Sensitivity of pH in a boreal stream network to a potential decrease in base cations caused by forest harvest

Anneli Ågren, Ishi Buffam, Kevin Bishop, and Hjalmar Laudon

Abstract: Increased forest harvest with more whole-tree utilization can decrease base cations (BC) in soils and stream runoff. This paper analyses how reducing stream BC changes the capacity of a boreal stream network to buffer pH changes. We estimated change in stream pH during spring snowmelt in 60 locations throughout a 68 km^2 boreal catchment in northern Sweden with different scenarios of BC removal from stream water ranging from 10 to 50 μequiv.·L^{-1}. The pH decreased in all scenarios, and if BC decreased by 50 μequiv.·L^{-1}, stream length with pH above the acid threshold pH 5 during spring snowmelt decreased from 82% to 44% of the stream network, whereas the stream length with pH above 5.5 decreased from 60% to 10%. The pH sensitivity of different stream reaches to reductions in BC was positively related to the slope of the catchment, forest cover, and forested mires, whereas it was negatively related to the percentage of agricultural fields. Because the long-term effect of different forestry practices on stream BC is unclear, there is all the more reason to evaluate BC sensitivity before, rather than after, eventual problems arise.

Résumé : La récolte accrue des forêts avec l'utilisation élargie des arbres entiers peut réduire les cations basiques (BC) dans les sols et l'écoulement des cours d'eau. Notre étude analyse comment la réduction des BC dans le cours d'eau modifie la capacité d'un réseau d'eau courante boréal à tamponner les changements de pH. Nous avons estimé les changements de pH dans les cours d'eau durant la fonte des neiges au printemps à 60 points dans un bassin versant boréal de 68 km^2 dans le nord de la Suède avec divers scénarios de retrait des BC des eaux courantes allant de 10 à 50 μequiv.·L^{-1}. Le pH a diminué dans tous les scénarios; lorsque les BC avaient diminué de 50 μequiv.·L^{-1}, la longueur de cours d'eau ayant un pH au-dessus du seuil acide de pH 5 durant la fonte des neige était réduite de 82 % à 44 % du réseau, alors que la longueur de cours d'eau avec un pH au-dessus de 5,5 avait baissé de 60 % à 10 %. La sensibilité au pH des diverses sections de cours d'eau en fonction de la réduction des BC est en corrélation positive avec la pente du bassin versant, la couverture de forêt et les tourbières forestières, alors qu'elle est en corrélation négative avec le pourcentage de champs agricoles. Parce que les effets à long terme des différentes stratégies forestières sur les BC des cours d'eau restent imprécis, c'est une raison de plus d'évaluer la sensibilité des BC avant, plutôt qu'après, l'arrivée éventuelle de problèmes.

[Traduit par la Rédaction]

Introduction

There is increasing interest in forest biomass harvest in many regions of the world. Plans to increase productivity and use new extraction methods, including whole-tree harvesting (WTH), are being put into action to meet an increasing demand for biofuel (European Commission 1997) and other forest products. In WTH, the whole aboveground biomass is extracted (in Sweden, the practice of removing the stump wood and roots has been implemented on a trial basis on 1% of the final cut area). The impacts of such forest management decisions on ecosystem services such as future soil productivity and water quality is a topic of current interest. One particular concern is how increased biomass removal from the catchment soils will affect the long-term export of base cations (BC, defined as the sum of Ca, Mg, Na, and K) to surface waters in acid-sensitive regions.

Soils and surface waters are closely linked by groundwater, which transports dissolved nutrients and other solutes from the terrestrial to the aquatic ecosystem. A consequence of this strong linkage is that a change in the soil biogeochemistry will ultimately affect stream water quality. As the BC concentration strongly controls acid-buffering capacity in streams, a decline in catchment soil BC concentration due to biomass removal will impact the pH in the stream network.

Forest harvesting has different effects on BC over different time scales. In the short term, BC often increase in surface waters following harvest (Neal et al. 1992) due to

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A. Ågren[1] and H. Laudon. Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, SE-901 83 Umeå, Sweden.
I. Buffam. Ecosystem and Landscape Ecology Lab, Department of Zoology, University of Wisconsin, Madison, WI 53706, USA.
K. Bishop. Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, P.O. Box 7050, SE-750 07 Uppsala, Sweden.

[1] Corresponding author (e-mail: anneli.agren@seksko.slu.se).

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increased mineralization, decomposition, and possibly leaching during nitrification (Kreutzweiser et al. 2008). In a longer time perspective, which is the focus of this study, harvesting of trees will remove BC from the watershed soils and eventually contribute to surface-water acidification (Neal et al. 1992). The environmental effect on surface waters of biomass removal, through loss of soil BC, will ultimately be determined by how sensitive the soils are to BC depletion. In Mediterranean forests, MAGIC (Model of Acidification of Groundwater In Catchments; Cosby et al. 1985, 2001) models predict little change in water quality due to forestry harvest, because there are high BC inputs from the atmosphere and the BC weathering rates are also high (Neal et al. 1995). However, in the more acid-sensitive soils in regions of the northeastern US and Canada, as well as in Scandinavia, models predict soil and surface-water acidification with different forestry scenarios (Larssen 2005; Clair et al. 2007; Aherne et al. 2008). Mass-balance calculations have demonstrated that Finnish soils will be depleted in base cations in the long term if WTH is practiced (Joki-Heiskala et al. 2003). Measurements from long-term experiments (15–16 years after harvesting) also report that WTH results in lower pools of exchangeable BC, as well as a decreased cation exchange capacity in the soil compared with stem-only harvesting (Olsson et al. 1996). Another survey of the same sites 25 years after harvesting showed that the effect of WTH on the pools of exchangeable BC persisted (Olsson et al. 2004). An investigation from Canada showed that reduction of BC in the soil would also reduce the export of BC in streamwater, in particular Ca (Molot and Dillon 2008). The effects of a change in forestry practice from stem-only to whole-tree harvesting on Finnish lakes were modeled using MAGIC (Aherne et al. 2008). The authors found that the long-term (by 2100) potential decrease in surface-water BC due to WTH was, on average, 10 μequiv.$\cdot$L^{-1}. In a Swedish application of MAGIC, WTH was found to cause long-term acidification of soils after one rotation period (on average, 98 years (79–141)), especially in areas with high stand productivity and low weathering capacity (Westling and Kronnäs 2006). Modeled deforestation was also predicted to decrease acid-neutralizing capacity (ANC) in runoff (1960–2060), with the decline ranging from about 20 μequiv.$\cdot$L^{-1} to almost 100 μequiv.$\cdot$L^{-1} depending on forest type and previous acidification history. Even without WTH, mass-balance calculations suggest that serious depletion of BC will occur after one to two rotations across large parts of Sweden (Akselsson et al. 2007).

Because of the limited understanding of how intensified forestry practice will affect the long-term sustainability of water quality at the landscape scale, there is a need for studies exploring potential impacts on aquatic ecosystems. The purpose of this study is to investigate the sensitivity of a boreal stream network to declines in streamwater BC ranging from 10 μequiv.$\cdot$L^{-1} to 50 μequiv.$\cdot$L^{-1}. We apply a well-tested charge-balance model for pH (Köhler et al. 2000; Hruška et al. 2003) on 60 stream segments during spring snowmelt in the Krycklan catchment network in northern Sweden (Laudon and Buffam 2008). Using this model, we examine how the potential removal of BC from the stream water (in the absence of other water chemistry changes) would affect the pH drop during spring snowmelt and how this would change the amount of suitable habitat for acid-sensitive biota in the stream network. Whereas other studies have focused on ANC, this paper focuses on pH, which is typically the key factor for acid-sensitive biota and can be used as an integrated benchmark of acid–base status in the watershed as a whole. The response in pH is analyzed in a landscape perspective, with empirical measurements of water chemistry providing the foundation.

Specifically, we ask the following. (*i*) In a mesoscale boreal catchment, given a uniform change in stream BC on the order of that expected from WTH, how much of the stream habitat will cross ecologically relevant pH thresholds? (*ii*) What are the characteristics of the stream reaches and subcatchments most sensitive to changes in BC?

Material and methods

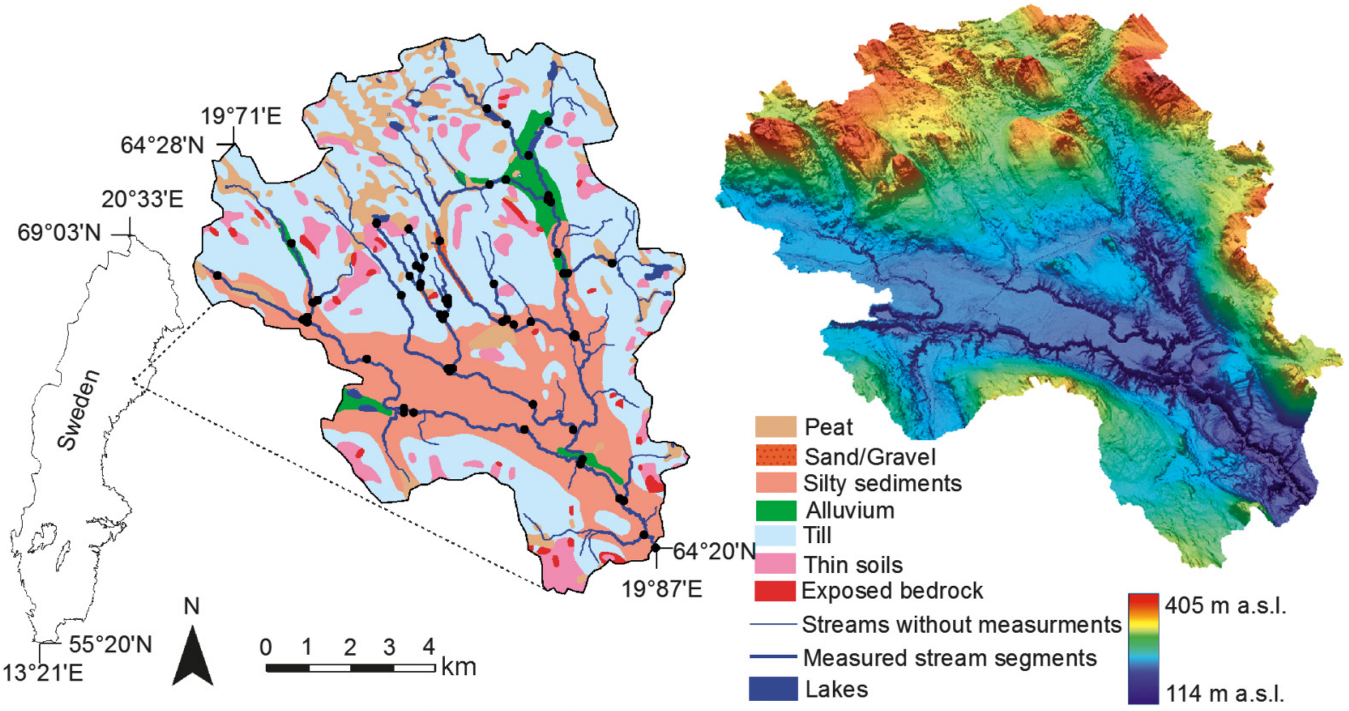
Study site

The Krycklan catchment (Fig. 1), a 68 km^2 area boreal stream network in northern Sweden, has been used as the model catchment for this study. The bedrock consists of Precambrian gneiss with intrusions of acid and intermediate metavolcanic rocks, granite, and pegmatite. The Quaternary deposits are dominated by till, with patches of peat, bare rock, thin soils, and fine sorted sediments. The Krycklan catchment ranges in elevation from 114 to 405 m above sea level (a.s.l.). In the lower part of the catchment, the streams traverse a postglacial delta, with thick layers of silty sediments where ravines and bluffs of up to 20 m can be found. In the till soils, higher up, well-developed iron podzols dominate the forest floor soils, but near the stream channels, the organic content increases, forming a riparian peat zone along the streams. The peatlands (covering 9% of the catchment) are dominated by *Sphagnum* species. These can be categorized as acid, oligotrophic, and minerogenic, with varying proportions of microtopographic units (e.g., hollows, hummocks, strings, lawns) (Rydin et al. 1999). Forests cover 84% of the catchment, clear-cuts, 4%, open or arable grounds, 3%, and lakes, 1%. The dominant tree species is Scots pine (*Pinus sylvestris*) in dry upslope areas, whereas Norway spruce (*Picea abies*) dominates in wetter, lower-lying areas. The Vindeln Experimental Forest covers 25% of the catchment area and has been protected since 1922, whereas the majority of the other 75% of the area is second-growth forest. The population in the catchment is less than 100 people. The mean annual air temperature is 1 °C, and the mean annual precipitation in the region amounts to 600 mm, of which approximately 50% becomes runoff. The area has on average five months of snow cover, and 35%–40% of the precipitation falls as snow (Eriksson 1991). The hydrology is characterized by a strong runoff peak in late April – early May due to snowmelt, with occasional rainfall-induced runoff peaks in summer and autumn. The streams are relatively humic (brown water) with dissolved organic carbon (DOC) levels ranging from 4 to 41 mg$\cdot$L^{-1} (Buffam et al. 2007).

Sampling

The stream segments used in this study were defined by Buffam and co-workers (Buffam et al. 2008). In short, stream chemistry was sampled at 60 locations in the stream

Fig. 1. The location of the Krycklan catchment with the Quaternary deposits map (1 : 100 000, Geological Survey of Sweden, Uppsala, Sweden) and the topography according to a digital elevation model based on LIDAR measurements (note that the topography map is tilted for a three-dimensional effect and that height is exaggerated five times for visualization purposes). The solid circles are the sampling points. The bolder blue lines indicate the measured stream segments, and the thinner lines indicate stream segments without measurements.



network, and the chemistry was then assigned to segments of the streams to be able to express the changes in proportion to stream length. The segments were constructed by extending to the halfway point between neighboring sampling sites. At the headwater sites, segments were extended halfway to the stream origin on the 1 : 100 000 map. The mean length of the segments was 941 m (68–2874 m). Those segments represented 56 km out of a total of 96 km in the whole network. We express the changes in stream length with chemistry as a percentage of the measured stream length (56 km). Based on results from studies on fish (Holmgren and Buffam 2005; Serrano et al. 2008) and stream invertebrate species (Fölster et al. 2007), pH 5.5 and pH 5.0 were used as thresholds in this study as these were found to be the most critical pH intervals for many acid-sensitive species.

The stream network was sampled at 60 sites during the rising limb, close to peak runoff during the spring snowmelt (22 April 2004) and concurrent with the minimum pH (Buffam et al. 2007). Samples for dissolved inorganic carbon (DIC) analysis were injected into N_2-filled 60 mL glass vials and acidified. For all other analyses, stream-water grab samples were collected in 250 mL high-density polyethylene bottles. All samples were stored in the dark and at cool temperatures until subsampling for chemical analysis. The samples were analyzed for major cations (K^+, Na^+, Mg^{2+}, Ca^{2+}), strong acid anions (SO_4^{2-}, Cl^-, NO_3^-), pH, DOC (after filtration with 0.45 μm MCE membrane filter), and DIC (using partial pressure of headspace CO_2). For details regarding the analytical procedures, refer to Buffam et al. (2008) and Laudon and Buffam (2008).

pH model

A charge-balance model that predicts pH in the stream segments was constructed based on the following equations (Laudon and Buffam 2008). Assuming that K^+, Na^+, Mg^{2+}, and Ca^{2+} were present in their free ionized form, the BC concentration was calculated as

$$\text{(1)} \qquad \mathrm{BC} = [\mathrm{K}^+] + [\mathrm{Na}^+] + 2[\mathrm{Mg}^{2+}] + 2[\mathrm{Ca}^{2+}]$$

The strong acid anions (SAA) were calculated as

$$\text{(2)} \qquad \mathrm{SAA} = 2[\mathrm{SO_4}^{2-}] + [\mathrm{Cl}^-] + [\mathrm{NO_3}^-]$$

BC and SAA were expressed as μequiv.·L^{-1} of charge. The acid-neutralizing capacity (ANC) was then calculated as BC – SAA. Another way to express ANC is

$$\text{(3)} \qquad \mathrm{ANC} = [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}] + [\mathrm{RCOO}^-] + [\mathrm{OH}^-] - [\mathrm{H}^+] - n[\mathrm{Al}^{n+}]$$

where DIC is used to calculate HCO_3^-, using Henry's law and carbonate equilibria equations. CO_3^{2-} did not affect the ANC in this case, as pH was always below 7.0 and CO_3^{2-} could therefore be excluded. $RCOO^-$ denotes dissociated organic acid anions calculated from DOC and pH using a three pK_a model following Hruška et al. (2003). Al^{n+} denotes positively charged inorganic monomeric Al species. Previous studies in these and similar high DOC streams have shown that inclusion of the monomeric labile Al fraction and Fe does not significantly improve the agreement between measured and model-predicted pH at the pH range of these stream water samples (Köhler et al. 2000, 2001; Laudon et al. 2000). Because inclusion of Al^{n+} does not improve the model for these waters (Köhler et al. 2000), it was excluded. Hence, H^+ can be calculated as

$$(4) \qquad [H^+] = [HCO_3^-] + [RCOO^-] + [OH^-] - BC + SAA$$

No model calibration was carried out in this study, but because HCO_3^-, $RCOO^-$, and OH^- are dependent on pH, this equation is solved iteratively, until pH was stable within 0.01 pH units.

BC scenarios

First we ran the model with present conditions at each of the 60 stream sites, and the modeled pH was compared with measured pH to assess the success of the model. Then we ran different scenarios in which ANC was changed (by changing BC). By keeping all other water chemistry constant, we studied the net effect of the BC removal on pH. In the scenarios, we removed 10, 20, 30, 40, and 50 μequiv.·L^{-1} of BC from present day BC ($BC_{present}$). The BC scenarios represent upper and lower bounds of possible effects of whole-tree harvest taken from the literature. Of course, it is unrealistic that the distribution of BC removal would be equal through the entire catchment system, but it is done to illustrate the point that different landscape units display different sensitivity. The range 0–50 μequiv.·L^{-1} corresponds to 0%–22% of the mean spring BC stream concentration in our study catchment. The key to our modeling approach is a charge-balance – H^+ buffering model, where we assume that any change in BC is offset by a change in H^+ and then allow the model to come to equilibrium given the other dissolved constituents present. Thus we use H^+ (not pH) for the modeling, but we use pH in the paper for descriptive and visual purposes because that is a more conventional way to show the changes at an ecologically relevant scale. To minimize the uncertainty of the modeling, the new pH was calculated from the measured [H^+] minus the modeled change in [H^+] (Laudon and Buffam 2008), as shown in eqs. 5–6. In this way, much of the uncertainty in the organic acid modeling is cancelled out.

$$(5) \qquad [H^+{}_{\Delta BC}] = [HCO_3^-] + [RCOO^-] + [OH^-] - (BC_{present} - \Delta BC) + SAA$$

$$(6) \qquad \Delta H^+ = H^+{}_{\Delta BC} - H^+{}_{\text{modeled at present conditions}}$$

$$(7) \qquad pH_{new} = -\log(H^+{}_{measured} + \Delta H^+)$$

It should be noted that the approach we used allows pH to be estimated at discrete points; the approach does not provide explicit spatial connectivity between observation points, i.e., mixing downstream. However, the sampling design is such that different sites can be taken to represent stream segments of varying length, as in Laudon and Buffam (2008).

To answer the question “What are the characteristics of the stream reaches and subcatchments most sensitive to changes in BC?” we performed a partial least squares analysis (PLS) using the SIMCA-P 11.0.0.0 statistical package (Umetrics AB, Umeå, Sweden). The PLS model was constructed with ΔpH from three simulations as *Y* variables and 27 landscape characteristics (derived from maps and a digital elevation model) on soil types, land cover, stream order, catchment area, slope of the catchment, average height of the catchment and tree volume from satellite data (by the *k* nearest-neighbor method; Reese et al. 2003) as *X* variables. Before construction of the model, the variables were transformed to fit normality and were converted to *z* scores. For this paper, the purpose of the PLS modeling was not to predict ΔpH, but rather to determine which catchment–stream variables are associated with high ΔpH. When refining the model, an emphasis was therefore placed on reducing the number of variables down to the significant variables (95% confidence interval) with high weight.

Results

During present conditions (measured values), the BC concentration in the 60 stream segments during the spring snowmelt of 2004 was 229 (±54) μequiv.·L^{-1} (mean ± standard deviation (SD)). The base cations showed a normal distribution, checked with a one-sample Kolmogorov–Smirnov test in SPSS Statistics 17.0 (SPSS Inc., Chicago, Illinois). The average pH was 5.49 (Table 1). The comparison of modeled and measured pH suggests that the model succeeded well in predicting the pH in the stream segments during spring snowmelt (Fig. 2). The root mean square error (RMSE) between measured and modeled values was 0.15 pH units.

To put the modeled pH changes in perspective, we compared them with the observed episodic pH drop during snowmelt. From the winter baseflow to the spring snowmelt, the average pH drop was 0.87 pH units (SD = 0.37 pH units) (Fig. 3). The model predicts a further decline in pH during spring snowmelt for the different BC removal scenarios. A decrease of 10 μequiv.·L^{-1} BC would lower the pH during spring snowmelt by another 0.10 pH units on average. A decrease of 30 μequiv.·L^{-1} and 50 μequiv.·L^{-1} BC would decrease pH by another 0.31 (Fig. 3) and 0.56 pH units on average, respectively.

The decrease in pH was not uniform among streams. The largest pH effect for a given decrease in BC was found in stream segments with a contemporary snowmelt pH between 5 and 6, where the average pH decline due to a decrease in BC of 30 μequiv.·L^{-1} was 0.37 pH units. For stream segments with pH below 5 or above 6, the decrease was less pronounced, and the average decline was 0.26 and 0.22 pH units, respectively. There was a large variation in the sensitivity of the stream segments, but the PLS model (R^2X = 0.39, R^2Y = 0.32, Q^2 = 0.26) indicated that subcatchments with a steep slope and high forest cover (and also forested wetlands) were the catchments that had stream pH most sensitive to a change in BC (Fig. 4). On the other hand, the subcatchments with open fields were less sensitive in terms of ΔpH.

At present, 82% of the stream length in the catchment had a pH above 5 during spring snowmelt. The stream segments with pH below the thresholds 5 and 5.5 presently are located in the upper central part of the catchment (Fig. 5). In the BC removal scenarios, the pH changed significantly. If BC were to decrease by 30 μequiv.·L^{-1} throughout the network, the proportion of stream length with a pH above 5 would decrease to 62% (Fig. 6). A similar change was found for the

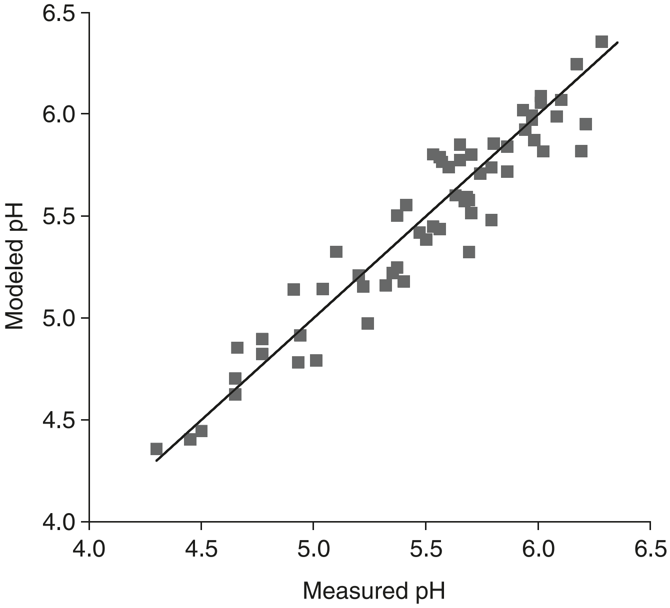
Table 1. Mean (standard deviation (SD)) of stream chemistry in the 60 stream segments during spring snowmelt of 2004.

Analyte	Mean (SD)
H^+ (μequiv.·L^{-1})	6 (9)
Ca^{2+} (μequiv.·L^{-1})	103 (31)
K^+ (μequiv.·L^{-1})	20 (11)
Mg^{2+} (μequiv.·L^{-1})	56 (12)
Na^+ (μequiv.·L^{-1})	49 (12)
SO_4^- (μequiv.·L^{-1})	81 (31)
NO_3^- (μequiv.·L^{-1})	4 (5)
Cl^- (μequiv.·L^{-1})	25 (6)
$RCOO^-$ (μequiv.·L^{-1})	118 (15)
HCO_3^- (μequiv.·L^{-1})	31 (27)
BC (μequiv.·L^{-1})	229 (54)
SAA (μequiv.·L^{-1})	106 (33)
ANC* (μequiv.·L^{-1})	123 (33)
DIC (μmol·L^{-1})	306 (68)
DOC (mg·L^{-1})	18 (4)
pH (pH units)	5.49 (0.49)

Note: BC, base cations; SAA, strong acid anions; ANC, acid-neutralizing capacity; DIC, dissolved inorganic carbon; DOC, dissolved organic carbon.

*ANC was calculated as BC – SAA.

Fig. 2. Modeled pH versus measured pH for the 60 stream segments. The 1:1 line is shown.



other pH threshold, where the stream length above pH 5.5 was 60% at present and would decrease to 35% with a BC drop of 30 μequiv.·L^{-1}. If BC were to decrease by 50 μequiv.·L^{-1}, the proportion of stream length with pH above the acid thresholds pH 5 and pH 5.5 would be 44% and 10%, respectively (Fig. 6). According to the most severe scenario, with a BC removal of 50 μequiv.·L^{-1}, the majority of the segments with a pH remaining above thresholds (marked in light green on the map in Fig. 5) would be located in the silty postglacial delta area and a few reaches would be found in areas with glaciofluvial sediments (Figs. 1 and 5).

Discussion

Impacts of harvest on watershed base cations

This section gives an overview of the impacts of harvest on watershed base cations based on a literature review. The watershed BC net-flux equation can be viewed as

$$(8)\quad \text{leaching} = \text{deposition} - \text{uptake} + \text{weathering} \pm \text{change in soil adsorbed pool}$$

Tree uptake of BC is balanced by the concurrent release of H^+, maintaining the charge balance in both tree roots and soil. Hence, forests acidify soils by trees taking up BC and releasing H^+; therefore, removal of the trees will result in a decreased BC uptake, which may increase BC leaching to streams in the short term. However, the large pool of BC removed in tree biomass by harvesting will, in the long term, likely result in reduced soil BC pools and reduced BC leaching to streams. How much BC will be removed will depend on the type of trees (Olsson et al. 1996) and the intensity of harvesting. Mass-balance studies indicate that WTH will increase the depletion of base cations in forest soils in the long term (Joki-Heiskala et al. 2003; Duchesne and Houle 2006; Akselsson et al. 2007). However, soil mineral weathering rates are difficult to assess and there are large uncertainties (Ouimet and Duchesne 2005). Therefore, despite decades of concern about surface-water acidification, the empirical basis for defining forest harvest influences on acidity status is not a sufficient basis for reliable predictions about how a more intensified silvicultural practice, in combination with climate change, will affect the BC export from the soil to surface waters.

In a model study using MAGIC in Sweden, the long-term effect of forestry practice on ANC in stream runoff was quantified (Westling and Kronnäs 2006). The authors calculated the change in ANC in runoff after the next rotation period using different forestry scenarios. The study showed that the response to WTH would be small in Scots pine *(Pinus sylvestris)* stands, whereas the soils in Norway spruce (*Picea abies*) stands are more sensitive and could show a substantial decrease of ANC in runoff (Westling and Kronnäs 2006). In a typical spruce stand in northern Sweden, WTH would decrease ANC by 20 μequiv.·L^{-1} in runoff compared with a stem-harvesting scenario. The same calculations on a catchment in the southern part of Sweden show that a whole-tree utilization scenario would give a reduction of 45 μequiv.·L^{-1} ANC in runoff. In the most extreme site among the 12 MAGIC modeling sites, the difference in BC in runoff between whole-tree and stem-only harvesting was almost 100 μequiv.·L^{-1} (Westling and Kronnäs 2006). A major reason for the difference between the sensitivity of the northern and southern parts of the country is that the southern parts have been subject to a larger anthropogenic acidification (at present, ca. 5 kg S·ha^{-1}·$year^{-1}$ and 13 kg N·ha^{-1}·$year^{-1}$ deposition compared with ca. 1 kg S·ha^{-1}·$year^{-1}$ and 1.5 kg N·ha^{-1}·$year^{-1}$ in the northern study catchment; Björkvald et al. 2009). This has depleted exchangeable BC in the southern soils, leaving them more sensitive to further acidification caused by forestry.

There is no consensus on the degree to which intensified forestry will contribute to surface-water acidification. Most of the studies on the effect of WTH study BC saturation in

Fig. 3. The shaded bars indicate the observed drop in pH in the 60 stream segments from baseflow to spring snowmelt. Baseflow data from Buffam et al. (2008). The solid bars indicate the further decline in spring snowmelt pH associated with a reduction in BC of 30 μequiv.·L^{-1}.

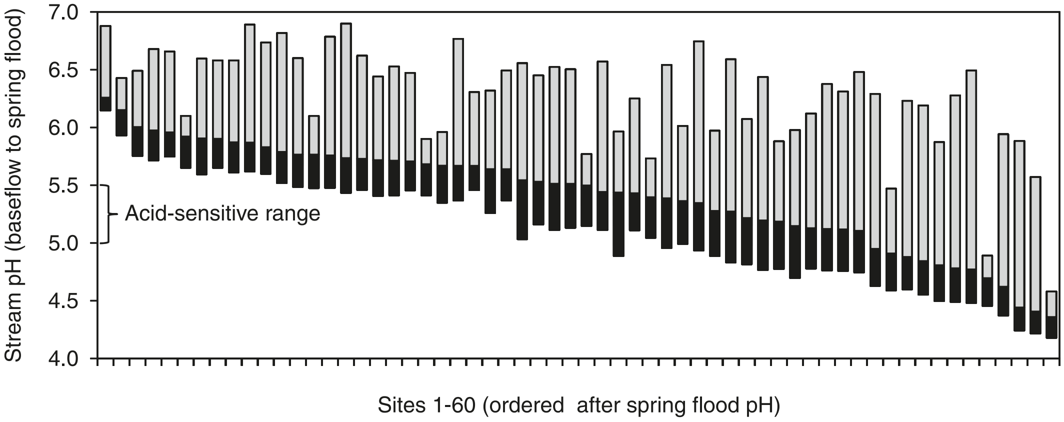
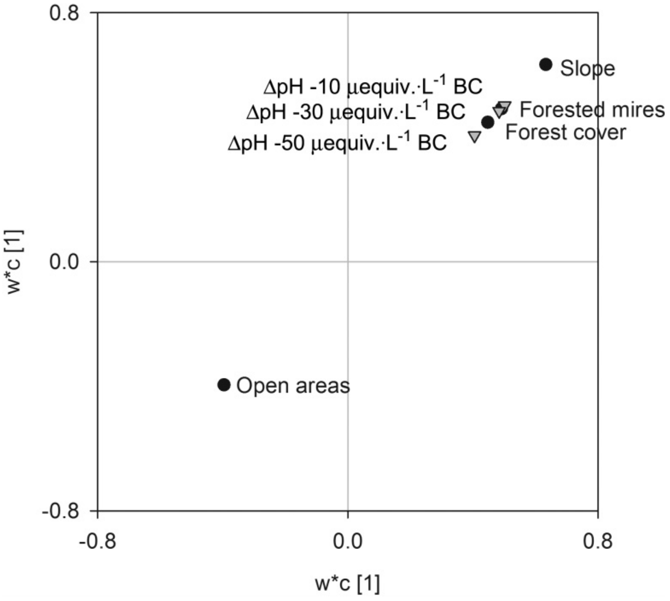


Fig. 4. Loading plot for the refined partial least squares (PLS) model with ΔpH from the different scenarios as dependent variables (shaded triangles) and four explanatory catchment characteristics variables (solid circles).



the soil, and few studies exist on runoff water. Comparison with long-term field experiments has shown that the soil hydrochemical MAGIC model might overestimate BC changes due to the lack of certain dynamic processes in the model. For instance, although second-rotation forest following WTH is expected to have a lower yield than the first rotation (in part due to soil BC depletion), this dynamic is not included in MAGIC. In long-term field experiments, the difference in acid load (in the soil) between stem-only and whole-tree utilization in measurements was only 10% of the potential (theoretical) effect (Staaf and Olsson 1991; Olsson et al. 2004). The evidence from experimental plots, mass-balance calculations, and modeling approaches indicates that intensified forestry will likely decrease BC in surface waters, but the quantification of that remains difficult. The response of stream BC dynamics to watershed BC depletion is expected to be complex and nonlinear, and we do not attempt to predict the dynamics of that response here. Rather, we present how sensitive stream pH is to stream BC change scenarios, of the same order of magnitude as those that might result from WTH. Based on literature studies, we would expect BC loss in streams to lie somewhere in the interval of 0 to 50 μequiv.·L^{-1}, but with variation between forest types (lower in pine and higher in spruce) and the location of the catchment (lower in the more pristine northern part of Sweden and higher in the more acidified areas in the south).

Impacts on stream pH distributions and ecological implications

During spring snowmelt, the pH drops in the study streams, and this study coupled with existing literature suggests that BC loss may result in further pH decline. Most of the pH drop (about 0.7–0.8 units) is due to natural variation resulting from dilution of ANC by the input of low ANC snowmelt water in combination with increasing levels of DOC (and associated organic acids) in the streams, which together typically result in the lowest annual pH (Bishop et al. 2000). At the end of the 1990s, about 0.1 to 0.2 pH units of the pH drop in the Krycklan catchment was due to acid deposition (Bishop et al. 2000); this part has now likely continued to decline as a result of the reduction in sulphur deposition (Laudon and Bishop 2002; Laudon and Hemond 2002). Spring snowmelt is the time when the streams would be most sensitive to BC removal because of the ANC decrease. In addition, during spring snowmelt, the water table rises, and the more superficial soil layers where we expect the largest WTH-derived changes in exchangeable BC (Olsson et al. 1996) contribute the majority of the snowmelt stream water (Bishop et al. 2004). In the scenarios, a removal of about 10–20 μequiv.·L^{-1} BC would affect pH of the same order of magnitude as acid deposition did at the end of the 1990s.

The study suggested that pH in the stream network was relatively sensitive to BC removal during spring snowmelt and that much of the stream length would decrease into the biologically sensitive range (pH 5–5.5) or below. Recent studies have shown that for many Swedish freshwaters, pH is the best predictor of brown trout mortality (Serrano et al. 2008), as well as the presence or absence of acid-sensitive fish species (Holmgren and Buffam 2005) and invertebrate

Fig. 5. Change in stream length with pH_{new} below or above the thresholds with different percentage removal of BC during the spring snowmelt.

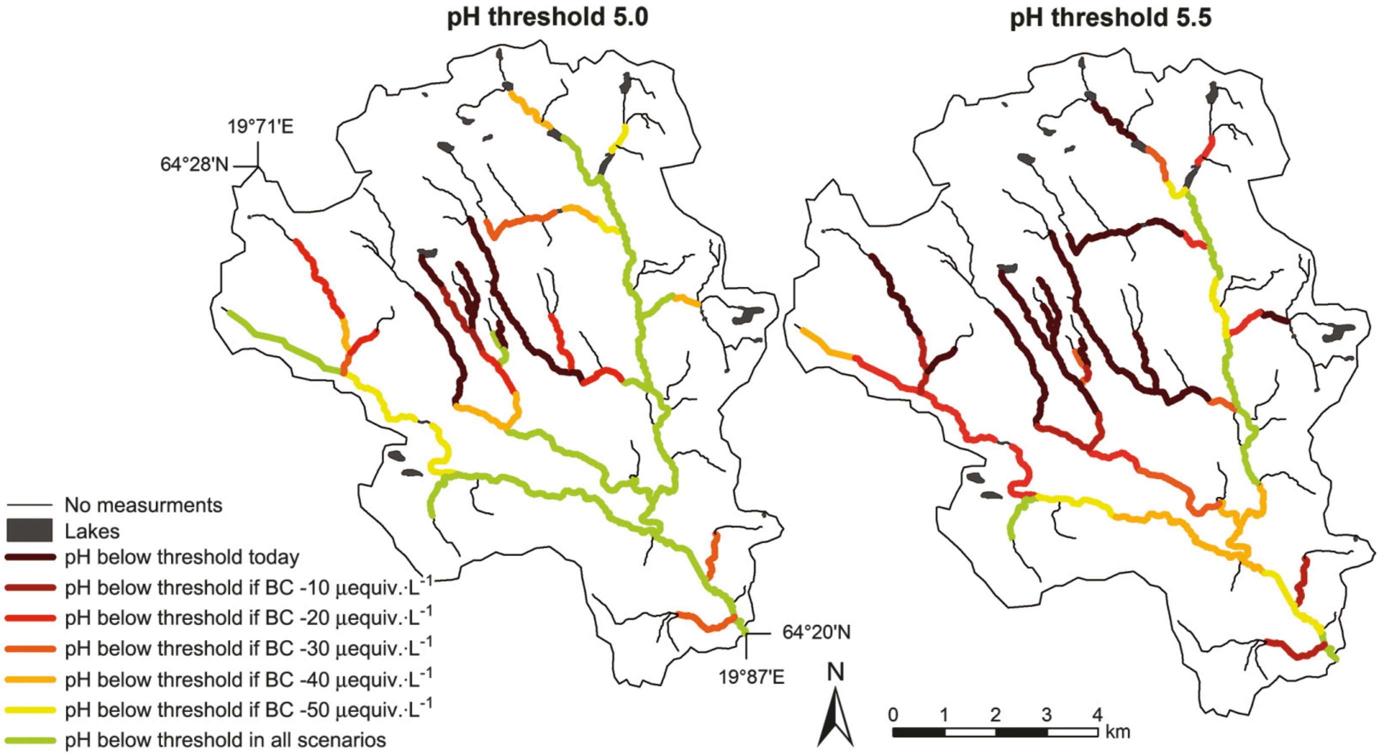
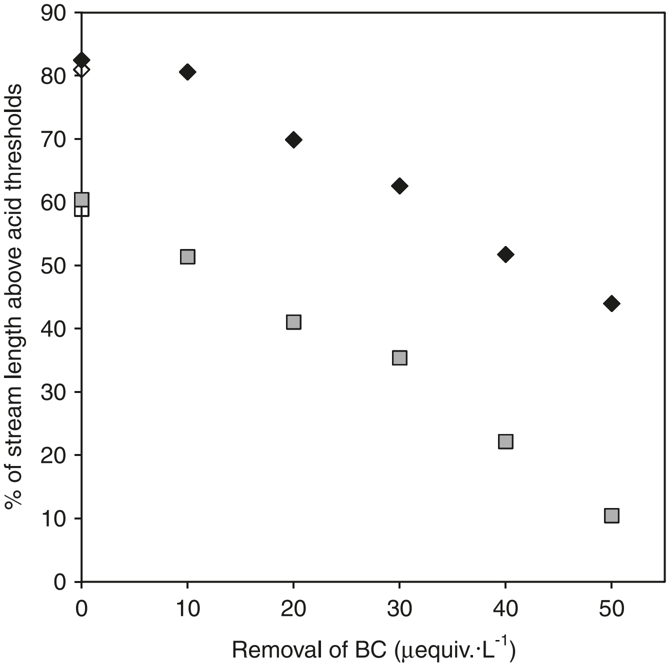


Fig. 6. Stream length affected by low pH during spring snowmelt in different BC removal scenarios: solid diamonds, stream length below pH threshold 5.0; shaded squares, stream length below pH threshold 5.5. To illustrate the model fit, we show both measured values (the open symbols) and modeled pH (solid symbols) on the *y* axis. Solid symbols indicate the stream length above acid thresholds calculated as pH_{new}.



species (Fölster et al. 2007). Although the spring snowmelt is a short period, it is extreme regarding pH changes and has been found to be an ecologically critical period for acid-sensitive biota (Lepori and Ormerod 2005). Removal of BC from the catchment is therefore likely to have an ecological impact on the habitats for a range of acid-sensitive aquatic species. According to the new Environmental Quality Guidelines from the Swedish Environmental Protection Agency, anthropogenic acidification at baseflow is classified as a human-induced pH drop of at least 0.4 units. However, during episodes, a change of 0.2 pH units is classified as anthropogenic acidification (Swedish Environmental Protection Agency (EPA) 2007). In the 30 µequiv.·L^{-1} removal scenario, that would mean that 58% of the stream length would be classified as anthropogenically acidified, and in the 50 µequiv.·L^{-1} scenario, 100% of the stream length would be classified as affected as a result of forestry effects alone.

pH was most easily affected between pH 5 and pH 6. Above pH 6, the bicarbonate becomes important for buffering pH changes, and for the lower pH range (below 5), the organic buffering becomes more significant. The sensitivity of pH to the BC-removal scenarios showed a clear spatial pattern in which downstream segments had a greater buffering capacity than the small headwaters. The PLS analysis supported the hypothesis that pH sensitivity was greatest in the small headwaters with a higher slope compared with the downstream areas with less topography. On the contrary, subcatchments with the open fields (agricultural areas on fine-grained soils) were better buffered and less sensitive to a removal of BC. This reflects the sensitivity of the catchments and the pH, BC, and ANC status of the different stream segments under present conditions (Buffam et al. 2008). The small, first-order catchments tended to be more acidic, whereas downstream catchments were better buffered. Stream pH has been found to vary with altitude and distance downstream in a predictable way in other studies as well (Likens and Buso 2006). This has been partly attributed to changes in flowpaths (Driscoll et al. 1988) where the downstream catchments, with a large accumulated stream length, will have a longer subsurface-water transit time. Hence, the groundwater will accumulate more ions from weathering of the mineral soils intersected en route to the stream. The downstream trend in pH can also be attributed to changes in soil types (Soulsby et al. 2006; Ågren et al. 2007; Buffam et al. 2008). The postglacial fine sediment (silty) area in the lower part of the catchment has a high specific surface area, which increases the opportunity for weathering and BC exchange between the mineral surfaces and the water. However, in the upper areas of the catchment, the soils are characterized by till, exposed bedrock, and thin soil (Ågren et al. 2007) and hence contain less BC that can be exported to the stream. The streams draining these upper areas are more prone to be adversely affected by BC removal. One notable exception is headwater wetland streams in which pH is largely buffered by high concentrations of organic acids. In our study, there was an overrepresentation (Buffam et al. 2008) of the downstream better-buffered catchments. Had we sampled more of the small, first-order catchments, it is possible that the increase in stream length with pH below biological thresholds would have been even greater in the different scenarios.

The PLS analysis also indicated that the subcatchments with a high proportion of forest cover and forested mires were more sensitive to a loss of BC. There is a large variation among catchments depending on soil types, distance downstream, and other variation, but there are plausible mechanistic reasons for the forest cover pattern. First, the lowest pH and BC are found in wetland areas and thus will not show a large pH change in our scenarios, partly due to the logarithmic scale of pH. At the other end of the scale, in streams with high pH and BC, the pH is buffered against change by bicarbonate (inorganic alkalinity). Many variables interact to create these high pH streams, but in brief, they are associated with agricultural areas, fine sorted sediments, lower lying stream reaches, and large accumulated stream length (Buffam et al. 2008). This means that downstream we get input of “old deep groundwater” into the streams that have had a long water subsurface transit time and also traversed the silty sediment area with a large specific area allowing for many ion exchange sites in the soil. Hence, this water is well buffered and rich in BC (Laudon et al. 2007; Buffam et al. 2008). Streams most sensitive to BC loss are instead those with upland forested catchments on unsorted till.

Although we have taken a simple approach with uniform BC removal in all streams for our scenarios, in reality, any response to an environmental perturbation would be more complex. The amount of BC that is removed from a catchment due to forestry would be affected by the forest coverage, tree species, different proposed rotation periods, stem-only or whole-tree harvesting, etc. The sensitivity of the catchment to the removal of BC is dependent on the weathering rates of the soils, which in turn are related to the Quaternary deposits. The hydrology of the catchment, the length of flowpaths, subsurface pathways, and residence time in the soil will also affect the sensitivity of the streams to catchment removal of BC, as will the historic acid deposition that may have reduced the base saturation of the soils (Jönsson et al. 2003). High nitrate fluxes have been observed in some studies following harvesting (Tremblay et al. 2009), and although this process only goes on for a couple of years after clear-cutting (Wang et al. 2006), the BC losses can be substantial during this period. Because we focus on the long-term perspective and nitrification is more short term, we decided not to go into this process any further. Also, the study region is severely nitrogen-limited, with very little leakage of nitrogen after clear-cutting (Löfgren et al. 2009). Future levels of acidifying pollutants may also affect the pH in the streams in the long term, even if the emissions have been reduced significantly. Nitrogen fertilization of forest soils to increase forest productivity is another scenario that might affect the pH in the streams, both due to increased removal of BC at harvesting and as a direct effect of nitrogen fertilization on nitrate fluxes. Reduced deposition, changed precipitation patterns, and higher temperatures may also affect the concentrations of organic acids in the streams in the future (De Wit and Wright 2008), as well as the weathering rate of BC (Egli et al. 2008). In the face of this complexity, we maintained a simple approach to testing the sensitivity of the stream network to BC loss, a likely effect of intensified forestry. The hope is that future research will provide a more detailed answer to the long-term effects that might be seen in stream pH, depending on the combination of factors listed above. Krycklan catchment is used as a case study, but the results here are probably informative for many sites with acid-sensitive soils in the northeastern US and Canada, as well as in Scandinavia where several modeling studies have predicted acidification with WTH (e.g., Joki-Heiskala et al. 2003; Clair et al. 2007; Aherne et al. 2008). Because the long-term effect of different forestry practices is unclear, there is all the more reason to evaluate BC sensitivity before, rather than after, eventual problems arise.

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