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## Spatial heterogeneity of the spring flood acid pulse in a boreal stream network<sup>☆</sup>

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### ABSTRACT

Spatial and temporal patterns in streamwater acidity are ecologically important, but difficult to measure in parallel. Here we present the spatial distribution of streamwater chemistry relevant to acidity from 60 stream sites distributed throughout a 67 km<sup>2</sup> boreal catchment, sampled during a period of winter baseflow (high pH) and during a spring flood episode (low pH). Sites were grouped based on pH level and pH change from winter baseflow to spring flood. The site attributes of each pH group were then assessed in terms of both stream chemistry and subcatchment landscape characteristics. Winter baseflow pH was high throughout most of the stream network (median pH 6.4), but during the spring flood episode stream sites experienced declines in pH ranging from 0–1.6 pH units, resulting in pH ranging from 4.3–6.3. Spring flood pH was highest in larger, lower altitude catchments underlain by fine sorted sediments, and lowest in small, higher altitude catchments with a mixture of peat wetlands and forested till. Wetland-dominated headwater catchments had low but stable pH, while the spring flood pH drop was largest in a group of catchments of intermediate size which contained well-developed coniferous forest and a moderate proportion of peat wetlands. There was a trend with distance downstream of higher pH, acid neutralizing capacity (ANC) and base cation concentrations together with lower dissolved organic carbon (DOC, strongly negatively correlated with pH). This apparent scale-dependence of stream chemistry could be explained by a number of environmental factors which vary predictably with altitude, catchment area and distance downstream—most notably, a shift in surficial sediment type from unsorted till and peat wetlands to fine sorted sediments at lower altitudes in this catchment. As a result of the combination of spatial heterogeneity in landscape characteristics and scale-related processes, boreal catchments like this one can be expected to experience high spatial variability both in terms of chemistry at any given point in time, and in the change experienced during high discharge episodes. Although chemistry patterns showed associations with landscape characteristics, considerable additional variability remained, suggesting that the modeling of dynamic stream chemistry from map parameters will continue to present a challenge.

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## 1. Introduction

Stream acidity provides a critical constraint for aquatic biota in many regions (e.g., Driscoll et al., 1980; Lacroix and Townsend, 1987). Temporal dynamics in stream acid chemistry are of particular relevance due to the prevalence of rain or snowmelt driven acidic episodes (e.g., Carline et al., 1992; Laudon et al., 2000; Lepori and Ormerod, 2005). For mobile aquatic organisms such as salmonids, the spatial distribution of acidity within a stream network at a range of scales is also of ecological consequence. Incorporation of a temporally dynamic and spatially explicit understanding of stream chemistry is thus an important step in assessing stream ecosystems and relating patterns in chemistry to distributions of fish and other aquatic organisms.

Spatial heterogeneity presents a challenge to the characterization of stream chemistry. Where spatially dense measurements of stream chemistry have been made, they have revealed highly heterogeneous chemistry, particularly in relatively small streams (Stutter et al., 2006; Temnerud and Bishop, 2005; Wolock et al., 1997). Likens and Buso (2006) found that in a snapshot of streamwater chemistry during a low flow period, the 40 km<sup>2</sup> Hubbard Brook stream network (New Hampshire, USA) varied in concentration by more than an order of magnitude for every measured solute, including H<sup>+</sup>, dissolved organic carbon (DOC) and inorganic aluminum. The most acidic sites were found in the headwaters (Likens and Buso, 2006).

Although small headwater streams contribute a substantial portion of the water and chemical character found in larger rivers (Alexander et al., 2007), measurements taken on a larger stream/river do not adequately characterize the range, or often even the average, of chemistry in the headwaters upstream of that point (Likens and Buso, 2006; Temnerud et al., 2007). Downstream trends in stream chemistry are observed in some regions, with larger streams/rivers commonly having higher pH and buffering capacity than their smaller tributaries (Eriksson, 1929; Johnson et al., 1981; Likens and Buso, 2006). These downstream trends have been typically attributed to variation in hydrology (Driscoll et al., 1988; Johnson et al., 1981; Soulsby et al., 2006), such as increasing length of flow pathways coupled with increased within-catchment water transit times with distance down a stream system. Lakes within stream networks tend to mineralize organic carbon resulting in lowered downstream DOC concentrations (Cole et al., 2007; Dillon and Molot, 1997; Temnerud et al., 2007), which may increase pH at sites below lakes. Shifts in forest type or sediment/soil type have also been hypothesized to contribute to observed altitudinal gradients in stream chemistry (Ågren et al., 2007; Driscoll et al., 1988; Soulsby et al., 2006), but for many monitored stream systems the mechanism(s) behind downstream trends remains unclear.

Aiding in the study of stream chemistry patterns, spatial variation in stream chemistry often roughly mirrors catchment characteristics such as soils, vegetation or topography (e.g., Ahearn et al., 2005; e.g., Creed et al., 2003; Hutchins et al., 1999). Using such correlations between catchment characteristics and stream chemistry coupled with a GIS, researchers have made recent advances in empirically modeling stream chemistry in entire stream networks using information on soil and geology (Cooper et al., 2004; Smart et al., 2001; Wade et al.,

1999), although these modeling efforts typically do not explicitly consider downstream trends.

Can temporal, episodic changes in stream chemistry also be predicted from catchment characteristics like soil or vegetation type? Evidence for this exists in northern Sweden, where forested and wetland catchments respond in hydrologically distinct ways to the spring snowmelt (Laudon et al., 2007). As a consequence, acid chemistry of streams draining these landscapes differs during spring flood. Forested headwater streams experience a large pH drop due primarily to increases in organic acids associated with dissolved organic carbon mobilized from soils, while the chemistry of headwater wetland streams has been observed to dilute from snowmelt and pH changes little (Buffam et al., 2007; Cory et al., 2006). However, little is known about the way in which these contrasting temporal behaviors combine in stream networks in a heterogeneous landscape, or how the headwater chemistry signals mix in larger order streams.

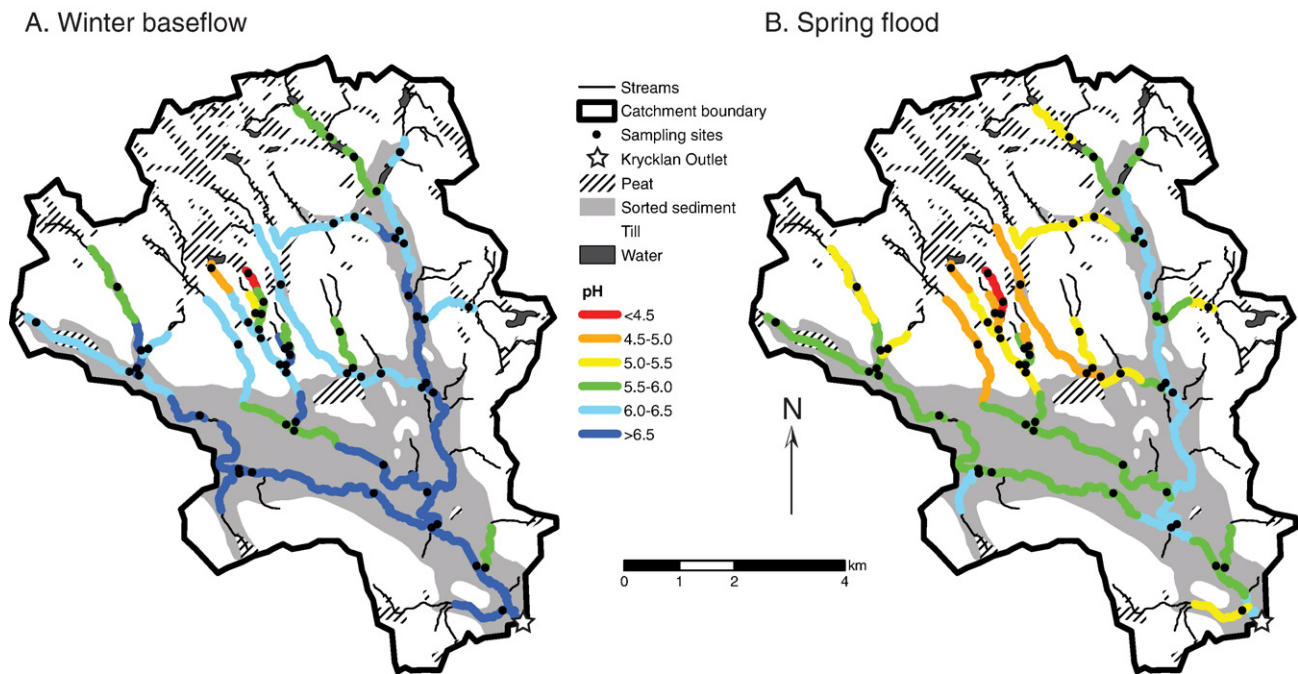
We present a case study from the Krycklan catchment, a 67 km<sup>2</sup> boreal catchment in northern Sweden which consists of a mosaic of wetlands and lakes interspersed in the forested landscape. Within the stream network of this catchment, observations indicate a wide range of pH values during spring flood, and a wide range of responses in terms of acid pulse during that period (Buffam et al., 2007). This is in spite of uniform parent geology and uniform (and relatively low) levels of anthropogenic acid deposition. In that context, the objectives of this study were to:

1. Compare the spatial distribution of stream acidity during winter baseflow with its distribution during spring flood.
2. Identify streamwater chemistry characteristics associated with a range of acid pulse behaviors relevant to aquatic biota during the transition from winter baseflow to spring flood.
3. Identify catchment/landscape attributes associated with the most/least acidic groups of streams, and with the most/least well-buffered groups of streams. Is there a shift to less acidic sites with distance downstream, as seen in other areas? If so, with which catchment/landscape characteristics is the shift associated?

The approach that we took was to carry out multiple spatial surveys (one during winter baseflow, one during spring flood) of stream chemistry throughout the stream network, then classify sites within the stream network by characteristic stream acid pulse behavior. Classification was done by grouping sites by spring flood pH (pH<sub>F</sub>) and by pH difference between winter baseflow and spring flood ( $\Delta$ pH). Following this classification, we quantified streamwater chemistry and catchment characteristics for each of the identified pH groups.

## 2. Site description

The study area is the upper 67 km<sup>2</sup> of the Krycklan River catchment in northern Sweden (Fig. 1). This catchment includes the Vindelns Experimental Forests, where climate data have been monitored at the Svartberget Research Station (64° 14' N, 19° 46' E) since 1980. Annual mean air temperature is 1 °C with ca. 600 mm annual mean precipitation, of which one-third falls



**Fig. 1** – Map of the Krycklan stream network in Northern Sweden. Stream segments are colored by interpolated values of pH, illustrating the spatial distribution of pH during (A) winter baseflow and (B) spring flood. Measured pH values from 60 sampling sites were assigned to stream segments extending up to the halfway point between sites, or upstream half the distance to the stream source for headwater streams. Values were not extended beyond stream junctions. Streams which were not sampled are shown as thin black lines. Primary surficial sediment deposits are shown in the background (Geological Survey of Sweden, Quaternary Deposits Map Ak19, ©1995).

as snow (Ottosson Löfvenius et al., 2003). Snowcover is present for 171 days on average (1980–1999), and spring snowmelt is the dominant hydrological event, with up to half of the annual stream flow occurring during a 3–6 week period in April–May.

Within the Experimental Forests, soil hydrologic parameters and stream flow have been monitored in the 50 ha Nyänget subcatchment since 1980 (e.g., Bishop et al., 1990). Subsurface pathways dominate stream flow delivery in forested sites, with overland flow rare due to high infiltration capacity of the surficial till and overlying soils (Bishop et al., 1990; Nyberg et al., 2001). Stream water chemistry has been monitored regularly at the Nyänget stream site for the past 25 years (Fölster and Wilander, 2002; Grip and Bishop, 1990).

The area currently receives on the order of  $2 \text{ kg ha}^{-1} \text{ yr}^{-1}$  each of S (as  $\text{SO}_4^{2-}$ ) and N (as  $\text{NO}_3^-$ ) from atmospheric deposition. Deposition peaked in the 1970's at about  $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$  of S, which was less than a quarter of that experienced in southwestern Sweden (Mylona, 1996). Analysis of spring flood episodes in northern Sweden has demonstrated that in this region the pulse of acidity associated with this annual episode is now typically derived primarily from an increase in naturally occurring organic acids in conjunction with the dilution of ANC (buffering capacity), with a smaller contribution from anthropogenically-derived acids (Bishop et al., 2000; Laudon et al., 2000).

The Krycklan study catchment ranges from 126 to 369 m above sea level (Table 1). Throughout the catchment, metasedimentary bedrock (primarily metagreywacke) is overlain by quaternary deposits dominated by till varying in thickness up to tens of meters (Ivarsson and Johnsson, 1988). Well-developed

iron-podzol soils are common. The lower 55% of the catchment is below the highest post-glacial coast line (current altitude 255–260 m in this area), and the postglacial sediments in this part of the catchment are composed largely of silt and fine sand which were deposited in the distal part of a postglacial delta (Fig. 1). These fine sorted sediment deposits form a thick layer through which the streams have deeply incised channels, in some cases forming ravines and bluffs of up to 30 m in height. Organic rich soils are common near stream channels (Bishop et al., 1995). The catchment is forested primarily with mature Scots Pine (*Pinus sylvestris*) in dry upslope areas and Norway Spruce (*Picea abies*) in wetter, low-lying areas. The forested landscape is interspersed with patches of naturally acidic sphagnum-dominated peat wetlands, making up 9% of the total catchment area, with >30% coverage in some of the smaller studied subcatchments (Table 1). Deciduous shrubs and trees, primarily birch (*Betula* spp.) but also alder (*Alnus incana*) and willow (*Salix* spp.), are found in the riparian forest along larger streams (Andersson and Nilsson, 2002). Brown trout (*Salmo trutta*), Bullhead (*Cottus gobio*) and Brook trout (*Salvelinus fontinalis*) are common in many of the streams (Buffam, 2007).

### 3. Methods

#### 3.1. Field sampling

Water sampling consisted of grab samples collected in acid-washed 250 ml high-density polyethylene bottles, with

**Table 1 – Median (and 5th–95th percentiles in parentheses) catchment characteristics for stream sites used in the study**

Variable	All sites (N=60)	Headwater sites (N=18) <sup>a</sup>	Krycklan outlet <sup>b</sup>
<i>Surficial sediment type (%)</i>			
Till	62.5 (45.4–95.9)	66.2 (17.1–99.5)	52
Peat	13.5 (0.0–29.8)	10.8 (0.0–55.4)	9
Sorted sediment <sup>c</sup>	7.4 (0.0–35.9)	0.2 (0.0–36.0)	29
Thin soils	7.7 (0.0–24.6)	8.5 (0.0–32.8)	8
Exposed bedrock	0.9 (0.0–4.6)	0.3 (0.0–7.7)	1
<i>Landcover (%)</i>			
Forest	82.3 (58.1–96.6)	84.8 (49.6–98.7)	84
Wetland	12.0 (2.5–28.8)	9.7 (1.3–50.4)	9
Clearcut	2.1 (0.0–10.0)	0.4 (0.0–32.9)	4
Open or arable	0.6 (0.0–3.7)	0.0 (0.0–4.6)	3
Lake	0.1 (0.0–4.1)	0.0 (0.0–5.8)	1
<i>Forest inventory</i>			
Birch volume (m <sup>3</sup> ha <sup>-1</sup> )	11 (7–18)	11 (6–21)	11
Spruce volume (m <sup>3</sup> ha <sup>-1</sup> )	37 (21–99)	29 (19–131)	33
Pine volume (m <sup>3</sup> ha <sup>-1</sup> )	50 (37–87)	47 (29–93)	50
Total volume (m <sup>3</sup> ha <sup>-1</sup> )	99 (72–180)	89 (61–225)	94
Mean tree stand age (yr)	58 (48–94)	59 (37–104)	57
Mean tree height (m)	10 (9–16)	10 (7–18)	10
<i>Other</i>			
Above former high coast line (%) <sup>d</sup>	72 (0–100)	90 (0–100)	45
Mean catchment slope (%)	9 (6–14)	9 (4–16)	11
Mean catchment altitude (m)	272 (224–295)	283 (207–299)	242
Site altitude (m)	198 (133–263)	238 (133–287)	126
Catchment area (km <sup>2</sup> )	3.3 (0.2–41.9)	1.5 (0.1–4.1)	67
Median subcatchment area (km <sup>2</sup> ) <sup>e</sup>	0.9 (0.1–2.4)	0.6 (0.1–2.1)	1.5

<sup>a</sup> Group of independent 1st and 2nd order stream sites, shown here to illustrate downstream trends in catchment characteristics from headwaters to outlet.

<sup>b</sup> Corresponding values for the entire 67 km<sup>2</sup> Krycklan catchment.

<sup>c</sup> Primarily silt and fine sand.

<sup>d</sup> Percent of catchment with altitude >257.5 m, which is the local altitude of the furthest extent of the sea following the last deglaciation.

<sup>e</sup> Median of the distribution of subcatchment areas draining into the stream cells within a given catchment.

multiple rinses of sample water. Samples were taken on two separate occasions (April 2004 and February 2005) at the same 60 stream sites distributed throughout the Krycklan stream network (Fig. 1). In order to represent all major stream reaches, samples were taken from 5–10 m above and 25–50 m below every junction in the stream network. These junction samples were supplemented with samples from sites near the middle of particularly long (>2 km) stream reaches, and from 15 easily

accessible sites which are part of a long-term monitoring program (Buffam et al., 2007; Cory et al., 2006). Several intended sites were not sampled, either due to inaccessibility during spring flood or due to lack of water flow during winter. During winter many of the smaller headwater streams froze solid, reducing the extent of the stream network. In total there were 67 sites for which both winter baseflow and spring flood samples were taken. Of these, 7 sites were removed from consideration due to high degree of overlap (>90% catchment area) with other sites, leaving 60 sites in all for our analysis (Fig. 1). Amongst these were 18 independent headwater (1st or 2nd order) sites (catchment areas 0.1–4.1 km<sup>2</sup>).

### 3.2. Chemical analyses

Following collection, water samples were kept dark and cool until they were subsampled for chemical analyses. pH (at natural pCO<sub>2</sub>, not air-equilibrated) was measured at room temperature with gentle stirring shortly after returning to the laboratory using a Ross 8102 low-conductivity combination electrode (ThermoOrion). For samples with pH>5.0 this method yields pH values slightly higher than closed cell (field) pH, as a result of CO<sub>2</sub> degassing during the analysis. However, measurements of CO<sub>2</sub> degassing rates and pH drift on selected samples demonstrated that the measured pH values were within 0.1 pH units of closed cell pH. DOC was measured by combustion and analysis as CO<sub>2</sub> using a Shimadzu DOC-V<sub>CPH</sub> analyser after acidification and sparging to remove inorganic carbon. Samples for DOC analysis were filtered using Millipore 0.45 µm MCE membrane filters (spring flood sampling) or left unfiltered (winter baseflow sampling) and then frozen until analysis. An intercomparison across sites and covering flow extremes determined that there was no measurable difference in concentration due to filtering. This result is in agreement with other studies of Swedish surface waters (Ivarsson and Jansson, 1994; Köhler et al., 1999) which found particulate organic carbon concentration to be negligible relative to the dissolved fraction. Thus, we use the term DOC for all samples in our study. Precision of the DOC analysis based on replicate injections was always better than 5%, and averaged less than 2%.

Samples for major cation analyses (K, Mg, Na, Ca) and total filterable aluminium (Al<sub>tot</sub>) were filtered (0.45 µm MCE membrane filters), preserved with ultrapure HNO<sub>3</sub> (1% v/v) and stored cool until elemental analysis by ICP-OES (inductively-coupled plasma optical emission spectroscopy) on a Varian Vista Ax Pro instrument. Samples for strong acid anions (SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) were stored at 6 °C (2004 samples) or frozen (2005 samples) until analysis, which utilized a Dionex DX-300 or DX-320 ion chromatograph system. The typical precision in anion and cation analyses based on measurements of certified standards was better than 2%. Analysis of NO<sub>3</sub> by flow injection analysis on selected samples which had been preserved by filtration and freezing until analysis (one-third of samples) revealed that concentrations were so low as to contribute insignificantly to the charge balance.

Base cation (BC) concentration was calculated as the sum of K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> concentrations expressed as µeq L<sup>-1</sup> of charge, with the assumption that these elements were present in their free ionized form. Strong acid anion (SAA) concentration

was calculated as the sum of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  expressed as  $\mu\text{eq L}^{-1}$  of charge. Acid neutralizing capacity (ANC) was calculated from the charge balance definition as the difference between strong bases and strong (mineral) acid anions (e.g., Munson and Gherini, 1993), expressed here as molar quantities:

$$\begin{aligned} \text{ANC} &= [\text{K}^+] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] \\ &= \text{BC} - \text{SAA} \end{aligned} \quad (1)$$

The concentration of dissociated organic acids ( $\text{OA}^-$ ) including both strong and weak acids was calculated from DOC and pH using a triprotic model (Hruška et al., 2003) with  $\text{pka}_1=3.04$ ,  $\text{pka}_2=4.42$ ,  $\text{pka}_3=6.7$  and an overall site density of  $10.2 \mu\text{eq/mg C}$ . The strong component of organic acids associated with DOC was not used in the calculation of ANC, nor was  $\text{Al}^{3+}$ , which is primarily organic-bound and contributes only in a minor way to charge balance in these waters (Cory et al., 2006).

### 3.3. Representativeness of sampling periods

The two sampling occasions were selected to represent the extremes experienced annually in northern Swedish boreal streams, both in terms of discharge and in terms of pH. Late winter baseflow is a period of sustained low flow associated with high pH, while the spring flood period typically gives rise to the highest annual flows and the longest period of sustained low pH (Buffam et al., 2007). The winter baseflow sampling occasion was from Feb. 17–28, 2005. Discharge during this period was stable and ranged from  $0.21\text{--}0.22 \text{ mm d}^{-1}$  at the Nyänget reference site, typical for winter low-flow discharge which averages  $0.18 \text{ mm d}^{-1}$  (mean daily flow during Jan–March over the 25-year discharge record). The spring flood sampling occasion was on the rising limb of the hydrograph during spring high flow, April 22, 2004. Discharge at the reference site on that day was  $3.0 \text{ mm d}^{-1}$ , while peak flood was reached two weeks later on May 4 with  $7.1 \text{ mm d}^{-1}$  of flow during a rain-on-snow event. Peak spring flow in 2004 was within the typical range of  $9.7 \pm 3.4 \text{ mm d}^{-1}$  for the 25-year mean of the daily peak spring flow at the reference site.

Data from 15 sites where stream pH was measured more frequently indicated that our two sampling occasions represented reasonably well the transition between the extreme situations winter baseflow and the rising limb of the spring flood. Most streams in this region experience an extended period of low pH beginning on the rising limb and extending through the period of highest spring flow (Laudon et al., 2000). The drop in pH is accompanied in most streams by an increase in DOC peaking on the rising limb, along with a more gradual dilution of BC, SAA, and ANC, which reach their lowest values at the time of highest flow (Buffam et al., 2007). Our sampling on the rising limb thus captured higher concentrations of most solutes than would be expected at peak flow. Based on the concentrations at the 15 temporally intensive sites, the spring flood survey samples were on average  $+0.1$  pH unit,  $+4 \text{ mg L}^{-1}$  DOC,  $+67 \mu\text{eq L}^{-1}$  BC,  $+17 \mu\text{eq L}^{-1}$  SAA,  $+51 \mu\text{eq L}^{-1}$  ANC and  $-15 \mu\text{g L}^{-1}$   $\text{Al}_{\text{tot}}$  relative to the values at peak flow. At the time of the survey the majority of the change in concentration between winter baseflow and peak flow had already occurred for all solutes. The analysis can thus be

considered a comparison between winter baseflow and the typical conditions early in the spring flood.

### 3.4. Subcatchment delineation and characterization

Subcatchment characteristics were determined along the Krycklan stream network (Table 1). All calculations were based on gridded elevation data (DEM) with a grid resolution of 50 m. A multiple-flow-direction algorithm (Seibert and McGlynn, 2007) was used to compute the downslope accumulation of catchment area until the stream network, which was derived from the 1:100000 scale digital land-cover map, (Lantmäteriet, Gävle, Sweden), was reached. This defined the local contributing area or local catchment area, i.e., all grid cells draining towards a certain stream cell. Along the stream network all area was routed towards the direction of the steepest gradient. Using the contributing area for the  $67 \text{ km}^2$  catchment outlet, the average of different catchment attributes was calculated for all cells along the stream network ( $N=1654$ ). As attributes we used map characteristics including surface sediment type from a 1:100000 scale digital Quaternary deposits coverage map (Geological Survey of Sweden, Uppsala, Sweden) and land-cover type from a 1:12500 scale digital land-cover map (Lantmäteriet, Gävle, Sweden). From the Quaternary deposits map, the categories “silt”, “glaciofluvial sediment”, “sand” and “gravel” were lumped to create a “sorted sediment” category. Silt was by far the most common of these, and the “sorted sediment” category is dominated by fine sediments in nearly all catchments. From the land-cover map, the categories “open” and “arable” were lumped to create an “open or arable” category. Additionally, forest information was estimated from satellite data from the national forest inventory by the  $k$  nearest neighbour ( $k\text{NN}$ ) method (Reese et al., 2003). Other parameters were calculated directly from the 50 m DEM as described in the caption to Table 1. In total, 22 different subcatchment characteristics were used to characterize each ( $N=1654$ ) stream grid cell in the entire stream network. For the sampled stream sites ( $N=60$ ) subcatchment characteristics were then extracted from the appropriate grid cells along the stream network.

Our selection of 60 sites covered a wide range of subcatchment characteristics (Table 1) and generally replicated well the distribution of potential sampling sites in the catchment ( $N=1654$  stream cells on 50 m grid) in terms of distribution of characteristics. However, we undersampled the smallest headwaters, giving our distribution of sample sites values of  $0.37 \text{ km}^2$ ,  $3.3 \text{ km}^2$ , and  $18 \text{ km}^2$  for the 10th, 50th, and 90th percentiles of area as compared to  $0.14 \text{ km}^2$ ,  $1.5 \text{ km}^2$ , and  $16 \text{ km}^2$  for the entire network. This under-representation can be explained by two factors: (1) we did not attempt sampling to the upper extent of the wetted channel in most streams, but instead typically took samples just above the first major stream junction; (2) during winter, some of the smaller headwater streams had frozen solid, reducing the size of the stream network relative to the perennial stream network recorded on the 1:100000 map. Distributions of other subcatchment characteristics (surface sediment, land-cover, forest parameters) for the 60 sites deviated little from the distributions of the entire stream network.

Because many landscape parameters which are expected to affect stream chemistry covary, it is difficult to disentangle

effects due to single characteristics. In order to address the issue of covarying landscape parameters, we used PCA (Canoco for Windows v.4.54) to reduce the number of landscape descriptor variables from 22 (Table 1) to several orthogonal principal components (PCs). Subcatchment characteristics of all stream cells in the entire stream network ( $N=1654$ ) were used as input for the PCA. The resulting PCs were then utilized as additional landscape variables in further statistical analyses.

### 3.5. Data analysis

#### 3.5.1. pH Groups

The bulk of the analyses utilized a site grouping approach. The 60 stream sites were classified (Table 2) based on spring flood pH ( $pH_F$ ) and change between winter and spring flood pH ( $\Delta pH$ ). Three categories of pH drop were defined: Stable ( $\Delta pH < 0.4$  pH units), Intermediate drop (0.4–1.0 pH units), and Extreme drop ( $> 1.0$  pH units). Four categories of  $pH_F$  were defined: Low ( $< 5.0$ ), Intermediate (5.0–5.5), High (5.5–5.9) and Very High ( $> 5.9$ ). The intermediate range of pH 5.0–5.5 was selected to correspond to a biologically relevant range where acidity thresholds commonly occur for many stream biota in the region. In a recent study conducted by the Swedish EPA reviewing all available national lake and stream water quality and biological data, pH was recommended as a preferred acidity index over inorganic aluminum ( $Al_i$ ), acid neutralizing capacity (ANC) and other potential chemical metrics. This was because pH was found to correlate as well or better than  $Al_i$  to the presence/absence of acid-sensitive fish species and stages (Holmgren and Buffam, 2005), and better than  $Al_i$  to the presence/absence of acid-sensitive invertebrate species (Fölster et al., 2007). Furthermore these studies suggested that the most critical pH interval for many acid sensitive species in Swedish surface waters is generally between pH 5.0 and 5.5. Thus, in this study the Low  $pH_F$  categories include sites that drop below critical biological thresholds, the Intermediate  $pH_F$  categories include sites right in the critical threshold range, and the High and Very High  $pH_F$  categories have sites

which remain above critical thresholds even during the spring snowmelt period.

When the 60 sites were divided up into these 12 potential combinations of pH criteria, only 7 of the categories contained more than 1 site (Table 2). These 7 categories were defined as the 7 pH groups of interest, and the remaining “lone” sites ( $N=3$  total) were each assigned to the group to which its pH behavior ( $pH_F$ ,  $\Delta pH$ ) was most similar (all 3 sites were within 0.1 pH unit of the group to which they were eventually assigned). These 7 groups of sites were then described and compared with one another in terms of differences in chemistry (baseflow, spring flood, and change between baseflow and spring flood) and catchment landscape characteristics.

#### 3.5.2. Comparison of pH group characteristics

The 7 pH groups each contained between 2 and 16 sites. We undertook to describe the chemical and catchment attributes which characterized each group, and in particular to identify attributes which were outstanding (above average or below average) for a given group of sites. There were two obstacles to direct statistical comparison of the members in each group: First, many of the groups contained sites which were upstream of other sites within the group, thus to some degree autocorrelated in both chemistry and landscape characteristics. Secondly, the groups contained unequal numbers of sites. In order to avoid autocorrelation, and consequently pseudoreplication issues, only “group-independent” sites were used for graphical and statistical evaluation of pH groups (i.e., sites which were independent of all other sites within the same pH group). In this way, only a single site is used to represent a particular part of the stream network in a certain pH category, instead of multiple sites. For each of the 7 pH groups, the maximum number of achievable independent sites was selected, resulting in a total of 2–8 sites per group for a total of 30 group-independent sites (Table 2). Where multiple solutions were possible (e.g., a string of sites with similar pH behavior along a single stream), the site which was spatially nearest to the center of the patch in question was selected. Sites which overlapped in catchment area by  $< 10\%$  were

**Table 2 – Division of 60 stream sites into 7 pH groups**

pH group <sup>a</sup>	$pH_F$	$\Delta pH$	Nr total sites	Nr independent sites <sup>b</sup>	Stream length represented (km) <sup>c</sup>
VHM	Very High ( $> 5.9$ )	Moderate drop (0.4–1.0 pH units)	12	2	16
HM	High (5.5–5.9)	Moderate drop (0.4–1.0 pH units)	16	8	12
HS	High ( $> 5.5$ )	Stable ( $< 0.4$ pH units)	7	4	6
IX	Intermediate (5.0–5.5)	Extreme drop ( $> 1.0$ pH units)	7	4	5
IM	Intermediate (5.0–5.5)	Moderate drop (0.4–1.0 pH units)	8	6	8
LX	Low ( $< 5.0$ )	Extreme drop ( $> 1.0$ pH units)	8	4	8
LS	Low ( $< 5.0$ )	Stable ( $< 0.4$ pH units)	2	2	1

<sup>a</sup> Groups are ordered from highest to lowest mean pH (weighting  $pH_w$  and  $pH_F$  equally).

<sup>b</sup> These “group-independent” sites were used for all figures and analyses involving comparisons of the pH group characteristics.

<sup>c</sup> Stream length represented estimated as described in caption to Fig. 1, further details can be found in Laudon and Buffam (2008).

**Table 3 – Median chemistry (and 5th–95th percentiles in parentheses) for the 60 stream sites used in the study during (1) winter baseflow, (2) spring flood, (3) change between winter and spring**

Variable		Winter baseflow chem	Spring flood chem	Change
pH		6.4 (5.5–6.9)	5.6 (4.5–6.2)	–0.8 (–1.5–0.2)
H <sup>+</sup>	( $\mu\text{eq L}^{-1}$ )	0.4 (0.1–3.4)	2.6 (0.6–31.2)	+2.0 (+0.3–+23.7)
DOC	( $\text{mg L}^{-1}$ )	9 (4–23)	17 (13–25)	+8 (+1–+12)
OA <sup>–</sup>	( $\mu\text{eq L}^{-1}$ )	76 (36–140)	117 (96–145)	+41 (–9–+79)
BC	( $\mu\text{eq L}^{-1}$ )	324 (205–506)	228 (138–323)	–114 (–249–19)
SAA	( $\mu\text{eq L}^{-1}$ )	128 (68–262)	100 (61–186)	–30 (–80–+11)
ANC	( $\mu\text{eq L}^{-1}$ )	206 (99–393)	123 (60–164)	–82 (–215–+4)
Ca <sup>2+</sup>	( $\mu\text{eq L}^{-1}$ )	142 (74–243)	101 (58–173)	–41 (–131–+7)
K <sup>+</sup>	( $\mu\text{eq L}^{-1}$ )	18 (11–37)	20 (7–36)	+2 (–10–+15)
Mg <sup>2+</sup>	( $\mu\text{eq L}^{-1}$ )	76 (43–134)	55 (36–77)	–26 (–66–3)
Na <sup>+</sup>	( $\mu\text{eq L}^{-1}$ )	95 (68–127)	48 (32–76)	–47 (–75–17)
Cl <sup>–</sup>	( $\mu\text{eq L}^{-1}$ )	29 (22–48)	24 (17–35)	–6 (–22–+3)
SO <sub>4</sub> <sup>2–</sup>	( $\mu\text{eq L}^{-1}$ )	98 (37–235)	75 (39–160)	–22 (–70–+9)
NO <sub>3</sub>	( $\mu\text{eq L}^{-1}$ )	5 (0–13)	2 (0–18)	–2 (–10–+12)
Al <sub>tot</sub>	( $\mu\text{g L}^{-1}$ )	125 (50–352)	177 (81–427)	+50 (–104–+260)

DOC=dissolved organic carbon; OA<sup>–</sup>=dissociated organic acids (modeled, including both strong and weak component); BC=base cations; SAA=strong acid anions; ANC=acid neutralizing capacity (BC–SAA).

considered independent of one another. This cutoff value was justified by an empirical variogram (cf. Ganio et al., 2005) using all possible pairwise comparisons of our 60 sites which demonstrated that similarity in pH between sites was increased only when sites overlapped by >10% (Data not shown).

Due to variation in the number of sites per group, a direct comparison of the distribution of catchment or chemistry characteristics between groups using parametric statistics was not possible. Instead, we estimated the likelihood of randomly achieving the observed median values for each attribute for a given pH group. Take as an example the catchment characteristic peatland %. The null hypothesis in this case is that peatland % does not influence pH, and thus sites with low and high peatland % would have an equal probability of being placed in any of the 7 pH groups. If we find that one of the pH groups has an unusually low or high peatland % associated with it (relative to the median peatland % of all 30 sites), then we can reject the null hypothesis and indicate a relationship between peatland % and pH. A Monte Carlo simulation using the statistical program R v.2.4.0 (R Development Core Team, 2006) was used for the analysis. In the simulation, the 30 sites (with associated chemical and catchment attributes) were each randomly assigned to a pH group such that all 7 groups were filled with the appropriate number of sites, and median group values were calculated for each respective attribute. This process was repeated 10000 times. The resulting normal distribution of medians was then compared to the actual observed medians for each respective pH group. A group was considered to have a higher than average value for a particular variable if the actual group median exceeded the 95th percentile of the random distribution, and a lower than average value if the actual group median was less than the 5th percentile. Prior to analysis, non-normally distributed attributes were transformed as appropriate (arcsine $\sqrt{p}$  transformation for proportional catchment cover variables, and log transformation for catchment area and selected skewed chemistry parameters). For chemistry parameters, separate comparisons were made using

winter baseflow values, spring flood values, and change between winter and spring flood.

## 4. Results

### 4.1. Stream chemistry—general

During winter baseflow, pH ranged from 4.6–6.9 (Fig. 1A), with 90% of the sites falling between pH 5.5 and 6.9 (Table 3). The 67 km<sup>2</sup> Krycklan outlet was the site with the highest pH, while there were only two sites with pH below 5 (Fig. 1A). These were both small headwater streams (catchment area <20 ha) with a high proportion of wetlands (>35%). Concentrations of all measured solutes at the different sites ranged considerably at winter baseflow (Table 3).

During spring flood, H<sup>+</sup> concentration increased by between 0 and 33  $\mu\text{eq L}^{-1}$  at the different sites (median 2  $\mu\text{eq L}^{-1}$ ) equivalent to a pH drop ranging from 0–1.6 pH units (median 0.8). This gave rise to a heterogeneous pattern in spring flood pH ranging from 4.3–6.3 (Fig. 1B), with 90% of the sites falling between pH 4.5 and 6.2 (Table 3). Again, the 67 km<sup>2</sup> Krycklan outlet had a higher pH than any of the upstream sites. The lower reaches of the two largest tributaries and the main stem of Krycklan maintained pH above 5.5 during spring flood, while many of the first and

**Table 4 – Linear correlation (Pearson's *r*) between pH and selected chemical parameters for independent headwater stream sites (N=18)**

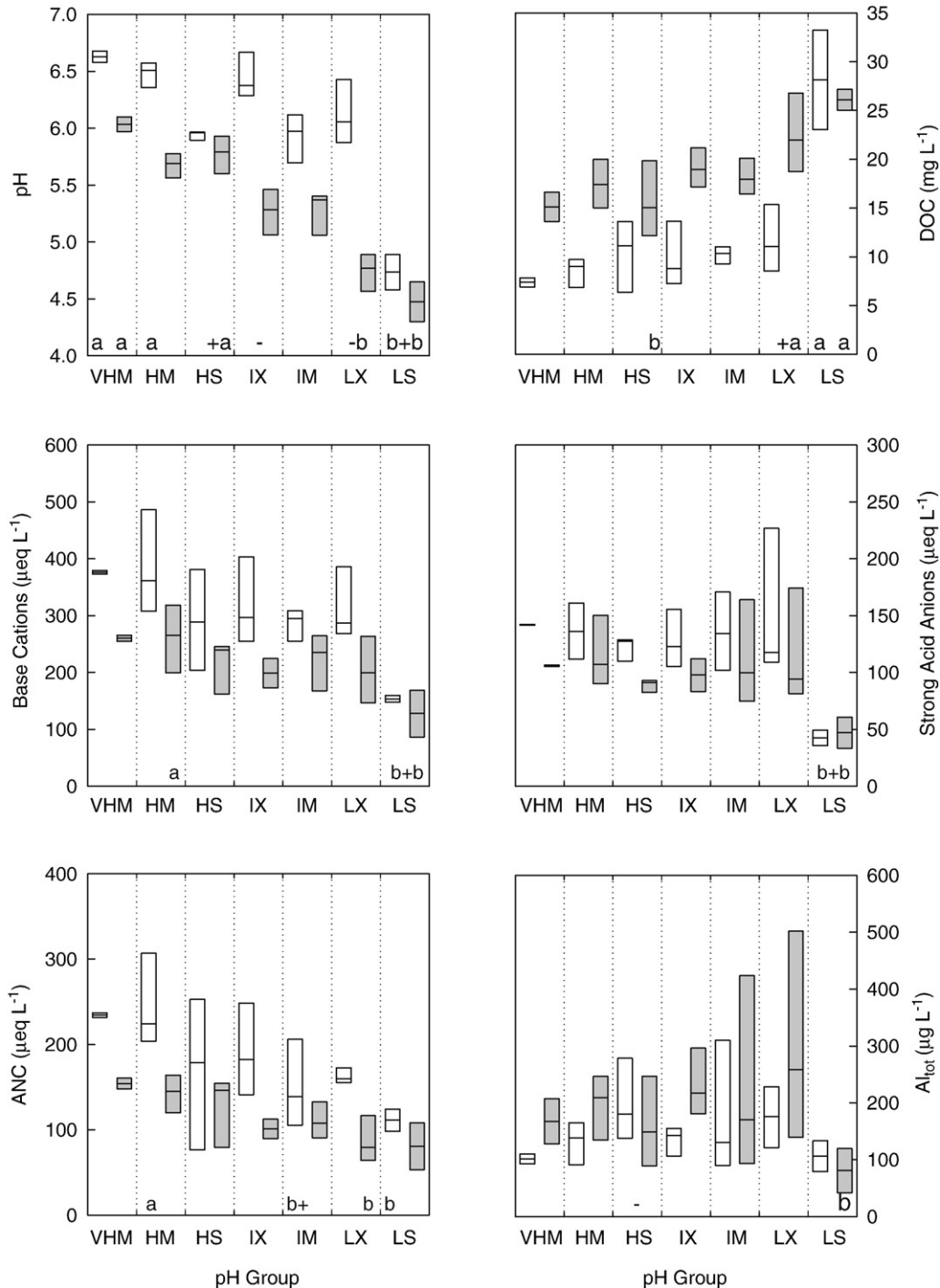
Period	DOC	BC	SAA	ANC	Al <sub>tot</sub>
Winter baseflow (pH <sub>w</sub> )	<b>–0.58</b>	0.24	0.19	0.29	–0.07
Spring flood (pH <sub>f</sub> )	<b>–0.85</b>	<b>0.52</b>	0.26	<b>0.63</b>	–0.19
Transition <sup>a</sup> ( $\Delta\text{pH}$ )	<b>–0.58</b>	–0.20	–0.24	–0.17	<b>–0.55</b>

Significant ( $p < 0.05$ ) relationships are shown in boldface.

<sup>a</sup> This row gives correlations for temporal change in pH ( $\Delta\text{pH} = \text{pH}_w - \text{pH}_f$ ) vs. change in other chemical parameters during the same period.

second order streams dropped to pH below 5.0, particularly in the central part of the catchment underlain by till and peat (Fig. 1B). The pH drop was accompanied at most sites by an

increase in DOC (median change +8 mg L<sup>-1</sup>) and a decrease in BC, SAA, and ANC (median change -114 μeq L<sup>-1</sup>, -30 μeq L<sup>-1</sup>, and -82 μeq L<sup>-1</sup> respectively). Al<sub>tot</sub> increased at 45 of 60 sites (median



**Fig. 2**–Boxplots (25th, 50th, 75th percentiles) with key chemistry parameters during winter baseflow (white) and spring flood (grey) at stream sites divided into 7 groups by pH behavior (Table 2). For groups VHM and LS, which have only 2 members, the mean and the two individual values are shown. At the bottom of each panel, the lowercase letters signify groups whose medians were significantly above (“a”) or below (“b”) average for that chemical attribute (see methods section for details of analysis). The symbols “+” or “-” denote groups which had a significantly more positive or more negative change between winter baseflow and spring flood chemistry as compared to the average change. For instance, the “a a” on the first panel for cluster VHM means that cluster VHM had above-average pH during both winter baseflow and spring flood. One small headwater site in group HS with outlier winter baseflow chemistry was excluded from the figure (see text of results for details).



change  $+50 \mu\text{g L}^{-1}$ ). At the time of the spring flood sampling, the range in concentrations of most measured solutes was reduced as compared to winter baseflow, with DOC having a particularly low spatial variability during spring flood (Table 3).

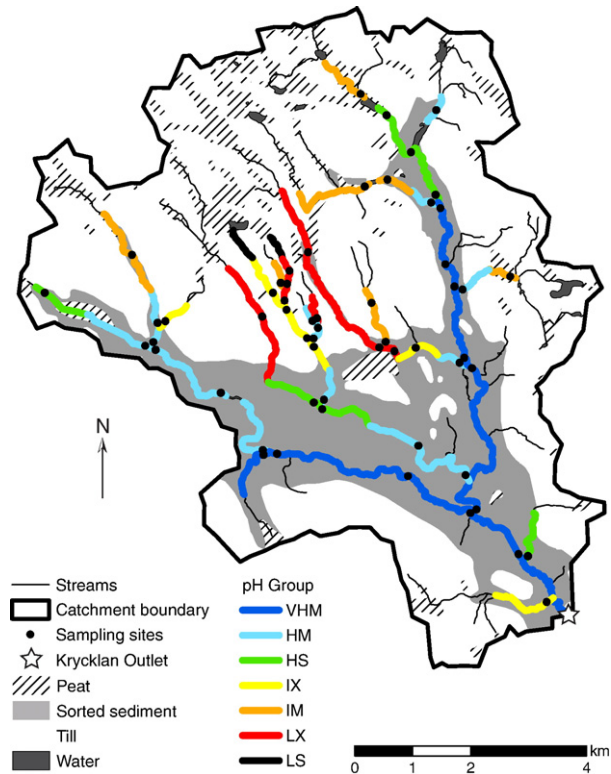
In a correlation analysis of all independent headwater sites ( $N=18$ ), pH was strongly negatively correlated with DOC during both winter baseflow and spring flood (Table 4).  $\Delta\text{pH}$  was also negatively correlated with  $\Delta\text{DOC}$  and  $\Delta\text{Al}_{\text{tot}}$ —that is, sites which decreased the most in pH during spring flood tended to be those that increased the most in DOC and  $\text{Al}_{\text{tot}}$ . Otherwise, there were few consistent correlations between pH and the other major chemistry measures, though spring flood pH was positively correlated with  $\text{BC}_F$  and  $\text{ANC}_F$ .

#### 4.2. Downstream trends in chemistry

During both winter baseflow and spring flood, pH was higher at the Krycklan outlet than at any of the other 59 upstream sites. There was a trend in essentially all tributaries of increasing pH with distance downstream (Fig. 1A and B). The largest jumps in pH typically occurred near the transition from the upper half of the catchment underlain by peat/till, to the lower half of the catchment underlain by large deposits of silt/sand (Fig. 1). During both winter baseflow and spring flood, larger downstream sites tended to have higher pH, BC, ANC,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  than headwaters (Table 5). During winter baseflow, DOC was lower in larger streams than in the headwaters, but during spring flood there was less of a difference in DOC between sites (Table 5).

#### 4.3. Stream chemistry—pH groups

The stream sites were organized into 7 pH groups (Table 2) based on spring flood pH ( $\text{pH}_F$ ) and change between winter baseflow and spring flood pH ( $\Delta\text{pH}$ ). The groups with higher pH (i.e. VHM, HM, HS) tended to have relatively low DOC, high BC and high ANC (Fig. 2), while SAA and  $\text{Al}_{\text{tot}}$  were less clearly associated with pH. The groups could be described as ranging between those indicating flowpaths interacting predominantly with



**Fig. 3**—Map of the Krycklan stream network. Stream segments are colored by pH group, with values extended from measured points as in Fig. 1. Primary surficial sediment deposits are shown in the background (Geological Survey of Sweden, Quaternary Deposits Map Ak19, ©1995).

**Table 5**—Comparison of headwater chemistry (median,  $N=18$  independent 1st/2nd order headwaters) with chemistry of the 4th order Krycklan Outlet

Variable	Winter baseflow		Spring flood	
	Headwaters	Outlet	Headwaters	Outlet
pH	6.1	6.9	5.4	6.2
$\text{H}^+$ ( $\mu\text{eq L}^{-1}$ )	0.8	0.1	4.3	0.6
DOC ( $\text{mg L}^{-1}$ )	10	5	18	16
$\text{OA}^-$ ( $\mu\text{eq L}^{-1}$ )	73	46	116	125
BC ( $\mu\text{eq L}^{-1}$ )	288	462	219	268
SAA ( $\mu\text{eq L}^{-1}$ )	125	160	95	109
ANC ( $\mu\text{eq L}^{-1}$ )	160	301	106	158
$\text{Ca}^{2+}$ ( $\mu\text{eq L}^{-1}$ )	115	214	93	102
$\text{K}^+$ ( $\mu\text{eq L}^{-1}$ )	15	32	16	33
$\text{Mg}^{2+}$ ( $\mu\text{eq L}^{-1}$ )	69	118	50	72
$\text{Na}^+$ ( $\mu\text{eq L}^{-1}$ )	90	98	44	60
$\text{Cl}^-$ ( $\mu\text{eq L}^{-1}$ )	26	44	23	30
$\text{SO}_4^{2-}$ ( $\mu\text{eq L}^{-1}$ )	98	117	73	79
$\text{NO}_3^-$ ( $\mu\text{eq L}^{-1}$ )	5	6	0	17
$\text{Al}_{\text{tot}}$ ( $\mu\text{g L}^{-1}$ )	135	61	175	196

mineral soils (high pH, high BC, high ANC, low DOC) and those indicating flowpaths interacting more with organic soils (low pH, low BC, low ANC, high DOC). There was a single site which did not follow this pattern, a small ( $0.5 \text{ km}^2$ ) headwater catchment with a large recent clearcut (33% by area). Although its spring flood chemistry was unremarkable, during winter baseflow, this site had the highest DOC of any of the 60 sites and concentrations of BC, ANC, SAA,  $\text{Al}_{\text{tot}}$  and DOC several-fold higher than any other site. The site represented only a tiny fraction of the stream network in terms of flow and area, but may warrant further study. For the purposes of visualization of the typical chemistry of the pH groups for this study, it was considered an outlier and was excluded from Fig. 2.

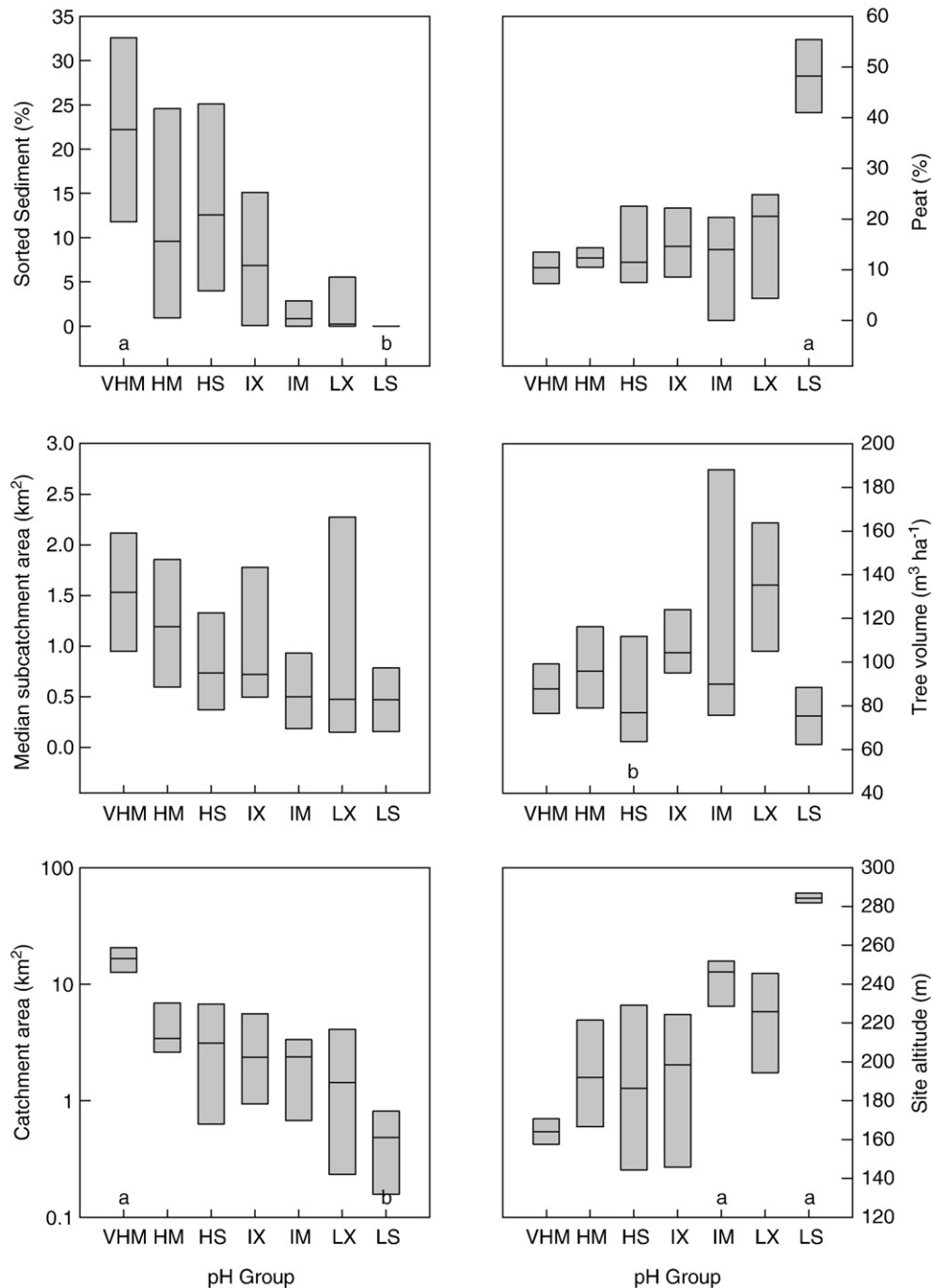
For all groups, changes in chemistry during spring flood (increasing DOC, decreasing pH, BC, ANC) were consistent with a shift towards greater influence of organic flowpaths coupled with the contribution of new snowmelt during spring flood. The most acidic group LS was characterized by low but stable pH (median  $\text{pH}_W=4.7$ ,  $\text{pH}_F=4.5$ ), high but unchanging DOC, and low, relatively constant BC, SAA, ANC and  $\text{Al}_{\text{tot}}$ . The other 6 groups all had winter baseflow pH above critical thresholds, but varied widely in  $\Delta\text{pH}$ . Differences in behavior of the intermediate pH groups are illustrated by the contrast between groups HS and LX. Group HS contained sites of intermediate pH which changed very little during spring flood, while group LX was characterized by a larger than average pH drop resulting in spring flood pH at potentially toxic levels (Fig. 2). These two pH

groups had similar chemistry during winter baseflow (Fig. 2). The main difference in chemistry aside from the difference in  $\Delta\text{pH}$ , was the fact that group LX had a significantly greater increase in DOC during spring flood (median  $\Delta\text{DOC} + 11 \text{ mg L}^{-1}$  to give a higher than average median  $\text{DOC}_F$ ) as compared to group HS (median  $\Delta\text{DOC} + 5 \text{ mg L}^{-1}$  to give a lower than average  $\text{DOC}_F$ ) (Fig. 2). Group LX also had lower than average  $\text{ANC}_F$  resulting from substantial ANC dilution, contributing to the low  $\text{pH}_F$ . Sites in the well-buffered group HS had an uncharacteristic dilution

of  $\text{Al}_{\text{tot}}$  (median  $\Delta\text{Al}_{\text{tot}} - 40 \mu\text{g L}^{-1}$ ) during spring flood, while group LX increased (median  $\Delta\text{Al}_{\text{tot}} + 101 \mu\text{g L}^{-1}$ ).

#### 4.4. Catchment characteristics—pH groups

Although no spatial consideration was taken in assigning the pH groups, several of the groups formed large continuous patches/clusters of sites of similar pH behavior to give a clear spatial pattern (Fig. 3). The pH groups roughly corresponded to



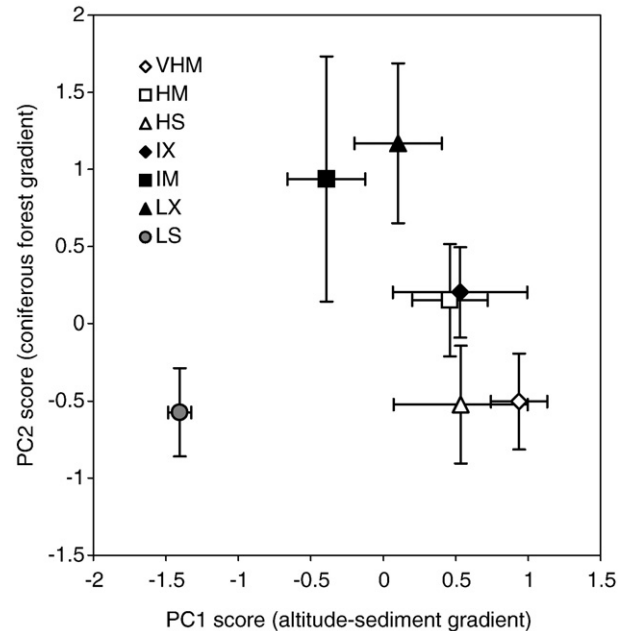
**Fig. 4**—Boxplots (25th, 50th, 75th percentiles) of selected landscape characteristics for subcatchments corresponding to stream sites in the 7 pH groups (Table 2, Fig. 3). For groups VHM and LS, which have only 2 members, the mean and the two individual values are shown. At the bottom of each panel, the lowercase letters signify groups whose medians were significantly above (“a”) or below (“b”) average for that attribute (see methods section for details of analysis).

characteristic catchment attributes for the respective sub-catchments (Fig. 4). The highest pH groups (VHM, HM, HS) tended to have catchments with a high proportion of sorted sediment, low/intermediate peat proportion, large catchment and mean subcatchment areas, low altitude and low tree volume. Group VHM had sites with significantly above average sorted sediment and catchment area. The acidic-but-stable group LS was comprised of 2 small headwater peatland catchments, which were distinguished by lower than average sorted sediment proportion and catchment area, and higher than average altitude and peat proportion.

The other five groups were generally intermediate in catchment characteristics between these two extremes (with the exception of tree volume). Group HM, with slightly lower pH than VHM, was similar in landscape characteristics, but was comprised of smaller streams (median area 3.4 km<sup>2</sup>) with lower sorted sediment coverages (median 10%). The exceptionally well-buffered group HS was characterized by intermediate sized catchments with fairly high sorted sediment coverage, and lower than average total tree volume (Fig. 4). Several of the sites in this stable pH group had lakes upstream in the stream network in the northeast portion of the catchment (Fig. 3). Group LX, which experienced the largest pH drop, had sites with the greatest total tree volume, owing to above average stand age, tree height and volume of Scots pine (data not shown). Sites in this group were also devoid of lakes and open/arable land, and had very low or no sorted sediments (Figs. 3 and 4).

In order to address the issue of covarying landscape characteristics, we used PCA to reduce the number of landscape descriptor variables from 22 (Table 1) to two major principle components (PCs). These PCs captured 80% of the overall variation in the subcatchment characteristics, and could be described as (PC1) an altitude-sediment gradient and (PC2) a coniferous forest gradient. PC1 described 54% of the total variation in the landscape dataset, and high PC1 scores were associated most strongly with sites with low altitude, below the former high coast line, and with high fine sorted sediment coverage (factor loading scores  $-0.97$ ,  $-0.87$ , and  $0.73$ , respectively). Also covarying with PC1, though more weakly, were catchment area ( $0.44$ ), open/arable land ( $0.41$ ), wetland ( $-0.55$ ), and peat ( $-0.53$ ). PC2 described 26% of the total variance, and was associated with sites with high total tree volume, high spruce volume, and high pine volume (factor loading scores  $0.97$ ,  $0.91$ , and  $0.82$ , respectively). PC2 was also associated with forest land cover ( $0.44$ ), high birch volume ( $0.50$ ), and till ( $0.41$ ).

The pH groups had distinct signatures in terms of the two landscape PC gradients. The groups with highest pH (VHM, HM, HS) scored high on PC1, i.e. were characterized by catchments with large area, low altitude, and a large coverage of sorted sediments (Fig. 5). The group with lowest pH (LS) scored negatively on PC1, i.e. was characterized by small catchments of high altitude with large peat deposits and no sorted sediment, while the intermediate pH groups had intermediate scores on PC1. The second PC axis correlated moderately well with the pH groups in terms of pH change. Relatively stable groups (VHM, HS, LS) scored negatively on PC2, i.e. were characterized by low coniferous forest density. The group with the largest pH drop (LX) had the highest loading on PC2 (highest



**Fig. 5 – pH Group scores (mean and standard error of the mean of independent sites from each group) on principle components describing major landscape variation. High PC1 corresponds to stream sites with low altitude and high proportion of fine sorted sediment in their catchments. High PC2 corresponds to stream sites with catchments containing high spruce and pine density.**

coniferous forest density, resulting from a high proportion of older stands of pine and spruce), while the other three groups scored intermediately on this PC axis.

## 5. Discussion

### 5.1. Stream acidity in a heterogeneous landscape

The analysis of a reasonably large number of sites distributed throughout the same network enabled us to see spatial patterns in the aquatic landscape at a scale that would not have been apparent from samples taken in separate independent streams. For the 60 stream sites in this mesoscale catchment, different chemical analytes varied spatially from 3-fold to 200-fold at a given point in time (Table 3). The pH drop and other chemical changes during spring flood also ranged considerably between sites. However, the chemical heterogeneity could be summarized into groups of similar pH which were often spatially aggregated, and this spatial aggregation of pH behavior corresponded roughly to patterns in the underlying landscape (Fig. 3).

During both time periods, the highest pH was found in groups of sites with catchments having a high proportion of fine sorted sediments, large area, and low altitude. The relatively high pH, high BC, low DOC conditions prevalent during winter baseflow gave way in most streams to an increase in DOC and dilution of BC and ANC during spring flood, resulting in a pH drop. These changes are characteristic

of spring flood events in the region (Laudon et al., 2000). Spatial heterogeneity was largely maintained in terms of all measured analytes except DOC, which became less spatially variable during spring flood as previously observed (Buffam et al., 2007). Changes could be attributed to a shift in most sites from deeper flowpaths intersecting mineral soils (at baseflow) to rising flowpaths intersecting organic soil horizons (during spring flood) coupled with influx of new dilute snowmelt (cf. Buffam et al., 2007; cf. Schiff et al., 1998). The magnitude of the acid pulse however varied greatly (0–1.6 pH units) between stream sites, resulting in a change in the spatial pattern of pH within the stream network. The largest pH drop was observed in groups of sites which increased greatly in DOC during spring flood, and which had small/intermediate sized catchments with high coniferous forest density, no fine sorted sediment, no lakes, and medium or high proportion of wetlands. DOC in this study and others in the boreal forested zone has been found to strongly influence pH by contribution of organic acids (e.g., Köhler et al., 1999). Lakes buffer temporal changes and mineralize DOC (Cole et al., 2007; Dillon and Molot, 1997; Temnerud et al., 2007), which likely explains why their presence was associated with groups with a smaller pH drop during spring flood (Fig. 3). High coniferous forest density is typically associated with acidic, organic-rich litter layer and soils, which may contribute to acidity when water tables rise into organic soil layers as during the spring flood.

### 5.2. Implications for sampling heterogeneous stream networks

Earlier studies in the Krycklan catchment with a smaller number of intensively studied sites have shown that sub-catchment proportion of wetlands strongly influences hydrological flow pathways (Laudon et al., 2007) and changes in DOC, ANC, pH (Buffam et al., 2007),  $Al_i$  and  $Al_{tot}$  (Cory et al., 2006) during the spring flood period. The current more spatially comprehensive study additionally highlights the importance of Quaternary deposit sediment characteristics, tree volume, altitude and catchment area. These and other landscape attributes should be considered when designing sampling programs to represent a stream network. As many of these factors covary, it may neither be practical nor desirable to sample all combinations of these variables in a factorial design. A logical starting point would be to represent the extremes (representatives of the pH groups in this study, for instance) using headwater catchments, and additionally follow changes with distance downstream for a few streams differing in landscape characteristics.

### 5.3. Scale issues and downstream trends

Notably, during both sampling periods the Krycklan outlet site had higher pH than any of the 59 upstream sites, and as a general rule BC, ANC and pH increased with distance downstream, while DOC decreased (Fig. 1, Table 5). These downstream trends are similar to those observed in previous catchment studies in Sweden (Temnerud and Bishop, 2005) and in other northern regions (Chapman et al., 1993; Driscoll et al., 1988; Likens and Buso, 2006). Particularly during winter baseflow, stream chemistry at the Krycklan outlet cannot be

explained by mixing of the headwaters alone. As the impact of in-stream processing on stream chemistry in the Krycklan stream network is believed to be relatively minor (Köhler et al., 2002), the observed trend implies a substantial additional contribution of high BC, high ANC, low DOC water in the larger streams, especially during winter baseflow. The most plausible source is deep groundwater.

Groundwater inputs with these characteristics are often associated with long subsurface water transit times, contact with relatively more weatherable minerals with high surface area, and flowpaths that do not intersect sources of organic matter in the riparian zone. Increasing length of flow pathways (Driscoll et al., 1988; Johnson et al., 1981) coupled with increased within-catchment water transit times with distance down a stream system have been implicated in other catchments to explain similar downstream trends. In Krycklan, water tables are much deeper in the low-altitude fine sediment zones than in the region of unsorted till (unpublished data), suggesting longer flow pathways. The groups of sites which had higher pH and were well-buffered (highest BC and ANC) tended to have both high catchment area and high median subcatchment area (Fig. 4). Median subcatchment area accounts for the spatial arrangement of stream networks in the landscape, and has been found to be correlated with within-catchment water transit time (McGlynn et al., 2003). This suggests longer within-catchment transit times for these sites, thus greater hydrological contact with mineral sediments which could increase BC, decrease DOC and thereby contribute to the observed downstream trends in pH. Additionally, by nature of having deeper stream channels and being lower in the landscape, the larger streams could be receiving a more consistent contribution of deep slow-moving groundwater than the headwaters.

Variations in sediment/soil type have been cited in other studies as contributing to similar altitudinal stream chemistry gradients (e.g., Soulsby et al., 2006). The dominant surficial sediment type in Krycklan shifts from till to fine sorted sediments (primarily silt) as the streams pass from above to below the former high coast line. Silt has a higher specific surface area than unsorted till and is therefore rich in mineral adsorption sites which bind DOC (Kalbitz et al., 2000), as well as having a greater surface area for weathering and release of BC. Based on a multi-year DOC flux study in Krycklan, the bulk of the DOC enters the network through small headwater streams in upper reaches of the catchment, and is then attenuated during passage into the lower lying areas underlain by fine sorted sediment (Ågren et al., 2007). This attenuation is attributed in part to differences in riparian zone soil characteristics. In the forested till headwater areas, peat builds up in the near-stream zones, serving as a source for stream DOC (Bishop et al., 1995, 2004) particularly during high flow episodes when water tables are elevated. In the lower-lying silty areas, stream channels are more deeply incised, water tables are deeper and organic soil horizons in the riparian zone are thinner (Ågren et al., 2007). Thus, subsurface hydrological flowpaths presumably rarely intersect riparian organic soils en route to the larger streams, resulting in lower stream DOC concentrations. As DOC and pH are strongly negatively correlated (Table 4), this DOC drop contributes to higher pH in the larger streams. Shifts in forest

type from coniferous to deciduous were cited as contributing to downstream trends in stream acidity in a North American study (Driscoll et al., 1988), but in Krycklan we found no evidence of a consistent shift in forest type or density with distance downstream or catchment size (Table 1, Fig. 4).

#### 5.4. Role of within-catchment spatial distribution

In the current study, stream pH and related chemistry was associated with lumped catchment characteristics like proportion of sediment type and peat coverage. Other studies in similar landscapes have found strong correlations between mean catchment characteristics and stream DOC concentration (Andersson, 2005; Creed et al., 2003). Gergel et al. (1999) found that for streams and rivers in Wisconsin, USA, bulk landscape characteristics were as good as or better than near-stream characteristics at predicting stream DOC. Does this indicate that within-catchment spatial arrangement is not an important controlling factor for the chemical parameters of interest? In a study over a range of scales, empirical models relating landscape characteristics to stream characteristics tended to fall apart for small (<1–10 km<sup>2</sup>) catchments, suggesting that spatial arrangement of landscape patches may become important at these scales (Strayer et al., 2003). For instance, the connectivity of wet areas to a stream network varies over time and plays a role in the temporal variation in stream chemistry (Buttle et al., 2004; Creed and Band, 1998). Furthermore, the importance of the riparian zone in giving a signature to stream chemistry has been established in northern Sweden (Bishop et al., 2004, 1995) as well as other regions (Buttle et al., 2004; Hinton et al., 1998). This implies that use of lumped catchment characteristics in correlating with stream chemistry as we have done here, may not always be appropriate. However, because riparian zone characteristics may follow upland characteristics, riparian–stream chemistry relationships may be obscured within mean catchment–stream chemistry correlations. In Krycklan for instance, as previously mentioned the riparian soil characteristics differ between till-dominated areas at higher altitudes and lower lying areas with fine sorted sediment. Explicit consideration of within-catchment spatial organization would likely add to our understanding of landscape–stream chemistry linkages.

#### 5.5. Implications for modeling stream water chemistry

Defining catchment characteristics for all stream cells in the stream network as we have done here could prove a promising foundation for modeling chemistry in a spatially continuous way at different time periods. Cooper et al. (2004) have for instance used a typology approach with soil/geology characteristics to create spatially distributed models of stream ANC. Evans et al. (2006) extended this approach to examine stream ANC behavior over time and with different acid deposition scenarios. For the Krycklan stream network and similar boreal catchments, modeling of this type should include surface sediment type (till vs. sorted sediment), peatlands, and degree of coniferous forest development. These all played a role in determining stream chemistry relevant to acidity and the size of the spring flood acid pulse. The pattern of decreasing DOC and increasing BC, ANC, pH

with distance downstream suggests that catchment/stream scale is also important to consider, though this might also be explained by covarying landscape characteristics (sediment type, slope, altitude, median subcatchment area). Furthermore, within-catchment spatial arrangements of wetlands are expected to be important in controlling stream chemistry, especially for smaller catchments. Thus, mixing models are expected to fall short in describing the spatiotemporal patterns in stream chemistry, unless they also account for scale-related processes such as water transit times and the spatial arrangement of landscape units.

#### 5.6. Implications for acid-sensitive biota

In this mesoscale catchment, there were large patches of many km in stream length which were well-buffered and maintained relatively high pH, while other patches/tributaries exceeded known pH toxicity thresholds during spring flood (Fig. 3). Acid-sensitive organisms might be expected to distribute themselves accordingly. However, in order to account for the chemical limitations placed on acid-sensitive organisms, distributions in both pH and inorganic aluminum (Al<sub>i</sub>) must be considered (Åtland and Barlaup, 1995; Buffam, 2007; Gensemer and Playle, 1999). In Krycklan, the spatiotemporal patterns in pH are different from those of Al<sub>tot</sub> and Al<sub>i</sub>. The current study suggests that the largest pH drop is seen in small/intermediate-sized catchments with mixed wetland (peat) and forest (till) land cover, and the lowest consistent pH in headwater wetland sites. However, a companion study in Krycklan found that spring flood Al<sub>i</sub> was highest in headwater forest (till) sites with no wetlands (Cory et al., 2006), at times exceeding 100 µg L<sup>-1</sup>. This exceeds acute toxic thresholds for sensitive salmonids (Gensemer and Playle, 1999). Consideration of spatial arrangement of some landscape elements (wetland patches) may therefore be important for field studies of acid toxicity. Spatial heterogeneity of chemistry in stream networks can also create toxic zones at stream junctions due to mixing of waters of different pH in the presence of dissolved Al (Åtland and Barlaup, 1995; Poléo et al., 1994), further arguing for spatially explicit description of acid chemistry in stream networks.

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