PARTICLE TRACKING MODELING OF MARINE SEDIMENT POLLUTION

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ABSTRACT

PARTICLE TRACKING MODELING OF MARINE SEDIMENT POLLUTION

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Drilling cuttings, chemicals and drilling mud that are discharged to the sea during drilling in offshore, affect sediment habitat at sea floor. The main stressors describing the impact of discharges on marine sediment are, burial, toxicity and free oxygen depletion. In order to determine the effects of mixing of the discharged material in the sediment column, one dimensional particle tracking model that utilizes the random walk method was developed for estimating the free oxygen, natural carbon and added chemical concentrations. This method can overcome numerical diffusion and boundary effects mainly faced in numerical methods as finite difference. The general transport equation with constant bioturbation coefficient and first decay of added chemical is solved with both analytical methods and finite different method to compare the results with particle model. In addition, the stressors are modeled by the diagenetic equations which are solved with finite difference and particle methods to show the consistency of the methods. In order to overcome the oscillations in the particle model due to random behavior of particles, a Kernel smoothing method is applied.

Results show that particle tracking method is a promising alternative to numerical solutions and has a stable behavior for different parameters and it is simple to apply in advection diffusion and first order decay reaction problems. On the other hand, since particle tracking method is an explicit solution, the implementation of reaction in diagenetic equations will lead to divergence between true model and particle model

Keywords: Discharge, drilling cuttings, marine sediment impact, diagenetic equations, particle tracking method

ÖZ

DENİZ TABANINDAKİ SEDİMAN TABAKASINDA OLUŞAN KİRLİLİĞİN PARÇACIK İZLEME YÖNTEMİYLE MODELLENMESİ

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Deniz sondajı sırasında denize boşaltılan sondaj kesintileri, kimyasallar ve sondaj çamuru deniz tabanındaki sedimanın yaşam alanını etkilemektedirler. Boşaltımın etkisini tarif eden en temel stres etkenleri; gömülme, zehirlenme ve serbest oksijen yitimidir. Boşaltım maddesinin sediman kolonunda karıştırılmasının etkilerini belirlemek ve serbest oksijen, doğal karbon ve eklenen kimyasalların konsantrasyonlarını hesaplamak amacıyla, düzensiz hareket metodunu kullanarak parçacık izleme modeli geliştirilmiştir. Bu metot, sonlu kalan gibi sayısal yöntemlerde karşılaşılan sayısal difüzsyon ve sınır etkisi probemlerinin üstesinden gelebilmektedir. Sabit biyotürbasyon katsayılı ve eklenen kimyasalların birinci derece bozulumlu genel taşınım denklemi sonlu kalan ve analitik yöntemlerle metotların tutarlılığını göstermek için çözülmüştür. Parçacık modeldeki düzensiz davranıştan kaynaklanan dalgalanmaları gidermek için bir Kernel düzeltmesi kullanılmıştır. Diyajenetik denklemler tarafından modellenen sistem, ayrıca sonlu kalan ve analitik yöntemler ile parçacık model sonuçlarını karşılaştırmak için çözülmüştür.

Sonuçlar parçacık izleme metodunun sayısal yöntemlere alternatif olarak ümit verici olduğu ve farklı parametreler için kararlı davranış gösterdiği gözlenmiştir. Ayrıca, adveksiyon, difüzyon ve birinci dereceden bozulma problemlerine kolaylıkla uygulanabilmektedir. Öte yandan, parçacık izleme yöntemi açık bir çözüm yöntemi olduğu için, reaksiyonun diyajenetik denklemlerde uygulaması gerçek model ve parçacık model arasında sapmalara neden olmaktadır.

Anahtar Kelimeler: Tahliye, sondaj kesintileri, deniz sediman etkisi, diyajenetik denklemler, parçacık izleme yöntemi

To My Beloved Family

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NOMENCLATURE

k_1	biodegradation (respiration) rate of natural organic matter (per hour)
k_2	biodegradation (respiration) rate of added chemical (per hour)
t	time (hour)
u	bulk velocity of pore water (cm/hour)
w	burial velocity from natural sediment deposition (cm/hour)
z	vertical space (cm)
C	concentration (mass/volume, kg/m^3, mg/dL)
$\hat{C}$	concentration of compound in pore water (mass/volume, kg/m^3, mg/dL)
D'	effective diffusion coefficient (cm^2/hour)
D_B	bioturbation coefficient (cm^2/hour)
D_{Bave}	average bioturbation coefficient (cm^2/hour)
D_0	diffusion coefficient for oxygen in pore water (cm^2/hour)
F	flux (mass/area/time)
K_{O_2}	Monod-type saturation constant
O_2	oxygen concentration (mg/L)
E	natural carbon concentration (g/kg dry sediment)
R	retardation factor
γ_1	Redfield number of natural carbon

γ_2	Redfield number of added material
θ	tortuosity
ϕ	porosity
nP	number of particles
nL	number of layers
$nLadd$	number of added layers

CHAPTER 1

INTRODUCTION

Oil and gas exploration and production expands through deep waters which directly affects the marine environment. Certain potential impacts linked to drilling activities arise from the disposal of drilling fluid and cuttings. Most of the cuttings, due to their particulate nature and higher densities, sink down on sea floor near the drilling rig. The major effects are due to the attached chemicals in the drilling muds. Chemicals can form larger particles called ‘agglomerates’ due to their sticky property. Three types of fluids are used in drilling activities to provide riskless and efficient operations which are water based muds (WBM), oil based muds (OBM) and synthetic based muds (SBM). Each has its own chemical content and its own harm on environment but OBMs are the most harmful fluids and in fact the usage of OBMs are prohibited in many countries (Frost et al., 2006). Although prohibition of the discharge of cuttings with regulatory arrangements and laws exists nowadays, the effects of former operations can be seen and in some cases disposal in marine environment can be the least expensive and simple choice. After disposed particles arrived at marine sediment, they exposed to some transport processes like advection, diffusion, aggregation, deposition (Breivik, 2012) and cause inhibition and smothering of the benthic organisms (Niu et al., 2009). The major effects of contaminated cutting discharge to marine sediment are (APPEA, 1998);

- toxicity,
- bioturbation of materials by biota,

- smothering effects on biota,
- oxygen depletion in sediment, sediment anoxia,
- biodegradation

The discharge may cause impact on both sediment and water column. Where the effects on water column can be seen quickly right after discharge, the impacts on sediment column can spread over a long time. The mathematical modeling of transport equations can be used to determine the effects of drilling discharges on marine sediment. Up until today, a number of models for effects of drilling discharges have been constructed which have their complexity and different type. In the study of Smith and Brandsma (2004), effects of discharged water and water based mud on water column are modeled with the Offshore Operators Committee Mud and Produced Water Discharge Model (the "OOC Model") in which ocean currents and factors that affect the discharge plume are obtained by field studies. The benthic boundary layer transport (bblt) model is developed by Niu et al. (2009) to simulate the transport and dispersion of discharges in the benthic layer by modeling the velocity of particles. The modeling of the release of materials is modeled with ParTrack model by Rye et al (2004). In the study of Rye et al (2006), a numerical model called Dose related Risk and Effect Assessment Model (DREAM) to simulate the fate of the discharge particles in water column and marine sediment. DREAM is a global model which employs several sub modules, including near field plume model, water column transport model, degradation models, sediment models etc. As a part of the global model in order to quantify environmental risk, Rye et al. (2006) presented their sediment model which is based on diagenetic equations estimating the effect of discharges of drill cuttings and mud. Following the descriptions from Rye et al. (2006), Durgut et al (2015) presented a sediment model to estimate the environmental risk of drilling discharges in the marine environment by incorporating the risk into the model which is a good first approximation to the uncertainties involved in model controlling parameters. In this study, the effects of released particles only on sediment layer is modeled by solving the diagenetic equations with particle tracking method, and the finite difference and the analytical methods are used to compare the results. The particle method is a random walk method which calculates the positions of randomly distributed and equal mass particles which moves with the effect of advection and diffusion (Cranmer, 2003). This method is used by Kenzelbach (1990) and Uffink (1988) to model the pollution in groundwater and to overcome the problems faced in numerical methods. Also, as in the study of Durgut et al. (2015) diagenetic equations from which the physical, chemical and biological changes in sediment subsequent to deposition can be calculated, is solved numerically by finite difference method and analytical methods which are supposed in the study of Genuchten and Alves (1982).

CHAPTER 2

THEORY OF DIAGENESIS

2.1 Diagenetic Equations

Diagenesis in a broader context refers to the sum of processes that bring about changes in a sediment or sediment rock subsequent to deposition. The processes may be physical, chemical and/or biological in nature. Early diagenesis term represents to the transformations during burial up to a few hundred meters where exalted temperatures are not observed and the deposited layers were not uplifted above sea level, so that the sediment pore spaces are always filled with water (Berner, 1980). Such as the precipitation of minerals, activities of microbes, alteration of larger fauna that live in the sediment, compaction due to self-weight of the particles and resuspension of the sediment due to currents and turbulence are subtopics of the diagenesis. The “early” word in front of the diagenesis as in the book of Berner (1980) designates that the changes occurring near sediment water interface that is approximately a few meters. (Boudreau, 2000). Further the scope of the studies investigating processes in marine sediments is usually narrowed down to benthic fauna where biological activities take place in few centimeters of sediment depth (10 to 20 cm). The processes included in those studies are commonly classified as bioturbation, biodegradation, diffusion, and burial which will be the processes to be studied in this thesis.

The equations that describe these processes are therefore called diagenetic equations. They are nonlinear partial differential equations. The derivation of diagenetic equations is based on defining the diagenetic processes mathematically. By using the mass conservation principle the decrease or increase in amount of a given constituent in the sediment (concentrations of naturally depositing chemicals or artificially deposited chemicals, oxygen concentration in pore water etc.) in a givensediment volume V in a time interval Δt is given by (Boudreau, 2000):

$$net\ acumulation = \int_{t}^{t+\Delta t}\int_{V} \frac{\partial C}{\partial t} dVdt \tag{2.1}$$

The C term is concentration of a species. The Eqn 2.1 can be expressed with the difference of fluxes through the surface of the volume and/or sink source terms in volume. The net flux is given by over the area of S as (Boudreau, 2000):

$$net\ flux = -\int_{t}^{t+\Delta t}\int_{S} F\ .n\ dAdt \tag{2.2}$$

where F represents the flux vector across the surface S, n is the unit normal vector and A is the area of the surface.

Source and sink terms can be constructed by geochemical reactions and transport processes that take place in a volume of V. The sum of the individual rates of every process and reaction, R_i at each point is the net flux (Boudreau, 2000):

$$net\ sink\ or\ source\ term = \int_{t}^{t+\Delta t}\int_{V} \sum R_i dV\ dt \tag{2.3}$$

Then the net accumulation is equal to;

$$\int_{t}^{t+\Delta t}\int_{V} \frac{\partial C}{\partial t} dVdt = -\int_{t}^{t+\Delta t}\int_{S} F\ .n\ dAdt + \int_{t}^{t+\Delta t}\int_{V} \sum R_i dV\ dt \tag{2.4}$$

By using divergence operator ∇ from Gauss's theorem the equation can be simplified from surface flux with integral over bounding surface to volume integral:

$$\int_{t}^{t+\Delta t}\int_{V}\left(\frac{\partial C}{\partial t}+\nabla . F-\sum R_i\right)dVdt=0 \quad (2.5)$$

where ∇ is the divergence operator and equals to:

$$\nabla = \boldsymbol{i}\frac{\partial}{\partial x}+\boldsymbol{j}\frac{\partial}{\partial y}+\boldsymbol{k}\frac{\partial}{\partial z} \quad (2.6)$$

There is only one way for Eqn 2.5 becomes zero that the inside of the integral at left hand side have to be zero for all volumes and time intervals. Then the mass conservation equation for sediment can be expressed as (Boudreau, 2000):

$$\frac{\partial C}{\partial t} + \nabla . F - \sum R_i = 0 \quad (2.7)$$

The diagenetic changes generally act in vertical dimension because while changes occur in sediments at horizontal directions on the scale of hundred meters, in vertical directions changes take place over a very short distance (Fig 2.1). This is related to geological time, thus horizontal variations are slow compared to vertical directions and can be neglected (Berner, 1980). Then the equation has the simple form as:

$$\frac{\partial C}{\partial t} = \frac{\partial F}{\partial z} - \sum R_i \quad (2.8)$$

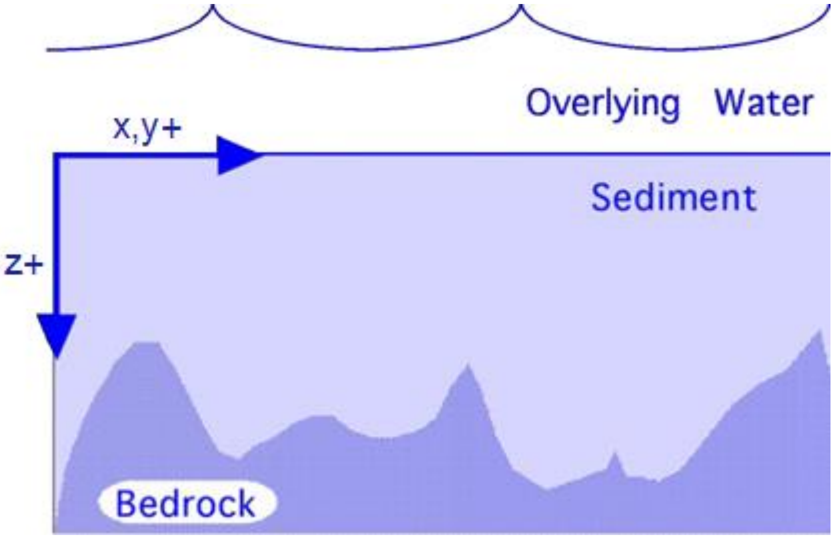

Figure 2.1: Representation of Cartesian coordinate system used in modelling early diagenesis in marine sediments (Boudreau, 1997).

2.1.1 Steady State Diagenetic Process

Let C represents the concentration of any property in a sediment or sedimentary rock, for instance, a certain chemical or oxygen concentration, z is depth in sediment and t is time. Because of neglecting the horizontal changes C is defined as a function of depth. and time:

$$C = f(z, t) \tag{2.9}$$

From the mathematical point the total changes which occur in sediment due to diagenesis is the total or material derivative of the bulk concentration. The total concentration change of a property in an observed small mass of either pore water or solid sediment is connected with changes in all independent variables and the transformation is expressed as (Boudreau, 1997):

$$\left(\frac{DC}{Dt}\right)_{fixed\ \ layer} = \left(\frac{\delta C}{\delta t}\right)_{fixed\ depth} + \frac{dz}{dt}\left(\frac{\delta C}{\delta z}\right)_{fixed\ time} \tag{2.10}$$

which is the total derivative of the bulk concentration. For the sake of simplicity, the subscripts can be removed not to cause any confusion:

$$\left(\frac{DC}{Dt}\right) = \left(\frac{\delta C}{\delta t}\right) + \frac{dz}{dt}\left(\frac{\delta C}{\delta z}\right) \tag{2.11}$$

The left hand side of the Eqn 2.11 is diagenesis and it is balanced by the changes in the right hand side. The dz/dt term is the velocity observed in layer as observed in the coordinate system. It is positive at downward direction and thus it is burial velocity in solids and expressed as w. The burial velocity is simply the rate of deposition (Berner, 1980):

$$\frac{dz}{dt} = w \tag{2.12}$$

If no diagenesis occurs, C within a fixed layer is constant,

$$\left(\frac{DC}{Dt}\right) = 0 \qquad (no\ diagenesis) \tag{2.13}$$

Thus,

$$\left(\frac{\delta C}{\delta t}\right) = -w\left(\frac{\delta C}{\delta z}\right) \tag{2.14}$$

Therefore, the changes in sediment are caused by burial of a time varying input (i.e. C). After a certain time Δt, the property changes at a fixed depth z_1 as shown in Fig 2.2. On the other hand if a chosen layer of sediment is followed (Layer A in the same figure), no change will be observed because of the absence of diagenesis and it will be just buried. Therefore it is called non steady state for a stable substance.

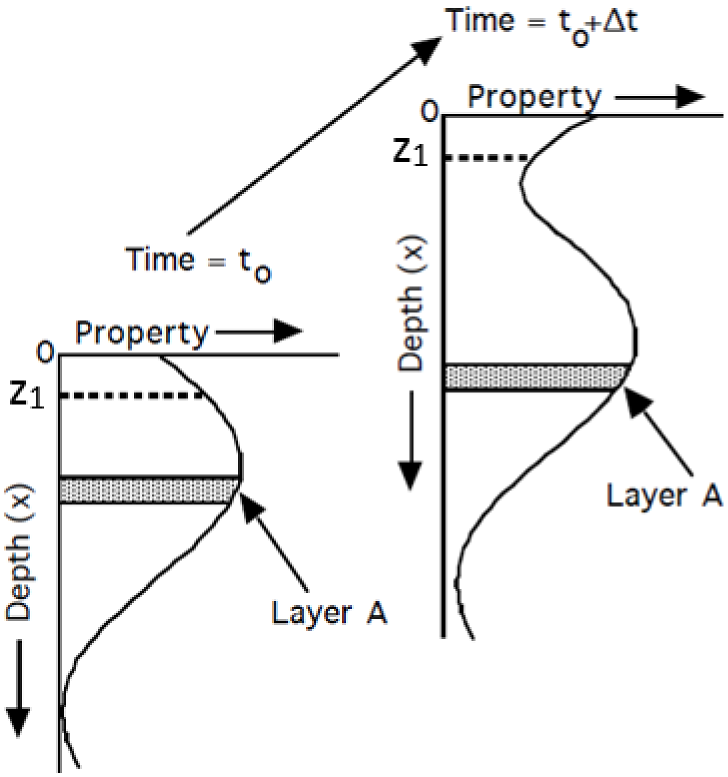

Figure 2.2: An example of a non-steady state diagenesis of a non-reactive substance at a certain layer A (Berner, 1980).

The opposite assumption is that when the concentration has the same value at the same depth which is called steady state diagenesis and expressed as,

$$\left(\frac{\delta C}{\delta t}\right) = 0 \tag{2.15}$$

Thus,

$$\left(\frac{DC}{Dt}\right) = w\left(\frac{\delta C}{\delta z}\right) \tag{2.16}$$

If a layer of sediment is chosen and followed while burial continues, change of layer concentration with time is the fact (Fig 2.3). However, at a fixed depth, z_1 no changes will be observed because change in fixed depth is balanced with continuous burial flux. The balance of the diagenetic changes expresses the steady state diagenesis. This assumption is useful to compare real diagenetic situations where the change with time is considered.

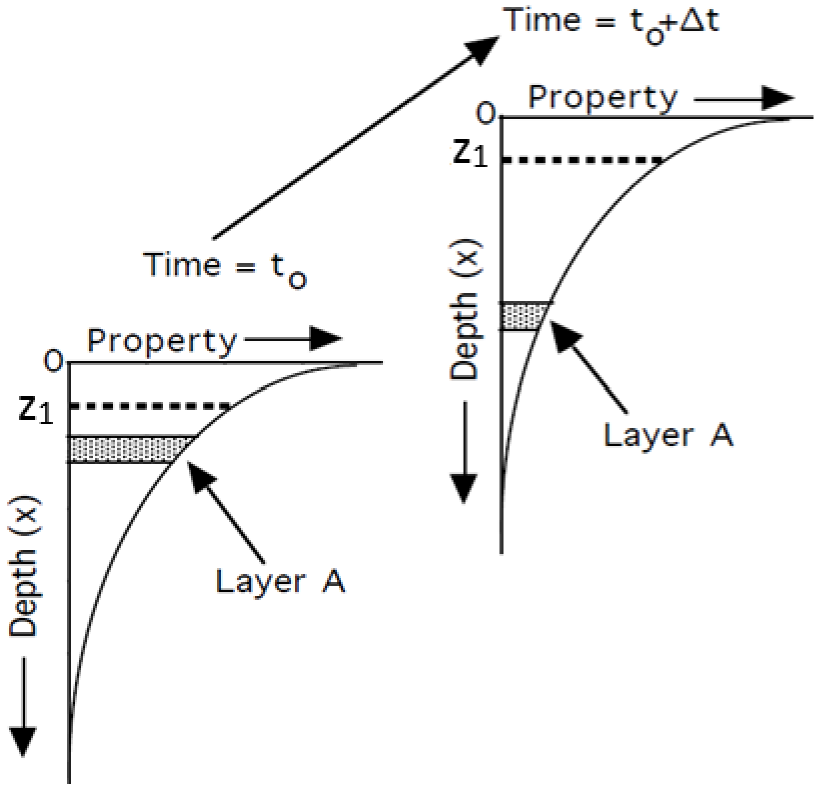

Figure 2.3: An example of steady state diagenesis of a decaying substance (Berner, 1980).

2.2 Types of Fluxes in 1-D

The transport process discussed herein consists of two types of flux; diffusive and advective. Diffusion of solids or liquids is a spreading process which cannot be reversed and is the result of random motions of particles. Advection is the bulk flow of the substance.

2.2.1 Advection

Advection is defined as the bulk flow of a fluid, so one dimensional advective mass flux of a given compound with the given the concentration C is defined as,

$$F = uC \tag{2.17}$$

where u is the bulk velocity of the compound.

If the process takes place in the porous media, u, will be the velocity of porewater along the principal direction of flow and the porosity term, ϕ appears in the equation:

$$F = u\phi\hat{C} \tag{2.18}$$

Note that the concentration, $\hat{C}$ is the concentration of compound in pore water and the porosity, ϕ is defined as:

$$\phi = \frac{volume\ of\ porewater}{volume\ of\ solid\ sediment + porewater\ volume} \tag{2.19}$$

The temporal rate of change of concentration that is proportional to spatial variation of substance flux has been stated earlier as Eqn 2.8. The same relation can be written for porous medium as follows:

$$\left(\frac{\partial\phi\hat{C}}{\partial t}\right) = \frac{\partial F}{\partial z} \tag{2.20}$$

Therefore advective transport in porous medium is expressed as:

$$\left(\frac{\partial \phi \hat{C}}{\partial t}\right)_{advection} = u\frac{\partial\left(\phi \hat{C}\right)}{\partial z} \qquad (2.21)$$

The velocity, u will be taken as w, burial velocity of solids. Burial, compaction and/or externally impressed flow can result in the advective flux (Boudreau, 1997). However appearance of the advection term in the equations is that the sediment water interface is used as reference. According to Berner (1980), burial rates are between 0.1-10 cm per thousand years in deep sea sediments and between 0.1-10 cm per year in near shore fine grained muds. If the effects of compaction and externally impressed flow can be neglected, advection of pore water will be equal to burial rate. On the other hand, in fine grained sediments the advection of pore water and particles can be due to compaction but in general, the effect of compaction is ignored in diagenetic equations because it is smaller than the velocity of the solids and thus porosity of a given layer does not change during burial.

At river entrances and at places that sediment build-up occurs, the burial velocity increases generally. According to Boudreau (1997), with increasing water depth, burial velocity has the tendency to decrease.

2.2.2 Diffusion

Diffusion is the net motion of substances from a high concentration region to low concentration and, in particular mixing of particles by the random motion of particles. It can be in the form of molecular, bioturbation, wave and current strings and diffusion. The main focus will be on molecular diffusion and bioturbation.

Molecular diffusion has the same definition with diffusion that is the process transport of particles one point to another point due to random molecular motion with a concentration gradient and for the porous medium it can be expressed with the Fick's First Law, (Fick, 1855)

$$F_D = -\phi D' \frac{\partial \hat{C}}{\partial z} \qquad (2.22)$$

where F_D is the diffusive flux, D' is the effective diffusion coefficient of the solute in the pores, ϕ is the porosity of the sediment. Because of the tortuosity of the flow paths in a porous system that are followed by molecules, the effective diffusion coefficient, D' and molecular diffusion coefficient in free solution D_o are not equal, because the path has its characteristic tortuosity,

$$D' = \frac{D_o}{\theta^2} \tag{2.23}$$

where θ is tortuosity which is greater than 1 and slows down the diffusion process in pores due to the presence of the grains but it is an unmeasurable parameter.

Fick's Second Law gives relation between change in concentration with time and space. Combining the Fick's First Law and Second Law,

$$\frac{\partial \phi \hat{C}}{\partial t} = -\frac{\partial F_D}{\partial z} = \frac{\partial (\phi D' \frac{\partial \hat{C}}{\partial z})}{\partial z} \tag{2.24}$$

and expanding the equation gives,

$$\frac{\partial \phi \hat{C}}{\partial t} = D_o \frac{\partial}{\partial z}\left(\frac{\phi}{\theta^2}\frac{\partial \hat{C}}{\partial z}\right)\frac{\partial \hat{C}}{\partial z} \tag{2.25}$$

If the porosity does not vary with depth, it simplifies to

$$\left(\frac{\partial \hat{C}}{\partial t}\right)_{\substack{molecular \\ diffusion}} = \frac{D_o}{\theta^2}\frac{\partial^2 \hat{C}}{\partial z^2} \tag{2.26}$$

Another form of diffusion is bioturbation (biodiffusion) which is the alteration, displacement and mixing of the sediment grains by organisms to locate food, build and maintain dwellings, hide from predators etc. (Boudreau, 2000) The upper part of the sediment is exposed to activities of benthic organisms and it will result with changes in the physical, chemical, and biological properties of the sediment. If the mixing process is rapid, small-scale and random, the bioturbation can be assumed as diffusive behavior, and it can be formulated as follows:

$$\left(\frac{\partial\phi\hat{C}}{\partial t}\right)_{bioturbation} = \frac{\partial}{\partial z}\left(\phi D_B \frac{\partial\hat{C}}{\partial z}\right) \quad (2.27)$$

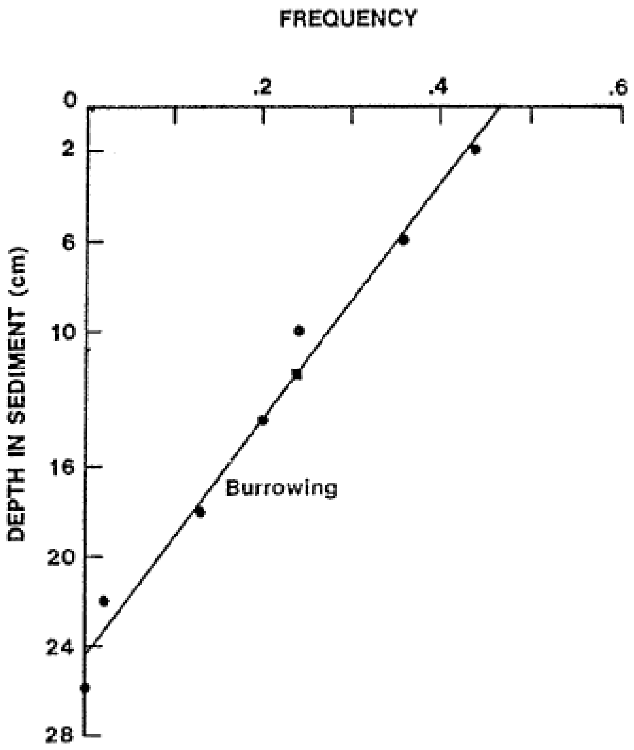

Figure 2.4: Example of burrowing frequency with respect to sediment depth

Also the analysis of bioturbation rate and depth of the sediment that the process occurs so-called mixed depth, L has done by Boudreau (1998) and stated that bioturbation rate is dependent on mixing depth. The bioturbation is highest at the sediment surface and decreases with depth and reaches to zero at bottom of the mixed depth. Although the general assumptions about constant bioturbation coefficient due to burrowing, as it is shown in Fig 2.4 is a function of sediment depth.

2.2.3 Reaction

The R expression in the diagenetic equations is the rate of each reaction in terms of mass per unit volume of total sediment per unit time. The reactions that can occur in advection diffusion transport models can be equilibrium controlled or rate limited sorption reactions.

Generally, equilibrium controlled sorption reactions involve mass transfer between the porous medium and dissolved substance (absorption and adsorption) (Zheng & Bennett, 2002).

The reaction term in this study refers to biodegradation process in sediment. Biodegradation is the process of decomposition of organic materials by microorganisms which causes oxygen depletion in sediment layer. Decomposition of organic matter or oxidation can be modeled by so called Monod kinetics (Boudreau, 1997),

$$R = \left(\frac{\partial \phi \hat{C}}{\partial t}\right)_{reaction} = -k\hat{C}\frac{O_2}{K_{ox} + O_2} \tag{2.28}$$

where $\hat{C}$ is the concentration of organic compound in pore water, O_2 is the pore water concentration of oxygen that is consumed for degradation, k is the biodegradation rate and K_{ox} is the saturation constant. The biodegradation rate of organic matter can be different for each chemical.

It is concluded that the Monod kinetics reaction equation is hyperbolic and first order in organic compound concentration (Fig 2.5). When $O_2 \gg K_{ox}$ the reaction is essentially independent of O_2 (zeroth order reaction). It may be approximated to first order reaction equation when $O_2 \ll K_{ox}$.

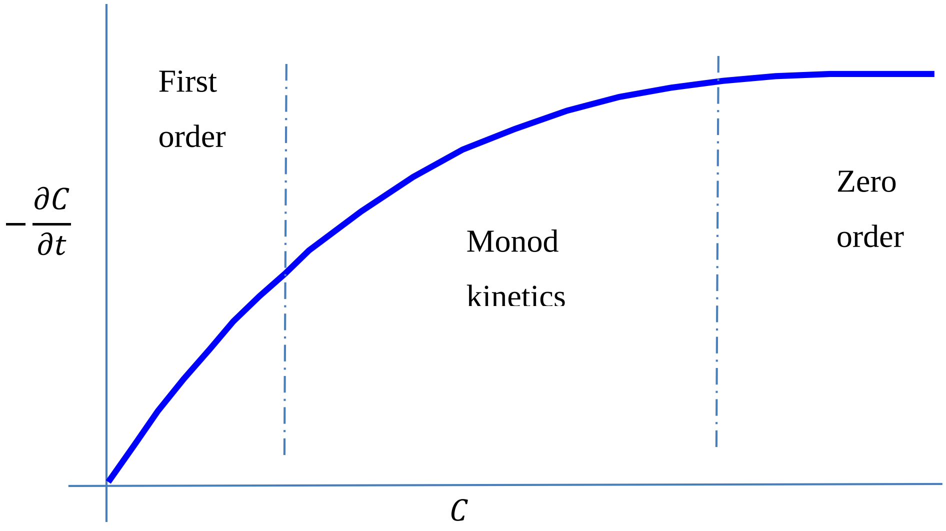

Figure 2.5: The graphic representation of Monod kinetics reaction equation.

2.3 The Standard Form of Diagenetic Equation

The general diagenetic equation obtained by considering accumulation of a certain compound in sediment, including effective diffusion, bioturbation, burial and reaction processes can be obtained by summing all the equations is defined as;

$$\frac{\partial \phi \hat{C}}{\partial t} = \frac{D_o}{\theta^2} \frac{\partial}{\partial z} \left(\frac{\partial \phi \hat{C}}{\partial z} \right) + \frac{\partial}{\partial z} \left(\phi D_B \frac{\partial \hat{C}}{\partial z} \right) - w \frac{\partial \phi \hat{C}}{\partial z} + \sum R \tag{2.29}$$

The sediment concentrations are usually measured as mass of a species per dry sediment weight or volume during surveillance. Therefore, setting the parameters of the equations to a value used in practice eases the comparison with field data. For instance, stating the polluting chemical concentration as mass of species per dry sediment volume solid concentration with $\hat{C}$ the pore water concentration can be obtained as;

$$\hat{C} = \frac{1-\phi}{\phi} C \tag{2.30}$$

In this study, the oxygen concentration is the pore water concentration while the organic compounds (either natural or artificially deposited) are given as mass per dry sediment volume in the model equation. Therefore according to the equations explained above, the free oxygen pore water concentration profile, O_2 is modeled by;

$$\frac{\partial O_2}{\partial t} = \frac{D_0}{\theta^2} \frac{\partial^2 O_2}{\partial z^2} - \frac{1-\phi}{\phi} R_{oxyg} \tag{2.31}$$

Porosity is assumed as constant and thus it is canceled out in right hand side and left hand side of the Eqn 2.27 but it has to be added to in front of the reaction term as expressed in Eqn 2.31 because the reaction process between carbon and oxygen takes place in pore scale. The burial term for oxygen equation is omitted because diffusion process is much larger than burial effect.

The biodegradable natural carbon concentration, C and the biodegradable chemical concentration, E are calculated from;

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(D_B \frac{\partial C}{\partial z} - wC\right) - R_{carb} \tag{2.32}$$

$$\frac{\partial E}{\partial t} = \frac{\partial}{\partial z}\left(D_B \frac{\partial E}{\partial z} - wE\right) - R_{chem} \tag{2.33}$$

Since reaction happens in the sediment scale, porosity term is canceled both sides of the equation and the main processes are the bioturbation and advection of the natural carbon and chemical particles.

2.4 General Transport Equation

The rate of the movement of a chemical or a substance through sediment is estimated by several transport processes. These processes in this study are identified as diffusion, advection and reaction (i.e. biodegradation specified by zero order or first order decay). The general one dimensional advection-diffusion-reaction (ADR) equation from which the change in concentration of a chemical or a substance, C can be calculated, is:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - kC \tag{2.34}$$

where retardation factor, R, diffusion coefficient, D, advection velocity, u and degradation rate, k are constants. The retardation factor makes the motion of the substance through sediment slower; however it is taken as 1 in this study. The diffusion term considers only mixing process and the advective term specify on movement of the substance under a velocity field. The decay of the chemicals with other substances is defined by the reaction term (Rubio, Zalts, & El Hasi, 2008).

Although the transport equation is difficult to solve because of its spatial first (advective motion) and second order (diffusive motion) terms which introduce hyperbolic and parabolic characters respectively, there are studies both numerically and analytically. In the study of Genuchten and Alves (1982) the equation is solved for several boundary conditions and reaction types for constant parameters. On the other hand, the equation is solved by several numerical methods as finite difference and finite element in the article of Kaya and Gharehbaghi (2014). Furthermore, Kenzelbach (1990) is used random walk method to estimate the movement of a pollutant in groundwater.

CHAPTER 3

STATEMENT OF THE PROBLEM

The primary aim of this study is to model the fate and effects of instant deposition of drill cuttings and discharges on the sea floor after disposal. In order to observe the effects of disposal, a one dimensional vertical profile of added chemical, natural carbon and oxygen concentrations are calculated with particle tracking model which can be used in depth dependent bioturbation equations and can overcome numerical diffusion and boundary effects faced in numeric methods. Moreover, the general transport equation with constant bioturbation coefficient and first order reaction for added chemicals is solved with analytical, finite difference and particle methods to show the effects of parameters and to compare the mathematical methods. The diagenetic equations for added chemical, natural carbon and free oxygen concentrations are solved with finite difference and particle methods to investigate the limitations of the methods and error analysis are done to verify the model.

CHAPTER 4

PARAMETER CHARACTERIZATION

The aim of this chapter is to describe briefly the mathematical models that are used to model solute transport in sediment. The focus is on the particle tracking method which is the main purpose of this thesis.

4.1 Model Description

In order to model pollution of marine sediments (e.g. deposition of the drill cuttings and mud that is discharged during offshore operations on the sea floor, or pollution due to spilled oil settled into to nearshore zones), a sediment bottom module is needed. Some of the processes interested in the study are illustrated in Fig 4.1. The effects of pollution that is modeled in this study can be listed as: (Rye, Reed, Durgut, & Ditlevsen, 2006b)

- Covering existing biota on the sea floor, burial effects
- Biodegradation of the added chemicals, oxygen depletion in turn
- Bioturbation of the naturally deposited and added chemicals

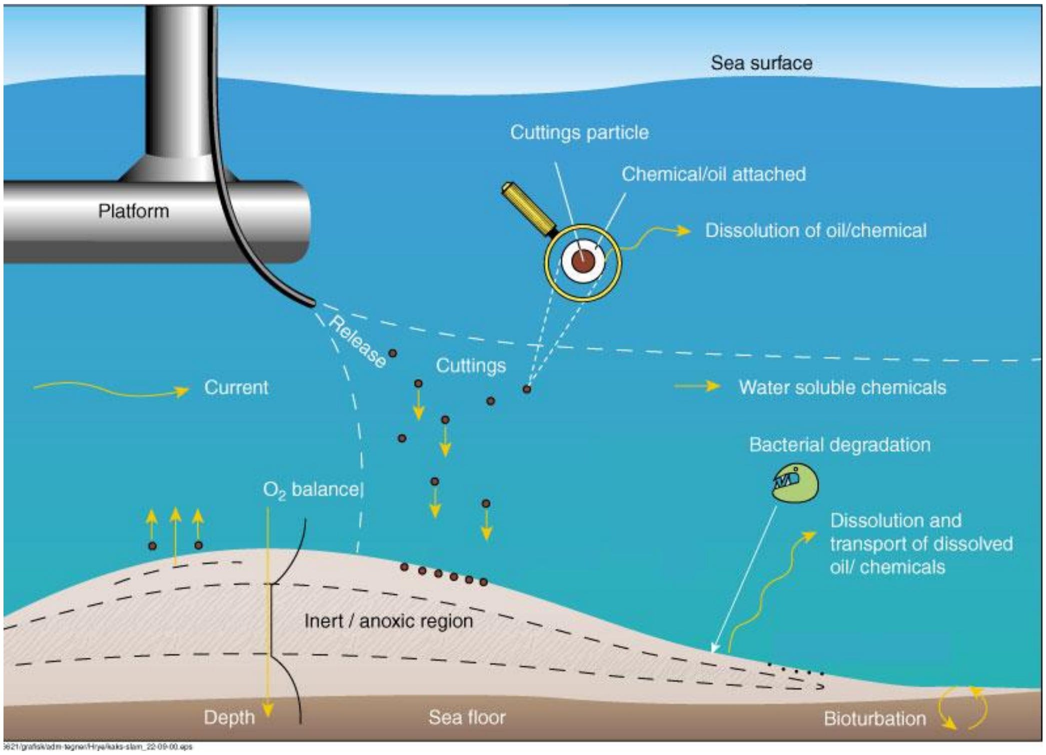

Figure 4.1: Illustration of some processes that occur at the bottom sediment module (Singsaas et al., 2007).

4.2 Sediment Characterization before Discharge

Defining and estimating the change in oxygen content is required for modelling the natural bottom sediment because the oxygen concentration changes with sediment depth and time. The vertical oxygen profile in sediment column should first be constructed before deposition, then it should be updated after the deposition. The factors that affect the oxygen profile in the sediment are:

- amount of biodegradable carbon
- diffusion of the free oxygen in the pore water
- consumption of the free oxygen

Also the steady state biodegradation of natural carbon has to be modeled before discharge because it moves downwards in the sediment due to burial and bioturbation. In order to model these processes the diagenetic equations are solved.

4.3 Stressors Acting on the Sediment

4.3.1 Burial Effects

An important parameter for the diagenetic processes, and in turn for the sediment model, is the natural deposition rate. When discharge occurs, new layer will be formed on the sediment surface. In the model burial is defined as added layer. Burial of the discharged material may affect the natural habitat or benthic fauna. The existing biota will be covered after deposition. Having the burial effects a new sediment layer will form and starts to mix with the old sediment due to bioturbation process which brings up the old sediment to surface. The added layer is mixed with old sediment and former benthic fauna can regain its territory by time. The burial thickness which is the thickness of the added layer in this case is reduced according to the amount of the old sediment in the initial thickness of deposition to overcome from these effects. The function of burial is expressed as follow (Durgut, Rye, Reed, Smit, & Ditlevsen, 2015):

$$Burial(t) = \int_{0}^{L_{dep}} \Phi(z,t)dz \tag{4.1}$$

where $\Phi(z,t)$ is the concentration of the added deposited particulate material and L_{dep} is the initial thickness of the deposition.

4.3.2 Oxygen Depletion

The settling of added particulate matters causes oxygen consumption. The oxygen consuming processes are classified in Fig 4.2 and the free oxygen in the pores of sediment is mainly compelled by benthic fauna (aerobic bacteria) in the top layer of the sediment. The anoxic biodegradation of natural carbon and added chemicals will reduce oxygen content in the deeper layers (Park & Na, 2002.).

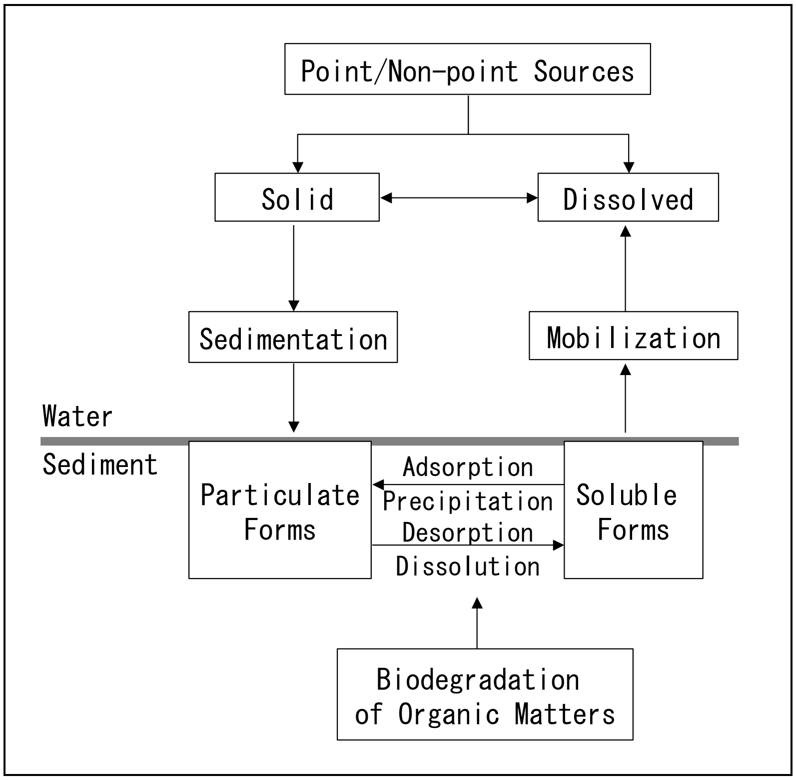

Figure 4.2: Processes that contaminants face in benthic sediment.(Park & Na, 2002.)

The water quality and marine biota in the sediment is related with the oxygen level. Microbial breakdown of organic matter and discharged cutting can cause rapid depletion of oxygen and thus can lead to anoxic conditions. The oxygen reduction can also result from organic matter advection due to sediment mixing (APPEA, 1998).

The dissolved oxygen concentration profile in vertical direction is integrated over the sediment column to calculate the oxygen depletion with time. Each time step the depleted oxygen can be calculated from;

$$Oxygen\ depletion(t) = \frac{\left[\int_0^L \phi O(z,t)dz\right]_{t>0} - \left[\int_0^L \phi O(z,t)dz\right]_{t=0}}{\left[\int_0^L \phi O(z,t)dz\right]_{t=0}} \tag{4.2}$$

where $O(z,t)$ is the concentration of oxygen in pore spaces as a function of time and space. The porosity, ϕ, appears in the equation because the amount of oxygen dissolved in pore water is considered in the model. However, in this study the porosity is taken out from integral and cancelled because it is assumed to be constant. The integral limit L is the sediment depth where the oxygen concentration is close to zero. This guarantees to include almost all the amount of dissolved oxygen in the sediment in calculations.

4.3.3 Toxicity

The deposition of heavy metals and chemicals attached to particles may cause toxic effects to benthic fauna. The concentration of these materials in the sediment (called toxicity) can be calculated as (Durgut et al., 2015) ;

$$Sediment\ chemical\ concentration = \frac{1}{L_{tox}} \int_{0}^{L_{tox}} C(z,t)dz \qquad (4.3)$$

where $\mathrm{C(z,t)}$ is the concentration of chemicals deposited on the sediment and L_{tox} is the toxicity calculation depth which is set to upper 3 cm of the sediment layer. The value of the depth is arbitrary, however since the upper 1 or 3 cm of the sediment layer is usually observed this value is taken. The other reason for this choice is that the benthic fauna is mainly concentrated on the first 3 cm of the sediment.

4.4 Diagenetic Equations Used in Model after Discharge

The stressors that are described are expressed with diagenetic equations. The free oxygen content in pore water, natural carbon in sediment and added chemical due to discharge are equated with partial differential equations and solved by finite difference and analytical models.

The priority is to calculate oxygen calculation which can be expressed as a balance between the diffused oxygen downward from free water to pore water and consumed by biodegradable organic matter that deposited on the sea floor. The deposited biodegradable organic matter reaches to sediment surface as particles and bioturbation and burial cause a distribution of these particles within the sediment layer. The reaction between biodegradable organic matter and oxygen leads to formation of CO_2 by consumption of oxygen in pore water. The balance of free oxygen flux from above is provided by the organic matter consumption in the sediment.

After instant discharge of disposable matter which can include biodegradable chemicals, the oxygen equation should be modified and an equation for chemicals should be added because deposition of these materials will lead to depletion in oxygen. After discharge the oxygen equation is evolved as; (Rye et al, 2006)

$$\frac{\partial O_2}{\partial t} = \frac{D_0}{\theta^2}\frac{\partial^2 O_2}{\partial z^2} - \frac{1-\phi}{\phi}\left[\gamma_1 k_1 C + \gamma_2 k_2 E\right]\frac{O_2}{K_{O_2} + O_2} \tag{4.4}$$

where E is the concentration of added chemical, γ_2 and k_2 are Redfield number and biodegradation rate of added organic chemical respectively. The unit of oxygen concentration is g/m^3 (or mg/L pore water) and the unit of natural carbon and chemical concentration are same which is kg/m^3 dry weight. Moreover, the equations for added chemical and biodegradable natural carbon concentration (both are considered as organic matter) are, respectively; (Rye et al, 2006)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(D_B\frac{\partial C}{\partial z} - wC\right) - \left[k_1 C\right]\frac{O_2}{K_{O_2} + O_2} \tag{4.5}$$

$$\frac{\partial E}{\partial t} = \frac{\partial}{\partial z}\left(D_B\frac{\partial E}{\partial z} - wE\right) - \left[k_2 E\right]\frac{O_2}{K_{O_2} + O_2} \tag{4.6}$$

The left hand side of the equations represent the rate of change in concentration of compounds in sediment (oxygen and organic matter). The first term on the right hand side for the oxygen equation represents the diffusion of oxygen through pores and for the organic matters (added chemical or biodegradable natural carbon) it is defined as bioturbation effect with natural burial. The second terms represent the reaction of organic matters with oxygen. On the other hand, consumption of oxygen and biodegradation of organic matter is calculated from the second part which is literally means formation of CO_2.

The equations should be solved numerically and simultaneously because they are nonlinear and coupled equations. The left hand side of the equations are set to be zero (steady state condition) to calculate the oxygen and organic matter concentration before discharge.

4.4.1 Parameters in Equations

4.4.1.1 Diffusion coefficient for oxygen and tortuosity

The tortuosity, θ appears in the Eqn 4.4 because molecular diffusion is dependent of existence of grains. Tortuous structure of sediments slow down the diffusion process of oxygen, so diffusion coefficient is divided by tortuosity squared.

Although tortuosity is defined by Berner (1980) as dl/dz, ratio of the actual length of a particle must travel in the pores, dl and direct distance, dz just the added path length in porous media is not enough according to Boudreau (1996). There are theoretical and empirical models that express tortuosity with porosity, ϕ. The three empirical models are discussed in Boudreau's study; Archie's Law, Burger-Frieke equation and a modified Weisseberg equation. According to the study, Weisseberg equation has the best fit with the observed values,

$$\theta^2 = 1 - b \ln \phi \tag{4.7}$$

In order to produce reasonable estimate of tortuosity for fine grained sediments, it is suggested that adjustable constant, b is equal to 2. Thus,

$$\theta^2 = 1 - \ln \phi^2 \tag{4.8}$$

Since porosity, ϕ is assumed to be constant, tortuosity can be taken as constant in this study.

The relation between the diffusion coefficient for oxygen, D_0 and the temperature viscosity ratio, T/μ is given in Fig (4.3) and calculated as (Boudreau, 1997);

$$D_0 = (0.2604 + 0.006383 \times (T/\mu)) \times 10^{-5} \tag{4.9}$$

T is the absolute temperature in pore water, F^{o}, and μ is dynamic viscosity, cp, which is calculated from;

$$\mu = 1.7910 - 0.06144 \times T^{*} + 0.001451 \times T^{*2} \qquad (4.10)$$

where T^{*} is the temperature in C°. The temperature of the pore water is taken as the water temperature at the bottom sea.

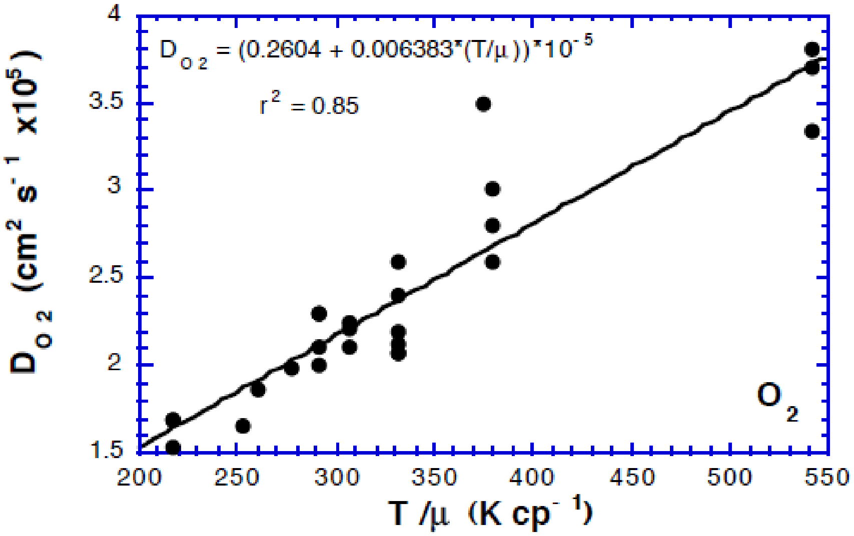

Figure 4.3: Data points of O_2 diffusion coefficient as a function of absolute temperature viscosity ratio (Boudreau, 1997).

4.4.1.2 Burial velocity and bioturbation coefficient

The magnitude of natural burial velocity, w is dependent on water depth. It generally increases close to river entrances and sediment build up regions. According to Boudreau's study (1997) natural burial velocity has tendency to decrease with increasing water depth (Fig (4.4)).

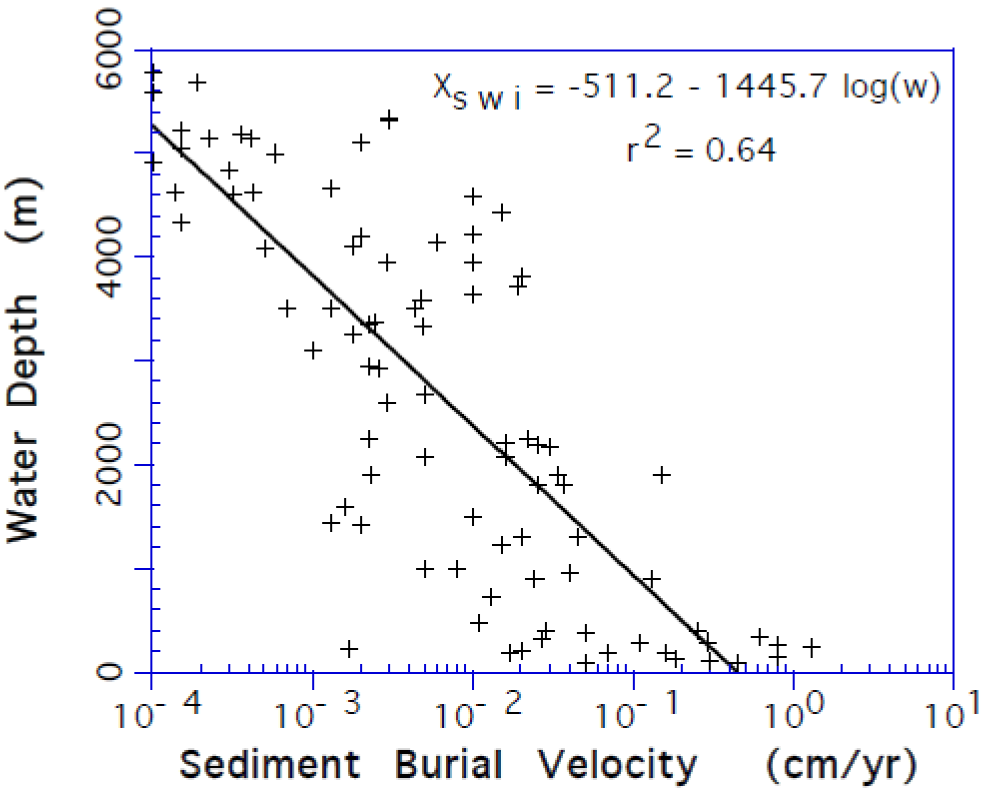

Figure 4.4: The relation between water depth and natural burial velocity (Boudreau, 1997)

In the model the burial rate can be defined by user but it has default definition as; (Trannum, Brakstad, & Neff, 2006)

$$\begin{cases} w = 3.5/H & H > 35\, m\, depth \\ w = 0.1\, cm/year & H < 35\, m\, depth \end{cases} \tag{4.11}$$

where w is the burial velocity in cm/year and H is the water depth. If it is not defined by user these conditions can be used for calculations.

The bioturbation (biodiffusion) coefficient, D_B can be calculated from the following sediment depth dependent function (Boudreau, 1997);

$$D_B(z) = \begin{cases} 3D_{Bave}(1 - \frac{z}{L})^2, & 0 \le z \le L \\ 0, & z > L \end{cases} \tag{4.12}$$

where D_{Bave} is the average bioturbation rate and L is the mixing depth that contains the living organisms and has a mean of 9.8 ± 4.5 cm which is accepted worldwide (Boudreau, 1998) (Fig (4.5)).

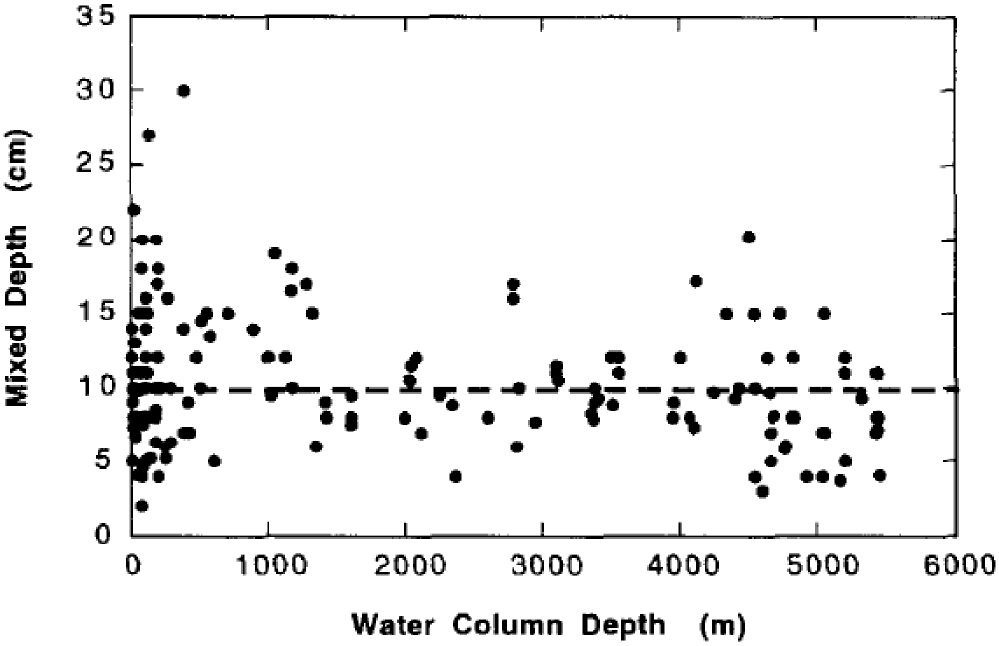

Figure 4.5: Plot of the tracer identified mixed layer thickness L of marine sediments as a function of overlying water column depth (Boudreau, 1998).

According to Boudreau's study (1997) on the relation between average bioturbation coefficient and burial rate, w is plotted with different tracers. (Fig (4.6)). From a large variety of different oceanic conditions the following equation is based on the best line of the graph,

$$D_{Bave} = 15.7w^{0.6} \qquad (4.13)$$

As the formula reveals, the bioturbation coefficient decreases with increasing burial rate. The bioturbation coefficient is in cm^2/year and burial rate is in cm/year.

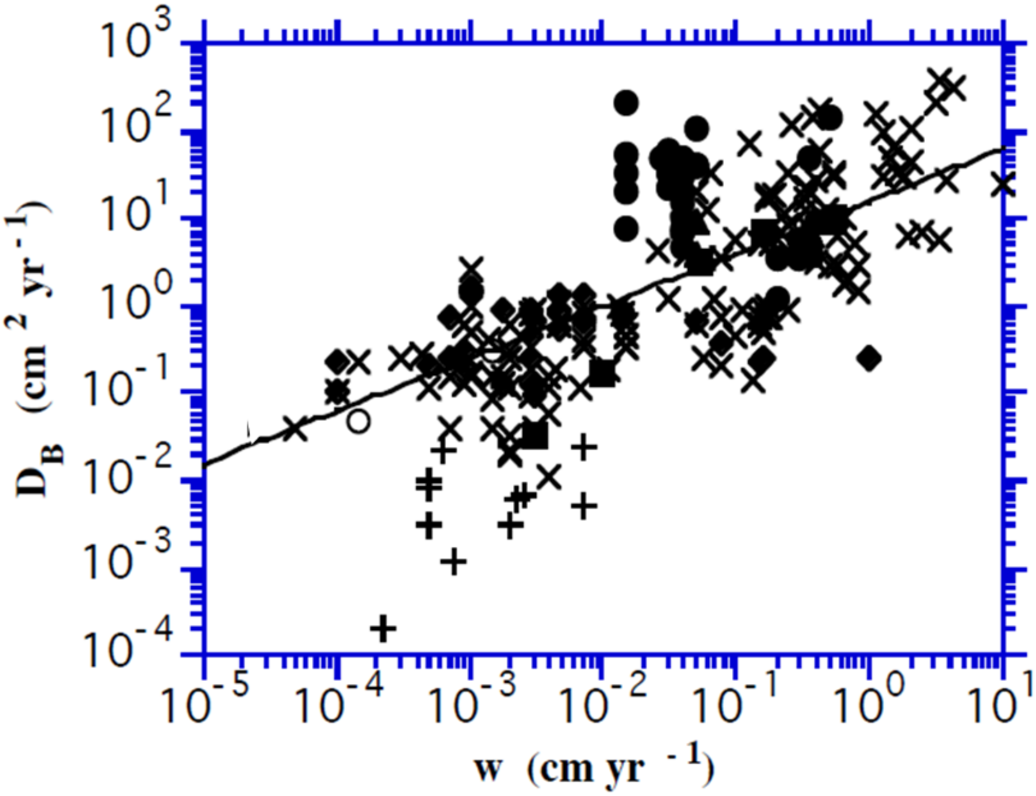

Figure 4.6: Relation between bioturbation coefficient D_B and burial rate w. Different symbols identify used tracer: ♦ 137Cs and 239,240Pu, Õ for 32Si, ● for 234Th and 228Th, X for 210Pb, + for tektites and ash,▲ for 7Be, and ■ for miscellaneous tracers and techniques. (Boudreau, 1997)

In the model the bioturbation coefficient can be taken as constant also. The choice is left to the user.

4.4.1.3 Redfield number, biodegradation rate of natural organic matter and Monod-type saturation constant

The Redfield number, γ_1 reflects the reaction between 32 grams of oxygen and 12 grams of carbon that compose carbon dioxide. It can be calculated from the oxygen to carbon reaction ratio and the ratio of g/mol O_2 and g/mol C product: $(138/106 * 32/12) = 3.47$

According to Boudreau (1997), the biodegradation rate depends on burial rate as in Figure 4.7 and it comprises two different contributions that are a reactive fraction decaying within top 10-20 cm of the sediment and characterizing organic matter biodegradation on a short time scale and a refractory component that oxidizes on a much longer time scale.

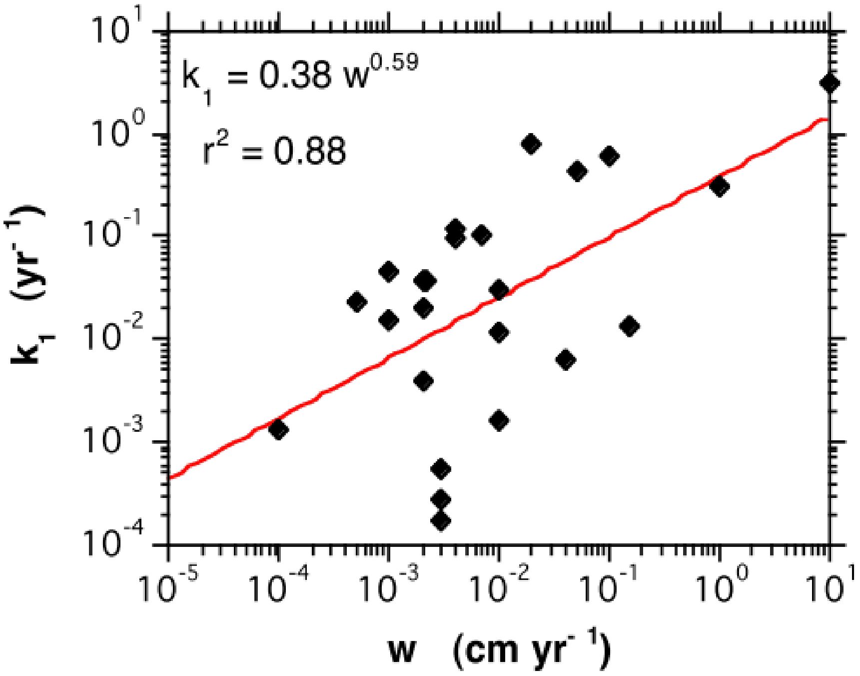

Figure 4.7: A plot of rate constant k_1 for organic matter against corresponding values of the burial velocities of the sediment, w. (Boudreau, 1997)

The relation between biodegradation rate, k_1 (per year) and burial velocity, w (cm per year) can be written as: (Boudreau, 1997)

$$k_1 = 3.0w^{0.6} + 0.4w^{0.6} \tag{4.14}$$

This equation stands for the best line of the graph of the data collected from oceanic conditions by Boudreau (1997).

In Eqs (4.5) and (4.6) the second group on the right-hand side of equations (i.e. the reaction terms) describe a specific type of biodegradation process which is derived from "Monod-type kinetics". The Monod-type reaction kinetics express that the maximum degradation rate attained when the dissolved oxygen concentration (defined per unit pore water volume) is sufficiently larger than a constant K called as the half saturation constant. Field measurements reported in the literature indicate that its value is small. Moreover in order to avoid unrealistic oxygen content values in the model which fail the simulations, small values are suggested (Rye et al. 2006). Therefore it is taken as 0.1 mg/L.

For added organic matter equation, although the form of the equation is the same as the natural carbon one, the Redfield number and biodegradation rate constants can be different.

4.4.2 Initial and Boundary Conditions

In order to numerically solve the equations of the system (Eqs (4.4), (4.5) and (4.6)), both initial and boundary conditions have to be defined. For initial conditions (t = 0) the $\delta/\delta t$ terms are set to zero in the equations. This bring about the stationary solution for O_2 and C which are obtained by a iterative method. The stationary solution is the representation of the oxygen and natural carbon before the discharge.

To establish the boundary conditions the sea floor (z = 0) and the bottom of the sediment layer (provided as input parameter to the model) is used. For the oxygen equation the upper boundary condition (sea floor) is taken as 9 mg/L and at lower boundary Neumann boundary condition with zero gradient (i.e. zero net flux across the boundary) is applied.

For natural carbon equation flux type boundary conditions is used which is the Mixed boundary conditions namely, Robin boundary conditions (Boudreau, 1997). This condition is used to express a flux of addition of organic matter to top of the sediment. The boundary condition is represented as flux of natural carbon and its advection and bioturbation effect:

$$Flux = wC_0 = -\left(D_B \frac{\partial C}{\partial z} - wC\right) \text{ at } z = 0 \qquad (4.15)$$

C_0 term is the natural carbon concentration above the sediment surface which is the required amount of biodegradable organic matter to balance the free oxygen concentration in the pore water of the sediment layer and it is different from the concentration at sediment surface (at z=0) that is the concentration at the first layer of the sediment. The lower boundary condition (at bottom of sediment layer) for natural carbon is the Neumann boundary condition with zero gradient. Since this boundary conditions requires to have zero gradient at the boundary, the organic matter is advected down with the burial velocity below the maximum sediment depth (L).

After the discharge, the boundary conditions for oxygen are the same as what they are before the discharge; at the sediment surface, the oxygen concentration is the same as the concentration in the sea water (9 mg/L) and at the maximum sediment depth it is the Neumann boundary condition. Also the boundary conditions for the natural carbon concentration remain the same. For the added organic matter, since there is instant discharge only at t=0, and it is assumed that no more discharge takes place later, no flow boundary condition is applied at the sediment surface and the Neumann boundary condition with zero flux gradient at the maximum sediment depth will be applied.

CHAPTER 5

MATHEMATICAL METHODS

5.1 Analytical Methods

Numerous analytical solutions to one dimensional advection-diffusion-reaction problem can be found in the literature. A summary of the methods used in publications is presented in the study of Genuchten and Alves (1982). The general partial differential equation is stated and by assigning boundary conditions and determining the type of reaction, the analytical solutions of corresponding equation are listed. The equations are characterized in three different forms: i) equation with no production and decay, ii) with zero order production only and iii) with zero order production and first order decay simultaneously. The upper and lower boundary conditions are classified into two category; concentration-type (first type) and flux type (third type).

The most appropriate equation and boundary conditions for the chemical concentration without reaction is chosen as:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - w\frac{\partial C}{\partial z} - k \tag{5.1}$$

$$C(z,0) = \begin{cases} C_1 & 0 < z < z_1 \\ 0 & z > z_1 \end{cases} \tag{5.2}$$

$$\left(-D\frac{\partial C}{\partial z} + wC\right)_{x=0} = \begin{cases} wC_0 & 0 < t < t_0 \\ 0 & t > t_0 \end{cases} \tag{5.3}$$

$$\frac{\partial C}{\partial z}(\infty, t) = 0$$

where R is the retardation factor that is taken as 1 in calculations, z_1 is the thickness of added sediment depth, C_0 is the concentration in the sediment surface before discharge, C_1 is added chemical concentration and t_0 is the discharge time which is a very short time scale. The analytical solution is given as (Genuchten & Alves, 1982);

$$C(z,t) = \begin{cases} C_1 A(z,t) + (C_0 - C_1)B(z,t) & 0 < t < t_0 \\ C_1 A(z,t) + (C_0 - C_1)B(z,t) - C_0 B(z, t - t_0) & t > t_0 \end{cases} \tag{5.4}$$

where,

$$\begin{aligned} A(z,t) &= \frac{1}{2} erfc\left[\frac{R(z - z_1) - wt}{2(DRt)^{1/2}}\right] \\ &+ \left(\frac{w^2 t}{\pi DR}\right)^{1/2} exp\left[\frac{wx}{D} - \frac{R}{4Dt}\left(z + z_1 + \frac{wt}{R}\right)^2\right] \\ &- \frac{1}{2}\left[1 + \frac{v(z + z_1)}{D}\right. \\ &\left. + \frac{w^2 t}{DR}\right] \exp\left(\frac{vz}{D}\right) erfc\left[\frac{R(z + z_1) + wt}{2(DRt)^{1/2}}\right] \end{aligned} \tag{5.5}$$

$$\begin{aligned} B(z,t) &= \frac{1}{2} erfc\left[\frac{Rz - wt}{2(DRt)^{1/2}}\right] + \left(\frac{w^2 t}{\pi DR}\right)^{1/2} exp\left[-\frac{(Rz - vt)^2}{4DRt}\right] \\ &- \frac{1}{2}\left[1 + \frac{vz}{D} + \frac{w^2 t}{DR}\right] \exp\left(\frac{vz}{D}\right) erfc\left[\frac{Rz + wt}{2(DRt)^{1/2}}\right] \end{aligned}$$

The ADR equation is solved by the method proposed in the study of Freijer et.al. (1998). In this study, velocity and diffusion coefficient are kept constant and only vertical direction advection and diffusion processes are assumed and the solution is evaluated by Laplace transform and separation of variables. The following dimensionless variables are defined where l is the added layer thickness;

$$\zeta = \frac{wz}{D}$$
$$\tau = \frac{w^2 t}{RD_B} \tag{5.6}$$
$$\epsilon = k_1 RD_B / w^2$$
$$\lambda = lw/D_B$$

and the solution is stated as;

$$C(\zeta,\ \tau\ ) = \frac{1}{2} C_0 \exp(-\epsilon\tau)\{P + \exp(\zeta + \lambda)\, Q\} \tag{5.7}$$

with;

$$P = erfc\left[\frac{\zeta - \tau}{2\sqrt{\tau}}\right] - erfc\left[\frac{\zeta + \lambda - \tau}{2\sqrt{\tau}}\right] \tag{5.8}$$

$$\begin{aligned} Q = (1 + \tau + \zeta + 2\lambda) erfc\left[\frac{\tau + \zeta + \lambda}{2\sqrt{\tau}}\right] - \frac{2\sqrt{\tau}}{\sqrt{\pi}} exp\left[\frac{-(\tau + \zeta + \lambda)^2}{4\tau}\right] \\ - (1 + \tau + \zeta + 2\lambda) erfc\left[\frac{\tau + \zeta + \lambda}{2\sqrt{\tau}}\right] \\ + \frac{2\sqrt{\tau}}{\sqrt{\pi}} exp\left[\frac{-(\tau + \zeta + 2\lambda)^2}{4\tau}\right] \end{aligned} \tag{5.9}$$

C_0 value is the added sediment concentration (mass/volume) and calculated as;

$$C_0 = \frac{Ch_{add}}{l(1 - \phi)} \tag{5.10}$$

Ch_{add} is the total mass of added chemicals (mass/area) and porosity is used for correction.

5.2 Finite Difference Method

As in the study of Rye et al. (2006), a numerical method that applies an implicit central difference discretization method is used to solve the diagenetic equations, because without specifying some assumptions, the system equations cannot be solved analytically.

In this method to discretize the system, the problem domain, $x = [0, L]$ is divided into N elements. The approximation for dissolved oxygen equation is;

$$\frac{O_i^{k+1} - O_i^k}{\Delta t} = \frac{D_o}{\theta^2} \frac{O_{i+1}^{k+1} - 2O_i^{k+1} - O_{i-1}^{k+1}}{(\Delta z)^2} - \frac{1-\phi}{\phi} [\gamma_C k_C C_i^{k+1} + \gamma_E k_C E_i^{k+1}] \frac{O_i^{k+1}}{K_O + O_i^{k+1}} \tag{5.11}$$

for biodegradable natural organic matter equation;

$$\frac{C_i^{k+1} - C_i^k}{\Delta t} = D_{B\,i} \frac{C_{i+1}^{k+1} - 2C_i^{k+1} - C_{i-1}^{k+1}}{(\Delta z)^2} + \left(\left. \frac{dD_B(z)}{dz} \right|_{z_i} - w \right) \left(\frac{C_{i+1}^{k+1} - C_{i-1}^{k+1}}{2\Delta z} \right) - [k_C C_i^{k+1}] \frac{O_i^{k+1*}}{K_O + O_i^{k+1*}} \tag{5.12}$$

for biodegradable added organic compound equation;

$$\frac{E_i^{k+1} - E_i^k}{\Delta t} = D_{B\,i} \frac{E_{i+1}^{k+1} - 2E_i^{k+1} - E_{i-1}^{k+1}}{(\Delta z)^2} + \left(\left. \frac{dD_B(z)}{dz} \right|_{z_i} - w \right) \left(\frac{E_{i+1}^{k+1} - E_{i-1}^{k+1}}{2\Delta z} \right) - [k_C C_i^{k+1}] \frac{O_i^{k+1*}}{K_O + O_i^{k+1*}} \tag{5.13}$$

where the subscript i shows the variable in z dimension and the superscript k specifies the time domain, thus $k + 1$ indicates the next time step where k is current time step.

In these equations there are three unknowns for each equation; O_i^{k+1}, O_{i+1}^{k+1}, O_{i-1}^{k+1}; C_i^{k+1}, C_{i+1}^{k+1},C_{i-1}^{k+1}; E_i^{k+1},E_{i+1}^{k+1},E_{i-1}^{k+1}. For each layer the equation of these variables are solved algebraically and in order to solve these unknowns the equations are written in a tridiagonal matrix form which has nonzero values only at its diagonals. Gaussian elimination is used to solve matrices.

The equations are solved with an iterative algorithm which calculates new time step by starting with previous time step calculations then substituting the previous iterations while checking the convergence of state variables. Since oxygen profile depends on natural carbon and added chemical concentrations, there is an order to solve the equations. First, Eqns 5.12 and 5.13 are solved, the oxygen profile from Equation 5.11 is calculated with the values from these equations. The subscript in equations indicates the values are obtained from previous iteration.

5.3 Particle Tracking Method

In this study, oxygen, natural carbon and added chemical concentrations are evaluated by particle tracking. The main aim of this study is to overcome numerical diffusion in finite difference method for convection diffusion equation without limiting spatial discretization. The reason of this behavior is the double nature of transport equation where diffusion part is a parabolic easy to solve equation, while advection part is a hyperbolic equation and the parameter that defines the false diffusion is Peclet number, Pe and calculated as (Kenzelbach, 1990);

$$Pe = \frac{w\Delta z}{D} \tag{5.14}$$

when Peclet number is higher, the equation becomes more hyperbolic and when it is lower the equation becomes more parabolic (Zimmermann, 2004). In order to avoid numerical oscillations, the Peclet number should be smaller.

The method of particle tracking solves a partial differential equation with updating the positions of particles in a stochastic manner (Cranmer, 2003). Since diffusion is a stochastic process in which particles is transported one place to another by random molecular motions it can be expressed as Monte Carlo based simulations. The motions of each molecule can be defined by the ‘random walk’ model by which the distance traveled by a molecule in a given time interval Δt, can be calculated (Crank, 1975).

5.3.1 Random Walk Method

The random walk method is used to analyze diffusion and dispersion processes through pore media in many studies. In the study of Cranmer (2003), the generalization of the Monte Carlo solution to diffusion problems is given by the help of Ito calculus. The one dimensional partial differential diffusion equation can be solved analytically by Fourier transform:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{5.15}$$

The analytic solution of this diffusion equation will be (Cranmer, 2003) :

$$C(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left[-\frac{(x)^2}{4Dt}\right] \tag{5.16}$$

The solution in Equation 5.15 is at the same form with a probability density function:

$$f_X(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \tag{5.17}$$

The equation is a normal (Gaussian) distribution probability density function with standard deviation of $\sigma = \sqrt{2Dt}$ and zero mean, $\mu = 0$. The distribution of the function is a bell shaped as in Fig (5.1). For any time, 68% of the total particles will fall within ±σ of the mean position, 95% will fall within ±2σ and 99.7% will fall ±3σ of the mean position.

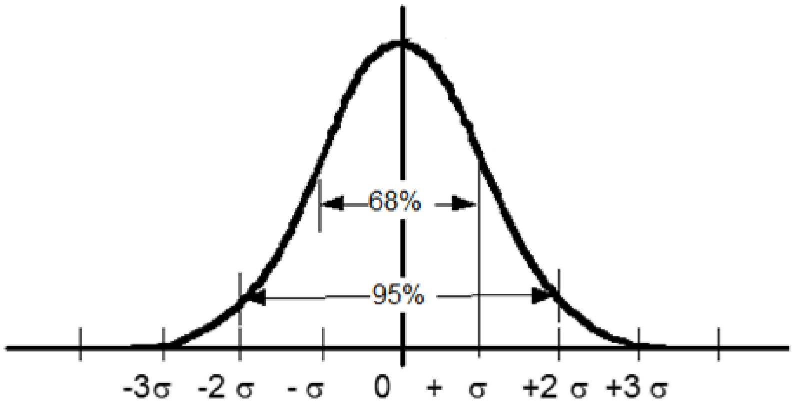

Figure 5.1: Normal distribution probability density function

Over time each particle moves forward and backward. Thus, updated position of a particle can be evaluated in the same manner. By setting N number of particles, the distance traveled by each particle, Δx, can be found from (Cranmer, 2003):

$$\Delta x = \mathcal{N}(\xi)\sqrt{2D\Delta t} \tag{5.18}$$

where $\mathcal{N}(\xi)$ is a normally distributed random number with zero mean and unit variance (i.e. Gaussian distribution):

$$\mathcal{N}(\ \xi\ ) = \frac{1}{\sqrt{2\pi}} e^{-\xi^2/2} \tag{5.19}$$

When the advection term is added to Eqn 5.18 the change position is calculated from:

$$\Delta x = w\Delta t + \mathcal{N}(\xi)\sqrt{2D\Delta t} \tag{5.20}$$

This equation is resulted from Ito calculus and for small time steps, Δt, the equation is valid for depth and time dependent diffusion coefficient and velocity which is the general form of Fokker Planck equation (Cranmer, 2003):

$$\frac{\partial C}{\partial x} = -\frac{\partial}{\partial x}[w(x,t)C(c,t)] + \frac{\partial}{\partial x}\left[D(x,t)\frac{\partial C}{\partial x}\right] \tag{5.21}$$

5.3.2 Initialization of Particle Model

The initial position of the chemical particles is set by multiplying the added sediment thickness with a random number from the normal distribution and the initial concentration of each particle is set to the added sediment concentration times the thickness divided by the total number particles. The initial concentration on every level can be calculated from the total of particle concentration at that level depth.

The diffusion parameter in the Eqn 2.31 for oxygen calculation is expressed as $\sqrt{2\frac{D_o}{\theta^2}dt}$ and the position of each oxygen particle and corresponding layer locations are calculated with the multiplication of random number and diffusion term in total significant depth.

Similarly, the initial position of natural carbon particles is estimated with the total depth of carbon and random number.

In order to calculate the initial concentrations of oxygen and natural carbon, the results from the finite difference method are used and the area under the graphs are evaluated from the trapezoidal rule for each layer. For the first layer, the concentration of oxygen particles are calculated as the ratio of the oxygen concentration at subsea (9 mg/L) and total number of particles. Concentration of each oxygen and carbon particles is assigned from the division of the calculated values from finite difference and depth of the sediment.

5.3.3 Modeling Accumulation of Particles

The main advantage of particle model when comparing with finite difference model, the bioturbation coefficient in equations can be taken as depth dependent variable. The relationship between depth and diffusion coefficient is constructed with Equation 5.12. Calculated bioturbation coefficient before that level of sediment depth is used in Eqn 5.29 to evaluate location of chemical and natural carbon particles and as for the velocity term burial is used. Concentration on each layer is the total concentration of particles at that level. The differences for the calculation of location of oxygen particles are the absence of the advection term because diffusion is dominant compare to advection process for oxygen and the diffusion coefficient explained in Equation 5.9 is used.

The reaction term is calculated from the solution of ordinary differential equation below:

$$\frac{\partial C(t)}{\partial t} = -RC(t) \tag{5.22}$$

where R is the degradation rate and the analytical solution is available for an incremental time step of Δt:

$$\Delta C = -\exp(R\Delta t)\, C_0 \tag{5.23}$$

The rate can be written for oxygen, natural carbon and added chemical concentration R term will be equal to with biodegradation constants, respectively:

$$R_{oxyg} = [\gamma_1 k_1 C + \gamma_2 k_2 E] \frac{O_2}{K_{O_2} + O_2} \,, \qquad R_{carb} = \frac{k_1 O_2}{\left(K_{O_2} + O_2\right)} \,, \tag{5.24}$$

$$R_{chem} = \frac{k_2 O_2}{\left(K_{O_2} + O_2\right)}$$

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Overall Model Behavior

The mathematical models of the system equations are constructed in MATLAB computing environment. The concentration profiles of added chemical, natural carbon and oxygen are calculated after instant discharge of cuttings to the marine sediment. One dimensional vertical direction model of concentration profiles of stressors is constructed by using finite difference (**red**), analytic (**black**) and particle (**green**) methods for every layer and the solution of each method is graphed. The main model is divided into two subcategories as Model 1 and Model 2. In Model 1, only added chemical concentration is calculated by solving the general transport equation (Eqn 2.34) using three mathematical methods with constant bioturbation coefficient and first order decay. On the other hand, oxygen, natural carbon and added chemical concentrations are studied in Model 2 with depth dependent bioturbation coefficient by using finite difference and particle methods for diagenetic equations given in Eqns (2.31), (2.32) and (2.33).

6.1.1 Assumptions in the model

In order to construct the model some assumptions have been made, which are listed below:

- One dimensional vertical deposition,
- Instant discharge only at $t = 0$,

- Constant burial velocity
- Constant porosity
- Constant grid size
- Closed upper boundary for added chemical and natural carbon,
- Open upper boundary (with buffer zone) for oxygen profile to compensate the concentration
- Open lower boundaries for all profiles. However, for lower boundaries in oxygen and natural carbon profiles, particles that exits the system are added from the top of the domain without mass in order to have constant particle numbers for both of the profiles.

6.1.2 Model inputs

The parameters set in the main model are listed in Table (6.1).

Table 6.1: Default model inputs

Input	**Value**
porosity, ϕ	0.60
layer length, dz	0.1 cm
time step, dt	1.0 hour
depth of sediment to simulate, Ls	100 cm
number of layers, n_L	100
number of added layers, n_{Ladd}	10
number of chemical particles, nP	2000
number oxygen particles, $nPox$	6000
number natural carbon particles, $nPcar$	6000
average bioturbation coefficient, D_B	0.01 cm^2/hours
burial velocity, w	0.05 cm/year
temperature at sea level, T	7°C
Monod-type saturation constant, K_{O_2}	0.1

Redfield number, γ	3.1417
biodegradation rate of natural organic matter, k_1	0.1 per year
biodegradation rate of added chemical, k_2	0.03 per day
total mass of added chemicals	2 gr/m^2
Natural carbon content at sea floor	0.3 % w/dry-w

6.1.3 Model Case 1: Solution of General Transport Equation

The concentration profile of added chemical after disposal is modeled in this case with explained mathematical methods and the stability of the methods are discussed with different parameters. The chemical concentration is initialized by dividing the concentration into added number of layers (n_{Ladd}) as in Fig (6.1).

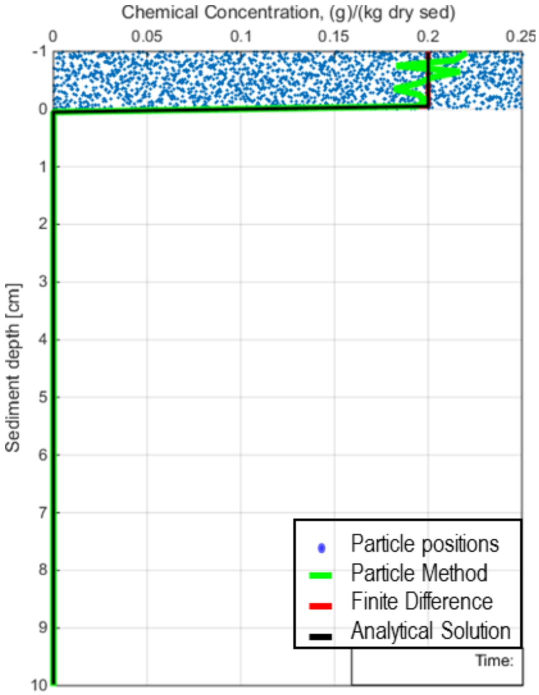

Figure 6.1: Initialization of chemical concentration profile.

In Fig (6.2), the consistency of the methods to calculate chemical concentration and the movement of particles by advection and diffusion with respect to sediment depth can be seen with the default inputs given in Table (6.1) and for different times.

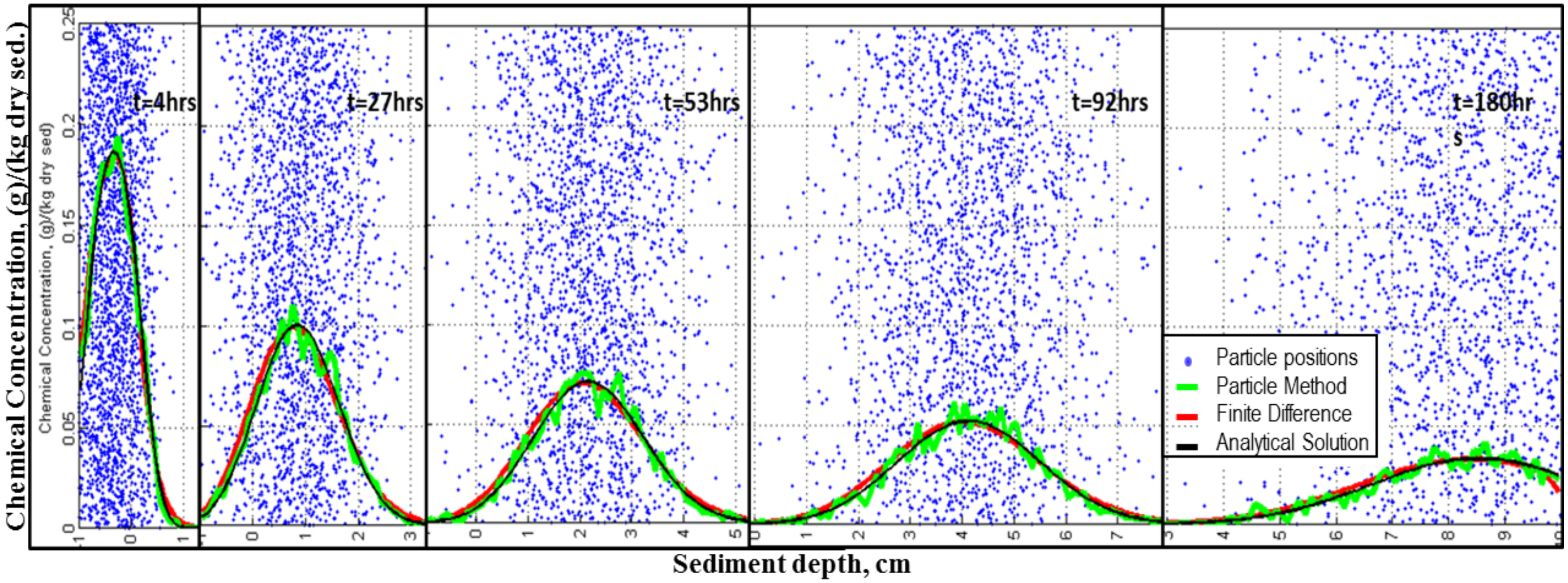

Figure 6.2: Added chemical concentration profile

However, some problems can be faced in numerical modeling of advection diffusion equations. The main problem is numerical diffusion which is seen in advection dominated flows where high Pe numbers ($Pe > 2$) are observed. In the model, parameters are changed to test the stability of the models. In Model 1, by changing the biodiffusion coefficient, D and also Peclet number, the effects are monitored and graphed in Fig (6.3) and (6.4). As in figures, finite difference method diverges significantly from analytical model while diffusion coefficient decreases and thus the problem becomes advection dominated. However, for all conditions the particle model converges to the true model.

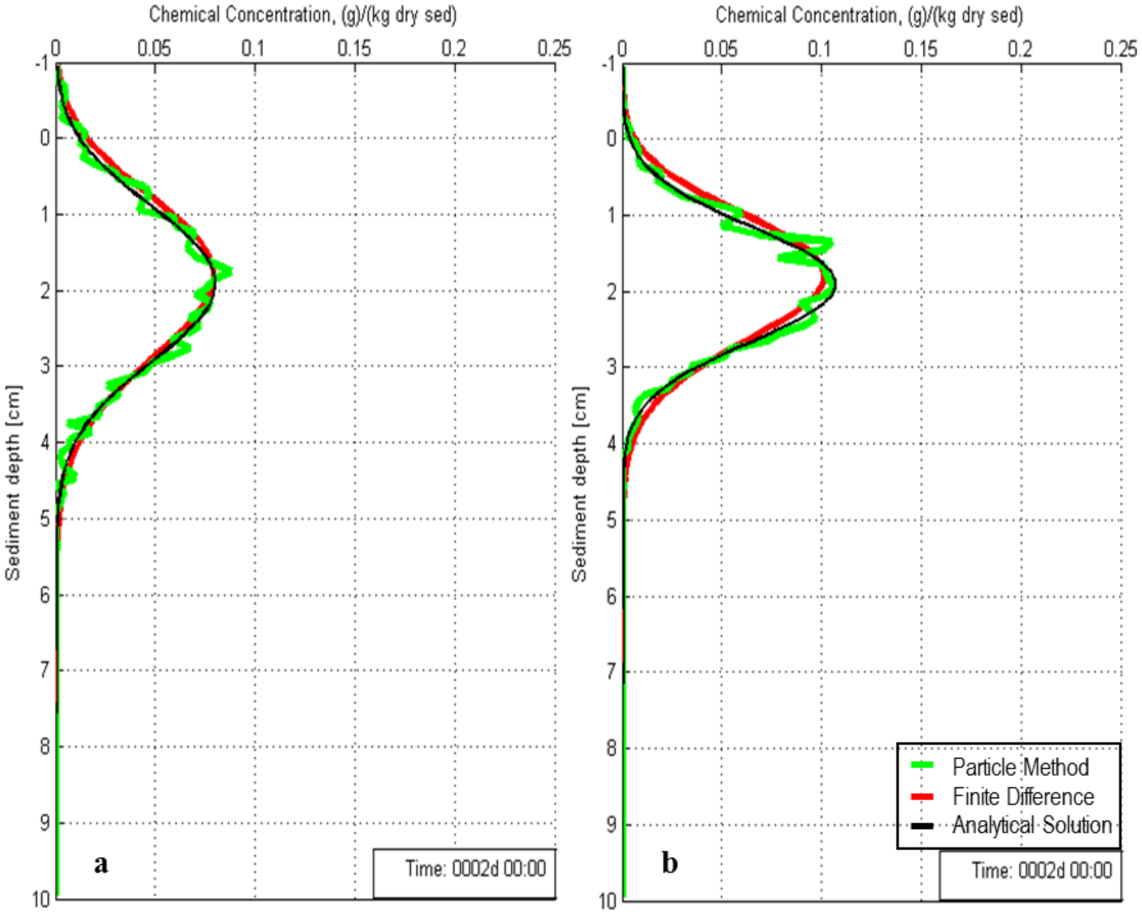

Figure 6.3: Peclet number effect, where (**a**) $D = 0.01$ and $Pe = 0.5$ (**b**) $D = 0.005$, and $Pe = 1.0$

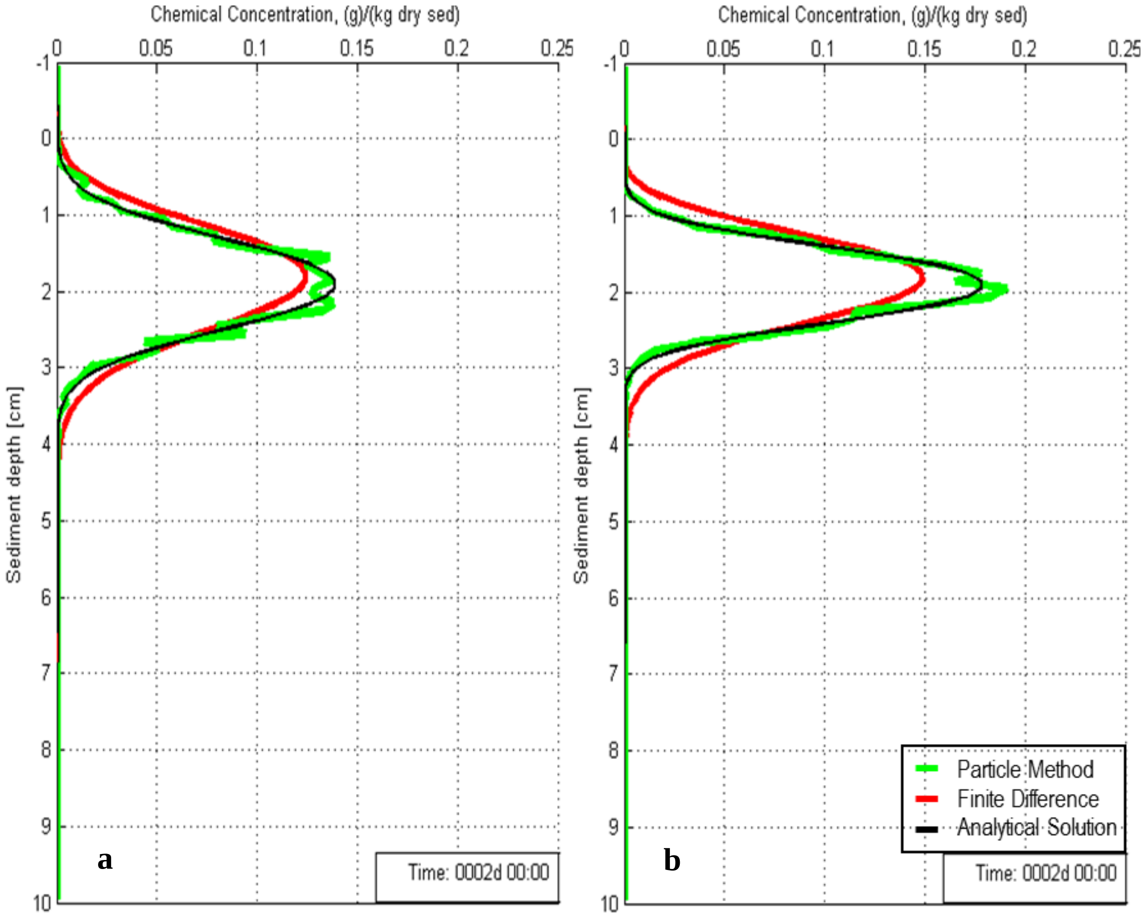

Figure 6.4: Peclet number effect, where (**a**) $D = 0.0025$ and $Pe = 2.0$ (**b**) $D = 0.001$ and $Pe = 5.0$

In addition, fractional error analysis is done to observe the effect of increasing Peclet number. In Fig (6.5), the error between analytical model and finite difference is increasing with increasing Peclet number.

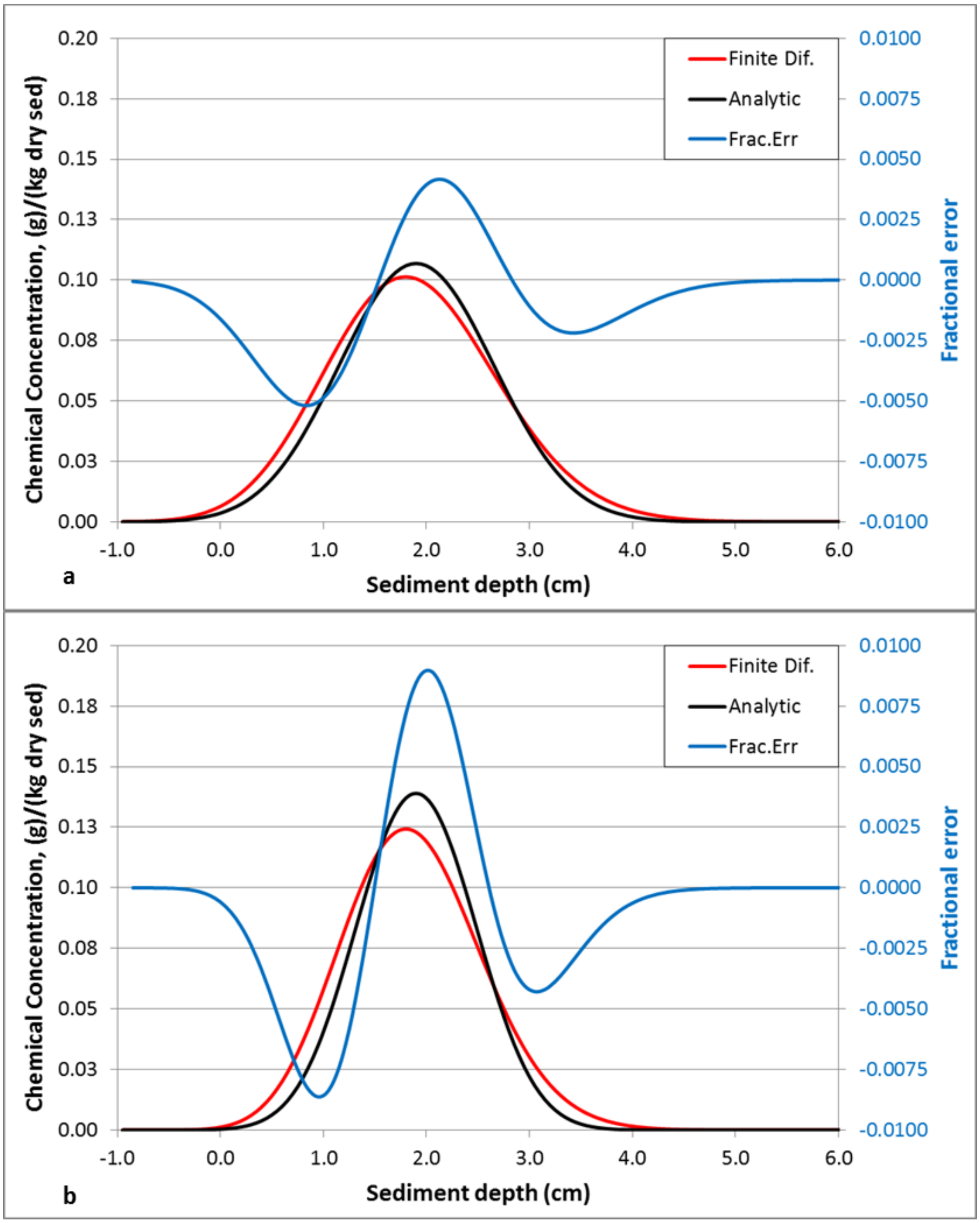

Figure 6.5: Error analysis between finite difference and analytical methods where (**a**) $Pe = 1$, (**b**) $Pe = 2$.

On the other hand, Peclet number is increased by increasing the burial velocity. The numerical diffusion is represented in Fig 6.6.

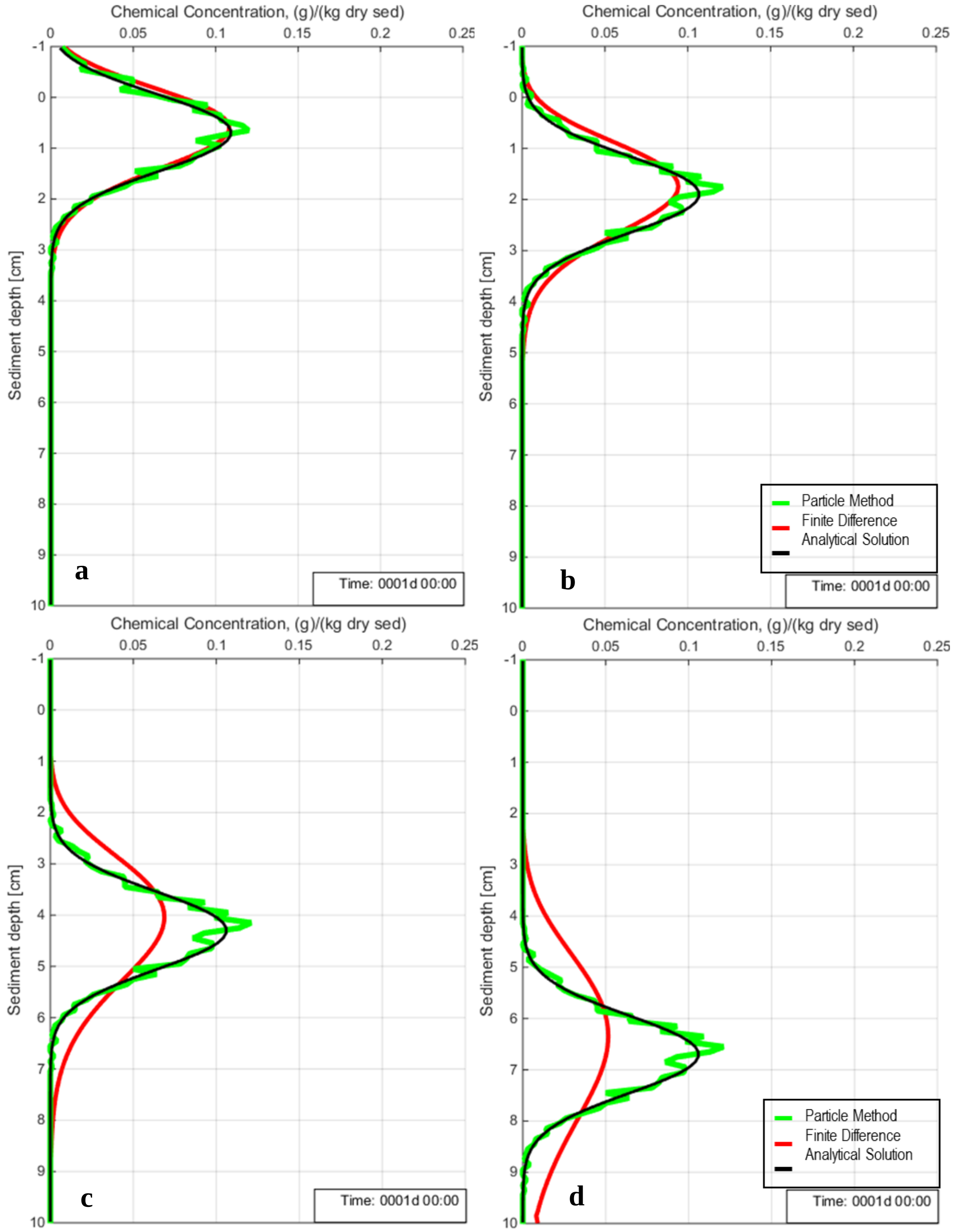

Figure 6.6: Peclet number effect, where (**a**) $w = 0.05$ and $Pe = 0.5$ (**b**) $w = 0.1$ and $Pe = 1.0$ (**c**) $w = 0.2$ and $Pe = 2$ (**d**) $w = 0.3$ and $Pe = 3.0$

Numerical diffusion also occurs when time interval is increased. In Figs (6.7) and (6.8) dt is taken as 1 and 4 hours and the effect of numerical diffusion can be clearly seen on both concentration profile and error analysis graphs for finite difference method, respectively.

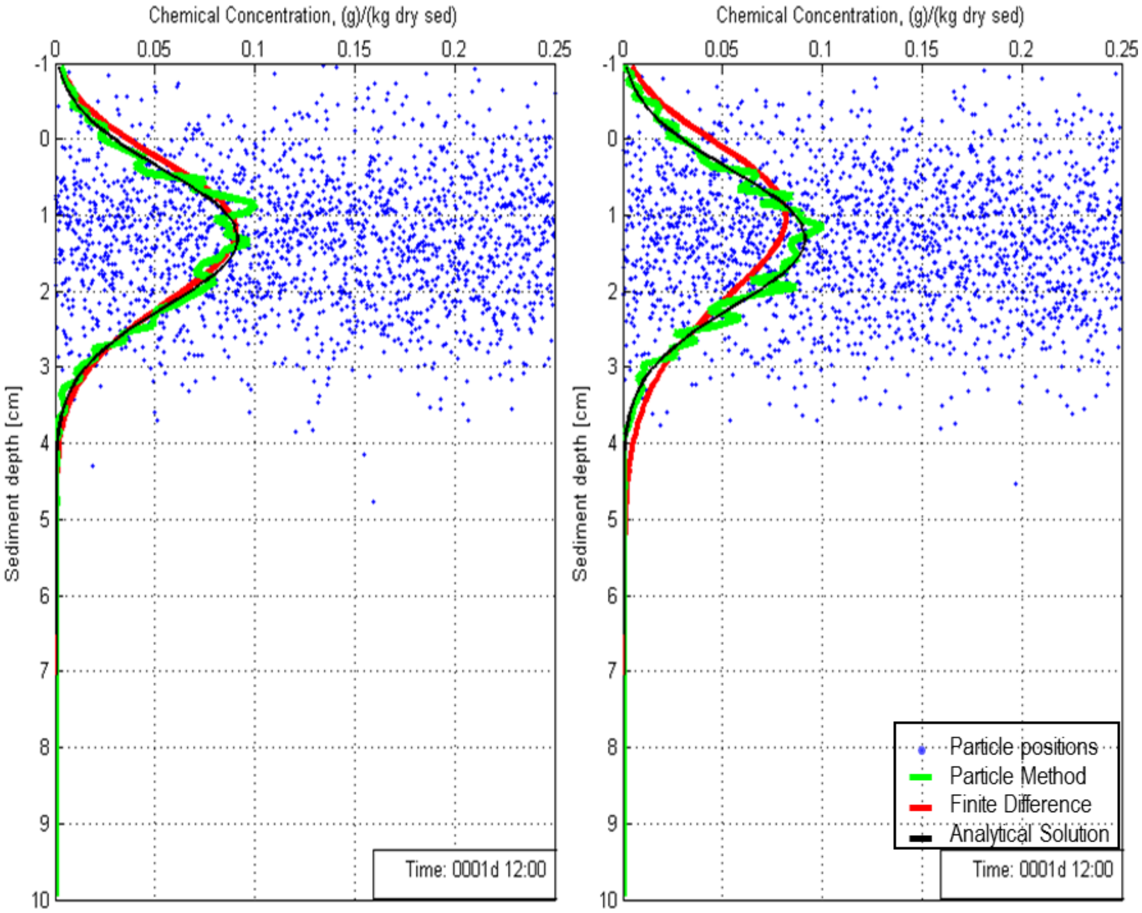

Figure 6.7: Monitoring the effect of time interval change on all methods where $dt = 1.0\ hour$ and $dt = 4.0\ hours$, respectively.

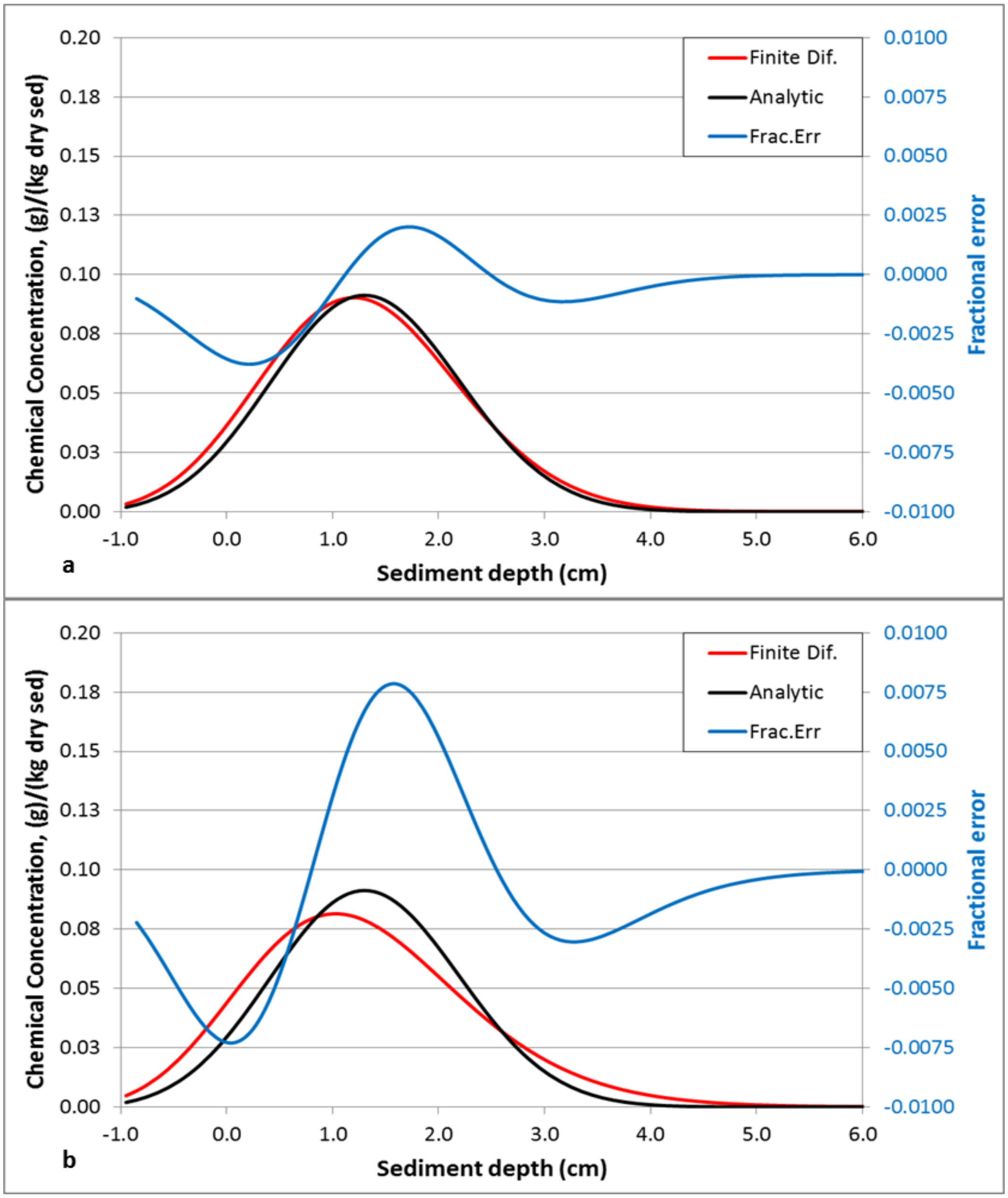

Figure 6.8: Error analysis between finite difference and analytical methods where (**a**) $dt = 1\ day$, (**b**) $dt = 4\ days$.

Moreover, the other problem encountered in the finite difference method is the boundary effect on the front of the concentration profile while it is propagating. The fractional error analysis between analytic and finite difference for added chemical concentration in Model 1 and the effects of boundaries are shown in Fig (6.9). It is indicated that the error increases when solution reaches boundaries of the model because of the nature of numerical solutions.

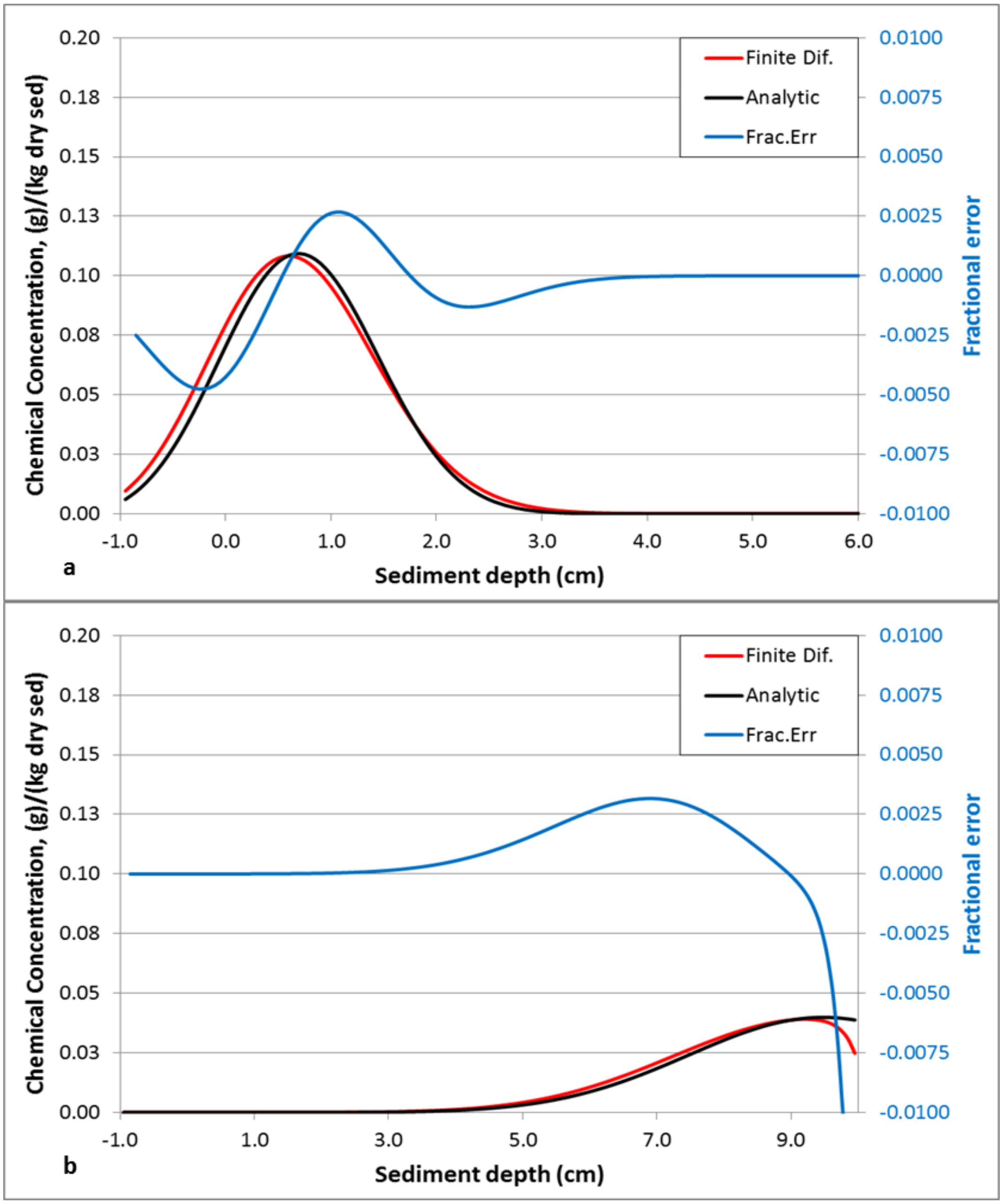

Figure 6.9: Error analysis between finite difference and analytical methods, where (**a**) $t = 1\ day$, (**b**) $t = 8\ days$

The error analysis between particle tracking method and analytic model is done in Fig (6.10) with particle number of 2000 and 20000. It is concluded that the error for both finite difference and particle model behaves similar at first time step for 2000 particles. Although there are oscillations because of random behavior of particles, the boundary effect does not occur in particle model and if the number of particle is increased, less oscillations will be observed.

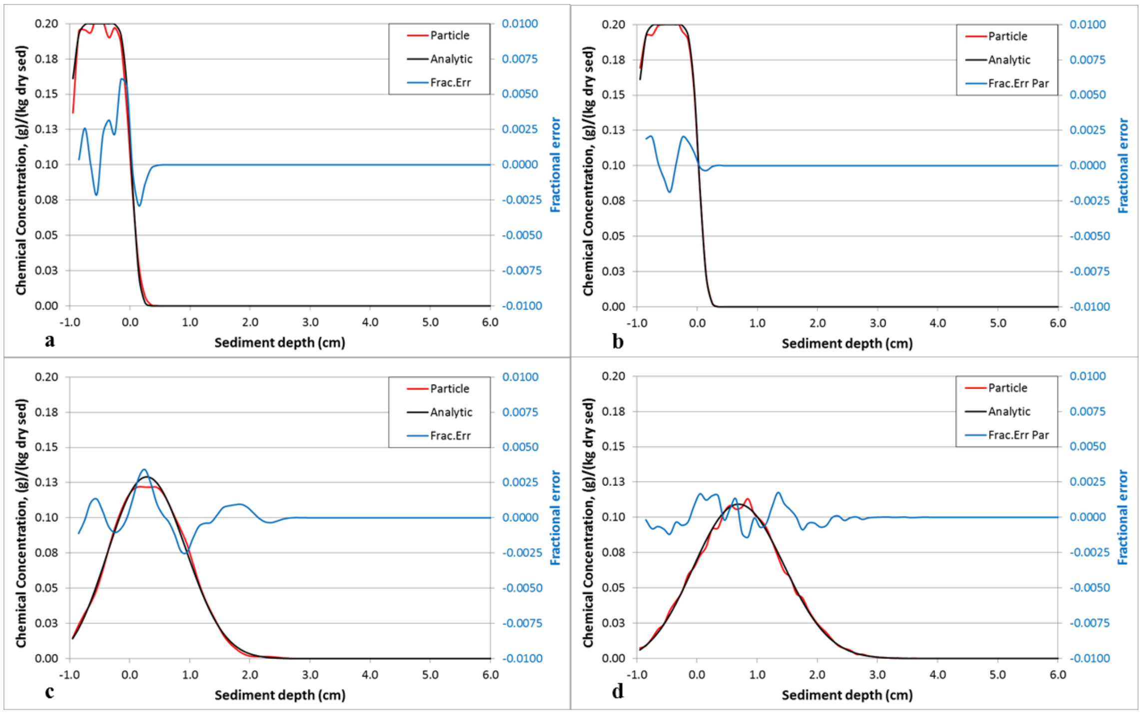

Figure 6.10: Error estimation of particle tracking method for chemical concentration, where $nP = 2000$ (**a**) $t = 30min$ (**b**) $t = 1day$ and $nP = 20000$ (**c**) $t = 30min$ (**d**) $t = 1day$ where $dt = 30min$

6.1.4 Model Case 2: Solution of Diagenetic Equations

In Model 2, the concentrations of oxygen, natural carbon and added chemical are modeled by particle tracking and finite difference methods with depth dependent bioturbation coefficient. Before disposal of cuttings and chemical, the corresponding sediment depth is divided into nL number of layers. After discharge $nLadd$ number of layers is added to the total sediment depth and the chemical concentration is initialized by dividing the concentration into layers. The oxygen concentration at the top of the sediment is set as 9 mg/l and the natural carbon concentration in the added layer is set to zero. The initial profile of both natural carbon and oxygen is calculated with finite difference approach (Fig (6.11)).

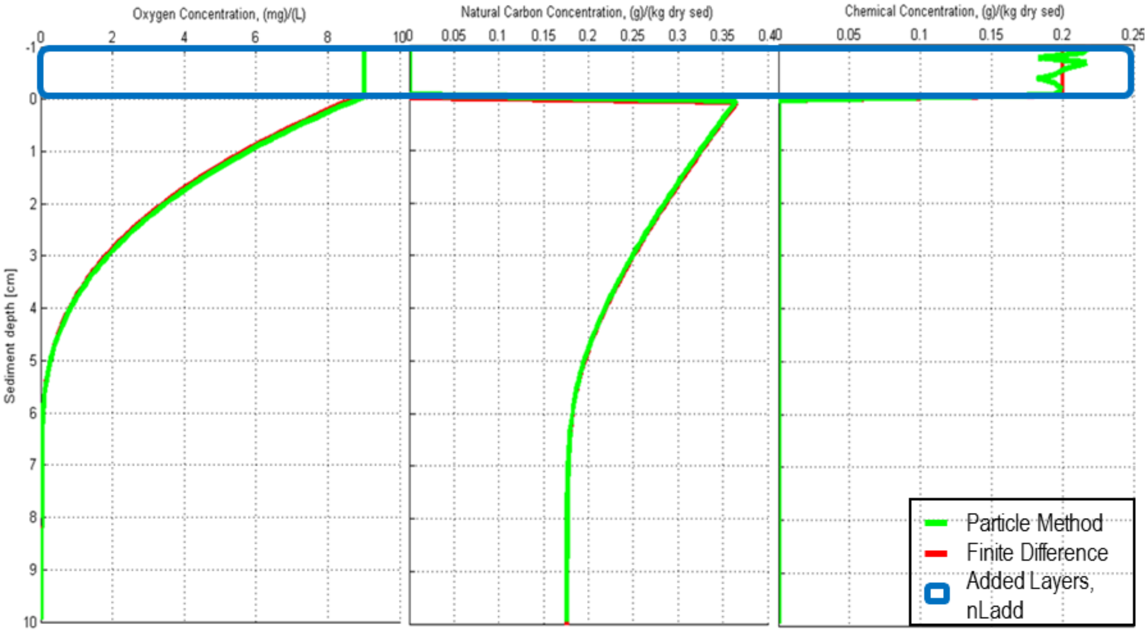

Figure 6.11: Initial profiles of oxygen, natural carbon and chemical.

The concentrations are modelled with the inputs in Table (6.1) for long time period. The depletion and restitution of oxygen and change in natural carbon concentration in sediment layer are graphed in Fig (6.12.a). After disposal, oxygen particles are depleted with biodegradation of chemicals and the depleted oxygen is replaced from the surrounding by diffusion. After 5 days later, nearly all oxygen is consumed due to degradation of chemicals in the deposited layers. The oxygen content returns its original concentration after almost 10 months later. The change in natural carbon concentration is shown in Fig (6.11.b). Unlike the oxygen profile, the recovery process is slower. In fact, after several years the natural carbon concentration profile can return its original pattern.

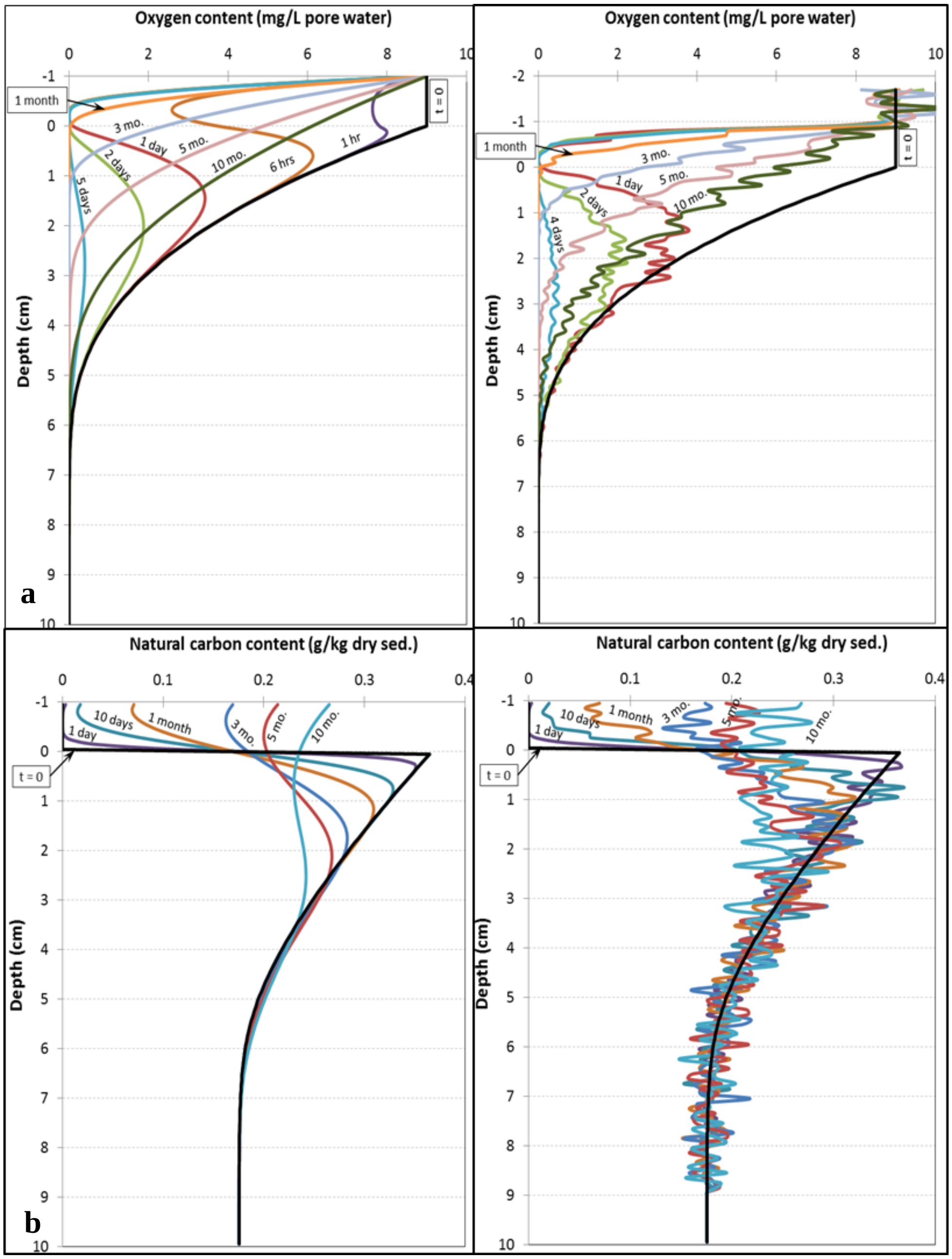

Figure 6.12: Depletion and restitution of oxygen concentration (**a**) and Change in natural carbon concentration (**b**) with time by using finite difference and particle methods.

As indicated in Table (6.1), 2 gr/m^2 of chemicals is deposited on the first layer of the system domain. In Fig (6.12), the concentration profile of added chemicals is represented.

Due to biodegradation and bioturbation, chemical particles are consumed and almost 5 months later all particles are degraded.

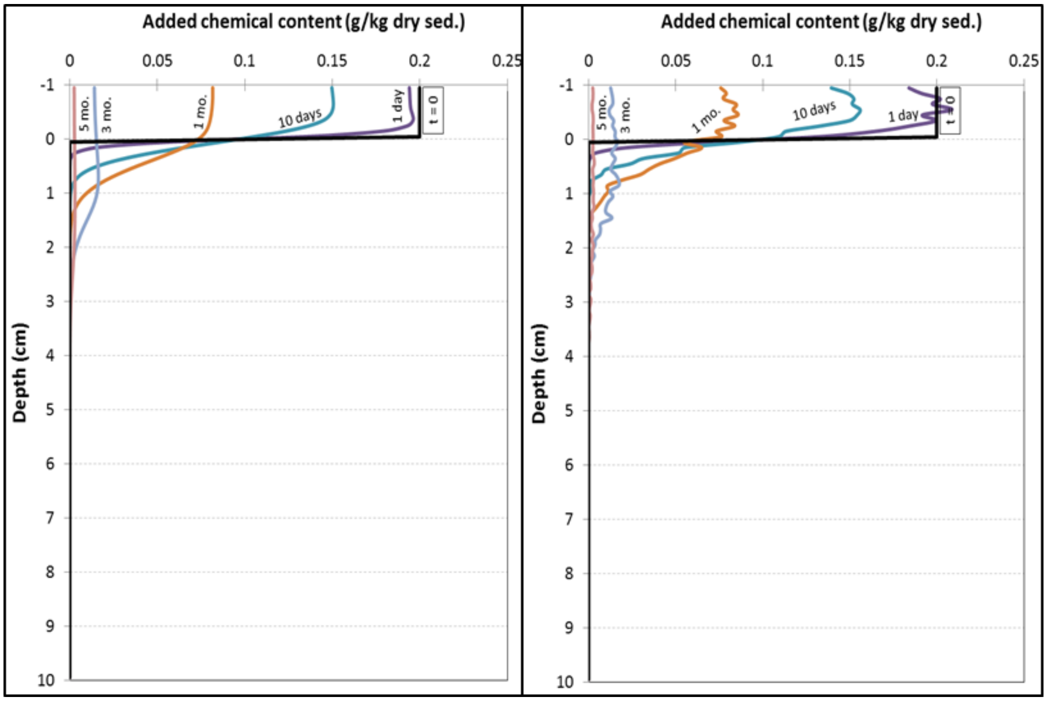

Figure 6.13: Change in added chemical concentration with time by using finite difference and particle methods.

Both mathematical models represent stable and reasonable results. In particle method, a special boundary implementation is used in which particles tend to move out from the system domain because of random motion. The oxygen and natural carbon particles that are out of system, are counted and their concentrations are calculated for each time step. Since, the oxygen equation is diffusion dominated, only the upper part of the system is controlled. On the other hand for the natural carbon equation the lower boundary is also checked for particles leaving the problem domain. Thus, total concentration of natural carbon particles that jump out of the system from top and bottom are added to the top layer in order to maintain the upper flux boundary condition for natural carbon.

The oxygen depletion and recovery, degradation of natural carbon and added chemicals and recovery of natural carbon content are summarized in Fig (6.13). In Fig (6.13) the oxygen profile is calculated with particle methods and total amount of oxygen in system domain and natural carbon and added chemical in the added layers are graphed with respect to time. After deposition of drilling material to sea floor, the amount of oxygen is greater than initial value, because sea water is trapped in the pores of added sediment layer. Also, in Fig (6.10) the increase in the area under the oxygen concentration curve can be seen in the added layer. This extra amount of oxygen is consumed approximately after 10 hours and the minimum oxygen concentration is reached after 4 to 5 days. Due to degradation of chemical material, oxygen amount start to recover after 2 to 3 months. The chemical matter is completely degraded approximately after a year as shown in the figure. The natural carbon content at the added layer is zero after sudden disposal and the recovery is slower than oxygen because the rate of deposited material from top of the sediment is small and bioturbation is a slow process. Therefore, after about a year when chemical content is degraded and oxygen reached to its initial level, natural carbon content is less than the initial amount which cause overshoot in oxygen profile. However, oxygen depletion process continues due to the existence of natural carbon.

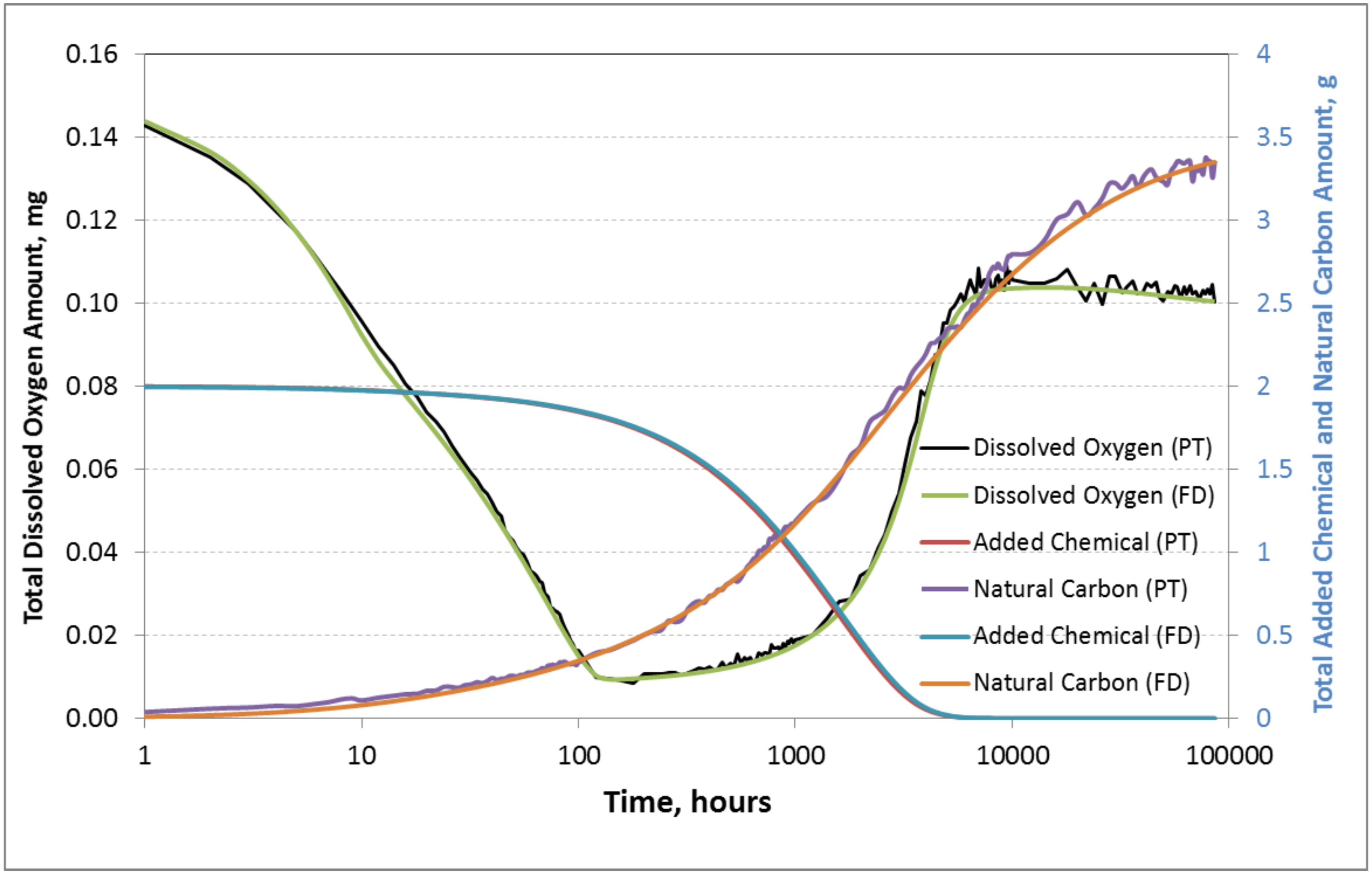

Figure 6.14: The total amount of dissolved oxygen, natural carbon and added chemical.

In particle tracking method, the modeling of reaction could lead some problems. When the time step is increased 4 times (i.e setting dt to 4 hours), there will be divergence between finite difference and particle model. In Fig (6.14), the total dissolved oxygen amount is shown for $dt = 4.0\,hours$. Since, in Equations 3.4-3.6 the oxygen concentration should be calculated implicitly as in finite difference method to model the biodegradation but in particle method it is not possible. Therefore, the reaction is calculated by using the oxygen concentration at previous time step in particle model and this leads to shift.

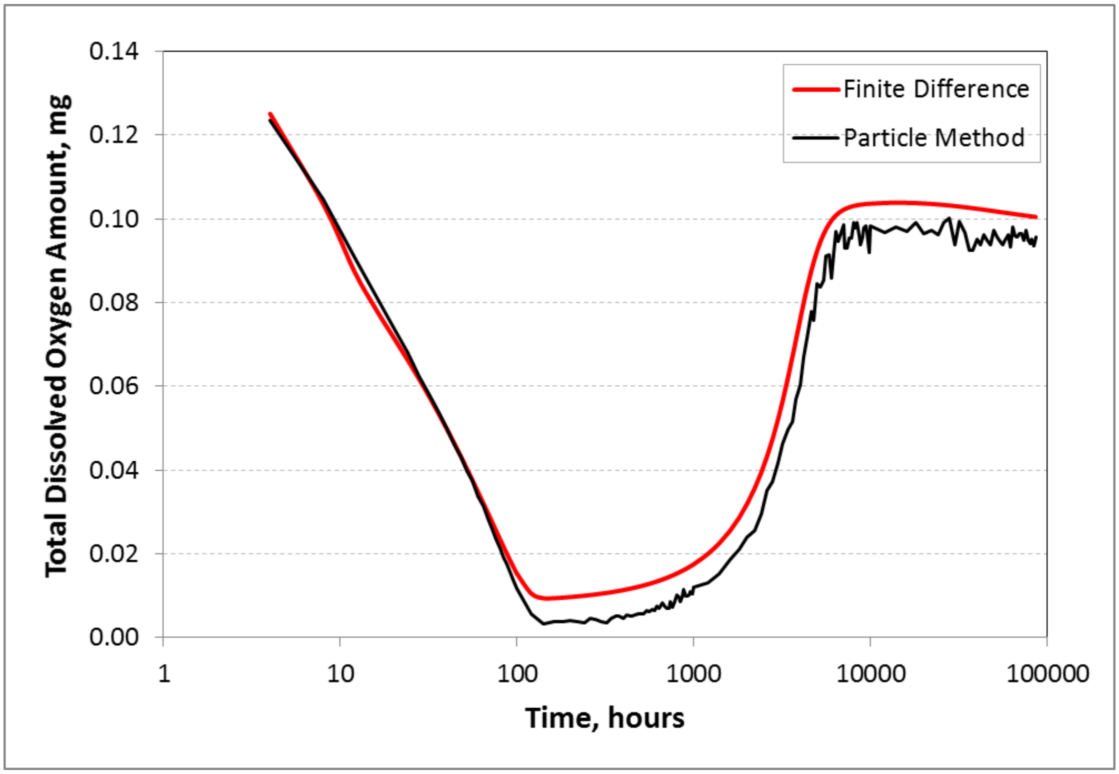

Figure 6.15: Shift in particle tracking model due to reaction with $dt = 4.0\ hours$

6.2 Kernel Smoothing

The box counting method is used to calculate concentrations which count the particles in a rectangular area (i.e. the grid layers) but this approach will cause oversmoothing or too much scattering in predictions at a given point in space (Haan, 1999). Increasing number of particles can be useful to deal with scattering issue but it will cause memory problems and will not be absolute solution. The Fig (6.15) shows the oscillations in box counting method.

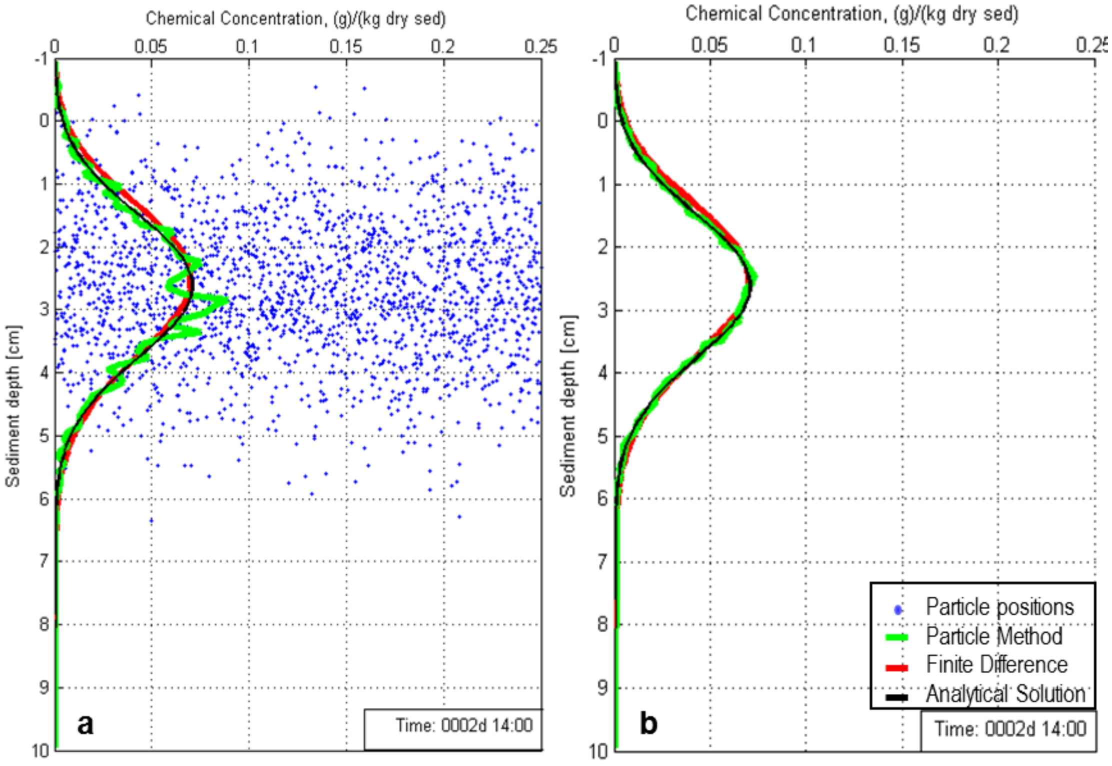

Figure 6.16: (**a**) $nP = 2000$ (**b**) $nP = 20000$ with box counting method.

In order to obtain smooth concentration profiles the density kernel method is proposed which give smoother concentrations with same accuracy. The kernel equation is:

$$K_a(x) = \begin{cases} C_{d,a}(1 - x^T x)^a & x^T x < 1 \\ 0 & otherwise \end{cases} \tag{6.1}$$

where $C_{d,a}$ are normalization constants listed in the Table (6.2). In this study, one dimensional triweigth kernel model is used which ensures that:

$$\int K_a dx = 1 \tag{6.2}$$

Table 6.2: Epanechnikov (a=1), biweight (a=2), triweight (a=3), quadweight (a=4) and quintweight (a=5) kernels for up to three dimensions.

$C_{d,a}$	$a = 1$	$a = 2$	$a = 3$	$a = 4$	$a = 5$
$d = 1$	$\frac{3}{2c_1}$	$\frac{15}{8c_1}$	$\frac{105}{48c_1}$	$\frac{945}{384c_1}$	$\frac{693}{256c_1}$
$d = 2$	$\frac{2}{c_2}$	$\frac{3}{c_2}$	$\frac{4}{c_2}$	$\frac{5}{c_2}$	$\frac{6}{c_2}$
$d = 3$	$\frac{5}{2c_3}$	$\frac{35}{8c_3}$	$\frac{315}{48c_3}$	$\frac{1155}{128c_3}$	$\frac{3003}{256c_3}$

In Fig (6.16), the proposed kernel model is used for 2000 chemical particles and it is seen that the profile introduced a better trend with analytical method.

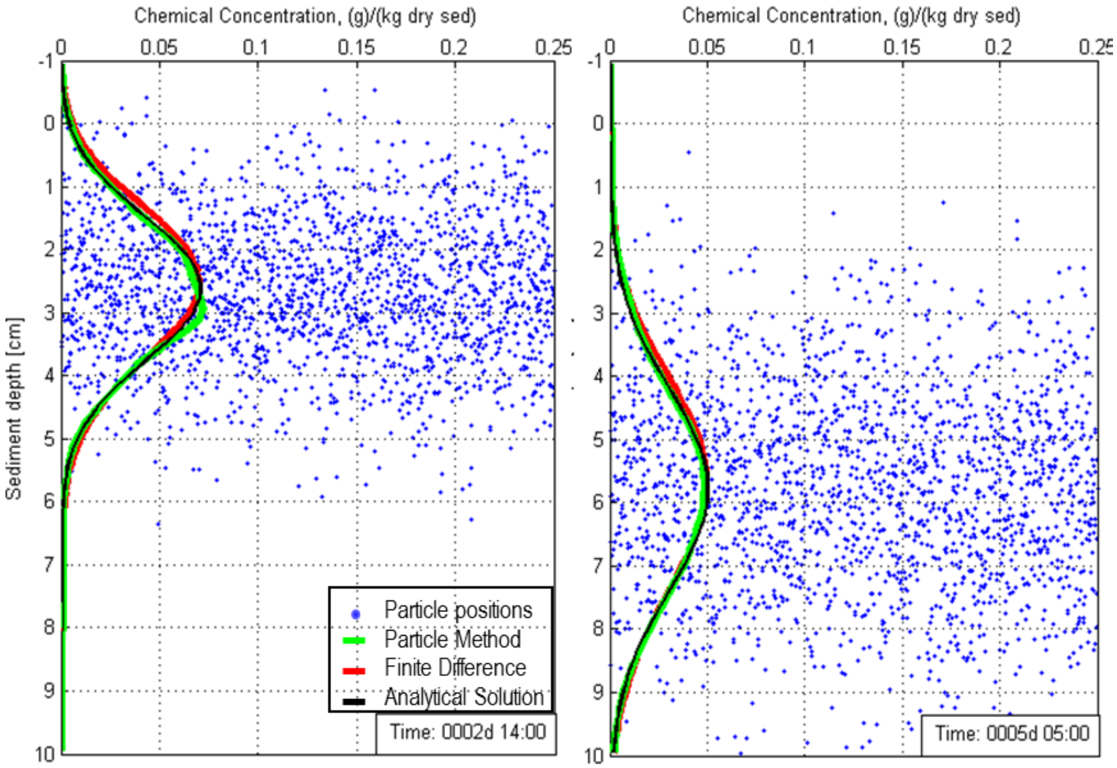

Figure 6.17: Kernel smoothing at different time steps for chemical concentration

This method is also applied to oxygen and natural carbon concentration calculations with particle model where for 3000 particles in Model 2. The Fig (6.17) shows oxygen and natural carbon concentrations before and after kernel smoothing, respectively.

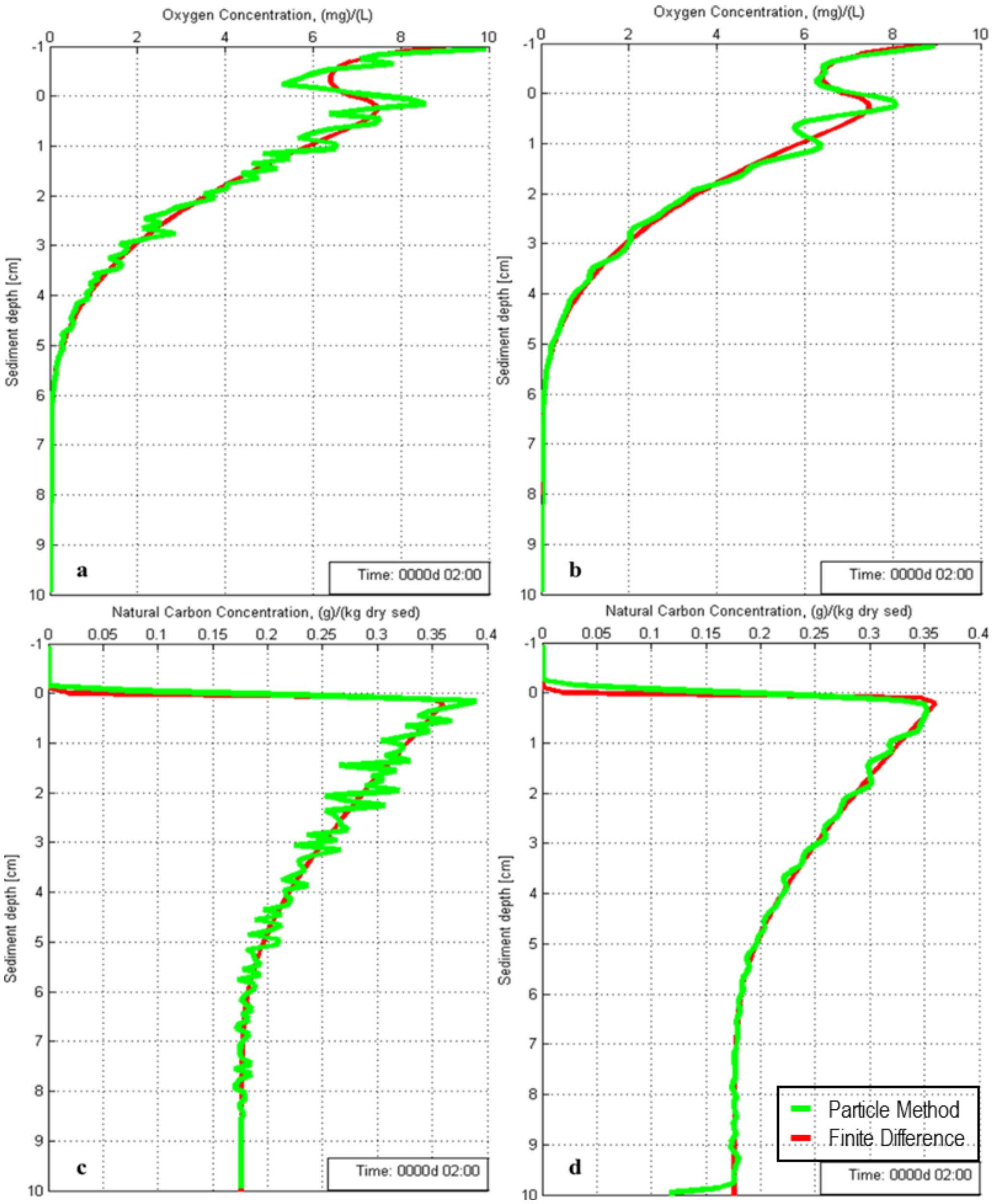

Figure 6.18: Oxygen concentration profile (**a**) without and (**b**) with kernel smoothing and natural carbon profile (**c**) without and (**d**) with kernel smoothing.

However, it can be seen from Fig (6.17.d) that there is a deflection at the bottom layer of carbon profile and when the advection velocity is decreased, these type of deflections may occur in the application of kernel smoothing on the top of the chemical particle profile. (Fig (6.18)).

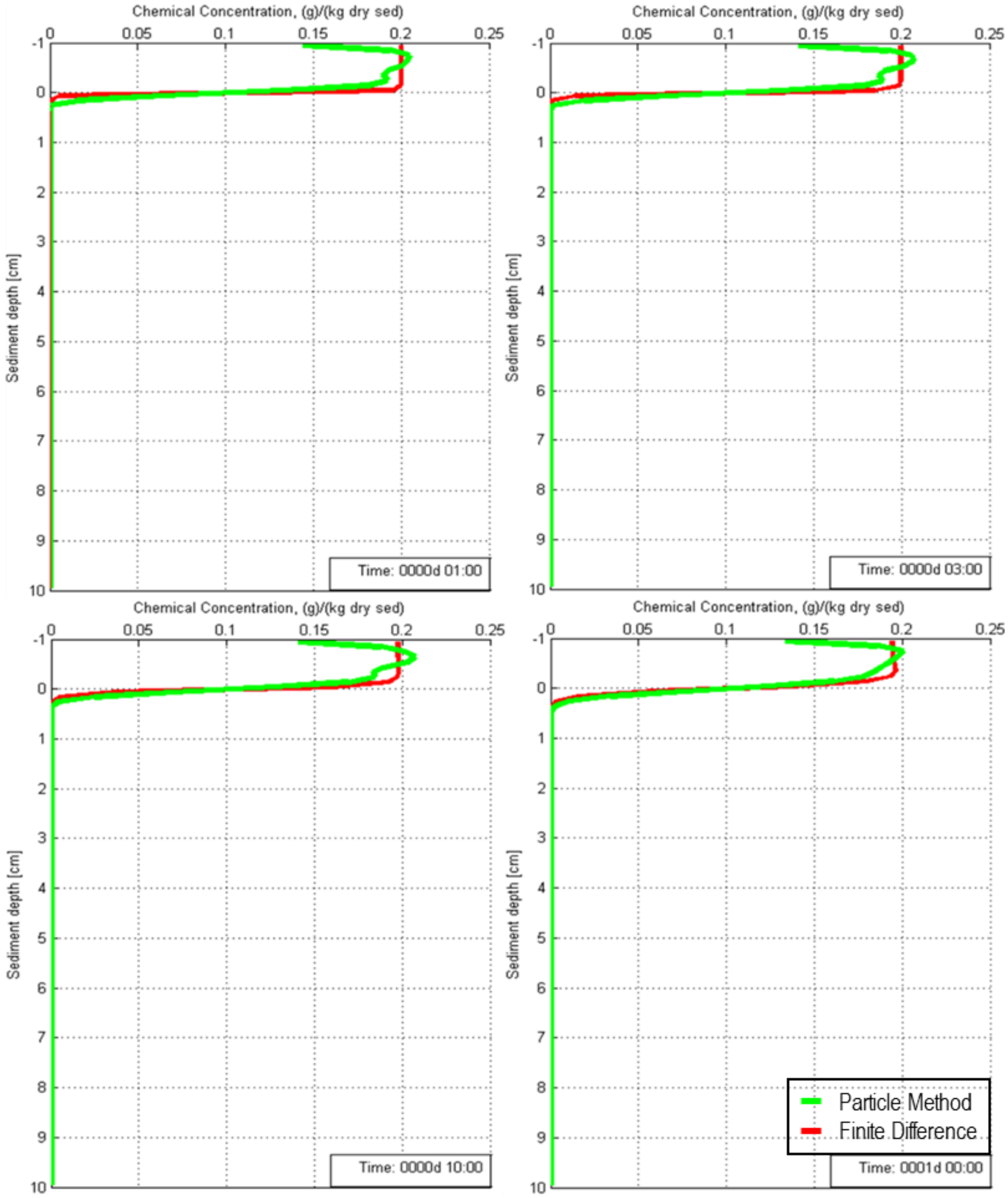

Figure 6.19: Deviations in kernel smoothing application for chemical concentration at different time steps.

As indicated in Eqn 6.2, the integral of kernel function is equal to 1. On the other hand, the integral of the top layer of chemical concentration is not because the particle concentration below the specified layer is zero. This is valid for bottom layer of natural carbon concentration. In order to overcome this problem, the integrals of top and bottom layers are calculated and the value is used to correct the kernel function (Figs (6.19) and

(6.20)). The application is working for oxygen profile because there is a buffer zone at the top of the system which will be explained in Section 6.3.

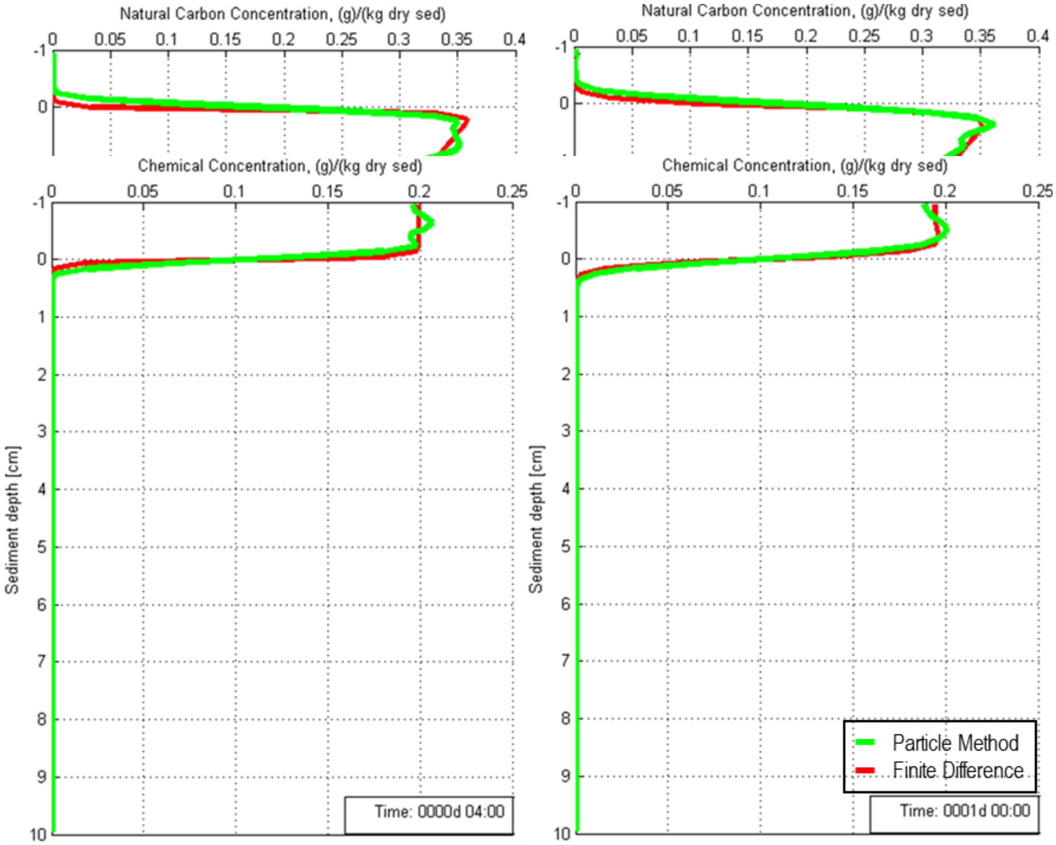

Figure 6.20: Corrected smoothed application for natural carbon concentration.

Figure 6.21: Corrected smoothing application for added chemical concentrations

6.3 Buffer Zone

In order to keep the upper boundary condition for oxygen concentration equal to 9 mg/L, a buffer zone is implemented for the oxygen particle modeling (Flekkøy, Delgado-Buscalioni, & Coveney, 2005). The oxygen profile before the buffer zone implementation is shown in Fig (6.21). The concentration on the boundary in particle model is under the required value and the particles that are escaping from the upper and lower part of the system do not compensate if they are added from top as in natural carbon profile. Thus, an imaginary layer with particles is added on the top of the system.

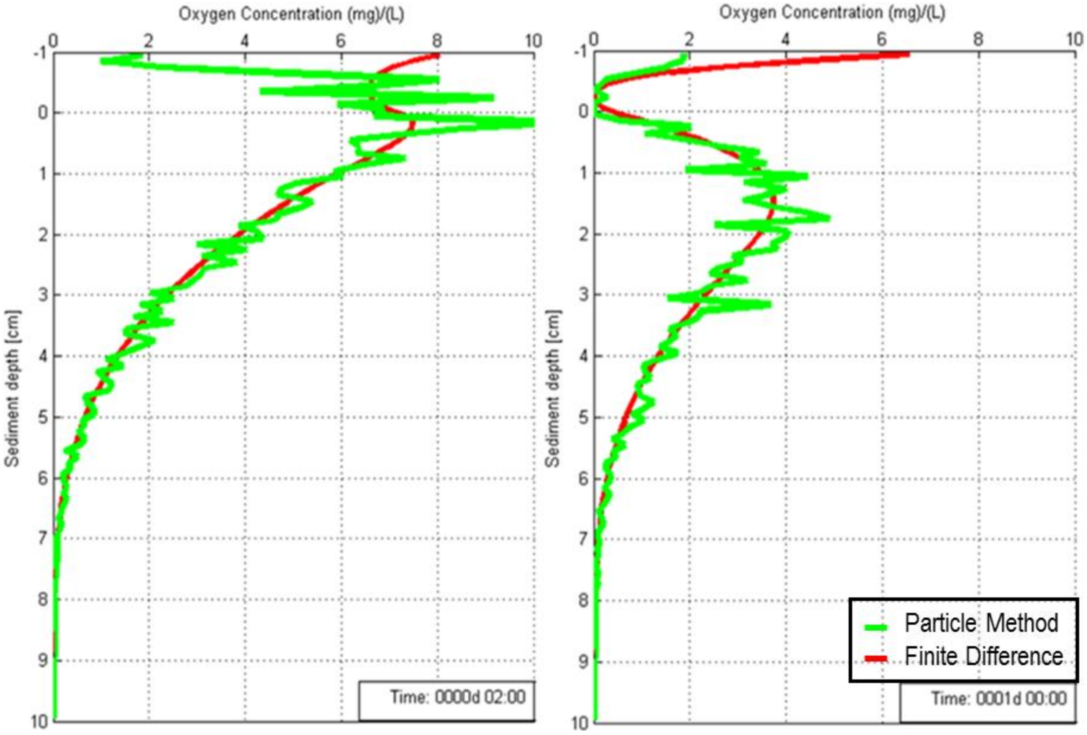

Figure 6.22.a: Oxygen concentration profile without buffer zone.

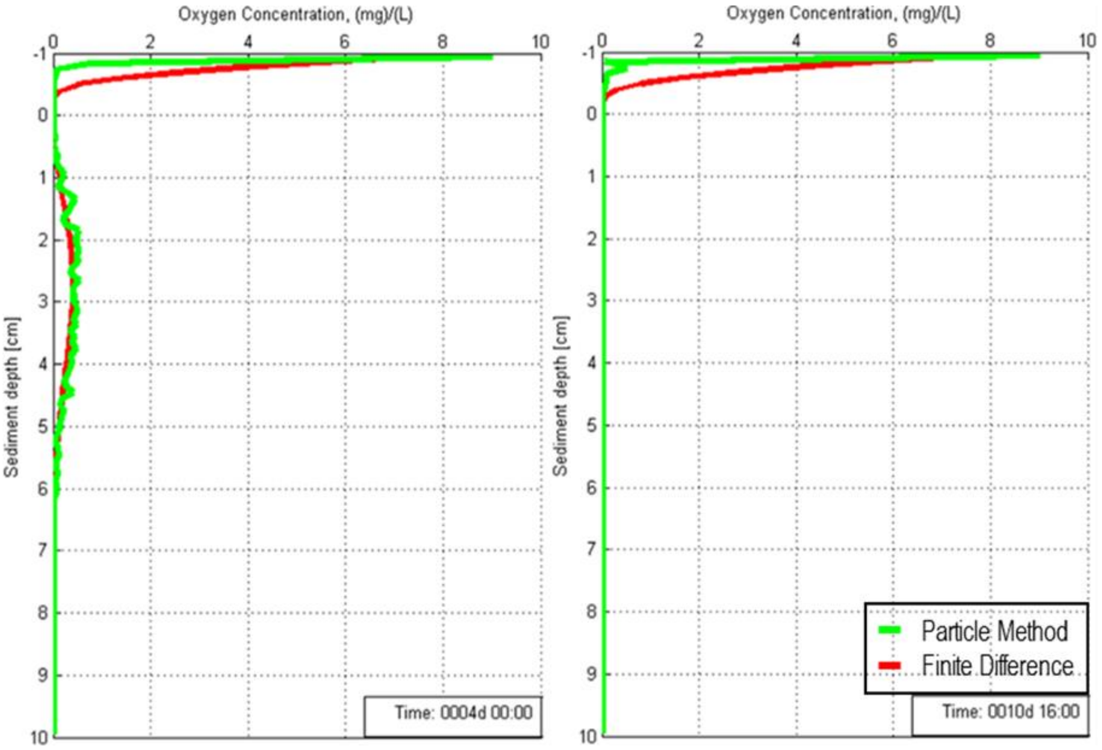

Figure 6.23.b: Oxygen concentration profile without buffer zone.

Buffer zone size is determined by an oxygen particle's travel distance which is forced by diffusive fluxes and expressed as in Eqn 5.18. For oxygen particles, the diffusion coefficient in Eqn 5.18 is taken as K_{O_2}/θ^2. This diffusive length is multiplied with 3 to fall particles into 99.7% confidence interval where mean is 3σ. The concentration of each oxygen particle is calculated by dividing the initial oxygen concentration, 9mg/L to total number of particles in the zone and it is multiplied by the ratio of buffer zone depth. The corrected oxygen profile is shown in Fig (6.23).

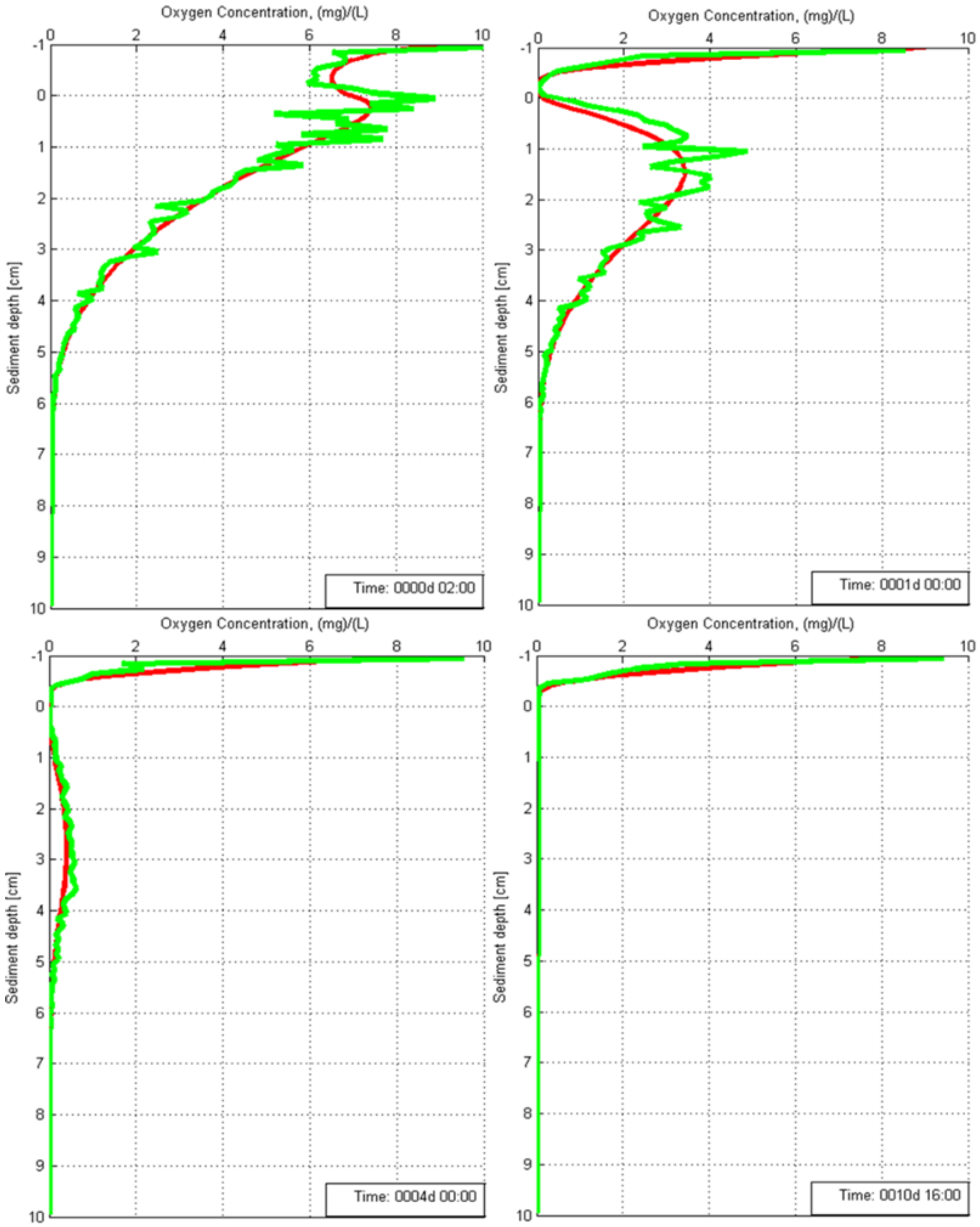

Figure 6.24: Oxygen concentration profile with buffer zone implementation

CHAPTER 7

CONCLUSION

This study offers a simple particle tracking method by which the general advection, diffusion, reaction equation can be modelled. In particular, this technique is used to model the transport of chemicals disposed to marine sediment by drilling operations and the effects of the disposal in marine sediment. Three of the stressors are modelled with particle tracking method: toxicity, oxygen depletion and biodegradation of natural carbon. Moreover, diagenetic equations that describe physical and chemical processes are solved with the finite difference and analytical methods to compare the results of proposed method.

The error analysis show that, random walk method does not show numerical diffusion when compared to finite difference model. Thus, it can be applied for applications that other methods are overwhelmed from numerical diffusion. Also, if Peclet number is taken greater than 2 or time interval is increased, finite difference method will diverge from the true model. However, particle method is not affected from the increase in Peclet number. Moreover, unlike analytical methods, this method can be used for transport equations with depth dependent diffusion coefficient.

Particle tracking method works better with higher particle numbers which decrease oscillations seen in the model. However, this will lead to increase in computation time and storage. The Kernel smoothing methods can be used to overcome oscillation which also slows down the simulation. In addition, increase in time interval will cause divergence between true model and particle model, especially for Monod type reaction transport equations, since particle tracking is an explicit method.

As a result, particle method can be a promising alternative to numerical methods when modelling the advection, diffusion and zero or first order decay of drilling cutting to marine sediment.

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