Inferring scale-dependent processes influencing stream water biogeochemistry from headwater to sea

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Abstract

Understanding how scale-dependent processes regulate patterns of water chemistry remains a challenge in aquatic biogeochemistry. This study evaluated how chemical properties of streams and rivers vary with drainage size and explored mechanisms that may underlie nonlinear changes with increasing scale. To do this, we contrasted concentrations of total organic carbon (TOC) with pH and cations (Ca and Mg) from 69 catchments in northern Sweden, spanning a size gradient from headwaters (< 0.01 km^2) to major rivers and estuaries ($> 100,000$ km^2). Across this gradient, we evaluated (1) changes in average concentrations and temporal variation, (2) scale breaks in catchment area-concentration relationships, and (3) the potential importance of groundwater inputs and instream processes as drivers of change. Results indicated that spatial and temporal signals converge at $\sim$2–10 km^2 as streams draining distinct headwater catchments coalesce and mix. Beyond 10 km^2, streams tended to lose headwater signatures, reflecting a transition from shallow to deep groundwater influence. This was accompanied by a second break at $\sim$70–500 km^2 corresponding to reduced spatial variability and a convergence of the response to snowmelt, as the dominance of deep groundwater influence increased with catchment scale. Larger catchments showed greater effect of instream processing on TOC, as concentrations predicted from the conservative mixing of upstream signals and dilution with deep groundwater were lower than measured. This study improves the understanding of scaling biogeochemical patterns and processes in stream networks, highlighting thresholds that imply shifts in the factors that shape variation in chemistry from headwaters to the sea.

One of the fundamental challenges in the aquatic sciences is to understand how large rivers integrate, process, and incorporate the biogeochemical signals from the diverse headwater environments they drain. A major obstacle to resolving these upstream-downstream connections is identifying how catchment processes change with spatial scale to shape emergent longitudinal patterns in hydrology and biogeochemistry (Sponseller et al. 2013). Such patterns potentially reflect important hydrologic and chemical thresholds, zones of interaction, and hotspots for microbial processing that ultimately regulate how large river basins function

biogeochemically (Palmer et al. 2015). This information is especially relevant to seasonally snow dominated catchments of the boreal zone, which store large quantities of organic carbon and are predicted to be strongly affected by climate change (Yigini and Panagos 2016).

Key to understanding how catchment processes change with scale is recognizing transitions in the dominant hydrological pathways and contributing areas that feed streams and rivers with water and solutes (Blöschl 2001; Creed et al. 2015). At small spatial scales, the chemistry of headwater streams often reflects the specific hydrological, ecological, and edaphic characteristics of surrounding uplands and riparian zones (Bormann and Likens 1967; Beven et al. 1988). As such, heterogeneity in landscape structure can generate distinct chemical patterns across headwater environments within a given drainage system (Schiff et al. 2002). For example, in boreal landscapes, variation in the relative cover of mineral (tills and sorted sediments) vs. organic (riparian soil and peatland) soils can lead to headwater streams in the same basin that are either locally rich in

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weathering-derived elements (Ca, Mg) or dissolved organic carbon (DOC), respectively (Tiwari et al. 2014).

As small streams coalesce into large rivers, chemical signals from distinct landscape patches are transformed, integrated, and ultimately lost at some scale where the emergent pattern reflects a mixture of the hydrological and biogeochemical properties of the variable, contributing headwaters (Jencso and Mcglynn 2011; Neubauer et al. 2013). While identifying the scale at which headwater signals are lost (or become averaged) has been an important goal in aquatic sciences (e.g., Wood et al. 1988; Asano and Uchida 2010), efforts to resolve this representative elementary area (REA) have been inconsistent (Peralta-Tapia et al. 2015), as the relevant scale varies across different hydrological and biogeochemical response variables.

Additionally, as small streams transition into larger channels, the dominant hydrological flowpaths that deliver water and solutes may also shift from shallow groundwater sources in the headwaters to deeper sources further downstream (Blöschl 2001; Creed et al. 2015). Water travels through different subsurface environments at various rates, with shallow flowpaths often having shorter residence times compared to deeper groundwater (Tetzlaff and Soulsby 2008). This transition has the potential to further alter patterns of stream chemistry, with small headwater streams reflecting flowpaths that interact with near-surface soil horizons and larger streams increasingly influenced by weathering processes within deeper alluvial sediments (Klaminder et al. 2011). In boreal landscapes, the consequences of this transition typically include declining DOC concentrations with corresponding increases in pH and base cations (BCs) with increasing drainage size (Peralta-Tapia et al. 2015). Although similar shifts in hydrological pathways with increasing spatial scale (here: catchment size) have been observed elsewhere (e.g., Shaman et al. 2004), the extent to which such transitions organize biogeochemical patterns from headwaters to large coastal rivers, and across seasonal flow conditions, remains poorly understood.

The relative importance of different flowpaths can also vary greatly during hydrological events, often resulting in dramatic changes to stream chemistry locally—as well as broader changes in longitudinal patterns. For northern latitude catchments, the most important annual hydrological event is snowmelt, which in places can generate more than 50% of the annual water load (Laudon et al. 2004; Lyon et al. 2010). Snowmelt has been found to cause increasing concentrations of DOC and a decrease in pH and BCs in till-dominated forest landscapes where surficial flowpaths during the flood intersect shallow organic rich soil horizons, rather than deeper mineral soils (Laudon et al. 2011). In contrast, in peatland-dominated landscapes, the large input of snowmelt water dilutes both DOC and BC (Köhler et al. 2008). Consequently, for larger streams, there is a seasonal shift in DOC source from dominance by peatlands (during baseflow) to forested soils (during peak flood). This variation in origin of DOC has important implications for microbial communities,

as well as for processing rates as the DOC quality from these different sources varies substantially (Berggren et al. 2007). At broader spatial scales, these different responses to snowmelt could potentially generate temporal shifts in the relationships between landscape variables and water chemistry that have not previously been accounted for.

In addition to the downstream mixing of different water sources, emergent longitudinal trends in chemistry may reflect biogeochemical transformations that occur within streams and rivers themselves. Increasing channel length as water travels from small headwaters to larger rivers leads to predictable increases in water residence time (Wollheim et al. 2006). This longer residence time increases the potential for instream processes, including microbial degradation, photo-oxidation, flocculation, and sedimentation of DOC (Köhler et al. 2002; Jones et al. 2015). However, there are currently conflicting views on the relative importance of instream processing for DOC. While there is evidence that labile fractions of the DOC pool can be rapidly mineralized in benthic and hyporheic sediments, the extent to which these processes remove bulk DOC from river systems remain debated (Mineau et al. 2016). Several studies suggest this processing may be minimal (Köhler et al. 2002; Wollheim et al. 2006) particularly for smaller streams where low water residence time precludes significant processing (Kothawala et al. 2015). One consequence of this residence time control is that usable forms of DOC from headwaters may be "shunted" downstream and processed in larger rivers (Raymond et al. 2016). At this broader scale, the presence of embedded lakes may provide additional opportunity for removal processes to influence DOC transport to the coast (Weyhenmeyer et al. 2012).

In this study, we ask how key biogeochemical properties of boreal streams and rivers vary with catchment size, from the smallest headwaters to large regional rivers and estuaries. We explored these patterns using data from 69 streams, rivers, and coastal monitoring stations in northern Sweden, spanning over seven orders of magnitude in drainage size (from < 0.01 km^2 to $> 100,000$ km^2) as well as data from deep groundwater wells (50–150 m). We hypothesized that emergent, regional patterns in stream/river chemistry are caused by nonlinear changes in the dominant hydrological processes that regulate local solute concentrations. We expected these hydrologic changes to generate scale-breaks in the relationship between surface chemistry, flood response, and catchment size that signify transitions in the key regulating processes from one scaling domain to the next. Specifically, we predicted that downstream mixing of headwaters would reduce the spatial and temporal variability in chemistry among small streams as catchment sizes become much larger than the areas of patches (e.g., wetlands) responsible for generating distinct chemical signals. We further predicted that the transition from small streams to larger rivers would coincide with a shift in dominance from near surface to deep groundwater sources that fundamentally change the chemical profile and flood response of
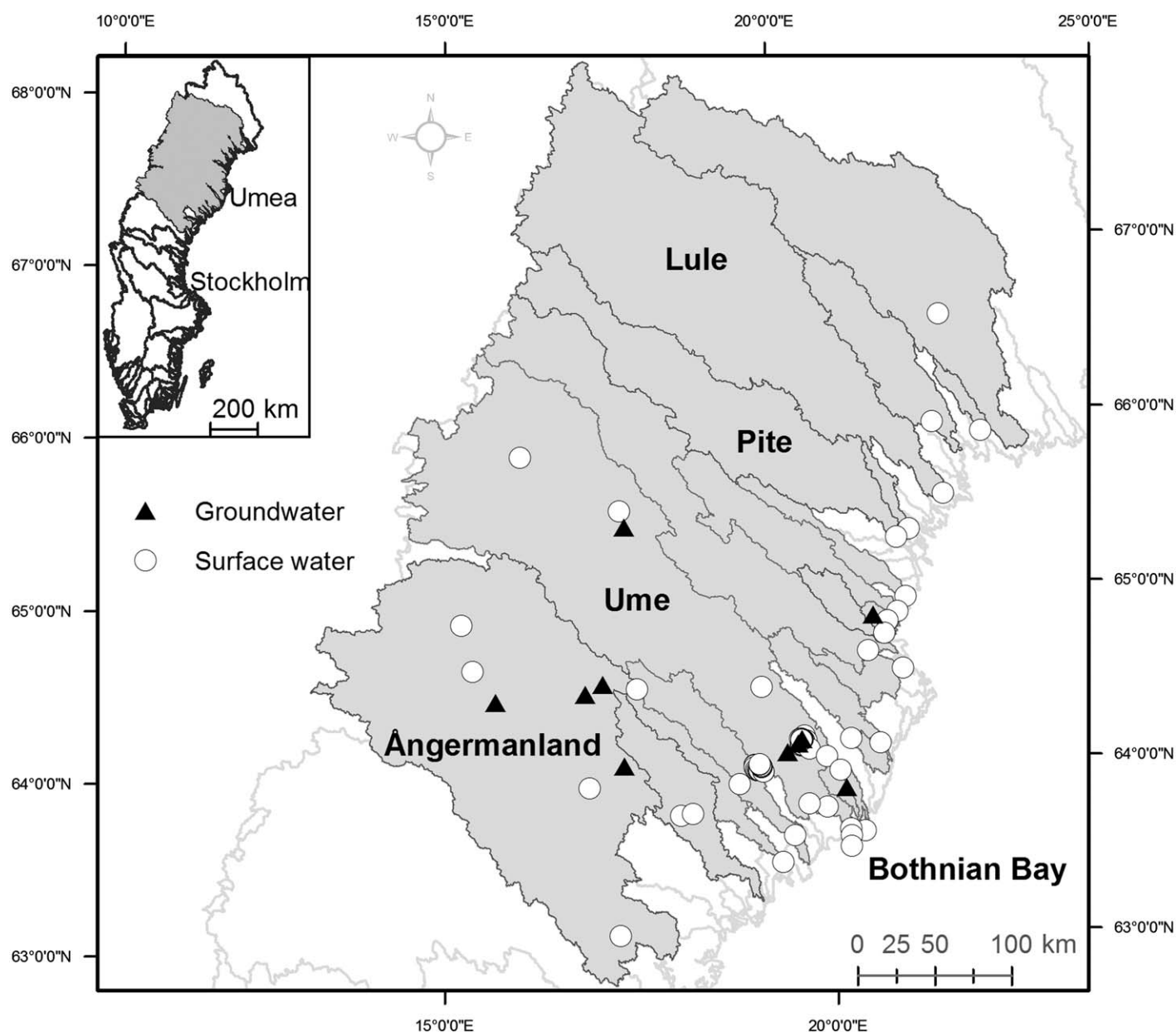
Fig. 1. The study area showing surface water and groundwater location in northern Sweden.

larger catchments. Finally, we tested whether removal processes within streams and rivers become important for shaping the trends for more biogeochemically active solutes (DOC) and if these effects are increasingly apparent for larger streams and rivers, which have longer residence times.

Methods

Study area

This study investigates the patterns in total organic carbon (TOC), Ca + Mg, and pH in catchments ranging from small headwaters (< 0.01 km^2) through larger rivers ($> 10,000$ km^2)

to the Bothnian Bay ($\sim 100,000$ km^2) in northern Sweden (Fig. 1). This included six regional drainage basins (the Ume-, Ångermanland-, Lule-, Pite-, Vindeln-, and Skellefte Rivers) which all originate on the Norwegian border and extend southeast to the Bothnian Bay (Fig. 1), except for the Vindeln River which flows into the Ume River at approximately 35 km upstream of the coast. A number of small headwaters and intermediate-sized rivers that drain into these larger systems, or directly into the Bothnian Bay were also included (Fig. 1). The Bothnian Bay is a northern sub-basin of the semi-enclosed Baltic Sea that is characterized by strong seasonality in temperature with regular ice-cover during winter. The depth of the Bothnian

Bay is less than 40 m with low salinity water (< 1 ppt) compared to the other parts of the Baltic Sea. The Bay is highly influenced, and primarily fed, by inputs of water from river discharge draining northern Sweden and Finland which results in brackish waters that freeze in November and melt in April–May (Granskog et al. 2006). Estuaries that connect the rivers to the bay have been found to be transformation zones for freshwater nutrients and DOC (Figueroa et al. 2016).

The landscape is characterized by lakes, peatlands, and forests dominated by Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), as well as some few deciduous tree species, primarily birch (*Betula* spp.). Geologically, the region consists of complex bedrock composed of amphibolites, schists, and sparagmites in the Scandinavian mountains, whereas the Baltic shield is of Precambrian origin with bedrock composed of predominantly granite and gneiss in the lower areas. The climate is characterized by cold winters and deep snow-packs with average January air temperature (1991–2010) of $-9.5 \pm 4.1°C$ and July temperatures $14.5 \pm 1.7°C$, recorded near the center of this region in the Krycklan Catchment (Oni et al. 2013). There is also a clear distinction between the coastal climate with average winter temperature of $-6°C$ and summer of $15°C$, and the mountain climate with average winter temperature of $-15°C$ and summer of $12°C$. The snowmelt period, which commonly occurs during April and May, accounts for approximately 40–60% of the annual runoff in the region.

Surface-water data

We compiled 3 yr of data (mid 2008–mid 2011) from different databases to assess regional patterns in chemistry. In total, our assessment included 2417 TOC, 2095 pH, and 2075 Ca + Mg samples, respectively, from 69 locations including the Bothnian Bay (Fig. 1). Data from the Bothnian Bay were obtained from the Swedish Meteorological and Hydrological Institute (SMHI) Shark database (http://sharkweb.smhi.se/). National Database files (Riks-inventory, Trend stations) hosted by the Swedish University of Agricultural Sciences (SLU) and collected within the National Environmental Monitoring Program (Folster et al. 2014) provided data for 34 monitoring stations within the study area that span a range of drainage sizes (http://miljodata.slu.se/mvm/). Data from additional headwater and intermediate catchments were also obtained from (1) the Krycklan Catchment Study database, which consists of 15 regularly monitored subcatchments (Laudon et al. 2013), (2) the Balsjö catchment consisting of six regularly monitored subcatchments (Löfgren et al. 2009*a*), and (3) from the Strömsjöliden catchment with 10 monitored catchments (Lucas et al. 2014).

TOC from the Krycklan and Strömsjöliden catchments were analyzed at the laboratory of the Department of Forest Ecology and Management, SLU. TOC from the Balsjö catchment, and the national monitoring database was analyzed at Department of Aquatic Sciences and Assessment, SLU (http://miljodata.slu.se/mvm/) (Löfgren et al. 2009*b*). TOC from the Bothnian Bay

was analyzed at the Swedish Meteorological, and Hydrological Institute (SMHI) using Swedish Board for Accreditation and Conformity Assessment accredited methods. Although TOC was collected and measured at different institutes, all measurements were made using standard methods and the same model instrument (Shimadzu TOC-V$_{PCH}$ analyzer) which should remove most bias due to measurement techniques. Previously, a difference of less than 5% was found between DOC and TOC concentrations, so TOC is essentially equivalent to DOC in Swedish surface waters (Gadmar et al. 2002; Laudon et al. 2011).

pH from the SLU database was determined potentiometrically at 25°C on the NBS/NIST scale calibrated with a buffers of low ionic strength at pH 4 and 7 (Temnerud et al. 2014), while pH from national monitoring stations was determined using a combination pH electrode adapted to low ionic strength using the same pH buffer (Lofgren et al. 2011). In the Krycklan and Strömsjöliden catchments, pH was determined using a Ross combination glassbody electrode again using pH buffers 4 and 7 (Orion Research, Beverly, Massachusetts, U.S.). Since all pH measurements were done using glass electrodes and standard measurement/calibration procedures, it is not expected that there should be strong bias in the different datasets.

Ca and Mg concentrations from all datasets were determined using inductively coupled plasma optical emission spectroscopy on a Varian Vista Ax Pro instrument (Köhler et al. 2008; Löfgren et al. 2009*a*; Lucas et al. 2014) and standard sampling methodologies. It is therefore unlikely that patterns in the data are due to among-dataset differences in sampling or analysis techniques.

Groundwater data

To explore variation in the influence of deep groundwater for catchments of different size, we also compiled data from seven groundwater wells in the region. Data from these wells (ranging 50–150 m deep) were obtained from the Swedish Geological Services (SGU) database where sampling and analysis was done according to ISO Standards using similar techniques and instruments as those of the surface-water analysis for TOC and Ca + Mg (Tunemar 2016).

Sampling

Samples were collected monthly at most sites for TOC and pH, yielding 36 observations over the 3-yr period. Where stations were sampled more frequently, we trimmed the dataset to 36 samples by selecting the sample closest to the date associated with the majority of other sites. For Ca and Mg, fewer samples were collected per year for most of the larger rivers (e.g., 4–6 times yr^{-1}), so we extended the time span of investigation to 2003–2011 to yield a comparable number of samples per site, evenly distributed across the seasons. To examine the temporal dynamics of stream chemistry in different catchments during snowmelt, we divided the data by seasons where January–February represented the winter period and April–May represented spring snowmelt.

Table 1. Catchment scales (km^2) where breaks in stream chemistry was identified using the piecewise linear regression in zone 1 (0–20 km^2) and zone 2 (20–1000 km^2).

Scale breaks	TOC (km^2)	pH (km^2)	Ca + Mg (km^2)
Zone 1	2.4–5	3–9.6	2.6–9.6
Zone 2	67–458	67–458	228–458

For groundwater data, 20 samples from each site were collected between 2000 and 2010 for TOC, pH, and Ca + Mg.

Spatial and temporal variability in stream chemistry from headwater to sea

We calculated the mean and SD of key water chemistry parameters (TOC, pH, and Ca + Mg) for each sampling location (Supporting Information Table 1). Variation in mean and SD as a function of catchment area were then used to explore scale-dependent shifts in the relative importance of different factors controlling stream chemistry. We used two methods to evaluate how the within-catchment (temporal) variability in stream chemistry changed with catchment size: (1) boxplots visually showing within-catchment variability, and (2) SD of the 36 measured values at a given site. We then fit LOESS (locally weighted average regression) curves based on both means and SD, as a function of catchment size. The LOESS curves were created using SPSS Statistics 22 (IBM Corp 2013) by fitting 60% of the points in a normal kernel. LOESS is a non-parametric graphic tool that is used to identify potential breaks in scaling relationships and depict natural relations between variables (Jacoby 2000). The strength of this tool lies in its simplicity to fit curves empirically rather than using stringent prior specifications.

To determine how catchments of different size responded to the spring snowmelt, we investigated the difference between the median winter and spring TOC concentration, pH, and Ca + Mg concentration as a function of drainage area. As above, a LOESS curve was used to evaluate how the response to snowmelt (as change in stream chemistry) varied as a function of catchment size.

Break point analysis using piecewise linear regressions

We used piecewise regression to identify nonlinear changes in the relationships between drainage size and stream/river chemistry. Piecewise regression has been widely used in ecological studies to show where breakpoints representing thresholds occurs using "broken-stick" models (Toms and Lesperance 2003; Toms and Villard 2015). The advantage of piecewise regression is that it identifies the points where the response variable changes within a few values of the explanatory variable. In this study, the breakpoints indicate the scale where the relationship between stream chemistry and catchment size changed. The piecewise regression analysis was conducted in R Core Team (2013) following the methods outlined in Crawley (2007) and Toms and Lesperance (2003). A prior
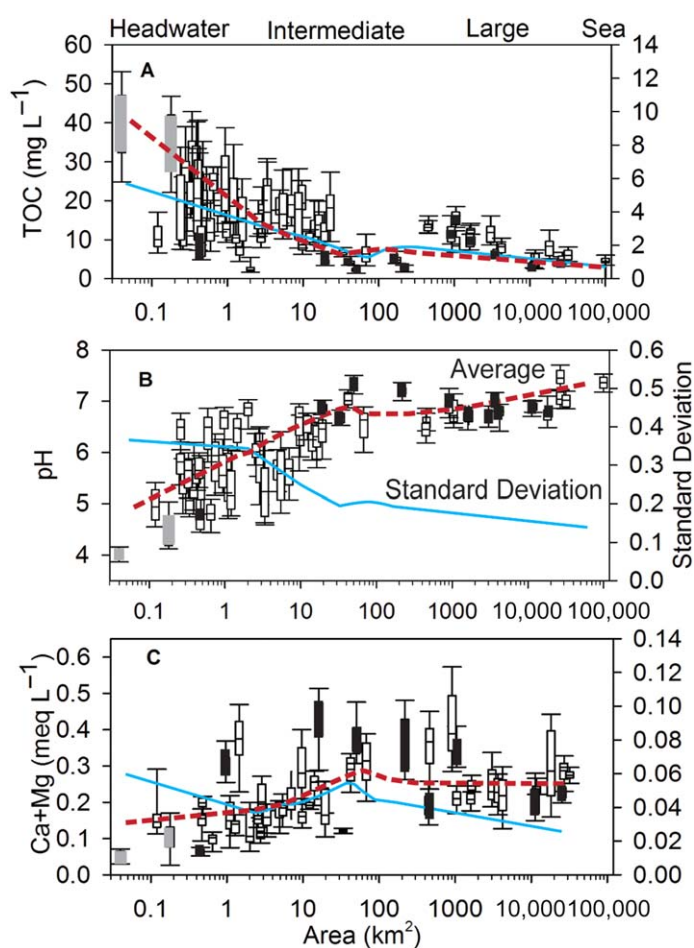

Fig. 2. Spatial and temporal variability of stream chemistry in catchments that are ranging in size from small headwaters to sea showing average (red broken line), SD (blue unbroken) for (A) TOC, (B) pH, and (C) Ca + Mg using a LOESS average of 60% of the nearest points. Black bars indicate catchments with more than 5% lake coverage while gray bars indicate catchment with > 50% peat coverage.

initial estimate for breakpoint locations were identified from the LOESS averages as areas with changes in the apparent relationship between stream variables and catchment area (Fig. 3), at ~ 10 km^2 and ~ 100 km^2 for all three variables. Wider scales were chosen to be conservative, and a linear regression was fitted to the first segment (0–20 km^2), after which an iterative process was used to determine the optimal location of the breakpoint(s) within that window, by calculating the residual mean square error (MSE) for each point, and iteratively shifting the location of the breakpoint to minimize MSE. The procedure was repeated for the segment 20–1000 km^2.

Two component mixing model for groundwater and surface-water interaction

To investigate the influence of deep groundwater in catchments of different spatial size, we used a two-component end-member mixing model to estimate mean groundwater inputs (GW%) as a proportion of total flow for each site using
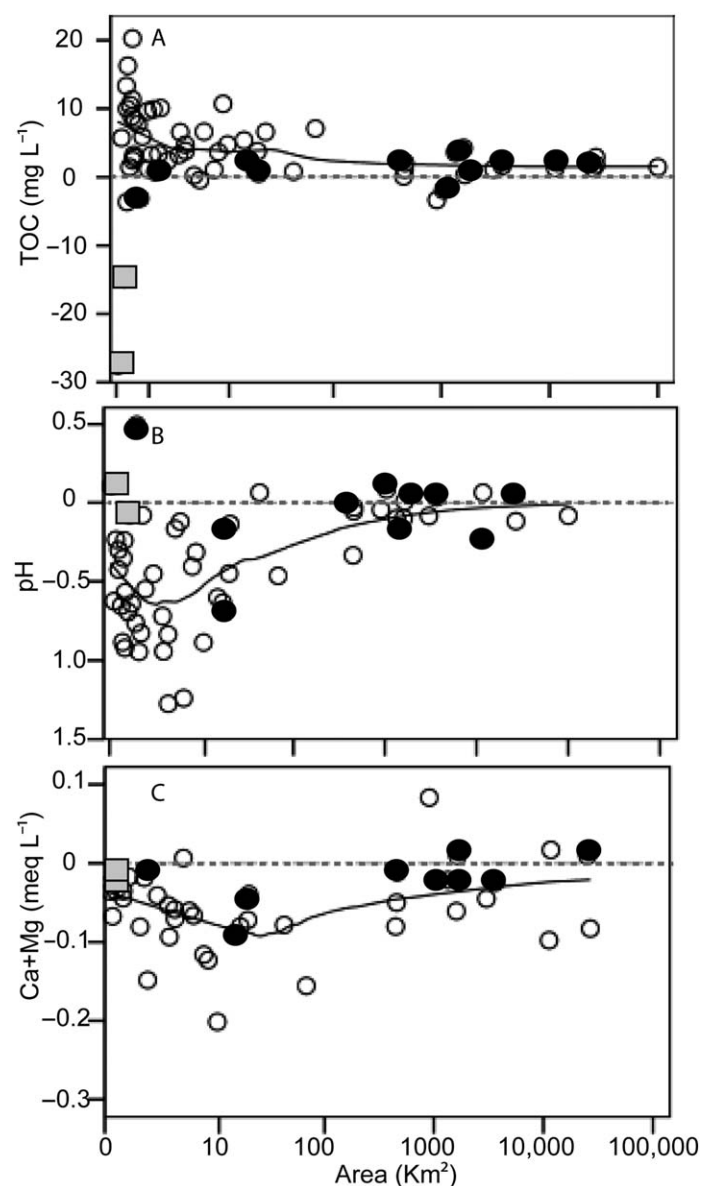
Fig. 3. The response of catchments to snowmelt illustrated by the difference between spring and winter TOC (**A**), pH (**B**), and Ca + Mg (**C**). Gray filled squares are catchments with more than 50% peat while black circles are catchments with more than 5% lakes and white circles are mixed catchments.

Ca + Mg concentrations (Eq. 1). The mixing model assumes that the difference in downstream concentrations and the mixture of upstream landscape signals (from dominant landscape types) can be explained by the input from deep groundwater. It also assumes that Ca + Mg are semi-conservative and are not likely to be affected by instream processes.

$$GW\% = (C_{Mixed} - C_{HW})/(C_{GW} - C_{HW}) * 100 \qquad (1)$$

Where C_{mixed} is the observed mean concentration at a given site, C_{GW} is the mean concentration of Ca + Mg for the

groundwater end-member (0.39 ± 0.15 meq L^{-1}), and C_{HW} is the modeled mean concentration of the headwater stream input end-member. The headwater catchments used for C_{HW} were selected based on previous studies (Laudon et al. 2011; Tiwari et al. 2014) which showed that the mixture of known chemical signatures of peatland and forested (underlain by mineral soil) headwaters was a good predictor of concentrations for smaller streams. The Krycklan C4 signals represented the peatland signal (Ca + Mg 0.10 meq L^{-1}) while the Krycklan C2 represented the forest signal (Ca + Mg 0.17 meq L^{-1}) which was then mixed corresponding to the relative proportion of each landcover type in the catchment in question. We obtained GIS data for lakes, peatlands, mineral soil, and catchment area from the SMHI database and calculations for areal coverage were carried out in Arc GIS 10.0. The landcover types (forest and peatlands) were chosen because they are the dominant features in the region, and they produce characteristic chemical signatures which are known to influence downstream chemistry (Laudon et al. 2011; Ågren et al. 2014).

Instream processing of TOC

We investigated the potential effect of instream processing of organic carbon for each site by comparing the observed mean TOC concentration to the TOC concentration modeled using the relative proportions of groundwater and headwaters end-members calculated using mixing model described above (Eq. 1, but in this case applied to TOC). The estimated TOC value for the headwater end-members was calculated for each catchment based on the relative proportion of peatland (mean TOC 35.3 ± 1.4 mg L^{-1}) and forested area (mean TOC 18.2 ± 1.0 mg L^{-1}) in the given catchment, while TOC value for groundwater was taken as 1.4 ± 0.13 mg L^{-1} based on the average measured from deep groundwater wells. We then plotted the difference between the measured and modeled TOC against catchment area to evaluate where, within these river systems, measured TOC concentrations were lower than modeled values. A lower measured TOC concentration at a given site compared to the modeled concentration is an indication that more TOC is lost to various aquatic processes than is accounted for by simple mixing and dilution.

Results

Spatial and temporal variation of stream chemistry from headwaters to sea

The analysis of stream chemistry based across the 69 locations in northern Sweden show marked spatial and temporal variability for TOC, pH, and Ca + Mg. For TOC, concentrations ranged from 2 mg L^{-1} to 41 mg L^{-1} ($N = 2417$), with lowest average values occurring at the outlet of the large lakes (e.g., Storvindeln (Supporting Information Table 2), while the highest occurred in the smallest headwater, which had a high wetland proportion in the watershed (Krycklan

C3). Generally, TOC concentrations decreased with increasing catchment size as shown by the LOESS average (Fig. 2A) starting with highest average in the headwaters and ending with the lowest concentrations in Bothnian Bay. The temporal variability in TOC concentration as measured by the SD (Fig. 2A) also showed a decreasing trend with increasing catchment scale.

pH ranged from 4.0 to 7.6 ($N = 2095$) with the lowest values observed in the smallest headwater catchment (Krycklan site 3) and the highest in the sea. As with TOC, the temporal dynamics of pH as measured by the SD showed that small catchments displayed the largest variability, which again decreased toward the Bothnian Bay (Fig. 2B).

Ca + Mg concentrations ranged from 0.04 meq L^{-1} to 0.4 meq L^{-1} ($N = 2075$) with the lowest values observed in the smallest headwater (Krycklan C3) and the highest in an intermediate-sized catchment (Ostvik). The LOESS average showed an increasing trend toward the intermediate sized catchments followed by a decrease toward larger catchments, beyond which concentrations remained constant. The temporal dynamics indicate a general decreasing variability with increasing catchment size, illustrated by high SDs in the headwaters, lower SDs in the large basin and a peak in the SD in the intermediate size catchments (Fig. 2C).

It should be noted that all of the stream chemistry (TOC, pH, and Ca + Mg) showed large changes in the average concentrations between headwater to intermediate-sized streams (< 100 km^2) (i.e., the largest decrease in the LOESS average TOC, while the LOESS average pH and Ca + Mg increased). Beyond 100 km^2, the changes in average values were smaller with increasing drainage size as indicated by a flattening of the LOESS curve.

Snowmelt responses from headwaters to sea

Investigating how catchments of different spatial extents responded to snowmelt showed that TOC, pH, and Ca + Mg in smaller catchments were more responsive to floods than in the larger basins and the sea. Specifically, TOC, pH, and Ca + Mg in smaller catchments (< 100 km^2) showed a greater response to snowmelt as shown by the larger deviation from zero (TOC 4.2 mg L^{-1}, pH 0.5, and Ca + Mg 0.06 meq L^{-1}) in the LOESS average values (Fig. 3). Catchments larger than 1000 km^2 had on average much smaller changes in chemistry from winter baseflow to spring snowmelt (TOC 1.7 mg L^{-1}, pH 0.03, Ca + Mg 0.03 meq L^{-1}, respectively) with TOC and pH showing little or no change for most of these larger catchments. Snowmelt response was also different across different types of headwater streams. TOC in smaller headwater catchments dominated by peat soils showed a dilution in TOC concentrations in response to spring flood, while most of the other catchments showed an increase (Fig. 3). Accordingly, variation among sites in the magnitude of TOC change during the spring flood declined with the percentage of peat cover in the respective

catchments ($r^2 = 0.43$, $p < 0.0003$, $N = 58$). By contrast, for nearly all catchments, pH and Ca + Mg were diluted during spring flood. The only exceptions to this were a few large basins with more than 5% lake coverage where Ca + Mg increased, and one small, peat-dominated headwater (C4) where pH increased (Fig. 3).

Break point analysis

The shape of the LOESS curves (Fig. 2) suggests that the relationship between stream chemistry with catchment scale is not linear and that there are distinct catchment sizes where changes in these scaling relationships occur. Piecewise regression gave further evidence for this nonlinearity, with MSE results highlighting two zones where scaling relationships between surface chemistry and drainage size changed (Supporting Information Fig. 1, Table 1). The first of these zones separated headwaters from larger streams (between 2 km^2 and 10 km^2, depending on the response variable); the second zone encompassed a broader range of drainage areas and distinguished intermediate-sized and larger rivers (67–500 km^2).

These zones of change separated three scaling domains (here: ranges of catchment size) within which the relationships between chemistry and drainage size were relatively constant. First, for catchments between 0.01 km^2 and 2 km^2, average TOC concentrations decreased from 40 mg L^{-1} to 14 mg L^{-1}, pH increased from 4.0 to 6.1, and Ca + Mg increase from 0.01 meq L^{-1} to 0.02 meq L^{-1}. In the second domain, from ~ 5 km^2 to 70 km^2, TOC decreased from 18 mg L^{-1} to 10 mg L^{-1}, pH increased from 5.6 to 6.5, and Ca + Mg increased from 0.03 meq L^{-1} to 0.07 meq L^{-1}. Finally, between 500 km^2 and 100,000 km^2, TOC further decreased from 6.1 mg L^{-1} to 4.4 mg L^{-1}, pH increased from 7.01 to 7.8, and Ca + Mg decreased from 0.02 to 0.03.

Groundwater surface-water interaction

Average deep groundwater TOC concentration was 1.3 mg L^{-1} compared to the surface-water concentrations, which ranged from 2 mg L^{-1} to 41 mg L^{-1}. Average groundwater Ca + Mg concentration was 0.44 meq L^{-1} compared to a range of 0.04–0.4 meq L^{-1} for surface waters. Smaller catchments had streams with higher TOC and lower Ca + Mg, while larger streams, rivers, and the sea tended to have lower TOC and higher Ca + Mg, i.e., more similar to the groundwater chemical signature (Fig. 4). To test the effect that deep groundwater input could have on the changing surface-water chemistry with increasing catchment size, we quantified the input of groundwater using the two component-mixing model (Eq. 1). Groundwater % contribution was positively correlated with catchment size ($r^2 = 0.43$; $p < 0.001$), suggesting that streams in the smallest catchments (< 2 km^2) received considerably less deep groundwater (12% on average) than rivers with the largest catchments (> 1000; 35% on average) (Fig. 5A).
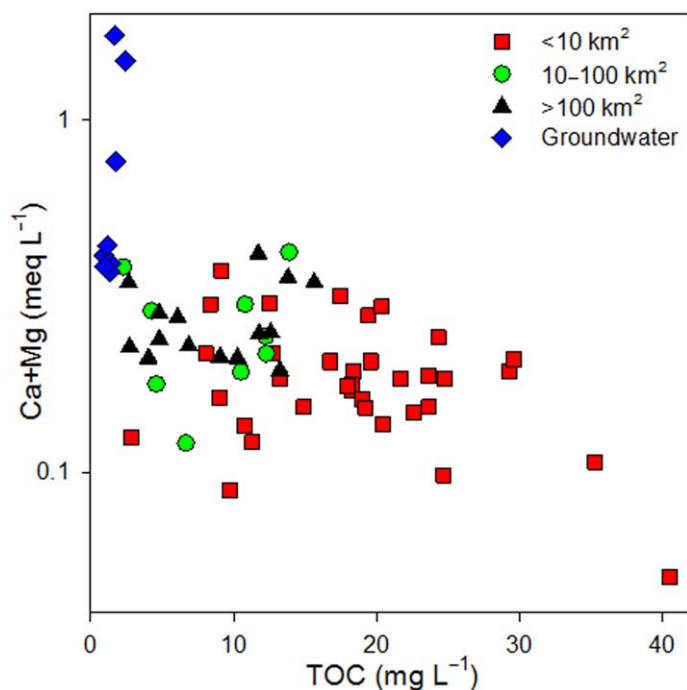
Fig. 4. Chemical signatures of surface waters (headwater, intermediate, large basins) and deep groundwater wells (50–150 m) in the study region of northern Sweden.

Inferred loss to instream processing

When TOC was predicted for each site using the modeled groundwater contribution and the mixing of upstream landscape signals (peatland and forested headwaters) in proportion to their landscape cover, the difference between modeled and measured concentrations increased with catchment area. For instance, in catchments < 10 km^2, the measured TOC concentrations were on average 2 mg L^{-1} higher than modeled concentrations; while in the larger basins (> 1000 km^2), measured TOC concentrations were on average 3 mg L^{-1} lower than measured concentrations (Fig. 5B).

Discussion

Spatial and temporal patterns of TOC, pH, and Ca + Mg, as well as catchment responses to snowmelt, all indicate that there are different processes operating at different spatial scales to generate the regional pattern observed as headwaters flow to the sea (Fig. 6). Within this region of northern Sweden, we identified two major breaks in the scaling relationship between drainage size and stream/river chemistry. These breaks separate scaling domains within which the dominant processes regulating the variability in surface chemistry very likely differ. For the first domain (0.01–2 km^2), we suggest that variation in TOC, pH, and Ca + Mg is driven by unique chemical signals derived
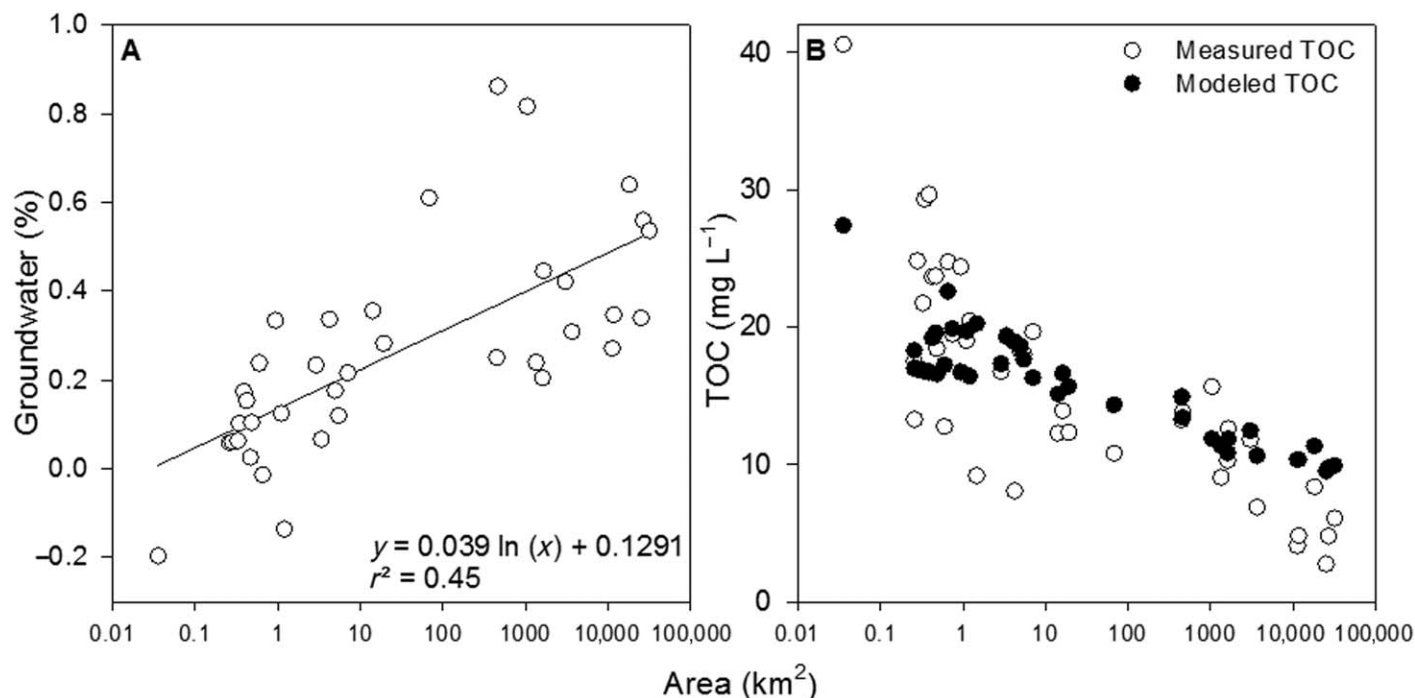

Fig. 5. Estimated groundwater input for each site derived from a two-component mixing model (**A**), and TOC concentration modeled from those same end-members, assuming conservative mixing and no in-stream processing (filled symbols, **B**) as well as actual measured TOC concentrations (open symbols). Measured TOC was less than modeled TOC for larger catchments, suggesting that in-stream processing or other mechanisms resulted in a loss of TOC en route.
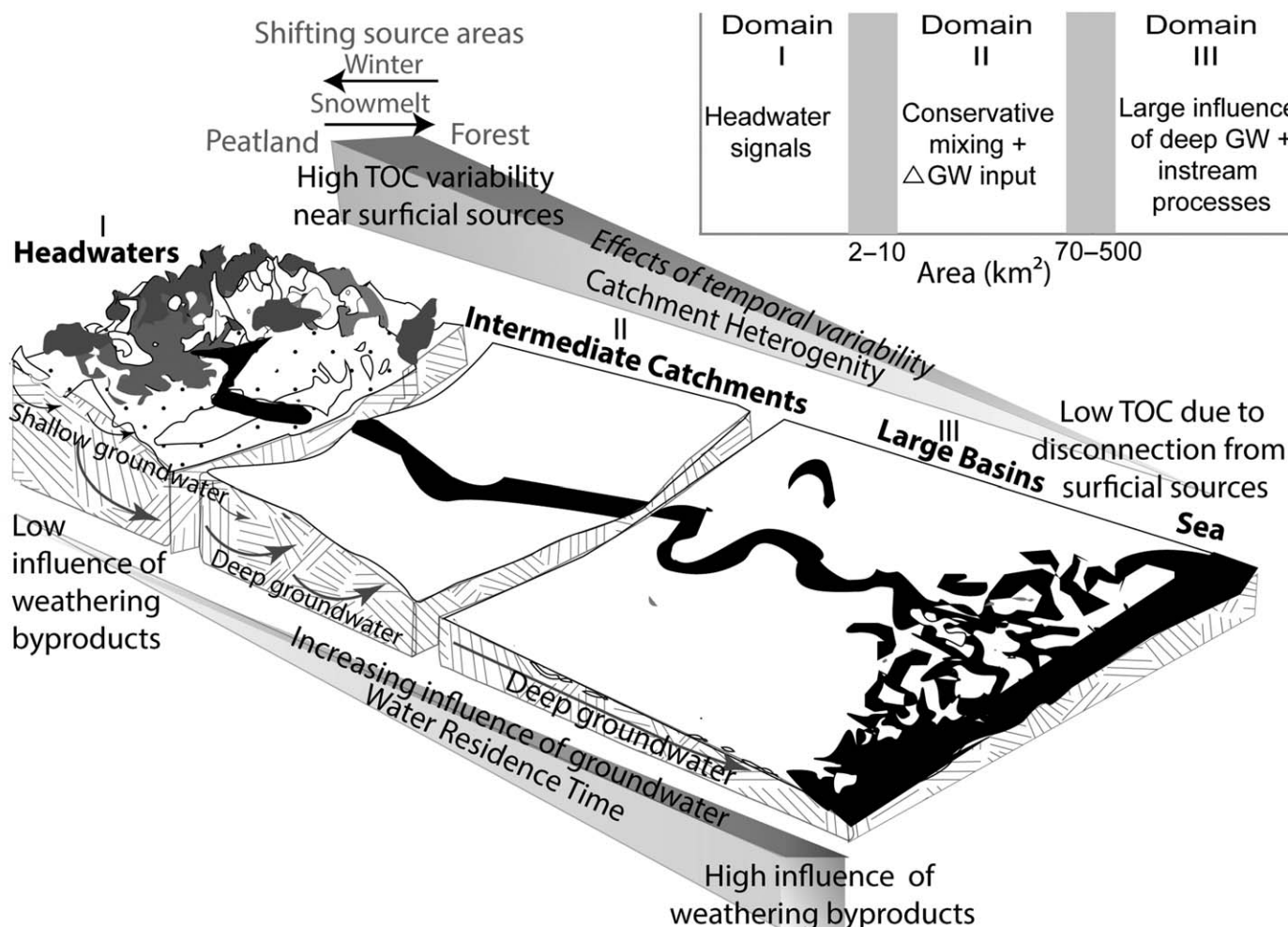
Fig. 6. Conceptual diagram of catchment processes affecting spatial and temporal variability of stream chemistry from headwaters to the sea. The main processes of the domains are related to (I) the distinct chemical signatures from headwaters, (II) the conservative mixing of headwater signals from different landscapes and the increasing input of deep groundwater, (III) the large influence of deep groundwater and the effects of instream processes. The two scale breaks (gray bars) at 2–10 km^2 and 70–500 km^2 are transition zones for stream chemistry.

from dominant landscape features (e.g., wetlands, lakes, and forests). For the second domain ($\sim$ 10–70 km^2), we suggest that variation in chemistry is shaped largely by the downstream mixing of headwater sources with variable inputs of deep groundwater that is low in TOC and high in BCs. For the third domain ($\sim$ 500–100,000 km^2), variation in surface chemistry becomes strongly influenced by a large and relatively constant contribution of deep groundwater sources and the influence of instream processes (Fig. 6).

At the smallest spatial scale considered, variation in landscape structure, primarily related to differences in peatland cover, generated variable chemical signals across headwater streams. However, these effects, both on average concentrations and on the seasonal changes associated with snowmelt, were restricted to the smallest streams. Indeed, with even small increases in drainage size, we observed reduced variability within catchments that likely reflects the convergence

and mixing of landscape signals from these distinct headwater settings. This convergence occurred at $\sim$ 2–10 km^2, where there was an abrupt decrease in TOC concentration with concomitant increases in Ca + Mg and pH. In general, these observations are consistent with the REA concept (Wood et al. 1988), which describes a decrease in hydrologic variability across streams with increased catchment area due to the mixing of various small-scale hydrological patterns and processes. While Wood et al. (1988) proposed a 1 km^2-catchment scale for the REA, Asano and Uchida (2010) estimated an REA of 1–10 km^2 in a mountainous catchment in central Japan, while Temnerud et al. (2007) showed a decrease in headwater TOC variability at $\sim$ 5 km^2 for a group of northern Swedish catchments. Differences in REA across these studies likely reflected the different landscapes and different individual parameters used to infer patterns (discharge, SiO$_2$, and TOC, respectively). Similar to this prior work, we show

that multiple elements, with varying catchment sources and degrees of reactivity, all point to a comparable range in the REA of around 2–10 km^2.

The effect of landscape heterogeneity on TOC during spring flood was strongest in the headwaters, when catchments dominated by specific patch types (e.g., peatlands, lakes, and forests) showed variable chemical responses to this seasonal event. Previously, Köhler et al. (2008) and Laudon et al. (2007) demonstrated that these patches indeed respond differently to the spring flood, such that source areas for TOC in the landscape shift from peatlands to mineral soils during this period. Here, we greatly expand the spatial scope of this assessment to show that the dilution of TOC commonly observed in peat-dominated streams during the snowmelt (Laudon et al. 2011) is rapidly lost with increases in catchment size—as the distance from major peat sources increase and the size of peat patches relative to the drainage area decreases (Fig. 6). Instead, most larger catchments showed increased TOC concentration during this event, indicating that meltwaters are adding TOC to river systems, most likely by flushing organic rich riparian zones that are characteristic of the boreal region (Grabs et al. 2012; Tunaley et al. 2016). Importantly, while the magnitude of this snowmelt response clearly declined with catchment size, even the subtle springtime increases in TOC observed in the largest rivers may have important ecological and biogeochemical consequences in estuaries of the northern Baltic Sea (Figueroa et al. 2016).

The distinction between catchments dominated by a specific landscape type (e.g., forest or peatland) were less obvious in the Ca + Mg responses to snowmelt because most stations showed decreasing concentrations, regardless of spatial scale. Because the main sources of Ca and Mg are from weathering of mineral soils (Klaminder et al. 2011), spring floods tend to dilute these concentrations as shallow groundwater and soil water enter streams (Campbell et al. 1995; Bishop et al. 2004). Therefore, surficial landscape heterogeneity, where hydrological and biogeochemical processes occur at the time scale of hours to days is less important for weathering derived elements. Instead, these inputs largely depend on groundwater flowpaths and variation in residence time in the catchment (Peralta-Tapia et al. 2015) (Fig. 6). Increased contact time for snowmelt runoff with mineral soils can explain the marked increase in Ca + Mg around catchment scale of 20 km^2 and above, since the mineral soils are a source of Ca + Mg (Tiwari et al. 2017). Nevertheless, the dilution of Ca + Mg in all catchments during snowmelt indicates that snowmelt plays an important role in regulating BC chemistry across all scales.

As small streams transition into rivers, the effects of landscape heterogeneity are lost and further altered as groundwater inputs shift from shallow to deeper sources with different chemical properties (Fig. 6). Deeper groundwater is characterized by longer water residence time in the catchment with more contact time with minerals which facilitates weathering and hence increased production of BCs and the mineralization of TOC (Klaminder et al. 2011). Previous work in the Krycklan Catchment has shown that this transition in water source is nonlinear with drainage size, and that during winter baseflow streams draining more than 10 km^2 may receive 70–80% of water from deeper sources (Tiwari et al. 2014; Peralta-Tapia et al. 2015). Our data encompass a broader range of seasonal conditions and therefore the average deep groundwater contribution at this same drainage size is lower (ca. 20–30% at 10 km^2), reflecting the importance of precipitation and more surficial inputs throughout the year (Fig. 5A). Regardless, as observed elsewhere (Shaman et al. 2004), our results show that the contribution of groundwater increases across a broad range of drainage sizes, and is notably high ($\sim$ 60%) for some of the largest rivers (Fig. 5A). Not surprisingly, this hydrologic shift was associated with declines in TOC and increases in pH and Ca + Mg along the transition from small streams ($\sim$ 10 km^2) up through to the intermediate-sized catchments at 70–500 km^2, after which we observed another shift in the chemical patterns. Hence, large inputs of deep groundwater with lower concentrations of TOC dampen the signals from the organic patches in the landscape, but also provide a source of Ca + Mg and buffers against pH change (Tiwari et al. 2014; Creed et al. 2015; Palmer et al. 2015) (Fig. 6). In addition to these impacts, large and persistent inputs of deep groundwater are very likely to reduce the variability in stream chemistry and sustain baseflow conditions (Thompson et al. 2011).

With increasing water residence time in larger catchments, there are also increased possibilities for processes such as microbial degradation, photo-oxidation, sedimentation, sorption, or flocculation to remove TOC from rivers. We investigated this potential by comparing measured and modeled TOC concentrations and show that the observed values, in many cases, were not simply the result of conservative mixing in combination with dilution by deep groundwater. Instead, we found lower than expected TOC concentrations for many of larger river sites (Fig. 5B), suggesting that removal processes are important at this spatial scale. In addition, this potential for removal appeared even stronger for rivers draining catchments with a relatively high lake percentage (Supporting Information Table 2, Fig. 2). Lakes can act as regulators of regional carbon cycling by increasing the water residence time within catchments, thereby giving time for various removal processes to occur (Weyhenmeyer et al. 2012; Müller et al. 2013). However, Müller et al. (2013) suggested that lower concentrations observed in lakes of intermediate-sized catchments could also simply be due to the combination of water input from rainfall, deep groundwater, and lateral tributary inflow due to their low landscape position. Similarly, Lottig et al. (2013) found in a study of low-gradient streams in northern

Wisconsin, U.S.A. that the presence of upstream lakes did not measurably alter mean DOC concentrations, but only delayed and attenuated the response of DOC to high flow events—suggestive of hydrologic buffering but minimal in-lake processing of DOC. In contrast, our results lend support to the notion that lakes may facilitate the internal aquatic processes that regulate TOC concentrations at larger spatial scales in the boreal landscape.

Conclusion

This study focused on improving the understanding of how spatial and temporal patterns change with scale, which remains a grand challenge for catchment biogeochemical modelers and hydrogeologists. By following scale-related changes in TOC, pH, and major BCs (Ca + Mg), we identify domains of scale within which different processes appear to regulate spatial and temporal patterns of stream chemistry. This analysis resulted in two main breaks in chemistry patterns, one at $\sim$ 2–10 km^2 and one at $\sim$ 70–500 km^2. We attribute the first break to convergence of small headwaters from heterogeneous patches in the landscape; the second to a transition from shallow to deep groundwater contribution. Larger catchments in general displayed a higher contribution of groundwater, which maintains stream flow and provides more constant stream chemistry relative to that observed in headwaters. Accordingly, headwater chemistry was more responsive to floods than larger catchments, with larger changes between winter and spring flood chemistry. This conceptual understanding of processes affecting stream water chemistry provides a framework that can aid in developing strategic management tools for dealing with environmental issues whose influence is potentially felt across a range of spatial scales, such as nutrient loading, forest harvest, and climate change.

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Conflict of Interest

None declared.