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Hydrology and water chemistry in a heterogeneous landscape

Process-based modelling of coupled surface water and groundwater flow across contrasting boreal catchments

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Hydrology and water chemistry in a heterogeneous landscape

Abstract

Surface water and groundwater are connected, and the exchange between them is a vital part of a catchment's hydrology. Along the flow paths through the catchment, biogeochemical processes can change the water's chemical composition. The degree of the chemical change depends largely on the water pathways and travel times through the subsurface environment. This thesis describes the application of a 3D coupled surface water and groundwater model to the well-studied Krycklan catchment to investigate the impact of hydraulic properties, landscape variability, and seasonal changes on the hydrology and water quality across nested catchments in a heterogeneous boreal landscape. The results show that variability in specific discharge and surface water and groundwater interactions can be linked to catchment characteristics such as soil properties and spatial variability in winter soil frost. Spatial variability of water quality, including weathering of base cations and locations of dissolved organic carbon-rich sources along the streams, was linked to different catchment characteristics affecting hydrology (including travel times and water pathways). Some catchment characteristics, such as soil frost, were found to not necessarily impact the modelling of streamflow dynamics from a large-scale perspective. However, soil frost was still important for the flow dynamics on smaller scales, and an important part of the spatial variability of stream water quality. This research highlights the importance of expanding our knowledge of the flow dynamics of different landscape components, surface water and groundwater interactions, and how hydrology can be linked to water quality across temporal and spatial scales.

Keywords: flow dynamics; temporal and spatial scales; solute transport; modelling

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Hydrologi och vattenkemi i ett heterogent landskap

Sammanfattning

Interaktionen mellan yt- och grundvatten är en viktig process som styr variationer i hydrologin och vattenkvaliteten inom ett avrinningsområde. Längs med grundvattens flödesvägar kan biogeokemiska processer förändra vattnets kemiska sammansättning. Omfattningen på den kemiska förändringen beror till stor del på vattnets transportvägar och uppehållstider i marken. Genom att applicera en 3D numerisk yt- och grundvattenmodell på det välstuderade avrinningsområdet Krycklan, undersöktes effekterna av hydrauliska egenskaper, vintertjäle och ackumulation av snö på hydrologin och vattenkvaliteten över delområden i ett heterogent borealt landskap. Resultaten visar att variationer i vattenflöde samt yt- och grundvatteninteraktioner kan kopplas till avrinningsområdenas egenskaper såsom fördelningen av olika jordarter samt rumslig variation av tjäle. Rumslig variation i vattenkvalitet, inkluderat vittring av baskatjoner och källor av organiskt material längs bäckarna, kunde i stor utsträckning förklaras av hydrologin. Vissa egenskaper, till exempel tjäle, påverkande inte nödvändigtvis modelleringen av flödesdynamiken på ett storskaligt perspektiv. Däremot var emellertid tjäle viktigt för flödesdynamiken på mindre skalor samt en viktig del som förklaring till den rumsliga variationen av vattenkvalitet. Sammanfattningsvis så belyser denna avhandling vikten av att utöka vår kunskap om hur flödesdynamik, yt- och grundvatteninteraktioner, samt hur hydrologi kan kopplas till vattenkvalitet och landskap på olika tidsmässiga och rumsliga skalor.

Nyckelord: flödesdynamik; tids- och rumsskalor; ämnestransport; organiskt kol; vittring

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Dedication

To my family, friends, and advisors

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. Jutebring Sterte, E., Johansson, E., Sjöberg, Y., Huseby Karlsen, R. and Laudon, H. (2018). Groundwater-surface water interactions across scales in a boreal landscape investigated using a numerical modelling approach. Journal of Hydrology. 560, 184–201.

II. Jutebring Sterte, E., Lidman, F., Lindborg, E., Sjöberg, Y. and Laudon, H. (2021). How catchment characteristics influence hydrological pathways and travel times in a boreal landscape. Hydrology and Earth System Sciences. 25(4), 2133–2158.

III. Jutebring Sterte, E., Lidman, F., Balbarini, N., Lindborg, E., Sjöberg, Y., Selroos, J.-O. and Laudon, H. (2021) Hydrological control of water quality – Modelling base cation weathering and dynamics across heterogeneous boreal catchments. Science of the Total Environment. 799, 149101.

IV. Jutebring Sterte, E., Lidman, F., Sjöberg, Y., Ploum, S. W. and Laudon, H. Hydrological regulation of stream dissolved organic carbon (DOC) across a heterogeneous landscape (Manuscript)

Papers I and III are reproduced with the permission of the publishers.

The contribution of Elin Jutebring Sterte (EJS) to the papers included in this thesis was as follows:

I. EJS took a leading role in model calibration and validation, and was also the primary person responsible for result analysis, writing and submission

II. EJS was the main person responsible for model setup, running the model, result analysis, writing and submission

III. EJS was the primary person responsible for model development, model calibration, model validation, result analysis and writing

IV. EJS was the main person responsible for model setup, model calibration, model validation, result analysis and writing

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1. Introduction

A key reason for the study of catchment hydrology is to improve our understanding and predictive power of where and when changes in water quantity and quality occur. Understanding of the influence and variability of catchment processes at different temporal and spatial scales remains limited, even though it is known that catchment characteristics can impact catchment hydrology in several ways (Karlsen et al., 2016; Laudon and Sponseller, 2018; McDonnell and Woods, 2004; Teutschbein et al., 2018). Such characteristics include catchment size, topography, soil heterogeneity, soil depth, and climate. In turn, catchment hydrology, including water pathways and travel times, can affect surface water and groundwater quality, and the functioning of both aquatic and terrestrial ecosystems (Godsey et al., 2009; Lindgren et al., 2004). Therefore, it remains important to analyse catchment characteristics and connect them to hydrological and water quality changes to understand better what controls these interconnected processes (Kirchner et al., 2000; Kolbe et al., 2020). Enhancing this knowledge can further facilitate improved predictions of ungauged catchments and models, which, in turn, can aid in assessing and managing water resources and water quality.

The work that this thesis and associated papers describe aims to investigate and improve our understanding of the hydrological functioning of a heterogeneous landscape. It seeks to link the hydrological functioning, including water pathways and travel times, to base cation and dissolved organic carbon (DOC) transport to gain new insights into the primary factors controlling base cation weathering variability and DOC stream contribution. The thesis is designed to deepen understanding of the catchment hydrology and water quality processes, with the main aim of the work divided into four parts:

- to explore surface and groundwater interactions and the impact and importance of seasonal soil frost on catchment of different sizes and characteristics (Paper I).
- to test modelled travel times against seasonal variations of stream chemistry and to find connections between travel times and catchment characteristics (Paper II).
- to test hydrology as the primary factor controlling base cation dynamics in streams and investigate potential export of base cations from deep soil (Paper III).
- to investigate groundwater travel times as a predictor of local riparian DOC sources, and stream water DOC concentration dynamics (Paper IV).

1.1 Catchment hydrology, water pathways and travel times

Historically, it has been common to treat surface and groundwater systems as separate entities but, over the last few decades, the interactions between them have been investigated in more detail (Barthel and Banzhaf, 2016; Diaz et al., 2020). However, as demonstrated by field-based empirical analyses and numerical modelling, we need to consider the interaction between both entities to improve our predictive capabilities (Ploum et al., 2018; Sophocleous, 2002; Zimmer and McGlynn, 2017). Another common assumption is that similar catchments respond similarly to hydrological forcing from agents such as precipitation or evapotranspiration (ET) changes. For example, extrapolating observed discharge from one catchment to another similar, and closely situated, non-gauged catchment is often used to estimate volumetric runoff (Archfield and Vogel, 2010). However, as shown by Karlsen et al. (2016), there can be considerable variability of discharge patterns between seemingly comparable catchments due to hydrological landscape variability of sub-catchments at smaller scales. Therefore, studying hydrological functioning on only a large-scale basis without process-based insights into the contributions of different parts of the landscape leaves a gap in our understanding of surface and groundwater interactions, and the origin of groundwater recipient contribution (Doyle et al., 2005; Sivapalan, 2006).

Furthermore, catchment heterogeneity can impact water pathways and water travel times (Sprenger et al., 2018). For example, the local and regional topography affects the partitioning of groundwater and the speed of flow (Wu and Selvadurai, 2016). Seasonal variations, such as temperature and ET changes, can impact different catchment features to varying degrees. Losses through ET can fundamentally impact catchment hydrology and vary in time and space (Feng et al., 2020). Low temperature can cause soil frost and precipitation to fall as snow. Soil frost depths and duration can seasonally influence some catchment landscapes and affect infiltration and groundwater flow. Snowmelt and snowpack accumulation can also seasonally impact groundwater recharge (Hardy et al., 2001; Niu and Yang, 2006; Oni et al., 2017).

Catchment characteristics control water pathways and travel times, which are important for surface and groundwater quality and have recently been being studied in greater detail (Hrachowitz et al., 2016; McDonnell et al., 2010; Weill et al., 2011). In a catchment, water age is defined as the time water spends in a catchment after entering it. In turn, the time that has passed since water entered the catchment is called the residence time. In comparison, travel time is defined as the time it takes for water to travel from one point to another, regardless of its "real" age (McGuire and McDonnell, 2006; Rodriguez et al., 2018). Water pathways, groundwater dynamics and travel times affect the transport, mobilisation, accumulation, and dispersal of reactive and non-reactive solutes, as well as biological processes. This includes, for example, the weathering and transport dynamics of DOC (Hrachowitz et al., 2016; Kralik, 2015; Tiwari et al., 2017; van der Velde et al., 2012). However, to draw conclusions from modelled travel times regarding such processes, it is important to test models against empirical data linked to spatial variability of travel times.

1.2 Base cation weathering and transport

Weathering is an important process for both terrestrial and aquatic ecosystems as it is the main source of base cations, including magnesium (Mg), potassium (K), calcium (Ca) and sodium (Na). Magnesium, K and Ca are essential plant nutrients and crucial for biological processes such as energy storage, cell signalling and photosynthesis (Lawlor, 2004; Zhu et al., 2016). Moreover, Mg and Ca are important drivers for freshwater community structures. Calcium is also crucial for eggshell formation and calcification of invertebrate exoskeletons (Hessen et al., 2017; Jeziorski et al., 2008; Weyhenmeyer et al., 2019).

It is not only the products but also the actual weathering process that is important for the water quality of soil and surface waters. During the weathering process, carbonic acid often functions as a proton donor and is converted to hydrogen carbonate. This process increases the solubility of inorganic carbon in the groundwater, decreases the release of carbon dioxide to the atmosphere and can eventually lead to the precipitation of carbonate minerals such as calcium carbonate ($CaCO_3$), which is an important sink for atmospheric carbon. Hence, weathering is a controlling factor for the carbon cycle over geological timescales and is, therefore, of interest for climate change discussions (Goddéris et al., 2006). The base cation weathering process is also one of the most important acid-neutralising reactions in the soil. Groundwater pH is increased by silicate weathering, the major mineral group, due to proton consumption (Likens et al., 1998; Lydersen et al., 2004) and can impact the water quality of surface water recipients (Gbondo-Tugbawa and Driscoll, 2003).

Despite decades of declining emissions that cause acid deposition, acidification of soils and surface water remains an important environmental issue (Broadmeadow et al., 2019; Geller and Schultze, 2009; Moiseenko et al., 2018; Swedish E.P.A., 2020). The trend in decreasing acid precipitation in combination with a greater demand for renewable energy sources has moved the focus to the impact of land use on soil acidity, such as forestry (Johnson et al., 2018; Lamers et al., 2013; Lynch et al., 2000). When vegetation grows, base cations are needed as nutrients, which are replaced by protons. The process leads to temporary acidification of the soil water, counteracted when the vegetation decomposes (Iwald et al., 2013). However, if the biomass is removed, the acidification becomes permanent. To a certain degree, weathering can counteract such acidification and contribute significantly to the acid-naturalising capacity (ANC), a measure of a water's acid-base status (Povak et al., 2013). Therefore, making informed decisions regarding the sensitivity of surface water to acidification and ensuring sustainable land use depends on applying methods such as assessing the ANC of the groundwater (Akselsson and Belyazid, 2018; Davies et al., 2005; Fanjaniaina et al., 2021).

Recently, research into base cation weathering has increased since the process is of interest for assessing the long-term safety of spent nuclear fuel and waste repositories. Nuclear waste contains several long-lived radionuclides, which must be isolated from humans and the environment (Shahkarami, 2017). Thus, safe disposal is a major challenge for the nuclear power industry. One of the more commonly proposed options is to store nuclear fuel and waste in repositories deep below the ground surface. One such storage method is currently being reviewed in Sweden (Hedin et al., 2011; SKB, 2011). Here, the storage is placed in sparsely fractured crystalline bedrock located approximately 500 m below the ground surface. The multi-barrier design of the repository includes a coppar canister, a bentonite buffer material, and the bedrock itself. Infiltration by dilute groundwater may be detrimental to this type of repository (SKB, 2011). While a prolonged period with a recharge of meteoric water may compromise the repository integrity, the buffering capacity of the soil may counteract the penetration of dilute water into the bedrock. Thus, in hydrogeological applications such as site-descriptive modelling of potential repository sites (Selroos and Follin, 2014b, Bosson et al 2008), and in safety assessments of such repositories (Selroos and Follin, 2014a, Bosson et al., 2010), the understanding and quantitative description of soil weathering processes as linked to hydrogeological processes are of importance.

The link between catchment function and base cation weathering is still undetermined. However, the effects of the catchment heterogeneity, particularly on the weathering process, can be observed as solute concentration differences between sub-catchments and concentration changes during low and high streamflow, the so-called Q-C relationship (Abbott et al., 2018; Ameli et al., 2017; Van Meter and Basu, 2017). Increasing base cation concentration in groundwater with soil depth has also been linked to older groundwater (Bouraoui and Grizzetti, 2011). Consequently, the weathering process has been strongly linked to mineral soil contact time (Benettin et al., 2015; Maher, 2010). However, studies of weathering rates are often primarily focused on shallow soil, up to a few meters depth, because the weathering is assumed to be strongest in this part of the soil (Casetou-Gustafson et al., 2019; Lebedeva and Brantley, 2020; Ouimet and Duchesne, 2005). Weathering rates calculated from studies of shallow soils can vary significantly from rates calculated using mass balance methods (comparing precipitation inputs to stream recipient outputs). The difference occurs, at least in part, because shallow soil methods exclude potential deep soil contributions (Brantley et al., 2013; Gu et al., 2020). It is also difficult to assess the contribution from different landscape types using mass balance methods. Without proper hydrological modelling, such methods can only give long-term or annual weathering rate estimates. Depending on circumstances, it could also be important to consider the contribution from deep soil sources. For example, although weathering below the root zone does not produce a source of nutrients for vegetation, it could still be important for the water quality of downstream recipients, such as streams and lakes (Larssen and Carmichael, 2000; Watmough et al., 2014). Likewise, for assessing the chemical conditions in deep groundwater, for example, in relation to a deep repository for nuclear waste, the importance of weathering below the root zone must not be overlooked.

1.3 Dissolved organic carbon (DOC) dynamics

In boreal landscapes, DOC is the most abundant form of organic carbon in surface water (Kasurinen et al., 2016). The flux of DOC can have implications for the carbon budget and is one of the most critical sources of organic matter for food webs in surface water (Gorham, 1991; Jansson et al., 2007a). Dissolved organic carbon is an essential part of determining surface water quality because it plays a key role in regulating stream water pH and the mobilisation of metals and organic pollutants (ElBishlawi and Jaffe, 2015; Hruška et al., 2003). The affinity of DOC to bind and impact the solid-liquid state of metals makes it an important controlling factor in the transportation of contaminants and the impact of solutes on the biological systems in freshwater (Aiken et al., 2011; Takata et al., 2012). Many elements, including several important radionuclides that would be insoluble under normal conditions, can be mobilised by DOC. Particularly for metals, the organically bound fraction can often dominate the speciation in the aqueous phase (Andersson et al., 2006; Claveranne-Lamolère et al., 2009; Dahlqvist et al., 2007; Vasyukova et al., 2010). Furthermore, especially in organic riparian soils, the mobility of otherwise insoluble elements can increase considerably with the presence of high DOC concentrations (Lidman et al., 2017). This has consequences, both for the surface water quality and the long-term fate of pollutants, nutrients, and other solutes in forest ecosystems. Therefore, DOC can be used as an indicator of environmental risk, including transportation of hazardous metals and radionuclides (Tomczak et al., 2019). A better understanding of freshwater sources and release dynamics of DOC is an important step to improve the predictability of natural and anthropogenic element transport.

The DOC transport dynamics for streams and lakes are regulated by several factors, including precipitation, temperature and the soil characteristics close to the discharge areas (Dick et al., 2015; Raymond and Saiers, 2010). A significant DOC source in headwater catchments is organic soil from peatlands and organic riparian zones. The riparian zone is the interface that connects the stream to the groundwater and is often characterised by a change in soil composition and vegetation growth caused by shallow groundwater (Ye et al., 2019). Shallow groundwater levels, combined with low temperatures, promote the build-up of organic material in near-stream riparian zones, creating conditions similar to wetlands (Jansson et al., 2007b; Lidman et al., 2017). The riparian zone can significantly impact the water quality of groundwater discharging to surface waters, regardless of upslope conditions (Berggren et al., 2009; McClain et al., 2003; Vidon et al., 2019) and are often a critical DOC source of streams and lakes (Ledesma et al., 2015). However, depending on the local hydromorphology, the placement and size of riparian zones can vary significantly across a catchment, creating scattered DOC rich sources (Grabs et al., 2012; Kuglerová et al., 2014; de Mello et al., 2018).

Several approaches have been developed to model DOC in the riparian zone, connecting the runoff from catchments to DOC stream concentration (Catalán et al., 2013; Humbert et al., 2015; (Kasurinen et al., 2016; Son et al., 2019). However, such modelling attempts leave a gap in the knowledge regarding the placement of DOC-rich riparian zones within catchments, which could be an important factor when predicting water quality. Some modelling studies have also been highly parameterised due to the complexity of the processes involved (Dick et al., 2015). Another approach is the Riparian Integration Model (RIM) model (Seibert et al., 2009), which is based on the exponential increase of DOC concentration with increasing groundwater level, and has successfully predicted the riparian DOC concentration of a small till-dominated catchment. One explanation for the greater accumulation of organic material in the shallower soils is the typical decreasing hydraulic conductivity with soil depth, creating greater lateral flows in the shallow groundwater (Nyberg, 1995). However, inferring DOC concentration from streams exiting such a catchment to larger catchments or catchments dominated by sorted sediments tends to overestimate the stream DOC concentration. A combination of model studies and field observations has led to the suggested linking of DOC concentration of the riparian zone to the proportion of old groundwater or the subsurface travel time dynamics, instead of the groundwater level (Ågren et al., 2007; Jantze et al., 2015; Tiwari et al., 2014). The connection has yet to be tested using a fully distributed and integrated surface water and groundwater model. However, this type of investigation could give new insights into the travel time connection to the DOC concentration of riparian zones within catchments and facilitate the search for local DOC-rich sources.

2. Study site, data, and methods

2.1 The Krycklan Catchment (Papers I–IV)

The Krycklan catchment (64.23°N, 19.77°E, 67.9 km^2) is situated in northern boreal Sweden (Figure 1 and Table 1). The annual precipitation is, on average, 600 mm, and the ET has been approximated to be 50 % of the precipitation (Laudon et al., 2013, 2021). The climate is characterised by long winters. Snow cover typically starts in late November and lasts until late April, when snowmelt causes almost 50 % of the annual streamflow.

Table 1. Krycklan catchment characteristics, including size and soil properties.

	Catchment size (km^2)	**Till (%)**	**Mire (%)**	**Sandy sorted sediments (%)**	**Silty sorted sediments (%)**	**Lakes (%)**
C1	0.5	91	0	0	0	0
C2	0.1	79	0	0	0	0
C4	0.2	29	42	0	0	0
C5	0.7	47	46	0	0	6.4
C6	1.1	51	29	0	0	3.8
C7	0.5	68	16	0	0	0
C9	2.9	64	14	7	4	1.5
C10	3.4	64	28	1	0	0
C12	5.4	70	18	6	0	0
C13	7.0	60	10	9	9	0.7
C14	14.1	46	6	24	15	0.7
C15	19.1	64	15	8	2	2.4
C16	67.9	51	9	21	10	1
C20	1.5	55	9	0	28	0

The landscape is dominated by coniferous forests, mainly consisting of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) (Lidman et al., 2016). In the upper regions of the catchments, mires and lakes are intertwined into the forested landscape. Here, the soil deposits mainly consist of glacial till reaching depths up to 15–20 m (Bishop et al., 2011; Seibert et al., 2009). At lower altitudes, the primary soil deposits consist of sandy and silty sorted sediments, reaching depths up to at least 50 m. The mineral soil has been found to consist mainly of quartz plagioclase and K-feldspar and, to a smaller extent, apatite, biotite, hornblende and pyroxene (Erlandsson Lampa et al., 2020; Nyberg et al., 2001).

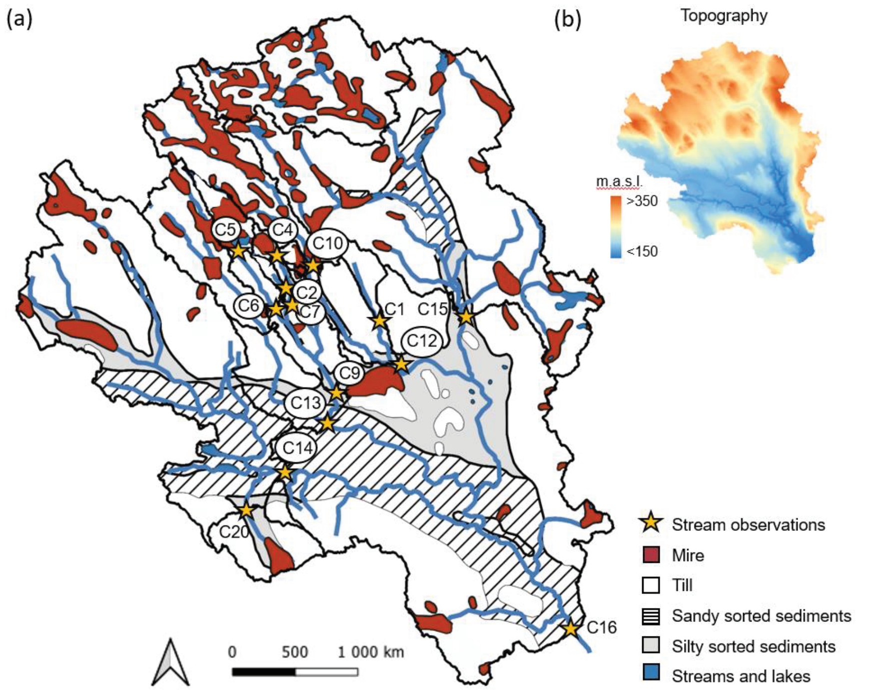

Figure 1. The Krycklan catchment. (a) Sub-catchment locations, stream network and main soil properties. Stream monitoring stations are marked with yellow stars. (b) Surface topography in meters above sea level (m.a.s.l.). Paper IV.

At the site, stream runoff, groundwater, and water quality have been monitored for more than 30 years, with the earliest data collection starting in the 1980s. The catchment is divided into sub-catchments with distinct features, with sizes ranging from 0.1 to 68 km^2. There is a discharge gauging station at each sub-catchment (Laudon et al., 2021). The central part of the data collected by the researchers and crew of the Krycklan Catchment Study (KCS), including water quality, stream, and groundwater measurements, can be acquired from the open Krycklan Database (www.slu.se/Krycklan). The mosaic landscape of forests, mires, and lakes, combined with the extensive datasets, give a unique opportunity to investigate the impact of spatial and temporal landscape variability on hydrology and water quality across scales.

2.2 Model tools and applications (Papers I–IV)

As described in Paper I, a hydrogeological flow model was established for the Krycklan Catchment and used in the research (Papers II–IV). The flow model was created in the fully distributed 3D Mike SHE tool and coupled to the simultaneously running streamflow model, Mike 11 (Figure 2, Paper I). Driven by time-varying climate data, topography, and soil properties, the model can calculate ET processes, saturated flow, unsaturated flow and overland flow across a catchment (Graham and Butts, 2005). In Mike SHE, ET processes are based on a methodology developed by Kristensen and Jensen (1975). Flow in the saturated zone is calculated in 3D using the Darcy equation, the flow in the unsaturated zone is calculated in vertical 1D using the Richards equation, and overland flow is calculated using Saint-Venant equations in 2D. The 1D Mike 11 model uses a high-order dynamic wave formulation of the Saint-Venant equations. Mike 11 allows for a more precise calculation of stream flows because it is not restricted to the grid size of Mike SHE. The Krycklan Mike SHE model was set to a horizontal resolution of 50 × 50 m. Vertically, the model was divided into ten computational layers, following the main stratigraphy of the soil. The unsaturated and saturated zone were fully integrated. When the soil is unsaturated, a finer unsaturated zone discretisation and equations are used.

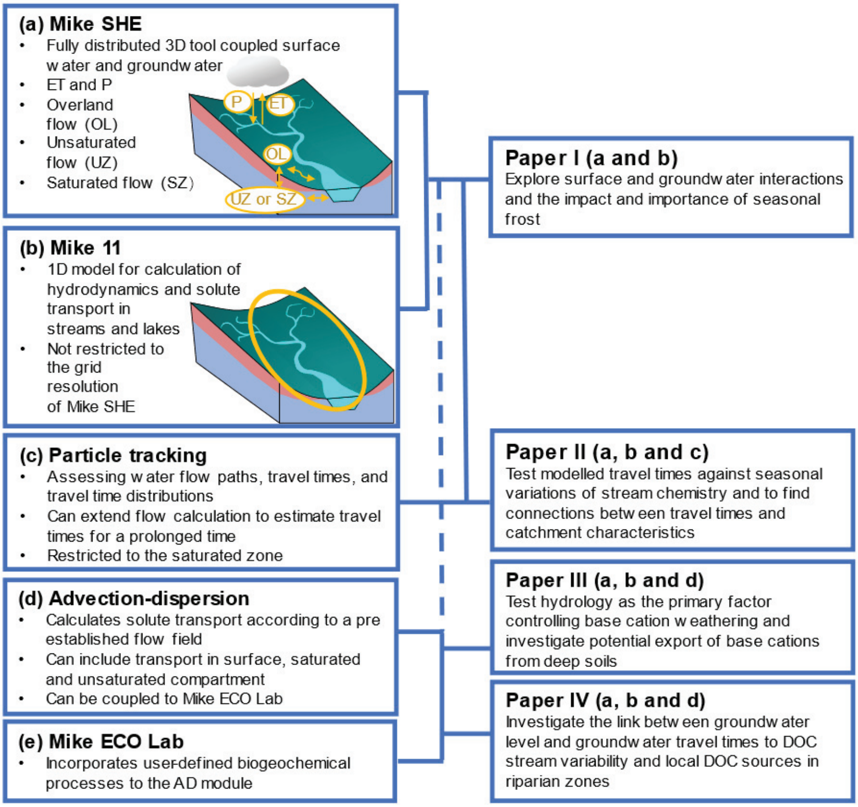

Figure 2. A schematic figure of model tools and applications. The figure shows the model tools used, the main usages for each tool and which were used in each paper of this thesis. The tools shown are (a) Mike SHE, (b) Mike 11, (c) Particle tracking (d) Advection-dispersion and (e) Mike ECO Lab.

As described in Paper II, particle tracking was used. It is a software module that can be added to Mike SHE to investigate groundwater travel paths and calculate groundwater travel time and travel time distributions (Figure 2, Paper II). Governed by the pre-calculated Mike SHE flow field, particles move in the groundwater by advection. Particle tracking in Mike SHE is restricted to the saturated zone only. However, it can repeat flow results and thereby extend the travel time investigations and, in turn, allow long-term travel time investigations. The methodology is further described in Bosson et al. (2010) and (2013).

For Papers III and IV, advection-dispersion methods were applied instead of particle tracking. The advection-dispersion module can be linked to an additional module called Mike ECO Lab, which can handle user-defined reactions (Butts et al., 2012). In each time step, the model calculates new concentrations for all cells. A cell's concentration can be changed by mixing, by pre-established sources or by reactions. Compared to particle tracking, all compartments (streams, lakes, overland flow, unsaturated flow, and saturated flow) can be included.

2.3 Surface water and groundwater interactions (Paper I)

In the work described in Paper I, the Krycklan model was calibrated to groundwater levels of 15 groundwater wells and the discharge of five sub-catchments (C2, C4, C5, C7 and C16), using data for 2009–2012. The calibration was a stepwise process based on four main actions, in order of increasing complexity of the involved processes (Figure 3). First, the overall water balance was calibrated at an annual and full-catchment scale (C16 and groundwater wells). The original PET, calculated using the Penman-Monteith formula, was stepwise reduced until the modelled ET-P ratio resulted in an accumulated flow at C16 close to observations (Step 1). Thereafter, remaining at a full-catchment scale, the properties of the dominating soils were calibrated (Step 2).

The calibration steps were evaluated using some of the smaller sub-catchments (C2, C4, C5 and C7). The small-scale catchments were used to separate mire and forest dominated sub-catchments, which allowed for an evaluation of the full-scale calibration on the function on these landscape types. The influence of the peat and soil properties on the flow dynamics of streams exiting these landscapes was evaluated (Step 3).

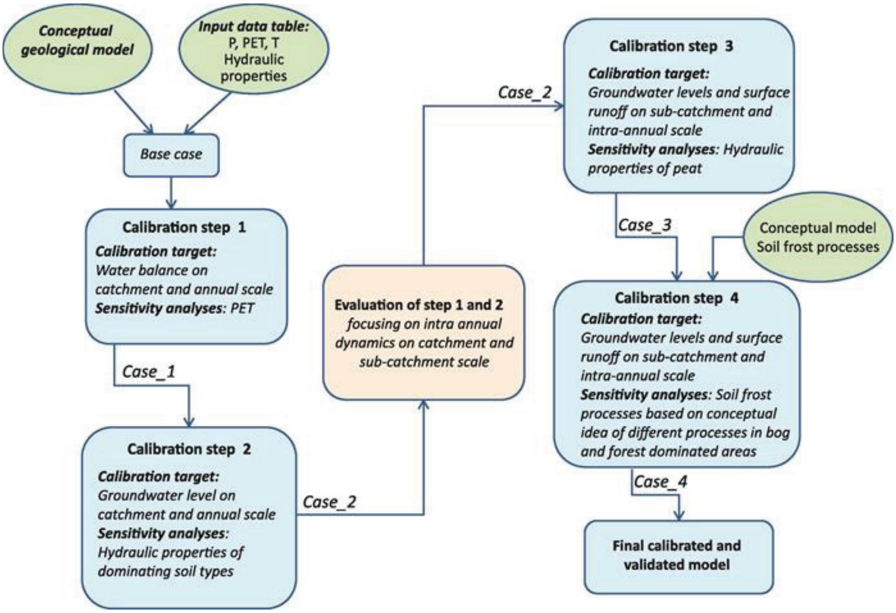

Figure 3. Calibration and evaluation procedure. The figure shows the stepwise calibration and validation process. Base Case: original model set up. Case 1: Water balance calibrated. Case 2: Hydraulic properties of the dominating soils calibrated. Case 3: Peat properties tested and evaluated. Case 4: Soil frost tested. Cases 1 and 2 were evaluated on a full catchment scale, while Cases 3 and 4 were calibrated on smaller sub-catchments. Case 4 was later validated in the final step on all sub-catchments. Paper I.

In a final step, the effect of soil frost was investigated (Step 4, Figure 3). Soil freezing was applied and tested by reducing infiltration and horizontal flow in soils during cold seasons (Johansson et al., 2015). Previous studies in the Krycklan catchment suggest greater event water ratios from mire-dominated catchments, with more water arriving at the streams as surface flow (Laudon et al., 2007; Peralta-Tapia, 2015). The event water is possibly caused by a greater impact of soil frost on the mires than forested soil. Seasonal soil frost may impact the surface and groundwater partitioning of catchments (Niu and Yang, 2006). In some cases, frozen soil may act as an impermeable layer preventing infiltration and increasing groundwater travel times (Brooks et al., 2012; Woo, 2012). The impact of soil frost is mostly visible during snowmelt episodes because the soil frost tends to produce more overland flow than unfrozen soils (Iwata et al., 2011; Orradottir et al., 2008). Soil frost was applied and tested for both forest and mire dominated sub-catchments in order to investigate the potential of soil frost to provide an explanation for the increased event water observed in mire-dominated sub-catchments (Figure 4).

The calibrated and validated model from Paper I resulted in a model that could simulate groundwater levels, intra-annual and accumulated stream flows. Although the main model setup remained the same for all the work (Papers I to IV), a few model updates were made, based on newly acquired data and specific catchment function insights, including adjustments to the location of the observation station at C5 and the hydrological conductivity of the silt. In Papers III and IV, the strength of the ET on the forest and mire was also slightly adjusted to account for higher ET from forested landscapes and lower ET from mire landscapes. However, at full scale, the average annual ET did not change. Instead, it was still approximately 50 % of precipitation, as with the previous model set up for the work described in Paper I.

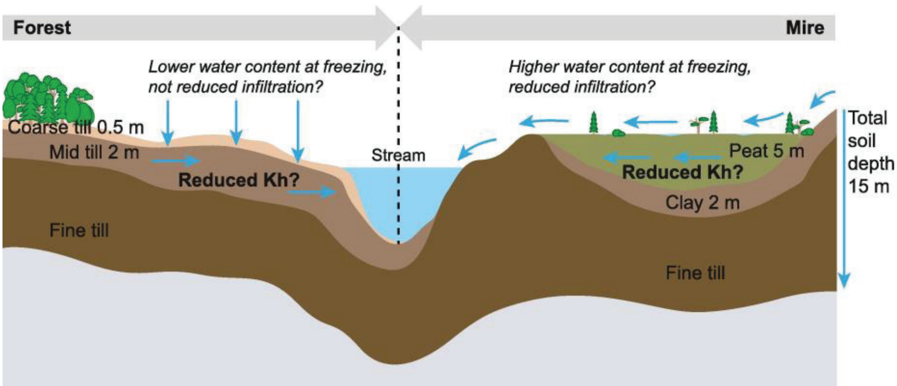

Figure 4. Soil frost. The conceptual model for the hydrological processes during soil frost conditions in a forest (left) and mire (right) dominated catchment. The two main frost processes evaluated are reduced flow in the upper part of the soil and/or reduced infiltration. Paper I.

2.4 Water travel times (Paper II)

For Paper II, modelled water travel times were tested against observed stream chemistry and later linked to catchment characteristics. Groundwater travel time was defined as the time from groundwater recharge to discharge in a stream and was calculated using particle tracking (Figure 2, Paper II). The particle tracking allowed investigation of long-term groundwater travel time because one year of flow results could be repeated, extending the particle tracking for several years. One year with normal precipitation and runoff was used and repeated, extending the particle tracking to 1000 years to capture the travel times of all discharging groundwater for all sub-catchments. The particle tracking module can only be used for the saturated zone of the model.

From the particle tracking, travel time distributions could be established for all sub-catchments. Several measures can describe the central tendency of these distributions, such as the arithmetic mean, median and geometric mean, all with advantages and disadvantages, depending on the distribution. For Paper II, a measurement was chosen that could describe the central tendency but could still take the length of the tail into account to distinguish the travel times of different streams better. The distributions became significantly skewed, making the arithmetic mean sensitive to the length of the tail. In comparison, the median does not take the length of the tail into account, that is, two distributions with the same median can have different tail lengths. Therefore, the geometric mean was used to analyse the central tendency of the distributions (MTT_{geo}) and was established on an annual and seasonal basis. The young water fraction was also established. For Paper II, the young water fraction was defined as the sum of groundwater fraction younger than three months together with the fraction of overland water (Lutz et al., 2018; Stockinger et al., 2019).

The model's performance was tested using the connection between water travel times and pathways to stream observations of $\delta^{18}O$ and base cation concentrations (Figure 5). Conceptually, the stream $\delta^{18}O$ variation is caused by seasonal variability in the precipitation signal (Figure 5). Winter precipitation is isotopically much lighter than that falling in summer, causing seasonal amplitude in the input signal, a difference that, to varying degrees, becomes replicated in the streams. The amplitude is reduced the more groundwater is mixed, and hence the longer water has, on average, resided in the soil before discharging to a stream. Therefore, conceptually, older groundwater generally has a signal closer to the long-term mean of the precipitation input. Due to precipitation falling as snow, the streams receive water from groundwater in winter only (Laudon et al., 2007; Peralta et al., 2015). Therefore, the winter signal can be more directly linked to groundwater travel times.

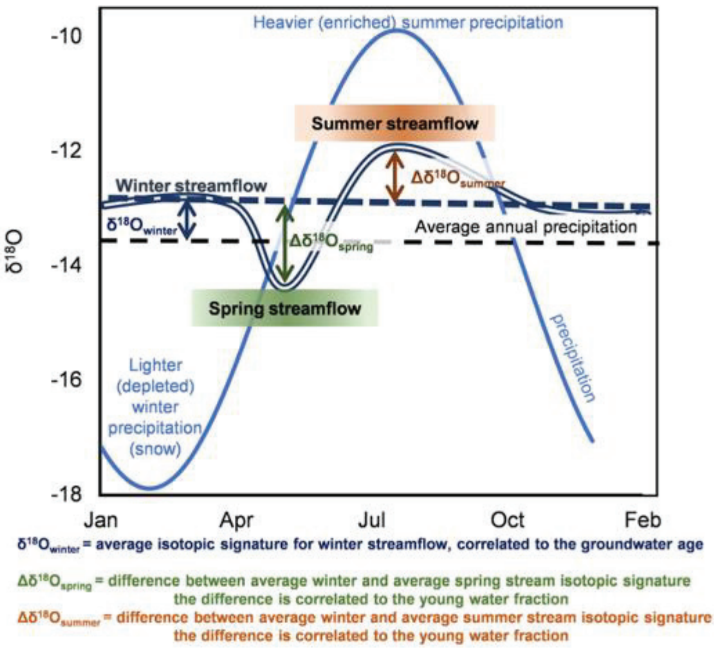

Figure 5. Conceptual figure of travel time to stream vs stream $\delta^{18}O$. The figure includes annual variations of $\delta^{18}O$ in precipitation and seasonal stream compositions. Paper II.

One issue using water isotopes to estimate travel time is that water older than 4–5 years often cannot be differentiated because the groundwater has reached complete mixing (Kirchner, 2016). However, the young water fraction may still be quantifiable even though there could be uncertainty regarding older water components (Benettin et al., 2020; von Freyberg et al., 2018). In spring, the stream winter signal is changed by the new input of melted snow with a much lighter signal (Laudon et al., 2004). Previous studies have also shown that the size of the young water fraction can be determined by calculating the difference between the spring and the preceding winter signal ($\Delta\delta^{18}O_{spring}$) (Laudon et al., 2007). Theoretically, the size of the young water fraction should also be distinguishable in summer, using the difference between the winter and summer signal ($\Delta\delta^{18}O_{summer}$). However, in summer, the precipitation is heavier than in winter. Therefore, in comparison to the negative relationship in spring, there should be a positive relationship.

Mineral soil weathering is the primary source of base cations in the boreal catchment system. Conceptually, increasing stream base cation concentration could be used as an indicator of travel time, or more explicitly, increasing soil contact time (Abbott et al., 2016; Erlandsson et al., 2016; Klaminder et al., 2011). Although no weathering occurs in mires (Lidman et al., 2014), the base cation stream concentration could still be used as an indicator of soil contact time by scaling it based on the mire proportion.

2.5 Weathering model (Paper III)

For Paper III, an advection-dispersion method was applied and coupled to a weathering model in Mike ECO Lab (Figure 2, Paper III). The weathering model was established to investigate the connection between base cation weathering and catchment hydrology (Figure 6). The weathering model was calibrated using groundwater base cation observations, and later validated using stream base cation observations. Two primary base cation sources, a constant precipitation source and soil weathering, were included. Weathering was permitted in the mineral soil and not allowed in lakes, streams, and mires. However, despite the lack of weathering, these landscape features could still receive base cations from surrounding areas. The weathering equation (Eq. 1) used in Paper III was based on a common method of estimating weathering (Ameli et al., 2017; Goddéris et al., 2006; Maher et al., 2009). In the weathering equation, the rate R depends on the maximum weathering rate (R_{max}), the concentration at the time (C^{t-1}), the equilibrium concentration (C_{eq}), and a brake constant which defines the dampening effect of an increasing concentration (b). The equation states that the concentration (C) at the time (t) is equal to the previous concentration (C^{t-1}) and increased by weathering.

$$C^t = C^{(t-1)} + R_{max}\left(1 - \frac{C^{(t-1)}}{C_{eq}}\right)^b dt \qquad \text{(Eq. 1)}$$

Four weathering rate equations were established, one for each base cation: Ca, Mg, Na, and K. The average from observed deep groundwater wells (>15 m) was used to establish C_{eq}, whereas R_{max} and b were calibrated using shallower groundwater observations. For Paper III, stream base cation exports and their link to catchment characteristics were evaluated. Mike SHE was also used to investigate weathering sources deeper than the first saturated calculation layer (>2.5 m).

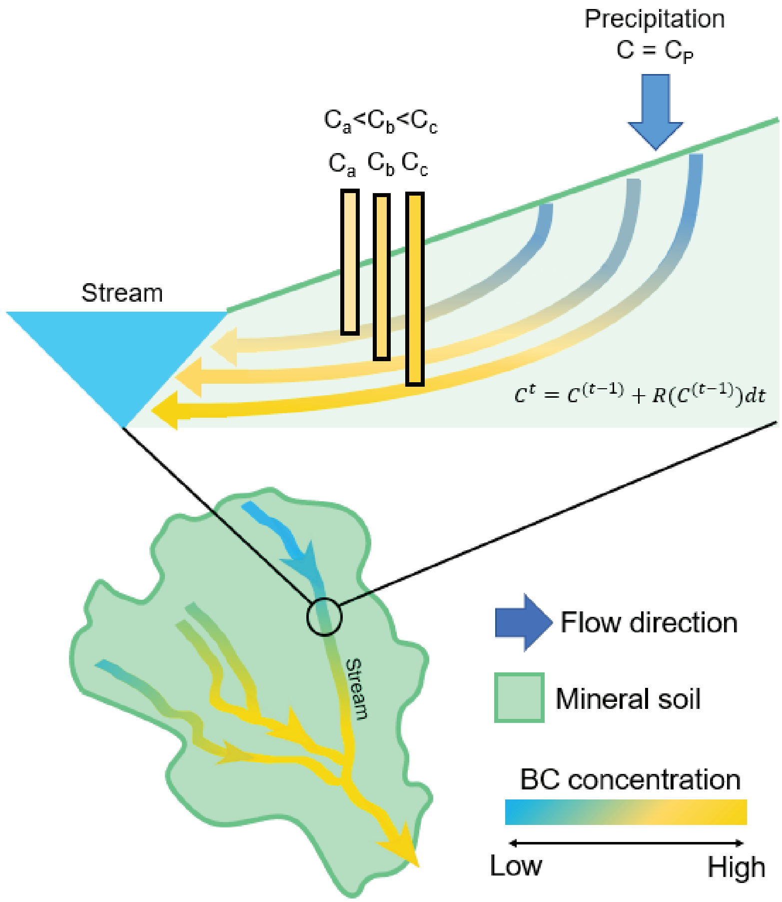

Figure 6. Weathering. A conceptual figure of the weathering model connecting increasing base cation (BC) concentration in the stream network to soil contact time. Streams receive groundwater with increasing concentrations due to weathering in the mineral soil. Paper III.

2.6 DOC model (Paper IV)

For Paper IV, a DOC model was established testing the stream DOC concentration connection to the groundwater level and travel times of the discharging groundwater. A concept established by Seibert et al. (2009), the so-called RIM model, was tested and further developed to allow an evaluation of MTT as a predictor of stream DOC concentration. The RIM model was based on an observed exponential increase in DOC concentration with an increase in groundwater level, as given in Eq. 2 (Figure 7a, Grabs et al., 2012; Laudon et al., 2007). In Eq. 2, C_{gw} describes the DOC concentration at a certain groundwater position (gw), C_0, is the surface groundwater concentration, and f is the shape factor of the exponential function:

$$C_{gw} = C_0 exp^{-f*gw} \qquad \text{(Eq. 2)}$$

The concept needs to be calibrated for a specific catchment. For example, deducing stream DOC concentration from small till-dominated soils overestimates the stream DOC concentration from larger catchments or catchments dominated by sorted sediments (Laudon et al., 2011). The overestimation may possibly be caused by less accumulation of organic material around riparian soils of sorted sediments (Grabs et al., 2012). It is also possible that the more even hydraulic conductivity may promote more even flow with soil depth, diluting DOC sources from shallower groundwater inputs (Figure 7b, Ågren et al., 2007; Tiwari et al., 2014). Larger catchments may also receive a greater input from deep and old groundwater (Tiwari et al., 2017). MTTs and groundwater levels are connected because MTTs of groundwater discharging to streams generally increase during low flow and are reduced during high flow (Hrachowitz et al., 2016). Deep groundwater and increased MTTs are both also associated with decreased DOC concentrations (Lessels et al., 2016; McDonough et al., 2020). However, MTTs may exhibit greater heterogeneity than groundwater levels because MTTs can vary across a catchment depending on the local soil properties and be affected by mixing different groundwater sources (Paper II, Ågren et al., 2014). Therefore, it is possible that MTT could be used as a predictor for DOC concentrations in the groundwater of riparian zones of a greater variety of catchments (Ågren et al., 2014; Jantze et al., 2015). Based on this conceptual knowledge and Eq. 1, a new model was developed and tested. It assumes a strong relationship between groundwater level and groundwater MTT:

$$C_{gw} = C_0 \exp^{-f*MTT} \qquad \text{(Eq. 3)}$$

In Eq 3., the groundwater level is replaced with MTT. C_{MTT} (mg l^{-1}) describes the concentration of the discharging groundwater based on daily changing MTT calculated with the help of Mike SHE. C_0 (mg l^{-1}) describes groundwater concentration with short travel times, and f describes the shape factor of the exponential function. In Paper IV, both the RIM (Eq. 2) and MTT (Eq.3) model was tested using daily changed groundwater level and MTT of the cells directly adjacent to the stream network.

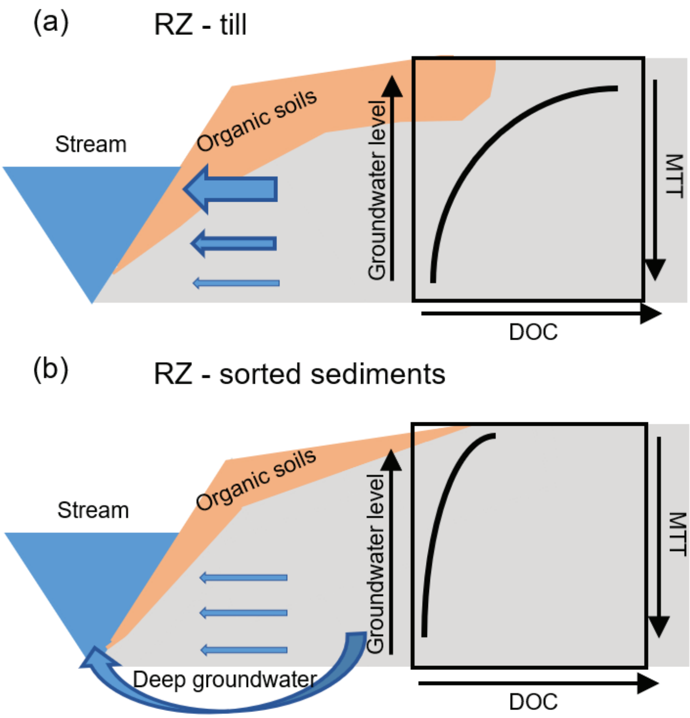

Figure 7. Conceptual figure: DOC in riparian soils. The relationship between increasing DOC release to streams based on groundwater flow (blue arrows), groundwater level and MTT in till soils. (b) Sorted sediments have a more stable hydraulic conductivity with soil depth promoting steadier flow regardless of groundwater level. Larger catchments may also be affected by dilution from deep groundwater sources. Paper IV.

Seibert et al. (2009) observed that shallow (young) groundwater in till soils could vary between approximately 20 mg l^{-1} to 80 mg l^{-1} with a shape factor varying between 0.5 and 4 and a strong seasonal relationship regarding the constant f and C_0. Generally, a higher C_0 and greater f can be expected in July to October, whereas a lower C_0 and f can be expected in May and June (Winterdahl et al., 2011). The seasonal variations in stream DOC concentrations are assumed to be related to soil temperatures and biological activity, with increased DOC concentrations in riparian zones during summer, reducing after the start of the spring snowmelt. Therefore, different exponential functions would be expected for different seasons. The DOC dynamic constants f and C_0 were calibrated using stream DOC observations from site C2 (till-dominated sub-catchment).

Peat dominated wetlands do not exhibit the same groundwater and DOC dynamics as till soils. The groundwater level is generally stable with consistently high DOC concentrations (Laudon et al., 2011). The main exceptions are the dilution in May–June due to the influence of the spring snowmelt, and the increase in July–Oct due to high ET. Therefore, the mires were given an average monthly concentration based on C4 (a mire-dominated sub-catchment) to test the groundwater level and MTT concept on sites including mires.

3. Summary of results and discussion

3.1 Surface and groundwater interactions (Paper I)

For Paper I, the Mike SHE model was established, calibrated, and validated. First, the general water balance was calibrated using the accumulated streamflow from the main outlet of C16 and the observed water levels of the scattered groundwater wells (Steps 1 and 2, Figure 3). The P-ET ratio was calibrated to approximately 50 %, close to previous estimates presented by Laudon et al. (2013). The two first calibration steps were then evaluated for some of the smaller sub-catchments. It was found that the modelling of the water balance of all sub-catchments had benefitted from the two first calibration steps. However, the discharge dynamics of the mire-dominated sub-catchments were not fully captured (Figure 8).

The mires had, at this point, been excluded from the calibration because of their relatively small proportion compared to other soil types at larger scales. The peat properties had little effect on the overall water balance. However, at smaller scales, their impact became more prominent for certain sub-catchments and determined much of the peak flow during rain events and the amount of water reaching the streams during spring snowmelt. Therefore, the functioning of the mires was evaluated using the peat properties and soil frost (Steps 3 and 4).

Modelling peat with higher hydraulic conductivities solved issues of streamflow being too rapid during intense rain events but resulted in too little water reaching the streams in spring. Frost was implemented in the model and tested on all soils from early winter until late spring, resulting in more water discharging to the streams as overland flow (Figure 4). In forest-dominated sub-catchments, the soil frost led to an overestimation of the amount of water reaching the streams. In comparison, in mire-dominated sub-catchments, the frost helped reduce the effect of the new peat properties in spring, increasing the amount of water reaching the streams. The results were supported by independent isotope studies and, later, by findings given in Paper II, that showed that surface and groundwater partitioning of the forest and mire during spring snowmelt function differently (Laudon et al., 2007; Peralta-Tapia et al., 2016). In the forest, snowmelt water is infiltrated and discharged to the streams as more slow-moving groundwater, while the peat frost results in more fast-flowing overland flow. The reason is most likely that the peat is saturated when it freezes, which creates an impermeable layer of soil frost. In comparison, the forests soils are unsaturated and, therefore, will remain partly permeable even when frozen.

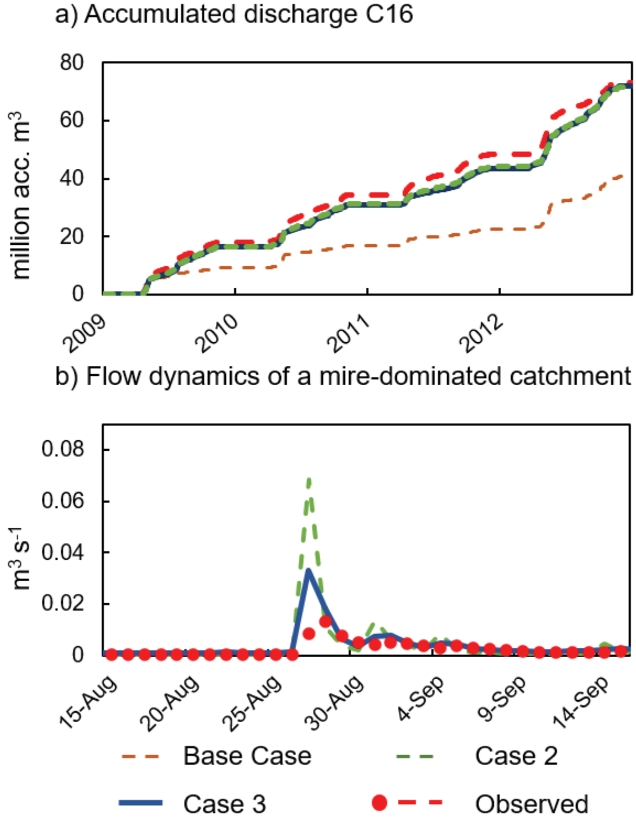

Figure 8. Flow results. The figures show the Base Case (before water balance calibration), Case 2 (full-scale calibration), Case 3 (peat properties). (a) The accumulated discharge of the full-scale catchment (b) discharge of C4 and the impact of peat during an example of a heavy precipitation event. Based on data from Paper I.

The final model was successful in reproducing the observed water balance, groundwater levels and general streamflow dynamics. The mean accumulated discharge error for all streams was 1 % ± 15 % (standard deviation) and an average groundwater level mean error of 0.1 m ± 0.23 m (standard deviation). The P-ET ratio was the most important calibration parameter for the overall water balance, while the soil properties were found to be more critical to the flow dynamics. To an extent, the model could capture the specific discharge patterns among the different streams as observed by Karlsen et al. (2016), even though the modelled P-ET ratio was similar for all sub-catchments. The results described in Paper I suggest that spatial ET variability may not be the only important factor controlling the differences in specific discharge among streams. Landscape characteristics, such as soil properties and soil frost, can also be important controlling factors. In particular, soil frost in mire-dominated sub-catchments was found to be important for the boreal landscape. The model (and, later, the work for Paper III) also indicated that there could also be deep groundwater flow paths, resulting in an import and export of groundwater between sub-catchments. Karlsen et al. (2019) also reported that soil properties combined with deep soil paths could be potential explanations of observed specific discharge variations between closely located sub-catchments. However, this needs to be further studied.

Paper I highlighted the importance of investigating catchments at smaller scales to find and characterise important factors controlling streamflow dynamics and surface water and groundwater partitioning. Improving our ability to describe the hydrological functioning of different landscape characteristics at smaller scales accurately is an important step in understanding the factors that affect water quality, including water pathways and travel times.

3.2 Water pathways and travel times (Paper II)

For Paper II, annual and seasonal MTT_{geo} and young water fractions were established for the water discharging to the streams of each of the 14 investigated sub-catchments. On an annual basis, the MTT_{geo} varied from 0.8 to 2.7 years. The longest MTT_{geo} was found in winter (MTT_{geo} = 1.2–7.7 years) due to accumulated snowpack and, subsequently, little groundwater recharge. In contrast, the shortest MTT_{geo} was found in spring during the snowmelt (0.5–1.9 years). The travel times fluctuated during summer due to ET variations and short, but sometimes intense, precipitation (Figure 9).

The results were supported by observed base cation and $\delta^{18}O$ records (Krycklan Database, 2013; Laudon et al., 2007). The seasonal travel times strongly correlated to the observed stream base cation records, with higher concentrations in winter and more diluted concentrations in spring (Figure 9). Additionally, sub-catchments characterised by discharging groundwater with overall longer travel times exhibited higher base cation concentrations. For example, C2, with shorter travel times, had a lower annual base cation concentration than C20 (Figure 9). As shown in Figure 9, spring and summer $\Delta\delta^{18}O$ strongly reflected the young water fractions (less than three months) for each stream. The streams with a greater discharge to overland flow and a greater fraction of young groundwater had a larger $\Delta\delta^{18}O$. Moreover, as shown in Figure 9, winter decreases in $\delta^{18}O$ signatures correlated with the isotopic composition ($r=-0.80$, $p<0.01$). The long-term precipitation average corresponded to older stream water (Figure 9).

The MTT_{geo} was mainly correlated to the areal coverage of silty sorted sediments ($r=0.90$, $p<0.05$), which overshadowed the impact of any other catchment characteristic, including catchment size previously found important by Peralta-Tapia (2015) and Tiwari et al. (2017). C20 best illustrated the importance of silty sorted sediments. Although the catchment is small, it still had the longest annual MTT_{geo}, suggesting that catchment size is not necessarily the primary factor controlling travel times. The catchment size was, however, an important factor for catchments with comparable soil distribution. Therefore, the results given in Paper II highlighted how the assumption that increasing catchment size leads to increased travel times might only be valid when the distribution of different soils is comparable.

The increasing young water fraction was mainly connected to the increasing areal coverage of mires, providing the streams with more overland flow. The mire effect was mainly visible in spring due to the mire frost. For example, the forest-dominated C2 area received less water as overland flow compared to the similar-sized and mire-dominated C4 area. The soil frost in C4 caused larger seasonal variation in travel times and young water fractions than in C2. Furthermore, the effect of silty sorted sediments was strongest in winter. Therefore, catchments which had both landscape features integrated, for example, peat and silt, such as in C20, exhibited larger seasonal variations in MTT_{geo} due to the seasonality of these landscape features. Longer travel times were seen in silty soils compared with catchments dominated by till soils. The pattern can be explained by the transmissivity feedback processes of till soils caused by the exponential decrease in the hydraulic conductivity with depth (Bishop et al., 2011). During precipitation events, the infiltrated water in till soil quickly raises the groundwater level, promoting groundwater flow in soils with greater hydraulic conductivity, reducing travel times. Therefore, even though groundwater in deeper till soils can be older and more stagnant, most discharging water is relatively young (Kolbe et al., 2020). In comparison, sorted sediments have a more uniform hydraulic conductivity with soil depth, increasing the proportion of deep groundwater discharging to the streams.

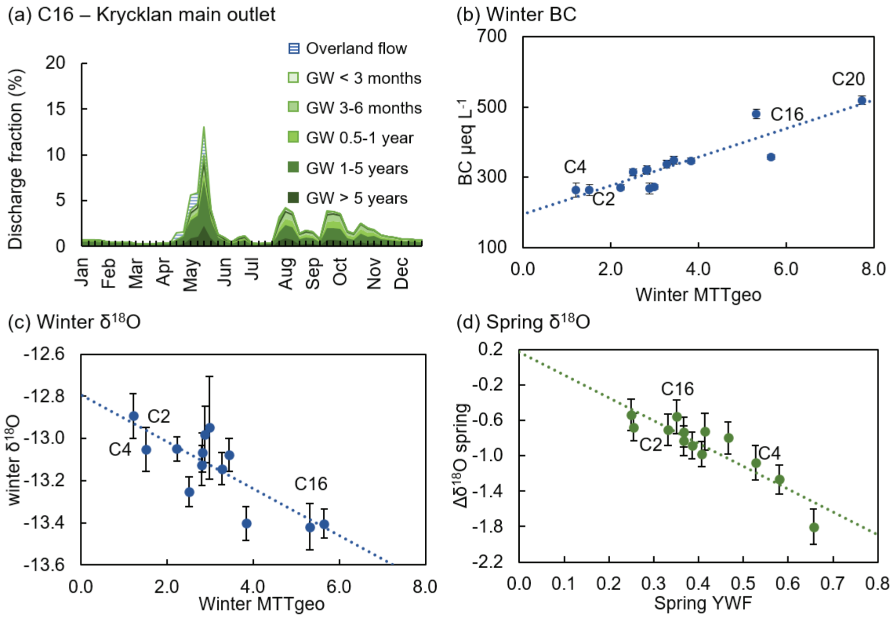

Figure 9. Mean travel time and stream chemistry. (a) The annual proportion of water discharging to the streams of the Krycklan catchment, including the proportion of overland flow and different travel time groups of groundwater. (b) Relationships of annual MTT_{geo} and annual base cation (BC) averages. (c) Relationships of winter MTT_{geo} and $\delta^{18}O$ (d) relationships of young water fractions (YWF) and $\Delta\delta^{18}O_{spring}$. Based on results from Paper II.

3.3 Base cation weathering rates and transport rates (Paper III)

The connection between weathering rates, hydrology, catchment characteristics and travel times was further explored for Paper III. A weathering model was applied and calibrated for the four base cations: Ca, Mg, Na and K (Eq. 1). The calibrated model captured annual and seasonal variations of Ca, Mg and Na for the 14 investigated streams effectively, with concentrations low in spring and high in summer (Figure 10). Although not all daily changes were captured, the general Q-C relationship was well predicted. The strong correlations emphasised hydrology, especially mineral soil contact time, as the primary factors affecting base cation weathering. Daily deviations could be flow-model based. Since stream concentrations were not measured daily, small inaccuracies in the timing of modelled discharge could reduce the accuracy of predicting concentrations. Inaccuracies may also be linked to biogeochemical processes not included in this model version, such as biological uptake and release (Campo et al., 2000; Moslehi et al., 2019); this is mainly noticeable for the most bioactive base cation K (Salmon et al., 2001; Tripler et al., 2006; Vitousek, 2004).

Supported by results from Paper II, those from Paper III showed that increasing stream base cation export was correlated to longer travel times (Benettin et al., 2015; Maher, 2010). However, the work described in Paper III gave new insights into the behaviour of the individual base cations (Table 2). Increasing concentrations of Ca, Mg and K were strongly correlated to longer travel times. Since Ca forms most of the Krycklan base cations, a strong correlation between the increasing total concentration of base cations and longer travel times could also be found. Moreover, streams received more base cations originating from deep soil sources with increasing travel times (Table 2). The results from Paper II also illustrated the strong connection between pH and base cation weathering (Table 2), supporting the importance of weathering as an acid-neutralising process (Larssen and Carmichael, 2000; Watmough et al., 2014).

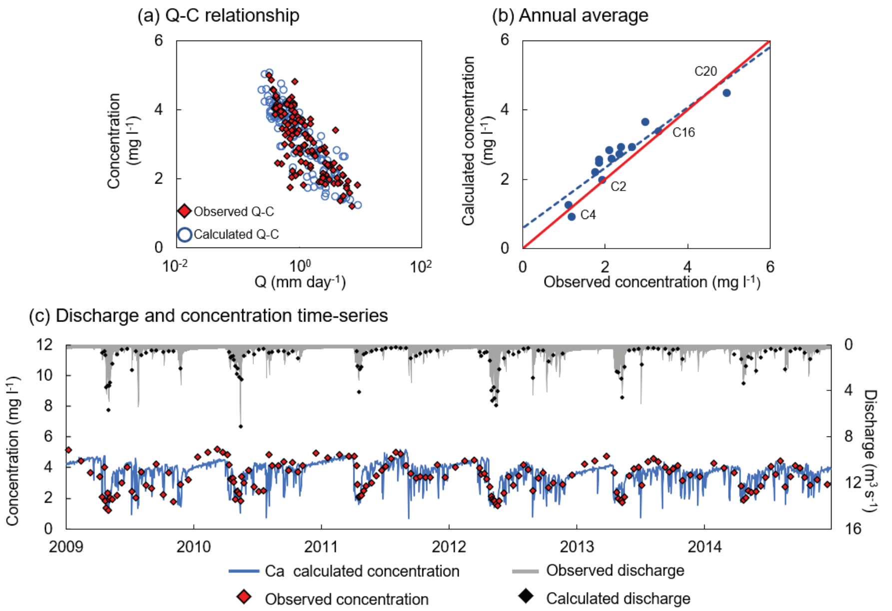

Figure 10. Weathering model results. (a) The Q_{model}-C_{model} and the $Q_{observed}$-$C_{observed}$. (b) Annual Ca concentration averages, calculations against observations (mg l^{-1}). (c) Modelled and observed Ca stream concentration (left y-axis) and modelled and observed discharge (right y-axis). Based on results from Paper III.

Na was the base cation least correlated with travel times. Instead, decreasing Na concentrations of the Krycklan stream correlated to the areal proportion of non-weathered landscape features, such as mires and lakes. The difference from the other base cations was mainly caused by the sharp decline in weathering in the shallower part of the soil (Table 2). This reduction in weathering is possibly caused by the groundwater reaching equilibrium with plagioclase in the shallow parts of the soils, one of the major Na-bearing minerals (Erlandsson Lampa et al., 2020).

A significant export from deep soils was described in Paper III. Even though weathering below the rootzone might not sustain forests themselves with nutrients, it could have implications for the pH and nutrient status of groundwater recipients, such as streams and lakes. However, methods to assess acidification of biomass removal are often focused on shallow soils (Akselsson and Belyazid, 2018). In Paper III, it was suggested that such methods might underestimate the weathering rates when hydrologically-active deep soils are present. Klaminder et al. (2011) noted that different methods tend to rank catchments weathering rates equally. However, they can provide vastly different estimates. Therefore, several methods should be used to assess weathering rates at the same site. The approach presented in Paper III could provide a complimentary method to assess the proportion of export from deep soils.

Table 2. Correlation matrix of base cation export to streams. The table shows the stream export rates of base cation (BC), Mg, K, Ca, Na and BC from deep soils (eq m^{-2} $year^{-1}$) and their correlation coefficient (r) to MTT_{geo}, (Paper II), log catchment size (Log A, km^2), the area proportion of mires and lakes (M & L, %), and pH. Paper III.

r	MTT_{geo}	Log A	M & L	pH
Log A	0.63	1.00		
Mires and Lakes	-0.50	-0.20	1.00	
pH	0.87	0.80	-0.52	1.00
Total export of BC	0.77	0.58	-0.69	0.80
Total export of BC: deep soils	0.86	0.69	-0.58	0.87
Total export of Mg	0.78	0.63	-0.70	0.83
Total export of K	0.78	0.58	-0.57	0.73
Total export of Ca	0.83	0.61	-0.64	0.84
Total export of Na	0.57	0.42	-0.79	0.58

3.4 Spatial DOC dynamics (Paper IV)

The link between the groundwater level and MTT to the stream DOC variability was investigated for Paper IV. Applying the groundwater level concept and calibrating the model with a small till-dominated catchment, resulted in an overestimation of the DOC concentration of stream exiting larger catchments and catchments dominated by sorted sediments (Eq. 2, RIM model). The dynamics of MTT of discharging groundwater was a better predictor of DOC stream concentration for different sub-catchments (Eq. 3 MTT model). The application of MTT reduced the concentration from sorted sediments associated with longer travel times while keeping the concentration from till soils high during high flows. On an annual basis, the MTT model could predict the DOC concentration of the Krycklan streams. Accounting for seasonal changes, the model could estimate seasonal stream concentrations and the observed spatial DOC variation of the riparian zones across Krycklan (Figure 11).

The variability of stream DOC dynamics has previously been linked to the heterogeneity of landscapes, with increased DOC concentration from till soils and decreased concentration from sorted sediments and larger catchments (Aitkenhead et al., 1999; Ivarsson and Jansson, 1994, 1995). The results described in Paper IV suggest MTT to be a strong predictor of DOC variability in riparian zones within catchments, supporting the idea that the hydrology strongly influences the heterogeneity of local DOC sources (Laudon et al., 2011; Raymond and Saiers, 2010). However, the mechanism behind the connection remains elusive and needs to be investigated further.

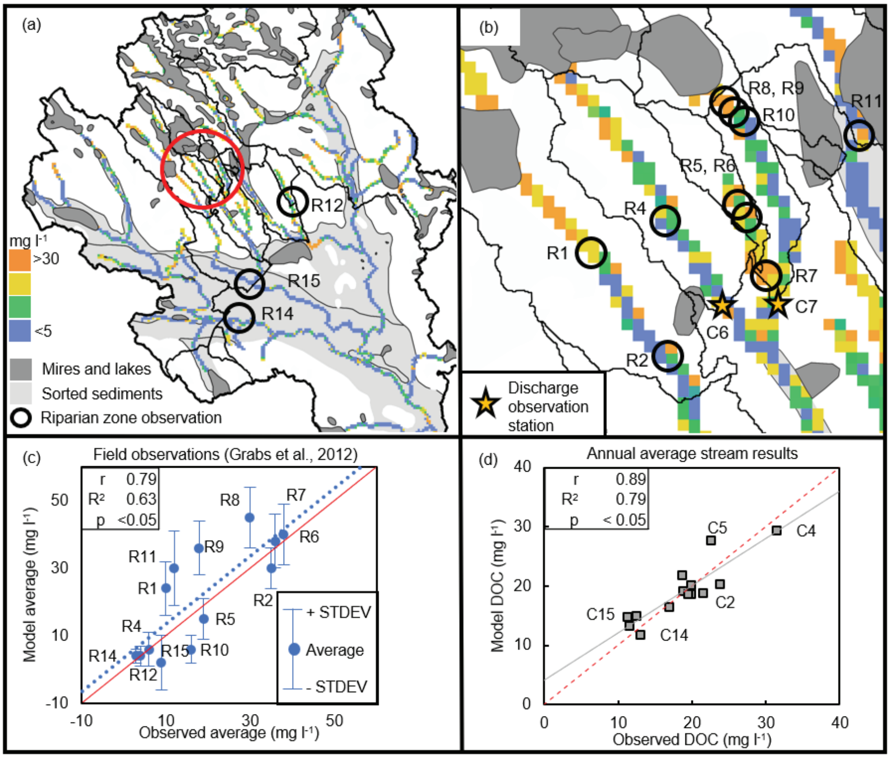

Figure 11. Modelled DOC concentration in the riparian zone. Results based on annual average from the MTT model. (a) Modelled DOC concentration and locations of riparian zone field station. (b) Magnification of area in red circle in (a), including the location of stream outlets C6 and C7. (c) Modelled against observed annual averages (Grabs et al., 2012), (d) annual model stream DOC concentration, including the 1:1 trend line (red) and the main statistics of the regression. Paper IV.

According to observations by Grabs et al. (2012), sorted sediments might not be as organic as till soils. A suggested explanation is that sorted sediments have a greater specific surface area, which increases the potential of mineralisation of DOC (Ågren et al., 2007; Kalbitz et al., 2000). Another suggestion is that a greater volume of deeper and older groundwater is discharged to streams exiting from sorted sediments, due to a more evenly distributed hydraulic conductivity with soil depth compared to till soils (Figure 7, Tiwari et al., 2014).

Even though there are models with greater predictive power on a daily timescale, most models must be calibrated for specific catchment characteristics (Kasurinen et al., 2016; Oni et al., 2014; Winterdahl et al., 2011). The model tested for Paper IV has advantages since one set of DOC parameters combined with a 3D flow model could estimate stream DOC concentration across contrasting catchment types and be used to find potential DOC-rich riparian zones. This type of model could be a useful tool in water quality studies, such as finding potential risk areas of transport of a wide range of hazardous metals and radionuclides, since these are strongly linked to the transport of DOC (Claveranne-Lamolère et al., 2009; Dahlqvist et al., 2007; Tomczak et al., 2019; Vasyukova et al., 2010).

Currently, the DOC model cannot account for processes occurring within streams and lakes. In Krycklan, due to the relatively short in-stream travel times, processes such as photochemical and microbial processes have been found to have negligible effect (Ågren et al., 2007; Tiwari et al., 2014). Lake processes, such as microbiological decomposition or DOC production, however, have been found to be much more important because of the prolonged time water spends in lakes (Weyhenmeyer et al., 2012). As described in Paper IV, lake processes could explain the relative overestimation of lake-influenced catchments such as C5, especially in summer. However, on an annual timescale, the overestimation is less significant, suggesting that the model could still be used to estimate annual stream DOC on catchments with short in-stream travel times and catchments where the proportion of the total area that is lake is smaller than at least 6%.

4. Summary of conclusions

The main aim of the work described in this thesis was to obtain a deeper understanding of the hydrological functioning across scales of a heterogenous catchment and link it to base cation weathering and DOC stream dynamics. Combining the 3D surface-groundwater flow model Mike SHE with data from the well-studied Krycklan catchment gave a unique opportunity to investigate these questions. The heterogeneous boreal landscape encompassed various catchment features, such as mires, forests, lakes, and a seasonal component consisting of periodic snow accumulation, snowmelt, and soil frost. The infrastructure and long-term monitoring data (including surface and groundwater flow and quality) allowed for investigations of sub-catchments with different scales and features along with extensive testing of the model results against real observations. Paper I described work that enhanced our knowledge of surface and groundwater interactions and the impact of small-scale features. The work described in Papers II to IV improved our understanding of travel times, base cation weathering, stream DOC variability and their interconnection to different landscape characteristics. The main lessons learned through this thesis work are:

- Small features, such as mires in the boreal Krycklan, can greatly influence the partitioning of surface and groundwater, affecting the water chemistry and travel times. Soil frost inhibits groundwater recharge and increases the amount of water arriving at recipients as overland flow. Consequently, overland flow dilutes streamflow chemistry from headwater down to larger catchments and increases the young water fraction across scales. Such small features may not have a major impact on the water balance on larger scales. Therefore, processes such as soil frost can be ignored in hydrological models.

- Soil properties and deep flow paths may explain variability in specific discharge and water quality. For example, the main factor controlling travel times was found to be soil property. Therefore, scaling hydrological features, such as specific discharge or travel times, to catchment size may only be an option when the distributions of different soils within the catchments are comparable.
- The fact that a complex hydrological model connected to a relatively simple weathering model was able to reproduce stream concentrations of different sub-catchments suggests a strong connection between the boreal catchment hydrology and the weathering of mineral soils. In Krycklan, the mineral soil contact time was the main controlling factor for catchment export of the base cations, specifically Ca, K, and Mg. In comparison, Na was not strongly linked to travel times because of the relatively fast weathering of Na in combination with Na reaching equilibrium in shallow soils. Instead, the concentration variability of streams was linked to the areal proportion of non-weathered features, such as mires and lakes.
- There might be significant base cation exports from deep soils when hydraulically-active deep soils in catchments are present. Deep soil weathering could counteract base cation dilution of groundwater and have implications for estimating nutrient and ANC exports. Depending on the topic at hand, deep soil sources may be important to consider in water quality studies.
- In Krycklan, MTT of groundwater was a useful predictor of stream DOC dynamics and the spatial variability of DOC in the riparian zone. Using the same parameters for all soils and sub-catchments, MTTs were found to be a better predictor of DOC concentration differences. The results detailed in Paper IV support the argument that hydrology is an important factor controlling DOC stream dynamics, and MTT could potentially be a useful DOC predictor for the riparian zone of other catchments.
- A well-calibrated and validated surface water and groundwater model, including spatial catchment characteristics such as soil and frost processes, can be a valuable tool to investigate catchment water chemistry at different spatial and temporal scales.

5. Future perspectives

The work this thesis describes strived to achieve an increased understanding of groundwater and surface water interactions across scales and the controlling factors of travel times, base cation weathering, and DOC dynamics. Together with the calibrated and validated Krycklan Mike SHE model, the knowledge and system understanding presented in this thesis opens up new opportunities for future research questions and directions. Here, I provide some possible future research topics as a way forward. These topics include climate change investigations, transport studies, and model developments.

5.1 Climate change investigations

Regions in northern altitudes, including the boreal forests, are potentially more sensitive to climate change because they are predicted to experience the largest increase in air temperatures and be subjected to precipitation changes (Diffenbaugh and Field, 2013; Gauthier et al., 2015). The boreal landscape is an important biome for forestry, and constitutes about 30% of the world's dense forests (Brecka et al., 2018). Climate change can profoundly influence the hydrology and water quality of the boreal landscape, impacting forestry, terrestrial and aquatic ecosystems.

Several interconnected factors can synergistically affect catchment hydrology, which can be difficult to predict. Landscape characteristics play a key role in catchment sensitivity to changing climate conditions (Teutschbein et al., 2018). For example, the increased temperature can result in shorter winters with less snow accumulation. A shallower snowpack may increase soil frost depth, increasing the thawing time and subsequently causing a larger fraction of overland flow in spring. However, a shallower snowpack can decrease the amount of spring snowmelt (Oni et al., 2015). The work this thesis describes has demonstrated a greater seasonality in travel times, young water fractions and stream chemistry caused by the shift from winter to spring. If the seasonality is reduced, it is possible that the seasonal water quality will change, having an impact on both terrestrial and aquatic ecosystems, which could be further explored. Jungqvist et al. (2014) also noted a disconnect between changing air and soil temperatures, increasing the difficulty to predict the effect of climate change on catchment hydrology and biogeochemistry.

The Krycklan flow model, which includes surface and groundwater flow in a 3D environment, gives a unique opportunity to investigate climate change impact on this biome and its integrated parts, as well as expand on the knowledge gained through the work described in Papers I and II. It would also be possible to study the hydrology and water quality of catchments in different climate regions, expanding on this thesis and other climate research. Currently, there is a Mike SHE model developed for three sites with an extensive dataset of hydrology and biogeochemistry data, including Greenland (arctic), Krycklan (boreal) and Forsmark (temperate), which presents opportunities for new studies of catchments along a climate gradient (Paper I, Bosson et al., 2013; Johansson et al., 2015).

5.2 Transport studies and model developments

Terrestrial and aquatic ecosystems are affected by their water quality, including base cation sources and water pH, both of which are impacted by soil weathering (Larssen and Carmichael, 2000; Watmough et al., 2014). Results from Paper III highlighted that there can be a significant portion of catchment export of base cations originating from deep soil sources, potentially important for surface waters. Investigating other catchments could give a clearer picture of the significance and proportion of deep soil contribution depending on catchment characteristics, soil depth and local mineralogy. It is also possible that specific discharge and travel time variability is caused by deep flow paths, causing import and export of groundwater between sub-catchments.

Results from Papers III and IV also suggested travel times to be a strong predictor of both base cation and riparian zone DOC variability. However, both the weathering and DOC model could benefit from supporting studies of other catchments to assess the real potential of the predictive power of travel times and the mechanisms regulating base cations concentration and DOC fluxes. Model studies of other catchments, applying the same or similar methodology as presented in Papers III and IV, could help unravel these underlying mechanisms. Such studies could also benefit from accompanying field studies that expand the monitoring to sites with other catchment characteristics and climates.

All papers greatly benefitted from the infrastructure and the long data series available at Krycklan, allowing investigations of several catchment characteristics at different scales, showcasing the importance of continuing and growing these types of interdisciplinary research infrastructures, where modellers and field research can come together and exchange data and knowledge. It is extremely useful to have access to an extensive dataset to test models against. However, groundwater and stream observation equipment cannot be installed everywhere, but can be installed in key areas. Therefore, it is also useful to test theories developed from field research on models to allow a larger scale perspective.

The model approaches presented in this thesis could also be further developed. For example, important biogeochemical reactions and sorption could be added. Then, the weathering model approach could be applied to solutes more reactive than base cations and possibly also better represent K fluxes (Paper III). For the transport modelling of more immobile elements in the landscape, the DOC model would also play an important role, since much of the transport of such elements in boreal waters is known to occur in the form of organic colloids (Claveranne-Lamolère et al., 2009; Dahlqvist et al., 2007; Vasyukova et al., 2010). The inclusion of lake and in-stream processes would also allow the DOC model to be applied to catchments with a larger proportion of lake and catchments with longer in-stream travel times (Paper IV).

Furthermore, establishment of water travel times in Mike SHE is, so far, restricted to the saturated zone only. Mike SHE uses a non-reactive fictive solute to track water flow paths and, to date, this method has only been developed for the saturated zone, due to numerical issues such as the effect of ET. However, it could be possible to develop particle tracing in the future to take such processes into account, allowing for travel time investigations for all Mike SHE model compartments.

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Popular science summary

Water quality and water supply in soils, streams and lakes depend, to a large extent, on which paths and at what speed water has travelled through the landscape. Rainwater falls onto the ground surface and either flows off the surface or seeps into the ground. In the ground, water then flows down through the landscape until it later gathers in lakes and streams. Soil properties, such as grain size, can affect how much water seeps into the soil and the speed of the water in the soil. Chemical and biological processes in the ground affect water quality. These processes, in turn, depend on the groundwater travel times. Seasonal variations in rainfall and soil frost can also affect areas within a landscape differently. It is important to gain a better understanding of which landscape properties affect the penetration of water into the soil, water pathways and what affects the speed of the water, to be able to manage water resources and water quality as well as build models. This is also important as a basis for studies on the impact of climate change. This thesis describes how small areas, such as small mires, can have a profound impact on the proportion of water that seeps into the ground. Later, this impacts the water quality in small streams, something that can also be traced in larger streams further down in the landscape. This work also shows that the time from rainfall to outflow in streams is more impacted by the soil properties than the distance from seepage to outflow. We can also show that the crucial processes for nutrition and water quality in soil, streams and lakes are affected by the characteristics of the landscape, the water flow paths, and the time water spends in the soil.

Populärvetenskaplig sammanfattning

Vattenkvalitet och vattentillgång i mark, sjöar och vattendrag beror i stor utsträckning på vilka vägar och i vilken hastighet som vatten tagit sig fram genom landskapet. Regnvatten faller ner och rinner antingen av på ytan eller sipprar in i marken. I marken flödar vatten sedan nedåt i landskapet tills det senare ansamlas i sjöar och vattendrag. Markens egenskaper, så som kornstorlek, kan påverka hur mycket vatten som sipprar ner i marken och därefter hastigheten på vattnet i marken. Kemiska och biologiska processer i marken påverkar vattenkvaliteten. Dessa processer beror i sin tur på markvattnets uppehållstider. Säsongvariationer i nederbörd och tjäle kan också påverka områden inom ett landskap olika. För att kunna hantera vattenresurser och vattenkvalitetsfrågor samt bygga modeller är det viktigt att få en bättre förståelse för vilka landskapsegenskaper som påverkar infiltration av vatten i mark, vilka vägar som vatten tar i ett landskap och vad som påverkar vattnets hastighet. Detta är också viktigt som en grund till studier av klimatförändringars påverkan på vattentillgång och vattenkvalitet. Denna avhandling visar på att små delområden, så som myrar, kan ha stor påverkan på andelen vatten som sipprar ner i marken. I ett senare skede påverkar detta vattenkvaliteten i bäckar, något som man kan spåra i större bäckar längre ner i landskapet. Denna avhandling visar också på att markens egenskaper har större påverkan på tiden vatten tillbringar i marken än avståndet från markinträngning till utflöde i en bäck eller sjö. Vi kan också visa på att processer i marken som påverkar näring och vattenkvalitet i mark, vattendrag och sjöar påverkas av landskapets egenskaper, vattens flödesvägar och tiden vatten spenderar i marken.

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Surface water and groundwater interactions, water travel times and pathways are all affected by catchment characteristics. These interconnected factors have an important influence on water quality, such as base cation weathering and locations of dissolved organic carbon-rich sources. The connection between these factors and water quality is not yet fully understood. This thesis highlights the importance of expanding our knowledge of the link between catchment characteristics, hydrology, and water quality across temporal and spatial scales.

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