Key Points:
- Water isotopes were used for partitioning groundwater sources during baseflow
- Old groundwater contributions increased with drainage size
- Partitioning of groundwater contributions regulate stream water chemistry

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Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments

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Abstract Understanding how the sources of surface water change along river networks is an important challenge, with implications for soil-stream interactions, and our ability to predict hydrological and biogeochemical responses to environmental change. Network-scale patterns of stream water reflect distinct hydrological processes among headwater units, as well as variable contributions from deeper groundwater stores, which may vary nonlinearly with drainage basin size. Here we explore the spatial variability of groundwater inputs to streams, and the corresponding implications for surface water chemistry, during winter baseflow in a boreal river network. The relative contribution of recent and older groundwater was determined using stable isotopes of water ($\delta^{18}O$) at 78 locations ranging from small headwaters ($0.12\ km^2$) to fourth-order streams ($68\ km^2$) in combination with 79 precipitation and 10 deep groundwater samples. Results from a two end-member mixing model indicate that deeper groundwater inputs increased nonlinearly with drainage area, ranging from ~20% in smaller headwater subcatchments to 70–80% for catchments with a $10.6\ km^2$ area or larger. Increases in the groundwater contribution were positively correlated to network-scale patterns in surface stream pH and base cation concentrations and negatively correlated to dissolved organic carbon. These trends in chemical variables are consistent with the production of weathering products and the mineralization of organic matter along groundwater flow paths. Together, the use of stable isotopes and biogeochemical markers illustrate how variation in hydrologic routing and groundwater contributions shape network-scale patterns in stream chemistry as well as patchiness in the relative sensitivity of streams to environmental change and perturbation.

1. Introduction

Understanding how catchment structure influences the hydrology and biogeochemistry of surface waters remains an important research challenge [*McDonnell et al.*, 2010]. A key aspect of this challenge includes identifying scale-dependent changes in the relative importance of different catchment processes that determine patterns of streamflow within drainage networks [*Blöschl*, 2001; *McGuire et al.*, 2005; *Rodgers et al.*, 2005]. Resolving these scale dependencies and understanding how processes at different scales interact to shape broader biogeochemical patterns have emerged as important prerequisites for predicting how riverine systems will potentially respond to changes in land use and climate [*McGuire et al.*, 2014]. Efforts to develop such scaling rules for stream networks have often sought to delineate thresholds, reported by some authors as the representative elementary area, which represents the drainage size at which variability in runoff processes among streams is sufficiently low to allow for the use of simple hydrological models [*Wood et al.*, 1988, 1990; *Shaman et al.*, 2004]. Below this threshold, locally variable structures and/or processes (e.g., related to surface-groundwater exchange) can lead to unique hydrological/biogeochemical patterns. Further, transitions across such thresholds in drainage size can be associated with sharp changes in the dynamics of water chemistry, temperature, and flow stability in the network [*Wolock et al.*, 1997; *Shaman et al.*, 2004].

The hydrological and biogeochemical characteristics of streams observed during baseflow can provide important insights into changes in water sources, sensitivity to perturbation, and for detecting scale-dependent processes [*Tetzlaff and Soulsby*, 2008; *Zimmer et al.*, 2013]. Baseflow is the portion of streamflow

that comes from groundwater storage and other delayed sources [*Hall*, 1968], representing an important "genetic component" of the hydrograph [*Smakhtin*, 2001] that has implications for the ecological structure and functioning of streams [*Doyle et al.*, 2005]. In many cases, baseflow conditions can also be used as a baseline to infer event-activated perturbations such as episodic acidification [*Bishop et al.*, 2000] and contaminant transport [*Bergknut et al.*, 2010]. Given its importance and potential utility for understanding hydrological and biogeochemical processes, many studies across the globe have sought to disentangle the sources of baseflow, using a variety of methods [*Vitvar et al.*, 2002; *Fan et al.*, 2013; *Krishnaswamy et al.*, 2013]. A key challenge to these efforts has been identifying windows of time when different catchment water sources can be separated. To more directly and reliably assess baseflow properties, an extended period of time without recent atmospheric inputs of water to a system is required. In high-latitude catchments, severe and prolonged frozen conditions in the surrounding terrestrial landscape create such conditions and therefore provide an opportunity for studying the properties of baseflow, including the relative importance of different water sources across scales of drainage size.

Natural stable isotopes of water [*Rodhe et al.*, 1996; *Soulsby et al.*, 2000; *Goller et al.*, 2005], often in combination with biogeochemical markers [*Richey et al.*, 1998; *Tetzlaff and Soulsby*, 2008], are increasingly used as tools for tracing the flow and sources of water through catchments. After the water enters the soil/groundwater system, the conservative behavior of the isotope ratios δ^{18}O and δ^2H (or D as in Deuterium) allows the use of mixing models to identify the relative contributions of "old" and "young" water sources to streamflow, and as such can provide a surrogate for catchment water residence time [*McGuire et al.*, 2005]. In contrast, elements such as major base cations (Ca and Mg), trace metals, and dissolved organic carbon (DOC) are subject to a range of reactions and transformations and thus are sensitive to the residence time, reactivity, and the sequence of various subsurface environment water encounters on route to streams [*Likens and Buso*, 2006]. As such, the dynamics and pattern of various elements in streams can provide valuable insights into the hydrological processes within catchments, including the extent of subsurface contact time [*Wolock et al.*, 1997; *Frisbee et al.*, 2011] and the location of biogeochemical hot spots [*Lidman et al.*, 2014]. Combining the use of conservative tracers with semiconservative elements can therefore provide a more mechanistic understanding of internal catchment processes and dynamics than any one method alone [*Kurtenbach et al.*, 2006; *Laudon et al.*, 2011; *Frisbee et al.*, 2012].

In this study, we explored the factors that influence the source of baseflow in a 68 km^2 boreal research catchment of northern Sweden [*Laudon et al.*, 2013]. The hydrology of the boreal region is characterized by marked seasonality linked to an extended period of frozen conditions, followed by rapid snowmelt in late spring and early summer [*Lowry et al.*, 2010; *Lyon et al.*, 2010]. In addition, boreal landscapes are commonly composed 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 streams [*Temnerud and Bishop*, 2005; *Peralta-Tapia et al.*, 2014]. At larger spatial scales, boreal landscapes are also characterized by variation in the distribution of till (and its composition), sorted sediment deposits, and in the influence of eskers, formations originating from previous deglaciations that now affect how deeper, older groundwater interacts with surface streams [*Tiwari et al.*, 2014]. Within this context, the objectives of this study were to (1) investigate the variability in groundwater contribution to surface streams across this drainage network during winter baseflow, (2) connect this variation in groundwater contribution with spatial patterns of stream chemistry, and (3) evaluate the degree to which groundwater contributions varied as a simple function of subcatchment size as compared to alternative descriptors of catchment structure (e.g., topography and local depressions). To do this, we used water isotopes to estimate groundwater inputs and compared this contribution to chemical markers surveyed from 78 stream sampling locations, spanning subcatchments that differ by nearly 3 orders of magnitude in drainage area.

2. Study Area

The study was carried out in the Krycklan Catchment (64°14′N, 19°46′E) located in northern Sweden (Figure 1; for further details, see *Laudon et al.* [2013]). Briefly, this catchment has a total area of 68 km^2 and includes 17 subcatchments that are monitored at semiweekly to monthly intervals and up to 100 additional sites that are occasionally sampled as part of spatially extensive campaigns (the number of sites in each survey varies, depending on flow conditions and accessibility).
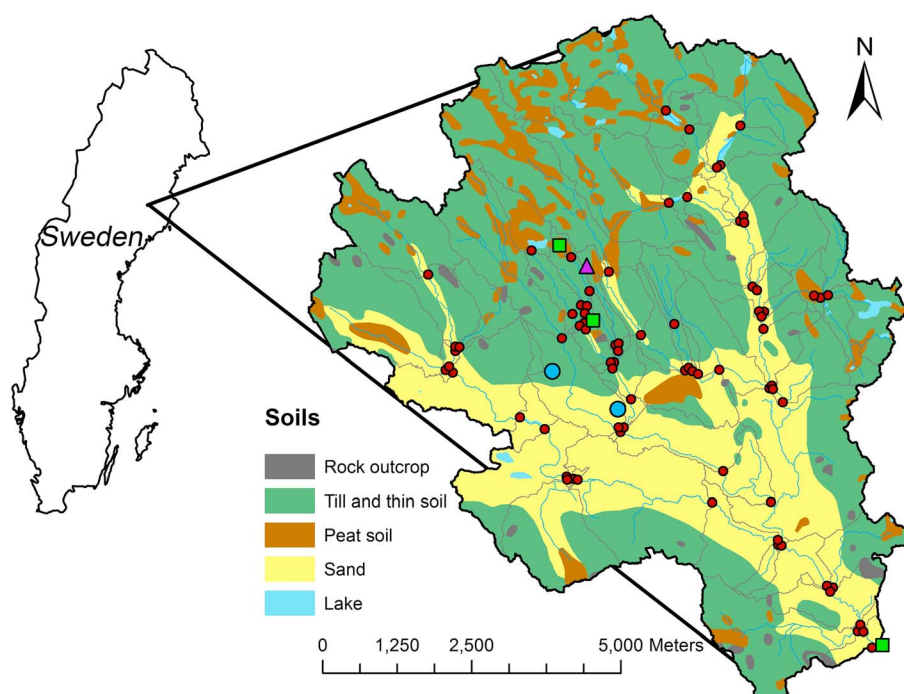
Figure 1. Krycklan Catchment: the red points show the sampling sites during the survey. The green rectangles show the deep groundwater well locations. The purple triangle shows the location of the Swedish Geological Monitoring (SGU) groundwater wells. The blue circles show where the rain gauges are located.

Over 87% of the Krycklan Catchment is covered by forests, mainly Scots pine (*Pinus sylvestris*), spruce (*Picea abies*), and birch (*Betula* spp.). Importantly, wetlands and lakes cover close to 10% and 1% of the entire catchment, respectively. Elevation ranges from 127 m above sea level (asl) at the outlet to 372 m asl at the highest point. The 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% are 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, larger channels are more incised, carving through floodplain sediments (i.e., silty/fine sands) that cover about 30% of the catchment (Figure 1). 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]. The mineralogy of the soils 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]. Mean annual precipitation in Krycklan from 1981 to 2007 was ~612 mm, 50% of which occurs as runoff as stream water. 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].

Subcatchments within Krycklan can be markedly variable in terms of vegetation, soils, and types of aquatic habitat [*Buffam et al.*, 2008]. Forest cover among the subcatchments ranges from 54 to 100%; mire coverage ranges from 0 to 44%. There are 24 subcatchments that have no lakes, while the remaining 54 include lake cover, ranging from 0.01 to 9.6% of their catchment (see Supporting Information S1 and Table S1 in the supporting information).

3. Methods

3.1. Sampling

Stream water samples were collected from 78 sites during winter baseflow in mid-February 2005 (Figure 1). As streams had been covered for several months with ice and snow, each site had to be dug out and surface ice drilled in order to access the underlying stream water. The 78 stream water samples were analyzed for stable

isotopes of water ($\delta^{18}O$ and $\delta^{2}H$), DOC, pH, and base cations (Ca, Mg, K, and Na). Seventeen regularly sampled stream stations described in previous studies of the Krycklan Catchment were included [*Laudon et al.*, 2013].

We analyzed all precipitation samples from snow and rain for 1 year preceding the stream water sampling. The snow that had accumulated in the catchment during the winter of the sampling was excluded because it could not have contributed to streamflow. In total, 79 precipitation samples of rain and snow from 13 December 2003 to 16 November 2004 were collected and analyzed for $\delta^{18}O$ and $\delta^{2}H$. Of these, 26 samples were from snow and 53 were from rain. The total snow volume equaled 165 mm in the winter of 2003–2004, and rain volume during the previous summer and autumn was 453 mm. All precipitation samples were collected manually on a daily basis after each event using standard precipitation gauges with a wind shield. Two rain gauges were used to measure the volume, and a third one, next to one of the other rain gauges, was used to collect samples for isotopic analysis (Figure 1). Precipitation signature and volume are assumed to be homogeneous across the Krycklan study site because of the catchment's relatively flat topography [*Laudon et al.*, 2007]. Precipitation samples for $\delta^{18}O$ analysis were collected in 50 mL, dark glass bottles. Archived frozen samples of precipitation were analyzed when the precipitation samples collected specifically for isotopic analysis were missing (24 samples). Those frozen samples had been stored in 100 mL high-density polyethylene bottles with minimal head space. To test if differences in sample storage influenced isotopic composition, more than 50 paired precipitation samples collected between 2002 and 2013 were analyzed using both unfrozen (refrigerated) and frozen water. Differences in isotopic signature between paired subsamples were all within the instrument's measurement error (see below), suggesting that the different methods did not bias results.

Groundwater was collected from different wells distributed across the Krycklan Catchment (Figure 1). On three sampling dates in 2004 (23 March, 11 May, and 11 June), water was collected from three nested wells, at depths of 3 to 5 m below the ground surface in the center of the study catchment, as part of national Swedish Geological Monitoring (SGU) network [*Klaminder et al.*, 2011]. These sampling data bracketed the snowmelt season, with March and June samples representing preflood and postflood, respectively. More recently, sets of nested wells (4–10 m deep) were installed across the longitudinal axis of the catchment, from the headwaters to the outlet stream, and later sampled in August and October of 2012 [*Laudon et al.*, 2013]. The latter wells were used to verify the constant signature of the deep groundwater along the longitudinal axis of Krycklan, testing the robustness of the assumption of a constant isotopic groundwater value in space and time.

3.2. Laboratory Analysis

Stable isotopes of water ($\delta^{18}O$ and $\delta^{2}H$) were analyzed with a Picarro cavity ringdown laser spectrometer (L1102-i) and the vaporizer module (V1102-i). Analyses were corrected for drift and memory effect. The serial standard deviation of the instrument was 0.1‰ for $\delta^{18}O$ and 0.2‰ for $\delta^{2}H$ on control waters. We chose to focus primarily on $\delta^{18}O$ as that has been the main focus in previous isotope work in the catchment [*Rodhe*, 1989; *Bishop et al.*, 1990; *Laudon et al.*, 2002, 2004, 2007; *Peralta-Tapia et al.*, 2014]. Isotopic signatures of water were corrected using laboratory standards, which were calibrated against three International Atomic Energy Agency official standards, the Vienna standard mean ocean water, the Greenland Ice Sheet Project, and the Standard Light Antarctic Precipitation [*Announcement*, 1995].

DOC was analyzed following combustion on a Shimadzu TOC-5000 (Shimadzu Corporation). pH was analyzed (at ambient pCO_2) at room temperature with gentle stirring shortly after returning to the laboratory using a Ross 8102 low-conductivity combination electrode (ThermoOrion) [*Buffam et al.*, 2008]. Samples for analysis of major cations (Ca, Mg, K, and Na) were acidified with HNO_3 (1% vol/vol) and refrigerated prior to analysis by inductively coupled plasma optical emission spectroscopy on a Varian Vista Ax Pro instrument.

3.3. Fractionation Correction

Evaporation from lake surfaces leads to fractionation of water isotopes that must be accounted for in order to estimate the groundwater contribution for sites with upstream lakes. Having variable evaporation effects upstream would be equivalent to having heterogeneous inputs in the isotopic signature in different subcatchments. To correct for such effects, we correlated both $\delta^{18}O$ and $\delta^{2}H$ with the percent cover of lakes in all subcatchments from the stream survey ($n = 78$) and applied this regression equation to factor
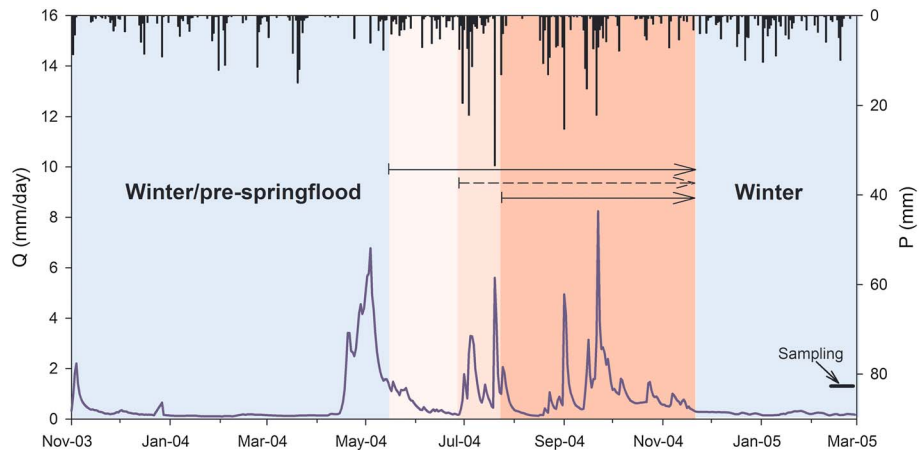
Figure 2. Precipitation (above) and discharge (below) from the beginning of the 2003/2004 winter until the baseflow sampling dates in February 2005. The arrows are a visual representation of the different scenarios used to estimate end-members for the bulking of precipitation in the mixing model. The shortest and the longest arrows are, respectively, the shortest and the longest feasible precipitation time windows. The dashed arrow represents the scenario with average signature of all time windows. At the lower right corner, the sampling period is represented by a bold line in black.

out the "lake effect" from all sites that had lake area different from zero ($n = 54$). The resulting regressions for sites with lake coverage greater than zero were

$$\delta^{18}O = 0.21 \cdot \left(\text{lake area km}^2\right) - 12.965 \left(r^2 = 0.70, \ p < 0.001\right), \quad \text{and} \tag{1}$$

$$\delta^2H = 1.12 \cdot \left(\text{lake area km}^2\right) - 92.81 \left(r^2 = 0.60, \ p < 0.001\right) \tag{2}$$

3.4. Calculation of Water Fractions

To partition the fraction of baseflow of recent groundwater (Q_{rec}) (originating from previous year's precipitation) from older groundwater sources (Q_{old}), we used a two-component mixing model:

$$Q_{tot} * C_{tot} = Q_{rec} * C_{rec} + Q_{old} * C_{old} \tag{3}$$

The old groundwater isotopic signature (C_{old}), which has a stable average value across the entire catchment, was used as one end-member for this model. The isotopic signature of recent precipitation inputs (C_{rec}) was used as the other. 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 10 consecutive days below 0°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*, largely following an approach developed by *Laudon et al.* [2002] for snowmelt separation. 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.

3.5. Statistical Analysis

To test which variables could explain the variability in groundwater inputs, we performed a number of regression analyses. First, we used simple linear regression with all sites to evaluate how $\delta^{18}O$ and the fraction of old groundwater inputs varied with subcatchment area (log transformed). Second, we performed a piecewise regression [*Toms and Lesperance*, 2003] between the old groundwater fraction and untransformed area to help identify potential threshold changes in the relationship between groundwater contribution and drainage size. The piecewise regression indicated a threshold in this relationship at
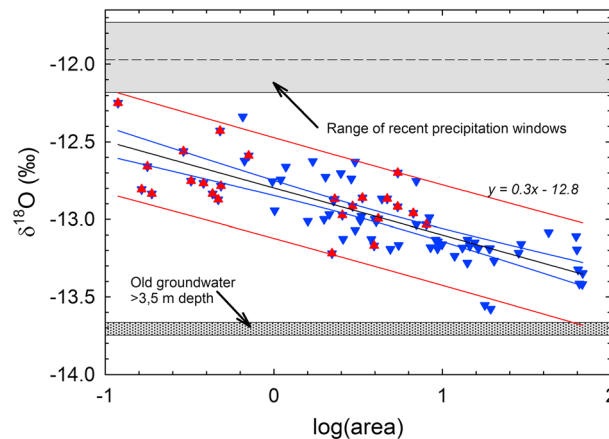
Figure 3. δ^{18}O versus catchment area (log). The blue lines are the 95% confidence interval of the regression; the red lines are the 95% prediction bands. The red triangles are the sites that have no upstream lakes. The blue triangles are the sites for which the lake effects on isotopic signals have been corrected. The upper band shows the recent precipitation window of possible averages represented with horizontal lines for giving a visual help to the reader. The dashed line represents the average signature mentioned in Figure 2. The lower band with dots represents the signature of the old groundwater.

10.6 km^2, below which there was a notable increase in the residual variation around the regression line. We therefore performed an additional analysis to investigate the possibility that other landscape variables may be influencing variation in groundwater inputs to these smaller streams. For this, we evaluated a number of digital terrain indices that had been calculated for this catchment in previous studies (see Ågren et al. [2014] for detailed methods).

A partial least squares regression (PLS; Simca 13.0, Umetrics) model was constructed with all digital terrain indices available from Ågren et al. [2014] to identify variables that best explained the variability in old groundwater fraction among catchments <10.6 km^2. Many of the tested terrain indices covary, but by selecting those with high explanatory power in the PLS model, that did not cluster in the loading plot (indicating low covariation), we identified three candidate variables that captured the topographic controls on hydrological flow paths at different scales. These were (i) the topographic position index (TPI), (ii) cartographic depth to water (DTW), and (iii) local depressions (called puddles in Ågren et al. [2014]). Topographic position index was calculated with a 100 × 100 m moving window and yields an index that describes the larger-scale topography, from hilltops to valleys. Cartographic depth to water (DTW) is the depth to a modeled groundwater level, where a low index indicates wet soils and where DTW < 1 is used to locate wet riparian soils along stream channels. Local depressions were calculated in comparison to a smoothed digital elevation model (9 × 9 cells), so this index describes the small-scale variability in topography.

To evaluate how much additional variability in old groundwater fraction these three digital terrain indices could explain, a multiple linear regression model was constructed using the residuals from the original regression model with catchment area (for subcatchments < 10.6 km^2). Finally, we used linear regressions to determine the relationship between old groundwater input (% contribution) and chemical parameters measured in all streams.

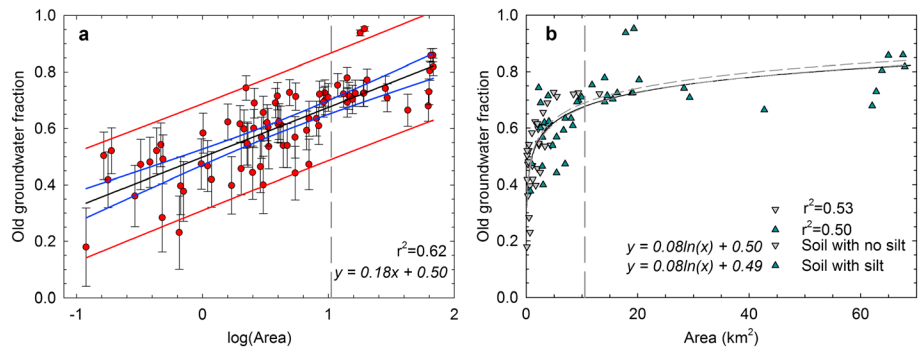## 4. Results

4.1. Temporal Dynamics in Isotopes

The δ^{18}O and δ^{2}H isotopic signatures of precipitation in the Krycklan Catchment were strongly seasonal; in general, it was tending toward more enriched values after the spring flood until summer and then declining to more depleted values during autumn and winter. Snow fall during the season previous to the sampling had a weighted average value of $-17.2‰$ (with a standard deviation, $\sigma = 2.8‰$) for δ^{18}O and of $-129.3‰$ ($\sigma = 23.8‰$) for δ^{2}H. Rainfall during the previous summer had a weighted average value of $-11.6‰$ ($\sigma = 3.0‰$) for δ^{18}O and of $-83.3‰$ ($\sigma = 24.1‰$) for δ^{2}H. The total isotopic-weighted average signatures of precipitation for the entire period were $-13.1‰$ for δ^{18}O and $-98.1‰$ for δ^{2}H (see Supporting Information S1 and Figure S1 in the supporting information).

4.2. Scale Dependencies

Isotopic signatures of stream water were more depleted in larger catchments ($r^2 = 0.62$, $p < 0.001$; Figure 3). Catchments that were corrected for lake influence fell within the 95% prediction bands for the regression of those without this correction. In general, larger subcatchments showed an isotopic composition closely

Figure 4. (a) Fraction of old groundwater (%), based on isotopic partitioning, against catchment (log). The error bars span the possible old groundwater fraction if the precipitation average is considered from May or from mid-August. The red points show the average value. (b) Fraction of old groundwater (%) versus catchment area (km^2). Logarithmic regression for all catchments (solid line), for catchments that had any presence of silt/fine sand (green triangles and dashed line), and for catchments that had no silt/fine sand (gray triangles and dot-dashed line). In Figures 4a and 4b, the dashed vertical line at 10.6 km^2 represents the piecewise regression threshold.

resembling deep groundwater, while smaller subcatchments suggested more influence from previous summer and fall precipitation (Figure 3). The old groundwater from sampling wells had an average $\delta^{18}O$ value of -13.7‰ ($\sigma = 0.04$‰, $n = 10$), presenting a more depleted signature than the stream water. In addition to drainage size, the isotopic signature of stream water was also slightly more enriched with increasing subcatchment elevation, although this statistical relationship was weak ($r^2 = 0.12$, $p = 0.02$).

Using both old groundwater and the previous summer/autumn precipitation (as the recent groundwater) water isotope signals as end-members, we calculated the fraction of old groundwater at each site (Figure 4a). The contribution of old groundwater ranged from 4% to 92% for a precipitation time window scenario from May to November and from 31% to 94% when the precipitation time window was defined as mid-August to November.

As was the case with stream isotopic signals, estimated old groundwater contributions also increased with the size of the catchment ($r^2 = 0.62$, $p < 0.001$; Figure 4a). Piecewise regression of estimated old groundwater contribution against untransformed drainage area suggested a break in this relationship at ~10.6 km^2 (SE $\pm$ 1.7 km^2; $r^2 = 0.62$, $p < 0.001$; Figure 4b). Higher drainage area resulted in comparatively high old groundwater contributions to surface streams (average = 76%) with a relatively narrow range (66–95%). Below this break, or threshold, old groundwater contributions varied markedly among locations, from 18 to 74%, highlighting a high degree of heterogeneity in local surface-subsurface connections across the smaller subcatchments in the network. Despite the large variability among the <10.6 km^2 subcatchments, area of the subcatchment remained the main predictor ($r^2 = 0.54$ for same regression curve as in Figure 4b but for catchments <10.6 km^2). However, additional variability could be explained by including the digital terrain indices; TPI ($r^2 = 0.11$, $p < 0.005$), DTW ($r^2 = 0.11$, $p < 0.005$), and local depression ($r^2 = 0.09$, $p = <0.005$). Taken together, the stepwise multiple linear regression using all terrain indices explained an additional 31% of the residuals from the correlation with size in small-scale catchments (<10.6 km^2). Finally, the relationship between the fraction of old groundwater and catchment area was independent of the soil type (silt/fine sand or till) in the catchment (Figure 4b). The relationship of ground water fraction for catchments with till versus silty/sand soils were similar ($r^2 = 0.50$, $p < 0.005$ and $r^2 = 0.52$, $p < 0.005$), respectively.

4.3. Linking Groundwater Contribution With Hydrochemical Patterns Observed During Baseflow

Surface water DOC decreased, and pH increased with increasing estimated contributions of old groundwater to streams ($r^2 = 0.40$, $p < 0.01$ and $r^2 = 0.40$, $p < 0.01$, for DOC and pH, respectively; Figures 5a and 5b). There were two outliers with low pH values, originating from headwater streams: one that was the most mire-dominated (pH = 4.59) and the other the most lake influenced (pH = 4.89) of all the subcatchments considered here, and that lake is as well fed by a mire. Similarly, the mire outlet had notably high concentrations of DOC relative to our estimate of relative water age at that site. Including these outliers marginally reduced the statistical strength for both the DOC- and pH-groundwater relationships ($r^2 = 0.34$, $p < 0.01$ and $r^2 = 0.36$, $p < 0.01$,
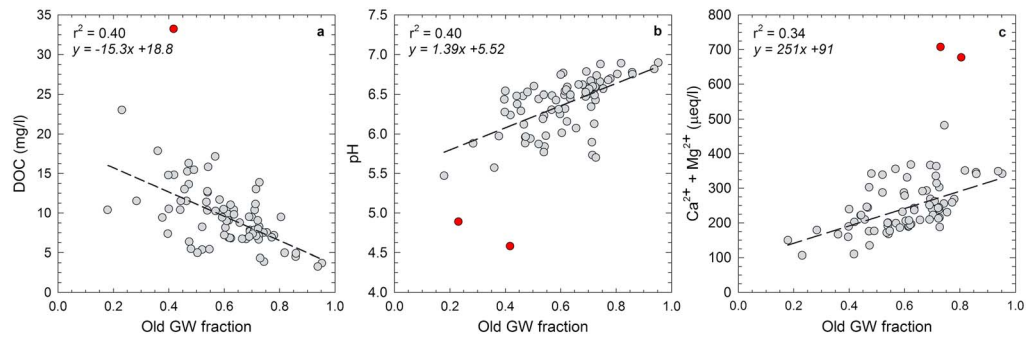
Figure 5. (a) DOC versus fraction of old groundwater based on isotopic partitioning. (b) pH versus fraction of old groundwater in the streams. (c) Ca + Mg versus fraction of old groundwater in the streams. The dashed lines represent the regression without including the outliers marked in red. The r^2 values and the equations in the three figures are calculated without considering the outliers.

respectively). As seen for pH, $Ca^{2+} + Mg^{2+}$ also increased across sample stations with a greater fraction of old groundwater ($r^2 = 0.26$, $p < 0.01$; Figure 5c). There were two outliers that when not considered, resulted in an improved regression model ($r^2 = 0.33$, $p < 0.01$). The outlier streams with the highest concentration of base cations were adjacent, and both had a catchment area of over $60 \, km^2$.

5. Discussion

5.1. Variability in Groundwater Contribution to Surface Streams Changes Across a Boreal Stream Network During Winter Baseflow

Hydrological and biogeochemical patterns observed during baseflow provide key insights into how surface streams interact with the groundwater system. In this study, we used stable isotopes of water and a two end-member mixing model to show how the contribution of older groundwater to stream baseflow varies across a channel network, primarily as a function of catchment area. In smaller subcatchments ($<10.6 \, km^2$), additional descriptors of catchment structure (TPI, DTW, and local depression) increased the predictability of variability in contribution of these older water sources by 31%. Network patterns of groundwater contribution were, in turn, directly related to spatial variation in stream DOC, pH, and major cations (Figures 5 and 6). This spatial characterization of heterogeneity in sources of stream water thus reveals how hydrological and biogeochemical patterns are regulated and linked during baseflow in this boreal watershed.

The contribution of older groundwater to surface streams increased nonlinearly with drainage area, indicating a threshold in contribution of 70–80% for catchments larger than ~10.6 km^2 (±1.7 SE). This overall pattern is generally consistent with *Klaminder et al.* [2011], who used $\delta^{18}O$ signals to estimate that old groundwater constitutes 25–80% for streams larger than 1 km^2 within seven of the Krycklan sites. However, the results presented here are derived from many more sampling points and include a
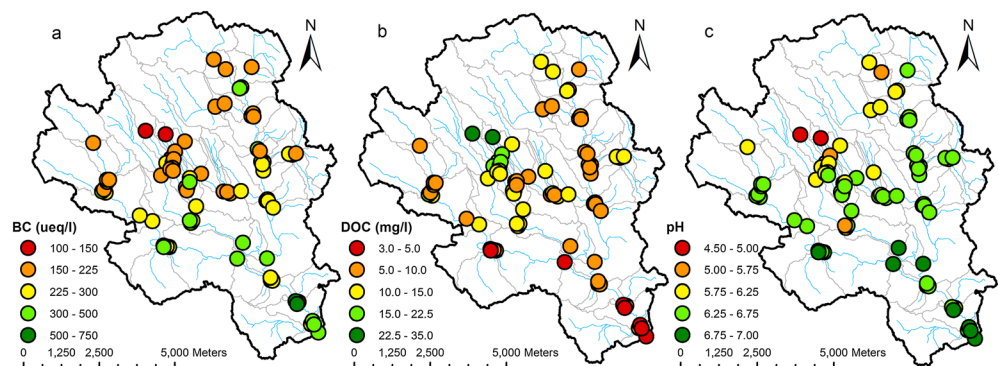
Figure 6. Maps of spatial distribution of (a) base cations, (b) DOC, and (c) pH in the 78 streams within the Krycklan Catchment.

correction for lake effects on isotopic signals, which allows for a more robust and spatially explicit assessment of groundwater inputs across this drainage network. Moreover, this threshold area is similar to that observed in a temperate forest watershed in North America [*Shaman et al.*, 2004], as well as in other boreal catchments of Sweden [*Temnerud and Bishop*, 2005]. In contrast, other studies have reported different catchment-scale thresholds associated with the emergence of this hydrological uniformity [*Wolock et al.*, 1997; *Tetzlaff and Soulsby*, 2008; *Asano and Uchida*, 2010], potentially because of different hydroclimatic, geological, and geomorphological settings that alter the magnitude of contributing flow paths [*Shanley et al.*, 2014]. The methods used may also lead to different results, as was the case for *Wolock et al.* [1997] and *Shaman et al.* [2004] who found different thresholds for the same catchment based on geochemical versus hydrological data. In contrast to these studies, *McGuire et al.* [2005] found that water residence time (a variable related to old groundwater inputs) did not correlate with area at all but instead with catchment structure (topography).

Results from our study also suggest that variation in catchment structure plays an important role in shaping heterogeneity in groundwater contribution for smaller streams within the network. Other studies have concluded that the hydrology of small streams is governed by the integration of hillslope responses, which in turn are strongly influenced by heterogeneous contributions of water flow from soils and bedrock [*Uchida et al.*, 2005]. Such heterogeneity helps to explain the large range in the fraction of older groundwater inputs across our smaller study sites. Indeed, we improved our ability to predict groundwater contributions for these smaller sites using three different catchment characteristics: topographic position index (TPI), cartographic depth to water (DTW), and local depressions. The two latter characteristics are related to the hillslope characteristics mentioned by *Uchida et al.* [2005] and the first to topographic controls as suggested by, for example, *McGuire et al.* [2005]. Our results hence confirm what others have found but further illustrate how multiple controls, including the scaling relationships with drainage area and landscape structure, may differentially contribute to water and solute sources across spatial scales in river networks.

A challenge when comparing observed scaling relationships across studies is that these efforts have often been addressed at different stages of flow, including high-flow events [*McGlynn et al.*, 2004]. Our results indicate relatively clear scaling rules that govern groundwater contributions in this drainage system, with the additional influence of topographic features in smaller subcatchments during winter baseflow. During more hydrologically active times of the year, other landscape features (e.g., wetlands and lakes) facilitate a comparatively rapid routing of water in this basin [*Peralta-Tapia et al.*, 2014; *Tiwari et al.*, 2014] when other water sources become connected. For example, patterns of new and older water contributions during the snowmelt in the Krycklan Catchment are linked to the upstream cover of wetlands, through which newer water is rapidly flushed [*Laudon et al.*, 2007]. Such preferential flow zones appeared to be maintained throughout the summer and autumn [*Peralta-Tapia et al.*, 2014], and as such are likely to have implications for network patterns in relative water age throughout much of the year. During the winter, the development of soil frost isolates—to some degree—these landscape features from the channel network [*Nyberg et al.*, 2001; *Ågren et al.*, 2008], which increases the relative importance of underlying deeper groundwater flow paths as a control on spatial patterns.

5.2. Linkages Between Variation in Groundwater Contribution and Spatial Patterns of Stream Biogeochemistry

Scaling hydrological and biogeochemical processes across drainage sizes continues to be an important research goal [*Egusa et al.*, 2013; *McGuire et al.*, 2014]. In this study, base cations and pH increased systematically while DOC declined with the modeled contribution of old groundwater in this relatively homogenous catchment. While the greater concentrations of base cations and higher pH values are directly related to weathering processes and older groundwater, high levels of DOC are typically associated with riparian soils in these northern landscapes and therefore contribution of more recent water [*Grabs et al.*, 2012; *Dick et al.*, 2014]. These statistical relationships underscore relatively predictable changes in hydrological response with catchment scale (Figure 7); however, the most important implication of this is the strong connection of hydrology and stream chemistry. Due to the relative geochemical homogeneity of the catchment and the large amount of subcatchments used for this study, our results make scaling up stream biogeochemical patterns possible under winter baseflow conditions.
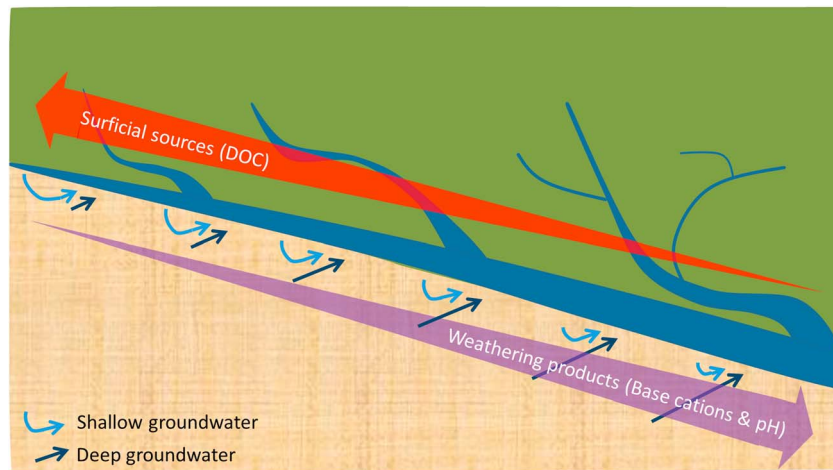
Figure 7. Conceptual model of downstream changes in the contribution to baseflow and implications for stream chemistry. Headwaters are shown on the left of the figure and larger outlet streams to the right. With increases in catchment scale, the dominance of shallow groundwater gives way to deeper water 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.

The mechanisms that underlie observed relationships between water age and stream chemistry appear to link geochemical and biogeochemical processing along flow paths of varying residence time. For example, *Klaminder et al.* [2011] found that weathering by H_2CO_3 (derived from DOC mineralization) and H_2SO_4 along deeper and slower hillslope flow paths in the Krycklan Catchment drives the dissolution of silicate minerals, which resulted in the production of base cations and concomitant reductions in DOC. In addition, *Wallin et al.* [2013] showed that the export of the HCO_3^- increased with catchment size in the same system suggesting that the flow paths coalesce and deliver older water with base cations, elevated pH, and reduced DOC concentrations to streams further down in the landscape. Research in other settings has also showed that the low-flow stream chemistry was systematically related to subsurface contact time and basin size [*Wolock et al.*, 1997; *Frisbee et al.*, 2011; *Zimmer et al.*, 2013]. While our results are consistent with these findings, the variance observed in groundwater contribution (and associated chemical signals) among smaller streams suggests that the spatial distribution and the scale at which these slower flow paths interact with the surface stream network are variable. These results are also consistent with those from *Tiwari et al.* [2014], who concluded that during low-flow conditions, downstream changes in the contribution of deeper groundwater sources act as the primary determinant of DOC concentration in this same system. In addition to the mechanisms described above, for the largest subcatchments considered here, deeper groundwater contribution derived from a large esker likely contributes to the observed hydrologic and chemical patterns (including lower DOC concentrations [*Tiwari et al.*, 2014]).

Links between variable groundwater contributions and water chemistry across the Krycklan Catchment suggest important network heterogeneity in the vulnerability of streams to disturbance. In particular, there is ongoing concern regarding the pH sensitivity of surface waters in response to past atmospheric deposition and future land use activities (e.g., forestry) that remove base cations from surrounding soils [*Dunford et al.*, 2012; *Harpold et al.*, 2013]. Acidity in streams of this region is driven largely by a combination of organic acids and acid neutralizing capacity [*Hruska et al.*, 2003], with strong temporal variation linked to snowmelt hydrology which has implication for the distribution of acid-sensitive biota [*Serrano et al.*, 2008]. In fact, by knowing the acid status of baseflow chemistry, the episodic pH decline can be predicted for individual streams [*Bishop et al.*, 2000; *Feeley et al.*, 2013] to entire regions [*Ågren et al.*, 2010]. So while the results from this study point to the potential for a relatively predictable variation in hydrologic routing and groundwater contributions to stream water in watersheds with low geological heterogeneity (Figure 7), it also provides a step toward an improved mechanistic understanding of the vulnerability to environmental changes across the stream network.

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