

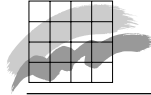


Ministry of Environment and Energy
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Theoretical evaluation of the sediment/water exchange description in generic compartment models (SimpleBox)

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July 2001

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Data sheet

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Abstract: It is shown how diffusion and deposition of solids drive the flux of substance between the water column and the sediment. The generic compartment models (Mackay type) use a one box model for the sediment in order to keep the calculations simple. However, when diffusion needs to be included in the calculations, the one box model needs to be evaluated in relation to a more complete solution of the differential equations for diffusion. General guidelines that are based on the system parameters are set up in order to establish the importance of diffusion and deposition respectively. These define the range where diffusion or deposition is negligible or where both processes must be included in order to describe the sediment-water substance exchange most appropriately.

Keywords: Molecular diffusion, Sedimentation, Deposition, Generic compartment model, Sediment.

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Summary

In this study generic compartment models are investigated. Such models are developed and used as described by e.g. *Mackay (1991)* and *Mackay et al. (1992)* and forms the basis in the European Uniform System for the Evaluation of Substances (EUSES) for risk assessment (*EC, 1996*).

In this investigation the environmental concentration is considered in relation to the substance exchange between the water column and the sediment.

The uncertainty analysis is crucial for mathematical models when they are used as decision support. A systematic approach is needed for determination of the total model uncertainty and in *Sørensen et al. (2001a)* one suggestion, where the overall uncertainty sources are divided in two types, is presented. This is also in agreement with definitions in *Etienne et al. (1997)*. The first type is input uncertainty attributed to the uncertainty in the input parameters for the model. The second type is the structural uncertainty as a result of the assumptions made in the model. Only the structural uncertainty will be considered in this investigation as the input uncertainty is investigated elsewhere (e.g. *Jager and Slop, 1995*, *Jager et al. 1997*; *Etienne et al. 1997*).

The structural uncertainty is difficult to quantify, because a validation can never be complete in reality. It may be possible to quantify the structural uncertainty by considering different elements (sub-models) in the model separately and for each sub-model formulate a more complete model to identify the discrepancy between the sub-model under investigation and the more complete model formulation. In this way the structural uncertainty related to the additional assumptions included in the sub-model under consideration compared to the more complete model will be quantified. This method is attractive for the generic exposure models because these models involve rather simple mathematical descriptions for the single compartments and the interaction between them. Thus, as a part of a structural uncertainty analysis it is possible to quantify the added uncertainty in the generic sub-models compared to more detailed and thus more complex models. The simplifications in the generic compartment models are natural consequences of the goal to perform manageable calculations for decision-makers. Thus, if the uncertainty related to the simplifications in the generic sub-models is acceptable (small) compared to the total obtainable uncertainty then the simple generic sub-models have to be selected.

In this investigation the structural uncertainty introduced in the simplified mathematical formulation of the diffusive sediment uptake will be evaluated on a regional scale. The sediment water system is important when hydrophobic substances are considered. Measurements of a series of hydrophobic substances actually show a high occurrence in the sediment layer (*Vikelsøe, et al. 2001*). In the generic compartment models a mean diffusive transport length approach is assumed for a sediment box of a specific arbitrary thickness (*Mackay et al. 1992*). The use of a single homogenous box is attractive in order to simplify the model, but the addi-

tional structural uncertainty due to the simplification needs to be quantified and related to the general uncertainty level of the model.

Two major transfer mechanisms for the water/sediment exchange can be relevant:

1. Transfer carried by net deposition of solids from the water column to the sediment surface
2. Transfer due to diffusion in the sediment pore structure

In relation to the description of diffusion between the sediment and water in generic models the following two questions appear relevant:

1. When will the transfer due to diffusion dominate the total substance mass transfer?
2. What is the uncertainty in the generic models introduced when the diffusion transfer is described using a single sediment box approximation?

In this report it is shown how diffusion and deposition of solids drive the flux of substance between the water column and the sediment, respectively. Initially when a substance is present in the water column (start of emission) the diffusion will dominate the sediment uptake due to large concentration gradients at the sediment surface. However, as the time progresses, the diffusion-induced flux will decrease rapidly, as the concentration gradients at the top of the sediment will level out because more substance enters the sediment layer. In contrast, the substance transfer due to deposition of solids will not display a high flux initially but rather a value that is proportional to the dissolved water column concentration.

The first case to be treated is when the dissolved water concentration is assumed constant in time and when the degradation in the sediment and the laminar boundary layer at the sediment/water column interface are neglected. In this case the initial diffusive flux will become infinitely high and decrease rapidly during time. The Flux due to deposition of solids will not display a high initial value but be constant during time and will thus become the dominating transfer mechanism after a specific time period. An equation is derived to calculate the time period after which the flux due to deposition is dominant. However, an additional time period needs to progress before the mass of substance in the sediment is governed by deposition. A maximum value of this time period is calculated.

Under some circumstances it is doubtful to neglect the degradation in the sediment. Even if degradation is included simple relationships are obtained by assuming a steady-state sediment concentration and a negligible laminar boundary layer at the sediment/water column interface. This yields an estimate of the flux due to diffusion and deposition, respectively, when steady-state is obtained in the sediment.

The description of diffusive transfer seems not well established in the generic compartment model, where the use of a mean transfer length for diffusion damages the nature of diffusion. The full solution of the governing equation for sediment diffusion indicates an extremely high rate of substance uptake, as long as the occurrence in the sediment is limited. On the other hand, the single sediment box approach yields a constant diffusion rate. After a specific time period the single box approach becomes more valid, however, that time period can easily be in the order of many years! In case of steady-state where the emission of substance into the

system is assumed equal to the sediment uptake by diffusion, the one box approach will always overestimate the dissolved water concentration in relation to the more complete sediment description. Obviously the discrepancy between the diffusive transfer descriptions will vanish as the transfer due to deposition of solids on the sediment surface starts to dominate in the total transfer of substance mass to the sediment. In many cases the deposition will dominate after a rather short time period and thus the concept in the compartment models will become acceptable simply because the diffusive transfer is negligible.

Thus, in conclusion, it appears that the one sediment box approach seems insufficient to include a realistic diffusion mechanism. But in many cases the deposition and thus the burial from the sediment box of fixed thickness will become the dominating factor in the sediment/water column exchange of substance and in those cases the inadequate description of diffusion will not be important.

In reality bio-turbation can be important for the substance transfer and one argument for using a single box to describe the diffusion in the sediment is that bio-turbation will tend to form a well mixed top layer at the sediment surface. However, the opposite argument seems more valid because bio-turbation will increase the diffusive rate of uptake, and thereby increase the structural uncertainty for the single box model, when the diffusive uptake is underestimated in general.

The reason for this confusion is due to the fact that the single box approach, as typically implied in the compartment models, is a mix between a diffusive model and a completely mixed model. The sediment layer is assumed completely mixed when the mass balance is made, where the layer is represented by a single concentration value. However, when the transfer of substance to the sediment layer is estimated a mean diffusive length of transfer is used, which assumes diffusive concentration stratification in the layer. If the sediment layer were assumed completely mixed in a consistent way then there would have been instantaneous equilibrium between the water column concentration and the sediment layer concentration.

The generic compartment models need to be mathematically simple in order to be applicable to decision support and a more realistic description of the diffusive transfer into the sediment will introduce a rather high level of mathematical complexity. Thus, an appropriate suggestion could be simply to accept the generic compartment models as valid when the diffusive description is negligible. However, more detailed models are necessary for the special cases where the diffusion controls the water/sediment exchange. This investigation ends up in a pragmatic guide for handling of this problem.

Resumé

I denne rapport er generiske compartment modeller undersøgt. Disse modeller er udviklet og brugt som beskrevet af f.eks. *Mackay (1991)* og *Mackay et al. (1992)* og danner basis i "European Uniform System for Evaluation of Substances" (EUSES), der anvendes til risikovurdering af miljøfremmede stoffer (*EC, 1996*).

I denne undersøgelse er de beregnede koncentrationer undersøgt i forbindelse stofudveksling mellem vandfase og sediment.

En usikkerhedsanalyse af matematiske modeller er afgørende når de anvendes til beslutningstagning. En systematisk tilgang er nødvendig når den totale modelusikkerhed skal bestemmes og i *Sørensen et al. (2001a)* er en fremgangsmåde præsenteret, hvor de samlede usikkerhedskilder er inddelt i to typer. En sådan definition er også foreslået i *Etienne et al. (1997)*. Den første type er usikkerheder fra modellens inputparametre. Den anden type er den strukturelle usikkerhed, der stammer fra modelstrukturantagelserne. Det er kun den sidstnævnte type der vil blive omhandlet her, da undersøgelser omkring inputusikkerheder kan findes i f.eks. *Jager and Slop, 1995*, *Jager et al. 1997*, *Etienne et al. 1997*.

Den strukturelle usikkerhed er svær at kvantificere fordi en validering aldrig vil være fuldstændig. Ved at dele modellen op i undermodeller og for hver undermodel at lave mere komplekse formuleringer, kan man få et bud på strukturusikkerheden som følge af ændrede proces- og strukturbeskrivelser. Denne metode er attraktiv for generiske modeller, da de involverer relativt simple matematiske udtryk for hver enkelt compartment og interaktionerne mellem dem. Som en del af en strukturel usikkerhedsanalyse er det således muligt at kvantificere usikkerhederne i de generiske undermodeller sammenlignet med mere detaljerede og komplekse modeller. Forenklingerne i de generiske compartment modeller er naturlige konsekvenser af ønsket om at udføre lettilgængelige beregninger for beslutningstagere. Hvis usikkerhederne relateret til forenklingerne i de generiske undermodeller er små sammenlignet med den totale usikkerhed, så skal disse simple modeller derfor anvendes.

I denne undersøgelse skal den strukturelle usikkerhed, forårsaget af de forenkledede matematiske beskrivelser af det diffusive sedimentoptag, evalueres i regional skala. Sediment-vand systemet er vigtigt i forbindelse med skæbnen af hydrofobe stoffer, hvilket understøttes af målinger der viser høje koncentrationer af hydrofobe stoffer i sediment (*Vikelsøe et al. 2001*). I generiske compartment modeller antages en gennemsnitlig diffusiv transportlængde i en sedimentboks af vilkårlig tykkelse (*Mackay et al. 1992*). Anvendelsen af en sådan længdeparameter i en homogent opblandet boks er attraktiv når modellen skal forenkles, men den tilføjede strukturusikkerhed forårsaget af forenklingerne skal kvantificeres og relateres til det generelle usikkerhedsniveau for modellen.

To overordnede transportmekanismer for vand-sediment systemet er relevante:

1. Transport ved netto-sedimentation af partikler fra vandet til sedimentoverfladen.
2. Transport ved diffusion i sedimentporestrukturen.

I relation til beskrivelsen af udvekslingen ved diffusion mellem vand og sediment i generiske modeller, er følgende spørgsmål relevante:

1. Hvornår vil transporten som følge af diffusion dominere den totale stoftransport.
2. Hvad er usikkerheden i de generiske modeller, som følge af at diffusionen beskrives ved en enkelt sediment boks.

I denne rapport vises det hvorledes henholdsvis diffusion af opløst stof og deposition af suspenderet stof driver fluxen af stof mellem vandfasen og sedimentet. I begyndelsen af en given emission, når stoffet første gang optræder i vandet, vil diffusionen dominere transporten til sedimentet på grund af en stor koncentrationsgradient ved sedimentoverfladen. Efterhånden som tiden går, vil den diffusive flux aftage hurtigt, fordi stofmassen i sedimentet vokser og gradienten aftager. I modsætning hertil vil stoftransporten forårsaget af deposition ikke være stor ved start men stige med tiden, da den er proportional med koncentrationen af opløst stof i vandet.

Det første tilfælde der behandles er, når den totale koncentration i vandet antages at være konstant i tiden og nedbrydningen i sedimentet er nul, ligesom det laminære vand-sediment grænselag er negligeabelt. I dette tilfælde, er den initiale diffusive flux uendeligt stor og vil aftage hurtigt med tiden. Fluxen ved deposition af suspenderet materiale vil være konstant og vil således blive dominerende efter et bestemt tidsinterval. En ligning opstilles til beregning af tiden hvor den diffusive flux er dominerende. En yderligere tidsperiode skal forløbe før den samlede stofmasse i sedimentet er styret af depositionen. En maximumværdi for dette tidsforløb er fundet.

I nogle situationer er det fejlagtigt at negligere nedbrydningen i sedimentet. Hvis den medregnes kan der opstilles nogle simple udtryk for steady-state koncentrationen i sedimentet, hvilket giver et estimat af den relative betydning af diffusion og deposition.

Beskrivelsen af den diffusive transport er ikke velunderbygget i den generiske compartment model, hvor anvendelsen af en middel transportlængde strider mod principperne for diffusionsprocessen. Den fulde løsning af sedimentdiffusionsligningen indikerer en ekstremt høj stofoptagsrate, så længe forekomsten i sedimentet er begrænset. I modsætning hertil, giver den enkelte sedimentboks i den generiske model en konstant diffusionsrate. Efter en given tidsperiode bliver enkeltboks tilgangen mere gyldig, men den nødvendige tidsperiode kan være mange år. I tilfældet hvor der er steady-state, det vil sige, hvor emissionerne af stof ind i systemet er lig med sedimentoptaget ved diffusion, vil enkeltboks modellen altid overestimere den opløste koncentration i vandet i forhold til den mere fuldstændige sediment beskrivelse. Det er givet at forskellen i diffusionsbeskrivelserne vil aftage efterhånden som depositionen af partikler til sedimentoverfladen begynder at overtage i den samlede transport.

Det kan konkluderes, at tilgangen ved de genetiske modeller ikke beskriver diffusionsprocessen i sedimentet tilfredsstillende. I mange tilfælde vil depositionen og den efterfølgende begravning af stof imidlertid dominere stoftransporten efter en bestemt tidsperiode og den resulterende uoverensstemmelse vil derfor blive acceptabelt på grund af det ubetydelige diffusionsbidrag.

Bio-turbation kan være vigtig for stoftransporten og et argument for at anvende en enkeltboks til at beskrive diffusionen i sedimentet er, at bio-turbation kan danne et opblandet overfladelag i sedimentet. På den anden side vil bio-turbationen øge den reelle diffusionsrate og herigennem yderligere øge den strukturelle usikkerhed hidrørende fra den i forvejen understimerede diffusionsrate.

Grunden til forvirringen omkring diffusionsbeskrivelsen er, at enkeltboks modellen er en blanding mellem en diffusionsmodel og en fuldstændigt opblandet model. Sedimentet antages at være fuldstændigt opblandet når massebalancen opstilles repræsenteret af én enkelt koncentrations værdi. Når diffusionstransporten skal beregnes, anvendes imidlertid en gennemsnits diffusionslængde, som danner en diffusionslagdeling i sedimentboksen. Hvis sedimentet antages at være fuldstændigt opblandet i alle beregningshenseende, så bør der være umiddelbar ligevægt mellem vandet og sedimentet.

Generiske compartment modeller skal være matematisk simple for at være anvendelige til beslutningstagning og en mere realistisk beskrivelse af diffusionstransporten i sedimentet vil indføre et højt matematisk kompleksitets niveau. En passende fremgangsmåde er, at acceptere de generiske compartment modeller som optimale såfremt diffusionen er ubetydelig. Mere detaljerede modeller er imidlertid nødvendige i de situationer hvor diffusionen styrer sediment-vand stofudvekslingen. Denne undersøgelse munder ud i en praktisk vejledning til håndtering af denne problemstilling.

1 Introduction

Basically the environmental risk of a chemical depends both on the toxicity and the expected environmental exposure level. Both of these quantities are difficult to predict, however, estimates are necessary in the risk assessment. The high uncertainty is compensated by introducing safety factors to form conservative estimates and thereby secure that no unaccepted harm will occur. The prediction of environmental exposure levels is a central topic in the risk assessment and the focus of this work. The predicted exposure level is often calculated using environmental fate models primary based on a compartment model paradigm, where the substance distribution within different compartments (media) is considered.

Generic fugacity models are developed and used in most cases to predict exposure as described by e.g. *Mackay (1991)* and *Mackay et al. (1992)*. This type of models forms the basis in the European Uniform System for the Evaluation of Substances (EUSES) system of models for risk assessment (*EC, 1996*). In EUSES the ratio between the effect concentration and the predicted concentration is calculated. In exposure assessment different spatial and temporal scales can be considered depending on the problem of concern. In some cases local problems needs to be analyzed e.g. at an outlet from a wastewater treatment plant, where the local stream is described in a local compartment model. In other cases the background concentration level is estimated for a larger area (regional, national or global scale). The time scale can also be different, where in some cases the peak concentration is related to the acute toxic effect or in other cases the long term exposure is of primary concern. In EUSES both a local and a regional exposure is calculated. These different scales in time and space induce different model setups and different sources of uncertainty. It is very important to consider the uncertainty of the model estimates and to gather as much empirical information as possible of actual measured exposure levels.

Measurements of some substances may give useful information to make predictions for new/not investigated substances. The system to be considered is rather complex and the resources for deducting investigations apparently will always be limited. Thus, the task is to accept, but minimize, the lack of knowledge (uncertainty). Neither the empirical knowledge nor the mathematical models can stand alone, because they have different weaknesses and benefits and thus need to be combined in order to obtain optimal knowledge in the exposure assessment.

The uncertainty analysis is crucial for mathematical models used as decision support. In principle when the uncertainty is not known, any model prediction will be useless. The model user may have a more or less intuitive idea about the actual uncertainty in a specific calculation or he/she may just use the model prediction to see if the result is in conflict with an 'expert judgement'. However, if the model predictions shall act as a powerful information source the uncertainty needs to be identified based on objective and well established methodologies. In such a methodology it is necessary to take a systematic approach in the uncertainty analysis in order to be sure that all uncertainty sources have been taken into account in the final uncertainty estimate. Otherwise the uncertainty analysis may

turn out to be more harmful than fruitful because a false reliability is added to the model prediction by the incomplete uncertainty analysis result and this is a pitfall in probabilistic risk assessment.

Different systematic approaches can be used to form a complete uncertainty analysis and one is described in *Sørensen et al. (2001a)*, where the overall uncertainty sources are divided in two types. The first type is input uncertainty attributed to the uncertainty in the input parameters for the model. The second type is the structural uncertainty as a result of the assumption taken in the model. This is also in agreement with definitions in *Etienne et al. (1997)*. Different attempts have been made to include input uncertainty analysis into the EUSES (*Jager and Slop, 1995, Jager et al. 1997; Etienne et al. 1997*). In general a series of methods exist to investigate the input uncertainty, however, it is more problematic to find a method to quantify the structural uncertainty.

The best way to quantify the structural uncertainty would be a validation using measured exposure values. This has to be done when possible. However, a validation will never be complete, because the system is too complex compared to the limited resources. The dilemma in the quantification of the structural uncertainty can be formulated as follows: If the structural uncertainty is going to be quantified completely then the model under consideration needs to be compared with a 'perfect' model. If this is possible then it is possible to replace the model under consideration by this 'perfect' model and avoid the structural uncertainty.

One possible way to quantify the structural uncertainty is to analyze a delimited sub-model from the generic compartment model. A more complete model is then formulated as an alternative to the sub-model and compared to the sub-modeling results. The discrepancy between the sub-model and the more complete model yields the structural uncertainty related to the additional assumptions which is used in the sub-model but not used in the more complete model. This method is attractive for the generic exposure models because these models involve rather simple mathematical descriptions for the single compartments and the interaction between them. Thus, as a part of a structural uncertainty analysis it would be possible to quantify the added uncertainty in the generic sub-models compared to more detailed and more complex models. The simplifications in the generic compartment model are natural consequences of the goal to perform manageable calculations for decision-makers. Thus, if the uncertainty related to the simplifications in the generic sub-models is acceptable (small) compared to the total obtainable uncertainty then the simple generic sub-models have to be selected.

The selection of sub models in this work is illustrated in Fig. 1.1. The sediment is selected because of the tendency to act as a sink, wherein exobiotics are accumulated and the sediment water system is, therefore, important when hydrophobic substances are considered. Measurements of a series of hydrophobic substances actually show a high occurrence in the sediment layer (*Vikelsøe, et al. 2001*). This project is a part of a larger project and both the references *Fausser et al. (2001)* and *Sørensen et al. (2001b)* are relevant for evaluation of the generic compartment models. The uptake into the sediment is relevant for the regional exposure model. At the local scale in EUSES the sediment is assumed in equilibrium with the water column, which eliminates the necessity for a description of the uptake.

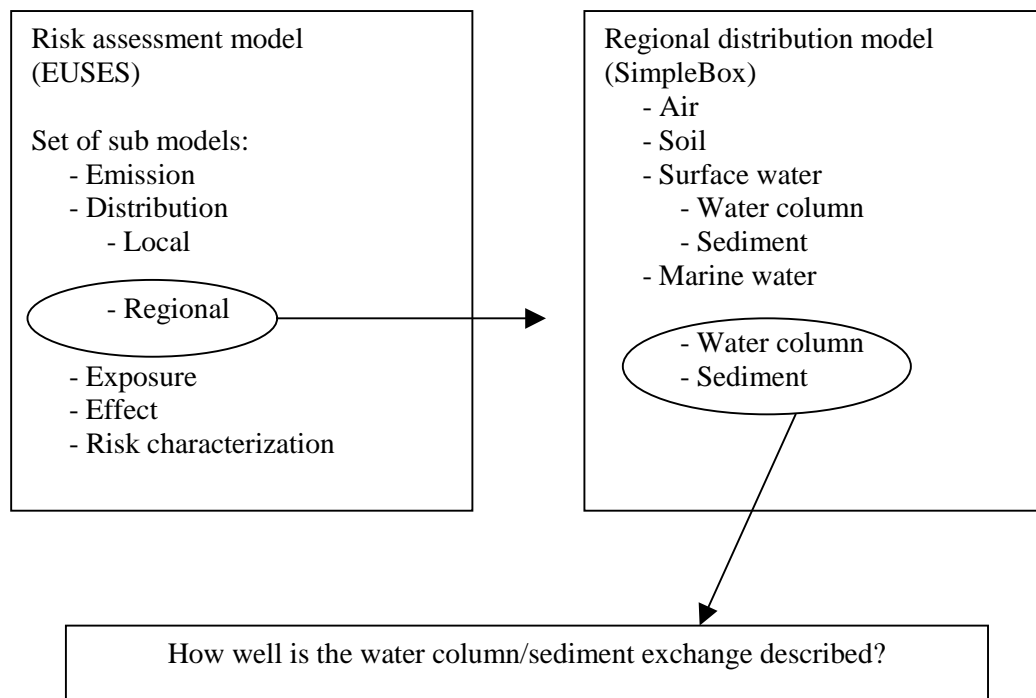


Figure 1.1 Selection of the sub model for further analysis in this investigation.

The generic risk assessment models (Mackay type) for exposure describes the water sediment exchange using a mean diffusive transport length approach for a single sediment box of a specific arbitrary thickness (L_{sed}) (Reuber *et al.* 1987 and Mackay, 1991). Consequently the single box will have a linear concentration profile. This is obviously a simplification compared to the solution of the local differential equation within the sediment layer having diffusion as transport phenomenon and the resulting structural uncertainty needs to be known by the user of the simple generic models. The difference between the generic model and a more realistic diffusion model is illustrated in Fig. 1.2

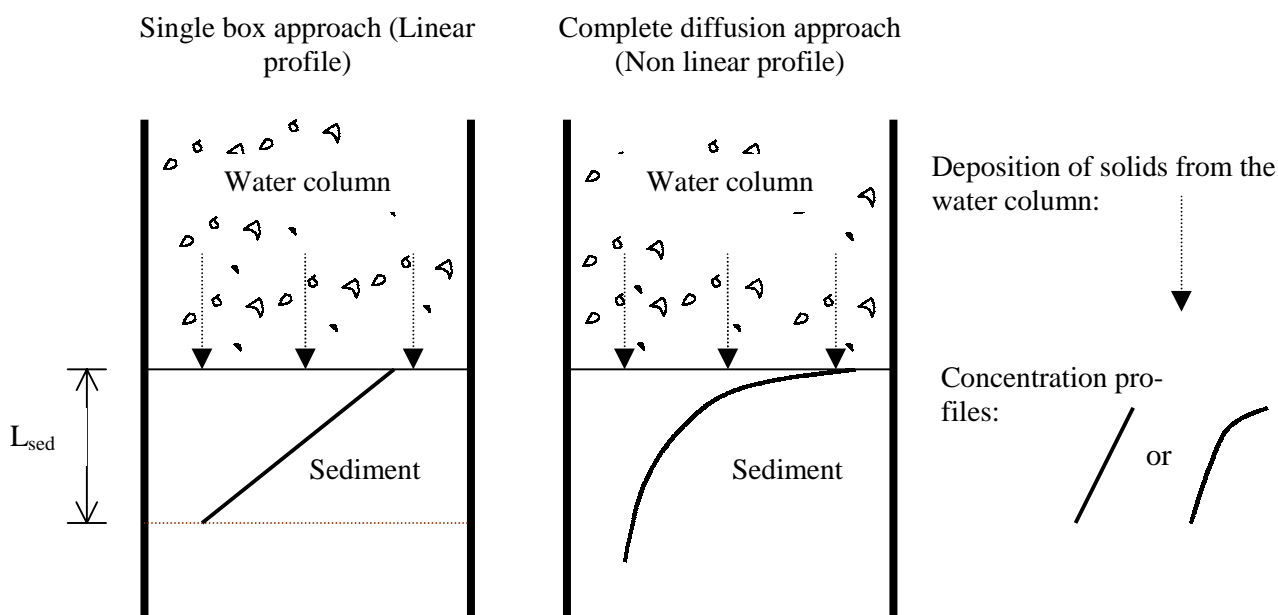


Figure 1.2 The principle in the two sub models analyzed in this investigation.

The transfer of substance between the water column and the sediment is governed by complicated conditions. Thus, any realistic model for describing the mechanism will be rough estimates of reality only. The following transfer mechanism can be relevant:

1. Transfer carried by deposition of solids from the water column to the sediment surface
2. Transfer carried by resuspension of solids from the sediment to the water column
3. Transfer due to advective flow between the sediment and the water column
4. Transfer due to diffusion into the sediment pore structure

The two first mechanisms will in this investigation will be considered as one net deposition. The actual deposition is assumed to be larger than the resuspension due to the primary production and supplement of solids from surface water and waste water treatment plants (the last one typically being of minor importance). Mechanism 3 will not be included in this study, as the advective transport into the sediment is not included in the generic compartment models. Mechanism 4 depends on the actual concentration profile in the very top of the sediment and is as such crucial when the sediment is described using a one box approximation as in the generic compartment models. In relation to the description of the sediment/water transfer in generic models the following questions appear relevant:

1. When will the transfer due to diffusion dominate the overall substance mass transfer?
2. What is the uncertainty in the generic models introduced when the diffusion transfer is described using a single box approximation for the sediment?

The answer to the first question will identify when it is important to consider the diffusion mechanism as crucial. Chapter 2 deals with this question, where the equations for diffusion and deposition are derived. In chapter 3 the generic compartment model equations for the sediment/water exchange is shown and related to the basic diffusion properties. In Chapter 4 the diffusion is solely investigated and the generic compartment model is compared to a diffusion model which takes into account the formed concentration profile. The conclusion ending up in a operational guide-line is given in chapter 5.

2 The sediment/water exchange using a diffusion/deposition description

The substance transfer between the water column and the sediment is assumed controlled by three mechanisms: (1) Diffusion of dissolved substance through the hydraulic laminar film at the sediment surface. (2) Net deposition of solids from the water column to the sediment surface constant in time. (3) Diffusion of dissolved substance within the sediment pores. The deposition and resuspension is considered in this investigation as a net deposition (deposition minus resuspension). First non-steady-state conditions for the sediment are described where degradation is neglected. Afterwards steady-state is assumed and the degradation in the sediment is included. The influence induced by the hydraulic laminar film will not be included in the equations but discussed separately.

2.1 Governing equation for the sediment concentration profile

The diffusion transport flux equation is

$$Flux_{diff} = -D \frac{\partial C_{diss}}{\partial x} \quad 2.1$$

where $Flux_{diff}$ is the substance flux (Mass/m²·s), C_{diss} is the dissolved substance concentration, D is the diffusion coefficient (m²/s) and x is the distance. A local mass balance for an infinite thin sediment layer (dx) in combination with Eq. 2.1. forms

$$\frac{\partial C_{s,diss}}{\partial t} = \frac{D_s}{R_s} \cdot \frac{\partial^2 C_{s,diss}}{\partial x^2}, \quad \text{where } R_s \equiv \theta + K_d \cdot \sigma \text{ and thus } C_{s,diss} = R_s \cdot C_{s,tot} \quad 2.2$$

where $C_{s,diss}$ is the dissolved concentration in the sediment pore water, D_s is the molecular diffusion coefficient modified for the sediment pore system, R_s is defined as the retention factor for the sediment as a result of adsorption to the sediment pore structure, θ is the porosity (volumetric water content) of the sediment, K_d is the linear adsorption coefficient for the sediment (l/kg) and σ is the dry bulk density (kg/dm³) of the sediment. The concentration $C_{s,tot}$ is the total concentration per sediment volume (µg/l) including both the dissolved and adsorped fraction.

The degradation of both substance and the sediment solids are neglected in Eq. 2.2. This equation is used in the following analysis in order to investigate the influence on the substance transfer due to both diffusion and the deposition of solids on the sediment surface. In a natural system continuous deposition of solids will take place on the sediment surface. These solids will adsorb substance in the water and thus participate in the transfer of substance from the water column into the sediment. The sediment surface will slowly be elevated due to this sedimentation as illustrated in Fig. 2.1. The diffusion in the sediment locally as described by Eq. 2.2 is still valid in this case, however the solution of the equation be-

comes more difficult due to the upward moving sediment surface. Thus, Eq. 2.2 is transferred into the moving space coordinates (x') from the fixed space coordinate (x) in order to fix the boundaries for the differential equation, see Fig. 2.1. The x' value is defined to be zero at the sediment surface.

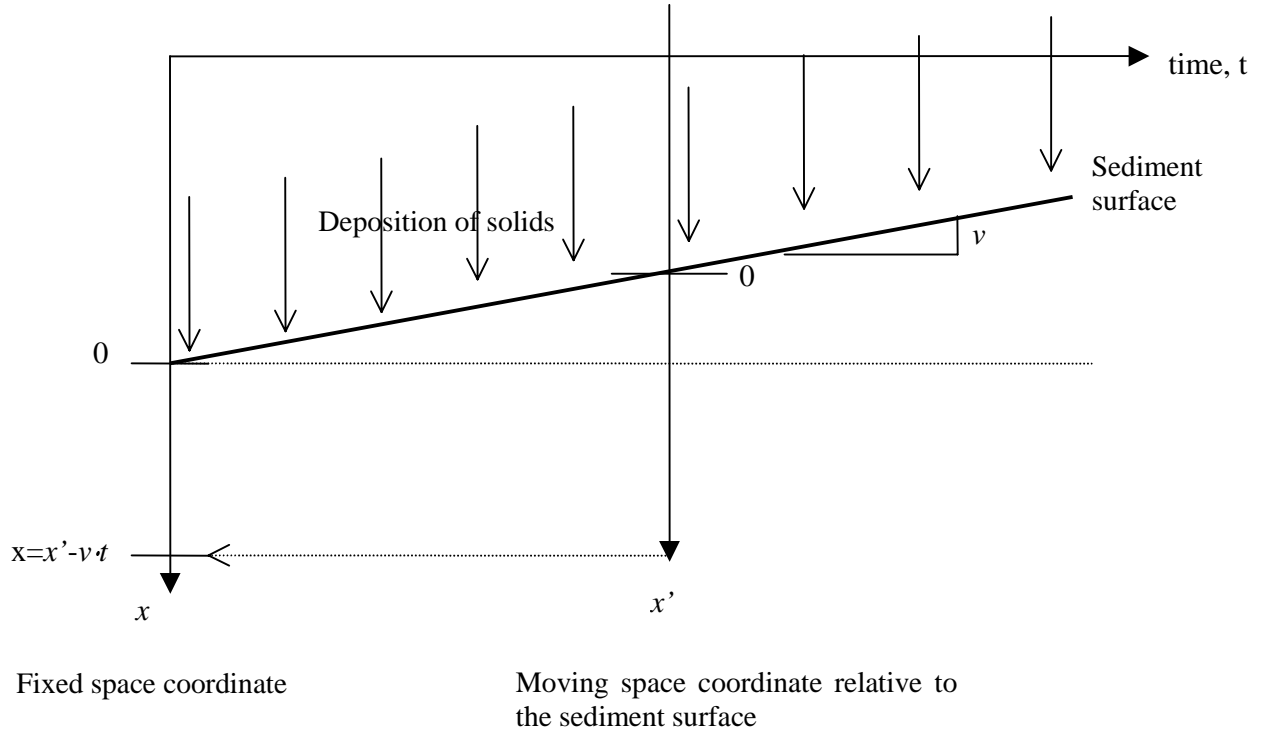


Figure 2.1 Illustration of the sediment build up due to deposition of solids. Definition of two space coordinates: A fixed coordinate (x) and a moving coordinate following the sediment surface (x').

In Fig. 2.1 the relationship between the two space coordinates is given as

$$x' = x + v \cdot t \quad 2.3$$

where v is the upward moving velocity of the sediment surface (m/s). The so-called chain rule is used to transfer the differential equation into the moving coordinate system:

$$\left. \frac{\partial C_{s,diss}}{\partial t} \right|_x = \frac{\partial C_{s,diss}}{\partial x'} \cdot \frac{dx'}{dt} + \left. \frac{\partial C_{s,diss}}{\partial t} \right|_{x'} \quad 2.4$$

where $\left|_x\right.$ and $\left|_{x'}\right.$ is the partial derivative in time for constant x and x' , respectively. A combination of the Eqs. 2.2, 2.3 and 2.4 yields a differential equation for the substance distribution in the x' coordinate system (relative to the sediment surface) as

$$\frac{\partial C_{s,diss}}{\partial t} = \frac{D_s}{R_s} \cdot \frac{\partial^2 C_{s,diss}}{\partial x'^2} - v \cdot \frac{\partial C_{s,diss}}{\partial x'} \quad 2.5$$

where v is the upward velocity of the sediment surface (m/s) due to the deposition of the solids which will be assumed constant in the solution.

This yields the following initial and boundary conditions

$$C_{s,diss}=C_{w,diss}, \text{ for } x'=0, t>0 \quad 2.6 \text{ a}$$

$$C_{s,diss}=0, \text{ for } x'>0, t=0 \quad 2.6 \text{ b}$$

where the dissolved concentration in the water column, $C_{w,diss}$, is assumed to be constant and $C_{s,diss}$ is the dissolved concentration in the sediment pores. The influence from the laminar film at the water/sediment interface is neglected by the condition of constant $C_{s,diss}$ value at the sediment surface (Eq. 2.6a).

2.2 Constant dissolved water column concentration

An analytical solution of Eq. 2.5. is manageable for constant concentration of dissolved substance in the water column ($C_{w,diss}$ constant in time in Eq. 2.6a). The solution of Eq. 2.5 is shown in Appendix A (Eq. A.11) and the dissolved concentration in the sediment pore water ($C_{s,diss}$) as a function of x' and t becomes

$$C_{s,diss} = \frac{1}{2} \cdot C_{w,diss} \cdot \left(\operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} - v \cdot \sqrt{t} \right) \right) + e^{-\frac{x' \cdot v \cdot R_s}{D_s}} \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} + v \cdot \sqrt{t} \right) \right) \right) \quad 2.7$$

The flux ($\mu\text{g}/(\text{m}^2\text{h})$) into the sediment by diffusion is described as

$$Flux_{diff} = -D_s \cdot \left. \frac{\partial C_{s,diss}}{\partial x'} \right|_{x'=0} \quad 2.8$$

Eq. 2.7 is differentiated at the sediment surface ($x'=0$) (see Appendix A, Eq. A.14) and combined with Eq. 2.8 to give an equation for the diffusive exchange between sediment and water column as

$$Flux_{diff} = \frac{1}{2} \cdot C_{w,diss} \cdot \left(2 \cdot e^{-\left(\frac{1}{2} \cdot v \cdot \sqrt{\frac{R_s \cdot t}{D_s}} \right)^2} \cdot \sqrt{\frac{D_s \cdot R_s}{\pi \cdot t}} - v \cdot R_s \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot v \cdot \sqrt{\frac{R_s \cdot t}{D_s}} \right) \right) \quad 2.9$$

In case of no deposition of solids on the sediment surface ($v=0$) the Eqs. 2.7 and 2.9 becomes:

$$C_{s,diss,v=0} = C_{w,diss} \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot x' \cdot \sqrt{\frac{R_s}{D_s \cdot t}} \right) \quad 2.10$$

and

$$Flux_{diff,v=0} = C_{w,diss} \cdot \sqrt{\frac{D_s \cdot R_s}{\pi \cdot t}} \quad 2.11$$

The two constants D_s and R_s needs to be known before this equation can be applied.

As a first approximation for D_s the following relationship between the molecular weight (MW) and the diffusion coefficient is useful (Schwarzenbach et al. 1993):

$$D_{w,unknown} = D_{w,known} \cdot \left(\frac{MW_{known}}{MW_{unknown}} \right)^{0.5} \quad 2.12$$

Benzen is used as known substance ($D_w = 10^{-9}$ m²/s and MW=78 g/mol, (Schwarzenbach et al. 1993)) in Eq. 2.12 to from the plot in Fig. 2.2, where the D_w value is estimated for different MW values.

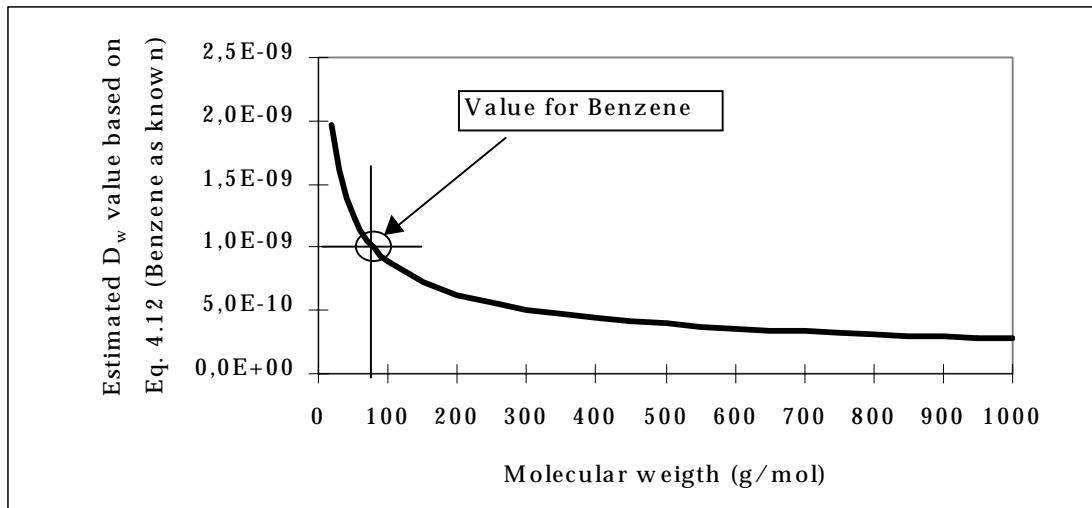


Figure 2.2 Estimated D_w values as a function of the molecular weight using Eq. 2.12 and Benzene as the known substance.

It is seen in Fig. 2.2 that the D_w value is rather constant for higher values of MW. Organic pollutants of higher hydrophobicity will often have a weight above 100-200 g/mol. Thus, according to Fig. 2.2, the D_w values will not exhibit large variation for such substances. It is further reasonable to assume a close relationship between D_s and D_w , so a rather constant D_w value indicates also a limited variability of the D_s value. Contrary, the R_s value can easily change dramatically due to differences in the sediment and substance adsorption properties. When D_s is involved in Eq. 2.9 the two parameters R_s and D_s always acts as pairs either as products or as ratios. Thus, a high uncertainty related to R_s compared to D_s will pin point the R_s parameter to be the dominating source of uncertainty when the sediment/water exchange has to be described in a mathematical model. Nevertheless, in this argumentation the bio-turbation is neglected, which may increase the effective diffusion into the sediment and thus introduce additional uncertainty into the D_s value.

The square root relationship between the diffusion coefficient and the $Flux$ (Eqs. 2.9 and 2.11) combined with Eq. 2.12, relating the molecular weight to the diffusion coefficient indicates nearly no effects on the $Flux_{diff}$ value due to different molecular weight. This can be illustrated by comparing the $Flux_{diff}$ for two different substances assuming $v=0$: (1) benzene and (2) a substance having the same R_s value as benzene but a different diffusion coefficient due to a different MW. The second substance is arbitrary and selected only to compare differences due to realistic differences in the diffusion coefficient value. The ratio between the diffusive flux of benzene ($Flux_{diff,benzene}$) and the flux of an arbitrary substance ($Flux_{diff,sub}$) can be calculated by combining Eqs. 2.11 and 2.12 as

$$\frac{Flux_{diff,sub}}{Flux_{diff,benzene}} = \left(\frac{MW_{benzene}}{MW_{sub}} \right)^{0.25} \quad 2.13$$

Eq. 2.13 is used in Fig. 2.3 using benzene as know substance and the $Flux_{diff}$ value for substances having a higher molecular mass than benzene is seen to be nearly constant independent on the molecule mass. In this analysis only the differences in the diffusion coefficient is considered while in reality the hydrophobicity (in terms of R_s) and thus the $Flux_{diff}$ value will indirectly be dependent on the molecular weight as well. Higher molecular weight will in general result in a large molecular volume and thus in a higher degree of hydrophobicity (higher R_s value) which will increase the substance flux into the sediment.

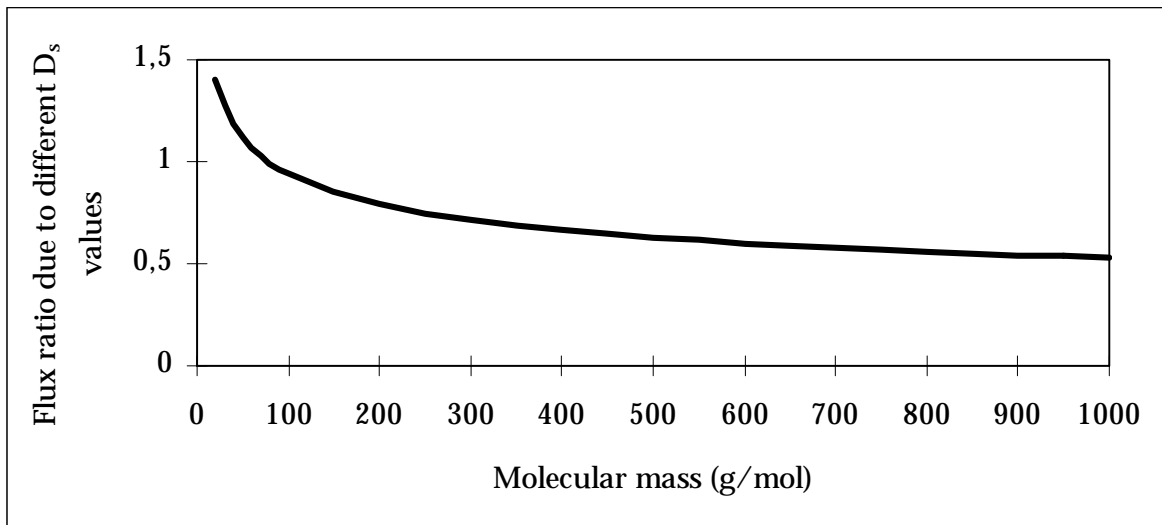


Figure 2.3 The ratio between the flux of benzene and the flux of a substance having different diffusion coefficient due to different molecular mass. All other properties are assumed the same.

The substance mass per unit area included in the sediment due to deposition of solids ($mass_{dep}$) during an infinitesimal short time step (dt) is described in Fig. 2.4.

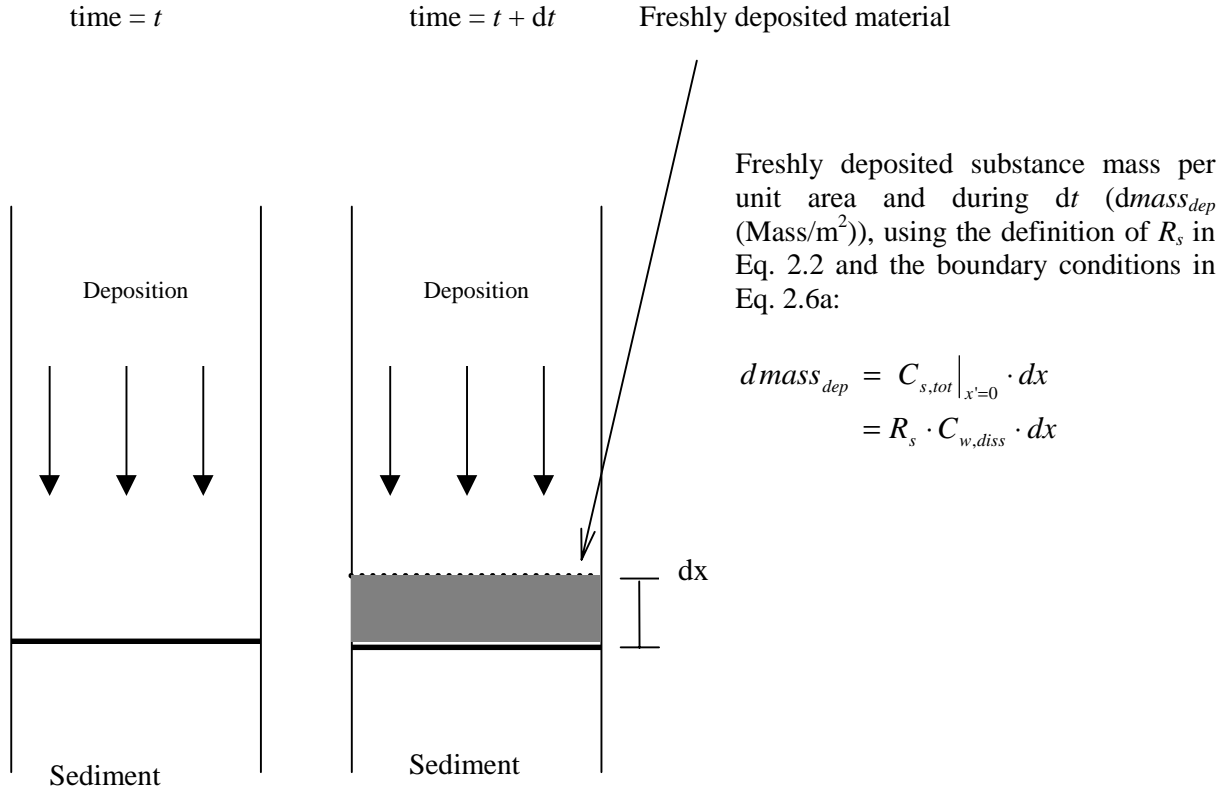


Figure 2.4 The substance mass included in the sediment as a result of deposition of solids on the sediment surface during the infinitesimal time step dt .

Using the relationship for $dmass_{dep}$ derived in Fig. 2.4 the following equation can be derived for the flux of substance to the sediment due to deposition:

$$Flux_{dep} = \frac{dmass_{dep}}{dt} = R_s \cdot C_{w,diss} \cdot \frac{dx}{dt} = R_s \cdot C_{w,diss} \cdot v \quad 2.14$$

where the retention factor R_s for the newly formed sediment is assumed similar to the value for the former deposited sediment layer below.

The following dimensionless factor is characteristic for the water/sediment exchange flux:

$$A \equiv v \cdot \sqrt{\frac{R_s \cdot t}{4 \cdot D_s}} \quad 2.15$$

because the flux due to diffusion ($Flux_{diff}$) is expressed in a simple way by combining the Eqs. 2.9, 2.11 and 2.15 as

$$Flux_{diff} = Flux_{diff,v=0} \cdot \left(e^{-A^2} - \sqrt{\pi} \cdot A \cdot erfc(A) \right) \quad 2.16$$

where $Flux_{diff,v=0}$ is the flux value due to diffusion in case of no deposition of solids ($v=0$) as described by Eq. 2.11. In a similar way Eq. 2.14 is rewritten as

$$Flux_{dep} = Flux_{diff,v=0} \cdot \sqrt{4 \cdot \pi} \cdot A \quad 2.17$$

From Eqs 2.16 and 2.17 it is seen that the ratio between $Flux_{diff}$ and the total flux ($Flux_{diff}+Flux_{dep}$) is a function only of A (note: The $Flux_{diff,v=0}$ cancels out in the flux ratio). The ratio $\frac{Flux_{diff}}{Flux_{dep} + Flux_{diff}}$ is shown as a function of A in Fig. 2.5.

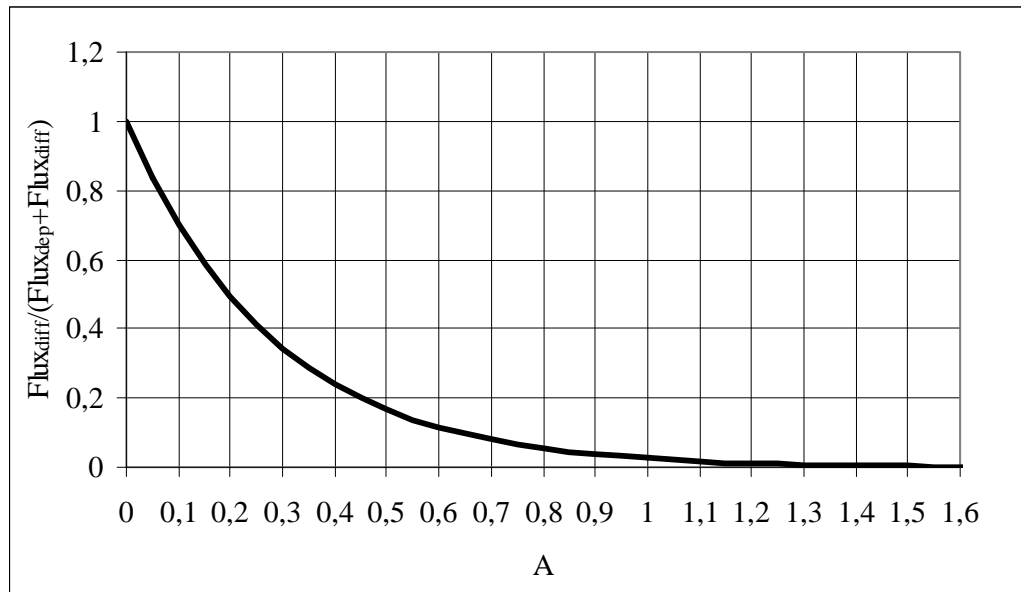


Figure 2.5 $\frac{Flux_{diff}}{Flux_{dep} + Flux_{diff}}$ as a function of A (Eq. 2.15) calculated using the Eqs. 2.16 and 2.17.

Critical values of A are useful in order to identify the predominant flux as either $Flux_{dif}$ or $Flux_{dep}$. The diffusive transport is seen to dominate when A is below about 0.2 (cf. Fig. 2.5) while the transport by deposition will dominate when the A value is above 0.2. Initially the diffusion will always be dominant because A is zero for $t=0$. But, the A value will increase during time and after a specific critical time period A will become above 0.2 indicating that the deposition of solids on the sediment surface starts to dominate. When the time has progress for a longer period the A value becomes above about 0,6 and the deposition will be the only significant transport mechanism for the flux.

The *specific Flux* (m/s) values are defined as:

$$specific\ Flux = \frac{Flux}{C_{w,diss}} \quad 2.18$$

Both the Eqs. 2.9 and 2.14 predict the actual $Flux$ to be proportional to the $C_{w,diss}$ value. Thus, the actual $Flux$ to a given time is simply the calculated *specific Flux* multiplied by the dissolved water concentration.

The specific mass per unit sediment surface area (m) can be calculated as

$$specific\ mass = \frac{mass}{C_{w,diss}} = \frac{1}{C_{w,diss}} \cdot \int_0^t Flux\ dt = \int_0^t (specific\ Flux)\ dt \quad 2.19$$

where $mass$ is the total mass of substance in the sediment per unit area ($Mass/m^2$). In the following the $mass$ of substance in the sediment as a result of diffusion will be denoted $mass_{diff}$ and the corresponding $mass$ due to deposition will be denoted $mass_{dep}$.

Using the values for DEHP: $D_s=2 \cdot 10^{-10}$ m^2/s , $R_s=10600$ and $v=2.5$ mm/year, as suggested by *Vikelsøe et al. (2001)* for Roskilde Fjord, the Eqs. 2.9, 2.14 and 2.19 is used to calculate the specific $Flux_{diff}$ and $Flux_{dep}$ respectively as a function of time in Fig. 2.6. The two $Flux$ values are equal after about 5 days, which is equivalent to at A value of 0,2, in agreement with the prediction in Fig. 2.5 of the $Flux_{diff}$ value being half of the total $Flux$.

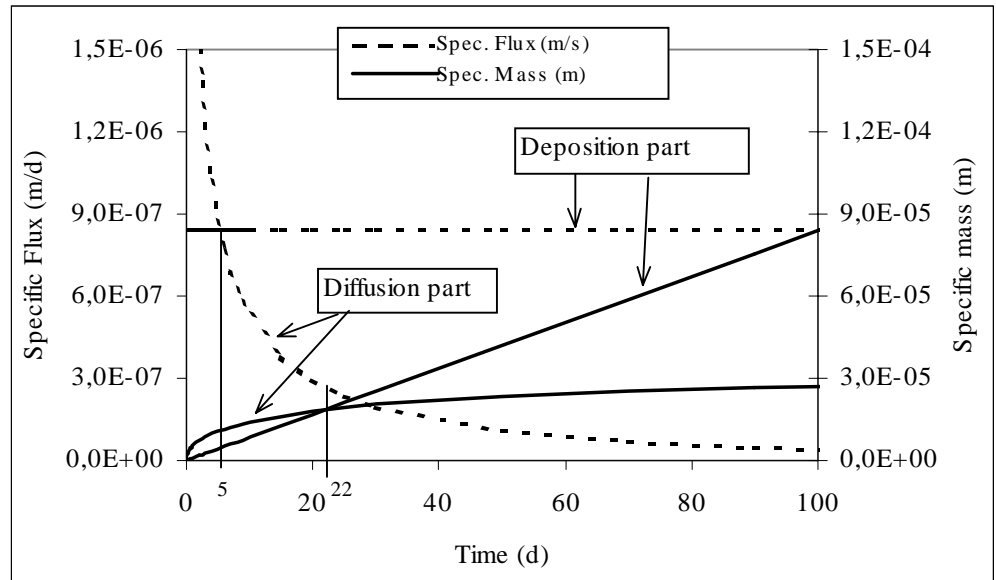


Figure 2.6 The specific flux and the specific mass (per unit sediment area) as a function of time due to diffusion and deposition, respectively.

After about 22 days the $specific\ mass_{diff}$ is equal to the $specific\ mass_{dep}$ and afterwards the deposition of solids at the sediment surface will be the dominating factor for the substance mass in the sediment. The $Flux_{diff}$ value is very high initially compared to the $Flux_{dep}$ value so the intersection between the $mass$ curves in Fig. 2.6 happens in a much later time period than the intersection of the $Flux$ curves.

The $specific\ mass_{diff}$ can be calculated by combining Eqs. 2.9 and 2.19. However, it is not possible to obtain an analytical solution of the integral (Eq. 2.19) to get a parametric functional relationship between time and $mass_{diff}$. Thus, only numerical integration of Eq. 2.9 is possible. Such numerical integration have been done and the following relationship is identified at any wanted numerical accuracy:

$$mass_{diff} = \frac{D_s}{v} \quad for \quad t \rightarrow \infty \quad 2.20$$

It is surprising that a complicated operation like a numerical integration of Eq. 2.9 yields a simple relationship as Eq. 2.20. It has not been possible to derive the relationship between Eq. 2.20 and Eq. 2.9 explicitly, due to the need for a numerical integration, so Eq. 2.20 is simply a result of a numerical experiment testing a combination of series of D_s , R_s and v values. The following parameter value intervals are tested: D_s below $1 \cdot 10^{-9} \text{ m}^2/\text{s}$, R_s above 100, and v above 0.5 mm/year. The R_s value was important for the rate of convergence as illustrated in Fig. 2.7.

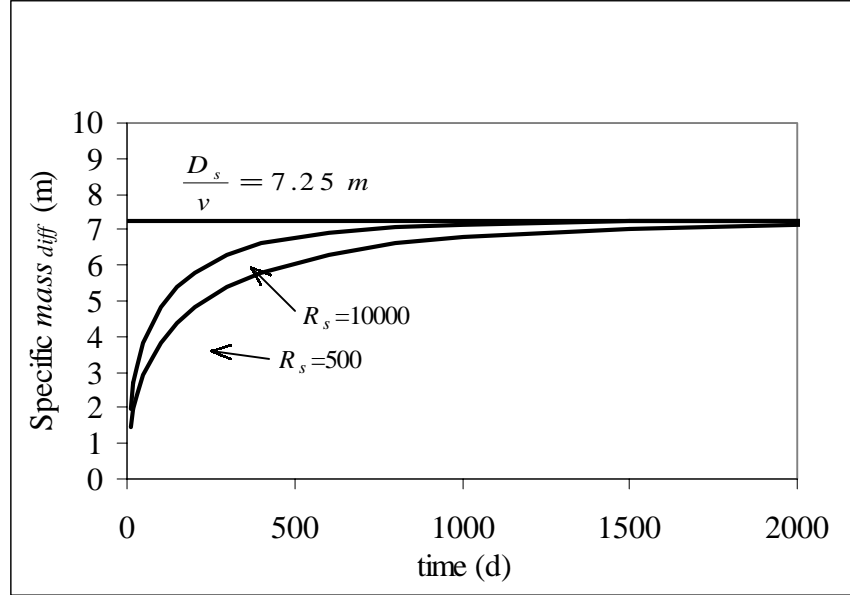


Figure 2.7 The convergence of the specific mass_{diff} for two different R_s values. $D_s=4,5 \cdot 10^{-10} \text{ m}^2/\text{s}$ and $v=2 \text{ mm/year}$.

From this analysis the following ratio can be defined using Eqs. 2.14, 2.19 and 2.20:

$$Ratio_{diff} < \frac{\text{specific mass}_{diff} \text{ for } t \rightarrow \infty}{\text{specific mass}_{diff} \text{ for } t + \text{Specific mass}_{dep}} = \frac{1}{1 + \frac{v^2 \cdot R_s \cdot t}{D_s}} = \frac{1}{1+B}, \text{ for } B \equiv \frac{v^2 \cdot R_s \cdot t}{D_s} \quad 2.21$$

where the parameter $Ratio_{diff}$ is smaller than the *maximum* ratio of substance mass in the sediment which can be attributed to diffusion. e.g. If the $Ratio_{diff}$ value is 0.1 then the diffusion mechanism will account for less than 10% of the total substance mass in the sediment at the time value t . B is a characteristic dimensionless parameter. The B factor will also be identified as characteristic in the next paragraph. If the time scales under consideration is so large that the Eq. 2.21 predicts the influence from diffusion to be negligible then it will be possible to neglect diffusion in the model for sediment water exchange because the deposition of solids will dominate.

2.3 Constant emission of substance to the water phase

The dissolved substance concentration in the water column was assumed to be constant in the above section, while in reality it may be more realistic to assume the emission of substance to the water compartment to be constant in time. In this case the dissolved water concentration ($C_{w,diss}$)

may change with time. In this case initially the flux into the sediment due to diffusion will be equal to the emission into the water, while in case of constant $C_{w,diss}$ value the initial $Flux_{diff}$ will be infinite. However, it seems more difficult to perform an analytical solution of Eq. 2.5 based on the assumption of constant emission compared to the previously solution (Eq. 2.7), where the $C_{w,diss}$ value was assumed constant. Therefore, a more approximately method using the thin layer diffusion assumption will be used to replace the differential equation Eq. 2.5.

The basic assumption in this theory is that the substance is transported though a layer having neither accumulation nor degradation. The space average of the $Flux$ value ($Flux_{av}$) within the layer at any time will be (Using Eq. 2.1):

$$Flux_{av} = \frac{1}{L} \cdot \int_0^L Flux \, dx = \frac{1}{L} \int_0^L D \frac{\partial C_{diss}}{\partial x} \, dx = \frac{D}{L} \int_{C_1}^{C_2} dC_{diss} = \frac{D}{L} (C_1 - C_2) \quad 2.22$$

where C_1 and C_2 are the upper and lower boundary value (just above and below the layer) respectively, for the dissolved concentration. Eq. 2.22 may seem surprising since a simple relationship for the spatial average flux is identified independently of the actual variation in the C value within the layer. This equation will always be true also in cases where the change in concentration values within the film is non-linear.

If no accumulation takes place in the layer then the amount of substance entering the film will be equal to the amount leaving and therefore, the flux will have the same value independently of distance within the layer. If the diffusion and retardation coefficient are assumed constant then a constant flux though the layer will give a constant concentration gradient which again yields a linear concentration profile. In this case the flux though the entire layer will be equal to the average flux given by Eq. 2.22.

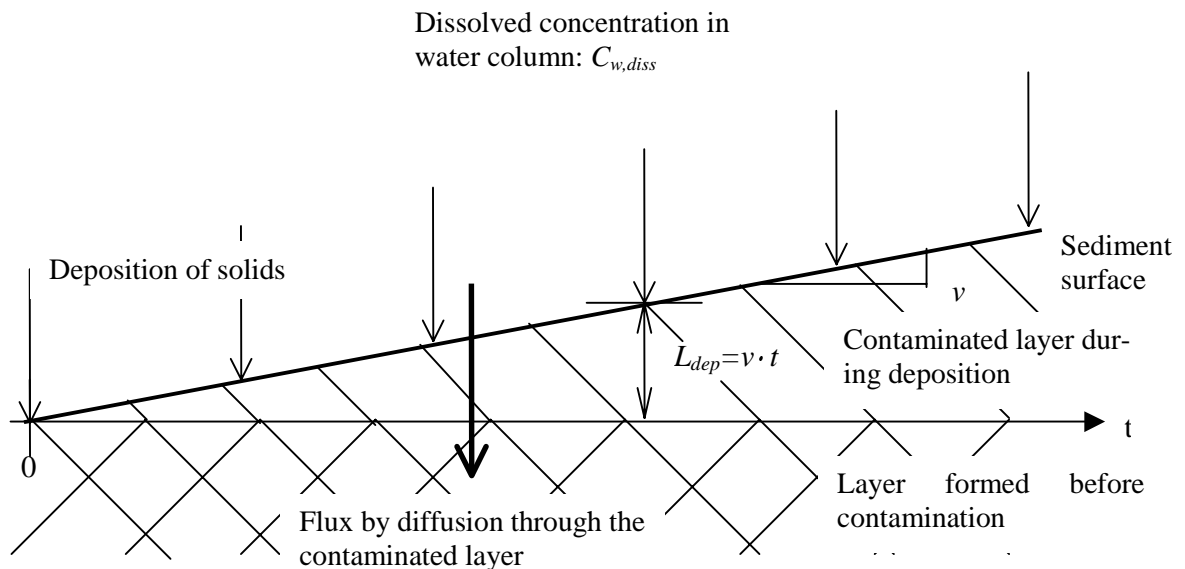


Figure 2.8 Formation of sediment as a result of deposition. The emission starts at $t=0$, the formed sediment subsequently being contaminated with substance. The thick arrow illustrates the diffusion pathway for substance to diffuse from the water column into the non-contaminated sediment.

The maximum *Flux* from the water column into the old sediment layer formed before the contamination took place can be calculated using the thin layer assumption (Eq. 2.22) for the new sediment layer (formed after contamination), where the substance concentration at the interface between the new sediment layer and old sediment ($C_{s,diss,x'=Ldep}$) is assumed to be negligible compared to $C_{w,diss}$ ($C_{w,diss} - C_{s,diss,x'=Ldep} \approx C_{w,diss}$) as

$$Flux_{max,diff} = \frac{D}{L_{dep}} \cdot C_{w,diss} = \frac{D}{v \cdot t} \cdot C_{w,diss} \quad 2.23$$

This equation describes the maximum possible value for two reasons: (1) The substance concentration at the interface between the newly formed and old sediment is assumed to be negligible compared to $C_{w,diss}$ ($C_{w,diss} - C_{s,interface} \approx C_{w,diss}$) and (2) All the substances which is transferred into the old sediment layer by diffusion comes from the water column and not from the newly formed sediment layer, which is a result of using the thin layer diffusion theory. The mass accumulation in the water column is assumed negligible so the total *Flux* entering the sediment by both diffusion and sedimentation is equal to the emission E (Mass/(m²·s)) defined as the total emission to the system divided by the sediment/water interface area. This gives the following relationship:

$$E = Flux_{max,diff} + Flux_{dep} \quad 2.24$$

where $Flux_{dep}$ is given by Eq. 2.14. The Eqs. 2.14, 2.23 and 2.24 is combined in order to find $C_{w,diss}$ as a function of time:

$$C_{w,diss} = \frac{E}{v \cdot R_s + \frac{D_s}{v \cdot t}} \quad 2.25$$

The total mass taken up from the water column by diffusion can now be calculated (overestimated) by combining Eqs. 2.23 and 2.25 and integrating with respect to time as

$$mass_{max,diff} = \frac{D_s \cdot E}{v^2 \cdot R_s} \ln \left(\frac{v^2 \cdot R_s \cdot t + D_s}{D_s} \right) \quad 2.26$$

where $mass_{max,diff}$ is an over estimation (max value) of the mass in the sediment attributed to diffusion. The total mass which has entered the sediment during the time t is simply $E \cdot t$ so the mass fraction between the $mass_{max,diff}$ and the total mass is

$$\frac{mass_{max,diff}}{mass_{total}} = \frac{mass_{max,diff}}{E \cdot t} = \frac{1}{\frac{v^2 \cdot R_s}{D_s} \cdot t} \cdot \ln \left(\frac{v^2 \cdot R_s}{D_s} \cdot t + 1 \right) = \frac{1}{B} \cdot \ln(B + 1) \quad 2.27$$

where B is defined in Eq. 2.21. Now two equations exist for determination of the substance mass fraction in the sediment due to diffusion (Eqs. 2.21 and 2.27) and both of them overestimate the actual influence from diffusion where E is constant. The best equation to select of these two is

the one, which is associated with the smallest over estimation of the actual mass ratio. Thus, the best choice between the two equations is to select the equation, which predicts the *mass* fraction to be smallest because both of them make an overestimation. The fact that both equations depends on B as the only variable makes this choice easy and a mass fraction calculated using Eq. 2.21 will always represent the smallest value. Thus, Eq. 2.21 is preferable to use although the governing assumption for the equation is a constant water concentration and not a more realistic constant emission to the system.

2.4 Steady-state including degradation in the sediment

It should be remembered that the degradation was neglected in the basic differential equation in this analysis (Eq. 2.5). Therefore, the calculation overestimates the sediment concentration especially after longer time periods. The differential equation including degradation is rather difficult to

solve analytically for the non steady-state situation where $\frac{\partial C_{s,diss}}{\partial t} \neq 0$. In

this case a numerical solution has been made by *Vikelsøe et al. (2001)*. In the steady-state solution the time changes is zero and the partial differential equation is reduced to a ordinary differential equation with respect only to x' (and not both x' and t). The solution of this equation becomes (*Vikelsøe et al. 2001*):

$$C_{s,diss} = C_{w,diss} \cdot e^{\left(\frac{v \cdot R_s}{2 \cdot D_s} - \sqrt{\left(\frac{v \cdot R_s}{2 \cdot D_s} \right)^2 + \frac{k_1}{D_s}} \right) x'} \quad 2.28$$

Where k_1 is the first order degradation coefficient with respect to the dissolved concentration.

The equation for the steady-state diffusive flux into the sediment is derived by differentiation of Eq. 2.28 (for $x'=0$) combined with Eq. 2.8 as

$$Flux_{diff} = -\frac{1}{2} \cdot C_{w,diss} \cdot v \cdot R_s \cdot \left(1 - \sqrt{1 + \frac{4 \cdot D_s \cdot k_1}{v^2 \cdot R_s^2}} \right) \quad 2.29$$

The ratio between the flux only attributed to diffusion ($Flux_{diff}$) and the total flux as a result of both diffusion and deposition of solids is calculated by using the Eqs. 2.14 and 2.29 as

$$Ratio_{Flux,steady} = \frac{Flux_{diff}}{Flux_{dep} + Flux_{diff}} = \frac{\sqrt{1+G} - 1}{\sqrt{1+G} + 1}, \text{ for } G = \frac{4 \cdot k_1 \cdot D_s}{v^2 \cdot R_s^2} \text{ or } G \equiv \frac{4 \cdot \ln 2 \cdot D_s}{v^2 \cdot R_s \cdot T_{1/2}} \quad 2.30$$

where the characteristic dimensionless G parameter is defined both in relation to k_1 and in the relation to the degradation half life time in the sediment $T_{1/2}$. The following key value comes out of Eq. 2.30: The transfer is dominated by deposition ($Ratio_{Flux,steady} < 0.5$) when $G < 8$ and dominated by diffusion ($Ratio_{Flux,steady} > 0.5$) when $G > 8$. The G parameter determines the flux ratio at steady-state after a sufficient long time period.

2.5 The importance of the laminar film at the sediment/water interface

Direct contact between the pore water in the sediment and the water column at the sediment surface has been assumed in the derived equations. However, it is well known that a laminar film will exist at the interface between the water column and the sediment. This film may cause an additional resistance for the transfer of substance, and diffusion equations in which this is neglected (Eq. 2.9) will thus over estimate the transfer by diffusion into the sediment. The laminar film will not affect the transfer of substance due to deposition of solids on the sediment surface, so, this film is only important in cases where the diffusion is identified as the dominating mechanism for substance transfer.

The *Flux* crossing the laminar film can be calculated using Eq. 2.22 and by assuming no accumulation and chemical transfer (e.g. degradation) within the film. The resulting equation is:

$$Flux_{lam\ film} = \frac{D_w}{L_w} \cdot (C_{w,diss} - C_{s,diss}|_{x'=0}) \quad 2.31$$

where D_w is the diffusion coefficient in the laminar film, L_w is the film thickness and $C_{s,diss}|_{x'=0}$ is the dissolved concentration in the sediment pore water at the sediment surface ($x'=0$). A critical parameter for the $Flux_{lam\ film}$ is seen to be the laminar film thickness, which depends on the actual hydrodynamic conditions. An equation is derived in Appendix B to estimate the L_w value and the conclusion is that the laminar film thickness L_w is inverse proportional to the spatial mean water velocity in the water column (V). Thus Eq. 2.31 combined with the results in Appendix B predicts the actual $Flux_{lam\ film}$ value to be directly proportional to V . In cases where the laminar film thickness in general can be the controlling factor for the sediment uptake there may still be time windows where the water velocity is so high due to tidal movements and wind friction that the sediment uptake happens without any inhibition from the laminar film. Due to the strong non-linear behavior of the diffusion flux into the sediment a relative small time period of high water velocity may be enough to ensure a nearly unaffected transport of substance into the sediment when the total transfer of substance mass is considered.

The existence of the laminar film will inhibit the diffusion keeping the flux due to deposition unaffected. Thus, the influence of diffusion will be over estimated when equations, where the laminar film is neglected are used. This will result in safe conclusions in cases where the diffusion is predicted to be insignificant. The main purpose of this part of the investigation is to identify when the Diffusion is insignificant. So, the laminar film will be neglected due to the following two reasons: (1) The laminar film is highly dynamic and difficult to interpret. (2) The predictions will still be valid when the diffusion is determined to be insignificant.

3 The one box sediment description of diffusive transport

In this chapter the diffusive transfer as described in the generic compartment models (*Mackay, 1991*) will be related to the basic equations derived in chapter 2. In the one box sediment description the sediment/water exchange by diffusion is described as two first order transfers: A transport from the water to the sediment and a transfer from the sediment to the water. This yields the following equation for the transport, where the notation for the coefficients are equivalent to SimpleBox as presented by *Brandes et al. (1996)*:

$$Flux_{diff, box} = XCH_{water-sed} \cdot C_{w,diss} - XCH_{sed-water} \cdot C_{s,tot} \quad 3.1$$

where $XCH_{water-sed}$ and $XCH_{sed-water}$ are the first order coefficient for the transport from the water column to the sediment and the transport from the sediment to the water column, respectively. In this investigation the $Flux_{diff, box}$ is considered to be per unit sediment surface area (equal the flux (Mass/m²·s)) so the XCH coefficients are described as

$$XCH_{water-sed} = \frac{kws_{water} \cdot kws_{sed}}{kws_{water} + kws_{sed}} \quad 3.2$$

where. Eq. 3.2. is based on a two film diffusion description, where the transport into the sediment is assumed to happen though two layer of resistance: One layer in form of the laminar water film at the sediment/water column interface and another layer in form of the sediment layer it self. The sediment thickness is defined to be 3 cm. The release from the sediment to the water column is described as

$$XCH_{sed-water} = \frac{XCH_{water-sed}}{R_s} \quad 3.3$$

The transfer coefficients kws_{water} and kws_{sed} can be explained by the so-called thin film diffusion theory. The basic assumption in this theory is that the substance is transported though the film having neither accumulation nor degradation in the film. If the transport is assumed diffusive and the diffusion coefficient constant in the film, the concentration change through the film will be linear as discussed at Eq. 2.22. Thus, in this case the flux though the entire film will be equal to the average flux given by Eq. 2.22 and the mass transfer coefficient becomes

$$kws = \frac{D}{L} \quad 3.4$$

The system is illustrated in Fig. 3.1.

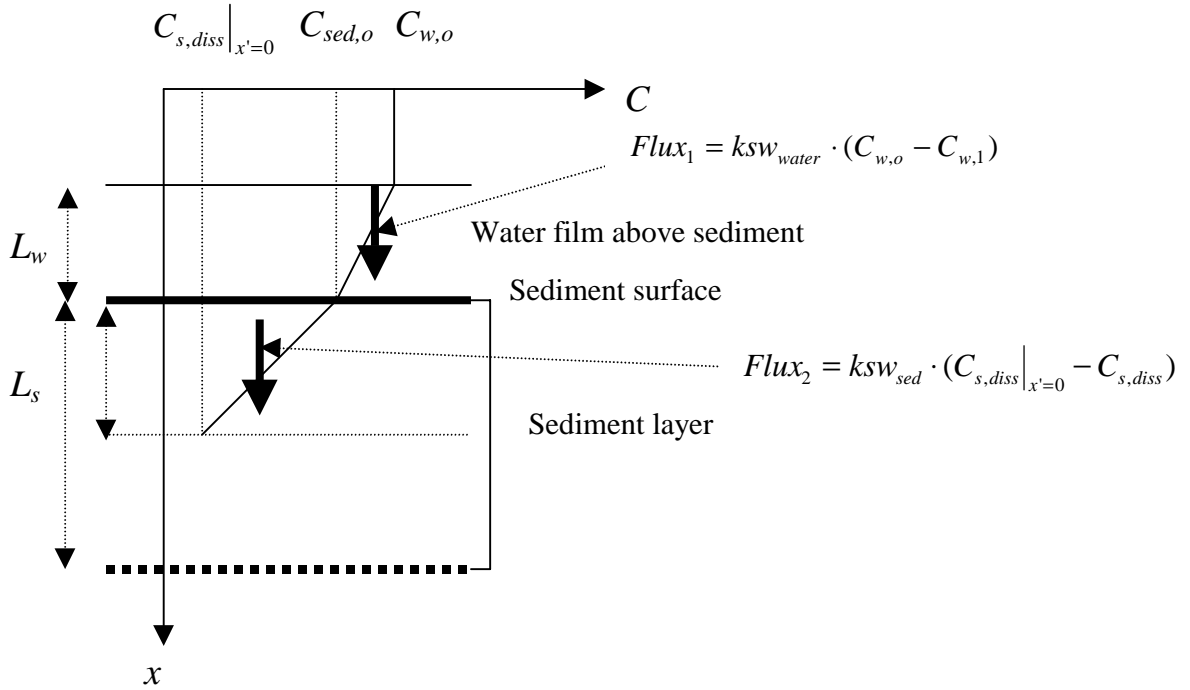


Figure 3.1 Schematic illustration of the sediment/water transfer description. L_w and L_{sed} are the thickness of the water film and the diffusion length in the center of the sediment layer, respectively. $Flux_1$ and $Flux_2$ are the flux of substance ($Mass/m^2s$) through the water film and to the center of the sediment layer, respectively.

Having no accumulation in the transporting films the fluxes $Flux_1$ and $Flux_2$ in Fig. 3.1 will be equal and the exchange between water column and sediment can be calculated as

$$\begin{aligned}
 Flux_1 = Flux_2 &\Leftrightarrow C_w - C_{s,diss} = Flux_1 \cdot \left(\frac{1}{kws_{water}} + \frac{1}{kws_{sed}} \right) \\
 \Leftrightarrow Flux_1 &= \frac{kws_{water} \cdot kws_{sed}}{kws_{water} + kws_{sed}} \cdot C_w - \frac{kws_{water} \cdot kws_{sed}}{kws_{water} + kws_{sed}} \cdot C_{s,diss}
 \end{aligned} \tag{3.5}$$

where the dissolved substance concentration at the sediment center ($C_{s,diss}$) is related to the total sediment concentration ($C_{s,tot}$) by the retention factor as

$$C_{s,tot} = R_s \cdot C_{s,diss} \tag{3.6}$$

For the water film Eq. 3.4 combined with the equation for $Flux_1$ in Fig. 3.1 yields

$$kws_{water} = \frac{D_w}{L_w} \tag{3.7}$$

where D_w is the diffusion coefficient in the water (m^2/s) and L_w is the laminar water film thickness (m) as illustrated in Fig. 3.1. The numerical value of kws_{water} is estimated in *Brandtes et al. (1996)* to be $2.778 \cdot 10^{-6}$ m/s and the value is assumed constant for all substances neglecting substance

related differences in the D_w value. A numerical value for ksw_{water} as $2.778 \cdot 10^{-6}$ m/s and a value for D_w as $5 \cdot 10^{-10}$ m²/s, which is estimated as a value for a larger molecule in Fig. 4.2, yields a water film thickness above the sediment (L_w) of about 0.2 mm. This value is related to a spatial mean water velocity (V) around 10 cm/s in Fig. B.1 (Appendix B). However, as discussed in Chapter 2, the actual L_w value may vary with time.

For the sediment an equation for the mass transfer coefficient is derived by combining Eq. 3.4 and the equation for $Flux_2$ in Fig. 3.1 as

$$kws_{sed} = 2 \cdot \frac{D_s}{L_s} \quad 3.8$$

where D_s is the effective diffusion coefficient in the sediment and L_s is the thickness of the sediment layer as illustrated in Fig. 3.1. The values of the two diffusion coefficients D_w and D_s may not be equivalent because of the increased travelling lengths in the pore system in the sediment. *Mackay et al. (1992)* suggested the following relationship between the two values: $D_s = D_w \theta^{1.5}$, where the porosity θ in the sediment is estimated to be 0.5. This gives the following numerical value: $D_s = 0.35 \cdot D_w$. In *Brandes et al., (1996)* a numerical value for kws_{sed} is assumed to be $2.778 \cdot 10^{-8}$ and the length to the center of the sediment box (L_s) is assumed to be 2 cm. These value for ksw_{sed} and L_{sed} leads to an D_s value of $2.778 \cdot 10^{-10}$ m²/s using Eq. 3.8. The assumed distance to the center of the sediment layer (2 cm) seems large compared to the total sediment thickness used in the same model (3 cm). In this analysis the distance to the center of the sediment layer is assumed to be half of the sediment thickness and equal to 1.5 cm. If the kws_{sed} value is fixed then a change in L_s value from 2 cm to 1.5 cm will induce a change in the estimated D_s value from $2.778 \cdot 10^{-10}$ m²/s to about $2.1 \cdot 10^{-10}$ m²/s. An actual value for D_s of about $2 \cdot 10^{-10}$ m²/s is in agreement with the use of $D_s = 0.35 \cdot D_w$ in combination with a value for D_w as $5 \cdot 10^{-10}$ m²/s. The kws_{sed} is assumed to be constant for all substances.

The kws_{water} value is 100 times higher compared to the kws_{sed} value, which makes it possible to simplify the Eq. 3.2 and thereby Eq. 3.3 as

$$XCH_{water-sed} \approx kws_{sed} \quad 3.9$$

$$XCH_{sed-water} \approx \frac{kws_{sed}}{R_s} \quad 3.10$$

Thus, the values selected by *Brandtes et al. (1996)* for the mass transfer coefficients, where the kws_{water} value is much larger than the kws_{sed} value removes the laminar water film at the sediment surface as important for the transfer.

An important conclusion from this analysis is that the rate of uptake by diffusion is independent on hydrophobicity and constant for all substances. This seems to conflict with the general tendency for a hydrophobic substance to enter the sediment at a higher rate compared to a more hydrophilic substance. The storage capacity in the sediment is related to

the hydrophobicity because the retardation factor R_s reduces the release from the sediment to the water (e.g. Eq. 3.3). Thus hydrophobic substances will tend to accumulate in the sediment but the rate of which it enters the sediment by diffusion is not affected by the hydrophobicity. This will be investigated in more detail by comparing this sediment box approach to a full description of sediment exchange by diffusion.

4 The discrepancy introduced in relation to the diffusive transfer by the one box sediment layer approximation

Only the diffusive flux is investigated because in this case the sediment box approximation differs from the more complete diffusion model forming a concentration profile in the sediment. The analysis will be divided up in two parts: (1) A transient situation where the sediment contamination changes during time. (2) A steady-state situation where the substance *Flux* in to the sediment equals the degradation. As the deposition of solids on the sediment surface is neglected the burial of solids below the sediment box will also be neglected. So the purpose in this chapter is to evaluate the performance of the generic compartment model compared to a more complete description of diffusion. This is relevant for cases where the transfer is dominated by diffusion and not by deposition and the resulting burial mechanism.

4.1 Transient conditions

The system to be considered in the following is a water sediment system having a size of one area unit (1 m^2) and where the dissolved water concentration ($C_{w,diss}$) is assumed constant. The mass uptake to the sediment ($mass_{diff}$ in Mass/m^2) is calculated using both the one sediment box approach and a continuously diffusion description for the sediment. The degradation in the sediment is neglected as only the transport of substance is investigated.

A mass balance for a unit area of the sediment yields the relationship:

$$\frac{d \text{mass}_{diff}}{dt} = \text{Flux}_{diff} \quad 4.1$$

where Flux_{diff} is the diffusive rate of uptake to the sediment ($\text{Mass}/\text{m}^2\text{s}$) and defined as positive downward. The Flux_{diff} value can be either calculated using the one sediment box approach (Eq. 3.1) or by introducing a concentration profile in the sediment.

Combining the Eqs. 3.1, 3.3, 3.8 and 3.9 and 3.10 yields

$$\frac{d \text{mass}_{diff,box}}{dt} = \frac{2 \cdot D_s \cdot C_{w,diss}}{L_s} - \frac{2 \cdot D_s}{L_s^2 \cdot R_s} \cdot \text{mass}_{diff,box} \quad 4.2$$

where the mass of substance in the sediment is related to the concentration as $mass_{diff,box} = L_s \cdot C_{s,tot}$. This equation has the form

$$\frac{dy}{dt} = -a \cdot y + b$$

and the solution of this linear differential equation is

$$y = \frac{b}{a} + (y_o - \frac{b}{a}) \cdot e^{-at},$$

where y_o is the y value at $t=0$. In our specific

case where y is replaced by $mass_{diff,box}$ the corresponding y_0 value is zero yielding the final solution ($y = \frac{b}{a} \cdot (1 - e^{-at})$) as

$$mass_{diff,box} = C_{w,diss} \cdot L_s \cdot R_s \cdot \left(1 - e^{-\frac{2 \cdot D_s}{L_{sed}^2 \cdot R_s} t} \right) \quad 4.3$$

This equation gives the sediment contamination per unit sediment area ($Mass/m^2$) as a function of time and the corresponding $Flux_{diff}$ as a function of time is derived by the following equation upon differentiation of Eq. 4.3 with respect to time:

$$Flux_{diff,box} = \frac{2 \cdot C_{w,diss} \cdot D_s}{L_s} \cdot e^{-\frac{2 \cdot D_s}{L_{sed}^2 \cdot R_s} t} \quad 4.4$$

This equation predicts the $Flux_{diff,box}$ to be close to constant in the beginning. This is easy to see using a Taylor series: $e^u = 1 + u + \frac{u^2}{2!} + \frac{u^3}{3!} \dots$. Using the first term (1) from this series as an approximation for the exponential function in Eq. 4.4 the following equation is obtained

$$Flux_{diff,box} \approx \frac{2 \cdot C_{w,diss} \cdot D_s}{L_s} \quad 4.5$$

where the $Flux_{diff,box}$ is seen to be constant independently on the R_s value (hydrophobicity). The Taylor series can be used to identify the time period in which Eq. 4.5 is valid. As the time progress the u value in the Taylor series above will increase and thus the higher order terms will tend to be more and more important. A critical u value will exist above which the “1” part of the series will be insufficient as an approximation for the exponential function. In this analysis the critical u value (u_{cr}) is defined to the value for which $u_{cr}=0.1$. Thus, when u is below u_{cr} then the first order term (u) in the Taylor series will have a value which is smaller than 10 % of the value for the zero order term (1). Using this value the constant $Flux_{diff,box}$ relationship as predicted by Eq. 4.5 is close to be valid as long as the exponent in Eq. 4.4 is below 0.1. From this condition the critical time period is derived as

$$t_{cr} = \frac{L_s^2}{20 \cdot D_s} \cdot R_s = \frac{(0.03 \text{ m})^2}{20 \cdot 2 \cdot 10^{-10} \text{ m}^2 / \text{s}} \cdot \frac{1}{3600 \text{ s} / \text{h} \cdot 24 \text{ h} / \text{d}} \cdot R_s \approx 2.6 \text{ d} \cdot R_s \quad 4.6$$

where the unit for t_{cr} is days and the values used are taken from *Brandes et al., (1992)* including the modification of the diffusion path length from 2 cm to 1.5 cm as discussed above. The prediction from this equation can be interpreted as the time period after which the rate of substance released from the sediment to the water column starts to have some degree of significance. At the time below this critical value the first term on the right hand side of Eq. 3.1 dominates while the second term may have some significant importance at later time values. The t_{cr} is seen to be very large, in the magnitude of many years, for hydrophobic substances where the R_s value easily exceeds 10000. It seems strange that the model predicts the rate of uptake to the sediment by diffusion to be constant and independent on the hydrophobicity for time period as long as this.

The sediment box approach for describing the sediment water column exchange will be further evaluated using an alternative diffusion model where the concentration profile is taken into account for the sediment layer.

The mass of substance per unit area transferred by diffusion and calculated without using the one box approach can be determined as the time integral of the equation of substance flux. If the deposition of solids is neglected ($v=0$) Eq. 2.11 replaces Eq. 2.9. Upon integrating the resulting equation for the mass per unit area becomes:

$$mass_{diff, v=0} = 2 \cdot C_{w,diss} \cdot \sqrt{\frac{R_s \cdot D_s \cdot t}{\pi}} \quad 4.7$$

where $mass_{diff, v=0}$ is the mass of substance per unit sediment area (Mass/m^2) calculated using the equations for the diffusion profile and neglecting the deposition of solids at the sediment surface. The ratios between the mass per unit area calculated using respectively the sediment box equation (Eq. 4.3) and the diffusion profile equation (Eq. 4.7) is:

$$\frac{mass_{diff, box}}{mass_{diff, v=0}} = \frac{L}{2} \cdot \sqrt{\frac{\pi \cdot R_s}{D_s \cdot t}} \cdot \left(1 - e^{-\frac{2 \cdot D_s \cdot t}{L_s^2 \cdot R_s}} \right) \quad 4.8$$

This equation predicts the mass ratio to vary as a function of time, however, it is difficult to make any general conclusion about this behavior from this equation because the time (t) is both in the denominator and in the exponent.

An analysis using the Taylor series $e^u = 1 + u + \frac{u^2}{2!} + \frac{u^3}{3!} \dots$, where the first two terms ($1+u$) are used for the exponential function yields

$$\frac{M_{s, box}}{M_{s, profile}} \approx \frac{1}{L_s} \cdot \sqrt{\frac{\pi \cdot D_s \cdot t}{R_s}} \quad 4.9$$

Using Eq. 4.9 it is possible to conclude that the mass ratio is zero initially and increases proportional to the square root of time. Thus, the box description predicts a mass radically smaller compared to the prediction using the profile description. Eq. 4.9 is only approximately for a first time period, whereas Eq. 4.8 predicts the ratio to approach zero for longer time periods, which again is a consequence of the fact that no degradation nor burial are involved in this analysis. With out burial in the box description the substance can only accumulated in the upper 3 cm of the sediment layer, while the diffusion profile model allows the diffusion to take place into deeper parts of the sediments.

Using specific values for DEHP as suggested by *Vikelsøe et al. (2001)*: $R_s=10600$, $D_s=2 \cdot 10^{-10} \text{ m}^2/\text{s}$ and a L_s as 1,5 cm, the two $mass$ values using the sediment box approach and the diffusion equation, respectively, are shown in Fig. 4.1. In Fig. 4.1 the diffusion equation is seen to predict a much larger mass compared to the on sediment box model during the first many years and the sediment box model seems basically insufficient to describe the diffusive flux into the sediment using the thin layer diffusion approximation.

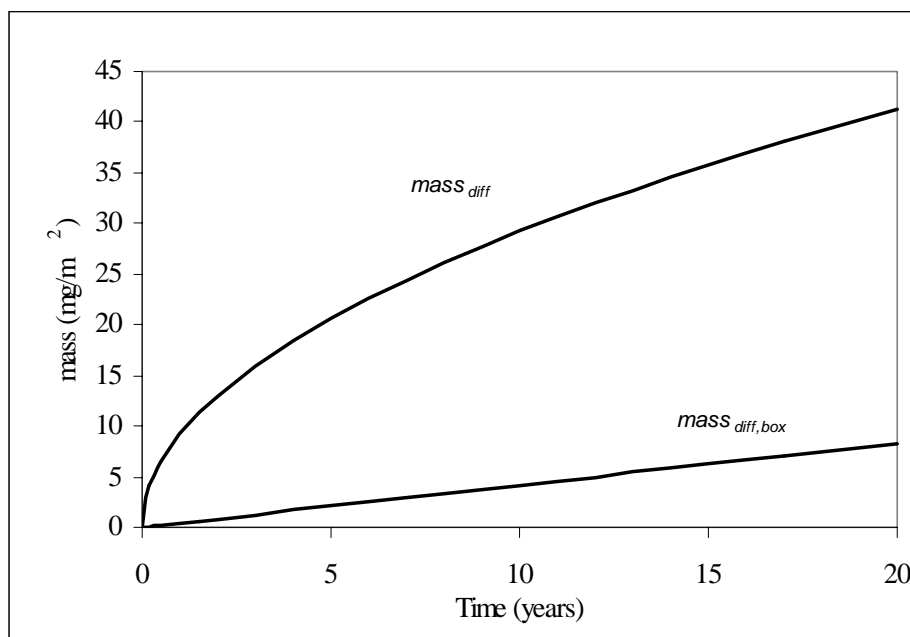


Figure 4.1 The calculated sediment content (DEHP) using both the Box description and the description based on a concentration profile in the sediment.

The parameter for DEHP can also be used to investigate the relative difference between the two models as described by Eqs. 4.8 and 4.9, see Fig. 4.2.

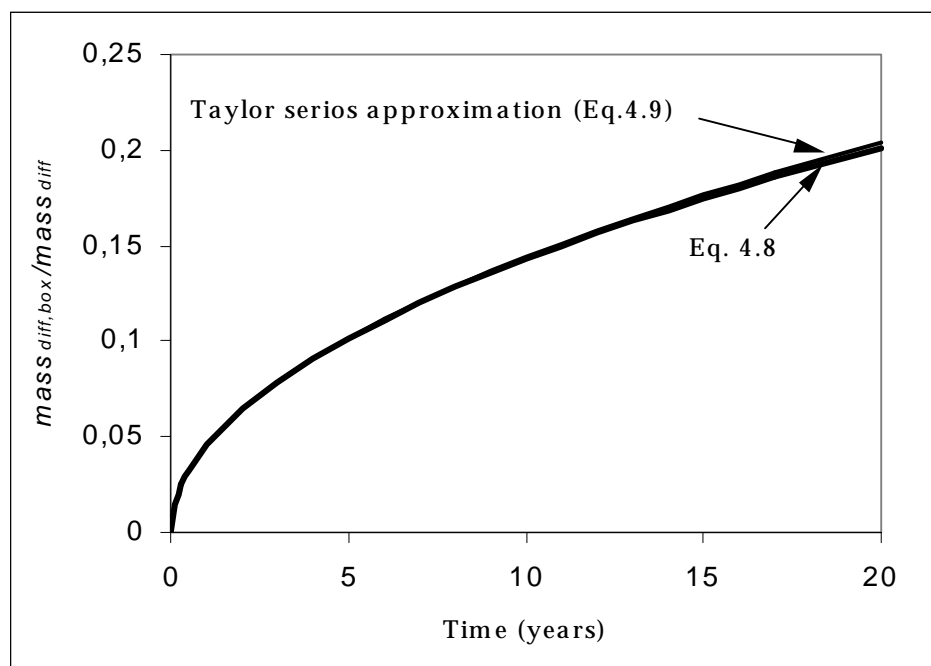


Figure 4.2 The mass ratio per m^2 sediment area (DEHP) between the box model and the model based on a concentration profile in the sediment (Eq. 4.8). The Taylor approximation (Eq. 4.9) is also shown.

4.2 Steady-state conditions

The preview section investigated transient sediment uptake while this section will consider a situation where steady-state exists. Steady-state sediment content will take place when the degradation processes in the sediment balances the net flux to the sediment. In this situation no further accumulation in the sediment is possible. This investigation is relevant for the steady-state calculations in the sediment box approach. A first order degradation relationship will be assumed. As in the preview section only the transfer due to diffusion will be considered.

As a simple case study a water sediment system is considered and illustrated in Fig. 4.3, where a constant rate of substance is introduced to the water (emission to the water body).

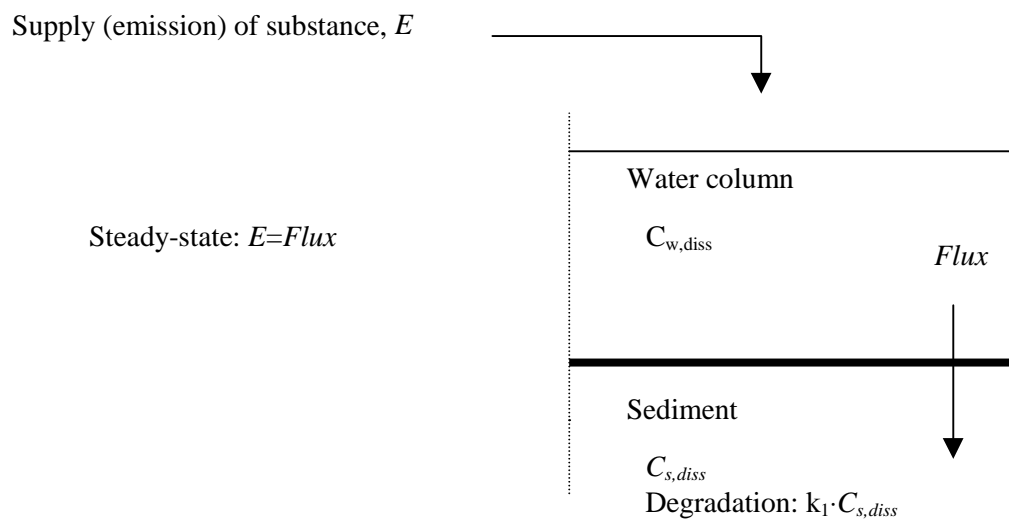


Figure 4.3 The case study system, where a water column of unit area receives substance at a constant rate and interacts with a sediment in where first order degradation takes place. The flux into the sediment needs to be equal the rate of supply at steady-state.

The concentration in the water column will increase during time and approach a steady-state concentration. The question is how a sediment box approach will determine the steady-state concentration compared to a sediment concentration profile model. First the equation for steady-state will be derived for both types of models and then calculation will be performed to compare them.

In the one sediment box approach the degradation in the sediment layer is given as

$$Degradation = k_1 \cdot C_{s,diss} \cdot L_s \quad 4.11$$

where k_1 is the first order degradation coefficient with respect to the dissolved concentration (1/s). The substance flux is described as $Flux_2$ in Fig. 3.1, which can be combined with Eq. 3.8 to form

$$Flux_{diff,box} = \frac{D_s}{L_s} \cdot (C_{w,diss} - C_{s,diss}) \quad 4.12$$

At steady-state the substance flux into the sediment is equal to the degradation, so these two equations can be set equal to each other in order to calculate the steady-state sediment concentration as

$$C_{s,diss,steady} = \frac{C_{w,diss} \cdot D_s}{k_1 \cdot L_s^2 + D_s} \quad 4.13$$

At steady-state the emission to the system is equal to the degradation (Eq. 4.11). Thus, Eq. 4.12 can be rewritten using Eq. 4.11 and the relationship $E=Flux_{diff}$ as

$$C_{w,diss,steady,box} = E \cdot \left(\frac{L_s}{D_s} + \frac{1}{k_1 \cdot L_s} \right) \quad 4.14$$

where $C_{w,diss,steady,box}$ is the steady-state water concentration as calculated using the sediment box approach. When a concentration profile in the sediment is considered the degradation processes have to be included in the basic differential equation so Eq. 2.5 must be extended by a first order degradation term as

$$\frac{\partial C_{s,diss}}{\partial t} = \frac{D_s}{R_s} \cdot \frac{\partial^2 C_{s,diss}}{\partial x'^2} - \frac{k_1}{R_s} \cdot C_{s,diss} \quad 4.15$$

where the deposition is neglected ($v=0$). At steady-state the left hand side of this equation will be zero leaving a ordinary second order differential equation with respect to the distance (x') from the sediment surface.

$$\frac{d^2 C_{s,diss}}{dx'^2} - \frac{k_1}{D_s} C_{s,diss} = 0 \quad 4.16$$

This equation is solved using a standard method for solving ordinary differential equations and the solution is

$$C_{s,diss,steady} = C_{w,diss,steady} \cdot e^{-\left(\sqrt{\frac{k_1}{D_s}}\right)x'} \quad 4.17$$

This equation describes the steady-state concentration profile which will be formed in the sediment after a period long enough to establish steady-state, where the degradation is balancing the diffusion. The equation for $Flux_{diff}$ is derived using Eqs. 2.8, 4.17 and the steady-state condition, where $Flux_{diff}$ equals the emission E . This yields an expression by which $C_{w,diss,steady}$ can be calculated when E is known:

$$C_{w,diss,steady} = \frac{E}{\sqrt{k_1 \cdot D_s}} \quad 4.18$$

The sediment box approach and the concentration profile type of model come up with two different equations for the steady-state water column concentration. The difference can be calculated as the ratio between re-

spectively Eqs. 4.14 and 4.18, where Eq. 4.14 (SimpleBox type) is divided by Eq. 4.18 (Concentration profile type). The resulting equation for this ratio is

$$\frac{C_{w,diss,steady,box}}{C_{w,diss,steady}} = Ratio = \sqrt{k_1 \cdot D_s} \cdot \left(\frac{L}{D_s} + \frac{1}{k_1 \cdot L_s} \right) = G + \frac{1}{G} \quad 4.19$$

where

$$G \equiv L_{sed} \cdot \sqrt{\frac{k_1}{D_s}} \quad 4.20$$

The minimum value of the Ratio is easy to find using the differentiation of Eq. 4.19 as

$$0 = \frac{d \text{ Ratio}}{dG} = 1 - \frac{1}{G_{\min \text{ Ratio}}^2} \Rightarrow G_{\min \text{ Ratio}} = 1 \quad 4.21$$

Putting a G value of 1 into Eq. 4.19 gives a minimum *Ratio* of 2. Thus, the sediment box approach will always overestimate the dissolved water concentration at steady-state by a factor larger than two. However, this overestimation can easily be much higher depending on the actual values of G .

5 Discussion and Conclusion

It is shown how diffusion and deposition of solids drive the Flux of substance between the water column and the sediment. Initially when a substance starts to be present in the water column (start of emission) the diffusion will dominate the sediment uptake due to a large concentration gradients in the sediment surface. However, as the time progresses, the diffusion-induced flux will rapidly decrease, as the concentration gradients at the top of the sediment will level out because more substance enters the sediment layer. In contrast, the substance transfer due to deposition of solids will not display a high flux initially but rather a value, which is proportional to the dissolved water column concentration.

Assuming constant water concentration and neglecting degradation and the laminar boundary layer at the sediment/water column interface

It is shown how the Flux changes from diffusion dominance to dominance of deposition of solids and the time value for this change is calculated. The diffusive Flux is initially infinitely high, but decreases rapidly with time. The Flux due to deposition of solids will not display a high Flux initially but a constant value when the dissolved concentration is assumed constant. There exists no lower limit for the deposition rate of solids below which the diffusion will become the dominating factor at infinitely long time scales. Thus, there will always be a time value after which the Flux due to deposition of solids is the dominating factor. The only question is the actual time before this transition will occur. In a time period after which the Flux due to deposition has started to dominate, there will still be more substance mass in the sediment as a result of diffusion. The substance mass in the sediment due to deposition will first be larger than the corresponding mass due to diffusion after an additional time and a maximum value of this time period is calculated.

Assuming steady-state sediment concentration and negligible laminar boundary layer at the sediment/water column interface

The partial differential equation for the concentration profile in the sediment can be transformed to a simpler ordinary differential equation by assuming a steady-state concentration in the sediment. In this case a rather simple solution is possible also when the degradation is included in the equation. From this solution the ratio between the flux due to diffusion and deposition alone, respectively, can be calculated. This yields an estimate of the final importance for diffusion and deposition, respectively, after steady-state has been achieved in the sediment. An easy measure for the time scale needed for steady-state to become valid is the half-life time in the sediment ($T_{1/2}$). After a time period much longer than the half-life with constant substance emission into the system, steady-state will have been established in the sediment layer. At that time the sediment contamination will not depend on the full history of exposure any more.

Calculating the laminar boundary thickness

The thickness of the laminar boundary layer is calculated using basic hydraulic theory and rough estimates results from the calculation. The actual thickness is seen to be strongly (inverse) dependent of the spatial mean water velocity in the water column. Water velocities introduced to open waters (open marine areas, bays or greater lakes) by tidal water movements and wind friction will in most cases be able to reduce the laminar boundary layer thickness to a magnitude of 0.1 mm. This means that the diffusion resistance in the layer becomes rather unimportant, however, the temporal change in the thickness seems to be large due to temporal changes in water flow velocity.

General guide lines for concerning the importance of diffusion and deposition respectively

Some general guidelines are the result of the equations for the sediment/water exchange and they are presented in Fig. 5.1.

- Estimate the time scale (time step) of the transient calculation (days, months and years): t_{scale}
- Estimate the half-life time for degradation in the sediment: $T_{1/2}$

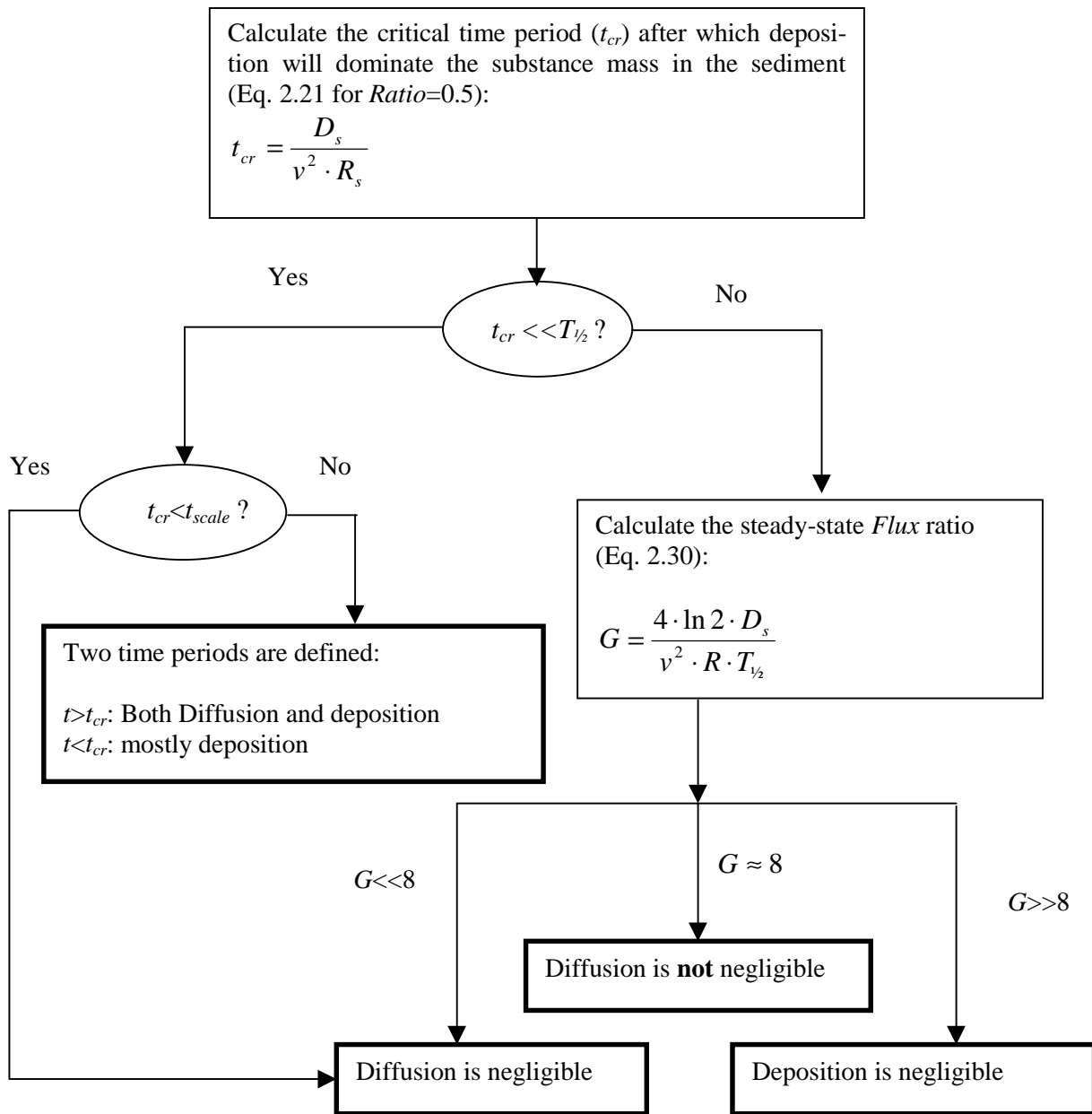


Figure 5.1 The decision rule scheme, which summarize the conclusion for the sediment uptake investigation.

In order to illustrate the use of the guide line numerical values are used from the investigation of DEHP (Vikelsøe *et al.*, 2001) in Fig.5.2. In this case the deposition is seen to be the dominating factor.

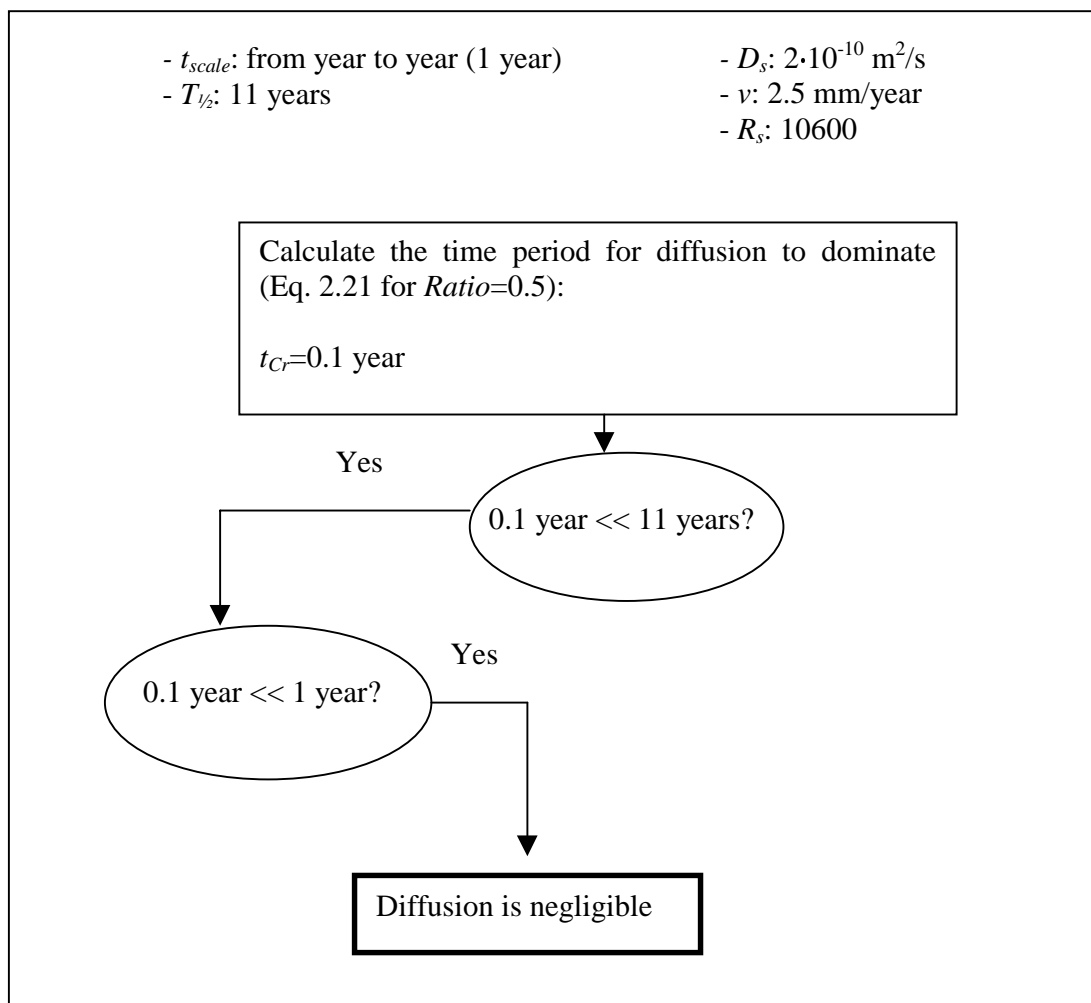


Figure 5.2 Use of the decision scheme in Fig. 5.1 using numbers for DEHP in a Danish bay (Roskilde Fjord) taken from Vikelsøe *et al.*, (2001). It relies on judgment how much one number needs to be larger than an other number before the << relationship is true. In case of fate modelling the uncertainty will typically be rather high and thus the << relationship can be considered to be true also for rather small differences.

Evaluation of the approach in the generic compartment models

The generic compartment models (Mackay type) use a one box model for the sediments in order to keep the calculations simple. However, when diffusion needs to be included in the calculation the one box approach needs to be evaluated in relation to a more complete solution of the differential equations for diffusion. The description of diffusive transfer is not well established in the sediment box model, where the nature of diffusion is damaged by using a mean transfer length for diffusion. In reality or as a result of the full solution of the governing equation for sediment diffusion the rate of substance transfer can be extremely high, as long the contamination in the sediment is limited. Contrary, the generic compartment model tends to have constant rate diffusion in the first time period for simulation. After a specific period the mean length approach becomes more valid, however, that time period can easily be in the magnitude of many years! In case of steady-state where the emission of substance into the system equals the sediment uptake by diffusion the one box approach

will always overestimate the dissolved water concentration compared to the more complete sediment description. Obviously the discrepancy in the diffusive transfer description will vanish as the transfer due to deposition of solids on the sediment surface starts to dominate in the total transfer of substance mass to the sediment. In many cases the deposition will dominate after a rather short time period and thus the concept in the generic compartment models will become acceptable simply because the diffusive transfer is negligible. Hence, the conclusion is that the one sediment box approach seems insufficient to include a realistic diffusion mechanism. However, in many cases the deposition and thus the burial from the sediment box of fixed thickness will become the dominating factor in the sediment/water column exchange of substance and in that case the inadequate description of diffusion will not be important.

The generic compartment models need to be mathematically simple in order to be usable as decision support and a more realistic description of the diffusive transfer into the sediment will introduce a rather high level of mathematical complexity. Thus, an appropriate suggestion could be simply to say that the generic compartment models are only valid when the diffusive description is negligible and otherwise more detailed models are necessary. The result in Fig. 5.1 gives the guidelines for when the diffusive transfer mechanism is negligible.

In this investigation the bio-turbation has been neglected, which may induce a vertical mixing of water and sediment solids. The effect of this is an increased substance transfer between the sediment and the water column. This can be considered as an enhanced diffusive transfer and included in the mathematical model as an additional contribution to the D_s value. This will increase the importance of the diffusive transfer and thus weaken the relevance of the sediment box approach. In case of high biological activity it may simply be possible to obtain reliable results by assuming the water column and the sediment layer to be in instant equilibrium.

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7 List of symbols

A	Dimensionless parameter defined by Eq. 2.15 (-).
B	Dimensionless parameter defined by Eq. 2.21 (-).
C_{diss}	Dissolved concentration ($\mu\text{g/l}$).
$C_{s,diss}$	Dissolved concentration in the sediment pores ($\mu\text{g/l}$).
$C_{s,diss,steady}$	Dissolved concentration in the sediment pores at steady-state conditions ($\mu\text{g/l}$).
$C_{s,diss,v=0}$	Dissolved concentration in the sediment pores having no deposition of solids on the sediment ($\mu\text{g/l}$).
$C_{s,diss,x'=L_{dep}}$	Dissolved substance concentration at the interface between the sediment layer formed by deposition during the period of contamination and the old sediment ($\mu\text{g/l}$).
$C_{s,tot}$	Total concentration per sediment volume ($\mu\text{g/l}$).
$C_{w,diss}$	Dissolved concentration in the water column ($\mu\text{g/l}$).
$C_{w,diss,steady}$	Calculated dissolved concentration in the water column at the steady-state conditions using the full diffusion equation ($\mu\text{g/l}$).
$C_{w,diss,steady,box}$	Dissolved concentration in the water column at steady-state conditions calculated using the generic compartment model ($\mu\text{g/l}$).
C_{tot}	The total substance concentration (dissolved and adsorbed) ($\mu\text{g/l}$).
D	Diffusion coefficient (m^2/s).
D_s	Diffusion coefficient in the sediment pores (m^2/s).
$D_{w,known}$	Known diffusion coefficient (m^2/s).
$D_{w,unknown}$	Unknown diffusion coefficient (m^2/s).
E	Emission of substance into the system per unity system area and per time unit ($\text{Mass}/(\text{m}^2 \cdot \text{s})$).
$Flux$	Substance flux ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{av}$	Average Flux ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{diff,benzen}$	Flux by diffusion estimated for benzen ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{dep}$	Substance flux due to deposition ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{diff}$	Substance flux by diffusion ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{diff,box}$	Substance flux by diffusion into the sediment box ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{diff,v=0}$	Substance flux by diffusion having no deposition of solids on the sediment surface ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{max,diff}$	Maximal possible flux due to diffusion (m^2/s).
$Flux_{diff,sub}$	Flux by diffusion for a specific substance ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
$Flux_{lam, film}$	Substance flux crossing the laminar film at the sediment/water column interface ($\text{Mass}/\text{m}^2 \cdot \text{s}$).
G	Dimensionless parameter for Eq. 2.30 (-)
K_d	Linear adsorption coefficient for the sediment ($1/\text{kg}$)
k_1	First order degradation coefficient with respect to the dissolved concentration ($1/\text{s}$).

kWS_{water}	The partial mass transfer coefficient at the water side of the sediment-water interface (m/s).
kWS_{sed}	The partial mass transfer coefficient at the pore water side of the sediment-water interface (m/s).
L	Fixed length (m).
L_{dep}	The thickness of the deposited layer during contamination (m).
L_s	The thickness of the sediment box in the generic compartment model (m).
L_w	The laminar film thickness at the sediment/water column interface (m).
$mass_{dep}$	Mass of substance per unit area in the sediment due to deposition (Mass/m ²).
$mass_{diff}$	Mass of substance per unit area in the sediment due to diffusion (Mass/m ²).
$mass_{diff,v=0}$	Calculated mass value assuming $v=0$
$mass_{max,diff}$	Over estimated mass of substance per unit area in the sediment due to diffusion (Mass/m ²).
MW	Molecular weight (g/mol).
MW_{benzen}	Molecular weight for benzene (g/mol).
MW_{known}	Molecular weight for a substance having a known D_s value (g/mol).
$MW_{unknown}$	Molecular weight for a substance having an unknown D_s value (g/mol).
O	Dimensionless parameter (Eq. 4.20) for the ratio between the generic model and the sediment profile model for the calculated dissolved concentration in the water column (-).
R_s	Retention factor (-).
$Ratio_{diff}$	Mass ratio of substance which can be attribute to diffusion (-).
$Ratio_{Flux,box}$	The ratio between the diffusive flux calculated using the sediment box approach and the diffusion profile description (-).
$Ratio_{Flux,steady}$	The ratio between the diffusive flux.
$specific\ Flux$	Flux of substance into the sediment relative to the dissolved concentration in the water column (m/s).
$specific\ mass$	Mass of substance per unit area in the sediment relative to the dissolved concentration in the water column (m).
t	Time (s).
$T_{1/2}$	Degradation half life time in the sediment (s)
U_f	Friction velocity (m/s)
v	The rate of increase in sediment height due to deposition of solids on the surface (m/s).
V	Mean horizontal velocity of the water column (m/s)
x	Distance (m).
x'	Downward distance form the sediment surface (m).
$XCH_{water-sed}$	First order mass transfer coefficients for the transfer of substance from the water column into the sediment (1/s).
$XCH_{sed-water}$	First order mass transfer coefficients for the transfer of substance from the sediment into the water column (1/s).

σ	Dry bulk density (kg/dm ³)
θ	Porosity or volumetric water content in the sediment(-)
ν	Kinematic viscosity (kg/(m·s))

Appendix A

The Equation to solve is

$$\frac{\partial C_{s,diss}}{\partial t} = \frac{D_s}{R_s} \cdot \frac{\partial^2 C_{s,diss}}{\partial x'^2} - v \cdot \frac{\partial C_{s,diss}}{\partial x'} \quad A.1$$

This equation is transformed into a more easy to solve equation using the transformation as

$$C_{s,diss} = w \cdot e^{\left(\frac{v \left(x' - \frac{v \cdot t}{2} \right) R_s}{2 \cdot D_s} \right)} \quad A.2$$

where w is defined to be an arbitrary function of x' and t . A combination of Eqs. A.1 and A.2 using the Chain Rule of differentiation yields

$$\frac{\partial w}{\partial t} = \frac{D_s}{R_s} \frac{\partial^2 w}{\partial x'^2} \quad A.3$$

The new boundary conditions for the w function are derived from the boundary conditions as Eqs. 2.6 a and b:

$$\left. \begin{aligned} w &= C_{s,diss} \cdot e^{-\frac{v \left(x' - \frac{v \cdot t}{2} \right) R_s}{2 \cdot D_s}} \quad \text{for } x' = 0 \Leftrightarrow w|_{x'=0} = C_{s,diss} \cdot e^{\frac{v^2 \cdot t \cdot R_s}{4 \cdot D_s}} \\ w &= 0 \quad \text{for } x' \rightarrow \infty \\ w &= 0 \quad \text{for } t = 0 \end{aligned} \right| \quad A.4$$

A Laplace transformation of Eq. A.3 yields the following ordinary differential equation:

$$\frac{D_s}{R_s} \cdot \frac{d^2 W}{dx'^2} = s \cdot W \quad A.5$$

where W is the Laplace transformation of w :

$$W \equiv \int_0^{\infty} e^{-s \cdot t} \cdot w dt \quad A.6$$

The boundary conditions described in Eq. A.4 also needs to be transformed using Eq. A.6 as

$$\left. \begin{aligned} W|_{x'=0} &= \frac{C_{s,diss}}{s - \frac{v^2 \cdot R_s}{4 \cdot D_s}} \\ w &= 0 \quad \text{for } x' \rightarrow \infty \end{aligned} \right| \quad A.7$$

Eq. A.5. is solved using the boundary conditions of Eq. A.7:

$$W = \frac{C_{s,diss}}{s - \frac{v^2 \cdot R_s}{4 \cdot D_s}} \cdot e^{-\sqrt{\frac{R_s \cdot s}{D_s}}} \quad A.8$$

The inverse transformation of Eq. A.8 to find w yields the solution of Eq. A.3 as

$$w = \frac{1}{2} \cdot C_{w,diss} \cdot e^{\frac{v^2 \cdot R_s}{4 \cdot D_s}} \left[e^{\frac{x' \cdot v \cdot R_s}{2 \cdot D_s}} \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} - v \cdot \sqrt{t} \right) \right) + e^{\frac{x' \cdot v \cdot R_s}{2 \cdot D_s}} \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} + v \cdot \sqrt{t} \right) \right) \right] \quad A.9$$

where erfc is a standard function called the complementary error function, which is defined as

$$\operatorname{erfc}(z) \equiv 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} \cdot d\eta \quad A.10$$

The equation for the dissolved substance concentration in the sediment as a function of depth and time is formed using Eqs. A.2 and A.9 as

$$C_{s,diss} = \frac{1}{2} \cdot C_{w,diss} \left[\operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} - v \cdot \sqrt{t} \right) \right) + e^{\frac{x' \cdot v \cdot R_s}{D_s}} \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} + v \cdot \sqrt{t} \right) \right) \right] \quad A.11$$

Differentiation of Eq. A.10 is needed in order to determinate the diffusive exchange of substance between the sediment and the water column. First we will differentiate the complementary error function (erfc). Using the so-called Leibnitz's Rule for differentiation of integrals Eq. A.10 is differentiated with respect to z as

$$\frac{d}{dz}(\operatorname{erfc}(z)) = -\frac{2}{\sqrt{\pi}} \cdot e^{-z^2} \quad A.12$$

Now Eq. A.11 can be differentiated using the relationship in Eq. A.12

and the chain rule ($\frac{d}{dx} \operatorname{erfc}(z) = \frac{d}{dz} \operatorname{erfc}(z) \cdot \frac{dz}{dx}$) as

$$\frac{\partial C_{s,diss}}{\partial x'} = \frac{1}{2} \cdot C_{w,diss} \cdot \left[\frac{v \cdot R_s}{D_s} e^{\frac{v \cdot R_s \cdot x'}{D_s}} \operatorname{erfc} \left(\frac{1}{2} \cdot \sqrt{\frac{R_s}{D_s}} \cdot \left(\frac{x'}{\sqrt{t}} + v \cdot \sqrt{t} \right) \right) - \sqrt{\frac{R_s}{D_s \cdot t \cdot \pi}} \cdot \left(e^{-\left(\frac{1}{2} \sqrt{\frac{R_s}{D_s}} \left(\frac{x'}{\sqrt{t}} + v \cdot \sqrt{t} \right) \right)^2} + e^{-\left(\frac{1}{2} \sqrt{\frac{R_s}{D_s}} \left(\frac{x'}{\sqrt{t}} - v \cdot \sqrt{t} \right) \right)^2} \right) \right] \quad A.13$$

At the sediment surface ($x'=0$) this equation can be simplified to:

$$\left. \frac{\partial C_{s,diss}}{\partial x} \right|_{x'=0} = \frac{1}{2} \cdot C_{w,diss} \cdot \left[\frac{v \cdot R_s}{D_s} \cdot \operatorname{erfc} \left(\frac{1}{2} \cdot v \cdot \sqrt{\frac{R_s \cdot t}{D_s}} \right) - 2 \cdot \sqrt{\frac{R_s}{D_s \cdot t \cdot \pi}} \cdot e^{-\frac{R \cdot v^2 \cdot t}{4 \cdot D_s}} \right] \quad A.14$$

Appendix B

The length scale of the laminar film thickness at the sediment water column interface is estimated in this appendix using a horizontal flow assumption. The used theory considers highly idealized condition so the results shall only be considered as length scale estimates. Important parameters for the laminar film thickness are:

1. The mean water velocity in the water column
2. The roughness of the sediment/water column interface

The water column in a marine/estuarine area or in greater lakes will always have a velocity different from exactly zero. This is mainly due to wind friction at the water surface and tidal movement of the water. The tidal movement can easily result in water velocities equal to the velocity in a fast flowing river and will periodically change direction. Thus, the water velocity is a very dynamic parameter and the resulting laminar film thickness will also change during time. The roughness of the bottom (sediment/water column interface) is more constant in time but related to the actual condition at the bottom. As the bottom conditions can vary between stones and sand etc. the spatial variation of the roughness may be large.

The following equations will not be derived because it will involve quite a lot of basic hydraulics which are presented in a series of text books (E.g. *Engelund and Pedersen, 1982*). Close to a solid surface (the bottom) there will exist a laminar layer in which a water molecule will flow in a fixed distance to the solid surface. The local velocity will increase from the solid surface and out in the water column and the friction from the water column to the solid surface is transmitted through the layer by 'friction' between the water molecules. At a give distance from the solid surface the flow will become turbulent and the water molecule will not have a fixed distance to the surface any more due to the formation of eddys. This distance from the surface where the conditions change from laminar to turbulent can be calculated by combining the laminar and turbulent flow theory as

$$L_w = 11.7 \cdot \frac{\nu}{U_f} \quad \text{B.1}$$

where ν is the kinematic viscosity ($\nu=1.3 \cdot 10^{-6}$ kg/(m·s) at 10° C) and U_f the friction velocity. The friction velocity is not a true velocity but a key parameter coming out of the basic flow theory. The relationship between the spatial mean velocity in the water column (V) and the friction velocity is

$$U_f = \frac{V}{6.4 + 2.45 \ln\left(\frac{d}{k}\right)} \quad \text{B.2}$$

where d is the depth of the water column, k is the length scale of the bottom roughness and V is the spatial mean water velocity. This equation is

valid for wide channels where the depth is much smaller than the width. In our case the width is in the length scale of km and the depth is in the length scale of m. Another assumption is that the flow needs to be strongly turbulent (In hydraulic terms: a Reynold number of several thousands). This will typically be true when the water depth is in the length scale of m, also for very low water velocity (in the size of 1 mm/s). The actual depth (d) varies and a reasonable interval could be between 1 to 50 m. The value of k depends on the conditions on the bottom and the value may vary from about 1 cm to several cm (20-50 cm). Summing up this variation a reasonable interval for the d/k ration can be 10-1000. When the depth of the water is larger than one meter the ration d/k will be much larger than one and the logarithmic function in Eq. B.2 will smooth out the variability in the d/k ratio. As a result of this a given variability in the d/k ratio will introduce a much smaller variability in the U_f and thus the L_w value in Eq. B.1. The U_f value will, on the other hand, be proportional to the mean water velocity (V) so the variability in the water velocity will tend to have rather high influence on the L_w value. L_w values are calculated as a function of V in Figure B.1, where a band of values is calculated for the d/k ratio interval of 10 to 1000 and for V values up to 50 cm/s.

The laminar film thickness is seen to be extremely variable as the water velocity decreases below about 10 cm/s. In a natural system where the actual water velocity varies from hour to hour due to wind and tidal movement it seems nearly impossible to consider the laminar film thickness as a fixed value. In cases where the laminar film thickness in general can be the controlling factor for the sediment uptake there may still be time windows where the water velocity is so high that the sediment uptake happens without any inhibition from the laminar film. Due to the strong non-linear behaviour of the diffusion flux into the sediment a relative small time period of high water velocity may be enough to ensure a nearly unaffected transport of substance into the sediment when the total transfer of substance mass is considered.

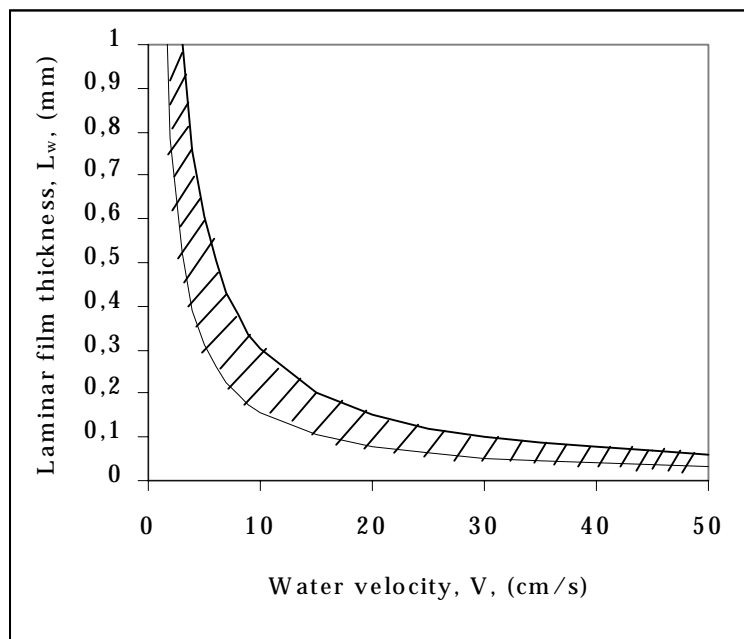


Figure B.1. The calculated laminar film thickness as a function of the spatial mean water velocity in the water column. The lower and upper boundaries represent respectively the d/k values of 10 and 1000.

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It is shown how diffusion and deposition of solids drive the flux of substance between the water column and the sediment. The generic compartment models (Mackay type) use a one box model for the sediment in order to keep the calculations simple. However, when diffusion needs to be included in the calculations, the one box model needs to be evaluated in relation to a more complete solution of the differential equations for diffusion. General guidelines that are based on the system parameters are set up in order to establish the importance of diffusion and deposition respectively. These define the range where diffusion or deposition is negligible or where both processes must be included in order to describe the sediment-water substance exchange most appropriately.

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