixed Layer
Contaminant Concentration at top of the Deep Sediment Layer ($C_{(s0)}$)	$\mu g/m^3$	Depends on Concentration of Mixed Layer
Suspended Solid Concentration in Water Column (S_w)	$\mu g/m^3$	100
Settling Velocity (V_s)	m/year	Calculated
Resuspension Velocity (V_r)	m/year	Calculated
Burial Velocity (V_b)	m/year	Calculated
Fraction of Contaminant in Particulate Form in Water (F_{dw})	Dimensionless	Calculated
Fraction of Contaminant in Dissolved Form in Water (F_{pw})	Dimensionless	Calculated
Porosity (ϕ)	Dimensionless	0.7
Density of Sediments (ρ_P)	g/m^3	Given in Table 6.3
Density of Water (ρ_w)	g/m^3	Calculated
Diffusive Mass Transfer Coefficient (V_d)	m/year	Given in Table 6.3

Table 6.5. The properties of the selected heavy metal concentrations used in the SWIM Model (Chemical Elements 2011)

Heavy Metal	**Copper**	**Zinc**	**Chromium**	**Nickel**	**Lead**
Initial Concentration in Water	0.001 mg/L	0.233 mg/L	0.089 mg/L	0.049 mg/L	0.506 mg/L
Initial Concentration in Deep Sediment	36.2 mg/L	781 mg/L	197.2 mg/L	161 mg/L	445.7 mg/L
Inflow Concentration	0.001 mg/L	0.0271 mg/L	0.089 mg/L	0.049 mg/L	0.506 mg/L
Molecular Diffusivity	$5.42*10^{-6}$ cm^2/s	$5.29*10^{-6}$ cm^2/s	$4.39*10^{-6}$ cm^2/s	$5.02*10^{-6}$ cm^2/s	$6.99*10^{-6}$ cm^2/s
Density of Sediment Solids	8.96 g/cm^3	7.14 g/cm^3	6.9 g/cm^3	8.9 g/cm^3	11.34 g/cm^3

Chromium concentration in the water layer decreased from 0.089 mg/L to 0.0302 mg/l in ten years (Figure 6.2), in the mixed layer it reached to 0.0429 mg/l (Figure 6.3) and in the deep layer it decreased from 192.7 mg/L to 0.00105 mg/l (Figure 6.4).

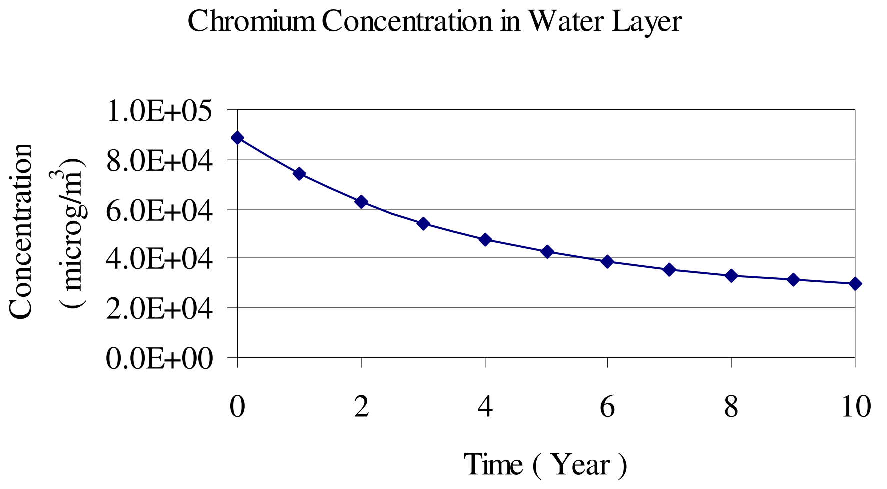

Figure 6.2. Chromium concentration in the water layer simulated by the SWIM model

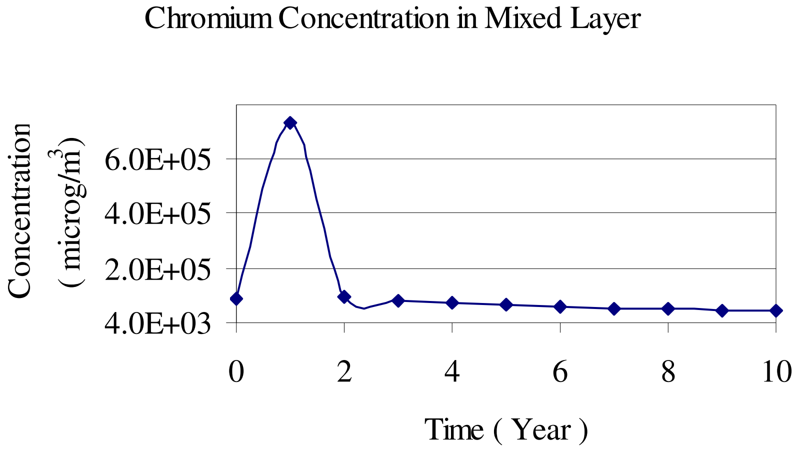

Figure 6.3. Chromium concentration in the mixed layer simulated by the SWIM model

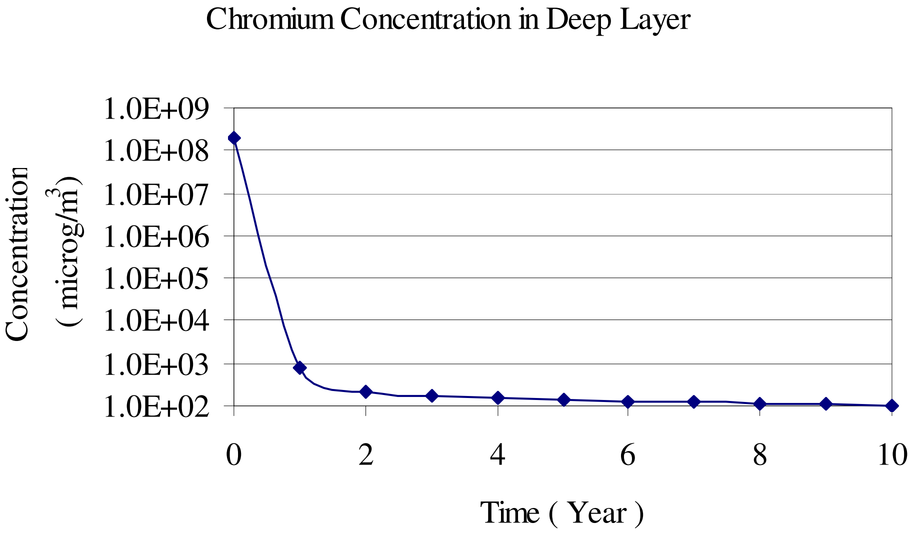

Figure 6.4. Chromium concentration in the deep sediment layer simulated by the SWIM model

Zinc concentration in the water layer decreased from 0.233 mg/L to 0.141 mg/l in ten years (Figure 6.5), in the mixed layer it reached to 0.235 mg/l (Figure 6.6) and in the deep layer it decreased from 781 mg/L to 0.079 mg/l (Figure 6.7).

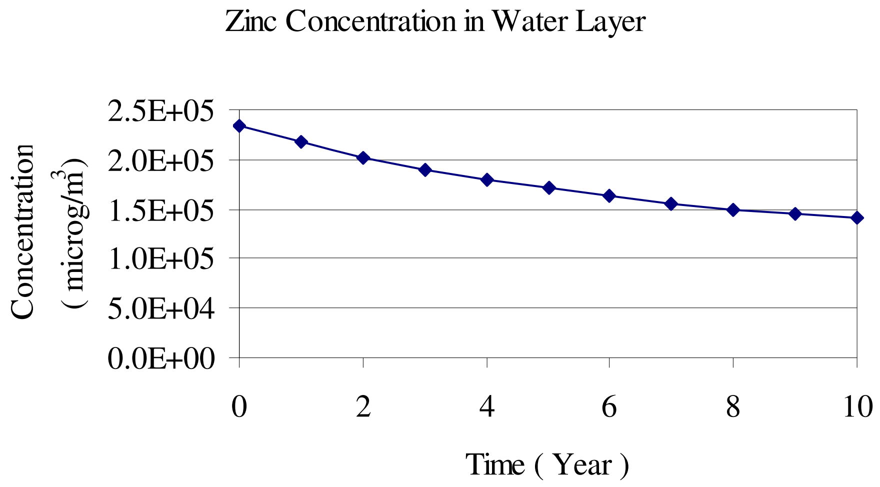

Figure 6.5. Zinc concentration in the water layer simulated by the SWIM model

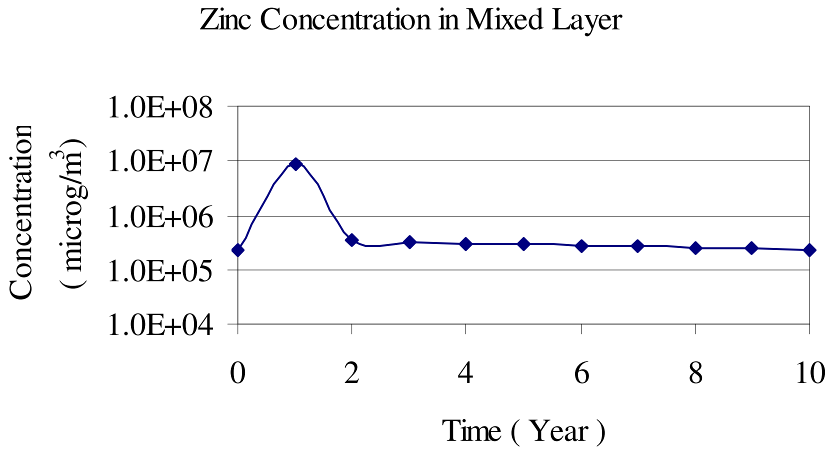

Figure 6.6. Zinc concentration in the mixed layer simulated by the SWIM model

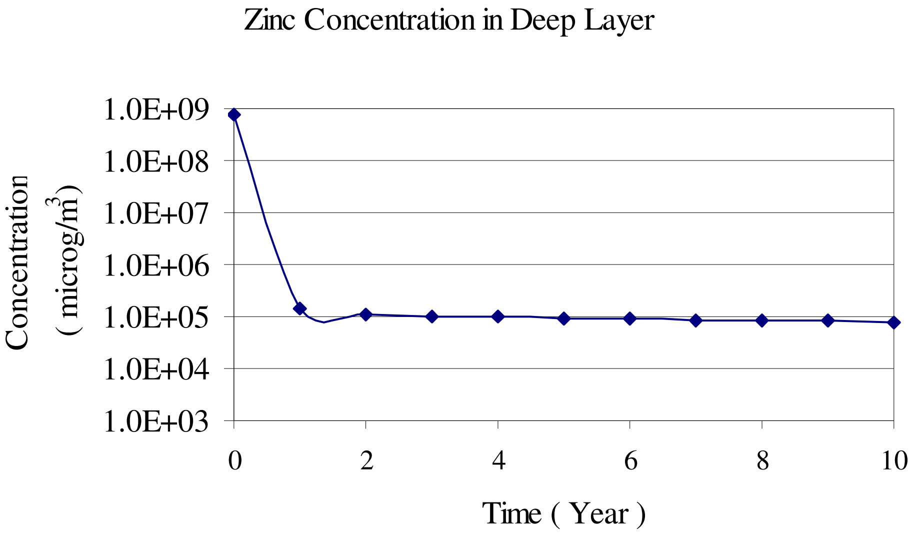

Figure 6.7. Zinc concentration in the deep layer simulated by the SWIM model

Lead concentration in the water layer decreased from 0.506 mg/L to 0.278 mg/l in ten years (Figure 6.8), in the mixed layer it reached to 0.595 mg/l (Figure 6.9) and in the deep layer it decreased from 445.7 mg/L to 0.628 mg/l (Figure 6.10).

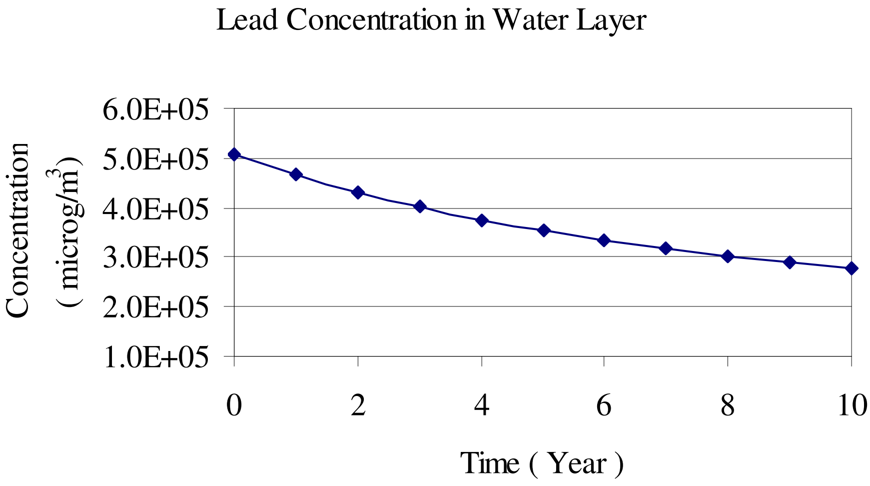

Figure 6.8. Lead concentration in the water layer simulated by the SWIM model

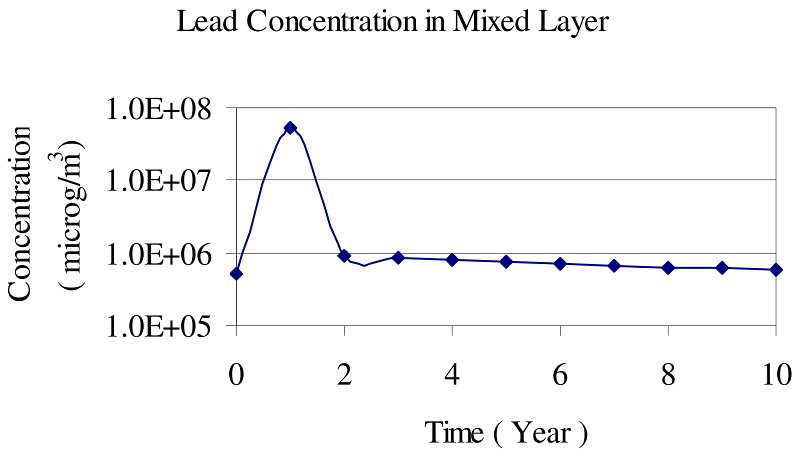

Figure 6.9. Lead concentration in the mixed layer simulated by the SWIM model

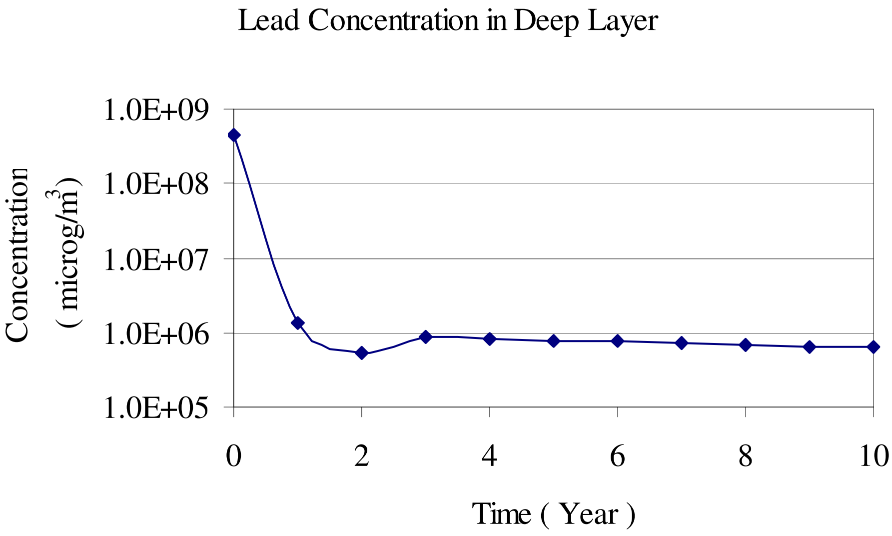

Figure 6.10. Lead concentration in the deep sediment layer simulated by the SWIM model

Nickel concentration in the water layer decreased from 0.049 mg/L to 0.0315mg/l in ten years (Figure 6.11), in the mixed layer it reached to 0.059 mg/l (Figure 6.12) and in the deep layer it decreased from 161 mg/L to 0.071 mg/l (Figure 6.13).

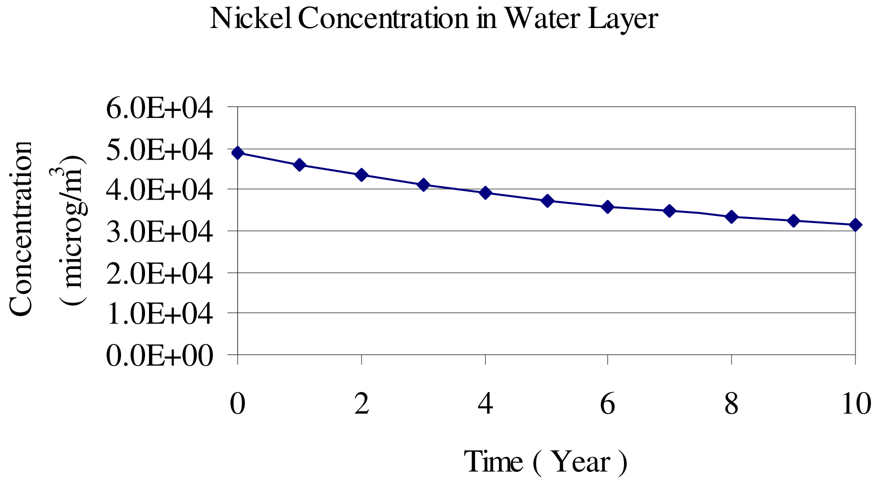

Figure 6.11. Nickel concentration in the water layer simulated by the SWIM model

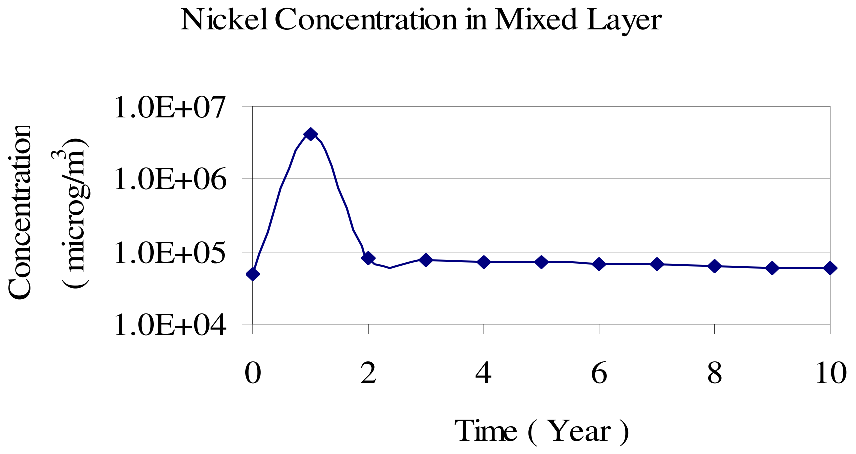

Figure 6.12. Nickel concentration in the mixed layer simulated by the SWIM model

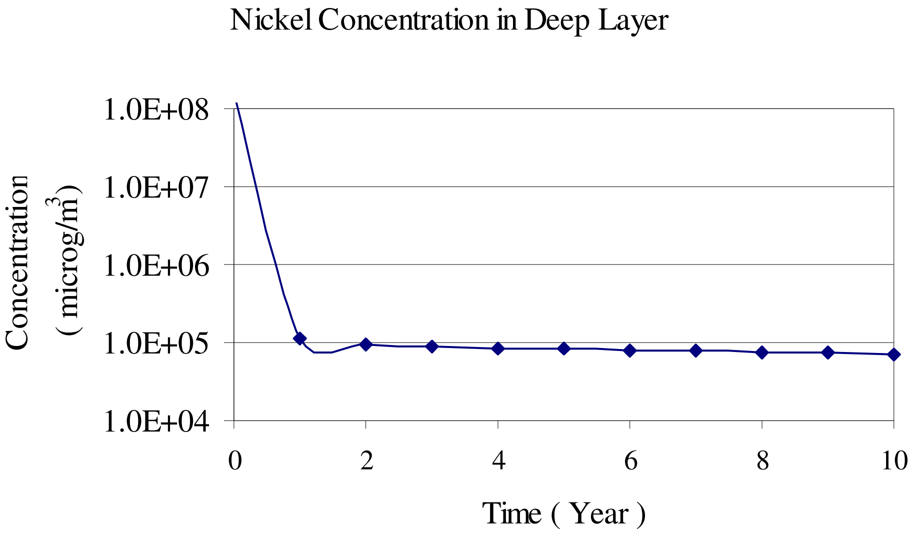

Figure 6.13. Nickel concentration in the deep sediment layer simulated by the SWIM model

Copper concentration in the water layer decreased from 0.001 mg/L to 0.00064 mg/l in ten years (Figure 6.14), in the mixed layer it reached to 0.0012 mg/l (Figure 6.15) and in the deep layer it decreased from 36.2 mg/L to 0.0038 mg/l (Figure 6.16).

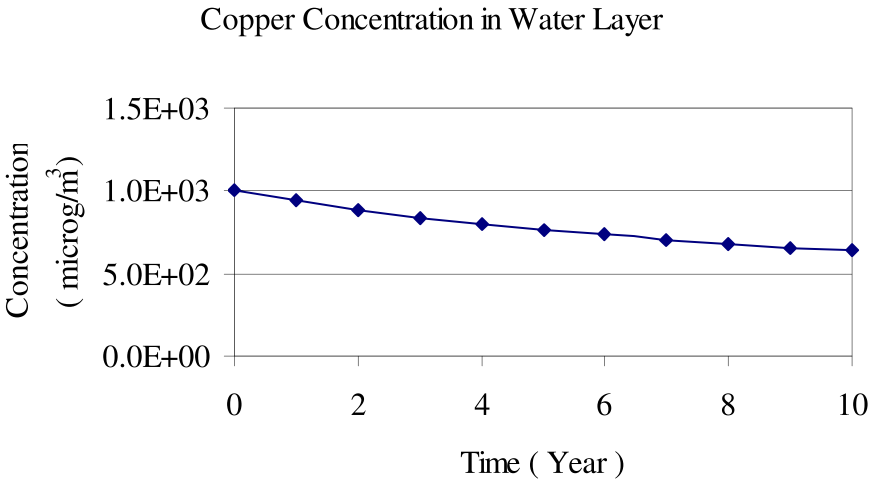

Figure 6.14. Copper concentration in the water layer simulated by the SWIM model

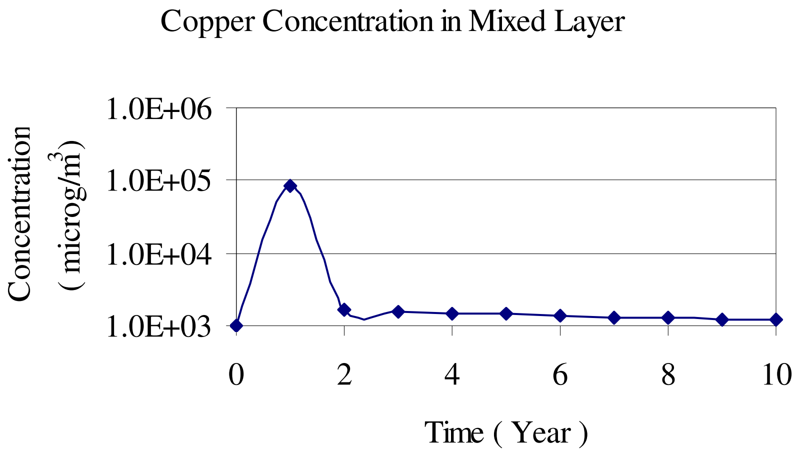

Figure 6.15. Copper concentration in the mixed layer simulated by the SWIM model

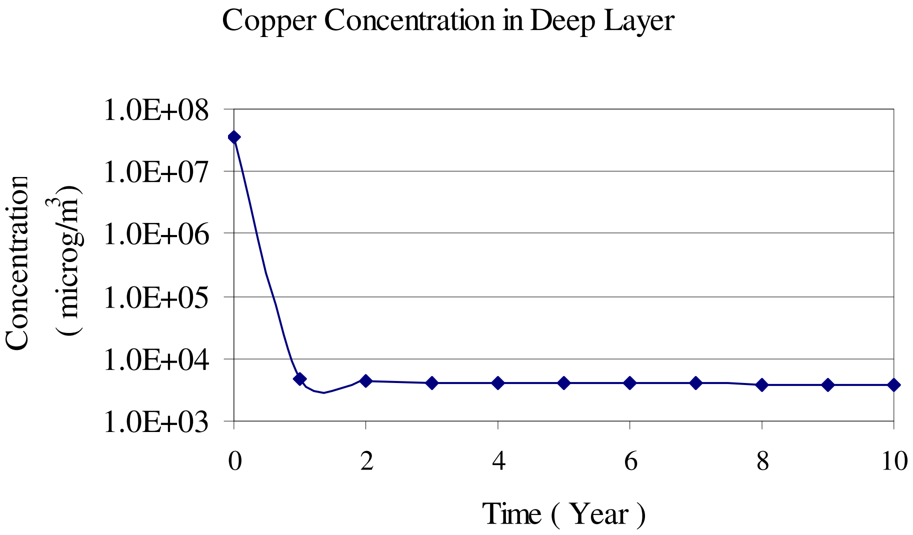

Figure 6.16. Copper concentration in deep sediment layer simulated by the SWIM model

6.1. Contaminant Concentration Results for Stratified Water Column Conditions :

Chromium concentration in the water layer decreased from 0.089 mg/L to 0.0292 mg/l in ten years (Figure 6.17), in the mixed layer it reached to 0.0303 mg/l (Figure 6.18) and in the deep layer it decreased from 192.7 mg/L to $2.82*10^{-4}$ mg/l (Figure 6.19) for stratified water column conditions.

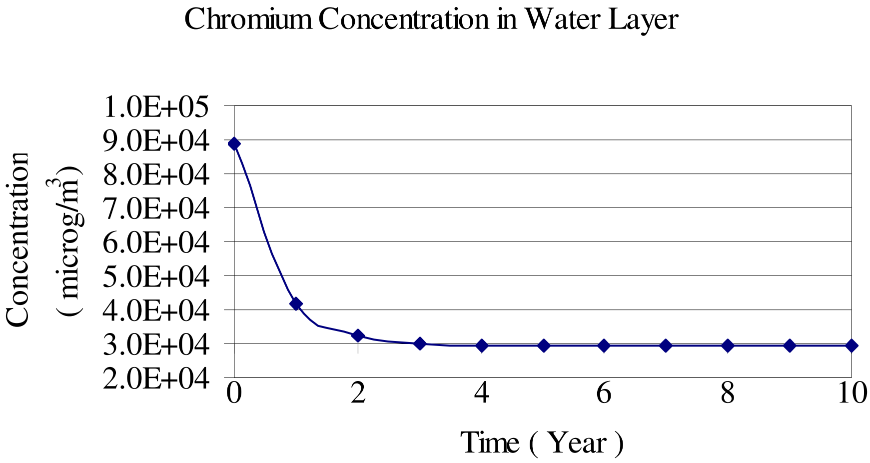

Figure 6.17. Chromium concentration in water layer simulated by the SWIM model for stratified water column conditions

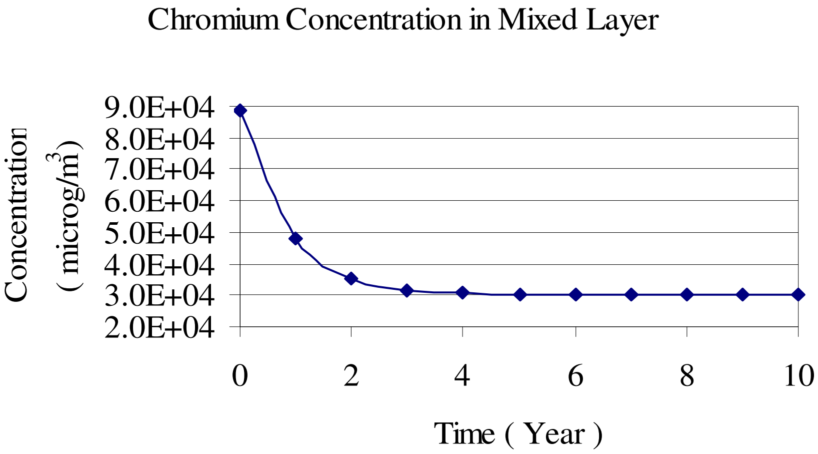

Figure 6.18. Chromium concentration in mixed layer simulated by the SWIM model for stratified water column conditions

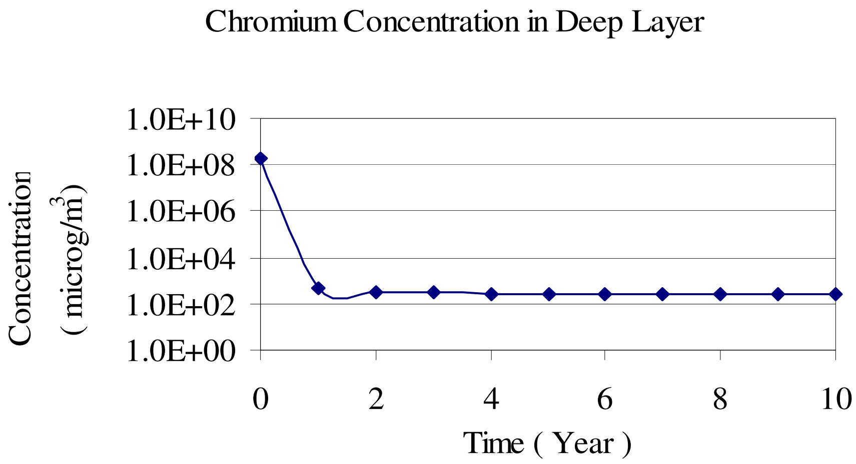

Figure 6.19. Chromium concentration in deep sediment layer simulated by the SWIM model for stratified water column conditions

Zinc concentration in the water layer increased from 0.233 mg/L to 0.112 mg/l in ten years (Figure 6.20), in the mixed layer it reached to 0.139 mg/l (Figure 6.21) and in the deep layer it decreased from 781 mg/L to 0.0322 mg/l (Figure 6.22).

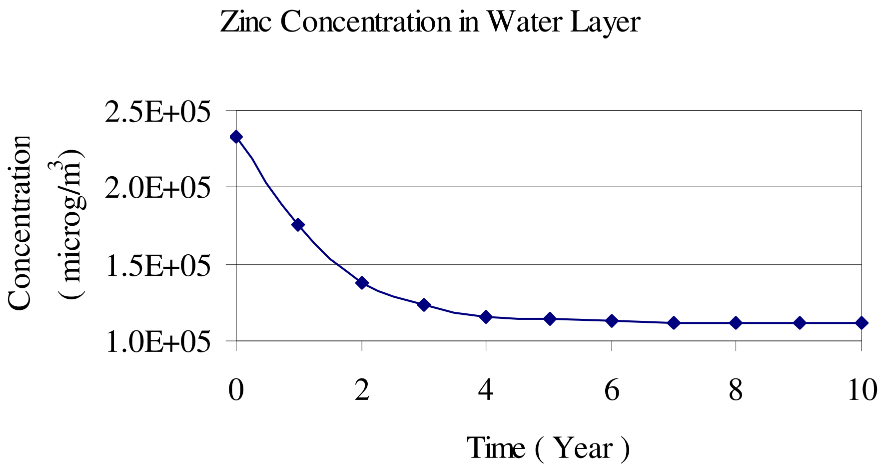

Figure 6.20. Zinc concentration in water layer simulated by the SWIM model for stratified water column conditions

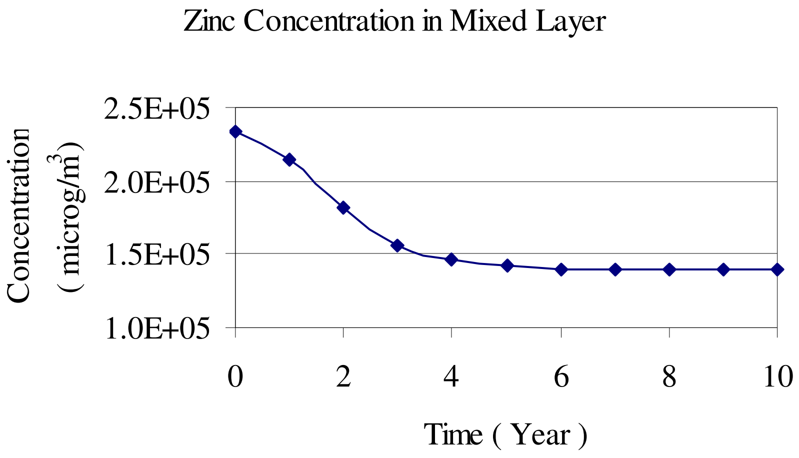

Figure 6.21. Zinc concentration in mixed layer simulated by the SWIM model for stratified water column conditions

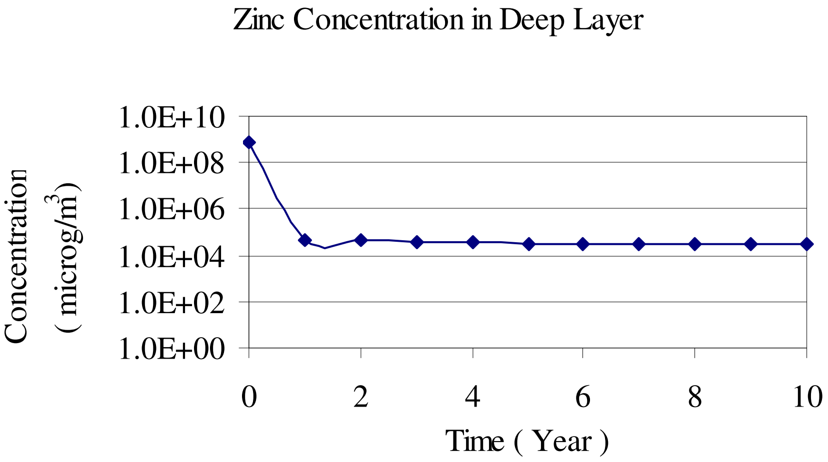

Figure 6.22. Zinc concentration in deep sediment layer simulated by the SWIM model for stratified water column conditions

Lead concentration in the water layer increased from 0.506 mg/L to 0.241 mg/l in ten years (Figure 6.23), in the mixed layer it reached to 0.336 mg/l (Figure 6.24) and in the deep layer it decreased from 445.7 mg/L to 0.257 mg/l (Figure 6.25).

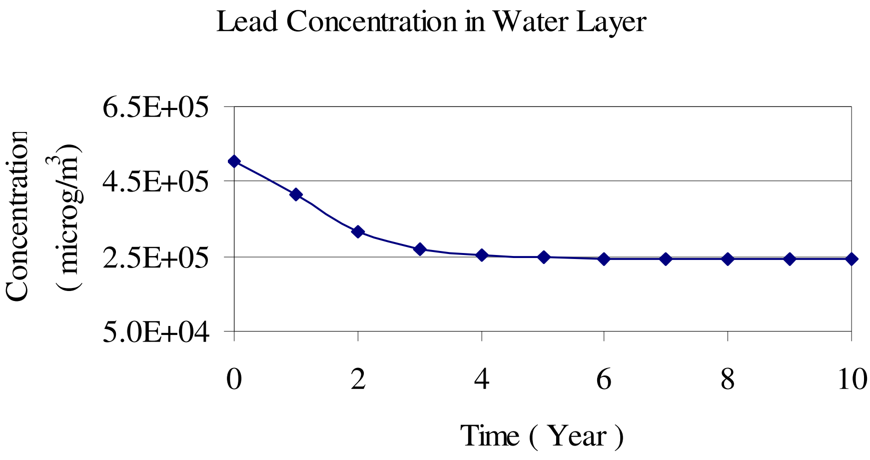

Figure 6.23. Lead concentration in water layer simulated by the SWIM model for stratified water column conditions

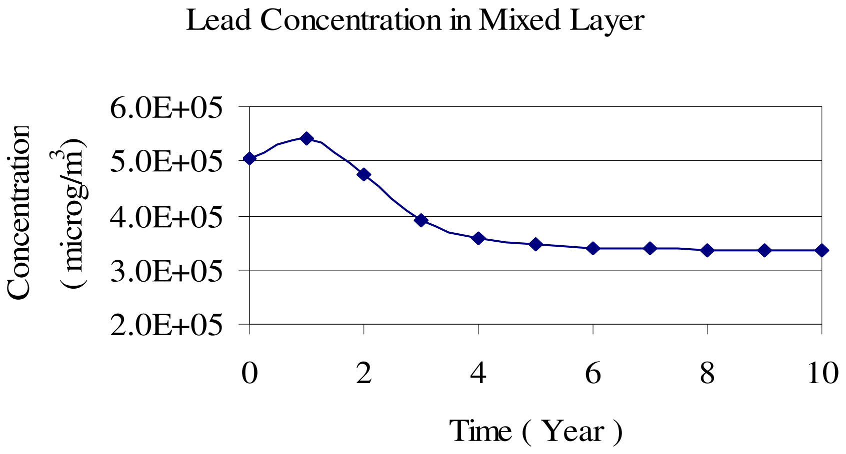

Figure 6.24. Lead concentration in mixed layer simulated by the SWIM model for stratified water column conditions

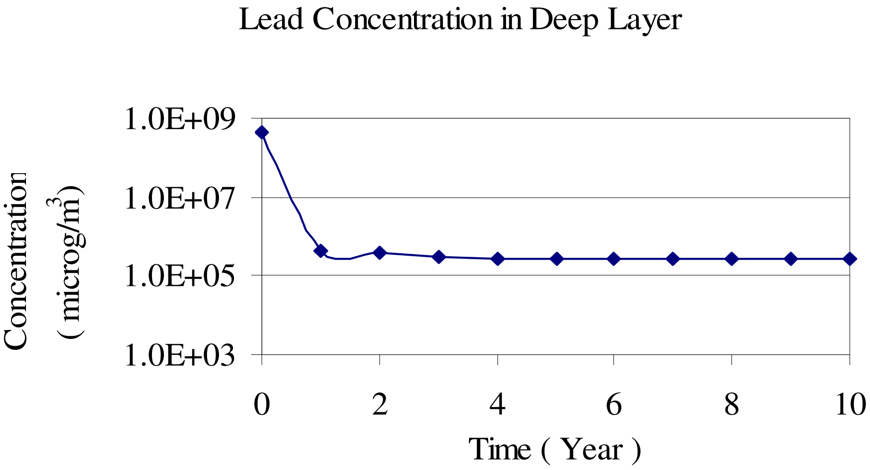

Figure 6.25. Lead concentration in deep sediment layer simulated by the SWIM model for stratified water column conditions

Nickel concentration in the water layer increased from 0.049 mg/L to 0.0251 mg/l in ten years (Figure 6.26), in the mixed layer it reached to 0.0335 mg/l (Figure 6.27) and in the deep layer it decreased from 161 mg/L to 0.0269 mg/l (Figure 6.28).

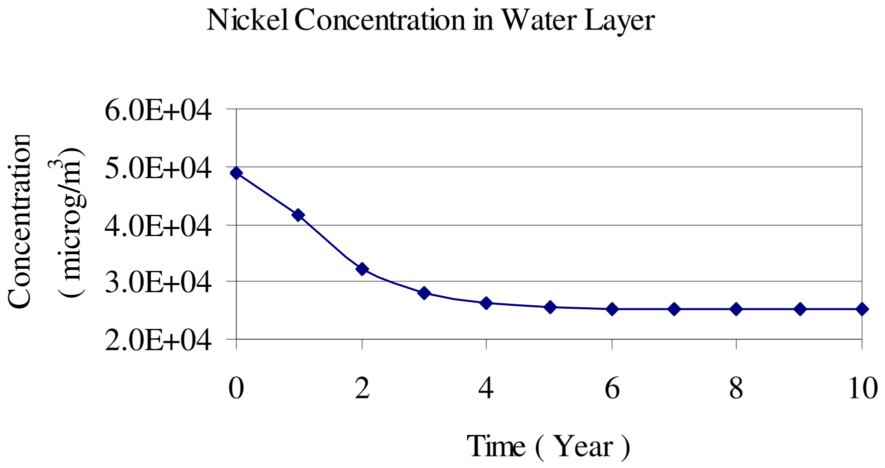

Figure 6.26. Nickel concentration in water layer simulated by the SWIM model for stratified water column conditions

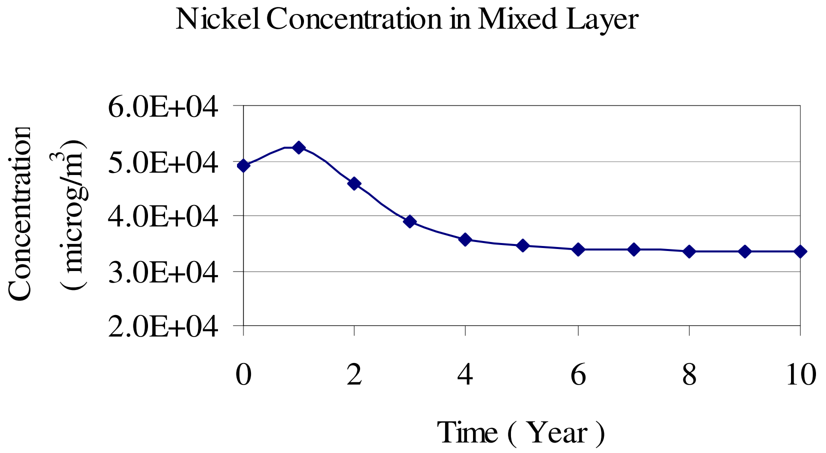

Figure 6.27. Nickel concentration in mixed layer simulated by the SWIM model for stratified water column conditions

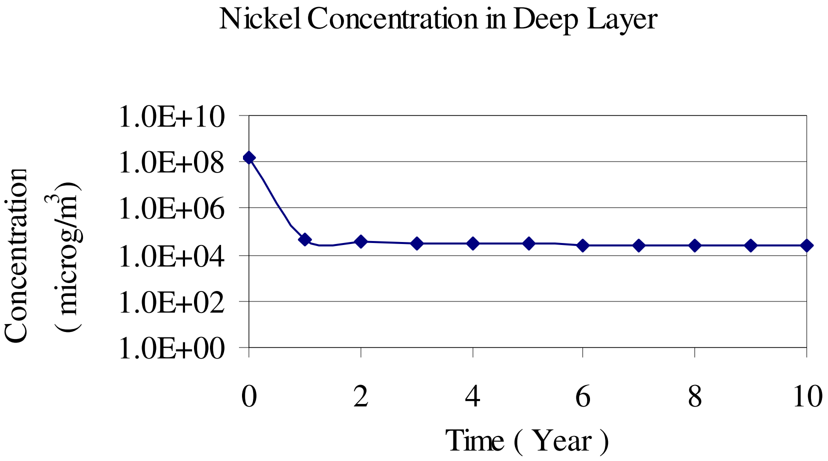

Figure 6.28. Nickel concentration in deep sediment layer simulated by the SWIM model for stratified water column conditions

Copper concentration in the water layer increased from 0.001 mg/L to $5.11*10^{-4}$ mg/l in ten years (Figure 6.29), in the mixed layer it reached to $6.84*10^{-4}$ mg/l (Figure 6.30) and in the deep layer it decreased from 36.2 mg/L to $5.49*10^{-4}$ mg/l (Figure 6.31).

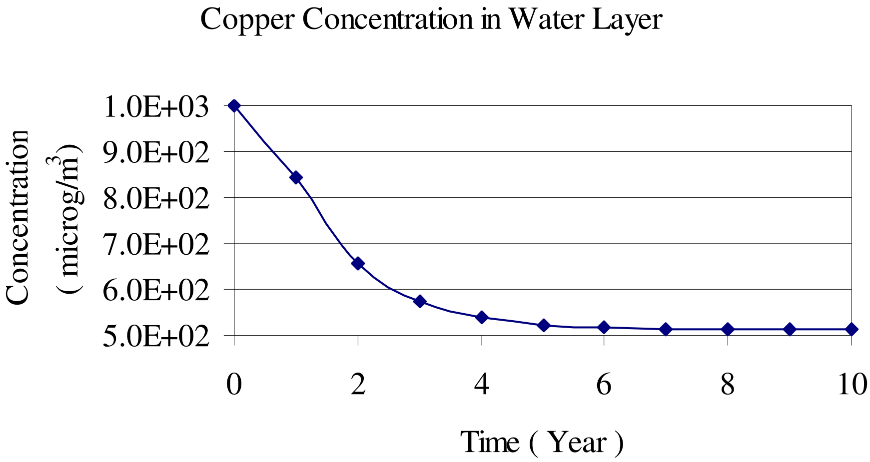

Figure 6.29. Copper concentration in water layer simulated by the SWIM model for stratified water column conditions

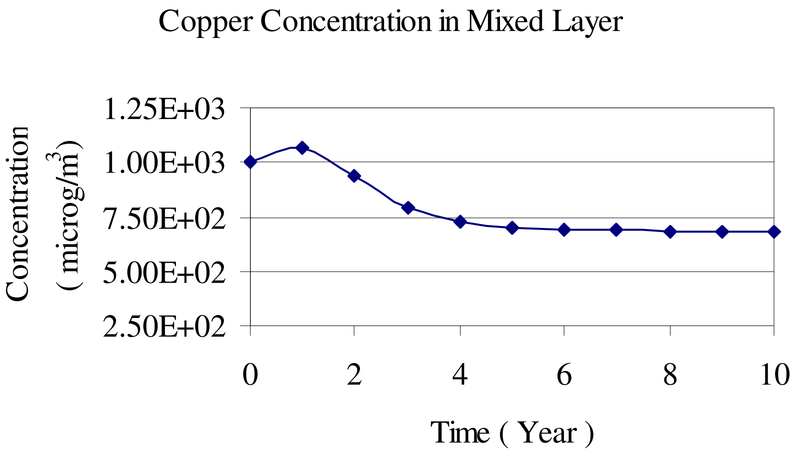

Figure 6.30. Copper concentration in mixed layer simulated by the SWIM model for stratified water column conditions

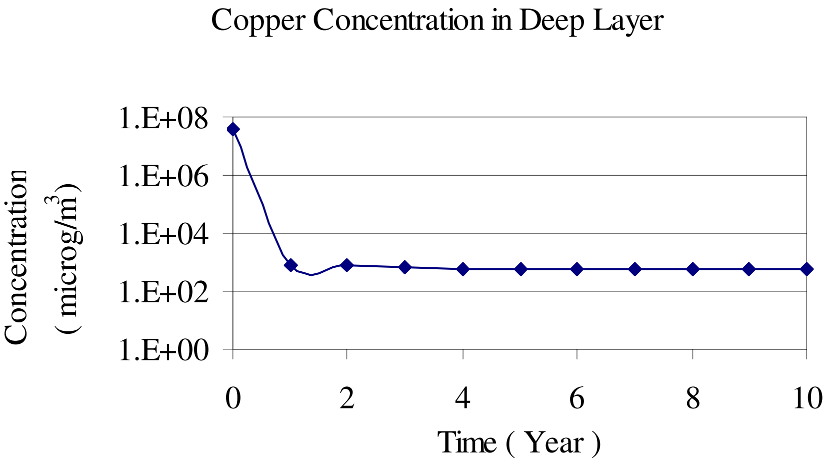

Figure 6.31. Copper concentration in deep sediment layer simulated by the SWIM model for stratified water column conditions

CHAPTER 7

CONCLUSIONS

This study investigates the life-long impact of submersed contaminated bottom sediments in projected reservoirs on surface water quality. A sediment-water interaction model (SWIM) is developed based on existing sediment water interaction models proposed by Ruiz (1998) and Gualtieri (2001). Unlike the existing sediment-water column interaction models assuming that the system is idealized as a well-mixed surface water layer underlined by a stratified sediment column, SWIM model can simulate stratified surface water which is the most common environment encountered in the nature. The calculations in SWIM are performed by utilizing Visual Basics Software. In one dimensional model, the system is idealized as stratified surface water layer underlined by a mixed sediment layer, underlined by two layers composed of both contaminated and clean deep sediment layers. In addition to this, the SWIM Model has the capability to select between two different settling velocities (Rubey and Stoke's) and it calculates the corresponding resuspension velocities based on the mass balance equation.

The model results indicated that particle size is an important parameter in calculating the settling velocities. In the simulations, SWIM Model is run using Rubey's and Stoke's equations and the simulated concentrations remained same only for the small particle sizes (less than 0.0002 mm) and greatly differed with respect to the formulation used for larger particles. Sensitivity of the model to other parameters such as initial concentration, inflow concentration and porosity are also investigated. When the initial concentration is increased, the simulated concentration in the water layer remained same whereas in the mixed layer and in the deep layer the values increased by up to 36 %. When the inflow concentration is doubled, the simulated concentrations are also doubled. Simulated contaminant concentration values increased in both water column and mixed sediment layer as the porosity increased.

The effect of stratification on settling velocities and projected contaminant concentration is also investigated and it is found that projected contaminant concentration increases as the water temperature increases. Concentration is significantly higher for the stratified water column conditions as compared with the mixed water suggesting that stratified conditions of the reservoir need to be accounted for in predicting contaminant concentrations.

The only existing sediment-water interaction model tested with field data, Recovery model, is used to compare simulated concentrations. For this purpose, first Dieldrin is utilized since its related model parameters are available in the literature. SWIM Model is run to calculate the projected contaminant concentration at all three layers and the results are compared to the results of the Recovery model for the same conditions. The computed error measures are calculated and are 0.0022 microg/L, 0.0018 microg/L, and 10.26% for RMSE, MAE and MRE respectively for the water column, 8.69E-04 mg/kg, 0.00073 mg/kg, and 23.3 % for RMSE, MAE and MRE respectively for the mixed layer and 180.3 microg/m^3, 143.6 microg/m^3, and 13.6 % for RMSE, MAE and MRE respectively for the deep layer.

SWIM and Recovery Models are also run to simulate DDE, since observed data are available in the literature from a flooded limestone quarry dosed with the insecticide, DDE. The quarry was periodically sampled, and the results are used to validate the numerical models. The results are in good agreement especially for the water column in both models.

The SWIM model is then applied to Çamlı Reservoir to predict the long term impact of the contaminants attached to the site sediments on water quality. For this purpose, soil samples taken and analyzed before the construction of the dam are obtained. The maximum values of the concentrations monitored along the main river are selected and used as initial concentrations in the water column and as inflow concentrations in the SWIM Model. Contaminant concentrations of the deep layer are set to the values determined from the analysis of the sediment samples obtained from the dam site. Other parameters such as density of sediment solids, molecular diffusivity and decay rate are obtained from the literature. Results of the reverse model utilized to predict contaminant concentration in the water column originating from the bottom sediments indicated that heavy metal concentrations (Copper, Zinc, Chromium, Nickel, and Lead) in the water layer increased significantly in ten years. In summary, chromium concentration in the water layer decreased from 0.089 mg/L to 0.0302 mg/l, zinc concentration decreased from 0.233 mg/L to 0.141 mg/l, lead concentration decreased from 0.506 mg/L to 0.278 mg/l, nickel concentration decreased from 0.049 mg/L to 0.0315 mg/l, copper concentration decreased from 0.001 mg/L to 0.00064 mg/l.

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APPENDIX A

SWIM MODEL

```
Sub Mixed_layer()


Dim cs(100), csnew(100)

Depth = 10 'm'
Q = 2 * 10 ^ 7  'm^3/y
Vw = 1 * 10 ^ 8  'Volume of water body m^3
Vm = 1 * 10 ^ 7  'Volume of mixed layer m^3

dx = 1
nn = Depth / dx

Ds = 132  'm^2/yr
Km = 0.22  '1/year
Kw = 0.22  '1/year
Kv = 7.536  '1/year
Aw = 1 * 10 ^ 7  'm^2
Am = 1 * 10 ^ 7  'm^2
Fpw = 0.393
Vd = 1.4406 * 10 ^ -6  'm/year
Fdp = 0.0048
Fdw = 0.606
ks = 0.22  '1/year
Fi = 0.7  'porosity




Sw = 1000  'g/m^3
Rop = 2.65 * 10 ^ 6  'g/m^3
alfa = 1.64 * 10 ^ -4
g = 9.81
d = 11.36 * 10 ^ -7  'm


s = 10 'C
mü = ((1.79 * 1.79) * (10 ^ -6)) / (1 + (0.0337 * s) + (0.000221 * (s ^ 2)))
Row = 1000 * (1 - (s + 288.9414) / (508929.2 * (s + 68.12963)) * (s - 3.9863) ^ 2)
```

```
dt = 0.004
T = 0



'INITIAL CONDITIONS
Ci = 0 'microg/m^3
CW = 1000 'microg/m^3
CW0 = 0 'mg/m^3
CMM = 50 * 10 ^ 3 'g/m^3
cs(0) = 0


11 For T = 0 To 10 Step dt
If T = 0 Then GoTo 1 Else GoTo 2
1 CW = CW0
  GoTo 3
2  CW = CWnew
3 Vs = (1.65 * g * ((d) ^ 2) / (18 * mü)) * 31.536 * 10 ^ 6
  Vb = Vs * alfa
  Vr = (Vs * Aw * Sw - Vb * Am * (1 - Fi) * Rop) / (Am * (1 - Fi) * Rop)
AA = Q * Ci - Q * CW - Kw * Vw * CW - Kv * Vw * CW - Vs * Aw * Fpw * CW +
Vr * Am * CMM + Vd * Am * (Fdp * CMM - Fdw * CW)
CWnew = AA * dt / Vw + CW
Cells((T + dt) * 250 + 1, 1) = T
Cells((T + dt) * 250 + 1, 2) = CWnew / 1000

If T = 0 Then GoTo 4 Else GoTo 5

4 CM = CWnew
  GoTo 6

5 CM = CMnew


6 AA = -Km * Vm * CM + Vs * Aw * Fpw * CWnew - Vr * Am * CM
  BB = -Vb * Am * CM + Vd * Am * (Fdw * CWnew - Fdp * CM)
  CC = Vd * Am * (Fdp * cs(0) - Fdp * CM)
  DD = AA + BB + CC


CMnew = (DD * dt / Vm) + (CM)
Cells((T + dt) * 250 + 1, 3) = CMnew / 120000


'INITIAL CONDITIONS FOR DEEP SEDIMENT LAYER

If T = 0 Then GoTo 7 Else GoTo 8
7  For i = 2 To nn
   cs(1) = CMnew * 10
```

```
   cs(i) = 0
   Next i
   cs(nn + 1) = cs(nn)
   GoTo 9

8  For i = 1 To nn
   cs(i) = csnew(i)
   Next i
   cs(0) = CMnew * 10
   cs(nn + 1) = cs(nn)

9 For i = 1 To nn

csnew(i) = cs(i) + (Fi * Fdp * Ds * (cs(i + 1) - 2 * cs(i) + cs(i - 1)) / dx ^ 2 - Vb * (cs(i +
1) - cs(i - 1)) / (2 * dx) - ks * cs(i)) * dt
Cells((T + dt) * 250 + 1, 4) = csnew(1)
Cells(i + 1, T + 5) = csnew(i)

Next i

cs(0) = cs(1)
Next T


If T > 10 Then GoTo 10 Else GoTo 11



10 End Sub
```

APPENDIX B

REVERSE MODEL

```
Sub Mixed_layer()


Dim cs(100), csnew(100)

Depth = 10 'm'

Q = 22.54 * 10 ^ 7 'm^3/year
Vw = 23.98 * 10 ^ 6 'm^3
Vm = 854 * 10 ^ 3 'm^3


dx = 1
nn = Depth / dx
dt = 0.005

Ds = 0.014 'm2/yr

Km = 7.05 * 10 ^ -4 '1/year
Kw = 7.05 * 10 ^ -4 '1/year
Kv = 0 '1/year
Aw = 854 * 10 ^ 3 ' m^2
Am = 854 * 10 ^ 3 ' m^2

Vd = 0 'm/year

Fi = 0.7 'porosity
ks = 7.05 * 10 ^ -4 '1/year

'FOR PARTITION COEFFICIENTS

kdw = 4.7
Sw = 100 'g/m^3
kds = 3.5
Fpw = kdw * Sw / (1 + kdw * Sw)
Fdw = 1 / (1 + kdw * Sw)
Fdp = 1 / (Fi + kds * (1 - Fi) * Rop)



Rop = 8960000 'g/m^3
```

```
alfa = 1.64 * 10 ^ -4
g = 9.81 'm^2/s
d = 11.36 * 10 ^ -7

s = 10 'C
mü = ((1.79 * 1.79) * (10 ^ -6)) / (1 + (0.0337 * s) + (0.000221 * (s ^ 2)))
Row = 1000 * (1 - (s + 288.9414) / (508929.2 * (s + 68.12963)) * (s - 3.9863) ^ 2)


t = 0
Fi = 0.7


'INITIAL CONDITIONS
cs(0) = 36.2 * 10 ^ 6 'microg/m^3
Ci = 1 * 10 ^ 3 'microg/m^3
CW = 1 * 10 ^ 3
CW0 = 36.2 * 10 ^ 6 'microg/m^3
CMM = 2 'g/m^3



1 For t = 0 To 0.5 Step dt
If t = 0 Then GoTo 1 Else GoTo 2

1 Cells(2, 11).Select
  Range(Selection, Selection.End(xlDown)).Select
  Selection.End(xlDown).Select
  ssat = ActiveCell.Row
  maxCW = Application.WorksheetFunction.Max(Range(Cells(1, 11), Cells(ssat, 11)))
  Cells(1, 1).Select
  CW0 = maxCW + CW


  GoTo 3

2 Cells(2, 11).Select
  Range(Selection, Selection.End(xlDown)).Select
  Selection.End(xlDown).Select
  ssat = ActiveCell.Row
  maxCW = Application.WorksheetFunction.Max(Range(Cells(1, 11), Cells(ssat, 11)))
  Cells(1, 1).Select
  CW0 = maxCW + CWnew



3 Vs = (1.65 * g * ((d) ^ 2) / (18 * mü)) * 31.536 * 10 ^ 6
  Vb = Vs * alfa
  Vr = (Vs * Aw * Sw - Vb * Am * (1 - Fi) * Rop) / (Am * (1 - Fi) * Rop)
```

```
AA = Q * Ci - Q * CW0 - Kw * Vw * CW0 - Kv * Vw * CW0 - Vs * Aw * Fpw *
CW0 + Vr * Am * CMM + Vd * Am * (Fdp * CMM - Fdw * CW0)
CWnew = AA * dt / Vw + CW0
Cells((t + dt) * 200 + 1, 1) = t
Cells((t + dt) * 200 + 1, 2) = CWnew

If t = 0 Then GoTo 4 Else GoTo 5
 CM = CW0

4  AA = -Km * Vm * CW0 + Vs * Aw * Fpw * CW0 - Vr * Am * CW0
  BB = -Vb * Am * CW0 + Vd * Am * (Fdw * CW0 - Fdp * CW0)
  CC = Vd * Am * (Fdp * cs(0) - Fdp * CW0)
  DD = AA + BB + CC

CMnew = (DD * dt / Vm) + (CW0)
Cells((t + dt) * 200 + 1, 3) = CMnew
dt = 0.005



5 CM = CMnew


  AA = -Km * Vm * CM + Vs * Aw * Fpw * CWnew - Vr * Am * CM
  BB = -Vb * Am * CM + Vd * Am * (Fdw * CWnew - Fdp * CM)
  CC = Vd * Am * (Fdp * cs(0) - Fdp * CM)
  DD = AA + BB + CC


CMnew = (DD * dt / Vm) + (CM)
Cells((t + dt) * 200 + 1, 3) = CMnew


'deep sediment

dt = 0.005


If t = 0 Then GoTo 7 Else GoTo 8
7  For i = 2 To nn
   cs(1) = CMnew
   cs(i) = 0
   Next i
   cs(nn + 1) = cs(nn)
   GoTo 9

8  For i = 1 To nn
   cs(i) = csnew(i)
   Next i
   cs(0) = CMnew
```

```
 cs(nn + 1) = cs(nn)

9 For i = 1 To nn

csnew(i) = cs(i) + (Fi * Fdp * Ds * (cs(i + 1) - 2 * cs(i) + cs(i - 1)) / dx ^ 2 - Vb * (cs(i + 1) - cs(i - 1)) / (2 * dx) - ks * cs(i)) * dt
Cells((t + dt) * 200 + 1, 4) = csnew(1)

Next i

cs(0) = cs(1)
Next t



If t > 0.5 Then GoTo 10 Else GoTo 11



10 End Sub




Sub Reverse()


Dim cs(100), csnew(100)

Depth = 10 'm'

Q = 22.54 * 10 ^ 7 'm^3/year
Vw = 23.98 * 10 ^ 6 'm^3
Vm = 854 * 10 ^ 3 'm^3

dx = 1
nn = Depth / dx

Ds = 0.014 'm2/yr
Km = 7.05 * 10 ^ -4 '1/year
Kw = 7.05 * 10 ^ -4 '1/year
Kv = 0 '1/year
Aw = 854 * 10 ^ 3 'm^2
Am = 854 * 10 ^ 3 'm^2
Vd = 0 'm/year
ks = 7.05 * 10 ^ -4 '1/year



'FOR PARTITION COEFFICIENTS
```

```
kdw = 4.7
Sw = 100 'g/m^3
kds = 3.5
Fpw = kdw * Sw / (1 + kdw * Sw)
Fdw = 1 / (1 + kdw * Sw)
Fdp = 1 / (Fi + kds * (1 - Fi) * Rop)



s = 10 'C
mü = ((1.79 * 1.79) * (10 ^ -6)) / (1 + (0.0337 * s) + (0.000221 * (s ^ 2)))
Row = 1000 * (1 - (s + 288.9414) / (508929.2 * (s + 68.12963)) * (s - 3.9863) ^ 2)

Rop = 8960000 'g/m^3
alfa = 1.64 * 10 ^ -4
g = 9.81 'm^2/s

d = 11.36 * 10 ^ -7
Fi = 0.7 'porosity

'INITIAL CONDITIONS

Ci = 1 * 10 ^ 3 'microg/m^3
CW = 1 * 10 ^ 3 'microg/m^3
CMM = 2 'g/m^3
cs(0) = 36.2 * 10 ^ 6 'microg/m^3

t = 0
dt = 0.005



11 For t = 0 To 0.5 Step dt

If t = 0 Then GoTo 3 Else GoTo 4

3 CM = CW
  CWnew = CW

GoTo 5

4 CMnew = CWnew
  CM = CMnew



5  Vs = (1.65 * g * ((d) ^ 2) / (18 * mü)) * 31.536 * 10 ^ 6
Vb = Vs * alfa
```

```
Vr = (Vs * Aw * Sw - Vb * Am * (1 - Fi) * Rop) / (Am * (1 - Fi) * Rop)



AA = -Km * Vm * CM + Vs * Aw * Fpw * CWnew - Vr * Am * CM
BB = -Vb * Am * CM + Vd * Am * (Fdw * CWnew - Fdp * CM)
CC = Vd * Am * (Fdp * cs(0) - Fdp * CM)
DD = AA + BB + CC


CMnew = (DD * dt / Vm) + (CM)
Cells((t + dt) * 200 + 1, 10) = CMnew



'FOR WATER LAYER

CWnew = CMnew

AA = Q * Ci - Q * CW - Kw * Vw * CW - Kv * Vw * CW - Vs * Aw * Fpw * CW +
Vr * Am * CMM + Vd * Am * (Fdp * CMM - Fdw * CW)
CWnew = AA * dt / Vw + CW
Cells((t + dt) * 200 + 1, 11) = CWnew

Next t

If t > 0.5 Then GoTo 10 Else GoTo 11

10 End Sub




Sub Mixed_layer()


Dim cs(100), csnew(100)

Depth = 10 'm'

Q = 22.54 * 10 ^ 7 'm^3/year

Vw = 23.98 * 10 ^ 6 'm^3
Vm = 854 * 10 ^ 3 'm^3
Aw = 854 * 10 ^ 3 'm^2
Am = 854 * 10 ^ 3 'm^2

dx = 1
nn = Depth / dx
```

```
dt = 0.005

Ds = 0.014 'm2/yr
Km = 7.05 * 10 ^ -4 '1/year
Kw = 7.05 * 10 ^ -4 '1/year
Kv = 0 '1/year
Vd = 0 'm/year
ks = 7.05 * 10 ^ -4 '1/year


Fi = 0.7 'porosity

Q = 22.54 * 10 ^ 7 'm^3/year
cs(0) = 36.2 * 10 ^ 6 'microg/m^3

'FOR PARTITION COEFFICIENTS
kdw = 4.7
Sw = 100 'g/m^3
kds = 3.5
Fpw = kdw * Sw / (1 + kdw * Sw)
Fdw = 1 / (1 + kdw * Sw)
Fdp = 1 / (Fi + kds * (1 - Fi) * Rop)


Rop = 8960000 'g/m^3
alfa = 1.64 * 10 ^ -4
g = 9.81 'm^2/s
d = 11.36 * 10 ^ -7

s = 10 'C
mü = ((1.79 * 1.79) * (10 ^ -6)) / (1 + (0.0337 * s) + (0.000221 * (s ^ 2)))
Row = 1000 * (1 - (s + 288.9414) / (508929.2 * (s + 68.12963)) * (s - 3.9863) ^ 2)


t = 0

Fi = 0.7

'INITIAL CONDITIONS
CMM = 2 'g/m^3
Ci = 1 * 10 ^ 3 'microg/m^3
CW = 1 * 10 ^ 3 'microg/m^3
CMcu = Cells(2, 4)


t = 0


11 For t = 0 To 0.5 Step dt
```

```
 Cells(2, 11).Select
  Range(Selection, Selection.End(xlDown)).Select
  Selection.End(xlDown).Select
  ssat = ActiveCell.Row
  maxCW = Application.WorksheetFunction.Max(Range(Cells(1, 11), Cells(ssat, 11)))
  Cells(1, 1).Select
  CW0 = maxCW



  Vs = (1.65 * g * ((d) ^ 2) / (18 * mü)) * 31.536 * 10 ^ 6
  Vb = Vs * alfa
  Vr = (Vs * Aw * Sw - Vb * Am * (1 - Fi) * Rop) / (Am * (1 - Fi) * Rop)

AA = Q * Ci - Q * CW0 - Kw * Vw * CW0 - Kv * Vw * CW0 - Vs * Aw * Fpw *
CW0 + Vr * Am * CMM + Vd * Am * (Fdp * CMM - Fdw * CW0)
CWnew = AA * dt / Vw + CW0
Cells((t + dt) * 200 + 1, 1) = t
Cells((t + dt) * 200 + 1, 2) = CWnew


dt = 0.005


CM = CWnew


AA = -Km * Vm * CM + Vs * Aw * Fpw * CWnew - Vr * Am * CM
BB = -Vb * Am * CM + Vd * Am * (Fdw * CWnew - Fdp * CM)
CC = Vd * Am * (Fdp * cs(0) - Fdp * CM)
DD = AA + BB + CC


CMnew = (DD * dt / Vm) + (CM)
Cells((t + dt) * 200 + 1, 3) = CMnew


dt = 0.005



If t = 0 Then GoTo 7 Else GoTo 8
7  For i = 2 To nn
   cs(1) = CMnew
   cs(i) = 0
   Next i
   cs(nn + 1) = cs(nn)
   GoTo 9
```

```
8 For i = 1 To nn
  cs(i) = csnew(i)
  Next i
  cs(0) = CMnew
  cs(nn + 1) = cs(nn)

9 For i = 1 To nn

csnew(i) = cs(i) + (Fi * Fdp * Ds * (cs(i + 1) - 2 * cs(i) + cs(i - 1)) / dx ^ 2 - Vb * (cs(i +
1) - cs(i - 1)) / (2 * dx) - ks * cs(i)) * dt
Cells((t + dt) * 200 + 1, 4) = csnew(1)
'Cells(I + 1, t + 5) = csnew(I)

Next i

cs(0) = cs(1)
Next t



If t > 0.5 Then GoTo 10 Else GoTo 11



10 End Sub





Sub Reverse()


Dim cs(100), csnew(100)

Depth = 10 'm'

Q = 22.54 * 10 ^ 7 'm^3/year
Vw = 23.98 * 10 ^ 6 'm^3
Vm = 854 * 10 ^ 3 'm^3
Aw = 854 * 10 ^ 3 'm^2
Am = 854 * 10 ^ 3 'm^2

dx = 1
nn = Depth / dx
dt = 0.005

Ds = 0.014 'm2/yr
Km = 7.05 * 10 ^ -4 '1/year
Kw = 7.05 * 10 ^ -4 '1/year
```

```
Kv = 0 '1/year
Vd = 0 'm/year
ks = 7.05 * 10 ^ -4 '1/year


Fi = 0.7 'porosity

Q = 22.54 * 10 ^ 7 'm^3/year
cs(0) = 36.2 * 10 ^ 6 'microg/m^3

'FOR PARTITION COEFFICIENTS
kdw = 4.7
Sw = 100 'g/m^3
kds = 3.5
Fpw = kdw * Sw / (1 + kdw * Sw)
Fdw = 1 / (1 + kdw * Sw)
Fdp = 1 / (Fi + kds * (1 - Fi) * Rop)


Rop = 8960000 'g/m^3
alfa = 1.64 * 10 ^ -4
g = 9.81 'm^2/s
d = 11.36 * 10 ^ -7

s = 10 'C
mü = ((1.79 * 1.79) * (10 ^ -6)) / (1 + (0.0337 * s) + (0.000221 * (s ^ 2)))
Row = 1000 * (1 - (s + 288.9414) / (508929.2 * (s + 68.12963)) * (s - 3.9863) ^ 2)


t = 0
Fi = 0.7 'porosity


CMM = 2 'g/m^3
Ci = 1 * 10 ^ 3 'microg/m^3
CW = 1 * 10 ^ 3 'microg/m^3


t = 0
dt = 0.005



11 For t = 0 To 0.5 Step dt


4 Cells(2, 2).Select
  Range(Selection, Selection.End(xlDown)).Select
  Selection.End(xlDown).Select
  ssat = ActiveCell.Row
```

```
  maxCW = Application.WorksheetFunction.Max(Range(Cells(2, 2), Cells(ssat, 2)))
  Cells(1, 1).Select
  CWnew = maxCW
  CM = CMnew



5  Vs = (1.65 * g * ((d) ^ 2) / (18 * mü)) * 31.536 * 10 ^ 6
   Vb = Vs * alfa
   Vr = (Vs * Aw * Sw - Vb * Am * (1 - Fi) * Rop) / (Am * (1 - Fi) * Rop)



  AA = -Km * Vm * CM + Vs * Aw * Fpw * CWnew - Vr * Am * CM
  BB = -Vb * Am * CM + Vd * Am * (Fdw * CWnew - Fdp * CM)
  CC = Vd * Am * (Fdp * cs(0) - Fdp * CM)
  DD = AA + BB + CC


CMnew = (DD * dt / Vm) + (CM)
Cells((t + dt) * 200 + 1, 10) = CMnew



AA = Q * Ci - Q * CWnew - Kw * Vw * CWnew - Kv * Vw * CW - Vs * Aw * Fpw *
CW + Vr * Am * CMM + Vd * Am * (Fdp * CMM - Fdw * CW)
CWtop = AA * dt / Vw + CWnew
Cells((t + dt) * 200 + 1, 11) = CWtop

Next t

If t > 0.5 Then GoTo 10 Else GoTo 11

10 End Sub
```