Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network

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[1] Acidity is well known to influence stream biota, but the less well-studied spatial and temporal distributions of acidity are likely to play a larger ecological role than average values. We present data on spatial variability of chemical parameters contributing to acidity during winter baseflow and spring flood periods in Krycklan, a fourth-order boreal stream network in northern Sweden. Fifteen stream sites were monitored in subcatchments spanning 3 orders of magnitude in size and representing a wide range of percent wetland. At baseflow, pH ranged from 3.9 to 6.5 at the different sites. Baseflow dissolved organic carbon (DOC) concentration varied by an order of magnitude and was positively correlated with subcatchment percent wetland, resulting in high spatial variability in dissociated organic acids (OA^-). During spring flood, DOC and OA^- increased in forested sites and decreased in wetland sites, resulting in reduced spatial variability in their concentrations. In contrast, base cations and strong acid anions diluted throughout the stream network, resulting in decreased acid neutralizing capacity (ANC) at all sites. The spatial variability of base cations increased slightly with high flow. As a result of the changes in OA^- and ANC, pH dropped at all but the most acidic site, giving a slightly narrowed pH range during spring flood (4.2–6.1). The transition from winter to spring flood stream chemistry could largely be explained by: (1) a shift from mineral to upper riparian organic soil flow paths in forested catchments and (2) dilution of peat water with snowmelt in wetland catchments.

1. Introduction

[2] Boreal stream networks are embedded in a mosaic of wetlands and lakes interspersed in the forest landscape. This mosaic results in complex and dynamic water chemistry that varies depending on stream size, catchment characteristics, season and flow. Untangling the processes underlying this complex water chemistry at a landscape scale is difficult, because most of our present process understanding is based on small-scale plots, hillslopes and very small catchments. Conversely, most questions about sustainability of water resources and protection of aquatic ecosystems concern the landscape scale. Knowledge about how different landscape units interact over a range of catchment sizes is fundamental for our understanding of processes and patterns in runoff chemistry at larger spatial scales. One relevant question is how the mosaic of wetlands and forested patches interact to control acidity in a stream network during snowmelt episodes.

[3] The patchy nature of acidity in stream and soil water occurs on scales ranging from plot [*Allan et al.*, 1993] to regional [*Cresser et al.*, 2000; *Hutchins et al.*, 1999]. This variation is typically related to natural variation in geology, soils, vegetation and/or sea-salt deposition [*Hutchins et al.*, 1999], or gradients of anthropogenic impact from point sources (e.g., mining) and atmospheric acid deposition [*Galloway*, 2001]. At the watershed scale, high spatial variability in stream water acidity has been noted in many regions including the temperate Catskill Mountain region of New York [*Wolock et al.*, 1997] and the boreal zone of northern Sweden [*Ivarsson and Jansson*, 1994; *Temnerud and Bishop*, 2005].

[4] Landscape heterogeneity has been cited as a driving factor in stream chemistry variability [*Humborg et al.*, 2004; *Hunsaker and Levine*, 1995; *Thomas et al.*, 2004]. Of particular relevance to the acid chemistry of boreal streams, streams draining wetlands generally have elevated dissolved

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organic carbon (DOC) [*Aitkenhead et al.*, 1999; *Creed et al.*, 2003; *Gergel et al.*, 1999; *Hope et al.*, 1994; *Mulholland*, 2003]. Boreal catchments with high-percent wetland thus commonly provide high concentrations of organic acids associated with DOC, resulting in acidic waters in areas where mineral weathering rates are low [*Urban et al.*, 1989]. In regions which have experienced relatively low levels of acid deposition, these naturally occurring organic acids frequently play a primary role in controlling the acidity of surface waters [e.g., *Campbell et al.*, 1992; *Kortelainen and Saukkonen*, 1995].

[5] A recent study of the stream networks in two Swedish boreal catchments at summer low flow found high variability in alkalinity, DOC and H^+ concentrations, each spanning an order of magnitude or more [*Temnerud and Bishop*, 2005]. *Ivarsson and Jansson* [1994] also found over an order of magnitude variation in DOC in small coastal streams in Sweden at baseflow, much of which could be explained by the extent of near-stream wetlands.

[6] In such boreal streams the spring flood episodes are likely to present a critical constraint on aquatic life, because these episodes deliver pronounced pulses of acidity along with half of the annual export of water and DOC [*Laudon et al.*, 2004a]. During the spring flood, Swedish boreal forest streams commonly increase in DOC concentration and dilute in acid neutralizing capacity (ANC), resulting in reduced pH [*Laudon and Bishop*, 1999]. The riparian zone has been proposed as the source of increased DOC in Swedish headwater boreal forest streams, by the mechanism of raised water tables intersecting near-surface organic-rich riparian soils [*Bishop et al.*, 2004]. The riparian zone has also been implicated as an important but spatially variable contributor to DOC during episodes in Precambrian shield watersheds in Canada [*Hinton et al.*, 1998].

[7] A picture emerges of a heterogeneous landscape which gives rise to highly spatially variable baseflow chemistry, and a variable response to high-flow episodes. However, changes in spatial variability within an entire stream network during this particularly acidic period of spring flood have not previously been thoroughly documented. The spatial patterns in acidity in a stream network context are likely to be important for mobile organisms such as the acid-sensitive Atlantic salmon (*Salmo salar*) and Brown trout (*Salmo trutta*), both commonly found in Swedish watercourses. Even during periods of episode-induced acid stress, stream reaches that are well-buffered may provide refugia patches. This raises the question: Does the body of surface water comprising a stream network become more or less heterogeneous during spring flood?

[8] We hypothesized that spatial variability in stream water chemistry would be reduced during the snowmelt-induced spring flood period as compared to baseflow, with the following rationale: At high flows, the dominant flow pathways in forested till catchments pass through riparian surficial organic soils [*Bishop et al.*, 2004; *Hinton et al.*, 1997], which are more similar to the organic rich flow paths that dominate in peat wetlands at all times.

[9] The objectives of this study are to (1) compare the behavior of streams from forested and wetland subcatchments in a Swedish boreal catchment with respect to changes in water chemistry during the transition from winter baseflow to spring flood, (2) compare the spatial

variability in acidity (as pH) and related chemistry (concentrations of strong acid anions, base cations, ANC, DOC and organic acids) between baseflow and spring flood in a Swedish boreal stream network, and (3) elucidate processes responsible for observed changes.

2. Site Description

[10] The study area is the upper 67 km^2 of the Krycklan River catchment in northern Sweden (Figure 1). This catchment includes the Vindeln 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 600 mm annual mean precipitation, of which one third falls as snow [*Ottosson Löfvenius et al.*, 2003]. Snow cover persists for 171 days on average (1980–1999), and spring snowmelt is the dominant hydrological event, exporting up to half of the annual stream flow during a 3- to 6-week period in April–May.

[11] 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 owing to high infiltration capacity of the till soils [*Bishop et al.*, 1990; *Nyberg et al.*, 2001]. Stream water chemistry has been monitored regularly for the past 25 years [*Fölster and Wilander*, 2002; *Grip and Bishop*, 1990].

[12] The Krycklan study catchment ranges from 130 to 369 m above sea level. Throughout the catchment, gneissic bedrock is overlain by till varying in thickness up to tens of meters [*Ivarsson and Johnsson*, 1988]. Well-developed iron-podzol soils are common. In the lower reaches of the catchment, larger streams have deeply incised channels carving through fine-grained floodplain sediments. 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 sphagnum-dominated peat wetlands, making up 8% of the catchment area, with up to 76% coverage in some of the smaller 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*) and Brook trout (*Salvelinus fontinalis*) are common in many of the larger streams.

3. Methods
3.1. Subcatchment Selection and Site Location

[13] Fifteen intensively studied subcatchments within Krycklan span a wide range of areal coverage of wetland and forest, the two major landcover types in the region (Figure 1 and Table 1). Year-round site accessibility was also considered in site selection. Boreal coniferous forest is present in all subcatchments and dominates in all but one, while four of the subcatchments have a small amount of arable land under cultivation (<4%). Peat wetland coverage ranges from 0 to 76%. One of the sites (Site 5, Stortjärnen Outlet) drains a small humic-rich lake, while another sub-
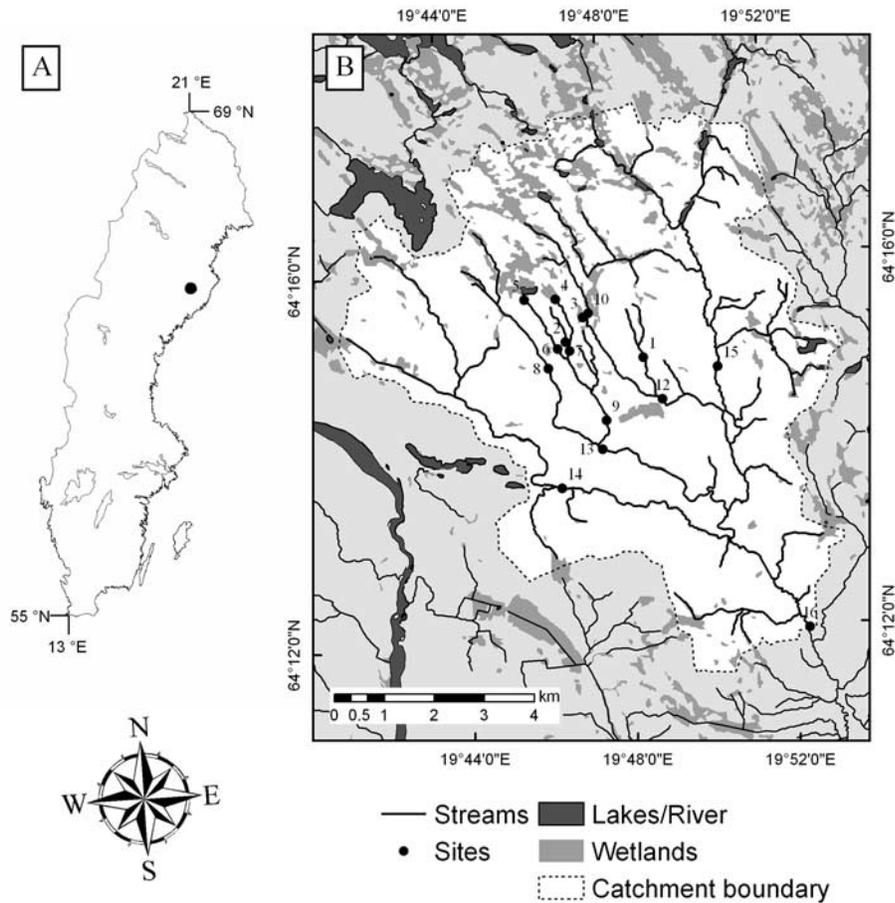
Figure 1. (a) Map of Sweden with Krycklan catchment location marked. (b) Location of stream sampling points throughout the Krycklan stream network within the catchment (catchment area shown in white). Wetland patches are shown in dark grey.

catchment (Site 15, Övre Krycklan) contains a large number of upstream lakes. Six of the larger streams include contributions of flow from upstream sampling sites (Figure 1).

3.2. Subcatchment Delineation

[14] Subcatchment boundary delineations were determined on the basis of a 50-m-grid digital elevation model (DEM) using software within the ArcGIS 8.0 framework.

For the smallest catchments (<2 km^2), field surveys updated catchment boundaries. Catchment area and percent of various landcovers were determined in ArcGIS using 1:50,000 scale digital maps (Lantmäteriet, Gävle, Sweden).

3.3. Field Sampling

[15] Water sampling consisted of grab samples taken at 15 stream sites (Table 1) weekly or biweekly during late

Table 1. Catchment Characteristics for 15 Stream Sites[a]

Site Number	Name	Stream Order	Area, km^2	Lake, %	Forest, %	Wetland, %	Arable, %	Landcover Type
1	Risbäcken	1	0.66	0	98.7	1.3	0	forested
2	Västrabäcken	1	0.13	0	100.0	0	0	forested
3	Lillmyrbäcken	1	0.03	0	24.0	76.0	0	wetland
4	Kallkälsmyren	1	0.19	0	59.6	40.4	0	wetland
5	Stortjärnen Outlet	1	0.85	4.7	59.0	36.3	0	wetland
6	Stortjärnbäcken	1	1.3	3.1	72.8	24.1	0	mixed
7	Kallkälsbäcken	2	0.50	0	85.1	14.9	0	mixed
8	Fulbäcken	2	2.5	0	88.7	11.3	0	mixed
9	Nyängesbäcken	2	3.1	1.3	84.9	13.8	0	mixed
10	Stormyrbäcken	3	2.9	0	74.2	25.8	0	mixed
12	Nymyrbäcken	3	5.4	0	84.1	15.5	0.3	mixed
13	Långbäcken	3	7.2	0.6	89.1	9.9	0.4	mixed
14	Åhedbäcken	3	14	0.6	90.4	5.1	3.9	mixed
15	Övre Krycklan	4	20	1.7	83.2	14.0	1.0	mixed
16	Krycklan	4	67	0.7	88.0	8.3	3.0	mixed

[a]Landcover type was defined by percent wetland coverage, with $<2\%$ wetland "forested", $2-30\%$ wetland "mixed", and $>30\%$ wetland "wetland." Site 5 is the outlet to a headwater humic lake.

winter and early summer and approximately every two days during the 5-week period encompassing spring flood. Water samples were collected in acid-washed 250-mL high-density polyethylene bottles, with multiple rinses of sample water. Hourly stream discharge was calculated for all sites using measurements of stream height and established height-discharge rating curves. For illustrative purposes we present discharge data from site 7 (Figure 2a), which has been monitored since 1980 using a 90° V-notch weir in a heated dam house. Measurements of discharge at the other 14 sites confirmed that changes in flow were generally synchronous, with maximum spring discharge at all sites occurring during a single 72-hour period.

3.4. Chemical Analyses

[16] Following collection, water samples were kept dark and cool until they were subsampled for chemical analyses. pH (at natural pCO_2, 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 > 4.8, this method yields pH values slightly higher than closed cell (field) pH, as a result of CO_2 degassing during the analysis. Measurements of CO_2 degassing rates and pH drift on selected samples demonstrated that the measured pH values were within 0.1 pH units of closed cell pH. Samples for DOC analysis were filtered using 0.45 μm MCE membrane filters and then frozen until analysis. DOC was measured by combustion and analysis as CO_2 using a Shimadzu TOC-V$_{PCH}$ analyzer after acidification and sparging to remove inorganic carbon. Precision of the DOC analysis based on replicate injections was always better than 5%, and averaged less than 2%.

[17] Samples for major cation analyses (K, Mg, Na, Ca) were preserved with ultrapure HNO_3 (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_4^{2-} and Cl^-) were stored at 6°C 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_3^- 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.

[18] Base cation (BC) concentration was calculated as the sum of K^+, Mg^{2+}, Na^+ and Ca^{2+} concentrations expressed as μeq L^{-1} 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 SO_4^{2-} and Cl^- expressed as μeq 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,

$$ANC = [K^+] + 2[Mg^{2+}] + [Na^+] + 2[Ca^{2+}] - [Cl^-] - 2[SO_4^{2-}]$$
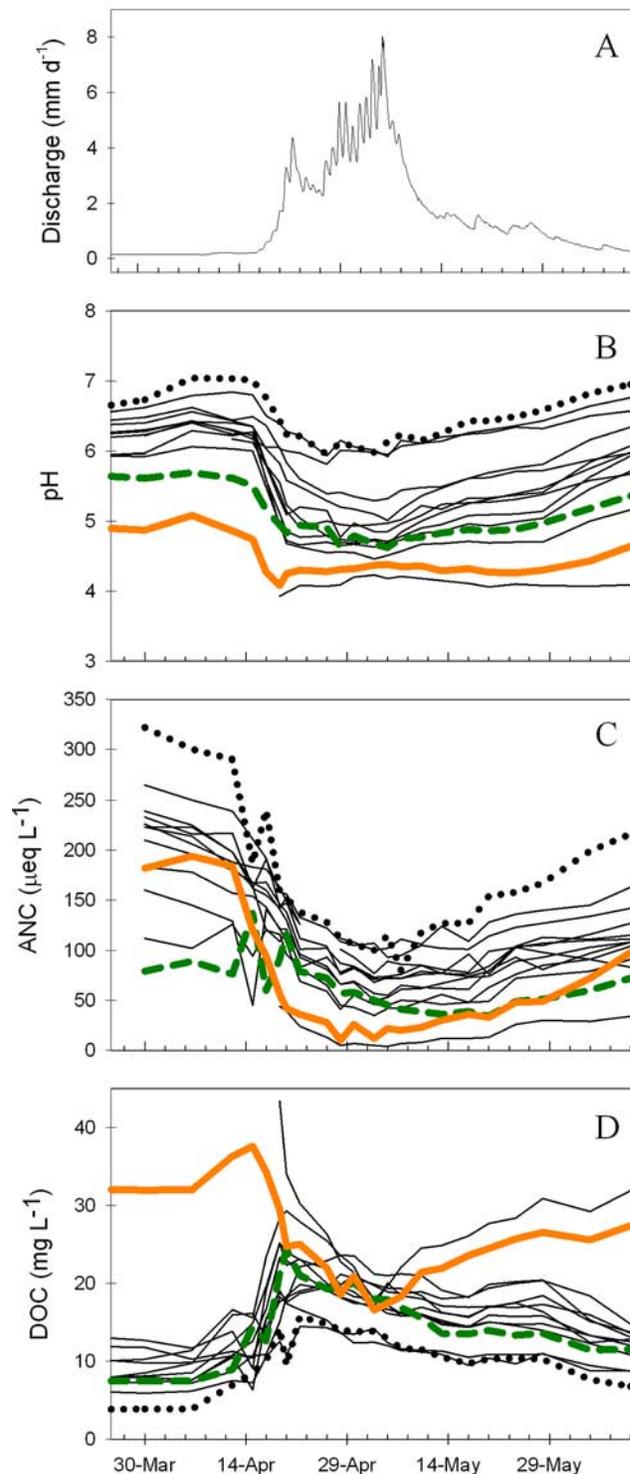$$= BC - SAA. \tag{1}$$

Figure 2. Timecourses of (a) discharge at a representative site, and (b, c, d) pH, ANC, and DOC, respectively, at all 15 stream sites during spring 2004. For illustrative purposes, chemistry timecourses at several sites are highlighted with thicker lines: Site 2 (headwater forested), dashed green line; Site 4 (headwater wetland), solid orange line; and Site 16 (Krycklan catchment outlet, a fourth-order stream), dotted black line.

Table 2. Mean Chemistry at Each of 15 Stream Sites During 2004[a]

Site Type	Site Number	DOC, mg L^{-1}	OA$^-$, µeq L^{-1}	SAA, µeq L^{-1}	BC, µeq L^{-1}	ANC, µeq L^{-1}	H$^+$, µeq L^{-1}	pH
Forested	1	8–20	60–117	215–124	324–190	108–66	1.2–12.9	5.9–4.9
	2	7–19	53–102	216–112	305–149	89–37	2.1–20.3	5.7–4.7
Wetland	3	41–20	152–85	51–26	111–32	60–6	125.9–62.6	3.9–4.2
	4	32–18	191–86	34–36	189–52	155–16	11.7–44.0	4.9–4.4
	5	20–22	120–111	61–42	143–83	82–41	11.1–33.6	5.0–4.5
Mixed catchments	6	12–20	89–108	109–53	301–100	192–47	1.2–20.4	5.9–4.7
	7	13–20	100–100	137–88	283–122	145–34	1.2–31.1	5.9–4.5
	8	10–22	76–121	128–70	357–131	229–61	0.7–19.1	6.1–4.7
	9	8–18	65–110	156–78	380–140	224–62	0.6–8.1	6.2–5.1
	10	8–17	63–92	121–76	363–105	242–29	0.6–21.5	6.2–4.7
	12	7–17	60–101	147–87	365–153	219–66	0.5–11.2	6.3–5.0
	13	11–18	84–117	146–80	403–165	257–85	0.6–4.8	6.2–5.3
	14	7–12	59–93	163–101	409–211	246–110	0.4–1.1	6.4–6.0
	15	6–13	53–101	138–88	369–178	230–90	0.3–1.0	6.5–6.0
	16	4–14	32–104	189–104	555–287	366–172	0.3–0.9	6.5–6.1
Mean (sd)		13 (10)–18 (3)	84 (41)–103 (11)	134 (52)–78 (27)	324 (108)–140 (62)	190 (80)–61 (40)	10.6 (31.0)–19.5 (16.9)	5.8 (0.7)–5.0 (0.6)
CV (%)		78–16	49–10	39–35	33–44	na	294–87	na
Range		38–10	158–36	182–99	444–255	306–166	125.6–61.7	2.6–1.9

[a]Cells show mean winter baseflow (to the left of dashes) and mean peak spring flood (to the right of dashes). DOC, dissolved organic carbon; OA$^-$, dissociated organic acids (including both strong and weak component); SAA, strong inorganic acid ions; BC, strong base cations; ANC, acid neutralizing capacity, BC − SAA. Sites are grouped by catchment landcover type as described in Table 1. Statistics (mean, standard deviation, CV and range of the 15 sites) at the bottom of the table summarize the differences between baseflow and flood periods. Here "na" denotes CV calculation not applicable for variables which do not scale to zero.

[19] The concentration of dissociated organic acids (OA$^-$) including both strong and weak acids was calculated from DOC and pH using a triprotic model [*Hruska et al.*, 2003] with pka1 = 3.04, pka2 = 4.42, pka3 = 6.7 and an overall site density of 10.2 µeq/mg C. Al cycling at the same sites has been extensively studied [*Cory et al.*, 2006], but was found to be a relatively minor contributor to charge balance and was excluded from analysis.

3.5. Data Analysis

[20] Samples were grouped into winter baseflow and spring flood periods. For each site, winter baseflow chemistry was taken as the mean chemistry of the samples (N = 2) collected during March 2004 for all sites except Site 3, which froze during late winter. At Site 3, the two samples bracketing the stable winter period were averaged to characterize winter baseflow chemistry. These two samples, from mid-November 2003 and mid-April 2004, had similar chemistry for all reported parameters (maximum difference 14%). For each site, spring flood chemistry was taken as the mean of the samples (N = 3) taken during the 7-day period of maximum flow.

[21] For both individual sampling occasions and for the winter baseflow and spring flood periods, mean (μ) and variation among the 15 sites was calculated for each analyte in terms of both standard deviation (δ) and coefficient of variation (CV),

$$CV = \frac{\delta}{\mu} \cdot (100\%). \qquad (2)$$

3.6. Chemical Signatures of Within-Catchment Reservoirs

[22] To aid in the interpretation of observed stream chemistry changes, water samples from various reservoirs in the Nyänget subcatchment (site 7) were periodically collected and analyzed for chemistry. These reservoirs included snow meltwater from open and forested areas (described by *Laudon et al.* [2004b]), peat pore water from wells at depths of 0.75–3.5 m in an 8 ha peat wetland (described by *Sirin et al.* [1998]), upslope mineral groundwater from wells at depths of 1–3 m (described by *Grip* [1994]), and soilwater from suction lysimeters in the organic-rich layer (depth 35 cm) of the riparian zone 4 m from a forested headwater stream (described by *Bishop et al.* [2004]).

4. Results

4.1. The pH

[23] Spatial variability in acidity as measured by the range of pH values across the 15 stream sites was high at winter baseflow (Table 2 and Figure 2b), encompassing nearly 3 pH units (range 3.9–6.5). Spring flood gave rise to an approximately 50-fold increase in flow, from 0.15 to 8.0 mm d^{-1} (Figure 2a). The episode resulted in a pH depression ranging from 0.4 to 1.5 pH units at fourteen of the 15 sites (Table 2). The lone exception was a small headwater wetland stream (site 3), in which pH increased from 3.9 to 4.2 during snowmelt. During peak flood, pH for the 15 sites ranged less than 2 pH units, from 4.2 − 6.1. Variability in pH was less at high flow than at baseflow, both in terms of standard deviation and range.

4.2. BC, SAA, and ANC

[24] At winter baseflow, interstream variability in SAA, BC and ANC was high, with a total range of 182, 444 and 306 µeq L^{-1} respectively, and CV between 30 and 40% for BC and SAA (Table 2). Baseflow SAA was lowest in wetland sites, intermediate in mixed sites and highest in headwater forest streams. Baseflow BC was lowest in wetland sites, intermediate in other headwater sites, and higher in the larger mixed sites, with the highest concentration of 555 µeq L^{-1} occurring at the 67 km^2 Krycklan outlet site. Variation in ANC was largely driven by BC
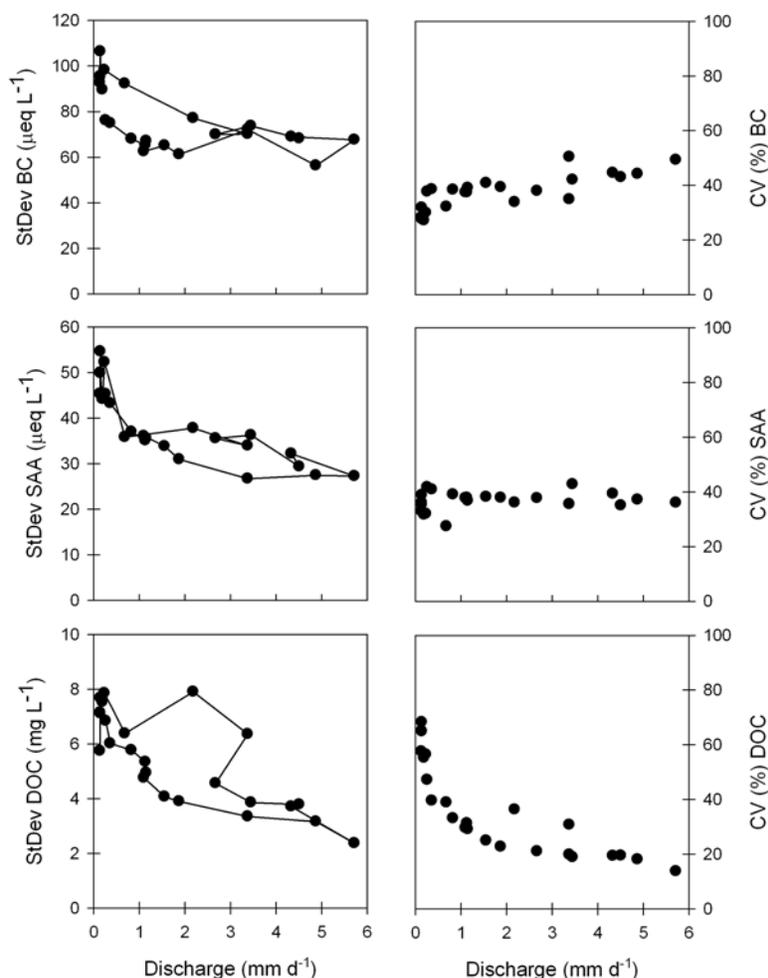
Figure 3. (left) Standard deviation and (right) coefficient of variation of base cations (BC), strong acid anions (SAA), and dissolved organic carbon (DOC) measured at 15 stream sites during spring 2004 as a function of flow at a representative site. All three analytes demonstrate hysteresis, with higher standard deviation on the rising than on the falling limb.

variation, and consequently baseflow ANC was lowest in wetland sites, intermediate in headwater forest sites and highest at the largest mixed sites (Table 2).

[25] During spring flood, all sites decreased in base cation (BC) concentration (mean decrease 58%, range 41–73%). BC percent dilution was least at the headwater lake outlet (site 5), and highest at the headwater wetland sites. Fourteen of the fifteen sites decreased in strong acid anion (SAA) concentration (mean decrease 39%, range 31–51%), while one headwater wetland site (site 4) increased by 5%. BC and SAA dilution combined to result in ANC decreases at all sites (mean decrease 128 μeq L^{-1}, range 41–213 μeq L^{-1}, Figure 2c). The range in SAA, BC and ANC shrank to 99, 255 and 166 μeq L^{-1} respectively (Table 2 and Figure 3). Spatial variability as measured by standard deviation of the concentrations of BC and SAA decreased during spring flood (Figure 3) with a clockwise hysteresis (higher standard deviation for sampling occasions on the rising limb than on the falling limb at equivalent flow). The changes in standard deviation were generally proportional however to changes in mean concentrations of BC and SAA, which were also higher on the rising limb. The calculation of

coefficient of variation (CV) by normalizing to the mean concentration on a given sampling occasion revealed that the spatial variability in SAA did not change while base cation CV was positively correlated with flow, increasing from 33 to 44% during spring flood (Figure 3 and Table 2).

4.3. DOC

[26] During winter baseflow DOC concentration ranged from 4 to 41 mg L^{-1} for the 15 sites, and was positively correlated with subcatchment percent wetland (Figure 4). OA$^-$ concentrations ranged from 32 to 191 μeq L^{-1} during winter, with the highest concentrations in the wetland sites (Table 2). At baseflow, OA$^-$ concentrations were lower than SAA at all sites except the two headwater wetlands and the headwater humic lake outlet (sites 3, 4 and 5). During spring flood, DOC increased markedly at 12 of the 15 sites (mean increase 118%, range 49–260%), bringing with it higher concentrations of organic acids (OA$^-$, mean increase 72%, range 1–221%). Of the other three sites, two were headwater wetland streams (sites 3 and 4), which decreased to approximately 50% of their baseflow DOC and OA$^-$ concentration. The third was a headwater lake outlet (site 5)
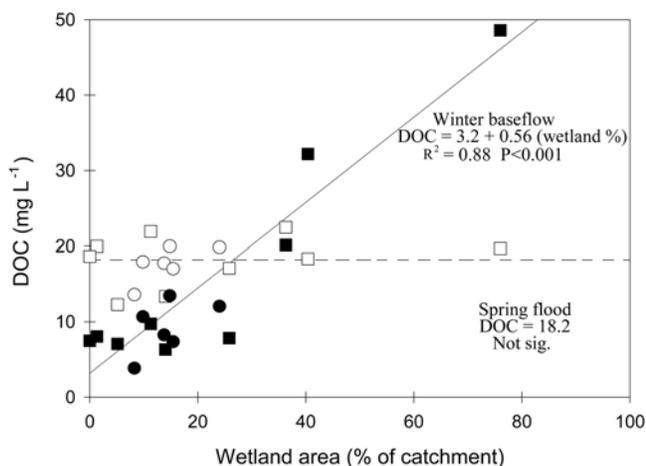
Figure 4. Correlation between catchment percent wetland and DOC during winter baseflow (solid symbols) and during spring flood (open symbols). Regressions were run using only the nine independent stream sites (square symbols), but the other six downstream sites are also shown (circles). Solid line is best linear fit to winter baseflow data. Dashed line is mean peak flood DOC. Relationship with percent wetland was not significant during spring flood.

with a high percent wetland catchment. This site remained virtually unchanged in DOC (+11%) and OA$^-$ (-7%) concentrations.

[27] As a result of these changes, DOC concentrations became more constrained during spring flood, even as mean DOC increased (Table 2 and Figure 2d). At the time of peak spring flow DOC concentrations were not significantly correlated with percent wetland (Figure 4), and ranged only from 12 to 22 mg L^{-1} with a mean of 18 mg L^{-1}. OA$^-$ concentrations were even less variable, with a total range of 85–121 μeq L^{-1} and no correlation with percent wetland. Both standard deviation and CV of DOC dropped substantially during spring flood, giving a negative relationship with flow (Figure 3). At the time of peak spring flood, calculated OA$^-$ concentrations were greater than SAA at all sites except the three with lowest percent wetland (sites 1, 2 and 14).

4.4. Shift in Chemical Signatures

[28] The changes in DOC and ANC during spring flood combined to give the bulk of the observed pH declines, as illustrated by the relationship between DOC, ANC and modeled air-equilibrated pH shown in Figure 5. Air-equilibrated pH values calculated from DOC and ANC (Figure 5) were close to the directly measured pH values (Table 2). Differences can be attributed to overpressures of CO$_2$ (which affects pH at pH > 4.8), buffering by other
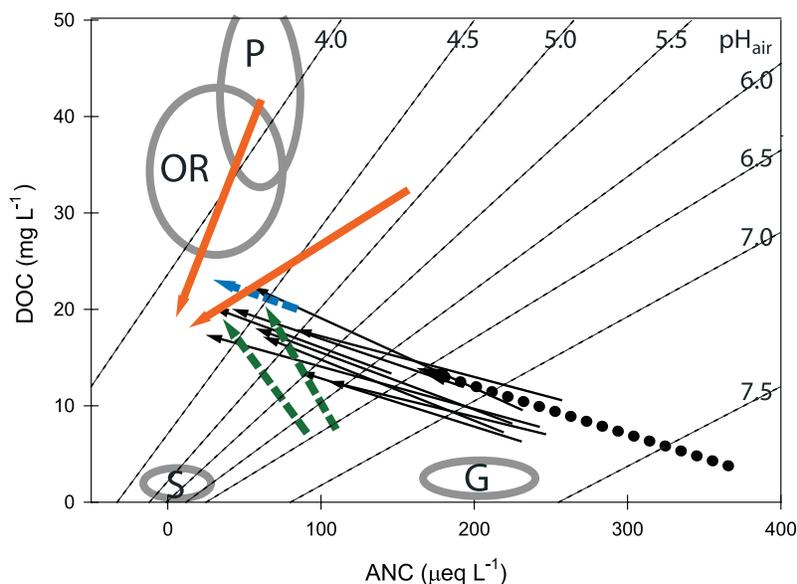

Figure 5. Arrows for each of 15 stream sites represent changes in DOC and ANC from winter baseflow (tail of arrow) to spring flood concentrations (head of arrow). Headwater wetland sites (thick solid orange lines), headwater forest sites (thick dashed green lines), humic lake outlet (thick dashed blue line), and the 67 km^2 Krycklan outlet site (thick black dotted line) are highlighted. To illustrate the impact of changes in DOC and ANC on pH, air-equilibrated pH isolines are shown as thin dotted lines ranging from pH = 4.0 to pH = 7.5. These are calculated from ANC (BC-SAA) and DOC using atmospheric pCO$_2$ of 380 ppm, charge balance equations and a triprotic organic acid model [Hruska et al., 2003] to convert DOC to OA$^-$ concentration. Grey ovals indicate measured chemical signatures for selected hydrological pathways/source reservoirs which have been monitored within the Krycklan catchment. Ovals are centered on mean value, with vertical and horizontal extent of oval determined by standard deviation of measurements. Pathways/reservoirs are: S, snow meltwater; P, peat pore water; OR, organic riparian soilwater; G, mineral groundwater.

elements such as aluminum not accounted for in the pH model [*Köhler et al.*, 1999] and/or analytical error. Headwater forested sites initially had chemical signatures (DOC, ANC) similar to a mixture of mineral groundwater and riparian organic soilwater, but shifted toward a riparian organic soilwater signature during spring flood. Headwater wetland sites initially had chemical signatures similar to peat pore waters, but shifted toward a snowmelt signature during spring flood. The headwater lake outlet (site 5) had intermediate chemistry initially and changed little during spring flood. The larger, mixed sites initially had ANC concentrations similar to groundwater, except the largest site (site 16) which had a higher ANC than groundwater. DOC concentrations of the mixed sites at baseflow were intermediate between that of groundwater and riparian organic soilwater. During spring flood, all mixed sites had a chemistry trajectory intermediate between those of the headwater forested and headwater wetland sites. This could be described as a shift from a groundwater chemical signature toward a more organic chemical signature, similar to that of the riparian organic soils.

5.　Discussion

5.1.　DOC and Wetlands

[29] As is typical for the Swedish boreal forest zone, the Krycklan catchment is dominated by patches of coniferous forest and peat wetlands. At baseflow, these two landcover types give rise to distinctly contrasting stream chemistry. For instance, Krycklan streams demonstrated a strong positive correlation between catchment percent wetland and DOC at baseflow. A similar relationship is frequently reported for other streams and regions, often with percent wetland or peat explaining a large portion of variance in DOC concentration or export [*Creed et al.*, 2003; *Hope et al.*, 1994; *Mulholland*, 2003]. Exceptionally strong correlations between percent wetland and stream DOC are observed for small catchments when detailed mapping of small-scale organic matter distribution is done, for instance by the identification of cryptic wetlands not shown on maps [*Creed et al.*, 2003] or by the calculation of topographic indices to identify wet areas [*Andersson*, 2005].

[30] On the basis of our observations in Krycklan however, this relationship may not hold true at all times of the year (Figure 4). In Krycklan, the lack of correlation between wetlands and DOC during spring flood was associated with a decrease in DOC spatial variability concurrent with increased flow (Figure 3, bottom). The decrease in DOC variability could largely be attributed to the contrasting behavior of streams draining forested and wetland catchments. In short, forested and mixed catchments increased in DOC during spring flood, while headwater wetland sites diluted from high baseflow concentrations to reach peak flow concentrations approximately equal to those of the other catchments. Snowmelt dilution of DOC in streams with high wetland contributions occurs in many boreal catchments and has been documented in Nova Scotia, Canada [*Gorham et al.*, 1998], in Ontario, Canada [*Fraser et al.*, 2001; *Hinton et al.*, 1997; *Schiff et al.*, 1998], in Wisconsin [*Gergel et al.*, 1999] and previously at one of the headwater wetland sites within the Krycklan catchment [*Bishop and Pettersson*, 1996; *Laudon et al.*, 2004a]. In central Ontario, Canada for instance, streams increase substantially in DOC during spring events in subcatchments without wetlands, while subcatchments with small wetland areas show minimal or no increase [*Hinton et al.*, 1997]. In those streams, wetland DOC dilution was attributed primarily to hydrological flushing of riparian peat resulting in a depleted DOC reservoir during periods of sustained high flow [*Schiff et al.*, 1998]. Mechanisms of DOC flow response in boreal regions have implications for carbon export, and the underlying processes warrant further study.

5.2.　Base Cations

[31] We hypothesized that high flow would bring organic-rich waters from shallow flow paths throughout the catchment giving rise to relatively homogeneous stream chemistry, but we found an unexpected increase in spatial variability of BC at high flow as measured by CV (Figure 3). This arose primarily owing to the behavior of the two headwater wetland sites (sites 3 and 4), which had the highest degree of BC dilution (>70%) in spite of beginning with the second and third lowest baseflow BC concentrations. However, even with these two sites removed from consideration, the CV was still higher (35 ± 3%) during the week of peak spring flood than during the rest of the measurement period (28 ± 4%).

[32] This suggests that there were more complex changes during spring flood than a shift to more similar flow paths at all sites. In particular, the high level of BC dilution in the wetland sites could result from increased overland flow of new snowmelt over frozen wetland surfaces as proposed by *Laudon et al.* [2004a], contrasting with forested till soils which remain pervious to infiltration even with soil frost [*Nyberg et al.*, 2001]. In other stream systems, increased similarity in base cation concentrations during periods of high flow was observed for streams in the Catskill mountains of New York State [*Murdoch and Stoddard*, 1993] and during the rainy season in Costa Rica [*Newbold et al.*, 1995]. The similarity at high flow in the Catskills was attributed to the influx of water from shallow soil flow paths and direct precipitation, thought to be more similar in chemical nature than the variety of deeper flow paths contributing water during baseflow. *Murdoch and Stoddard*'s [1993] study would not be expected to pick up snowmelt-specific processes since they pooled data from all seasons, perhaps explaining the different trends observed in our study and theirs.

5.3.　Baseflow Chemistry: Link to Patterns in Landscape

[33] At baseflow, the horizontal distribution of soil organic matter across the landscape appears to play a primary role in controlling stream water chemistry, at least in terms of DOC. Patterns of peat wetlands interspersed in the landscape give rise to regions of high-DOC stream water where flow paths pass through peat en route to the stream, while forested catchments give rise to regions of low-DOC stream water where flow paths through mineral soils predominate. This is illustrated in Figure 5 by the wide separation in baseflow chemistry between high-DOC wetland sites, low-DOC forested sites, and intermediate DOC mixed sites (see also Figure 4).

5.4. Spring Flood Flow Paths: Forested and Mixed Sites

[34] As shown in Figure 5, the chemical signatures of forested and mixed sites at baseflow lie between those of groundwater and organic soil water, suggesting contributions from both sources. During spring flood, these sites shift toward a signature (high DOC, low ANC) more like that of organic soil water. (Figure 5). These changes are consistent with the hypothesis that vertical gradients in soil solution chemistry are responsible for the chemistry trajectory observed in forested and mixed subcatchments during spring flood. On the basis of previous ^{18}O tracer studies water in these forested headwater streams comes almost exclusively from the soil matrix during spring flood, with only a minor contribution from new melt water [*Laudon et al.*, 2004b]. The changes in stream water chemistry can thus be attributed to rising water tables intersecting upper organic soil layers which are high in DOC [*Bishop et al.*, 2004; *Laudon et al.*, 2004b]. The riparian zone is a particularly important contributor of DOC, since a thick peat layer forms in the surficial riparian zone of many streams, and during snowmelt subsurface flow intersects these zones just before entering the stream [*Bishop et al.*, 1995; *Nyberg et al.*, 2001]. ANC dilution during spring flood in forested and mixed sites can also be attributed to rising water tables intersecting vertical gradients in soil solution characteristics, since BC and ANC in soil solution often increase with depth in forested catchments [e.g., *Bishop et al.*, 2004; *Hazlett et al.*, 2001]. However, upslope soil horizons as well as riparian zone are likely to contribute to the observed stream ANC signature.

5.5. Spring Flood Flow Paths: Wetland Sites

[35] As illustrated in Figure 5, the two headwater wetland sites had chemistry signatures indicative of peat pore waters at winter baseflow, then shifted during spring flood to a signature between those of snowmelt and peat pore waters. The DOC and ANC dilution trajectory supports previous ^{18}O tracer studies [*Bishop et al.*, 1995; *Sjöblom*, 2005] which implicate a substantial contribution (40–50%) of new snowmelt water to wetland streams during spring flood. Relative to forested sites, headwater wetland sites route a much higher proportion of snowmelt water quickly to the stream, particularly early in the melt period [*Sjöblom*, 2005]. This is believed to result primarily from overland flow over frozen surfaces and/or completely saturated peat soils, as suggested for some northern wetland catchments [*Hayashi et al.*, 2004; *Woo and Winter*, 1993]. Additionally, because hydraulic conductivity is higher near the peat surface, even small increases in water table have the potential to result in rapid near-surface horizontal flow during spring flood. This hydrological flushing could result in the depletion of DOC in peat pore waters at high flow [*Schiff et al.*, 1998] and likely also contributes to the observed dilution in the wetland streams.

[36] The basic patterns of changes in stream chemistry observed during spring flood in the Krycklan catchment were consistent with control by variations in hydrologic flow path and soil chemistry. On the basis of DOC and ANC concentrations in stream water and catchment reservoirs, the major changes in stream chemistry during spring flood could be qualitatively explained by two basic processes, both illustrated in Figure 5: (1) a shift from mineral to superficial, riparian organic soil flow paths in forested and mixed catchments and (2) dilution by snowmelt in wetland catchments. Temporal variation in source reservoir chemical signatures resulting from hydrological processes such as flushing [*Creed and Band*, 1998; *Hornberger et al.*, 1994] or chemical processes such as cation exchange likely also occur and add additional complexity to the soil-stream connection, but were not explicitly considered in this study.

5.6. Spatial Variability in Acidity

[37] The coupled effects of elevated OA$^-$ concentrations at most sites and dilution of ANC led to increased acidity in the Krycklan stream network during spring flood, with a peak flood pH range of 4.2–6.1. However, the dilution of DOC and OA$^-$ at the most acidic, high-DOC wetland sites resulted in a muted or absent acid pulse for these sites. As a result, the spatial variability in acidity as measured by pH range decreased slightly during the snowmelt period. Additionally, during spring flood there was a shift in most sites from mineral acidity at baseflow to organic acidity at peak flow. A companion study on Aluminum (Al) during spring flood at the same sites also highlighted the importance of flow pathways and the influence of landscape on stream chemistry [*Cory et al.*, 2006]. Forested sites underlain by mineral soils gave rise to higher total Al concentrations and greater inorganic Al proportions than catchments with substantial wetland areas, despite significantly higher pH. This was attributed to source limitation of Al in peat wetlands. Furthermore, the largest proportional increases in Al during spring flood were observed in headwater forested streams, which already had the highest concentrations at baseflow, suggesting increased spatial variability of stream Al during spring flood. Because of the distinct and sometimes contrasting influence of landscape on pH and Al, the spatial distribution of both should be considered when acid toxicity is of concern.

6. Conclusions and Implications

[38] Our hypothesis of decreased interstream variability during spring flood was borne out for DOC, but the opposite occurred for BC, while SAA variability remained unchanged. Decreased DOC variability resulted from the contrasting behavior of DOC in wetland and forested catchments. Forested and mixed catchments increased in DOC during spring flood, while headwater wetland sites diluted from high baseflow concentrations to reach peak flow concentrations approximately equal to those of the other catchments (mean for all sites 18 mg L^{-1} DOC during peak flood). During spring flood, BC and SAA were diluted throughout the stream network by an average of 58% and 36%, respectively. Changes in DOC and ANC (BC-SAA) during spring flood combined to decrease pH at 14 of 15 sites, resulting in a slight reduction in the spatial variation of pH. Even at peak flow however, the stream network maintained a spatially variable distribution of pH (range 4.2–6.1) which could provide areas of refuge for moderately acid sensitive fish during spring flood as long as other potentially limiting parameters (e.g., inorganic Al concentrations) are of acceptable levels. In forested till

catchments, the changes in stream water chemistry from winter baseflow to spring flood could be qualitatively explained by a shift in hydrological flow path from mineral to organic soils. In headwater wetland catchments, the changes were consistent with dilution of peat pore waters with snowmelt. These processes are expected to play a role in controlling snowmelt chemistry in stream networks with similar landscape and hydrogeological conditions, i.e., extensive areas of the boreal zone.

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