Effect of Hyporheic Exchange on Conservative and Reactive Solute Transport in Streams

*Model Assessments Based on Tracer Tests*

BY

KARIN JONSSON

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Abstract

Understanding of the processes affecting solute transport in flowing water is important for the possibility to predict the evolution with time of polluted stream systems.

This thesis presents tracer experiment methodology and model developments for solute transport in streams, with special focus on retention processes and their effect on solute stream transport. Results are presented from a tracer experiment in the Såva Stream, Uppland County, Sweden, where both a conservative (2H as tritiated water) and a reactive (63Cr as trivalent chromium ion) tracer were injected simultaneously. The time and length scales of the experiment were prolonged compared to previous studies, which allowed for new critical tests of different model concepts.

It was found that the hyporheic exchange greatly affected the solute transport of both tracers. However, the retention of chromium was significantly more pronounced. About 76% of the injected chromium was lost from the stream water phase directly after the passage of the pulse 30 km downstream of the injection point. The inventory of chromium in the sediments indicated that the main part was retrieved in the hyporheic zone.

Both a diffusive and an advective hyporheic exchange model were developed and evaluated versus independent observations in the stream water and hyporheic zone. Analytical expressions for the central temporal moments of the breakthrough curve and semi-analytical solutions for the solute concentration in the Laplace domain were derived. Both models were found useful in representing the observations.

For the transport of the reactive solute, it was found essential to consider a kinetic sorption on to particulate matter in the hyporheic zone. The time needed for a wash-out of 75% of the maximum uptake in the hyporheic zone was found to be ~85 times longer for the reactive solute, compared to the conservative solute. Neglecting the sorption kinetics in the transport model yielded significant errors in the central temporal moments, which implied an incorrect description of the wash-out process from the hyporheic zone. Independent observations in the stream water and hyporheic zone as well as choice of evaluation method are essential for a correct interpretation of the processes.

A first attempt was also made to link model parameters such as the residence time in the hyporheic zone with measurable parameters of the stream. Such a relationship offers the possibility to generalize results for other streams and stream conditions. A generic study of the transport of an inert solute in the Lule River, Sweden, using this kind of relationship, indicated that the hyporheic exchange can have a large practical implication.

Keywords: conservative, hyporheic exchange, model, reactive, retention, solute, sorption kinetics, stream transport, temporal moments, tracer experiment

Karin Jonsson, Department of Earth Sciences, Villav. 16, Uppsala University, SE-75236 Uppsala, Sweden

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"Många bäckar små blir till en stor å"

Swedish proverb
List of papers included in the thesis

This thesis is based on the following papers, which are appended at the end of the thesis and referred to in the text by their Roman numerals:


The papers are reproduced with the kind permission of Elsevier, American Geophysical Union and American Society of Civil Engineers.
The contribution to the papers by the author is as follows:

I) Responsible for the model development and parts of the writing. The first and the second author equally shared the main responsibility for the planning, performance and evaluation of the field experiment.

II) Responsible for the main part of the analyses, evaluation and writing.

III) Responsible for the main part of the analyses, evaluation and writing.

IV) Contributed with experimental data and part of the evaluation.

V) Responsible for the main part of the analyses, evaluation and writing.

VI) Responsible for the main part of the model development and analyses. The authors wrote the text on a collaborative basis.
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1 Introduction

1.1 Background

Transport in stream and river systems dominates the flow of various chemical elements from continent to ocean. Today, a large number of surface water systems with underlying sediment around the world are polluted due to different kinds of emissions, e.g. from industries, sewage treatment plants, agriculture, mining activities, nuclear power plants and accidental spills (e.g. Beneš et al., 1994; Karuppiah and Gupta, 1996; Chang et al., 1998; Hudson-Edwards et al., 2001). Releases into the water system can be from diffuse or point sources, instantaneous from an accidental spill, or more sustained from an industrial activity.

For example, in recent years failures of tailing dams of mine reservoirs in Romania, Spain, Bolivia and Sweden have caused accidental releases of metals and other substances to the surrounding water systems (Achterberg et al., 1999; Hudson-Edwards et al., 2001, Macklin et al., 2003). The dam failure at Baia Mare in Romania in January 2000 led to the release of 100,000 m$^3$ of waste water with a high concentration of, for example, cyanide into the adjacent river. The observed concentration of cyanide in the stream water due to this accident, as high as $\sim$100 times the maximum limit for drinking water, severely damaged the biotic life in the river system (UN/OCHA, 2000).

One example of more sustained contaminant sources is the leakage of nutrients from agricultural land, which has been an increasing source of nutrients, especially since the introduction of artificial fertilizers. Nutrients transported with the rivers will eventually enter the ocean and alter the nutrient budget. The phosphorous and nitrogen loads in the Baltic Sea have increased by a factor of 8 and 4, respectively, since the beginning of the twentieth century (Larsson et al., 1985). This has resulted in problems with algal blooms and oxygen deficiency in deep water and sediment (Larsson et al., 1985).

Another sustained contaminant sources is the leakage of metals from metallurgical and mining activities. For example, in Poland this has caused
extensive pollution of the Vistula and Odra Rivers. Measurements of Cd concentration in the Vistula River sediment show that these concentrations are some of the highest to be found in river sediments in Europe (Helios Rybicka, 1996). The retention of the contaminants in the sediment causes the system to be polluted for a long time.

Initially when a stream system is polluted, the concentration in the stream water is higher than in the sediment and the sediment will act as a sink for the contaminant. Depending on the characteristics of the contaminant, the substance will be more or less retained within the sediment. If the input of the contaminant into the stream system eventually ceases, the sediment can then act as a source when the contaminant accumulated in the sediment is released back into the stream water.

Considering the examples of polluted river systems, exemplified above, it is obvious that there is a need for an understanding of the processes governing the transport and retention of solutes in order to predict the evolution of a polluted system. In reality, numerous different processes are present that influence the transport. However, finding representative model parameterizations for the dominating processes will allow for a model formulation that can be used for predictions.

The focus of this thesis is on the transport and particularly the retention processes of conservative and reactive solutes in streams. The thesis presents experimental methodology, model parameterizations, solution techniques and solutions to formulated model equations.

1.2 Retention processes for solutes in streams and rivers

The recovery time for a polluted river system can be very long, depending on which retention processes that are present and dominating in the stream or river. Retention can be caused either by physical processes such as different mixing processes that will temporarily immobilize the solute in certain spatial zones or by solute reactions, where the properties of the solute are crucial for the extent of the retention.

Different processes will act on different temporal and spatial scales and all processes are not necessarily present in every watercourse and for all substances. Examples of physical processes causing retention of substances in watercourses are:

- **Hyporheic exchange**
  
  Hyporheic exchange, i.e. the exchange between the streaming water and the subsurface bed sediment, can occur due to different hydraulic mechanisms and retards the solute transport.
Observations in streams and rivers as well as detailed laboratory observations reveal that pressure differences over bed forms and flow obstructions induce the transport of dissolved solutes into the hyporheic zone (Huettel et al., 1996; Thibodeaux and Boyle, 1987; Elliott and Brooks, 1997; Packman et al., 2000; Marion et al., 2002). Depending on the residence time in the hyporheic zone and the exchange velocity, this uptake leads to a more or less pronounced retention in the water system.

Stream meander bends can also generate hyporheic exchange and thereby retention, but here on a larger spatial scale than the hyporheic exchange due to the above-mentioned bed forms. In this case, the flow path formed where the stream water leaves the stream will travel lateral to the stream for some distance before re-entering the stream channel (Wroblicky et al., 1998).

Furthermore, stepped-bed morphology can control the stream-subsurface water exchange (Harvey and Bencala, 1993). Transport of water into the hyporheic zone has been found where the stream water slope increases at the transition from pools (<1%) to steeper channel reaches (5-20%), while transport from the hyporheic zone has been found at the transition from steeper reaches to pools (Harvey and Bencala, 1993). The dissolved solutes will consequently be temporally retained in the subsurface.

- **Flooding and storage in overbank sediments**
  Temporal flooding of rivers can transfer solutes to the river floodplains, where storage in overbank sediments can retard the transport through the system (Macklin and Klimek, 1992; Walling et al., 1999; Hudson-Edwards et al., 2001). For example, in the Vistula basin, the overbank sediment polluted by past and present industrial and mining activities, constitutes today the most important secondary source of metal contaminants in the stream water (Macklin and Klimek, 1992).

- **Changes in geomorphology**
  Erosion processes can change the morphology of a watercourse basin and thereby the access of a substance. For example, in a meandering river, there is a deposition in the inner bends of the river that can cause “burial” of particulate-bound solutes and an erosion in the outer bends, which can release substances previously retained in the sediment.

In spite of the physical mixing processes, solute reactions can also prolong the residence time in a stream system, thereby causing a further retardation of the solute transport. Some examples of such reactions, present in watercourses, are:
• **Chemical processes**
  Chemical processes such as sorption onto particulate material and precipitation can give rise to an additional retention of the solute transport, where the effect is highly dependent on the reactivity of the substance, i.e. the fraction of the solute that is immobilized due to the reaction.

  Changes in, for example, redox potential and pH can alter the charges on to the adsorbent or cause changes in the oxidation state of the solute. This in turn means that the properties of a solute can change to or from a more reactive state, which can cause more or less retention due to sorption (Salomons and Förstner, 1984).

• **Biological processes**
  Biological uptake can cause temporarily retention of solutes and occasionally also biological transformations (Svendsen and Kronvang, 1993). Solutes are often released back to the stream water when the plant decomposes or settles down with the decomposing material on the sediment.

  As previously mentioned, the importance of the specific processes to the solute retention depends on the scale considered as well as the type of watercourse and substance. In a river like the Vistula, it is probably important to consider the flooding of, and retention in, the overbank sediments. However, for many streams, flooding and changes in geomorphology do not occur, and the exchange with the hyporheic zone due to pressure variations is likely to be a dominating hydraulic process that regulates the solute retention in the system. Examples are the northern Swedish rivers used for hydropower production. These rivers rarely undergo flooding, with the exception of short reaches when, occasionally, an ice jam occurs during the spring ice melting. Further, the river beds are covered with natural armour layers and not subject to significant geomorphological changes.

  To be able to predict the spreading of an accidental spill or the transport of pollutants or nutrients from continent to ocean, it is important to understand the fundamental principles of the processes acting in a stream or river system. Reaching this goal warrants detailed investigations of all relevant processes, where the development of model concepts is combined with empirical knowledge gained from field experiments. This thesis treats mainly the retention process due to hyporheic exchange and the retention of reactive solutes due to sorption on to particulate matter. The exchange with the hyporheic zone is important for the geochemistry in a stream system (Harvey and Fuller, 1998), and secondary effects of the retention might be
impact on the availability of nutrients (Svendsen and Kronvang, 1993) or the dissolved oxygen concentration in the sediment (McMahon et al., 1995). The availability of such essential solutes is important for the existence of biotic life. The prime focus in this study is, however, on basic hydraulic and chemical exchange processes.

1.3 Objectives

An overall objective of this study was to gain fundamental information on hydraulic and chemical processes affecting solutes in streams and rivers. The focus is on retention processes in stream systems, particularly the hyporheic exchange of dissolved solutes and sorption within the hyporheic zone, and its implication for solute transport. The overall goal is to find physical frameworks, which in the future could be used to generalize results for other streams and stream conditions. This thesis serves as a beginning of the work needed to be done to reach this final goal.

A specific aim was to make a detailed evaluation of the transport mechanisms by performing a tracer experiment with both a reactive and a conservative solute in a small-scale stream. This work involved the development of tracer experiment methodology as well as mathematical models, solution techniques and interpretation of physical mechanisms. The use of tracer experiments to obtain empirical data for model evaluations is a commonly applied technique (Bencala and Walters, 1983; Kennedy et al., 1984; Harvey et al., 1996). The resulting distortion of an introduced tracer breakthrough pulse (concentration versus time) gives a summarizing picture of the numerous hydraulic, chemical and biological processes present in the stream.

As mentioned, this thesis focuses on the hydraulic and chemical processes. Compared to previous studies, the experiment performed within this study was prolonged over larger length and time scales than ever before. The simultaneous injections of a conservative and a reactive tracer also allow for a differentiation of their transport characteristics. Further, the extensive simultaneous sampling of both stream water and bed sediment was intended to yield new empirical information that allows for detailed cross-testing of proposed model concepts versus several independent observations. The exchange with the hyporheic zone is investigated, and both an advective and a diffusive exchange model are evaluated. One specific objective is also to find an applicable parameterization of the sorption mechanisms and to investigate the influence of sorption kinetics on solute stream transport.

The knowledge gained from the evaluation of the tracer experiment in the small-scale stream will then be applied on a large-scale river to exemplify
the importance of hyporheic exchange to solute transport in a large-scale river. The regulated Lule River, northern Sweden, was chosen for this effect study. An investigation of how the effect of hyporheic exchange differs between a regulated and an unregulated system will also be done.
2 Transport and retention mechanisms in streams and hyporheic zones - model parameterizations

A number of hydraulic, chemical and biological processes in the flowing water and streambed will influence solutes in a stream system (Fig. 1). The main transport mechanism responsible for solute transport along the stream is advection, i.e. the transport of a substance due to the mean flow velocity in the stream. The spreading of an introduced solute cloud is termed dispersion, which is a combined effect of longitudinal differential advection and transversal mixing (turbulent and molecular diffusion). Temporal storage in side pockets with more or less stagnant or re-circulating water along the stream (Thackston and Schnelle, 1970; Schmid, 1997) and storage in the hyporheic zone surrounding the stream channel (Bencala and Walters, 1983; Papers I and III) will cause retention of the solute transport.

Fig. 1. Conceptual figure of hydraulic and chemical processes in a stream. Boxes denote mass phase species and arrows mass transfer mechanisms. The figure shows a model concept that applies for a sorbing solute (from Paper II, slightly modified).
In addition to the hydraulic mechanisms, biological and chemical processes can also significantly affect the transport, depending on the properties of the solute under consideration. For example, biological processes can be important for the transport and retention of nutrients (Svendsen and Kronvang, 1993), while metals, for example, are not equally affected by biology. Unlike conservative substances, heavy metals and other polluting substances often have a high particle affinity, which enhances the retention in the stream system. Exchange with the hyporheic zone and sorption on to particulate material is the predominant retention mechanisms in many streams.

In a box-type (zero dimensional) model, the mass transfer between the stream and the hyporheic zone can be expressed in terms of $\frac{\partial g_T}{\partial t}$, where $g_T$ is the dissolved solute mass in the hyporheic zone per unit volume of pore water (kg/m$^3$). Details will be given in the next section. In a spatially distributed description of the transport in the hyporheic zone, the mass conservation in the hyporheic zone can be expressed as (e.g. Berner, 1980):

$$\frac{\partial(\eta g_i)}{\partial t} = \frac{\partial J_i}{\partial z} + \sum q_i$$

where $g_i$ is the solute mass of component $i$ in the sediment per unit volume of pore water (kg/m$^3$), $\eta$ the porosity [-], $z$ the lateral co-ordinate (m), $J_i$ the solute flux of component $i$ in terms of mass per unit area of total sediment per unit time (kg/(m$^2$s)), $q_i$ the rate of chemical and biological reactions affecting component $i$ in terms of mass per unit volume of total sediment per unit time (kg/(m$^3$s)) and $t$ is the time (s). The solute flux in Eq. (1) expresses the exchange of solute mass between the hyporheic zone and the stream water if $J_i$ is evaluated at their interface, $J_i|_{\text{interface}}$.

As was exemplified in section 1.2, many processes affect solute transport in streams and for different temporal and spatial scales the different processes will be more or less important. This section will describe the hyporheic exchange and sorption mechanisms with possible adherent model parameterizations (for the exchange and reactions).

### 2.1 Hyporheic exchange parameterization

Many of the existing models for solute transport in streams are based on mass conservation in terms of the advection-dispersion equation, used early on in stream water studies by, for example, Fischer et al. (1979). Results from tracer experiments in streams indicated that the advection-dispersion equation model does not accurately represent the skewness in the breakthrough curves (BTCs). As the tails of the breakthrough curves
observed in the stream water were markedly prolonged in comparison with
the predictions by the advection-dispersion equation, the use of storage
zones or “dead zones” along the stream was included in the model concepts
(Hays, 1966; Thackston and Schnelle, 1970; Bencala and Walters, 1983). An
advection-dispersion model including a parameterized temporal
immobilization in the storage zones was found to provide an acceptable
representation of the observed skewness in the breakthrough curves.

The transient storage of water and solutes between the stream water and
stagnant zones and the surrounding hyporheic zone has since then been
described with different parameterizations. Concurrently, mainly three
different concepts are used alone or in combination to describe the exchange.

One commonly applied approach is to describe the exchange as a first-
order mass transfer exchange, where the concentration in the storage zone is
uniform and the exchange is driven by the difference in concentration in the
stream water and storage zone (Bencala, 1983; Bencala and Walters, 1983;
Schmid, 1995; Choi et al., 2000) (Fig. 2). This is the zero dimensional
approach mentioned in the previous section.

![Diagram of transient storage concept with first-order mass transfer](image)

In this “box model” parameterization, the transfer of dissolved solute
mass across the stream water/hyporheic zone interface can be expressed as:

$$\frac{\partial g_d}{\partial t} = \alpha(c_d - g_d)$$

\[ (2) \]
where $g_T$ is the total solute mass in the hyporheic zone per unit volume of pore water (kg/m$^3$), $\alpha$ an exchange coefficient (s$^{-1}$), $c_d$ the dissolved solute mass in the stream water per unit volume of water (kg/m$^3$) and $g_d$ is the dissolved solute mass in the hyporheic zone per unit volume of pore water (kg/m$^3$). Different reactions can be added to the mass conservation equation in a similar way as for the spatially distributed description (Eq. (1)). This kind of box-model concept is used in section 6 (Paper VI), where the effect of hyporheic exchange in a large-scale river influenced by hydro-power regulation is investigated.

A second alternative is to assume that the concentration in the storage zone is spatially distributed in the vertical direction according to Eq. (1) and that the exchange between the storage zone and the stream water can be described as diffusive and driven by the concentration gradient at the sediment/water interface (Forsman, 2000; Jackman et al., 1984; Wörman, 2000) (Fig. 3).

Fig. 3. Schematics of the transient storage concept with a diffusive mass transfer ($D$ – exchange diffusion coefficient, $c_d$ – dissolved concentration in the stream water, $g_d$ – dissolved concentration in the pore water in the hyporheic zone, $\eta$ – porosity). In the spatially distributed model of the mixing process in the hyporheic zone, the concentration generally decreases with depth during the uptake phase.

In this parameterization, the transfer of solute mass between the hyporheic zone and the stream water (in Eq. (1)) can be expressed as:

$$J_{\text{interface}} = J_{z=0} = \eta D \frac{\partial g_d}{\partial z}_{z=0}$$

(3)
where $D$ is the exchange diffusion coefficient (m$^2$/s), $g_d$ the dissolved solute mass in the hyporheic zone per unit volume of pore water (kg/m$^3$) and $z$ is the lateral co-ordinate (m). This concept is evaluated in section 5.1.1 (Papers I, II and III).

A third alternative is to describe the exchange with the hyporheic zone as advective. Different laboratory studies report pressure-driven advection as the main mechanism for the exchange over bedforms. A higher pressure is found on flow obstructions opposing the flow, while a lower pressure is found on the downstream side, where the flow is accelerating over the bedform (Thibodeaux and Boyle, 1987; Huettel et al., 1996; Elliott and Brooks, 1997). The higher pressure on the upstream face induces an advective transport into the bed, while the lower pressure on the downstream side yields a recharge of the water transported into the bed in the high-pressure zones (Fig. 4).

Fig. 4. Schematics of the transient storage concept with advective storage path exchange transfer ($c_d$ – dissolved concentration in the stream water, $g_d$ – dissolved concentration in the pore water in the hyporheic zone, $V_{pore}$ – pore water velocity, $\eta$ – porosity, $T$ – residence time in transport paths).

Concepts with advective storage paths can be parameterized using a residence time distribution within the hyporheic zone (Papers IV and V). In an advective exchange model the transfer of solute between the hyporheic zone and the stream water (in Eq. (1)) can be expressed as:

$$J_{|_{\text{interface}}} = \eta \left[ V_{pore} c_d \right]_{t=0} - \left[ V_{pore} g_d \right]_{t=T} +$$

(4)

where $c_d$ is the dissolved solute mass in the stream water per unit volume of water (kg/m$^3$), $g_d$ the dissolved solute mass in the bed sediment per unit volume of pore water (kg/m$^3$), $V_{pore}$ the pore water velocity (m/s) and $\eta$ is the porosity [-]. Note that the two terms in Eq. (4) reflects the in- and outflowing
section of an advective transport path in the hyporheic zone. This concept is evaluated in section 5.1.2 (Papers IV and V).

2.2 Chemical reaction parameterization

For reactive solutes, the degree of particle association has to be taken into consideration in transport modelling, as chemical reactions can contribute to short- or long-term immobilization of solutes ($q$-term in Eq. (1)). This reversible or irreversible exchange can cause a marked retention of the solute transport. In reality, a number of different chemical processes may occur, e.g. sorption, precipitation, dissolution, complex formation with organic and inorganic ligands (Salomons and Förstner, 1984). These processes are also affected by different environmental conditions, e.g. pH, conductivity and alkalinity. In the stream water transport modelling context, it is impossible to relate functionally all these different processes to underlying factors. All data needed for the evaluation of the functions are seldom available. A single sorption isotherm is therefore often included to represent all the above-mentioned particle association processes.

Sorption may occur either on to suspended particulates in the stream water or in the hyporheic zone. It is important to consider above all the retention due to sorption in the hyporheic zone in predictions of long-term changes of solutes in streams, as shown in Papers II, III and V.

From studies of different substances in both laboratory and field environments it is well known that sorption on to particulate material is often kinetically controlled (e.g. Nyffeler et al., 1984; Jannasch et al., 1988).

A commonly used parameterisation for kinetically controlled sorption is to assume a first-order linear relationship between dissolved ($C_d$) and adsorbed ($C_a$) solute concentration (Fig. 5).

![Fig. 5. Conceptual model of adsorption ($C_d$ - dissolved concentration, $C_a$ - adsorbed concentration, $k$ - rate coefficient).](image)

Based on the assumption of a single sorbed state, the parameterized equations can be expressed as:
where $C_d$ is the dissolved solute mass in the water per unit volume of water (kg/m$^3$), $C_a$ the adsorbed solute mass in the water per unit volume of water (kg/m$^3$) and $k$ is the sorption rate coefficient (s$^{-1}$).

The same type of relation is often expressed also for the desorption isotherm. Hence, assuming $C_a(t=0)=0$ and $C_d(t=0)=C_0$, the adsorbed solute concentration can be expressed as:

$$\frac{C_a}{C_0} = 1 - e^{-kt}$$

Depending on the value of the rate coefficient, $k$, the kinetics can be more or less pronounced (Fig. 6) and might therefore be more or less important to consider. A low value of the rate coefficient, $k$, indicates a pronounced kinetic sorption. In the special case where $k\to\infty$, an instantaneous sorption is assumed and it is possible to describe the partitioning with an equilibrium distribution coefficient.

Fig. 6. Sorption isotherms representing a linear adsorption with different pronounced effect of kinetics.

The sum of all the $q$-terms in Eq. (1) describes all the reactions present. Considering sorption, both the adsorption and the desorption can then be parameterized as above for inclusion in the equation.
The adsorption of different substances has also been found to be kinetically controlled in a two-step process (e.g. Smith and Comans, 1996; Hansen and Leckie, 1998; Strawn et al., 1998). The equations stated above can then be used in each step to describe both adsorption and desorption.

For very high concentration of solutes it might be important to consider a non-linear sorption isotherm, as the adsorbed mass increases with increasing concentration only until the surface sites are saturated. In the present thesis, however, the chromium concentrations are very low (Paper III) and the non-linearity will probably not be of importance.

In section 3, the diffusive and the advective hyporheic exchange parameterizations are combined with kinetic sorption parameterizations and longitudinal transport in a stream. The formulated modelling frameworks are used to interpret the effect of the retention, caused by hyporheic exchange and kinetic sorption, on solute transport in streams. In transport models, prevailing equilibrium chemistry has often been assumed (Berner, 1980).

Bencala (1983) presented a transient storage model for the transport of solutes in streams, which takes into account adsorption on to sediment particles. In this model, the exchange between the stream water phase and the sediment is kinetic, but there is no kinetic representation of the exchange between the dissolved and the adsorbed phase within the sediment, i.e. no distinction is made between the hydraulic and the chemical mechanisms. The commonly used OTIS model described by Runkel (1998) also applies this concept for reactive solute uptake. Other theoretical studies of the effect of sorption kinetics on the transport in open-channel flows have been performed, but sorption onto sediment particles suspended in the flowing water is then often only considered (Ng and Yip, 2001; Revelli and Ridolfi, 2002).

There is a lack of studies where the effect of sorption kinetics in the hyporheic zone is evaluated by means of a combination of theoretical development and necessary experimental data. The present thesis presents for the first time a thorough evaluation of the effect of kinetics on solute transport in streams, where the results from an extensive tracer experiment have been combined with model evaluations. In section 5.2, the relative importance of sorption kinetics is evaluated in terms of the relationships between the timescales of sorption, residence of solutes in the hyporheic zone and residence in the stream system.
3 Modelling and solution methods for solute transport in streams

To be able to evaluate the effect of different mechanisms, it is first necessary to find a model parameterization that can describe observed experimental data. As the hyporheic zone has been found important in the context of uptake and retention of solutes, it is essential to include this uptake mechanism in a model of solute transport in streams.

This section presents two different model concepts, both based on the advective-dispersion equation but with different representations of the hyporheic exchange and the sorption mechanism. The mathematical solutions and solution techniques needed for theoretical analyses and for the evaluation of these concepts versus tracer experiment data are derived here.

In the present thesis, mainly two different solution techniques have been suggested for evaluating the proposed model concepts versus observations in stream water and hyporheic zone. One technique applied is to derive closed-form solutions in the Laplace domain to the partial differential equation system constituting the model and use numerical Laplace inversion to obtain solutions of the tracer concentration with time (Papers I, III, IV and V). Numerical inversion is utilized to transform the Laplace space solution to the real domain. By means of these solutions, the model can then be fitted “by eye” to observed curves. Another technique is to derive analytical expressions of the temporal moments of the breakthrough curves from the system of equations (Papers II, IV and V). The temporal moments, $m_i$, of a function can be calculated by differentiations of the Laplace transform of the function $f(t)$ as:

$$m_i = \int_0^\infty t^i f(t) dt = (-1)^i \frac{\partial^i L[f]}{\partial p^i} \bigg|_{p=0} \quad i = 1, 2, \ldots$$  \hspace{1cm} (8)

where $L$ represents the Laplace transform, $t$ the time and $p$ is a positive number defined by the Laplace transform.
Fig. 7. The temporal moments of order $i$, $m_i$, can be used to formulate the central temporal moments, which express statistical properties such as expected value, $\mu$, variance, $\sigma^2$, skewness, $S_t$, and kurtosis, $K_t$. An infinite number of the moments exactly characterize the distortion of the breakthrough curve.

The central temporal moments of the breakthrough curve will express statistical properties such as expected value, variance, skewness and kurtosis of the breakthrough curve (Fig. 7). The distortion of the solute breakthrough curve can therefore be characterized using these properties, and the models can be evaluated by optimization of temporal moments versus stream water tracer data.

3.1 Model with diffusive hyporheic exchange (Papers I-III)

A conceptual model with a diffusive hyporheic exchange including one adsorbed and one dissolved solute phase in both the stream water and the hyporheic zone and first-order sorption kinetic transfers (as in Fig. 1) can be expressed in four mass conservation relations as:

Mass conservation for solute in dissolved phase in stream water

$$\frac{dc_d}{dt} + \frac{1}{A(x)(1 + K_R)} \left( c_d \frac{\partial Q(x)}{\partial x} + Q(x) \frac{\partial c_d}{\partial x} \right) = \frac{1}{A(x)(1 + K_R)} \frac{\partial}{\partial x} \left( A(x)E \frac{\partial c_d}{\partial x} \right) + k_1(K_d c_d - c_a) \left. \frac{P(x)}{A(x)} \frac{\partial g_d}{\partial \eta} \right|_{z=0}$$

$$\mu = m_1/m_0 \quad \sigma^2 = m_2/m_0 - (m_1/m_0)^2 \quad S_t = m_3/m_0 - 3\sigma^2 \mu - \mu^3 \quad K_t = m_4/m_0 - 6\mu^2 \sigma^2 - 4\mu S_t - \mu^4$$
Mass conservation for solute in adsorbed phase in stream water

\[
\frac{\partial c_a}{\partial t} + \frac{1}{A(x)(1 + K_R)} \left( c_a \frac{\partial Q(x)}{\partial x} + Q(x) \frac{\partial c_a}{\partial x} \right) - \frac{1}{A(x)(1 + K_R)} \frac{\partial}{\partial x} \left( A(x) E \frac{\partial c_d}{\partial x} \right) = 0
\]

Mass conservation for solute in dissolved phase in hyporheic zone

\[
\frac{\partial g_d}{\partial t} - D_s \frac{\partial^2 g_d}{\partial x^2} + k_2 (K_d g_d - g_a) = 0
\]

Mass conservation for solute in adsorbed phase in hyporheic zone

\[
\frac{\partial g_a}{\partial t} - k_2 (K_d g_d - g_a) = 0
\]

where \( c_d \) is the dissolved solute mass in the stream water per unit volume of water (kg/m³), \( c_a \) the adsorbed solute mass on particulate matter in the stream water per unit volume of water (kg/m³), \( g_d \) the dissolved solute mass in the hyporheic zone per unit volume of wet sediment (kg/m³), \( g_a \) the adsorbed solute mass on particles in the hyporheic zone per unit volume of wet sediment (kg/m³), \( t \) the time (s), \( A(x) \) the cross-sectional area of the main stream (m²), \( K_R \) the ratio of the cross-sectional area of the side pockets and the cross-sectional area of the main stream [-], \( Q(x) \) the flow in the stream \((Q(x) = V A(x))\) (m³/s), \( E \) the longitudinal dispersion coefficient (m²/s), \( k_1 \) the sorption rate coefficient in the stream water (s⁻¹), \( K_d \) the equilibrium distribution coefficient in the stream water \((K_d = [c_d/c_a]_{eq}) [-]\), \( D_s \) the exchange diffusion coefficient in the pore water (m²/s), \( x \) the longitudinal coordinate (m), \( z \) the lateral coordinate (m), \( P(x) \) the wetted perimeter of the stream (m), \( \eta \) the porosity in the hyporheic zone [-], \( K_h \) the equilibrium distribution coefficient in the hyporheic zone \((K_h = [g_a/g_d]_{eq}) [-]\) and \( k_2 \) is the sorption rate coefficient in the hyporheic zone (s⁻¹). Eqs. (9) and (10) presuppose that \( \frac{\partial}{\partial t} (A(x)(1 + K_R)) / \partial t = 0 \).

To be able to theoretically investigate the influence of sorption kinetics on solute stream transport, analytical expressions for the central temporal moments of the breakthrough curves were derived in Paper II. For the case where \( k_1 => \infty \) (i.e. instantaneous sorption in the stream water phase), no dispersion, a boundary condition in the sediment expressing an impermeable surface at a certain depth, \( L \) (m) (i.e. \( \frac{\partial g_d}{\partial z} \bigg|_{z=L} = 0 \)), and a pulse with a constant concentration during a finite time \( A(s) \) applied at the boundary, the temporal moments can be written as (Paper II):

\[
\mu_t = \frac{x}{u_e} \left[ 1 + \left( \frac{4}{A} \right)^2 \right]
\]
\[
\sigma_i^2 = \frac{x}{u_e} F \rho \left[ 1 + \frac{\kappa}{\rho} \right] + \frac{\Delta^2}{12} \tag{14}
\]

\[
S_i = \frac{9}{5} \frac{x}{u_e} F \rho^2 \left[ 1 + \frac{\kappa}{\rho} \left( \frac{5}{3} + \frac{5}{3\rho K_k} \right) \right] \tag{15}
\]

\[
K_i = \frac{x}{u_e} F \rho^3 \frac{153}{35} \left[ 1 + \frac{42\kappa}{17\rho} + \left( \frac{35}{17} + \frac{70}{51K_B} \right) \left( \frac{\kappa}{\rho} \right)^2 + \frac{35(1+K_B)^2}{51K_B^2} \left( \frac{\kappa}{\rho} \right)^3 \right] + 3 \left( \sigma_i^2 \right)^2 + \frac{\sigma_i(\Delta=0)^2 \Delta^2}{2} + \frac{\Delta^4}{80} \tag{16}
\]

where \( F = \frac{L \eta (1+K_B)}{h (1+K_d)}, \) \( \kappa = \frac{2K_B}{k_2(1+K_B)}, \) \( \rho = \frac{2}{3}(1+K_B) \frac{L^2}{D_s}, \) \( u_e = V/(1+K_B), \)

\( \mu, \) the expected value of the breakthrough curve, \( \sigma_i^2 \) the variance of the breakthrough curve, \( S_i \) the skewness of the breakthrough curve and \( K_i \) is the kurtosis of the breakthrough curve.

In order to evaluate the importance of including a kinetic description of sorption, relative errors in the expected value, variance and skewness of the BTC resulting from disregarding sorption kinetics (and thereby assuming instantaneous sorption) was determined in Paper II according to:

\[
\varepsilon_\theta = \frac{\theta_k - \theta_e}{\theta_e} \tag{17}
\]

where \( \theta \) represents the expected value, variance or the skewness in the representations, subscript \( k \) stands for the kinetic sorption and subscript \( e \) for the equilibrium chemistry (i.e. instantaneous sorption).

The effect of sorption kinetics in the stream water was also investigated by means of corresponding expressions for the above-mentioned moment equations. These expressions are significantly more complex and are therefore not presented in closed form. The analyses in Paper II indicated, however, that it was not just as important to consider the sorption kinetics in the stream water as the kinetics in the hyporheic zone in the context of its influence on temporal moments. One explanation is that the total number of available adsorption sites in the stream water is naturally less than in the bed sediment. This implies that there is a comparatively small fraction of adsorbed ions in the water and that the sorption mechanism in the stream water is not as essential as that in the bed, regardless of differences in the kinetics. The effect of sorption kinetics in the stream water has not been further investigated in the later papers of this thesis. Instantaneous sorption is assumed to prevail in the stream water, whereas the effect of sorption
kinetics in the hyporheic zone is further evaluated in Papers III and V (see section 5.2).

The boundary and initial conditions for which a solution of the total concentration in the stream water and the inventory curve in the hyporheic zone was derived are expressed as:

\[ c_T(x = 0, t \geq 0) = \frac{M}{Q_0} \delta(t = 0) \]  
\[ c_T(x = \infty, t \geq 0) = 0 \]  
\[ g_d(z = \infty, t \geq 0) = 0 \]  
\[ g_d(z = 0, t \geq 0) = c_d(x, t \geq 0) \eta \]  
\[ c_t(x > 0, t = 0) = g_d(z, t = 0) = g_d(z, t = 0) = 0 \]

where \( M \) is the amount of solute introduced in the system (kg), \( Q_0 \) the discharge at the upper boundary (m³/s) and \( \delta(t) \) is Dirac’s delta function (s⁻¹).

The discharge variation along the sub-reaches is assumed to fulfil the condition \( 1/Q \partial Q/\partial x = \) constant, which is the case when the discharge increases exponentially along the sub-reaches. For sufficiently small dispersion coefficients, as in the present study, the exact discharge variation is, however, not essential. This can be concluded from the solution when dispersion is negligible \( (E=0) \), where a scaling factor appears in front of the solution to the problem without dilution (Paper III). Forsman (2000) showed this for a linearly increasing flow in a model without dispersion. Hence, the main effect of dilution for a sufficiently small dispersion coefficient is therefore only a scaling of the concentration distribution.

To be able to evaluate the model concept versus independent observations in both stream water and hyporheic zone, solutions for the breakthrough curve in the stream water and the inventory curve in the hyporheic zone has to be derived. The solution for the total concentration in the stream water, \( c_T(=c_a+c_d) \), is derived here in the special case where \( k_f=\infty \), i.e. instantaneous sorption in the stream water phase, and can be written in the Laplace domain as (Paper III):

\[ -c_T = \frac{M}{Q_0} \exp \left[ u_c^2 \left( \frac{1}{2E} \right) \sqrt{u_c^2 + \frac{p}{E} + \frac{D_s \eta}{E(1 + K_d)h} \left[ \frac{p(1 + K_B + k_f)}{p + k_f} \right] \frac{D_s}{D_s} + \frac{u_c \phi}{E} } \right] \]

\[ (23) \]
where \( u_e = V/(1 + K_R) \) (m/s), \( \phi \) a flow dilution coefficient (m\(^{-1}\)), \( p \) the Laplace operator and \( h \) is the hydraulic radius \((h = A(x)/P(x))\) (m).

To obtain the real domain solution of Eq. (23), a numerical inversion algorithm described by De Hoog et al. (1982) and implemented by Hollenbeck (1998) was applied. The concentration at a section \( x \), \( G_x \), for an arbitrary variation of the boundary concentration, \( G_{BC} \), is given by the following convolution integral:

\[
G_x(t) = \int_0^t \frac{c_{x}(t - \tau)}{M/Q_0} G_{BC}^{(\tau)} d\tau
\]

where \( \tau \) is a convolution variable.

Solving the equation system for the total inventory of solute mass in the hyporheic zone \((M_{tot})\) down to a certain depth \((z_{int})\) per unit bed area when a unit pulse is introduced at the boundary between times \( t_1 \) and \( t_2 \), the solution in the Laplace domain can be stated as (Paper III):

\[
\tilde{M}_{tot} = \int_0^{z_{int}} \tilde{g}_{tot} dz = \left(1 + \frac{K_R k_2}{p + k_2}\right) \frac{\eta c_T}{K_d + 1} \sqrt{\frac{D_p}{\theta}} \left(1 - e^{-\frac{\theta}{\sqrt{D_p}z}}\right) \left(e^{-t_2\theta} - e^{-t_1\theta}\right) \frac{e^{-t_2\theta} - e^{-t_1\theta}}{p}
\]

where \( \theta = p + k_2 K_R - \frac{K_R k_2^2}{p + k_2} \).

As above, the numerical Laplace inversion algorithm was used to obtain the real-domain solution for a unit pulse. Superposition of the real-domain solutions of Eq. (25) for all the pulses that constitute the boundary condition gives the total amount of tracer in the sediment for a variable concentration in the stream water.

### 3.2 Model with advective hyporheic exchange (Papers IV and V)

In the modelling framework referred to as the Advective Storage Path (ASP) model, the longitudinal transport in the stream is coupled with flow-induced (advective) uptake in the hyporheic zone (as in Fig. 4) (Paper IV).

Different lengths of the individual exchange flow paths in the hyporheic zone lead to different residence times before sub-surface water re-enters the stream water. To describe this, we use a distribution of residence times. A mass conservation relationship in the main stream including the processes advection, dispersion and a net solute flux in the dissolved phase across the stream water/hyporheic zone interface is expressed as (Paper IV):

\[
\bar{M}_{tot} = \int_0^{z_{int}} \bar{g}_{tot} dz = \left(1 + \frac{K_R k_2}{p + k_2}\right) \frac{\eta c_T}{K_d + 1} \sqrt{\frac{D_p}{\theta}} \left(1 - e^{-\frac{\theta}{\sqrt{D_p}z}}\right) \left(e^{-t_2\theta} - e^{-t_1\theta}\right) \frac{e^{-t_2\theta} - e^{-t_1\theta}}{p}
\]
\[
\frac{\partial c_T}{\partial t} + \frac{1}{A_T} \frac{\partial (AUc_T)}{\partial x} - E \frac{\partial^2 c_T}{\partial x^2} = J_S \frac{P}{A_T} 
\] 
(26)

\[
J_S = \frac{1}{2} \int_0^\infty f(T) \xi(\xi V_Z(t,T) \Big|_{\tau=0} - g_d(t) \Big|_{\tau=0}) dt
\] 
(27)

where \(c_T\) is the total solute mass in the stream water per unit volume of water (kg/m\(^3\)), \(c_d\) the dissolved solute mass in the stream water per unit volume of water (kg/m\(^3\)), \(g_d\) the dissolved solute mass in the bed sediment per unit volume of pore water (kg/m\(^3\)), \(t\) the time (s), \(A\) the cross-sectional area of the main stream (m\(^2\)), \(A_T\) the cross-sectional area of the main stream including side pockets (m\(^2\)), \(U\) the average flow velocity in the main stream (m/s), \(Q\) the discharge (Q=UA) (m\(^3\)/s), \(E\) the longitudinal dispersion coefficient (m\(^2\)/s), \(x\) the longitudinal co-ordinate (m), \(P\) the wetted perimeter of the stream (m), \(J\) the net solute flux in the dissolved phase across the stream water/hyporheic zone interface (kg/(m\(^2\)/s)), \(\tau\) the residence time along a hyporheic flow path (s), \(T\) the total residence time from inlet to exit of the hyporheic zone (s), \(f(T)\) the probability density function (PDF) of \(T\) weighted by the velocity component normal to the bed surface, \(V_n\) the infiltration of exfiltration Darcy water velocity (=pore velocity×porosity) (m/s) and \(\xi\) is an area reduction factor equal to \(V_n/V_Z\) that accounts for the fact that the stream lines are not necessarily always perpendicular to the bed surface. The first term in the integral in Eq. (27) expresses the flow of solutes into the bed sediment while the second term expresses the flow of solutes out of the bed sediment. By integrating over all transport pathways, the net solute mass flux in the dissolved phase can thereby be expressed.

In Paper V, the ASP model presented in Paper IV is extended to include also the transport of reactive substances, i.e. the retention due to sorption is also taken into account. For the reasons mentioned in section 3.1, we assume instantaneous sorption in the stream water. The partition ratio at chemical equilibrium of the adsorbed solute mass per unit volume of stream water, \(c_a\) (kg/m\(^3\)), and the dissolved solute mass per unit volume of stream water, \(c_d\) (kg/m\(^3\)), are defined by the distribution coefficient, \(K_d = [c_a/c_d]_{eq}\) [-]. On the assumption that there is a two-step sorption process in the hyporheic zone, where the first sorption step is assumed to be instantaneous and the second kinetic (Fig. 8), the mass conservation equations representing the transport in the hyporheic zone become (Paper V):

\[
\frac{\partial g_d}{\partial t} + \frac{k_3}{1 + K_{B1}} (K_{B2} K_{B1} g_d - g_{a2}) + \frac{1}{\eta(1 + K_{B1})} \frac{\partial V_Z g_d}{\partial z} = 0
\] 
(28)

\[
\frac{\partial g_{a2}}{\partial t} - k_3 (K_{B2} K_{B1} g_d - g_{a2}) = 0
\] 
(29)
where \( g_{a2} \) is the adsorbed solute mass in the interior of the grains/grain clusters per unit volume of pore water (kg/m\(^3\)) (slow sorption phase), \( g_{a1} \) the adsorbed solute mass on readily available grain/grain cluster surfaces per unit volume of pore water (kg/m\(^3\)) (rapid sorption phase), \( k_3 \) a kinetic rate coefficient (s\(^{-1}\)), \( K_{B1} = \frac{g_{a1}}{g_d} \) and \( K_{B2} = \frac{g_{a2}}{g_{a1}} \) equilibrium distribution coefficients [-], \( z \) the curve-linear co-ordinate in the direction of the hyporheic flow (m) and \( \eta \) is the porosity [-].

![Diagram](image)

Fig. 8. Conceptual model of the different mass phases in the advective storage path model and the type of transfer between these phases. Boxes represent mass conservation relationships and arrows mass transfer relationships (see the text for an explanation of the variables) (from Paper V).

For this concept, too, different types of solutions are derived (Papers IV and V) to allow for several evaluations by means of independent observations in both stream water and hyporheic zone. Different optimization criteria are also tested, both a formal optimization of the temporal moments and a fit of the model to breakthrough curves “by eye”.

The system of equations is solved for a unit Dirac pulse, whereby the boundary conditions are expressed as:

\[
c_r(x=0, t) = \frac{M}{Q_0} \delta(t = 0) \tag{30}
\]

\[
c_r(x=\infty, t \geq 0) = 0 \tag{31}
\]

where \( M \) is the total amount of solute introduced in the system, \( Q_0 \) the discharge at the upper boundary (m\(^3\)/s) and \( \delta(t) \) is Dirac’s delta function. The discharge variation was assumed to fulfil the condition \( \frac{\partial Q}{\partial x} = \text{constant} \). This condition is fulfilled when the flow increases exponentially along the sub-reaches as \( Q = Q_0 e^\phi x \), where \( x \) is the distance (m) and \( \phi \) a proportionality coefficient (m\(^{-1}\)).
The boundary condition for the solute flow in the hyporheic zone is defined as an equal concentration in the dissolved phase at the water/sediment interface:
\[ g_{z}(z = 0, t) = c_{d}(x, t) R \]
where \( R \) is a focusing factor for the concentration of reactive solutes \((R > 1)\). The initial conditions for the tracer test used in the evaluation of the model are given by:
\[ c_{0}(x > 0, t = 0) = g_{0}(z, t = 0) = g_{d}(z, t = 0) = 0 \]

Provided the boundary and initial conditions Eqs. (30)-(33), the solution for the total concentration in the stream water in the Laplace domain can be expressed as (Paper V):
\[ \bar{c}_{r} = \frac{M}{Q_{0}} \exp(\Theta) \]
where
\[ \Theta = \frac{U_{e}}{2E} \left[ \left( \frac{U_{e}}{2E} \right)^{2} + \frac{U_{e} \phi}{E} \right] \frac{1}{2E A_{r}} R \bar{\xi} \frac{V_{Z}}{1+K_{d}} \left( e^{-\left(1+K_{n}+\frac{K_{n}K_{x}}{1+K_{n}}\bar{\xi} \right)} - 1 \right) \]

The real domain solution for a pulse of finite duration is obtained by means of numerical Laplace inversion and faulting as described in section 3.1.

Analytical expressions for the temporal moments are derived as a tool to interpret the effect of hyporheic exchange and sorption and especially to identify governing dimensionless parameters.

Several different distributions for the residence time PDF in the hyporheic zone (uniform, exponential, log-normal) were tested versus tracer data in Paper IV. Both the exponential and the log-normal distribution provided an acceptable representation of the data, but the log-normal distribution was found to best represent the tail of the breakthrough curve (Paper IV).

In the derivation of the temporal moments presented below, a log-normal distribution was therefore assumed. Schmid (2002) presented a relationship between the temporal moments at the upper boundary with the moments arising at the downstream boundary, which is applied in the moment equations below. When disregarding the longitudinal dispersion, the central temporal moments due to an arbitrary boundary concentration can be expressed as (Paper V):
\[ \mu_{t} = \frac{x}{U_{e}} \left( 1 + F(< T >) \right) + \mu_{0}[t] \]
\[ \sigma_{t}^{2} = e^{\rho_{r}^{2}} \frac{x}{U_{e}} F(< T >) \left( \frac{\kappa}{\rho(< T >) e^{\rho_{r}} + 1} \right) + \sigma_{0}^{2}[t] \]
\[ S_t = e^{\beta t} \frac{x}{U_e} F(< T >) \rho^2(< T >) \left[ 1 + \frac{\kappa}{\rho(< T >)} \left( \frac{3}{e^{3\beta t} \rho(< T >)} + \frac{3}{e^{2\beta t}} \right) \right] + S_0[t] \quad (37) \]

\[ K_t = e^{\beta t} \frac{x}{U_e} F(< T >) \rho^3(< T >) \left( \frac{3(1 + K_{B1} + K_{B1}K_{B2})}{e^{3\beta t} K_{B2}^2 K_{B1}^2} \left( \frac{\kappa}{\rho(< T >)} \right)^3 + \right. \]
\[ \left. \left( \frac{6}{e^{\beta t} K_{B2} \left( 1 + \frac{1}{K_{B1}} \right) + \frac{9}{e^{\beta t}} \left( \frac{\kappa}{\rho(< T >)} \right)^2 + \frac{6\kappa}{\rho(< T >)} + 1 \right) + 3(\sigma^2)^2 + K_0[t] \right) \quad (38) \]

where \( F(< T >) = P \xi V R < T > (1 + K_{B1} + K_{B1}K_{B2})/(2A_T(1 + K_d)), \)
\( \rho(< T >) = < T > (1 + K_{B1} + K_{B1}K_{B2}), \kappa = 2K_{B2}K_{B1}/(K_3(1 + K_{B1} + K_{B1}K_{B2})), \)
\( < T > \) is an arithmetic mean value of the residence times, \( \beta \) a coefficient in the log-normal residence time PDF defined from the expression \( \sigma^2_T / < T >^2 = e^{\beta t} - 1, \)
\( U_e = Q/A_T \) the effective flow velocity in the main stream channel corrected for side pockets with stagnant water, \( \mu \) the expected value of the BTC, \( \sigma^2 \) the variance of the BTC, \( S_t \) the skewness of the BTC, \( K_t \) the kurtosis of the BTC, \( \mu_0[t] \) the expected value of the inflow BTC, \( \sigma_0^2[t] \) the variance of the inflow BTC, \( S_0[t] \) the skewness of the inflow BTC and \( K_0[t] \) is the kurtosis of the inflow BTC.

To be able to evaluate the model versus inventory curves in the hyporheic zone, the net solute flux in the dissolved phase across the sediment/water interface is with the help of Eqs. (27)-(29), (32) and (33) expressed in the Laplace domain as (Paper V):

\[ J_s = -\frac{\xi V Z}{2} R \left( \frac{c_T}{1 + K_d} - L^{-1} \left( \frac{\bar{c}_T}{1 + K_d} e^{-\left( \frac{1 + K_{B1} + K_{B1}K_{B2}}{s + \kappa_0} \right)} \right) \right) \quad (39) \]

where \( L^{-1} \) represents the Laplace inversion of the expression and \( s \) the Laplace operator. Integrating the flux into the hyporheic zone with time yields the accumulated flux in the hyporheic zone. The Laplace inversion is evaluated numerically.
4 Experimental and evaluation methodology

4.1 Tracer experiment in the Säva Stream

Introducing a tracer not naturally existing in a stream or with a concentration significantly above the natural background level allows for a detailed study of the transport mechanisms, where it is possible to evaluate, for example, the exchange with the hyporheic zone. A tracer experiment with simultaneous injections of the radioactive isotopes tritium ($^{3}\text{H}$ as tritiated water) and chromium ($^{51}\text{Cr}$ as Cr(III) (aq.)) was therefore performed in the Säva Stream in Uppland County, Sweden (Fig. 9).

The stream flows through a 197 km$^2$ watershed, where the upper part of the stream is surrounded mainly by coniferous forest, whereas the lower part is situated in arable land. The two tracers were chosen so as to get one tracer that represents solutes that adsorb on to particulate matter ($^{51}\text{Cr}$) and one that represents the water flow (or inert solutes) ($^{3}\text{H}$). Simultaneous injections of a
conservative and a reactive tracer were chosen to allow for a differentiation of physical transport characteristics and retention processes for reactive solutes. A total amount of 74 and 92.5 GBq of tritium and chromium, respectively, was injected as pulses into the stream water phase at a constant rate for 5.3 h.

The fact that the tracers were radioactive made it possible to determine the tracer concentration independently of the oxidation state and chemical speciation of the solute, i.e. even if these change after its injection into the system.

The concentration was monitored in both the stream water and in the bed sediment along a 30-km-long reach of the stream. Stream water was sampled manually during the passage of the pulse at eight stations (Fig. 9). To obtain complete breakthrough curves, also the tails of the BTCs were monitored over a long period of time. Sediment samples were taken at two stations during several (~5) months. On each sampling occasion, 5 to 7 sediment cores were taken down to a depth of at least 10 cm, but some of the cores were taken down to a depth of 21 cm. To get information about the vertical distribution of the tracers, the sediment cores were vertically sectioned. The contents of tritium and chromium in the samples were then analyzed with a beta-scintillation counter and a gamma-spectrometer, respectively. In addition, the hydraulic conductivity and hypsographs along the stream, the chromium’s particle association and the spatial variability of the uptake were determined. For a detailed description of the performance of the experiment, see Papers I and III.

To be able to evaluate the mechanisms causing the retention of solutes in streams, the experimental findings are used in the evaluation of the proposed model parameterizations.

4.2 Evaluation methodology using tracer experiment data

As previously mentioned, the retention in the hyporheic zone will distort a solute pulse travelling in the stream system, where, for example a more spread-out and skewed breakthrough curve than the injected pulse results from the exchange mechanisms. A detailed study of the spatial and temporal changes in the stream water breakthrough curves from a tracer experiment can therefore be used to evaluate parameterized models, describing the retention processes in the stream. The tail of the stream water BTC is mainly the part of the curve that contains conclusive information about the exchange processes relating to the hyporheic zone. It is therefore of importance in the evaluation of these processes. The sampling time after the passage of the
main peak in the stream water should therefore be sufficiently long, to allow for an interpretation of the information available in the BTC tail.

The methodology suggested in this thesis is to evaluate the model concepts by means of the solutions proposed in section 3 versus the independent observations of the tracers in both the stream water and the hyporheic zone made during the experiment in the Säva Stream.

The equations expressing the central temporal moments, derived in section 3, can be used to evaluate the different processes by means of optimization of the moments versus the stream water breakthrough curves. In this calibration procedure, it should be important that the data used for moment optimisation is of a high quality concerning sampling frequency and total sampling time. The stream water breakthrough curves used for calibration in this study were therefore sampled over as long period of time as the detection limit of the analytical procedure allows.

By means of the simultaneous injections of a conservative and a reactive tracer it should also be possible to differentiate the hydraulic mechanism from the chemical processes. The hydraulic model parameters are first determined by means of a calibration versus the tritium data. These parameter values are then fixed, when the chemical processes are to be evaluated, i.e. for the reactive tracer the effect of sorption is added to the effect of the hydraulic mechanisms (evaluated from the conservative tracer).

Using the equations giving the concentration in the stream water and hyporheic zone in the Laplace domain in section 3, the model could be calibrated independently versus the different kinds of observations. One type of calibration is based on the total tracer inventory observed in the hyporheic zone down to a depth of 10 cm as a function of time. Another type of calibration is based on the breakthrough curves in the stream water, which reflect the time evolution of the solute mass per unit volume of water. Such independent calibrations are done to investigate whether the parameter set-ups calibrated from the stream water phase also provided a correct representation in the hyporheic zone. In this way, it should be possible to conclude what kinds of observations that are needed to make a correct interpretation of different mechanisms, i.e. how to determine a parameter set-up that provides a correct representation in both the stream water and the hyporheic zone. The different kinds of observations should also reveal whether the timescales of the processes are accurately captured within the time-span of the observations, or whether there is any difference in what can be concluded from the different observations. Most importantly, the independent observations reveal if the model provides a physically relevant basis in addition to a nice curve fit. Such a model feature is important for generalizations of the results.
5 Retention of conservative and reactive solutes in the hyporheic zone and its implication for solute transport in streams

5.1 Effect of hyporheic exchange

It can be concluded from the experimental results in Paper I that there is a clear retention of the two tracers along the stream and that the retention of the reactive tracer chromium is more pronounced than that of the conservative tracer tritium (Fig. 10). By normalizing the concentration at each station along the stream with the plateau concentration at station A, it is possible to see that a comparatively smaller fraction of the solute is found for chromium than for tritium in the stream water.

![Fig. 10. Differences in the stream water breakthrough curves at stations A-D due to different retentions of tritium and chromium in the hyporheic zone (from Paper I, slightly modified).](image)
A 76% loss of chromium relative to tritium was found in the stream water directly after the passage of the pulse in the stream water 30 km downstream of the injection point (Table 1).

Table 1. Mass balance of chromium along the Säva Stream calculated by integrating the stream water BTCs to obtain the remaining mass in the stream water (and thereby the approximate loss to the sediment) directly after the passage of the pulse at each station (from Paper III).

The retention is mainly caused by uptake within the hyporheic zone. A rough estimation yields that the inventory of chromium in the sediment constitutes ~93% of the loss found from the stream water BTCs (Paper III). The missing mass not found in the sediment might be attributed to a loss to vegetation in the stream. A tentative evaluation of the uptake onto vegetation in Paper III reveals that the concentration onto the surface of the vegetation can be high. However, if it is to cause any considerable loss in comparison with the loss to the bed sediment, the vegetation has to be very dense. It might be important, however, to carry out a future investigation also of this uptake to clarify all sinks for the solutes, but this has not been the primary focus of this thesis. For the reactive tracer chromium, sorption is an important mechanism to consider, since it prolongs the residence time within the hyporheic zone compared to that of the conservative tracer tritium. The wash-out time representing a 75% decrease of the maximum uptake in the sediment, for example, was found to be ~85 times longer (i.e. ~45 days) for chromium than for tritium at the sampling station 125 m downstream of the injection point (Fig. 11).
Another consequence of the reactivity of chromium is that the penetration depth within the sediment is reduced compared to the conservative tracer tritium, which can penetrate deeper into the sediment (Fig. 12). From the
depth profiles we can conclude that most of the solute mass for both tracers is located in the upper 10 cm of the sediment.

Since the data in this study comprised independent observations of both a reactive and a conservative tracer in both the hyporheic zone and the stream water and the quality of the data was rather high, the proposed concepts could be evaluated in a way that was not previously possible.

5.1.1 Diffusive exchange model

The diffusive flux parameterization of the hyporheic exchange was found capable of describing the retention of the conservative solute in both stream water and sediment, where both the peak values and the distortion of the stream water breakthrough curves, as well as the time course of the mass inventory in the sediment were correctly represented (Figs. 13, 14 and 15) (Paper III). The diffusion coefficient calibrated versus the stream water data, varied in the range $5 \times 10^{-9} - 4 \times 10^{-6}$ m$^2$/s with a coefficient of variation of 181% along the whole investigated reach. A similar magnitude of the coefficient was found from the calibrations versus the independent observations in the bed sediment. See Paper III for a complete presentation of the calibration results.

Fig. 13. Observed and simulated BTCs of tritium in the stream water at stations B-D along the Säva Stream using the diffusive exchange model. The diffusive exchange model gives a good representation of both peak values and the distortion of the solute pulse (from Paper III).
Fig. 14. Observed and simulated BTCs of tritium in the stream water at stations E-G along the Säva Stream using the diffusive exchange model. The diffusive exchange model gives a good representation of both peak values and the distortion of the solute pulse (from Paper III).

Fig. 15. Diffusive exchange model fitted to the observed tritium inventory in the uppermost 10 cm of the sediment at station A ($D_s=9\times10^{-9}$ m$^2$/s). Both the uptake and the wash-out were fairly well reproduced by means of the diffusive exchange model (from Paper III).
5.1.2 Advective exchange model

The ASP model (Advective Storage Path) was evaluated in Papers IV and V with the intention of finding a concept based on a more physically correct description of the hyporheic exchange. This concept, too, was found to be capable of representing the observations during the tracer experiment.

The first evaluation of this concept, in Paper IV, versus the conservative solute tritium, concerned the application of an exponential residence time distribution to describe the retention of a solute in the hyporheic zone. By means of hydrodynamic principles, a relation was found where the residence time in the hyporheic zone could be related to basic hydrodynamic quantities according to:

\[
\frac{<T> K}{h} = C \frac{gh}{U^2}
\]

(40)

where \(<T>\) is the mean residence time, \(K\) the hydraulic conductivity, \(h\) the hydraulic radius, \(C\) a proportionality coefficient that depends on geometrical properties of the bed sediment, \(g\) acceleration due to gravity and \(U\) is the flow velocity in the stream channel.

The proportional coefficient was determined by plotting the dimensionless time \(<T> K/h\) versus the inverse of the Froude number squared, \(gh/U^2\). The parameters were evaluated from the tracer experiment for an exponential distribution of residence times (Fig. 16).

There should preferably have been a larger number of reaches for the evaluation of this expression. However, the indications from this evaluation nevertheless yielded two trend lines for the different reaches of the stream flowing in either forest or agricultural land. The probable explanation for this is that the constant \(C\), which depends on geometrical properties of the streambed, varies with land use along the Säva Stream. Further investigations by Salehin et al. (2003) in the same stream but in another year and season strengthened this conclusion. Their solute transport results, from a sub-reach of the experimental reach studied in this thesis (in agricultural land), all fell along the trend line for agricultural land in Fig. 16. Their conclusion was therefore that the residence time in the storage zone could have been predicted well, based on the relationship Eq. (40) in combination with the value of the proportional coefficient, \(C\), in Fig. 16 and the stream flow conditions prevailing during the studied time period. Thus, relating the residence time to measurable properties of a stream provides relationships where results from one stream or stream condition can be generalized to another one. A further investigation of this relationship is however needed before it can be used with certainty.
Fig. 16. Evaluation of the effect of stream morphology on hyporheic exchange using the ASP model with an exponential distribution of residence times. The solid lines represent the trends between the dimensionless time and the stream Froude number. Different proportional coefficients were found for the land types agricultural land and coniferous forest (from Paper IV).

In Paper IV, it was also found that a log-normal residence time PDF provided the best description of the long-term retention expressed in the tails of the BTCs. The residence time distribution of the solute in the hyporheic zone was found to be best represented by the log-normal distribution.

Paper V describes an extension of the ASP concept, where the transport of reactive solutes could also be treated. Since reactive solutes primarily have a marked impact on long-term retention, i.e. affect the tails of the BTCs, the log-normal residence time distribution was retained in the evaluation of both the hydraulic and the chemical processes.

Calibration of the model parameters using optimization of temporal moments versus stream water data was found inappropriate in the context of representing long-term solute changes. The reason for this is that the observed moments are often underestimated and the optimized solution does not yield a good representation of the BTC tails (Fig. 17) (Paper V).
Fig. 17. Tritium observations in stream water at station B and simulated curve based on parameters optimized from the central temporal moments. If long-term changes of the solute concentration are of interest, the method of optimization of the moments is not appropriate, as the fit to the tail is unsatisfactory (from Paper V).

A fit “by eye” method was therefore found more useful for assessing the long-term changes, reflecting the wash-out from the hyporheic zone (Fig. 18). In this evaluation, the tails of the BTCs for tritium and chromium were also evaluated with a greater accuracy by representing the BTCs in a log-normal visualization during the fit and by using the independent observations in both stream water and hyporheic zone.

The ASP model with a log-normal residence time PDF was found to be useful for representing the tritium data in both the stream water and the hyporheic zone. However, calibrating the model solely versus the stream water BTC does not yield a unique parameter set-up. This may lead in particular to an incorrect representation of the uptake and wash-out in the hyporheic zone. Figures 18 and 19 show two different parameter set-ups that yield quite similar fits within the time period of the observations in the stream water, but with completely different representations of the wash-out in the hyporheic zone. Since it is possible to detect the concentration in the hyporheic zone (the bed sediments) over a longer period of time than the concentration in the stream water, we can detect from these data valuable information on long-term changes of hyporheic processes, which is not possible with the stream water BTC.
Fig. 18. Example of model fits to tritium stream water data at station B using the ASP model with two different parameter set-ups. Within the time period of the observations both parameter set-ups yield quite similar fits. For sufficiently long times, however, the tails of the BTCs will deviate from each other (from Paper V).

Fig. 19. Observed and simulated (using the ASP model) normalized tritium inventory in the hyporheic zone at station A for two parameter set-ups yielding appropriate representations of the stream water BTC. The normalization was based on the maximum uptake (from Paper V).
5.2 Effect of sorption kinetics

The chemical extraction of the sediment samples revealed that chromium mainly adsorbs on to substrate types of Fe and Mn oxides, humic matter and mineral constituents. The results also indicated a change in binding strength with time (Paper III), which is consistent with the relatively slower and slower decay of the tail in the mass inventory BTCs (Fig. 11). The rate-limited sorption was further interpreted by including a kinetic sorption representations in both the diffusive and the advective exchange model.

5.2.1 Diffusive exchange model

The importance of including a kinetic description of sorption for the reactive tracer in the stream water and hyporheic zone in the diffusive exchange model was evaluated in Paper II. The study comprised theoretical analyses of the analytical expressions of the central temporal moments Eqs. (13)-(16). It was found that the sorption rate coefficient in the stream water phase, \( k_1 \), influences the expected value, but with a decreasing error when the travel distances increases. When higher-order moments are considered, the sorption rate coefficient in the hyporheic zone, \( k_2 \), is also found to influence the error. For sufficiently large distances, the variance error was found to be more pronounced when sorption kinetics in the hyporheic zone was disregarded than when sorption kinetics in the stream water was disregarded.

Using the model with the diffusive parameterization reveals that the \( F \)-parameter \((F=\eta L\eta(1+K_B)/((h(1+K_B)))\) defined in the moment equations (13)-(16) is a typical retardation factor. For a conservative solute \((K_B=0)\), this retardation is determined by the extension of the hyporheic zone, \( L \), in proportion to that of the stream water, \( h \). For reactive solutes, this retardation factor will increase as \( K_B \) increases, since a larger fraction of the solute is then adsorbed in the hyporheic zone. An increase in \( K_B \) will instead reduce the value of the \( F \)-parameter, as the amount of solute in the dissolved phase, available for solute exchange with the hyporheic zone, then decreases. The retardation will, however, not be dependent on the sorption kinetics in the hyporheic zone. The kinetics in the sorption process in the hyporheic zone is expressed by the \( \kappa \)-parameter \((\kappa=2K_B/(k_2(1+K_B)))\), which will influence the moment of second order or higher, i.e. sorption kinetics is important for the spread and skewness of the breakthrough curve but not for the expected value. The \( \rho \)-parameter \((\rho=2L^2(1+K_B)/(3D_s))\) relates the extension of the hyporheic zone to the exchange diffusion coefficient and expresses a typical residence time in the hyporheic zone that is prolonged for reactive solutes. As for the kinetics, this typical residence time will only influence moments of second order or higher. From the errors derived in Paper II using the
moment equations, it is apparent that applying an equilibrium model instead of a kinetic representation of the sorption in the hyporheic zone will provide maximum errors for intermediately sorbing solutes for the variance and skewness.

The further evaluation of the chromium BTC, where the hydraulic parameters determined by the tritium data were used, also indicated that the sorption within the hyporheic zone was kinetically controlled (Figs. 20 and 21). As shown, a concept with instantaneous sorption in the hyporheic zone yielded too high a concentration in the tail of the stream water BTC and the wash-out from the hyporheic zone was too fast. A concept with a first-order kinetic sorption could significantly better describe the observations in both the stream water and the hyporheic zone. Such a description provided in particular a more correct representation of the tails of the stream water BTCs and a more correct representation timewise of the inventory in the hyporheic zone. The calibration versus the chromium inventory curve in the hyporheic zone was needed to limit the possible range of the value of the distribution coefficient, as the value of the distribution coefficient yielding a satisfactory representation in the stream water (Fig. 20) gave an unsatisfactory fit in the hyporheic zone (Fig. 21). Due to the high spatial variability of the uptake of chromium in the hyporheic zone, a more extensive sampling of sediment would, however, provide data of a higher quality (in the context of being more representative), which might lead to a slightly different evaluation. The $K_D$-value yielding the best fit versus the hyporheic inventory curve yielded, an appropriate representation also of the stream water breakthrough curve (Fig. 22).
Fig. 20. The diffusive hyporheic exchange model with a kinetic ($k_2 = 3 \times 10^{-8} \text{ s}^{-1}$) and an instantaneous ($k_2 = \infty$) sorption model fitted to the observed chromium BTC at station D (from Paper III).

Fig. 21. The diffusive hyporheic exchange model with different representations of the sorption process within the sediment fitted to the chromium inventory in the uppermost 10 cm of the sediment at station A (from Paper III).
Fig. 22. The diffusive hyporheic exchange model with a kinetic sorption model fitted to the observed chromium BTC at station D using the $K_B$-value yielding the best fit in the hyporheic zone.

5.2.2 Advective exchange model

The detailed evaluation of the hydraulics governing the conservative exchange (using the ASP model described in section 5.1.2) was an important prerequisite for a detailed evaluation of the sorption process, due to the reliable distinction between the effects of the hydraulic processes and those of the chemical exchange processes.

The indications from the model evaluation of the diffusive hyporheic exchange model that the sorption within the hyporheic zone was kinetically controlled, were also found by the fit of the ASP model. In this more detailed evaluation of the sorption parameterization, the concept with a single sorption step however, was found insufficient to represent the observed data. This is due to the model’s inability to represent the long-term retention visible in the tails of the BTCs, using a single sorption step parameterization. A two-step sorption process was found to follow the observations best, where the first instantaneous sorption step was followed by a second rate-limited step. The second step was found to be pronouncedly kinetic. A very high rate coefficient (approaching that of nearly instantaneous sorption) consequently provided a trend that clearly diverged from the observed BTC (Fig. 23).
Fig. 23. Fit of ASP model to chromium stream water data at station B for both a rapid (close to instantaneous) sorption ($k_3=2\times10^{-2}$ s$^{-1}$) and a pronounced kinetic sorption ($k_3=2\times10^{-8}$ s$^{-1}$) ($K_B1=6$, $K_B2=2000$) (from Paper V).

This result is in agreement with several previous studies, where the sorption of different reactive substances has been reported to follow a two-step sorption process with a rapid and a slow sorption step (Smith and Comans, 1996; Hansen and Leckie, 1998; Strawn et al., 1998). Here we also show that it might be important to incorporate such a sorption parameterization in a solute stream transport model framework to represent the long-term retention of reactive solutes along a stream. The importance of including a kinetic description in the models depends, however, on the effect variable under consideration. Sorption kinetics is not so important for estimations of when the main part of the solute mass has passed a certain point. However, if the interest is in the long-term wash-out of contaminants from the hyporheic zone, reflected in the tail of the stream water BTC, disregarding sorption kinetics may cause large errors. A correct representation of the long-term concentration changes can be of importance to, for example, the prediction of the recovery time after pollution, i.e. the time until the concentration has decreased below the limit for hazardous impacts.

Exclusion of the kinetic description of the sorption process introduces errors in the observed temporal moments of the BTCs (Paper V). In this thesis, analytical expressions of these relative errors have been derived and can be represented as isopleths as shown in Fig. 24. According to Eqs. (35)-
the kinetic sorption will influence temporal moments of the second order or higher, whereas the first moment is not affected by sorption kinetics. The error is largest for intermediate values of the distribution coefficient, $K_{B2}$, while it will decrease for extremely high or low values. We can also draw the conclusion that the errors in variance, skewness and kurtosis increase with decreasing hydraulic residence time in the hyporheic zone.

Fig. 24. Isopleth diagram of the relative error in variance when the kinetics in the ASP model is disregarded in the sorption process in the hyporheic zone (from Paper V).

By comparing the equations for the temporal moments using the ASP model with the corresponding expressions for the diffusive exchange model, it is possible to see that the expressions are quite similar. The same type of parameters (the $F$-, $\rho$- and $\kappa$-parameters in Eqs. (13)-(16) and (35)-(38)) appear in an identical functional type in both model representations. Thus, the $F$-parameter ($F(<T>)=P<>V_{z}R<T>(1+K_{B1}+K_{B1}K_{B2})/(2A_{f}(1+K_{B}))$) in the ASP concept also expresses the retardation in the system. As is the case with the diffusive exchange model for a conservative solute, this group relates the extension of the hyporheic zone ($-V_{z}<T>$) to that of the stream water ($h=A_{f}/P$). The $\rho$-parameter ($\rho(<T>)=<T>(1+K_{B1}+K_{B1}K_{B2})$) clearly expresses a typical residence time in the hyporheic zone that will be more pronounced for a reactive solute, when $K_{B1}=K_{B2}>0$. Finally, the $\kappa$-parameter ($\kappa=2K_{B2}K_{B1}/(K_{B}(1+K_{B1}+K_{B1}K_{B2}))$) expresses the kinetics in the sorption.
To get a critical evaluation of the ASP concept and the two-step sorption, it would be necessary to evaluate this concept versus high-quality data (in the context of getting representative sediment samples) in the hyporheic zone. The data available in this study are not of such a high quality due to the spatial variability in the uptake. An even more extensive sampling of the hyporheic zone should, however, provide data for the reactive tracer in the hyporheic zone that would allow for an independent evaluation. In this study, the aim of the model evaluations was, however, not to evaluate the parameters, but rather to investigate qualitatively the types of functions that can represent the processes acting in the stream.
6 Case study: Importance of hyporheic exchange in the regulated Lule River, northern Sweden (Paper VI)

Based on the relationship found by evaluating the ASP model in the Säva Stream, a case study was performed by generalizing this knowledge to the regulated Lule River in northern Sweden. The ASP model implies that the residence time for solutes in the hyporheic zone can be related to basic hydrodynamic quantities, which makes the theory suitable for generalizations, especially for predicting the effects on the transport due to changes in, for example hydraulics. This study is only tentative and the beginning of a research effort aiming at understanding the influence of hyporheic exchange on solute transport in large rivers. It should therefore only be considered as an example of how hyporheic exchange might influence inert solute transport in a river of this size. Further, a first evaluation was made to investigate whether river regulation alters the hyporheic zone interactions.

Fig. 25. Example of the changed flow pattern after regulation of the Lule River. Observed regulated and estimated unregulated discharge at Vietas hydropower station on the Lule River. The time period plotted is from June 20, 2000 to May 31, 2001.
Due to the regulation, the flow pattern in the Lule River has changed in the sense that the large seasonal flow variations have been smoothed out (Fig. 25). The residence time in the river system, too, has increased from a few hundred to a few thousand hours due to the regulation (Paper VI).

A modelling framework was developed, where the hydraulic model was uncoupled from the solute transport model (Paper VI). The hydraulic model takes into account spatial variation in hypsographs along the river and temporal changes in the discharge. By applying the Manning equation and a stepwise solution to the energy equation, the flow conditions were determined which were later used in a simplified box model for solute transport. The exchange intensities between the stream water and the hyporheic zone evaluated in Paper IV for coniferous forest and agricultural land (i.e. $C = 0.14$ and $C = 0.0013$ in Fig. 16), were recalculated to exchange coefficients in the box model and used with an estimated hydraulic conductivity, $K$, of $10^{-3}$ m/s in the effect studies of hyporheic exchange. The exchange coefficient between the river water and the hyporheic zone, $\lambda$, was then determined according to:

$$\lambda_{12} = \lambda_{21} = \frac{\alpha U^2}{h^2 g}$$  \hspace{1cm} (41)$$

where $\alpha = K/C$ ($\alpha = 0.0071$ m/s and $\alpha = 0.0769$ m/s, respectively), $U$ the stream velocity, $h$ the hydraulic radius and $g$ the acceleration due to gravity (m/s²).

To study the influence of hyporheic exchange, a short pulse of an inert substance was applied at a section coinciding with the location of Vietas hydropower station on the Lule River. The simulations were then performed to evaluate the retardation (i.e. the prolongation of the expected residence time) and the distortion (expressed as a relative spread), of the pulse due to hyporheic exchange. The relative spread, $RS(t)$, was defined as 

$$RS(t) = \frac{t_{75\%} - t_{25\%}}{t_{50\%}},$$

where $t_{75\%}$, $t_{50\%}$ and $t_{25\%}$ represents the time for 75%, 50% and 25%, respectively, of the mass to pass.

For both the regulated and the unregulated Lule River, the effect of hyporheic exchange on solute transport was significant, being most pronounced for the unregulated case. For the particular study period of interest, the hyporheic exchange in the unregulated river could increase the retardation of the solute pulse by as much as ~100% compared to the situation where no hyporheic exchange would be present (Fig. 26 a). The relative spread was even more affected by hyporheic exchange (Fig. 26 b). During unregulated conditions the relative spread could increase by ~1000% compared to the situation where no hyporheic exchange was assumed to be present. In the regulated river, the corresponding increase was ~100%. Consequently, the hyporheic exchange alters the solute transport by lowering the effective transport velocity and by smoothing out temporal variations in
solute transport. The importance of the hyporheic exchange should have been much more pronounced before the regulation than after it. In both cases, hyporheic exchange is probably an important mechanism that to a large extent influences the solute transport in the Lule River. More investigations on this matter are, however, warranted, where these theoretical results should be verified (or confuted) versus empirical knowledge.

Fig. 26. (a) Retardation and (b) change in the relative spread of a solute pulse in the regulated and unregulated river for different release times ($t_{50\%}$ represents the time needed for 50% of the mass to pass, $RS(t)$ stands for the relative spread defined as $(t_{75\%}-t_{25\%})/t_{50\%}$ and $\alpha$ is the hyporheic exchange intensity).
7 Discussion and Conclusions

An improved understanding of the transport mechanisms acting on solutes in streams has been achieved with this thesis. The work comprised both theoretical developments and analysis of stream transport models, and methodology for evaluations versus stream tracer data.

The results from the stream tracer experiment with simultaneous injections of a reactive ($^{51}$Cr) and a conservative ($^{3}$H) solute, made it possible to differentiate between, and critically test, model parameterizations of hydraulic and chemical processes, in a way that has not previously been possible. This is due to the long experimental time and length scales in combination with the extensive sampling of independent observations in both stream water and hyporheic zone.

It has been shown that hyporheic exchange greatly affects the transport of solutes in streams by causing retention in the stream system. Retention markedly influenced chromium. A 76% loss from the stream water relative the conservative tracer was found directly after the passage of a solute pulse, 30 km downstream of the injection point. The inventory of chromium in the hyporheic zone indicated that the loss was mainly due to uptake and sorption within the hyporheic zone. It was, therefore, found to be highly important to include these exchange mechanisms (i.e. hyporheic exchange and sorption) in solute stream transport models.

By studying the distortion of a solute pulse injected to the stream, information on the exchange processes can be obtained. In this type of analysis it was found important to consider the tail of the breakthrough curve, as this is the part of the curve that contains conclusive information on wash-out processes.

The main theoretical contribution includes the development of solute transport models as well as solutions and solution techniques needed for the evaluation. This work involved derivations of semi-analytical solutions for the solute concentration in the Laplace domain and analytical expressions for the temporal moments of the breakthrough curves. Both the diffusive and the advective parameterization of the hyporheic exchange were found to provide accurate representations of the observations of the conservative solute.

The effect of sorption on the solute stream transport could be evaluated in detail, as the conservative and reactive transport properties could be
separated by (in a first step) utilizing the tritium data to determine the hydraulic properties. For the long-term retention of the reactive solute, it was found that the sorption in the hyporheic zone had to be described as a rate-limited process in a stream transport model. Exclusion of the sorption kinetics by assuming instantaneous sorption introduces significant errors in the central temporal moments of second order or higher of the breakthrough curves. The errors were found at their maximum for intermediate values of the distribution coefficient, while for lower or higher values the errors decrease. Further, the errors increase with decreasing hydraulic residence time in the hyporheic zone. Hence, the kinetic description in the hyporheic zone was not important for the expected residence time of a solute pulse but for the variance, skewness and kurtosis. This implies that disregarding sorption kinetics in the hyporheic zone yields an incorrect description of the tails of the stream water breakthrough curves and an incorrect representation of the timescales of the wash-out of solutes from the hyporheic zone.

The evaluation of the diffusive exchange model indicated that the sorption in the hyporheic zone could be described as a kinetic process in one step. The more detailed evaluation of the advective exchange model indicated instead that the sorption follows a two-step reaction, with the first step instantaneous and the second pronouncedly kinetic. This is in accordance with several previous laboratory sorption experiment, however, seldom implemented in stream transport models. Also, the physical basis of the advective exchange model indicates that the results on the sorption process obtained with this model are probably reliable.

The commonly used temporal moment method (optimization of the model versus observed moments of the BTC in the stream water) was further found to be inadequate for the evaluation of the long-term exchange with the hyporheic zone. The tails of the observed breakthrough curves in the stream water are often too short and the observed moments are therefore underestimated. This causes a bias of model representation of the tails of the breakthrough curves. It is therefore essential to observe stream water breakthrough curves during tracer experiments over a sufficiently long period of time to be able to interpret the information on exchange processes available in the tails of stream water BTCs. A log-normal representation of the breakthrough curve provided the best representation of the tails and, thus, the best basis for evaluation of the sorption process.

Monitoring solely the solute concentration in the stream water was not found to be sufficient for the model calibrations in all cases. The uptake and wash-out in the hyporheic zone could then be completely misinterpreted. Hence, it is important that the data used to evaluate the different processes accurately captures the timescale of the process. The results in this study indicate that the tracer observations in the hyporheic zone have to be taken in...
account during the evaluation of the sorption mechanism in the hyporheic zone, using the diffusive model. A calibration versus solely the stream water data could provide an incorrect evaluation of the sorption parameters, yielding an incorrect representation of the mass inventory curves in the hyporheic zone and thereby an incorrect interpretation of the processes occurring. For the advective exchange parameterization, it was necessary to reduce the uncertainties also in the hydraulic exchange parameters by means of the observations in the hyporheic zone.

By relating the dimensionless residence time in the hyporheic zone (i.e. the product of the residence time in the hyporheic zone and the hydraulic conductivity divided by the hydraulic radius) to the stream Froude number, it was found that the hyporheic exchange rates increases and the residence time decreases with the Froude number. This relationship allowed for a first attempt to generalize the results from the model evaluation versus the Säva Stream data to other streams and stream conditions.

A tentative effect modelling study of the influence of hyporheic exchange on inert solute transport in the Lule River, northern, Sweden, revealed that the transport in the river was significantly affected. The hyporheic exchange caused both a retardation and a spreading of the pulse travelling in the river system. The effects were found both during regulated and unregulated conditions, but they were most pronounced for the unregulated case. The expected residence time and relative spread of a pulse, in the unregulated case, could increase by as much as \(\sim 100\) and \(1000\%\), respectively, compared to the situation where no hyporheic exchange was assumed to be present. Hence, the hyporheic zone alters the solute transport by lowering the effective transport velocity and by smoothing out temporal variations in solute transport. This can be important for water quality aspects were naturally or anthropogenic inputs to the river can be smoothed out.

Future research should search for physically based relationships between measurable parameters in the stream and model parameters. An attempt to find such expressions for reactive solutes should bring us a step closer to finding relationships useful to predictions of contaminant transport in streams. Reaching this goal, however, requires more research based on a continued interplay of model developments and tracer experiments with high-quality data. The present thesis gives some indications of useful constitutive equations as well as modelling approaches and how the model concept can be evaluated versus data (see also Appendix A). This knowledge is of importance to the future development of models for solute transport in streams.
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/Karin
References


Appendix A. Summarizing practical guidance for future performance and evaluation of tracer experiments

The experience from this study concerning performance and evaluation of tracer experiment in streams can be used as guidance for future experiment. Listed below are aspects that should be considered:

- A simultaneous injection of a conservative and a reactive tracer is of outermost importance to be able to differentiate the effect of hydraulic and chemical processes.
- The use of radioactive tracers allow for a determination of the tracer concentration independent of oxidation state and chemical speciation.
- Sampling of independent observations is important since different observations have different possibilities to accurately capture the timescale of the processes. For example, sediment samples could be used to reduce uncertainties in model parameters calibrated versus stream water data. Independent observations reveal if the model provides a physically correct representation in addition to providing a nice curve fit. This is important in the context of generalizing model results to other streams and stream conditions.
- Sampling of the tail of the stream water BTC over a sufficiently long time is important due to the fact that it contains conclusive information about exchange processes with the hyporheic zone.
- The time necessary for sampling of the hyporheic zone depends on tracer and sediment characteristics. For tracers with similar sorption characteristics as chromium and for similar sediment characteristics as in the Säva Stream, it should be necessary to sample sediment over a period of several months to capture accurately the uptake and wash-out from the hyporheic zone.
- Due to the spatial variability of the uptake of reactive solutes in the sediment, the number of samples at each occasion must be rather high in order to obtain a mean value that is representative for the location. In the present study, the 5 to 7 sediment cores at each sampling occasion should preferably have been higher. In the present study most of the uptake in the hyporheic zone was found in the upper 10 cm of the stream, indicating
that a depth of ~20 cm should be enough for sediment samples in streams of a similar magnitude.

- The commonly used temporal moment method (optimization of the model versus observed temporal moments of the stream water BTC) often provides an underestimation of the observed moments, which provides a bias of the model representation of the tail of the BTCs. It is therefore important to sample the stream water BTC tails over a sufficiently long period of time.

- A log-normal representation of the stream water BTC during a fit by eye calibration would provide a higher weight to the tail of the BTC. It would then be possible to consider the long-term changes in concentration due to the exchange with the hyporheic zone. A correct interpretation of this exchange is important for the model development of solute transport in streams utilized for predicting the time-evolution of contaminated systems.
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