From Precipitation to Stream

Isotopic Insights into Hydrological Flow Paths and Transit Times in Boreal Catchments

Andrés Peralta-Tapia
Faculty of Forest Sciences
Department of Forest Ecology and Management
Umeå

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Abstract

Understanding the journey water makes from precipitation entering a catchment, traveling through soils, and the time it takes before it exits as stream water are questions of great relevance for both scientists and environmental managers. Natural stable isotopes such as $\delta^{18}O$ and $\delta^{2}H$ have been extensively used over the last decades to trace water through diverse catchments across the world. In this thesis I analyzed over 2500 isotope samples to create long-term time series of precipitation and stream water data, as well as studying spatial and temporal variability of flow pathways in the Krycklan catchment in Northern Sweden. Based on these isotope samples, I observed that streams draining forested catchments were fed by soil water from different horizons throughout the year. In contrast, stream water from mire dominated catchments was linked primarily to one hydrological active layer with the exception of the winter season when both catchment types showed influence of old/deep groundwater. $^{234}U/^{238}U$ isotope ratios further enhanced the mechanistic understanding of old groundwater where $\delta^{18}O$ signature could not be used to disentangle sources. During a winter baseflow survey I found a the contribution of old groundwater to stream water among 78 sub-catchments, which increased with area ranging from ~20 % contribution in the smaller headwater sub-catchments up to 70-80 % for catchments with areas 10.6 km^2 or larger. Additionally, I found that the spatial variability of old groundwater contribution to catchments below ~10.6 km^2 was influenced by differences in structural properties across sub-catchments. Furthermore, dissolved organic carbon (DOC) was negatively correlated with old groundwater contribution, while base cations and pH were positively correlated. Finally, annual water transit time in the snow-dominated boreal catchment with the most complete isotopic record ranged between 300 and 1400 days and was negatively related to annual rain input. This relationship may have implications for our understanding of future hydrological and biogeochemical processes in boreal regions, given that warmer winters are forecasted, which would translate to larger proportions of precipitation falling as rain. Overall, this thesis has taken us one step further in the search for mechanistic understanding of hydrological flow paths and transit times in small to meso-scale boreal catchments.

Keywords: Isotopes, path ways, natural tracers, transit time, spatial variability, baseflow, time series, Gamma distribution.

Author's address: Andrés Peralta-Tapia, SLU, Department of Forest Ecology and Management, 901 83 Umeå, Sweden
E-mail: andres.peralta.tapia@slu.se

Dedication

A mi papelito, mi mami, Mundi, Muri, Ambar, Rocío…
… y a Carlitos

”… *al andar se hace camino*
y al volver la vista atrás
se ve la senda que nunca
se ha de volver a pisar
caminante no hay camino
sino estelas en la mar…”
Antonio Machado

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 A. Peralta-Tapia, R. Sponseller, D. Tetzlaff, C. Soulsby and H. Laudon (2014). Connecting precipitation inputs and soil flow pathways to stream water in contrasting boreal catchments. *Hydrological Processes*. Accepted online.

II F. Lidman, A. Peralta Tapia, A. Vesterlund and H. Laudon. $^{234}U/^{238}U$ in a boreal stream network – relationship to hydrological events, groundwater and scale. Submitted manuscript.

III A. Peralta-Tapia, R. Sponseller, A. Ågren, D. Tetzlaff, C. Soulsby and H. Laudon (2015). Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. Journal of Geophysical Research – Biogeosciences. Accepted online.

IV A. Peralta-Tapia, D. Tetzlaff, C. Soulsby, R. Sponseller, K. Bishop and H. Laudon. Hydroclimatic Controls on Non-Stationary Transit Time Distributions in a Boreal Headwater Catchment Over a 10 Year Period. (manuscript).

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1 Introduction

Understanding how water enters a catchment, travels through soils and bedrock, and exits as stream water are questions of great interest and relevance for both scientists and environmental managers [*McGuire and McDonnell*, 2006; *Tetzlaff et al.*, 2015]. A growing awareness that water quality to a great extent is regulated by the contribution of water sources from overland flow, shallow flow pathways, and deeper groundwater has led to an increasing interest in how surface waters can be partitioned into its contributing sources. In northern ecosystems, where long winters, intermittent soil frost, and large snow melt events during spring/summer are defining features, a better understanding of water pathways are of special relevance. Seasonally snow covered areas are of particular concern because of their importance as freshwater resources and habitats for aquatic organisms, but also because these areas are currently experiencing relatively rapid climate warming and increased pressure from natural resource extraction [*Kovats et al.*, 2014; *Romero-Lankao et al.*, 2014]. Great advances have been made in the last decades, but large knowledge gaps still needs to be filled in order to better understand the challenges that lie ahead of us when it comes to predicting and protecting water quality in the future.

1.1 Natural tracers

Natural, or environmental, tracers are solutes, isotopes or other dissolved compounds that are present in different concentrations or activities in the environment, and therefore can be used to trace, separate, and quantify different sources of water. Natural tracers have been used in catchment science for understanding the linkages between precipitation inputs, soil/groundwater routing, and surface flow for several decades [*Maulé and Stein*, 1990; *Soulsby et al.*, 2000; *Goller et al.*, 2005]. Depending on bedrock geochemistry, soil characteristics and precipitation chemistry, different hydrochemical constituents can be utilized. This includes the use of individual solutes such as silica [*Maulé and Stein*, 1990], base cations [*Bishop et al.*, 2000] or other hydrochemical or hydrophysical metrics such as electrical conductivity [*Nakamura*, 1971] and water temperature [*Bense and Kooi*, 2004]. In addition, flow-variant biogeochemical tracers such as dissolved organic carbon (DOC) or alkalinity can be applied to determine geographic sources of runoff in terms of near-surface or deeper groundwater processes in some systems [*Soulsby et al.*, 2007]. In more complex catchments, suites of ions and solutes can be useful to distinguish geologically different water sources and the influence of different land uses on water chemistry at different flow conditions (e.g. *Fröhlich et al.*, 2008).

However, compared to most other tracers, water isotopes $\delta^{18}O$ and $\delta^{2}H$ (or D as in Deuterium), behave conservatively once the water has entered the soil/groundwater system and therefore represent an integrated tool for resolving water sources and pathways. The natural abundance of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios are $0.20 \cdot 10^{-3}$ and $1.56 \cdot 10^{-4}$, respectively compared to all oxygen and hydrogen of water in the ocean [*Kendall and Caldwell*, 1998]. By international agreement, all $^{18}O/^{16}O$ and $^{2}H/^{1}H$ are measured against the respective ratio at the ocean, where negative δ values mean the sample has less heavy isotopes than mean ocean water [*Coplen*, 1996]. Since the 1950's when the first scientific studies were published demonstrating the variability in ^{18}O and ^{2}H abundance in precipitation and fresh waters due to isotopic fractionation [*Dansgaard*, 1954, 1964; *Gonfiantini and Picciotto*, 1959; *Ehhalt et al.*, 1963], scientists have use these isotopes to understand the movement and pathways of water in catchment systems [*Dinçer et al.*, 1970; *Mcdonnell et al.*, 1990; *Laudon et al.*, 2007; *Capell et al.*, 2012].

Fractionation between water molecules holding the common ^{16}O atom and those with the slightly heavier ^{18}O occurs particularly in connection with partial phase transitions such as evaporation from the world's oceans and condensation in the atmosphere (*Figure 1*). The fractionation effect is temperature dependent, and especially strong at higher latitudes, giving rise to traceable signals that vary during events and across seasons. Thus, the variability in input signal can be used to trace water flow pathways through diverse surface/subsurface environments. However, because of the much larger intra-annual variation in $\delta^{18}O$ compared to inter-annual changes, it is often difficult to separate more long-lasting water source variability without very extensive time series records of input and output signals [*McGuire and McDonnell*, 2006; *Tetzlaff et al.*, 2015]. Hence, the use of $\delta^{18}O$ to directly trace water sources is mainly limited to time spans ranging from events to a few years.

In contrast to the use of $\delta^{18}O$ requiring long, consistent, and frequent time series of input (rain and snow) and output (stream and river water), the combination with other isotopic tracers can provide valuable complementary information for partitioning water into different sources. The radioactive isotopes of $^{234}U/^{238}U$ are one such example [*Andersen et al.*, 2007; *Bagard et al.*, 2011]. Although the half-lives of ^{234}U (245 ka) and ^{238}U (4.46 Ga) are long enough to make the decay practically negligible in many applications, the radioactivity is central for the fractionation process, since it tends to cause a preferential mobilization of ^{234}U. First, the more short-lived ^{234}U occurs in the natural decay chain of the primordial ^{238}U. Over time (ca. 1 Ma), the activity of ^{234}U will approach the activity of ^{238}U in a closed system. The ratio $^{234}U/^{238}U$ (activity) provides important information about the status of the aquifer, particularly the historical intensity of the weathering and therefore indirectly the source of the element. Second, the radioactivity leads to much stronger fractionation and, accordingly, much more distinct isotope signals, which can be used to trace sources of solutes and water.

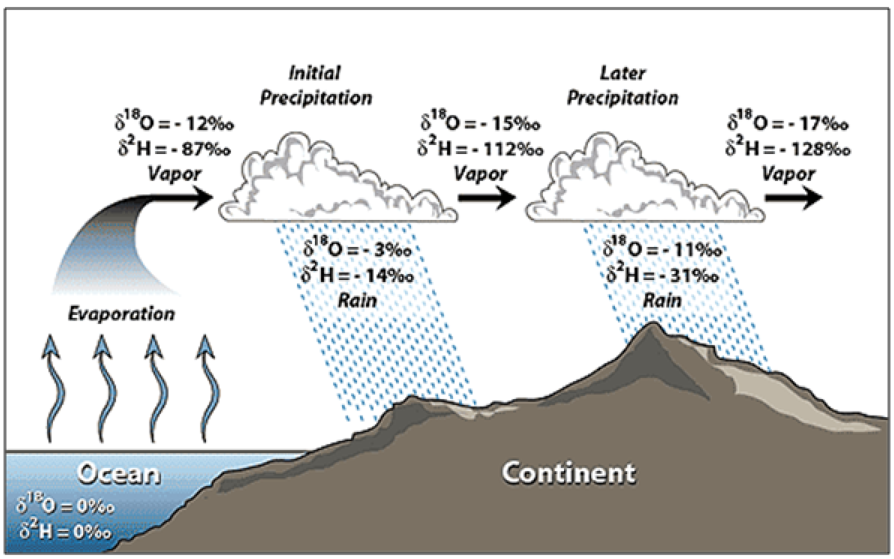

Figure 1. Schematic hydrological cycle showing how $\delta^{18}O$ with evaporation and precipitation events (based on Hoefs, 1997 and Coplen et al., 2000).

1.2 Spatio-temporal variability

1.2.1 Boreal landscapes

The Boreal Biome makes up only 8% of the global land area, but constitutes one third of the world's forests and store about 30% of the global terrestrial carbon pool [*Gorham*, 1991; *Turunen et al.*, 2002]. Boreal landscapes are commonly comprised of a mosaic of terrestrial and aquatic patches, including coniferous forests, lakes, and mires that have distinct influences on the hydrology and chemistry of associated surface waters [*Laudon et al.*, 2004; *Shaman et al.*, 2004]. As this is a region which is expected to undergo major climatic transitions in the coming decades due to climate change, a better understanding of hydrological processes and pathways across the heterogeneous landscape is of great importance [*Tetzlaff et al.*, 2013]. While understanding the hydrological functioning needs to be a central question in all water quantity and quality work, it is primarily the impact on water resources for human consumption and transport of nutrients and contaminants to downstream recipients that is most central for society. In a more long-term perspective, increased leakage of the large carbon pools to surface water and alteration of surface water habitats are other important issues that also are strongly connected to the issue of water pathways and transit times in headwater catchments.

1.2.2 Variability

Snow-dominated boreal catchments are characterized by marked seasonality with corresponding shifts in the potential water sources to streams (e.g. groundwater, snow melt, rain) causing a strong hydrological variability over time. Additionally, boreal catchments are formed by the contrasting landscape mosaic of forests, mires and lakes creating an additional layer of spatial variability [*Laudon et al.*, 2007]. Despite this potential complexity, studies of the hydrology and biogeochemistry of snowmelt-dominated catchments have often focused solely on the spring flood period because it represents a large portion of the annual water yield [*Rodhe*, 1981; *Maulé and Stein*, 1990; *Laudon et al.*, 2004; *Barnett et al.*, 2005]. However, providing a better picture of how different landscape elements behave hydrologically throughout all seasons is required for a more complete understanding of the functioning of boreal catchments.

1.2.3 Baseflow

Baseflow is the portion of stream flow that comes from groundwater storage and other delayed sources [*Hall*, 1968]. This source of stream flow represents an important ‘genetic component’ of the hydrograph [*Smakhtin*, 2001] that has implications for the ecology and biogeochemistry of streams [*Doyle et al.*, 2005]. In small streams baseflow is of critical importance as it determines the extent of habitat for many aquatic organisms, including many fish species [*Mitsuo et al.*, 2013]. Therefore, there is a strong motivation to have a better understanding on how catchment structure influences the hydrology during baseflow in boreal catchments.

1.2.4 Transit time

A missing piece of the puzzle after approaching the spatial and temporal issues of boreal catchments is to quantify the time that water spends in the subsurface system. Transit time of the water is commonly defined as the elapsed time when the molecules from a particular input event exit a flow system [*Bolin and Rodhe*, 1973; *McGuire and McDonnell*, 2006]. It can hence be used for disentangling information about flow paths and water storage and is a door to better understanding biogeochemical patterns and processes along catchment flow paths [*Burns et al.*, 2003]. Despite the importance of transit time to catchment function, it cannot be measured experimentally with the exception of manipulated catchments where all inputs can be controlled [*Rodhe et al.*, 1996]. Therefore, transit time distributions are most commonly inferred using models with time-series of input and output of natural tracers. Despite the numerous efforts to estimate transit times in different northern catchments [*Dinçer et al.*, 1970; *Maloszewski et al.*, 1983; *Lyon et al.*, 2010], studies based on sufficiently long time series in catchments with 4-5 months completely snow-covered are scarce in the literature [*Tetzlaff et al.*, 2015].

1.3 Objectives

The overarching goal of this thesis was to provide an improved mechanistic understanding of hydrological functioning of boreal catchments. To this end, I addressed the following specific objectives in the respective Papers:

- Evaluate how differences in flow path properties across forests, mires, and lakes influence the connectivity of these landscape units with their receiving streams (Paper I).
- Examine the variability in isotopic composition of soil water and groundwater in the two dominant boreal landscape elements (i.e. forested mineral soils and wetland peat soils) across depths, along horizontal flow paths, and over seasonal timescales (Paper I).

- Advance our understanding of the contribution of different water sources during the spring flood by combing the use of $\delta^{18}O$ and $^{234}U/^{238}U$ ratios in groundwater and stream water (Paper II).
- Investigate the variability in groundwater contribution to stream water as a function of sub-catchment size and alternative structure descriptors (e.g., topography, local depressions) during winter baseflow (Paper III).
- Connect this variation in groundwater contribution with spatial patterns of stream chemistry (Paper III)
- Improve our understanding of water transit time using a 10-year time series, evaluating inter-annual variability in relation to variation in precipitation inputs (Paper IV).

2 Methods

2.1 Study Area

The data for this thesis was collected in the Krycklan Catchment (64°14'N, 19°46'E) located in northern Sweden (Figure 1; *Laudon et al*., 2013). The catchment has a total area of 68 km^2 and includes 115 sub-catchments that have occasionally been sampled as part of spatially extensive campaigns (the number of sites in each survey have varied, depending on flow conditions and accessibility). Within these, 17 sub-catchments have monitored at daily, weekly to monthly intervals since 2003, whereas three of the sub-catchments have been regularly monitored since the early 1980's.

The four papers of this thesis were developed using different sets of sub-catchments of the Krycklan catchment (*Figure 2*). In short, in Paper I we studied three contrasting headwater sub-catchments characterized by complete forest cover (C2), extensive wetland (mire) cover (C4), and a lake outlet (C5). In Paper II we investigated seven nested sub-catchments and the main Krycklan outlet, including the three sub-catchments from Paper I and the sub-catchment studied in Paper IV. Paper III encompassed 78 sub-catchments including the main outlet and all sub-catchments studied in the other Papers. Finally, Paper IV was based on only one sub-catchment (C7) that includes two of the headwater sub-catchments of Paper I (C2 and C4).

The 30-year mean annual temperature (1981-2010) in the catchment has been recorded as 1.8 ˚C, with an average January and July temperature of -9.5 and +14.7 ˚C, respectively. The annual precipitation for the same period was 614 mm and annual runoff (at C7) 311 mm. This gives rise to an average annual average evapotranspiration of 303 mm. The average period of snow cover during this period was 168 days [*Haei et al.*, 2010]; overall, about 35-50 % of annual precipitation falls as snow [*Oni et al.*, 2013].

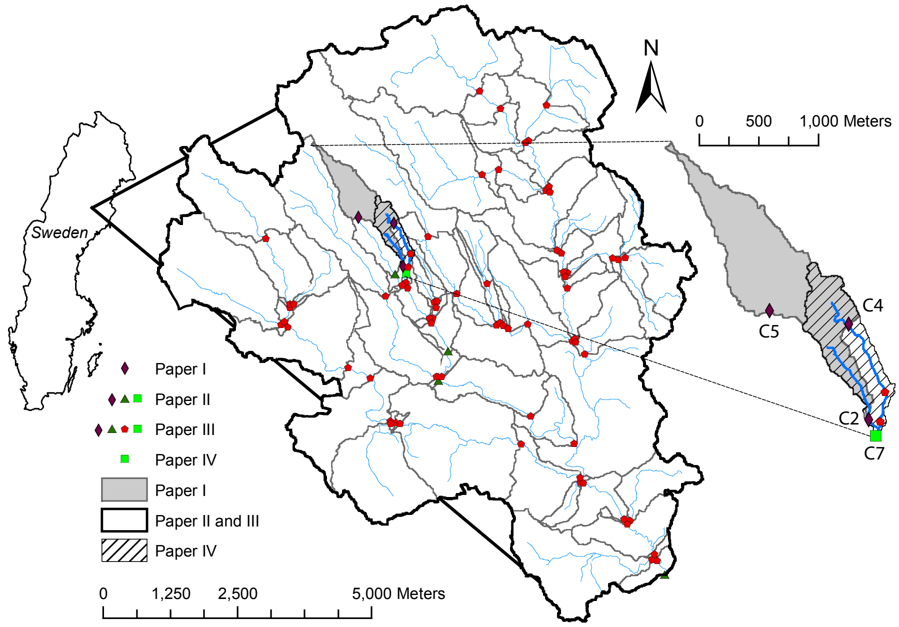

Figure 2. Study areas and sampling sites for this thesis.

Sub-catchments within Krycklan can be markedly different in terms of vegetation, soils, and types of aquatic habitat (*Buffam et al.*, 2008, Paper III). Forest cover in the 78 studied sub-catchments range from 54 to 100 %; while mire coverage range from 0 to 44 % (see appendix in Paper III, Table S1). Over 87 % of the Krycklan Catchment is covered by forests, mainly Scots pine (*Pinus sylvestris)*, spruce (*Picea abies*), and birch (*Betula spp.*). Importantly, mires and lakes cover close to 10 % and 1% of the entire catchment, respectively. Elevation range from 127 m.a.s.l. at the outlet to 372 m.a.s.l. at the highest point.

Soil mineralogy in the catchment is relatively homogeneous in space, consisting of quartz (31-43%), plagioclase (20-25%), K-feldspar (16-33%), amphiboles (7-21%), muscovite (2-16%), and chlorite (1-4%) [*Ledesma et al.*, 2013]. The soil geochemistry varies slightly but is independent of grain size and soil characteristics [*Lidman et al.*, 2014].

The Krycklan catchment is underlain by 93% paragneissic bedrock that is interspersed by younger metavolcanic intrusive rocks of which 4% are acid and intermediate granitic rocks, and 3 % basic metavolcanic rocks [*Ågren et al.*, 2007]. This bedrock is covered by a layer of till that varies in thickness from a few centimeters up to tens of meters. In the lower areas of Krycklan (included in Paper II and III), larger channels are more incised, carving through floodplain sediments (i.e., silty/fine sands) that cover about 30% of the catchment. These sediments are derived from a postglacial delta which covered an esker that followed the Vindel River for approximately 143 km [*Tiwari et al.*, 2014].

2.2 Sampling

A total of 2493 samples for isotopes ^{18}O and ^{2}H were collected and used in this thesis. These can be divided into 895 precipitation samples used as input signal and to create a Local Meteoric Water Line (LMWL), 256 snow melt samples from snow lysimeters (Paper IV), 883 stream samples from all sub-catchments in Krycklan (all papers), 261 soil water samples (Paper I), 158 groundwater samples from nested mire wells (Paper I and II), and 37 deep groundwater well samples through-out Krycklan (Paper I, II and III).

All ^{18}O samples were preserved in +4 °C in dark glass 50 ml bottles (10 ml from 2012), except soil water samples (Paper I) that were stored frozen in 100 ml high-density polyethylene bottles. All samples were collected and subsequently stored with minimal head space. We replaced missing glass bottles with frozen subsamples. To test whether differences in sample storage influenced $\delta^{18}O$ signals, more than 50 precipitation and stream water samples were analyzed, including both refrigerated and frozen samples. Differences between paired subsamples were all within instrument error, suggesting that these different storage methods did not bias the results.

There were three WMO standard rain gauges placed in two locations in Krycklan (Figure 1 in Paper III) used in this work. Precipitation samples were collected in one of the rain gauges and the other two (in different locations) were used to measure the precipitation volume. All rain gauges were heated during winter to avoid snow accumulation in the collection funnels.

All stream water samples used in this work were grab-sampled. Saturated and unsaturated soil water samples (S4, S12 and S22 in Paper I) were collected using suction lysimeters at different depths in a transect from the stream at 4, 12 and 22 meters following the groundwater flow [*Laudon et al.*, 2004]. Snow lysimeters (Paper IV) were sampled manually during snow melt. The nested mire wells (Paper I and II) were sampled with a peristaltic pump. Groundwater wells (Paper I, II and III) were sampled initially with a peristaltic pump and later with a submersible propeller pump.

2.3 Laboratory analysis

The isotopes $\delta^{18}O$ and δ^2H were measured using a Picarro L1102-i cavity ring down spectrometer coupled to a vaporizer module (V1102-i) until December 2012, and from July 2013 we used a Picarro L2130-i cavity ring down spectrometer with a vaporizer module (A0211). Both instruments were connected to a LEAP Technologies CTC Analytics HTC-PAL auto-sampler. For the first instrument, the protocol consisted of analyzing each sample five times using an injection volume of 1.8 µL, but only the average of the three last runs was used in order to avoid memory effects. The analyses were corrected for drift by placing control water samples throughout the batch. For the latter instrument, we used the method proposed by *van Geldern and Barth* (2012) to correct for memory effect and drift. Isotopic signatures of water were calibrated using internal laboratory standards calibrated against three International Atomic Energy Agency official standards, the Vienna Standard Mean Ocean Water (VSMOW), the Greenland Ice Sheet Precipitation (GISP), and the Standard Light Antarctic Project (SLAP). The $^{18}O/^{16}O$ ratios are expressed using delta notation ($\delta^{18}O$) relative to VSMOW [*Anon*, 1995; *Coplen*, 1996]:

$$\delta^{18}O(‰) = \left(\left(\frac{^{18}O}{^{16}O}\right)_{sample} \Big/ \left(\frac{^{18}O}{^{16}O}\right)_{\mathrm{VSMOW}} - 1 \right) \cdot 1000 \qquad \text{(Equation 1)}$$

The historical standard deviation of the instruments was 0.1‰ for $\delta^{18}O$ and 0.2‰ for δ^2H based on control water measured. We chose to focus primarily on the use of $\delta^{18}O$ as that has been the basis of most previous isotope work in the catchment [*Rodhe*, 1987; *Bishop et al.*, 1990; *Laudon et al.*, 2002, 2004, 2007].

Analyses of other hydrochemical parameters used in Paper II and III, e.g. Ca, Mg and DOC, were done by third parties following the standard protocol used in the Krycklan Catchment Study [*Buffam et al.*, 2007] and available at www.slu.se/Krycklan. Soil samples used in Paper II were collected and analyzed as well by third parties with thin connection with the installation of the groundwater wells and analyzed by X-ray fluorescence spectroscopy (XRF) at Umeå University [*Boes et al.*, 2011]. Finally, total uranium concentrations and $^{234}U/^{238}U$ ratios analyses used in Paper II were measured at the Swedish Defence Research Agency (FOI) in Umeå using ICP-SFMS [*Rameback et al.*, 2008].

2.4 Model analyses

In order to approach the spatial and the time variability in Krycklan, two models were used. We applied a simple mixing model in Paper III to separate recent and old groundwater during baseflow, and a gamma distribution model in Paper IV to calculate transit time of the water.

2.4.1 Mixing model

A two component mixing model was applied to the 78 subcatchments to partition the fraction of recent water (Q_{rec}) (originating from volume weighted previous year's precipitation) from older groundwater sources (Q_{old}) during winter baseflow using isotopic $\delta^{18}O$ signature:

$$Q_{tot} * C_{tot} = Q_{rec} * C_{rec} + Q_{old} * C_{old} \qquad \text{(Equation 2)}$$

The old groundwater isotopic $\delta^{18}O$ signature (C_{old}), which has a stable average value across the entire catchment, was used as one end member for this model. The weighted average isotopic $\delta^{18}O$ signature of recent precipitation inputs (C_{rec}) was used as the other. C_{tot} was the stream water isotopic signature, where 54 sub-catchments that had lake presence presented an evaporation effect which was corrected before applying the mixing model. We used daily air temperature to determine precipitation events that could be considered recent inputs. We assumed that recent groundwater potentially comes from all of the precipitation delivered to the catchment after the previous years' spring flood, but before the onset of winter (Figure 2), which was defined as ten consecutive days below 0 ^{o}C average air temperature. The inputs of precipitation during the previous summer and autumn are variable in magnitude and isotopic signature and we assumed that these input waters make up a well-mixed pool in the soil (see below) which we call *recent groundwater*. However, to address potentially important variation in the seasonal isotopic signal of summer and autumn precipitation in our mixing model, we used the minimum and maximum volume-weighted $\delta^{18}O$ values observed during this period. By having a variable precipitation signal as one end-member in our model, we obtained a range of possible values that are all plausible. Thus, the resulting partitioning between recent and old groundwater contribution to winter baseflow does not become one value, but rather an ensemble of possible values of which we show the average and range.

2.4.2 Transit time model

We applied a transit time model to a $\delta^{18}O$ signature 10-year time series in Paper IV, which greatly reduces the uncertainties in model fitting often encountered when using shorter time series. The model was used to calculate the mean transit time for the total period and to calculate annual transit time for each year. For the calculation of transit time of the water in the catchment, we used a script written in R by *Capell et al*. (2012), which uses a convolution equation (Equation 3) that includes a weighting of the input data in the simulations [*Stewart and McDonnell*, 1991] as follows:

$$C_{out}(t) = \frac{\int_0^\infty g(\tau)w(t-\tau)C_{in}(t-\tau)d\tau}{\int_0^\infty g(\tau)w(t-\tau)d\tau} \qquad \text{(Equation 3)}$$

where C_{out} and C_{in} are the signature values of the stream and the precipitation respectively. The weighting factor is defined as w, which was the daily precipitation adjusted for evapotranspiration, winter period, and the snowmelt. Here t represents calendar day and the integration is carried out over the transit times τ. The system response function specifying the transit time distribution of the water in the equation is defined as $g(\tau)$, in our study we used the gamma distribution model (Equation 2) to estimate the transit time:

$$g(\tau) = \frac{\tau^{\alpha-1}}{\beta^\alpha\Gamma(\alpha)}e^{-\tau/\beta} \qquad \text{(Equation 4)}$$

where the parameters α and β are adjusted to fit the observed stream isotopic response. For the parameter α , also known as the shape factor, it has been shown that values near 0.5 allow for representation of both advection and dispersion of spatially distributed inputs in the system [*Kirchner et al.*, 2001; *Godsey et al.*, 2010].

3 Results and Discussion

In this thesis I analyzed isotopic tracers in water samples from precipitation, groundwater, stream water, soil water and snow lysimeter water with the purpose of finding spatial and temporal links among them. I found that stream water in forested catchments presented a more damped response than stream water in mire and mire-lake dominated catchments in the annual cycle. However, during winter streams from all landscapes were partially fed with deep groundwater (deeper than 3-5 meters depth) in Paper I and later confirmed with more quantitative fractions in Paper III. The consistency of stable isotopes like $\delta^{18}O$ allowed determining the sources of the stream water during spring flood when combined with uranium isotopes analyses in Paper II. On the other hand, the limitation that stable isotopes $\delta^{18}O$ presented when groundwater is older than a couple of years benefitted from the additional use of radioactive uranium isotopes that aid in partitioning the differences in deep groundwater contributions among the different catchments (Paper II). Finally, I calculated the annual Mean Transit Time (MTT) variation obtaining a strong relationship with precipitation during snow-free seasons in Paper IV.

Precipitation is the main water input source to the system. The average volume weighted $\delta^{18}O$ signature during the measurement period from 2003 to 2012 was -13.6 ‰ (n=854). Similarly, the average deep/old groundwater $\delta^{18}O$ signature in the Krycklan catchment was -13.6 ‰ (n = 33). However, the volume weighted $\delta^{18}O$ average from the C7 stream water (the site with most samples analyzed) was -13.1‰ suggesting fractionation, likely caused by evaporation. Nevertheless, when plotted against the Local Meteoric Water Line (LMWL) we cannot confirm an evident evaporation effect since all average values lie over the LMWL (*Figure 3*). In any case, in *Figure 3* we can observe a probable evaporation effect in some individual samples at C7. Additionally, while the seasonal precipitation of $\delta^{18}O$ ranged between -31.6‰ in winter to -2.4‰ in summer, stream water (C7) $\delta^{18}O$ signature varied from -15.4‰ during spring flood, to -10.5‰ in late summer (*Figure 3, inset*). Despite the large intra-annual precipitation $\delta^{18}O$ signature, no seasonal variability in deep groundwater was observed, suggesting that this is a mixture of several years' precipitation. Nonetheless, precipitation and groundwater averages in this thesis strengthened the importance of using long-term datasets to understand pathways and transit times of water in headwater catchments.

In the following sub-sections I summarize the most important results and discussion points from the Papers included in this thesis.

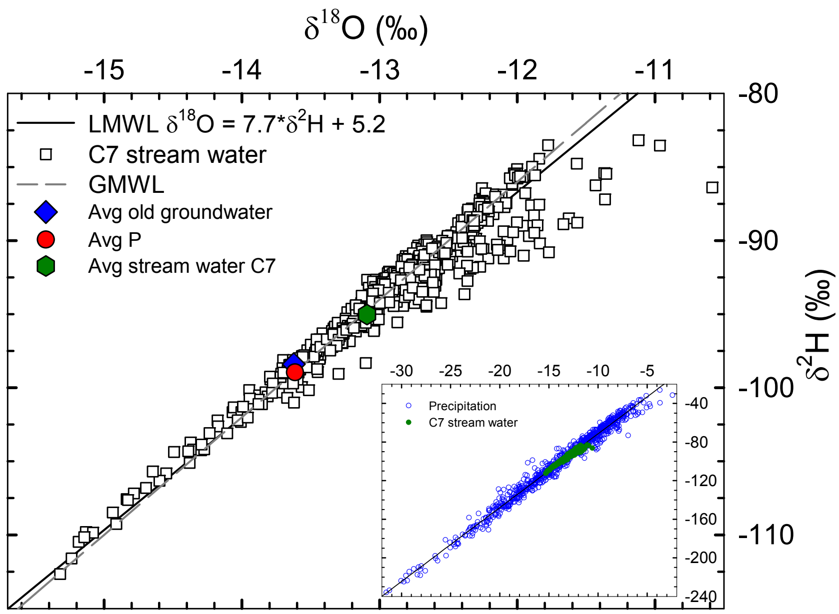

Figure 3. Representation of water from C7 during 2003-2012, average value of old groundwater, weighted average value of precipitation and of C7 with the Local Meteoric Water Line and the Global Meteoric Water Line. Local Water Line was based on 895 precipitation samples from 2002 and 2012. Inset: the entire isotopic range of precipitation is plotted with the stream water at the C7 stream.

3.1 Landscape variability drives catchment response (Paper I)

The seasonal stream water $\delta^{18}O$ signature displayed contrasting behaviors in forested (C2), mire (C4) and lake-mire (C5) dominated catchments. The annual isotope signature in C2 ranged between -13.5‰ and -12.5‰. Thus, the landscape dominated by coniferous forests showed a more damped response to the initial precipitation seasonality, as it has been observed in previous hydrological studies in the same catchment [*Rodhe*, 1981; *Laudon et al.*, 2007] and in other catchments in the world [*Rodhe*, 1981; *Sklash et al.*, 1986; *Buttle*, 1994]. On the other hand, the annual isotopic signature in C4 and C5 ranged from -14.6‰ to -11.6‰ and from -14.4‰ to -10.6‰ respectively. Having a signature range in the mire and lake dominated landscapes three times larger or more than in the forest stream suggests a more rapid routing of precipitation inputs in the former landscapes. These distinct hydrological characteristics of each landscape unit were most strongly apparent during the snowmelt season, but were also evident throughout the rest of the year.

Riparian soil lysimeter (S4) data at C2 suggested a temporally variable pattern of flow path to the respective stream (*Figure 4*). Overall, we observed that the surface stream and different soil levels were connected depending upon season. However, there was an exception during winter where all soil lysimeters had a heavier (more enriched) signature than the stream (approaching -13.6‰; *Figure 4*) suggesting greater contribution from old groundwater. The results obtained during spring flood agrees largely with previous work done in the same catchment by *Laudon et al.*, (2007) where the more surficial layers of the soil contribute to runoff, while the lower layers are less active. However, results from the rest of the year suggest that when the water level drops down, these previously less active lower layers get activated and contribute to stream flow. Thus, a combination of shallow, intermediate, and deep flow paths seem to contribute to surface runoff at the forested site, varying the proportions of their contribution along the year.

In contrast to the forest soil profile, the mire profile had one hydrologically active layer at 2-3 m depth that was connected to the stream water of C4 for most of the year (*Figure 5*). However, during winter the mire water was heavier than the stream water, suggesting a hydrological isolation of the mire and a larger contribution of old groundwater to the stream flow. While rapid hydrologic responses have been previously demonstrated for wetlands in these catchments during snow melt [*Rodhe*, 1987; *Sirin et al.*, 1998; *Laudon et al.*, 2007], this is the first time such patterns have been shown during summer and autumn seasons, when soil frost is not the mechanism partitioning water into distinct surface and subsurface flow pathways.

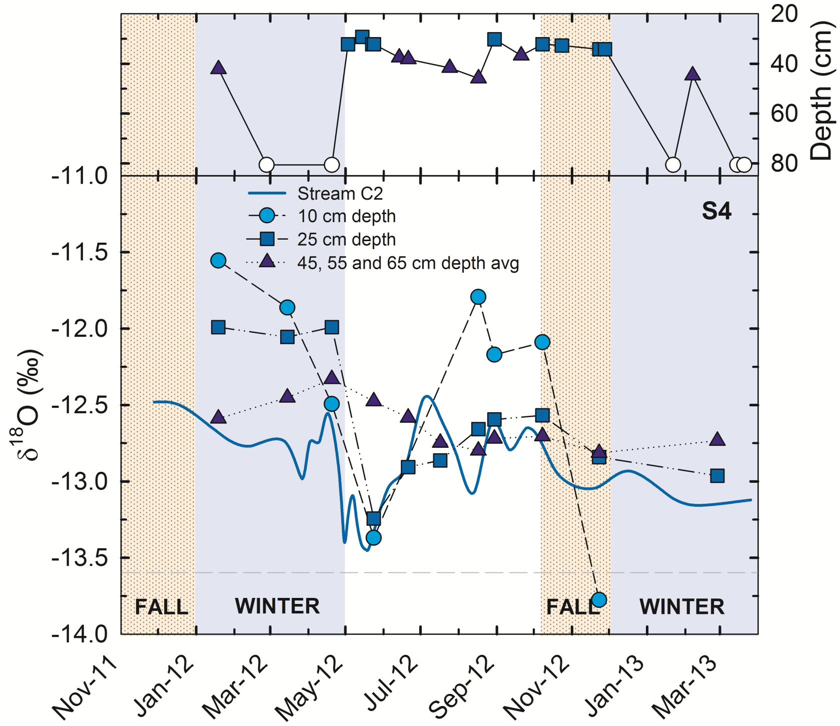

Figure 4. The $\delta^{18}O$ signature of stream and soil water (S4) and deep groundwater (dashed gray line) at the lower panel. Upper panel is the groundwater level with the color scheme and shape suggesting what levels are activated at different times (i.e: when there is a light blue square the water level is high enough for the 25 cm depth and deeper layers to be active). The white circles represent a dry well, meaning that the water level could be lower (Figure from Paper I).

3.2 Groundwater and stream variability using $^{234}U/^{238}U$ and $\delta^{18}O$ (Paper II)

Combining spatiotemporal information of $\delta^{18}O$ with uranium isotope ratios in groundwater and stream water gave consistent results that strengthened our mechanistic understanding of the hydrological processes during the spring flood. Lower $^{234}U/^{238}U$ ratios were observed derived from environments where the weathering has been more intense - essentially near-surface weathering. We observed that the $^{234}U/^{238}U$ ratio in the stream decreased during spring flood (snow melt) in most cases, indicating more superficial sources of water; which was consistent with the $\delta^{18}O$ isotopes. We also observed that stream $^{234}U/^{238}U$ increased with drainage size, suggesting deeper flow pathways and longer residence times in the larger catchments, which again was consistent with $\delta^{18}O$ isotope patterns.

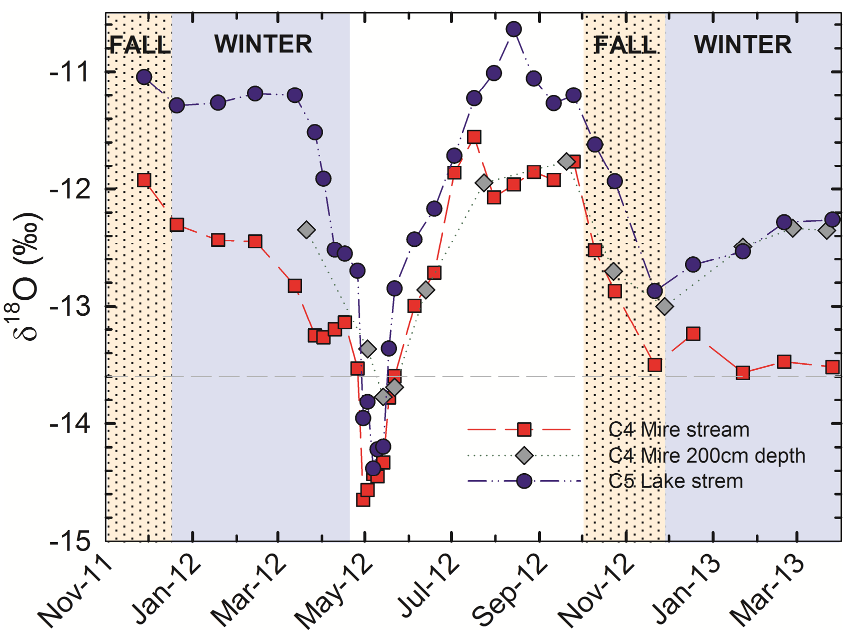

Figure 5. Temporal variation of δ^{18}O signature at mire stream C4, lake stream C5, mire groundwater piezometer (200 cm depth), and deep groundwater. The blue shaded periods represent the winter season with frozen and snow covered soils. The dotted shaded periods represent the selected autumn period for comparison reasons (Figure from Paper I).

We observed higher ^{234}U/^{238}U isotope ratios in deeper groundwater wells further down in the catchments, where δ^{18}O signature had reached already a constant value. In other words, ^{234}U/^{238}U isotope ratios were capable of tracing water over longer timescales, particularly in old groundwater where there was no more observable fractionation of δ^{18}O isotopes. Therefore, using both isotopic methods provided complementary information, since δ^{18}O was a better hydrological tracer (behaving conservatively unlike uranium), thus provided a clearer patterns and better resolution of the variable water sources across the heterogeneous catchment.

3.3 Winter baseflow spatial variability (Paper III)

The δ^{18}O corrected for lake-evaporation signal was used in the mixing model (described in 2.4.1) and the average old groundwater fraction of the baseflow streams ranged from 18% to 95%. The average old groundwater fraction increased logarithmically with catchment area (Figure 4 in Paper III). A piecewise regression of estimated old groundwater fraction against the catchment area suggested a break in this relationship at ~10.6 km^2 (SE: ± 1.7 km^2; $r^2 = 0.62$, $p < 0.001$; Figure 4b in Paper III). The same logarithmic regression explained only 54% in the sub-catchments below this threshold. Therefore, a step-wise regression on the residuals of the latter regression was used. The residual analysis indicated that three descriptors of catchment structure explained an additional 31% of the groundwater fraction. These additional factors where all related to digital terrain indices, including topographic position index (TPI), depth to water (DTW), and local depressions. Finally, the old groundwater fraction was positively correlated to pH and base cations and negatively correlated to DOC (Figure 5 in Paper III).

The large number of sub-catchments included in this study allowed us to observe a robust trend across the network and correct for the 'lake effect'. A size threshold of ~10.6 km^2 was found, indicating a catchment size after which the groundwater input stopped increasing. This threshold in drainage area was similar to other studied catchments in the world [*Shaman et al.*, 2004; *Temnerud and Bishop*, 2005], whereas as others have reported smaller [*Woods et al.*, 1995; *Asano and Uchida*, 2010] or larger thresholds [*Tetzlaff and Soulsby*, 2008] potentially caused by differences in hydroclimatic, geological, and geomorphological settings [*Shanley et al.*, 2014].

To conclude, within the spatial variability demonstrated in Paper III, we found a strong connection between the changes in groundwater inputs and the geochemical signals in surface streams (*Figure 6*). These relationships highlight potentially important spatial heterogeneity in stream chemistry, which can be translated to environmental changes vulnerability across this channel network.

3.4 Transit time annual variability (Paper IV)

To complement the previous papers, we quantified the overall transit time of water in one of the studied catchments and evaluated how this central hydrological descriptor responded to variation in climate. The best fit mean transit time (using the method described in 2.4.2) for the complete time series was 650 days, whereas the inter-annual mean transit time varied from 300 days to almost 1400 days (*Figure 7*; Table 2 in Paper IV). Correlation of these inter-annual mean transit times with annual precipitation excluding snow melt was significantly better than with annual precipitation including snow melt (*Figure 7*). The snow melt provided a considerable annual input, varying between 20 and 40 % of the annual precipitation input during the study period. A previous study that calculated transit time in the Krycklan for 2004 using only the snow melt as an input [*Lyon et al.*, 2010] suggested a shorter transit time (~90 days) compared to our estimation (~400 days). However, the better fit in *Figure 7b* indicates that despite being a large fraction of the annual input, given the short length of the snow melt season, the precipitation during the rest of the year is a stronger driver of the inter-annual differences in transit time. Therefore, the climatic trend towards warmer winters (less snow, more rain) in boreal areas [*Laudon et al.*, 2013; *Kovats et al.*, 2014; *Romero-Lankao et al.*, 2014], could cause our study catchment to have shorter transit times, with direct impacts on mineral weathering, nutrient removal, and pollutant exports from the catchment.

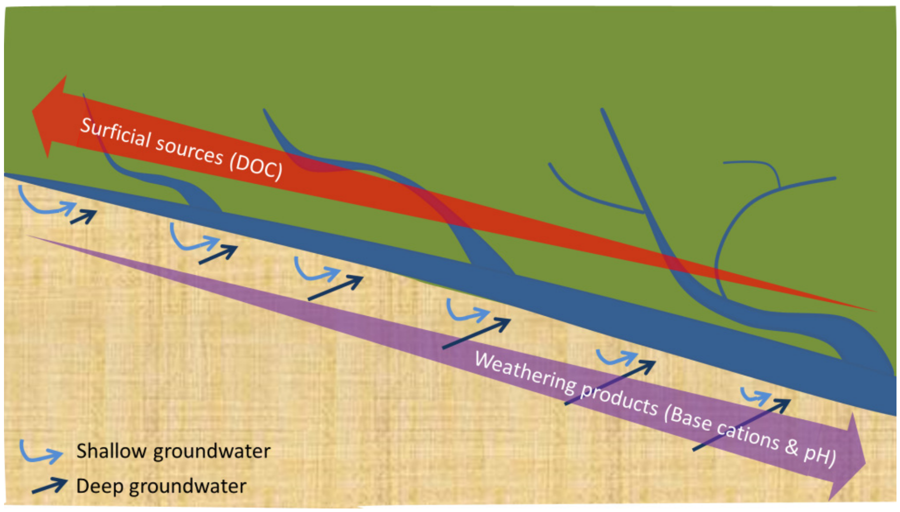

Figure 6. Conceptual model of downstream changes in the contribution to baseflow and implications for stream chemistry. Headwaters are shown on the left of the figure and larger outlet streams to the right. With increases in catchment scale the dominance of shallow groundwater gives way to deeper water sources during winter baseflow. These hydrological patterns result in higher concentrations of surficial sources of solutes (e.g. DOC) in small streams, which decrease with scale. Stream concentrations of weathering products (e.g. base cations and pH) mirror this landscape gradient, increasing with greater catchment size and contribution of water from deeper groundwater sources (in Paper III).

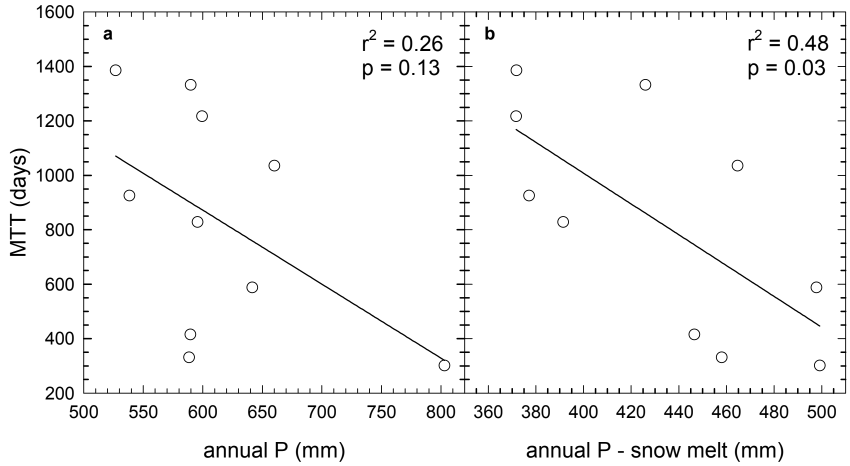

Figure 7. a) Modeled best fit mean transit time (MTT) vs. annual precipitation. b) Modeled best fit MTT vs. annual precipitation excluding snow melt water volume.

The Shape parameter α determines if the distribution of the water transit behaves exponentially or as a gamma function (i.e., a larger amount of event water initially with long tail, see *Kirchner et al.*, 2000). All years adjusted well to a gamma function with the exception of the wettest year 2012 (over 30 % more precipitation than the average) when α was 1, suggesting that the distribution that year behaved more as an exponential function. *Godsey et al.* (2010) explored these transit time distributions across several catchments, of which many were also best described by a gamma function; while others (usually catchments with lakes) best fitted an exponential function. The difference in these distributions was found to be related to the characteristics of the catchment and the shape of their transit time distribution. It is interesting that while C7 transit times fit a gamma function in the overall 10-year time series, when precipitation surpassed a threshold this distribution shifted to an exponential function, despite the lack of lakes in the catchment. This observation reinforces the importance of long time records to encompass a potentially wide range of hydrological variability. These results also highlight the necessity to better understand the behaviors of the transit time distributions around the world, in particular in the face of altered precipitation regimes.

4 Conclusions and Final remarks

The compilation of the Papers in this thesis has taken our mechanistic understanding of hydrological flow paths and transit times in boreal catchments forward. Specifically, my work has led to the following findings:

- The contrasting stream hydrological dynamics in forest, mire, and lake dominated catchments are strongly marked during spring flood, but are also observable throughout the rest of the year (Paper I).
- Forest stream water is fed by water from different soil horizons throughout the year; in contrast, the mire stream water was linked to only one hydrological active layer with the exception of winter time when both streams had a larger influence of old (deep) groundwater (Paper I).
- $^{234}U/^{238}U$ ratios and $\delta^{18}O$ provided a consistent picture of the hydrological functioning of the landscape, emphasizing the importance of deeper hydrological pathways and longer groundwater residence times in larger catchments and the activation of more superficial flow pathways throughout the landscape during spring flood (Paper II).
- In agreement with Paper I and II, winter baseflow showed increasing contribution of old groundwater to stream water among 78 sub-catchments from first to fourth order during winter baseflow (Paper III).
- Spatial variability of old groundwater contribution to stream water depended on catchment area and in the case of the Krycklan Catchment, groundwater inputs to sub-catchments smaller than ~10.6 km^2 were further influenced by structural descriptors of the landscape (Paper III).
- Variability in DOC, base cations, and pH was related to old groundwater contribution during winter baseflow (Paper III).
- Annual water transit time in snow-dominated boreal catchments was related primarily to the snow-free precipitation; while total annual precipitation did not correlate with transit time (Paper IV).

- Boreal catchments are likely to change their distribution of their annual water transit time when increasing the snow-free precipitation (Paper IV).

4.1 Future research directions

One emerging question at the completion of this thesis is whether or not the results obtained in Paper IV can be extrapolated to better understand transit time of water in other boreal catchments. In order to find a solution to this question it would be beneficial to follow the approaches described in Paper I, studying variable landscape elements, and implementing the transit time distribution study on these other catchment types similarly to what I studied in C7 (Paper IV).

Additionally, in the application of the transit time model, I did not consider the old groundwater contribution calculated in Paper III. Therefore, it would be an interesting way forward to test other transit time models that could implement the interaction with groundwater storage to evaluate our results. Importantly, such an effort would allow for an additional test of the relationship of snow-free precipitation and transit time, which has obvious implications for our understanding of boreal catchments in the face of climate change.

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