Linking groundwater travel times to stream chemistry, isotopic composition and catchment characteristics

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Key Points:

- A numerical model was used to simulate groundwater travel times across the Krycklan catchment in the boreal region of northern Sweden.
- The modeled annual mean travel times of groundwater in 14 partly nested sub-catchments ranged from 0.5-3.6 years
15 - The modeled travel times were consistent with both observed stream chemistry (base cation concentration and pH) and stable water isotopes ($\delta^{18}O$ and δ^2H)
- Hydraulic conductivity of the regolith was the most important factor regulating the variation in groundwater travel times between different sub-catchments

20 **Abstract**

Understanding travel times of rain and snowmelt inputs transported through the subsurface environment to recipient surface waters is critical in many hydrological and biogeochemical investigations. In this study, a particle tracking model approach in Mike SHE was used to investigating the travel time of stream groundwater input to 14 partly nested, long-term monitored boreal sub-catchments. Based on previous studies in the area, we hypothesized that the main factor controlling groundwater travel times was

25 catchment size. The modeled mean travel time (MTT) in the different sub-catchments ranged between 0.5 years and 3.6 years. Estimated MTTs were tested against the observed long-term winter isotopic signature (δ^2H, δ^{18}O) and chemistry (base cation concentration and pH) of the stream water. The underlying assumption was that older water would have an isotopic signature that resembles the long-term average precipitation input, while seasonal variations would be more apparent in catchments with younger water. Similarly, it was assumed that older water would be more affected by weathering, resulting in higher concentrations of base

30 cations and higher pH. 10-year average winter values for stream chemistry were used for each sub-catchment. We found significant correlations between the estimated travel times and average water isotope signature (r=0.80, p<0.001 for δ^{18}O; r=0.81, p<0.001 for δ^2H). We also found a strong correlation between MTT and base cation concentration (r=0.77, p<0.001) and pH of the streams (r=0.54, p<0.01), which strengthened the credibility of the model. There was no statistical correlation between catchment size and MTT of groundwater, hence refuting our hypothesis. Instead, one landscape characteristic, low conductive sediments, were found

35 to be most influential. Its areal proportion was found to positively affect MTT.

1 Introduction

The age and origin of stream water is a widely discussed research area in contemporary hydrology. This interest has emerged due to the important role water age, and flow pathways have for hydrological and biogeochemical processes (McDonnell et al., 2010; Sprenger et al., 2018). Such processes include transport and dispersal of contaminants (Bosson et al., 2013; Kralik, 2015), weathering (Burns et al., 2003), and accumulation and mobilization of organic carbon and associated solutes (Tiwari et al., 2017). These processes have received increasing attention also in snow-dominated landscapes due to their importance as water resources (Barnett et al., 2005) and their susceptibility to climate change (Aubin et al., 2018; Tremblay et al., 2018; Price et al., 2013). In the vast boreal region, the landscape often consists of heterogeneous patches of lakes, mires, and coniferous forests regulated by sometimes contrasting hydrologic mechanisms. This heterogeneity emphasizes the need for an enhanced understanding of hydrological and biogeochemical processes and their inter-linkage (Winnick et al., 2017; Waddington et al., 2015; Demers et al., 2010).

Travel time to streams provides valuable information about catchment sensitivity to changes in land use and climate as well as the input of contaminants and nutrients (van der Velde et al., 2012). The travel time distribution can vary substantially in time and space, depending on numerous catchment characteristics and hydrological conditions (McGuire and McDonnell, 2006; Scanlon et al., 2001). Therefore, estimating travel times for various contrasting landscape elements may enhance our process understanding and ability to more correctly quantify the contribution of water and various solutes derived from catchments. Groundwater is an especially important component of the hydrology and a regulator of many biogeochemical processes. From a surface water perspective, groundwater is a source of recharge for streams, lakes and, wetlands. Groundwater is the part of stream water contribution which is not linked to a specific hydrological episode and can, therefore, be used as a reference point to study solute transport, water quality and other event-activated processes (Bergknut et al., 2010; Doyle et al., 2005; Olson & Hawkins, 2012; Pinder & Jones, 1969). Northern landscapes with long-lasting snow cover and prolonged frozen conditions without the input of new surface water can give a unique opportunity to investigate stream groundwater input conditions (Peralta-Tapia et al., 2015).

Stable water isotopes and biogeochemical tracers are some of the most common tools in field investigations to locate sources of water and follow its pathways through the landscape (Barthet al., 2007; Goller et al., 2005; Maulé and Stein, 1990; Rodhe et al., 1996; Tetzlaff and Soulsby, 2008). Isotopic tracer dampening can provide an estimate of water travel times (McGuire et al., 2005; Peralta-Tapia et al., 2016; Uhlenbrook et al., 2002; van Geldern et al., 2014), and, more elaborate time-series analysis can provide quantitative assessments of water age (Danesh-Yazdi et al., 2016; Harman, 2015). Many solutes will react and transform differentially during their route to the stream (Ledesma et al., 2018; Lidman et al., 2017). Such transformations and reactions depend on the specific soil environment and can give information about travel time through the mineral soils and groundwater flow pathways (Frisbee et al., 2011; Wolock et al., 1997; Zimmer et al., 2012). Therefore, combined information from conservative and reactive tracers can provide an enhanced understanding of hydrological and biogeochemical processes in the catchment (Laudon et al. 2011). However, field investigations often require tracer inputs and outputs to be adequately controlled and can hence be impractical at larger temporal and spatial scales.

A complementary approach to field experiments is numerical modeling, which can be useful for achieving a system understanding of catchment hydrology. Lumped hydrological models can describe catchments as single integrated entities. In contrast, distributed numerical models can consider spatial heterogeneity in input parameters. Therefore, they have the potential to represent catchment processes in a more realistic manner, which can lead to a more process-based understanding of hydrology and biogeochemistry at the catchment-scale (Brirhet and Benaabidate, 2016; Soltani, 2017). Models, however, need – as far as possible – proper tests against real observations to build confidence in their outputs, and as a rule, this requires large amounts of empirical data.

In this study, advective travel times groundwater input to streams were investigated in the well-studied Krycklan catchment in the boreal region (Laudon et al. 2013) using a physically based distributed numerical model, Mike SHE (Graham and Butts, 2005). The model calculates saturated (3D) and unsaturated (1D) groundwater flow and is fully integrated with the surface water as well as evapotranspiration. The model setup previously presented by Jutebring Sterte et al. (2018) was used and has been calibrated and

80 validated to observed discharge and groundwater levels throughout the Krycklan catchment. The complexity of the model allows for an in-depth investigation of advective travel times by non-reactive particle tracking simulations in a transient flow field.

Based on previous work in Krycklan (Peralta-Tapia et al., 2015), we hypothesize that sub-catchment size is the primary factor determining groundwater travel times since the study site has a relatively uniform glacial history, geology, and climatic conditions. Firstly, we tested the credibility of the model results by comparing particle travel times from 14 long-term monitored sub-

85 catchments to ten-year winter δ^{18}O and δ^{2}H signatures, as well as ten-year winter base cation and pH records from the Krycklan network. Thereafter, we tested our hypothesis by linking the estimated particle travel times to various catchment characteristics to evaluate and generalize the regulating landscape factors.

2 Method

2.1 Site description

90 The Krycklan study catchment, located in the boreal region at the transition of the temperate/subarctic climate zone of northern Sweden, is spanning elevations from 114 to 405 m.a.s.l. The characteristic features of this boreal landscape are the dominance of Scots pine (Pinus sylvestris) and Norway spruce (Picea abies) covering most of the catchment (Laudon et al., 2013). Krycklan has a landscape distinctively formed by the last ice age (Ivarsson and Johnsson, 1988; Lidman et al., 2016). At the higher altitudes to the northwest, which are located above the highest postglacial coastline, the regolith can reach up to 15-20 m in thickness (Figure

95 1, Table 1). Here, the regolith primarily consists of sandy-silty till, and the landscape is intertwined with lakes and mires. Previous studies have indicated that the hydraulic conductivity of the till decreases with depth with the significant part of the flow occurring in the upper half meter of the regolith (Ågren et al., 2014; Bishop et al., 2004). The decreasing hydraulic conductivity with depth is characteristic for glacial tills in northern Sweden (Bishop et al., 2011; Seibert et al., 2009) with conductivities close to $5 \cdot 10^{-5}$ m s^{-1} at the soil surface and exponentially decreasing with depth (Nyberg, 1995). The high conductivity near the surface causes the

100 main lateral groundwater transport to occur in the shallower parts of the till. At lower altitudes, the regolith mainly consists of fluvial deposits of silty clay and sand. Compared to the regolith at higher altitudes, these sandy deposits can reach thicknesses up to approximately 60 m or more and are more homogeneous with depth.

The catchment, which is used for multi-disciplinary biogeochemical and hydrological research (Laudon & Sponseller, 2018), is divided into 14 nested sub-catchments, called C1 to C20, of which 14 were used in this study. Connected by a network of streams,

105 the different sub-catchments have distinct characteristics, which allow for an evaluation of the effects of catchment characteristics on hydrologic transport, including type regolith, vegetation, and differences in topography.

Table 1: Sub-catchment characteristics. The table includes all 14 monitored sub-catchments in Krycklan, called C1 to C20, in order of catchment size (see Fig. 1). The table includes sub-catchment area, average elevation, and average slope. Further

110 description of these characteristics can be found in Karlsen et al. (2016). The table also includes soil type based on the regolith map (1:100,000) from the Swedish Geological Survey. The area proportions were calculated from the 50*50 m map created in Mike SHE. The numbers in brackets represent the proportion of the sub-catchments that are assumed to be more silty sediments, i.e., with low conductive soils (LCS).

	Catchment size (km²)	Average elevation (m.a.s.l.)	Slope (°)	Till (%)	Mire (%)	Sorted sediments (%)	Lakes (%)
C2	0.12	273	4.75	79	0	0	0
C4	0.18	287	4.24	29	42	0	0
C7	0.47	275	4.98	68	16	0	0
C1	0.48	279	4.87	91	0	0	0
C5	0.65	292	2.91	47	46	0	6.4
C6	1.10	283	4.53	51	29	0	3.8
C20	1.45	214	5.96	55	9	28 (28)	0
C9	2.88	251	4.25	64	14	11 (4)	1.5
C10	3.36	296	5.11	64	28	1	0
C12	5.44	277	4.9	70	18	6	0
C13	7.00	251	4.52	60	10	18 (9)	0.7
C14	14.10	228	6.35	46	6	39 (15)	0.7
C15	19.13	277	6.38	64	15	10 (2)	2.4
C16	67.90	239	6.35	51	9	31 (10)	1
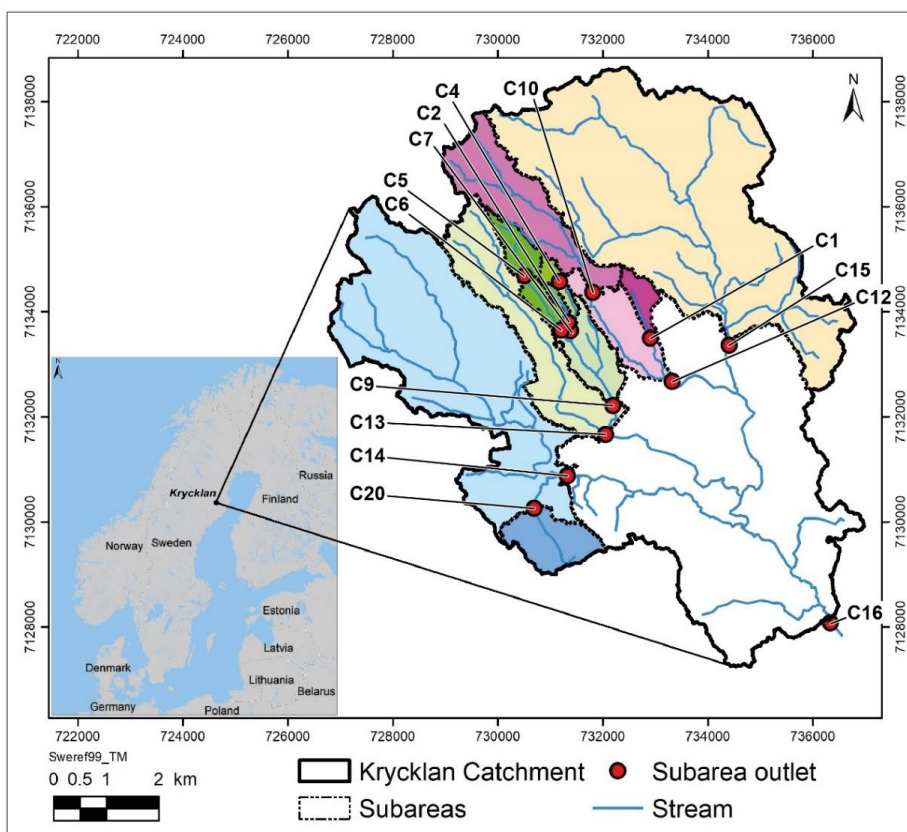
Figure 1: Location of sub-catchment and sub-catchment outlets (red circles). The areas are color-coded based on their stream network connections, e.g., all green sub-catchments connect before reaching the main outlet, C16. For further details of the catchment characteristics, see Table 1. The scale and coordinate system refer to the local figure over the catchment.

2.2 Model setup

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The Mike SHE model used in this study was a slightly updated version of the previously established and validated surface and groundwater model presented by Jutebring Sterte et al. (2018). The model has a horizontal grid resolution of 50*50 m. Vertically the model is divided into ten calculation layers and reaches a depth of 100 m below ground. The calculation layers follow the regolith stratigraphy with one exception: the uppermost layer thickness was set to 2.5 m. This exception was due to the numerical

125 implementation of the unsaturated zone and the evapotranspiration processes in Mike SHE, which only are fully active in the uppermost calculation layer. Therefore, the uppermost layer has to be deep enough to cover the part of the regolith influenced by evapotranspiration processes and capillary rise of groundwater. This depth averages several regolith types into one calculation layer, which may underestimate the observed high horizontal hydrological conductivity in the shallowest parts of the till (Peralta-Tapia et al., 2015). Numerically this is accounted for by implementing a depth-dependent drainage function, which increases the

130 flow velocity in the shallowest part of the till (Bosson et al., 2008). For more information regarding the model setup, see Jutebring Sterte et al. (2018). For this study, a few changes were made to the original Krycklan Mike SHE model. Most importantly, new field data from Krycklan gave a more precise location and the threshold level of the lake outlet of C5. The corrections and additions did not influence the model results in any substantial way.

Particle tracking in Mike SHE enables groundwater travel time investigations, as described in detail by Bosson et al. (2010, 2013).

135 Particles in the model will only follow the saturated groundwater flow by advection. In Mike SHE, it is possible to release particles, with unique identification numbers, at any depth and location. During the particle tracking, the particle locations (x-, y- and z- coordinates) from the release point to the sink where it leaves the saturated zone are stored, for example, through the unsaturated zone, through the river network or the model boundaries. The particle tracking calculations in Mike SHE are applied to a pre-calculated flow field. Hence, in the first step, the water movement calculation is performed, while in the second step, the tracing

140 of particles, from a source point to a sink, is executed. This method allows for long-term transport calculations where the particle tracking simulations can be run for several annual cycles based on the same, transient or steady-state, flow field. The porosity of the regolith and the bedrock were added to drive the particle tracking calculations (Table 2).

Table 2

Porosity values for different soil types used in the Mike SHE model

Soil type	Porosity
Gravel[a]	0.32
Sand[b]	0.35
Silt[c]	0.45
Clay[b]	0.55
Silt-clay[d]	0.50
Till[b]	0.30
Peat[b]	0.50
Bedrock[b]	0.0001
Bedrock fractures/deformation zones[b]	0.001

145 [a]Average of Morris and Johnson (1967). [b]Joyce et al. (2010). [c]Average value between sand and clay. [d]Average value between silt and clay

2.3 Numerical method

Particle tracking was used to assess travel times for each sub-catchment. The particle tracking was run to simulate several years to capture the travel times of most of the released particles in the area. One year of calculated flow results from Jutebring Sterte et al.

150 (2018) was cycled multiple times to extend the particle tracking simulation for several years. The year 2010 was selected, as the

precipitation and evapotranspiration data for this year were close to the long-term annual averages observed for the Krycklan catchment (approximately 600 mm and 300 mm, respectively (Laudon et al., 2013)).

The number of particles had to be restricted due to numerical constraints. Particles were released at the top of the transient groundwater table during the first year. We released one particle per cell per 5 mm average modeled groundwater recharge to

155 capture the timing of general recharge patterns, i.e., ca 24,000 particles per km^2 and year. The time it took for particles to reach a stream or lake (onwards called 'travel time') was calculated for each sub-catchment. Simulated travel time distributions were analyzed using five statistical measures, the arithmetic mean, the geometric mean, the median, the standard deviation, and the skew. If the standard deviation is higher than half of the arithmetic mean, the geometric mean may be a better measure of the central tendency of a data set (Taagepera, 2008), and this can often be the case with travel time distributions with long tails. The

160 standard deviation and skew were therefore used to evaluate which measure of central tendency was best for describing the simulated travel times. To identify the minimum simulation time needed for robust travel time estimates, we compared simulated median travel times for varying lengths of simulations. We assumed that the calculation was run for enough time when the median of the travel time was stabilized for all sub-catchments. The median stabilized after 500 years of simulation time, but in the end, we let the simulation run in total 1000 years to ensure that the results were stable for all parts of the catchments. Thereafter, we

165 used the entire simulation (the year 2010 cycled 1000 times) to calculate mean travel times for each sub-catchment.

2.3.1 Observations of stable isotopes

Stable water isotopes are often used to track pathways of precipitation inputs to a stream network. In this study, we used a time series of stable isotopes (δ^{18}O and δ^2H) in stream water to compare to modeled travel times (Peralta-Tapia et al., 2014). Water was collected at 13 of the 14 sub-catchments included in the study. Hydrological patterns emanating from differences in the landscape

170 structure can be seen in the isotopic composition of stream and groundwater (Ala-aho et al., 2017).

In this study, we compared the isotopic signature of winter baseflow, defined here as streamflow from December to February, to calculated winter groundwater travel times. During this season, the primary input to stream water comes from the groundwater due to the prolonged freezing temperatures at these times. In Krycklan, the winter is usually much longer than that, but since even minor melting episodes can have an influence on the isotopic composition and the chemistry of the stream water, only December-

175 February were considered. Therefore, the isotopic stream signature of these months was assumed to describe the isotopic signature of the groundwater the best. The average isotopic signatures of approximately ten years of field observations (the year 2008 to the spring of 2018) were calculated, which consists of approximately 35 measurements from each sub-catchment. Parts of the dataset has been published by Peralta-Tapia et al. (2016), where sampling and analyses are described in detail, and it has since been expanded using the same methodology. We used the average of the stable isotope signature from these years as a representation of

180 baseflow. These averages were also compared to the average (weighted average calculated by precipitation amount) of the long-term precipitation, calculated using approximately 1160 precipitation measurements of both δ^{18}O and δ^2H between 2007 and 2016.

The underlying assumption in this approach is that the strong seasonal signature from precipitation will be reduced with travel time due to mixing in the soil. With infinitely long travel times, the stream water signature should equal the long-term average of

185 precipitation inputs, while short travel times should make the stream water signature reflect the input signal from the precipitation. There should, therefore, be a significant relationship between the simulated travel times and the observed winter isotopic stream signature provided that the model performs well. Some of the sub-catchments are, however, affected by evaporation from lake surfaces that result in isotopic fractionation (Leach and Laudon, 2019). This fractionation must be accounted for in order to use the signature as a representation of the groundwater. The isotopic composition was corrected with respect to the percentage of

190   lakes in each sub-catchment, and a regression equation for each isotope was determined and applied to sub-catchments containing lakes. We used the same principle as in Peralta-Tapia et al. (2015) but adjusted it for newly acquired data with approximately 270 samples from each site (2008-2018). The long-term regression equations for each isotope for sub-catchments are as follows:

$$18O = 0.18(lake\ coverage\ [\%]) - 13.20\ (r^2 = 0.87,\ p < 0.001) \qquad \text{Eq. (1)}$$

$$2H = 0.81(lake\ coverage\ [\%]) - 96.03\ (r^2 = 0.68,\ p < 0.001) \qquad \text{Eq. (2)}$$

195   **2.3.2 Observations of stream chemistry**

Comparisons were also made to the long-term annual and winter averages of stream chemistry. Previous attempts to follow the chemical development of groundwater in the Krycklan catchment have shown that pH and the concentration of base cations increase along the groundwater flow pathway because of weathering (Klaminder et al., 2011). Therefore, a general agreement between the concentration of base cation and pH on the one hand and modeled travel times on the other would strengthen the

200   credibility of the model results. pH is generally expected to increase with the groundwater age since protons are consumed in the weathering of silicate minerals. In addition, the decomposition of organic acids over time will also increase the pH. The base cations are mainly derived from weathering of local soils in the Krycklan catchment, with only a minor contribution from atmospheric deposition (Lidman et al., 2014).

Modeling of weathering rates in a soil transect in the Krycklan catchment has indicated that there is kinetic control of the release

205   of base cations in the soils (Erlandsson et al., 2016). The release of base cations suggests that the longer the groundwater is in contact with the mineral soils, the higher base cation concentrations can be expected, similarly to what was observed by Klaminder et al. (2011). Since base cations have been observed to behave relatively conservatively in these environments (Ledesma et al., 2013; Lidman et al., 2014), we used their combined concentration as a proxy for water age, i.e., subareas with longer travel times would hypothetically exhibit higher base cation concentrations and higher pH. It has been observed, however, that mires have a

210   negative impact on the concentration of cations in the streams within the Krycklan catchment. The reason is that the peat does not contain any appreciable amounts of minerals, so groundwater passing through mires will not acquire cations at the same rate as when it passes through mineral soils (Lidman et al., 2014). In practice, this will cause cations in specific subareas to be diluted by groundwater from the mires in a manner that is not related to the groundwater travel time. The cation concentrations were therefore adjusted for the influence of mires according to:

215   $$Adjusted\ cation\ concentration = Observed\ cation\ concentration\ /\ (1 - mire\ coverage) \qquad \text{Eq. (3)}$$

All pH and base cation data were taken from the open Krycklan database, and the collection methodology and analysis are reported in Laudon et al., 2013. The base cation and pH data comprise approximately 25 (2008-2017) and 20 (2011-2018) observations for the winter period (December to February) for each stream, respectively (Table 3, an extended table can be found in Supporting

220   information 1). Since pH and base cations are less impacted by precipitation, compared to water isotopes, the annual average was also considered. The annual base cation and pH data comprise approximately 235 (2008-2017) observations and 180 (2011-2018) observations, respectively.

Table 3: Stream chemistry of Krycklan in order of catchment size

unit	$\delta^{18}O$ [a] winter ‰	δ^2H [a] winter ‰	Base cations [b] winter	annual (μeq L^{-1})	pH [c] winter	annual (-)
C2	-12.8	-94.5	257	229	5.29	4.99
C4	-12.9	-95.5	250	248	4.40	4.39
C7	-13.0	-95.3	271	246	5.25	4.88
C1	-12.9	-94.8	277	258	5.71	5.36
C5	-11.7	-90.3	257	228	4.74	4.82
C6	-12.3	-92.5	321	291	5.73	5.41
C20	(-)	(-)	520	495	6.61	6.40
C9	-12.7	-94.6	350	303	6.07	5.74
C10	-13.2	-96.7	315	288	5.83	5.23
C12	-13.1	-96.1	319	277	6.09	5.52
C13	-13.0	-95.3	338	284	5.73	5.55
C14	-13.2	-97.2	358	338	6.47	6.23
C15	-12.9	-95.3	347	324	6.45	6.30
C16	-13.2	-97.0	481	383	6.64	6.46
Long term precipitation average [d]	-13.5	-98.9	70	70	(-)	(-)

[a] Average measured winter isotope signature (2008-2018), sub-catchments with lakes have been adjusted according to Eqs. 1 and 2, respectively.

[b] Average measured winter and yearly cation signature (2011-2018), sub-catchments have been mire adjusted according to equation 3

[c] Average measured winter and yearly pH signature (2008-2017)

[d] Measured precipitation average for isotopes (2007-2016) and measured base cations (year 1997 to 2003)

2.3.3 Catchment characteristic investigation

To test the hypothesis that the catchment size is the primary factor affecting the groundwater travel time, the correlations between the calculated MTT and different catchment characteristics were investigated. The characteristics tested included important terrain factors such as size and slope as well as soil types. As many factors can affect the hydrology of a catchment, we list the main descriptive landscape characteristics in Table 1, which together describe the landscape variability of Krycklan. Karlsen et al. (2016) also suggested that these factors are some of the most important landscape characteristics affecting the hydrology of the catchment. The simulated specific baseflow to the streams, as well as the mean travel distance (MTD) of the particles, were also calculated to investigate if they could help explain the travel time patterns in the landscape (Table 4).

3 Results

3.1 Estimation of mean travel time

The simulated yearly mean groundwater travel time (MTTy) for all sub-catchments ranged between 0.5 to 3.6 years. The geometric mean was used to describe the central tendency of travel times, because of the skewed distribution (Table 4, extended table in

245 Supporting information 1). The travel time distribution as reflected by the MTTy, with, for example, C2 having the youngest mean age and the largest proportion of young particles. In comparison, C20 had the oldest age and the largest proportion of old particles (Table 4, Fig. 2).

Over a year, a small fraction of the water reaches the stream as surface flow, which may enhance or dilute various stream solutes in different ways. Winter baseflow conditions may, therefore, be a better representation of the groundwater chemistry. From

250 December to February, there was no input of precipitation due to freezing conditions, resulting in that the only input to the streams came from the groundwater. The mean simulated travel time of winter baseflow (MTTw) was older for all sub-catchments compared to MTTy. According to the simulation, winter baseflow (Dec-Feb) accounts for approximately 5-15% of the total yearly stream contribution.

255 **Table 4: Particle tracking results for all sites in Krycklan.** Statistics of particle tracking results with a simulation time of 1000 years. The table is ordered by increasing sub-catchment size. The statistics are calculated for each sub-catchment and include the MTT (MTTy is the yearly mean travel time, and MTTw is the winter (Dec-Feb) mean travel time), skew, and standard deviation (SD). Further statistical information can be found in Supporting information 1. MTD is the mean travel distance of the particles. Winter baseflow is the fraction of the total annual runoff generated during Dec-Feb.

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	Simulated results					
	MTT$_y$	MTT$_w$	Skew	SD	MTD	Winter groundwater fraction
unit	Year	Year			m	%
C2	0.5	0.8	6.2	5.2	50	6.3
C4	1.1	2.6	9.3	15.5	74	10
C7	1.3	2.6	4.6	16.6	70	13.1
C1	1.1	2.6	3.8	26.3	120	14.1
C5	1.0	1.6	11.3	25.3	90	5.8
C6	1.0	1.7	10.8	23.2	70	8.5
C20	3.6	7.5	8.0	50.2	110	13.0
C9	1.6	3.2	5.7	28.4	80	12.6
C10	1.3	2.6	7.3	26.4	70	12.7
C12	1.6	3.3	5.5	29.3	90	14.2
C13	1.5	2.9	7.0	28.8	85	13.3
C14	3.2	5.4	8.7	47.2	145	16.3
C15	1.9	4	7.3	30.8	85	11
C16	2.8	5.1	9.9	37.9	135	15.2
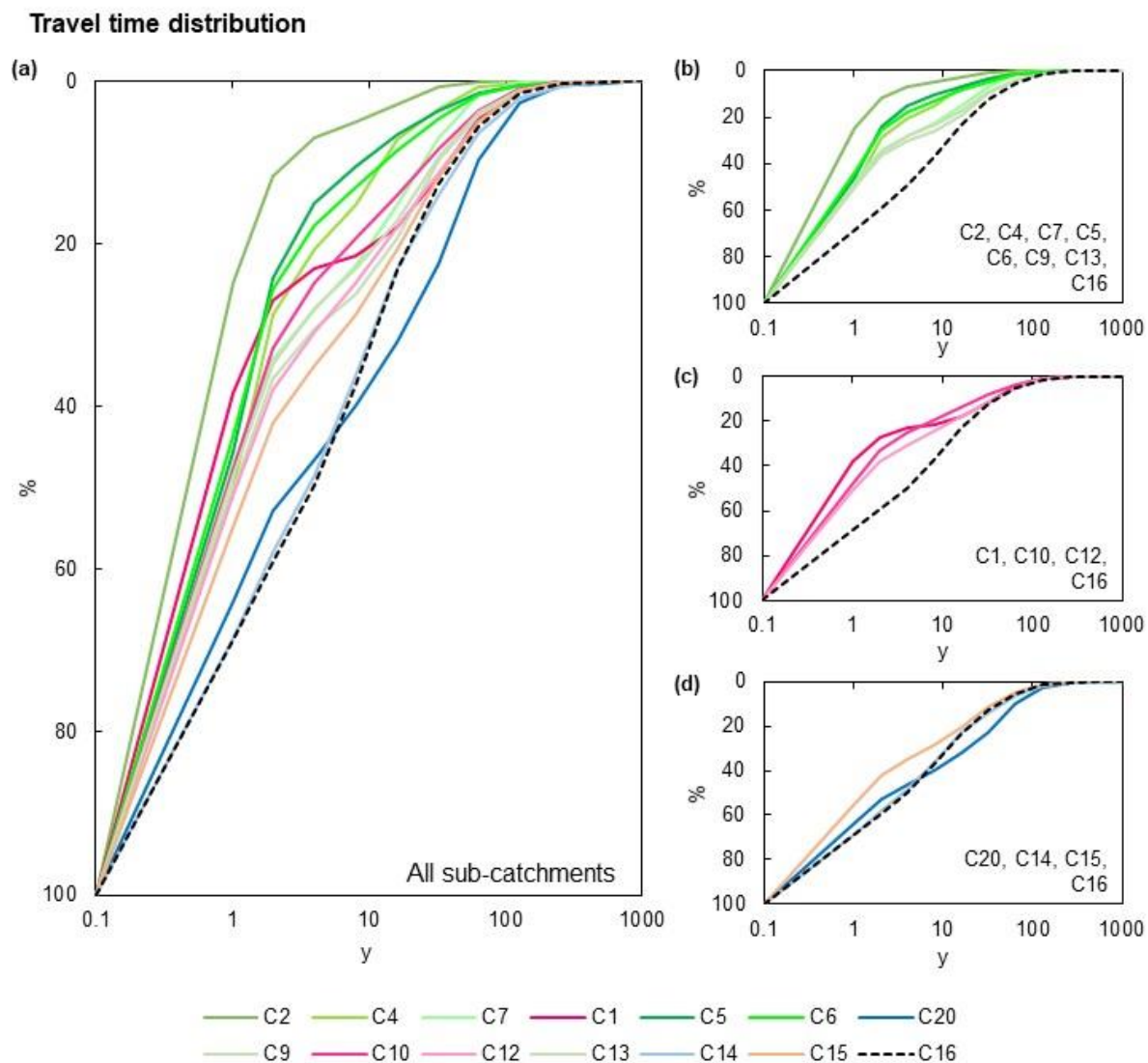
Figure 2 Simulated travel time distribution of the groundwater in Krycklan. C16 is used as a visual reference in all panels. The figure includes all 14 investigated sub-catchments, color-coded as Fig. 1 and displayed in the legend in size order from left to right with C2 being the smallest and C16 the largest sub-catchment. The figure is divided into (a) all sub-catchments, (b) the sub-catchments of C13, (c) the sub-catchments of C12 and, (d) the sub-catchments of C14 and C15.

3.2 Stable isotopes and stream chemistry

The simulated winter mean travel times (MTTw) were compared to the measured winter isotope signature for each site, as well as to the measured average winter cation concentration and pH, using linear regressions (Fig. 3). There was a significant correlation between the calculated mean winter travel times and both $\delta^{18}O$ (r=0.90, p<0.001) and δ^2H (r=0.90, p<0.001). Both $\delta^{18}O$ and δ^2H

decreased with travel time, approaching the long-term precipitation average of -13.46 ‰ and -99.88 ‰, respectively. There was also a significant correlation between the measured winter base cation concentration and the simulated travel times (r=0.88, p<0.001; Fig. 3). pH had a similar behavior, but the correlation was somewhat weaker (r=0.73, p<0.001). The main outliers were the mire-dominated sub-catchments C4 and C5, which have high concentrations of organic acids that influence pH negatively. Note that there are isotope data for 13 sub-catchments and chemistry data for 14 sub-catchments (isotope data excludes C20, see Table 3). The yearly mean travel times (MTTy) were also compared to the yearly average of base cations and pH, with significant results for both pH (r=0.83, p<0.001) and base cations (r=0.90, p<0.001).

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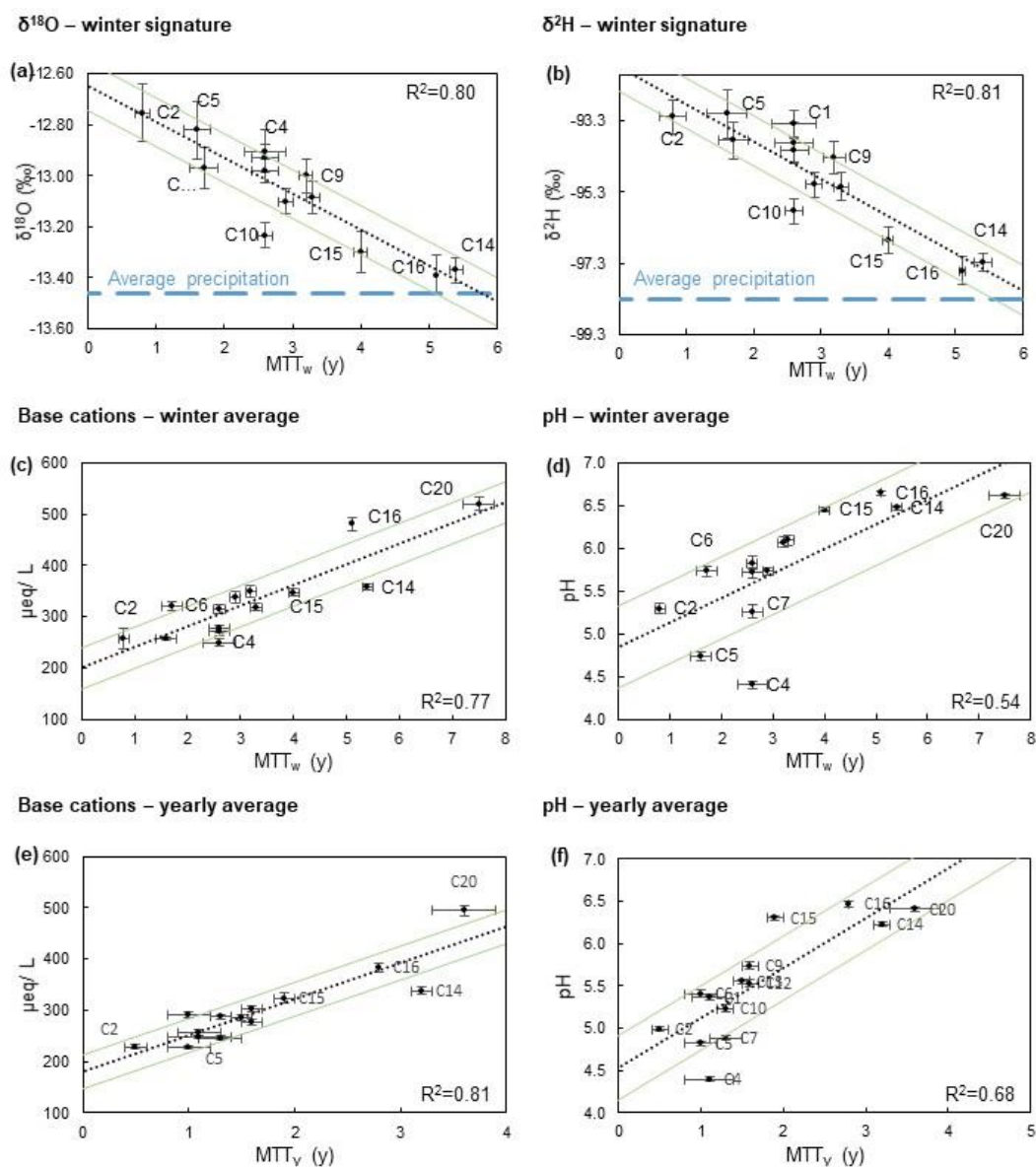
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Figure 3: Linear regressions of stream chemistry and calculated geometric mean travel times (MTT). The black line is the regression line, and the green lines are the 95% prediction bands. The plots also show the SEM (standard error of the mean) of the calculated average travel time and the chemistry observations (see Supporting information 1). (a) and (b): Average winter isotope signature, $\delta^{18}O$, and $\delta^{2}H$ (‰), against MTTw. Here the long-term average of precipitation signature is shown as a

285   horizontal blue line in each graph (-13.46 $\delta^{18}O$ and -99.88 $\delta^{2}H$ for the years 2007-2016). (c): Average winter base cation concentration (µeq/L, mire adjusted according to table 3 and eq. 3) against MTTw. (d): Average winter pH against MTTw. E: Average yearly base cation concentration (µeq L^{-1}, mire adjusted according to table 3 and eq. 3) against MTTy. F: Average yearly pH against MTTy.

3.3 Catchment characteristics

290   There was no significant correlation between sub-catchment size and calculated mean annual travel time (MTTy) (Fig. 4), C20 being the main outlier. Furthermore, when comparing the MTTy to other catchment characteristics, there was no significant correlation to the proportion of mires, till or lake area. However, there were significant (although weak) correlations between MTTy and mean travel distance (MTD) (r=0.76, p<0.01) and MTTy and catchment slope (r=0.73, p<0.01). A strong significant correlation between the MTTy and the proportion of low conductive sediments (LCS) (r=0.90, p<0.001), was also found. By using

295   multiple regression, two simple relationships could be established between the sub-catchments and three characteristics (further description of this relationship can be found in Supporting information 2). These show that although there is a correlation between the MTTy on one hand and slope (Eq. 4) or MTD (Eq. 5) on the other hand, the most significant parameter is the LCS:

$$MTT\ (y) = -0.33 + 0.31 * Slope[°] + 0.09 * LCS[\%]\ (R^2 = 0.90\ , p < 0.001) \qquad \text{Eq. (4)}$$

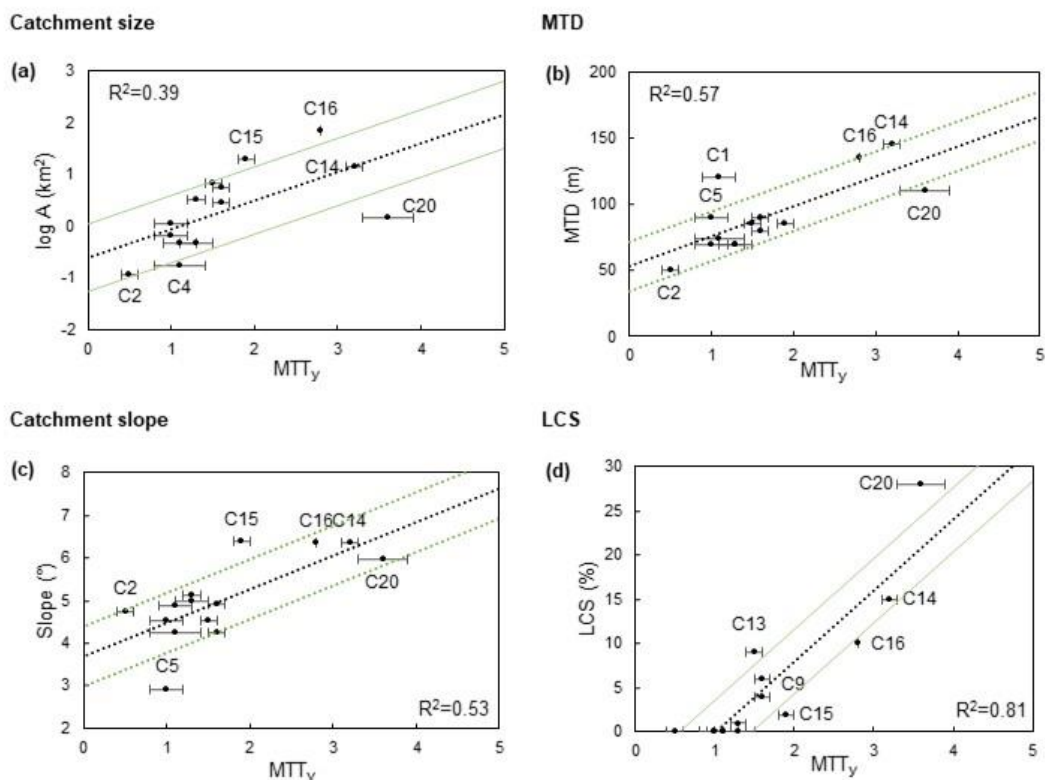
$$MTT\ (y) = 0.19 + 0.01 * MTD\ [m] + 0.08 * LCS[\%]\ (R^2 = 0.90, p < 0.001) \qquad \text{Eq. (5)}$$

300

Figure 4: Linear regression of catchment characteristics and calculated mean annual travel times (MTTy). The black line is the regression line, and the green lines are the 95% prediction bands. The plots also show the SEM (standard error of the mean) of the simulated average travel time (see Supporting information 1). (a): Catchment area against MTTy. (b): Mean travel distance of particles (MTD) against MTTy (c): Catchment slope (°) against MTTy. (d): Low conductive sediments (LCS) (%) against MTTy.

305

4 Discussion

4.1 Simulated travel times are consistent with the isotopic signal and stream chemistry

We used the stream winter isotopic composition and chemistry to test Mike-SHE's ability to capture the variability of groundwater travel times in the 14 Krycklan sub-catchments. Based on this, we found significant and robust correlations between the winter

310 isotopic signature of both $\delta^{18}O$ and $\delta^{2}H$ as well as the stream chemistry, on the one hand, and the calculated travel times on the other (Fig. 3). Theoretically, infinitely long travel time would result in a stream water isotopic signature approaching the long-term average precipitation input, while the base cation concentration of the stream water would increase until it reaches thermodynamic equilibrium with the soil mineral composition (Erlandsson et al., 2016). The strong statistical agreement between both the observed winter isotopic composition and stream chemistry and the particle travel times on the other supports the credibility of the model

315 results.

A comparison of these results to previous studies of MTT for one of the Krycklan sub-catchment (C7) shows that the different approaches gave similar results. While this study estimated the long term mean travel time to 1.3 years, Peralta-Tapia et al. (2016)

calculated a ten-year average travel time of 1.7 years using isotopic data and a gamma transformation method. In a non-distributed modeling study using the same data, but another travel time distribution technique, the median of the travel time distribution was
320   approximated to 0.9 years in the same catchment (Ala-aho et al., 2017).

The simulated travel times were compared to stream pH and base cation concentrations. Since the weathering rates generally are kinetically controlled, i.e., related to the travel time, such stream chemistry variables can be used as a relative indicator for stream water age. This study showed that the modeled travel times were significantly correlated to the observed pH and base cation concentrations. The use of pH and cations as tracers for groundwater residence times should be done with caution since both are
325   involved in several biogeochemical processes. Reducing weathering to a matter of travel times only may be an oversimplification. Weathering is affected by chemical conditions, differences in mineralogy and particle size distributions. However, previous research in the Krycklan catchment has indicated that the chemical composition of the local mineral Quaternary deposits is surprisingly homogeneous, even when comparing unsorted till and sorted sediments (Erlandsson et al., 2016; Lidman et al., 2016; Peralta-Tapia et al., 2015; Klaminder et al., 2011). Therefore, we do not expect mineralogical differences between soil types to
330   have a significant impact on the release of cations. The one exception is peat deposits, which strongly affect the cation concentrations, and that was accounted for by adjusting the concentrations for the influence of the mires following Lidman et al. (2014). Differences in particle size distribution may be important because coarser regolith will have less surface area per volume unit, therefore allowing for less weathering. However, such Quaternary deposits can also be expected to have higher hydraulic conductivities, leading to higher flow velocities and, consequently, less time available for weathering. Therefore, differences in
335   area-volume ratios between different soil types would not counteract the effect of travel times on the weathering, rather enhance it. Accordingly, base cation concentrations should still be a useful indicator of transit times. The pH of some sub-catchments has also been shown to be affected by mires, especially C4 and C5 (Buffam et al., 2007), due to high concentrations of organic acids that influence pH, especially when the buffer capacity is low (Hruska et al. 2003). This effect can be observed in the results of the mire dominated sub-catchments, which fall below the 95 % prediction line (Fig. 3D and 3F). Hence, we do not think that these
340   deviations contradict the credibility of the model results.

It can also be argued that pH is not a mixable quantity and therefore unsuitable as a tracer. Still, the purpose of the comparisons to stream water chemistry was not to mechanistically explain the evolution of stream water chemistry, but instead to compare the modeling results to some parameters that could be expected to reflect the groundwater travel times. Such tests are crucial for the credibility of the model results. Because pH increases as a result of silicate weathering, it is likely that pH would increase with the
345   groundwater travel time, albeit not necessarily in a linear manner. Complementing isotopic tracers with transported solutes for testing simulated travel times provide more insight into catchment processes. Despite the arguments that can be made against the use of pH and cations as tracers, they still offer a complementary possibility to test the performance of the model. As emphasized by McDonnell and Beven (2014), the inclusion of tracers in hydrological models is necessary to ensure that a model does reproduce the speed of flow, which is a crucial parameter when assessing travel time distributions. In catchment-scale models, this could be
350   an isotopic tracer or a solute that is transported with the water (Fenicia et al., 2010; Hooper et al., 1988; Hrachowitz et al., 2013; Seibert et al., 2003). Although neither the travel time distribution nor the kinetics of weathering is fully understood, the strong agreement between the calculated travel times and the observed stream water chemistry strengthens the credibility of model results and, more specifically, the chances that the model is producing credible results for the right reasons.

Strengthening the credibility of particle tracking in Mike SHE to produce travel time distributions enables the use of particle
355   tracking as a useful complement to other similar studies in the future. For example, stable water isotopes and biogeochemical tracer tests can be affected by dilution or chemical reactions, and here particle tracking could be a useful complement. Further extensions in the Mike SHE family (Graham & Butts, 2005) also allow the incorporation of solutes or isotopes with more complex

biogeochemical behaviour. These extensions could be used for further calibration and validation of the hydrological model
(McDonnell and Beven, 2014) as well as investigation of biogeochemical processes in the catchment. A more mechanistic
360 investigation of the relationship between groundwater travel times and stream water chemistry would require such extensions.

4.2 Catchment slope and hydraulic conductivity control travel times

Contrary to our hypothesis, the main factor controlling the groundwater travel times was the hydraulic conductivity and slope of
the catchment rather than the catchment size itself. In agreement with previous studies by Capell et al. (2012), Muñoz-Villers et
al. (2016), and Tetzlaff et al. (2009), there were significant correlations between catchment slope and travel time (Fig. 4). However,
365 the most significant factor was found to be the proportion of low conductive sediments (LCS), which overshadowed both the slope
of the catchment and the travel distance of particles. Earlier studies by Peralta-Tapia et al. (2015) and Tiwari et al. (2017) have
suggested that the MTT of groundwater is linked nonlinearly to the catchment size, i.e., the travel times increases with the
catchment size. However, we found C20 to be a distinct outlier to this pattern (Fig. 4). The long travel times in relation to the
relatively small catchment size means that the groundwater flow velocity generally is lower than elsewhere. Nevertheless, the
370 average catchment slope of C20 is steeper than comparably sized sub-catchments in the till areas, so the topographical possibilities
to build up high hydraulic gradients that can drive the water transport should be larger (Table 1; Fig. 4). This is probably related
to the fact that C20 is the only relatively small sub-catchment (1.45 km^2) in the area largely covered by LCS. However, the fluvial
deposit fraction may also explain the relatively long travel times of C14 and C16. For example, although C14 is smaller than C15,
it still has longer MTT. In contrast, C15 is much closer to C12 and C13 in MTT, even though C15 is almost twice as large. This
375 suggests that the critical difference between these sub-catchments and other sub-catchments is related to the hydraulic conductivity
of the regolith, rather than the catchment size. Without the contribution of water from headwater catchments with fine regolith
(such as C20), the MTT of sub-catchments like C14 and C16 would probably have a MTT much closer to the other smaller till
dominated sub-catchments. The results, therefore, emphasize that one cannot generally assume that the travel time would increase
with catchment size unless the distribution of regolith is comparable throughout the landscape.

380   5 Summary remarks

The Mike SHE model showed promising results in its ability to capture groundwater travel times, which was firmly related to
winter stream isotope signatures. The simulated travel times were, in turn, well correlated to the base cation concentration and pH
of the streams. In contrast to our hypothesis, we found that the catchment size itself is not the main factor determining groundwater
travel times. Instead, we found the hydrologic conductivity of regolith to be the most important parameter, but also that the
385 catchment slope and travel distance of the groundwater could have an impact. This essentially points back to Darcy's law, which
states that the groundwater flow is governed by the pressure gradient (approximated by the catchment slope in this case) and the
hydraulic conductivity of the medium (approximated by soil types). In that sense, the results are in line with theory. However, it is
far from evident that precisely these catchment parameters would stand out as most important in the complex landscape of the
Krycklan catchment or, for that matter, the boreal landscape at large. It is also important to note that catchment size may not be as
390 significant as previously thought.

6 Data availability

The Data from the Hydrological Research at Krycklan Catchment Study is available in Svartbergets open database
(www.slu.se/Krycklan).

7 Author contribution

395   Elin Jutebring Sterte was responsible for the design, conceptual idea and evaluation of results in collaboration with all the co-authors. Elin Jutebring Sterte and Emma Lindborg were responsible for the numerical modelling. Elin Jutebring Sterte prepared the manuscript and figures. All co-authors contributed to the writing of the paper.

8 Competing interests

The authors declare that they have no conflict of interest

9 Acknowledgments

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