

Separating Natural Acidity from
Anthropogenic Acidification in the
Spring Flood of Northern Sweden

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Abstract

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Spring flood is an occasion for transient hydrochemical changes that profoundly effect the biodiversity of the aquatic ecosystem. Spring flood is also very susceptible to anthropogenic acidification. Belief that acid deposition is primarily responsible for pH decline during spring flood has been an important factor in the decision to spend close to one billion Swedish crowns to lime surface waters in northern Sweden during the last decade.

The objective of this work is to present an operational tool, the Boreal Dilution Model (BDM), for separating and quantifying the anthropogenic and natural contributions to episodic acidification during spring flood episodes in northern Sweden. The limited data requirements of 10-15 stream water samples before and during spring flood make the BDM suitable for widespread use in environmental monitoring programs. This creates a possibility for distinguishing trends and spatial patterns in the human impact as well as natural pH decline.

The results from applying the BDM, and a one point "pBDM" version of the model, in northern Sweden demonstrate that the anthropogenic component associated with spring flood episodes is now generally limited. Instead it is the combination of natural organic acidity and dilution of the buffering capacity that is the major driving mechanism of episodic acidity during spring flood events in the region. While the anthropogenic component of episodic acidification generally contributes 0.1 to 0.3 pH units to the natural pH decline of up to 2.5 pH units, the current regional extent of areas that are severely affected by anthropogenically driven episodes is approximately 6%.

Prior to the initiation of the Swedish Environmental Protection Agency's "Episode Project", the limited spring flood data together with lack of a systematic methodology for determining liming candidates forced the liming authorities to base the remediation strategy in northern Sweden on biological indications. But, since there are more reasons why acid sensitive species may be absent or not thriving, including natural acidity, physical habitat degradation, or an earlier period of anthropogenic acidification that ceased many years earlier, biological indicators are not a reliable guide to the contemporary acidification status. Instead hydrochemical models, such as the BDM, are needed.

Key words: anthropogenic acidification, DOC, episodic acidification, natural acidity, northern Sweden, operational model, spring flood.

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Appendix

Papers I-V

This doctoral thesis is based on studies reported in the following papers, which will be referred to in the text by the corresponding Roman numerals.

- I. Bishop, K., H. Laudon and S. Köhler. 2000. Separating the natural and anthropogenic components of spring flood pH decline: A method for areas that are not chronically acidified. *Water Resources Research* 36(7), 1873-1884.
- II. Laudon, H., O. Westling and K. Bishop. 2000. Cause of pH decline in stream water during spring melt runoff in northern Sweden. *Can. J. Fish. Aquat. Sci.* 57, 1888-1900.
- III. Laudon, H., O. Westling, S. Löfgren and K. Bishop. 2000. Modeling pre-industrial ANC and pH during the spring flood in northern Sweden. (In review.)
- IV. Laudon, H., O. Westling, A. Bergquist and K. Bishop. 2000. Episodic acidification in northern Sweden: A regional assessment of the anthropogenic component. (Manuscript.)
- V. Bishop, K., H. Laudon, J. Hruška, P. Kram, S. Köhler and S. Löfgren. 2000. Does acidification policy follow research in northern Sweden? The case of natural acidity during the 1990's. (In review.)

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Sammanfattning

Vårfloden är, för många organismer i norrländska vattendrag, den ekologiskt viktigaste händelsen på året. Upp till hälften av årsavrinningen kommer i små och medelstora vattendrag under de tre till fyra veckorna på våren som snösmältningen pågår. Det uppträder även dramatiska vattenkemiska förändringar i samband med vårfloden, som utgör naturliga begränsningar för allt levande i ekosystemen. Tyvärr är vårfloden i Norrland också utsatt för en försurningsbelastning som medför en påverkan på flora och fauna utöver den naturliga och i värsta fall kan slå ut vissa känsliga arter. Försurningssituationen under snösmältningen försvåras ytterligare av att våren är en tid på året då många fiskarter befinner sig i känsliga utvecklingsstadier.

I Norrland påbörjades storskalig kalkning 1991 efter det att biologiska studier i vattendrag indikerat en avsaknad av vissa arter. Dessa biologiska indikationer tillsammans med Naturvårdsverkets bedömningsgrunder för kalkning (där alla vattendrag med ett pH under 6,0 någon gång under året kunde erhålla kalkningsbidrag) medförde att en storskalig verksamhet drogs i gång i många län. Idag, nästan tio år senare, har totalt närmare en miljard kronor spenderats på kalkning i Norrland. Av dessa pengar har en stor del gått till att förhindra ekologiska skador i samband med vårfloden.

Orsaken till att drastiska pH sänkningar, så kallade surstötter, uppstår i samband med vårfloden är dock mycket komplex och sur nederbörd är bara en av många möjliga faktorer. Naturliga faktorer kan ge upphov till minst lika kraftiga surstötter. Det är också svårt att utifrån biologiska indikationer i form av minskad fiskförekomst fastställa den depositionsbetingade (som orsakas av luftföroreningar) försurningens utbredning i Norrland, eftersom andra faktorer som skogsbruk, flottning, vandringshinder och överfiskning kan ge liknande effekter. Dessutom kan det ta flera årtionden innan biologin återhämtar sig trots reella förbättringar i vattenkemin. Den tidigare avsaknaden av en tillförlitlig metod för att separera naturlig surhet från antropogen försurning i samband med högflöden har därför försvårat en prioritering mellan objekt för att undvika att kalka naturligt sura vattendrag i Norrland.

Huvudsyftet med ”episodprojekt”, finansierat av Naturvårdsverket och där detta arbete är en del, har varit att öka den vetenskapliga basen för kalkningsverksamheten i Norrland. Syftet med det arbete som resulterat i denna avhandling har varit att ta fram en ”episodmodell” som kan särskilja naturlig respektive antropogen försurningspåverkan under surstötter.

Episodprojektet och byggandet av episodmodellen har följts av en bred referensgrupp med deltagare från Naturvårdsverket, länsstyrelserna i Norrland samt ett tiotal forskare från Sverige och Norge. Detta samarbete har lett till att vi idag bättre förstår vårflodens komplexa natur. För att möjliggöra en så korrekt beskrivning som möjligt av försurningspåverkan från luftföroreningar i samband med högflöden i

norrländska vattendrag samt för att testa olika kritiska aspekter av surstötdynamiken så har en mängd olika delprojektet, bl.a. ett fiskprojekt, ingått i episodprojektet.

Episodmodellen, som även kallas BDM (Boreal Dilution Model), är ett verktyg som kvantifierar hur stor del av ANC ("Acid Neutralisation Capacity" eller buffertkapacitet) och av pH-minskningen som orsakas av luftföroreningar respektive naturliga källor under surstötter. Modellen beräknar hur kemin i ett vattendrag skulle vara i samband med vårflods- och kraftiga regnepisoder utan inverkan av försurande luftföroreningar, det vill säga en naturlig vattenkemi. Episodmodellen möjliggör att i enskilda vattendrag avgöra hur stor del av de observerade surstöterna som kommer från naturliga respektive depositionsbetingade källor på ett sätt som tidigare inte varit möjligt. Framför allt är modellen tänkt att användas i områden där försurningspåverkan är episodisk, t.ex. i Norrland. I framtiden kan dock episodmodellen komma att användas i andra delar av landet då försurningsproblematiken, i samband med minskande surt nedfall, övergår från kronisk till mer episodisk karaktär.

Den användarvänliga beräkningsmodellen där episodmodellen står som grund, är redan i bruk inom ramen för olika miljöövervakningsprogram i landet. Modellen finns nu att tillgå i en internetbaserad version (<http://www.sek.slu.se/personal/hlaud/hjalmar.htm>). Modellen ger tjänstemän och andra intresserade möjlighet att använda ett avancerat utvärderingsverktyg utan att fastna i komplex kemisk jämviktsmodellering.

Resultaten från de över 20 vårflodsepisoder som presenteras i denna avhandling visar att naturliga källor, framförallt organiska syror och utspädning, i de allra flesta fall står för de största bidragen till de uppkomna surstöterna. Generellt bidrog luftföroreningar endast med 0,1 till 0,3 pH enheter av den observerade pH nedgången på upp till 2,5 pH enheter. I en regional studie som också presenteras i denna avhandling visas att endast ca 6% av Norrlands yta idag fortfarande är försurningspåverkat i samband med vårflodsepisoder. Den största andelen av dessa vatten ligger i den sydvästra fjällregionen.

Ett viktigt resultat som framkommit ur det här doktorsarbetet är att försurningsproblematiken i samband med vårfloden är starkt kopplad till koncentrationen av försurande ämnen i snön. Detta visar att en förändring av försurningsbelastningen i Norrland ger omedelbara effekter på vattenkemin. Eftersom det tar avsevärt längre tid innan de vattenkemiska förbättringarna leder till biologisk återhämtning så är det omöjligt att säga något om dagens försurningspåverkan med biologiska indikatorer. I stället behövs vattenkemiska verktyg, som t.ex. episodmodellen, för att utröna de naturliga respektive antropogena surstötsfaktorernas betydelse under rådande försurningsbelastning. En viktig slutsats från detta arbete är att det beslutsunderlag som idag används för att bedöma vilka vattendrag som ska kalkas i Norrland måste revideras så att en kalkning av naturligt sura ytvatten, till skillnad från idag, kan undvikas.

Background

Surface waters acidification has been the focus of much environmental research during the last 30 years. Despite large scientific advances in this field of research, though, fundamental questions about the effects of acid deposition on soils, surface waters and biology are still frequently discussed (e.g. Frink, 1996; Binkley and Högberg, 1997). A central question for regions on the boreal fringes of acidification that has long remained unanswered is the role of anthropogenic deposition during snow melt and storm runoff. For even though the acidity of surface waters often reach exceptionally high levels during these periods of high flow, there is a significant contribution from natural sources to these pH declines. One such boreal region on the fringe of acidification is northern Sweden where levels of acid deposition are relatively low but surface waters commonly experience low pH in conjunction with hydrological episodes, especially spring flood runoff.

To determine if surface waters are acid is not a difficult task since it is just a matter of measuring pH. But to determine if that same water has been acidified by acid deposition, is much more difficult. The term acidification defines a process moving from one chemical state to another, more acidic condition. Acidification of surface waters can be “chronic” due to permanent changes in surrounding soils, or “episodic” driven by hydrological events caused by snow melt runoff or rain storms. These processes can be entirely natural but also anthropogenic. Natural and anthropogenic acidification can also be superimposed upon each other. This latter situation is the case during episodes of high flow in northern Sweden, but this has not always been recognized, much less quantified.

The acidification debate in Sweden started with a Swedish newspaper article in October 1967 by Svante Odén (Odén, 1967). This article by Odén was the first time distant pollution source was cited as the explanation for declining fish populations in many surface waters in southwestern Scandinavia. His findings also served as the starting point of a chain reaction that, among many things, led to an almost immediate reduction of sulfur emissions in Sweden (Lundgren, 1991). Since Odén’s newspaper article, Swedish authorities have taken great strides in both international negotiations to reduce emissions and by remediation of anthropogenic surface water acidification.

In northern Sweden the acidification debate did not start until the beginning of the 1990’s. The stage for that debate was set by a report (Ahlström and Isaksson, 1990) which claimed that there was large scale biological damage in the region caused by acid deposition. No mention was made in that report of natural causes of acidity. Despite this shortcoming, or perhaps because of it, that report was instrumental in a decision by the Parliament to increase funds for liming so that the authorities also in northern Sweden could lime acid surface waters.

Biological indications of acidification were an important basis for the interpretation of the low pH found in northern Sweden, especially during episodes. The reliance on biological indicators resulted partly from an interest in fish status and partly from a lack of adequate hydrochemical measurements. This contributed to the failure to recognize the presence of natural acidity and the importance of separating those natural causes from anthropogenic acidification.

Biological acidification studies without adequate hydrochemical information can rarely elucidate the cause and extent of anthropogenic acidification in northern Sweden since a lack of older biological studies in the region often hinders such an analysis (e.g. Ahlström et al., 1995). Furthermore, several other factors besides acidification, such as damaged spawning grounds, migratory restraints, overfishing and introduction of new species could have caused the diminished fish stock in small lakes and streams in the region observed by many older residents of the region with an interest in fishing.

Despite the limitations in the tools for interpreting the causes of acidification in northern Sweden presented by Ahlström and Isaksson (1990) the report came to form the basis of the multimillion crown liming program in the region. Since 1991, the Swedish liming program has been subsidized by the Swedish government with between 150 and 200 million Swedish crowns annually. Approximately half of the national liming subsidy, or close to one billion Swedish crowns during the last decade, has been spent in northern Sweden. A further expansion of that liming program, with a focus on northern Sweden, was recently suggested for the coming 10 year period (SEPA, 1999).

During the 1990's a liming strategy based on the national policy guidelines for liming (SEPA, 1988) has been pursued. This policy states that all surface waters with a pH below 6.0 or alkalinity below $50 \mu\text{eq L}^{-1}$ at any time during the year are eligible for nationally subsidized liming. The official liming guidelines are now being revised (SEPA, in review). The official version now in review suggests that liming should focus on protecting and reestablishing the natural biodiversity. In the new proposed guidelines three levels of pH are given as the minimum tolerable pH at any time of the year depending on the level of natural acidity (6.3, 6.0, and 5.6).

Throughout the 1990's there has been a considerable concern that liming is not appropriate in northern Sweden since natural acidity is at least partly responsible for the low pH and alkalinity in the region (Bishop, 1991; Kullberg et al., 1993; Ivarsson and Jansson, 1995; Warfvinge et al., 1995; Bishop, 1997; Warfvinge et al., 1998). The opposition and debate has been driven by the fear that liming naturally acid systems would not only artificially raise pH to unnaturally levels but would also eliminate natural temporal and spatial variations in stream water chemistry. While an artificially raised pH will give negative effects on the natural biodiversity of such systems (Blomqvist et al., 1995), a homogenization of surface water chemistry could lead to less genetic variation and a competitive advantage for new species (Poléo, 1998).

A limitation of the early opposition to liming in northern Sweden was the difficulty of quantifying the natural sources of acidity. An important development for the improved understanding of the role of natural acidity was therefore the paleolimnological findings that no regional pH decline had occurred since pre-industrial times in the two most northern counties (Västerbotten and Norrbotten), despite the generally low contemporary pH of the lake water in the study (Korsman, 1993; 1999). However, since the diatom reconstructions of historic lake pH values respond to gradual changes in lake chemistry, and therefore do not necessarily reflect the transient change in pH associated with acid episodes, the findings by Korsman did not address the issue of how large the anthropogenic acidification component in northern Sweden was during episodes. Instead, the paleolimnological evidence brought the issue of spring flood episodes even more into the focal point of the acidification debate in northern Sweden.

In 1995 the Swedish EPA organized a workshop on the liming controversy in northern Sweden. The consensus document from that workshop called for an improvement in the scientific basis for understanding the problem of episodic acidification in northern Sweden (Löfgren and Bertills, 1995). In order to improve the scientific involvement in the liming program, the Swedish EPA Research Division and Liming Program jointly financed the multi-investigator Episode Project. The project, which has been running since the fall of 1996, has involved researchers from several universities in Sweden and Norway as well as representatives from both national and regional environmental protection authorities. The Episode Project consists of four parts; 1) monitoring and modeling chemical driving mechanisms of episodic acidification, 2) studying fish physiological response associated with spring flood pH decline, 3) modeling changes in baseflow chemistry in northern Sweden due to acid deposition and land-use, and 4) integration of biological and chemical results.

Objectives

The purpose of this thesis is to present the results from the first part of the Episode Project on monitoring and modeling chemical driving mechanisms of episodic acidification (although some results from the other parts will also be presented). The more specific objectives of the water chemistry part of the Episode Project were to:

1. Establish a protocol for data collection when monitoring episodic acidification.
2. Collect relevant data since limited data was available at the outset of the project.
3. Develop an operational model for separating natural acidity from anthropogenic acidification.
4. Provide recommendations to improve liming activity in northern Sweden.

Spring flood pH decline

Most naturally acid boreal environments have been acidified by slow processes since the last glaciation (Renberg et al., 1993). These acidification processes is due to production of organic acids in the top soil which leach the mineral soil as precipitation percolates down through the soil profile. This produces acid podzols. In low-lying areas paludification has led to the development of peats and wetlands. The podzolization and aging of the soil decreases the flux of base cations while the wetlands increase the flux of organic acids to surrounding surface waters. These natural processes have led to a situation where 8%-16% of the over 70,000 lakes (and probably a larger proportion of the almost one million km of streams) in northern Sweden are naturally acid i.e. have a natural pre-industrial pH below 6.0 (Lars Rapp, unpublished data). However important these slow natural processes are for forming the natural background environment in boreal regions, the transient changes associated with hydrological events superimposed on those baseflow conditions are often the major chemical constraints for many aquatic species in the region.

Transient changes in stream water chemistry associated with increasing discharge during rain or snow melt events often induce large declines in pH and acid neutralization capacity (ANC). The episodic pH decline is typically preceded by a change in the concentration of most major dissolved solutes due to a shift in the sources and pathways of water. During low flow periods (baseflow conditions) water is derived mainly from deeper mineral soil horizons and the groundwater zone with longer water residence times, where the accumulated effect of mineral weathering renders the water relatively alkaline. During hydrological events, rain or snow melt input generates a rising water table activating water flow through more superficial layers. These upper soil horizons are often more acidic due to higher concentrations of natural organic acidity and/or acid deposition. In northern Sweden, the upper horizons typically have a higher hydraulic conductivity allowing a more rapid transfer of water through the soil to the stream (Rodhe, 1987). Thus the pH and buffering capacity of the surface water originating from these episode-activated hydrological reservoirs are often depressed considerably relative to baseflow (Bishop et al., 1990). Recent research has shown that, contrary to popular belief, soil frost does not often alter the hydrology of spring flood in the boreal forest (Nyberg et al., in press; Stähli et al., in press).

The spring flood of many boreal environments has large ecological significance (e.g. Simonin et al., 1993). Not only do the natural transient changes in hydrology and hydrochemistry form the basis for the life cycle and competitive advantages of certain aquatic species (Poléo, 1998), the spring flood also has important implications for the nutrient transport and microbiology of surface waters (Jansson et al., 1999; Stepanauskas et al., 2000). Furthermore the spring flood in northern Sweden is of large hydrological interest since up to 50% of the annual runoff in small catchments occurs during the three to four week snow melt period.

However, since approximately half of the annual acid deposition load can accumulate in the winter snow pack and many of those acidifying compounds are released from the snow during the initial stages of melting (Johannessen and Henriksen, 1978), spring flood is particularly vulnerable to anthropogenic acid deposition. The sensitivity towards unnatural effects on the timing, duration and decline in pH during the spring flood is of particular concern since this is a period when many aquatic species are at sensitive life stages of their development (Vanoffelen et al., 1994).

Despite both the potential threat to the biodiversity in northern Sweden and the large government spring flood liming subsidy, surprisingly few episodic acidification studies have been conducted in the region. The isolated studies prior to the initiation of the Episode Project, demonstrate that both anthropogenic (Jacks et al., 1986; Ahlström, 1994) and natural factors (Jansson and Ivarsson, 1994; Löfgren, 1996) can be the main source of the increased acidity during spring flood events. The significance of the findings from the first episodic study (Jacks et al., 1986) for the situation today needs to be considered circumspectly though, because the acid deposition levels in the region have decreased substantially since that study was conducted 15 years ago. The limitation in the number of earlier observations also prevented an analysis of the geographic spread of anthropogenic acidity. The previous studies did, however, demonstrate that before the need for liming could be assessed, there was a need both for a systematic approach to separating natural sources of acidity from anthropogenic sources, as well as a more synoptic approach to the problem in northern Sweden (Löfgren and Bertills, 1995).

Although the problem of episodic acidification associated with snow melt received limited scientific attention in Sweden during the 1980' and early 1990's, the problem received more attention in other seasonally snow covered regions where transient changes in pH and ANC were a threat to aquatic organisms. Extensive reviews of these early developments in the understanding of episodic acidification are provided by Wigington et al. (1990) and Eshleman et al. (1992). Among the first to use a time series approach to estimate sources of episodic acidification was a study from central Ontario in Canada by Molot et al. (1989). The model developed by Molot et al. (1989), quantifies the relative contribution of dilution as well as strong acid anions to the decline in buffer capacity during episodes. Similar approaches have been used by a number of subsequent episode studies to estimate episodic sources of ANC decline (DeWalle and Swistock, 1994; Evans et al., 1995; Hyer et al., 1995; Wigington et al., 1996; Laudon and Bishop, 1999a) and increases in H^+ concentrations (Campbell et al., 1992; Kahl et al., 1992). While the approach first suggested by Molot et al. (1989) and later used in numerous studies was a great step forward to a better understanding of the mechanisms driving episodic acidification, these models did not solve the fundamental question for northern Sweden about the relative importance of natural and anthropogenic sources for the pH decline in areas with high levels of organic acidity.

Sources of acidity during spring flood

The pH decline of boreal surface waters associated with spring flood is often the result of several natural factors. In areas of anthropogenic deposition these natural factors can interact with the effects of acid deposition to produce toxic acid surges. These natural processes include, dilution of the buffering capacity, input of organic acids, oxidation of sulfides in marine sediments and bedrock, supersaturation of CO₂ and sea salt episodes. The anthropogenic sources originate mainly from airborne acid deposition, but could also include oxidation of natural soil sulfur due to land drainage. (Fig. 1)

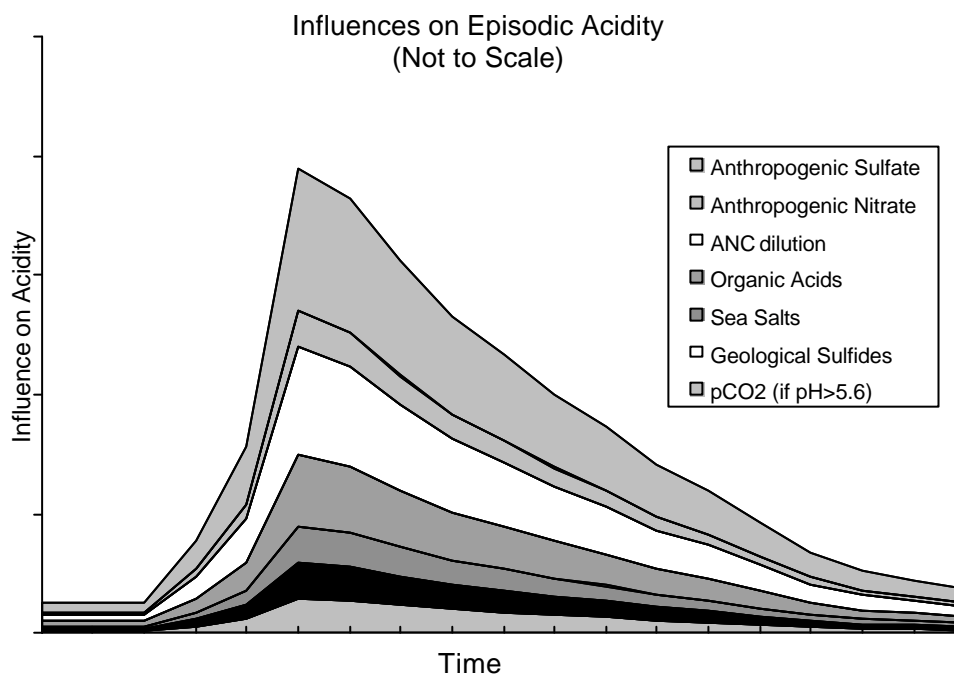


Fig. 1. Conceptual diagram of the potentially natural and anthropogenic influences on episodic acidification during spring flood and rain events.

Anthropogenic sources of acidity

Sulfate

Anthropogenic SO₄²⁻ deposition has caused extensive damage to soils and surface waters world wide (Rodhe et al., 1995). Reports on the chronic long term effect due to SO₄²⁻ deposition have proliferated in the scientific community for more than three decades (e.g. Odén, 1968; Henriksen, 1979; Mason, 1990; Likens et al., 1996). Studies in eastern USA and Canada (Tranter et al., 1994), as well as in Europe (Davies et al., 1992; Wigington et al., 1992), have also concluded that anthropogenically derived SO₄²⁻ is one of the most important factors depressing pH and ANC during hydrological episodes. In northern Sweden episode studies in weakly buffered streams have also cited anthropogenic SO₄²⁻ as having a major

influence on the stream water chemistry during hydrological episodes under certain circumstances (Jacks et al., 1986; Ahlström, 1994; 1999; Laudon and Bishop, in review A).

During the initiation phase of acidification, most of the deposited SO_4^{2-} is neutralized in the soil, which implies that the negatively charged SO_4^{2-} is co-transported with positively charged base cations leached from the soil rather than protons and toxic aluminum species. In later stages of soil acidification, base cations will be depleted, allowing more protons and inorganic aluminum to follow the mobile SO_4^{2-} anion to surface water (Reuss and Johnson, 1986). Therefore, in a short time perspective, acid deposition will not lead to an acidification of the runoff leaving the catchment. In a longer time perspective, though, exhaustion of base cations and acidification of the soil will result in surface water acidification.

Schematic models of SO_4^{2-} dynamics often state that the export of SO_4^{2-} from a catchment should equal the deposition input (e.g. Bernes, 1991). Mass-balance studies of sulfur, however, often show that there is a large seasonal variation in the export due to an internal temporal storage and more permanent retention of sulfur in many soil systems. The seasonal variation is due to an accumulation of SO_4^{2-} during the winter and summer periods. Only a part of the accumulated deposition is often washed out during high flow events during the spring flood and fall rain storms (Steele and Buttle, 1994; Allan, 1995). Steele and Buttle (1994) demonstrated that much of the anthropogenic SO_4^{2-} released during snow melt was transported and stored in the unsaturated zone. They concluded further that this storage was only partially depleted at the end of the melting and that a large portion of the sulfur may be lost as a result of deep groundwater flow, biological uptake or may undergo transformation to less mobile organic forms. In wetland areas the SO_4^{2-} retention has been found to be as large as 80% of the SO_4^{2-} input under certain hydrological conditions (Devito and Hill, 1997). This is similar to the approximately 65% retention of SO_4^{2-} , with the retention being positively correlated to wetland area, associated with spring flood found in the Episode Project (Laudon, 1999). In northern Sweden there is also a large unused SO_4^{2-} retention capacity in the soil that can retain SO_4^{2-} more permanently (Karlton, 1995). Retention of SO_4^{2-} in the soil decreases the acidification effect on both the soil and runoff. Recently, however, it has been shown that large amounts of organically bound sulfur can be mineralized and released from forest soils, delaying the recovery from soil and water acidification in southern and central Sweden (Mörth et al., 1999; Löfgren, 2000). Karlton (1995) concluded that soils in central and northern Sweden have a higher total capacity to retain SO_4^{2-} than soils in the southern part of the country. This implies that soils in the north have a higher capacity to neutralize deposited SO_4^{2-} and therefore are less susceptible to soil and surface water acidification compared to catchments in southern Sweden.

The contemporary deposition level of SO_4^{2-} in northern Sweden is ca. 1-3 kg S- SO_4^{2-} ha^{-1} yr^{-1} of which approximately half is deposited during the winter months (Kindbom et al., in press). Scenarios of historic SO_4^{2-} deposition in Sweden suggest that the

peak in SO_4^{2-} deposition was ca. 1970 (Mylona, 1996). The subsequent decline in SO_4^{2-} deposition is mainly due to decreasing European sulfur emissions (Lövblad et al., 1995) although relatively large inter-annual variations driven by variations in precipitation amounts have been observed (Kindbom et al., in press). From the 1970 deposition level in northern Sweden, the decline to the beginning of the 1990's was approximately 65% (S. Mylona, unpublished data). That decline has continued until today and was, on average for northern Sweden, approximately 50% between the mid 1980's and late 1990's (Kindbom et al., in press). Fulfillment of the Gothenburg Protocol to the United Nations Economic Commission for Europe Geneva Convention on Long Range Transport of Pollutants will lead to a further 25% reduction of sulfur deposition from the present value in northern Sweden (G. Lövblad, unpublished data).

Nitrate

Nitrate is another anthropogenic source of acidification. It can influence the pH of surface waters during hydrological episodes, especially spring flood (Galloway et al., 1987; Schaefer et al., 1990). Uptake and neutralization is a more significant process for NO_3^- than for SO_4^{2-} since it is an important and often limiting nutrient in the boreal forest. Anthropogenic NO_3^- has proved important in surface water acidification in some coastal areas in southern Sweden and Norway where the deposition of NO_3^- is high and the C/N ratio of the soil is low (Dise et al., 1998; Bertills and Näsholm, 2000). In northern Sweden, where the annual NO_3^- deposition normally is less than 1 kg ha^{-1} (Akselsson, 2000), no study, so far, has shown that NO_3^- leakage should be of importance in surface water acidification.

Natural sources of acidity

Dilution

One of the most important natural factors promoting acid surges during high flow events is the dilution of the more well buffered baseflow by ionically weak, low buffering snow melt water (Björnberg, 1983; Wigington et al., 1996; Laudon and Bishop, 1999a). Dilution can only reduce the total buffering capacity toward zero since no strong acidity is produced. After the carbonate buffering system is exhausted (around pH 5.2-5.5) and before the aluminum buffering system takes over (below ca. pH 4.5), organic acidity is the major pH buffer and thus determines how far dilution alone can depress pH. The larger the melt water fraction during the spring flood, the larger the dilution will be (Fig. 2). In areas of steep slopes and thin soils, such as mountainous catchments, the dilution is larger than in low elevation boreal forest catchments with thick soils where the fraction of melt water often is smaller (paper IV).

Buffering Dilution with Snowmelt

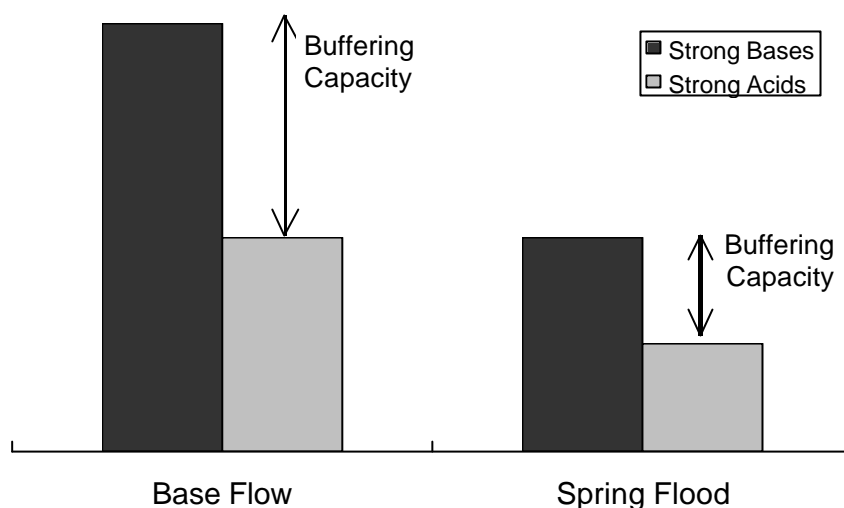


Fig. 2. Schematic figure of how the buffering capacity is diluted by snowmelt. The buffering is calculated as the difference between the strong bases and strong acid anions (c.f. equation 5). By diluting the strong bases and strong acid anions in the same proportion, the buffering capacity will be diluted similarly.

Organic acidity

The large influence of organic acidity, normally measured as TOC (total organic carbon), DOC (dissolved organic carbon) or color, on the acid-base chemistry of surface waters has been known for more than a decade (Oliver et al., 1983; Eshleman and Hemond, 1985; although Rosenquist (1978) already in the 1970's suggested that the expansion of coniferous forests was an important factor in lowering pH of surface waters in Norway). Several studies have also demonstrated that DOC can play an important role in controlling the pH decline during both rain driven flow events (Bishop et al., 1990; Laudon and Bishop, in review A) and during snow melt driven events (Campbell et al., 1992; Kortelainen and Saukkonen, 1995; paper I and III). A difficult task in quantifying the role of DOC on the pH during high flow events is modeling the acid-base character of the DOC. Recent work by Köhler et al. (1999) has successfully done this for the conditions in northern Sweden. This enables a more accurate description of DOC's role in driving the pH decline during spring flood.

The importance of DOC in controlling the pH in boreal forest streams is due to the generally high levels of DOC in surface waters of the region (generally ranging from 10 to 25 mg L⁻¹ of DOC). During high flow the DOC, contrary to most other dissolved constituents, often increases in concentration (Bishop et al., 1991; Bishop and Pettersson, 1996; Laudon and Bishop, 1999a; Laudon et al., 1999; paper I and II). Bishop and Pettersson (1996) suggested that the increased DOC concentration during the spring flood is driven by a rising groundwater level that activates new, more superficial source areas.

While the effect of dilution is that the water becomes more acid sensitive, DOC is the driving mechanism of the pH decline. The combined effect of dilution on the buffering capacity and the naturally increased flux of organic acidity during spring flood can cause a pH decline of over 2 pH units as well as forcing pH down to pH 4.5 or below under certain circumstances (Fig. 3; paper I and III).

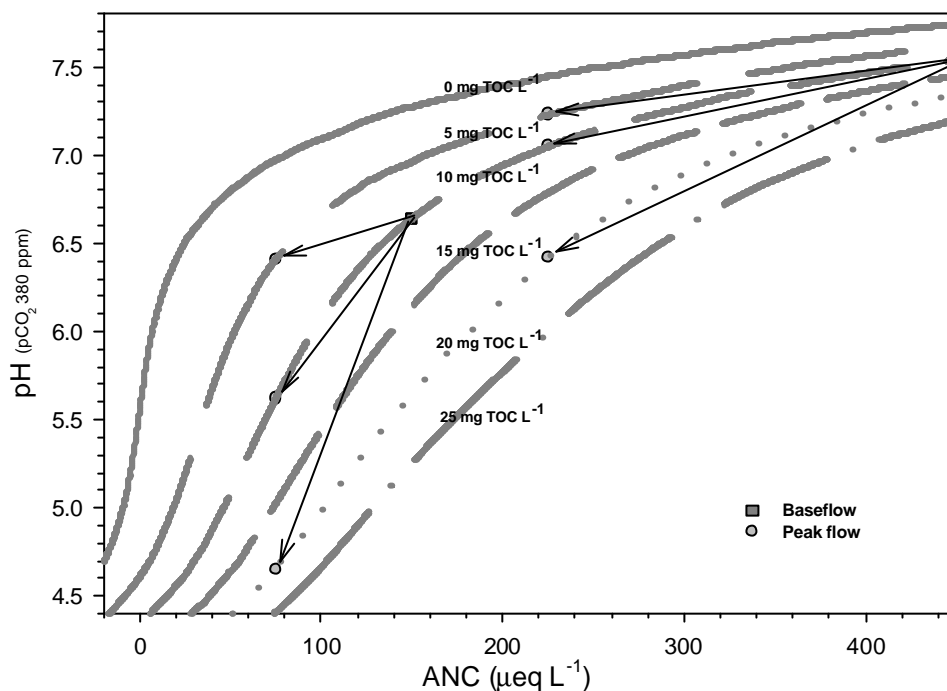


Fig. 3. The relationship between ANC and pH at different levels of TOC. In the figure two theoretical streams are shown with different baseflow ANC and three different changes in TOC during the episode. During an episode with a 50% dilution, the resulting pH will depend on baseflow ANC and on the relative TOC change.

Other natural sources of acidity

Natural sources of SO_4^{2-} and NO_3^- can, under certain circumstances, inhibit a straight forward analysis of whether the main driving mechanism of episodic acidification is natural or anthropogenic. Climatic variations, especially extremely cold weather, can increase the flux of nitrate leaching from forested soils (Mitchell et al., 1996). It is therefore possible that some previously reported cases of nitrate loss associated with snow melt episodes could be caused by natural variations in weather and not due to anthropogenic deposition. However, the separation between different sources of nitrate is of marginal importance in northern Sweden since nitrate is not an important hydrochemical component in surface waters of the region where forests are nitrogen limited.

Natural sources of SO_4^{2-} can be more difficult to separate from anthropogenic sources in northern Sweden since both fine sediment soils (Ivarsson and Jansson, 1995), and sulfide-rich till and bedrock (Andersson et al., 1999) can cause elevated levels of SO_4^{2-} during both baseflow and episodes. Fine post-glacial marine sediments

have been found up to 120 m above sea level in the county of Västerbotten (Granlund, 1943), suggesting that all catchments with fine sediments or wetland complexes below this level potentially could have elevated sulfate levels due to natural sources. SO_4^{2-} leakage from these fine sediment soils are an important cause of pH decline during the spring flood in the coastal area of Västerbotten (Ivarsson and Jansson, 1995). Large areas of the coastal zone in Västerbotten also have a very complex and heterogeneous geology with narrow dikes of sulfide-rich bedrock. The largest sulfur anomalies in the bedrock and overlying till are found in the contact zone between coastal gneiss and graywacke in the coastal area of northern Sweden (Dahlström and Johansson, 1997). Variation in bedrock and soils can hence give rise to large variation in the SO_4^{2-} of both baseflow and episode chemistry.

Supersaturation of CO_2 is also a natural factor which greatly can affect pH in many surface waters (e.g. Köhler, 1999). The CO_2 supersaturation is due to in-lake respiration of allochthonous carbon and from inputs of runoff from soils and wetlands high in TOC and CO_2 (Hope et al., 1996). Since CO_2 in combination with water produces bicarbonate and hydrogen ions, supersaturation will lead to a production of acidity. Significant effects on pH can, however, only be expected for pH above 5.0.

Sea salt in precipitation can have large effects on the episodic acidification of many coastal regions (Heath et al., 1992; Lydersen and Henriksen, 1995). Infiltration of snow melt or rain water with high sea salt concentrations will lead to cation exchange between base cations and hydrogen ions/aluminum bound to soil particles. The resulting runoff chemistry can have toxic effects on the biology of surface waters (Hindar et al., 1994). During heavy precipitation events, sea salt deposition can be higher than normal in the whole of Sweden, but especially in the mountain range along the border to Norway (Akselsson, 2000).

Operational model

One of the main objectives of the Episode Project has been to develop an operational model which can be used to separate and quantify the extent of anthropogenic and natural driving mechanisms during hydrological episodes. One important criteria for this work has been the need to develop an “operational” model that can readily be used by local, regional and national authorities for the evaluation of the acidification status in individual streams. The model developed here, called the Boreal Dilution Model (BDM), can be used to calculate the separate contributions from natural and anthropogenic sources of episodic pH decline (paper I). The BDM is an extension of the ADM (ANC Dilution Model) which was developed to separate and quantify driving mechanisms of ANC decline during hydrological episodes (Laudon and Bishop, 1997; 1999a).

Aquatic organisms are primarily affected by changes in pH (and pH dependent changes in the Al-speciation). The pH of the surface water is therefore of uttermost interest when attempting to model changes in the acid-base chemistry driven by atmospheric deposition. Since the pH of surface waters is controlled by the ANC and the presence of weak acids in the water, a shift in at least one of these two controlling factors must occur to drive a change in pH.

The fact that ANC is conservative with respect to dilution makes it a perfect candidate for the modeling purpose of the BDM. The pH on the other hand, is closely related to ANC and TOC. Thus the pH can be calculated. The foundation of the BDM rests on the charge balance definition of ANC (e.g. Stumm and Morgan, 1981) (Eq. 1).

$$\text{ANC} = \sum \text{proton acceptor} - \sum \text{proton donors.} \quad (\text{Eq. 1})$$

Alternatively, ANC can be expressed as Eq. 2.

$$\text{ANC} = \sum \text{weak acid anions} - \sum \text{weak cations} \quad (\text{Eq. 2})$$

According to the electroneutrality principle for natural waters, the sum of cations must equal the sum of anions (Eq. 3).

$$\sum \text{weak acid anions} + \sum \text{strong acid anions} = \sum \text{weak cations} + \sum \text{strong base cations} \quad (\text{Eq. 3})$$

ANC can, therefore, also be calculated using standard chemical analyses (equation 4 and 5).

$$\text{ANC} = \sum \text{strong base cations} - \sum \text{strong acid anions} \quad (\text{Eq. 4})$$

A strong acid is defined as being fully dissociated in the pH range of natural waters (Stumm and Morgan, 1981), which implies that it does not buffer the solution against protons at any pH of a natural system. A weak acid can range from entirely dissociated to practically undissociated in the pH range of natural waters, depending on its equilibrium pH, and can therefore act as a buffer in a certain pH interval. Most mineral acids are classified as either strong or weak. The organic acid component of DOC behaves as both a strong and a weak acid since DOC does not consist of one well-defined acid-base molecule but instead of an array of acid functional groups. The equilibrium pH of the individual organic acids varies over the whole pH range (e.g. Oliver et al., 1983). A portion of the organic acids should hence be included in the latter ANC calculation (equation 4) as strong acids for a more precise measure of the buffering capacity (Munson and Gherini, 1993). Some recent work on episodic acidification has also included the strong organic acid in the ANC calculation (Eshleman et al., 1995, Laudon and Bishop, 1999; Laudon et al., 1999). When quantifying and separating the anthro-

pogenic influences of episodic acidification from the natural factors it is, however of limited importance whether or not the DOC is referred to as a strong acid. Since there is an uncertainty in how much of the DOC should be defined as a strong acid (Köhler, 1999), DOC is often not included in the ANC calculation (Hyer et al., 1995; paper I and III). This is also the standard method in Swedish environmental protection monitoring work for calculating ANC (Wilander, 1999) as well as in international negotiation work (Posch et al., 1997). DOC is therefore excluded from the calculations of strong acids in the BDM.

Pre-industrial ANC

The BDM is based on the observed ANC ($ANC_{(obs,t)}$; Eq. 5), a dilution index ($DI_{(t)}$; Eq. 6) at any time “t” during the flow event and an organic acid model. The sum of base cations ($BC = 2 \cdot [Ca^{2+}] + 2 \cdot [Mg^{2+}] + [Na^+] + [K^+]$) are used as the DI which simulates the natural dilution of both BC and the anthropogenically significant anions of strong mineral acids ($ANSA = 2 \cdot [SO_4^{2-}] + [NO_3^-]$) during runoff episodes. Chloride dynamics are considered natural and are hence not diluted to follow the DI. The natural, pre-industrial ANC ($ANC_{(preind,t)}$) is predicted using equation 7. The difference between the predicted pre-industrial ANC ($ANC_{(preind,t)}$) (Eq. 7) and the observed ANC ($ANC_{(obs,t)}$) (Eq. 5) is interpreted as the human influence on the ANC ($\Delta ANC_{(poll,t)}$; Eq. 8) during the episode.

$$\begin{aligned} ANC_{(obs,t)} &= 2 \cdot [Ca^{2+}]_{(t)} + 2 \cdot [Mg^{2+}]_{(t)} + [Na^+]_{(t)} + [K^+]_{(t)} - [Cl^-]_{(t)} - 2 \cdot [SO_4^{2-}]_{(t)} - [NO_3^-]_{(t)} \\ &= BC_{(t)} - ANSA_{(t)} - [Cl^-]_{(t)} \end{aligned} \quad (\text{Eq. 5})$$

$$DI_{(t)} = BC_{(t)} / BC_{(base)} \quad (\text{Eq. 6})$$

$$ANC_{(preind,t)} = DI_{(t)} \cdot (BC_{(base)} - ANSA_{(base)}) - Cl_{(t)} \quad (\text{Eq. 7})$$

$$\Delta ANC_{(poll,t)} = ANC_{(preind,t)} - ANC_{(obs,t)} \quad (\text{Eq. 8})$$

The subscript “obs” denotes “observed” while “base” denotes baseflow conditions.

Pre-industrial pH

Since ANC also can be determined as the difference between weak acid anions and weak cations (Eq. 2), ANC can also be calculated using equation 9. By rearranging equation 9 and excluding species that will not significantly affect pH in the study streams, the natural, pre-industrial pH ($pH_{(preind,t)}$) can be calculated (Eq. 10). The difference between the pH_{preind} (Eq. 10) and the observed pH is interpreted as the human influence on the pH ($\Delta pH_{(poll,t)}$; Eq. 11) during the episode (although natural sources of SO_4^{2-} can inflate $\Delta pH_{(poll,t)}$, see “discussion”).

$$\text{ANC} = [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{RCOO}^-] + [\text{OH}^-] - [\text{H}^+] - n \cdot [\text{Al}^{n+}] \quad (\text{Eq. 9})$$

$$[\text{H}^+]_{(\text{preind}, t)} = [\text{HCO}_3^-]_{(t)} + [\text{RCOO}^-]_{(t)} + [\text{OH}^-]_{(t)} - \text{ANC}_{(\text{preind}, t)} \quad (\text{Eq. 10a})$$

$$\text{pH}_{(\text{preind}, t)} = -\log([\text{H}^+]_{(\text{preind}, t)}) \quad (\text{Eq. 10b})$$

$$\Delta\text{pH}_{(\text{poll}, t)} = \text{pH}_{(\text{preind}, t)} - \text{pH}_{(\text{aerated}, t)} \quad (\text{Eq. 11})$$

RCOO^- is calculated with a calibrated, pH dependent pK_a model described in paper **II**. Since several of the components in Eq. 10 are pH dependent, the $\text{pH}_{\text{preind}}$ must be solved for iteratively. Note that since pCO_2 is an important component in the pH modeling a set partial pressure is needed. In this work the atmospheric pCO_2 of 3.42 (380 ppm) is used for both modeling and for air equilibration.

A description of the BDM in Swedish is presented in Laudon and Bishop (1999B) and Laudon et al. (in press). A model for limed waters have also been developed (Laudon and Bishop, 2000). A computerized, user-friendly version of the BDM can be downloaded from <http://www.sek.slu.se/eng/personal/hlaud/hjalmar.htm>.

Results and discussion

This thesis presents the Boreal Dilution Model for separating and quantifying the anthropogenic and natural sources of episodic pH decline associated with spring flood episodes in northern Sweden (paper **I**) together with data and modeling results from the over 20 spring flood episodes from the region collected within the frame work of the Episode Project (Paper **II** and **III**). A synoptic overview of the severity of the anthropogenic component during spring flood episodes using deposition data and lake monitoring data from northern Sweden is also presented (paper **IV**). Finally, an analysis is provided of how the scientific advances in understanding the role of acid deposition during spring flood has been (and might be) used to develop the liming policy in northern Sweden (paper **V**). The results in this thesis are mainly based on the hydrochemistry component of the Episode Project but implications of these results for other parts of the project will also be discussed.

Paper I

This first paper presents the Boreal Dilution Model for separating and quantifying the natural and anthropogenic acidity in stream pH decline during spring flood or other hydrological episodes in areas that are not chronically acidified. The BDM is applied to one spring flood episode in northern Sweden. Three important assumptions in the BDM are discussed and quantified;

1. Variations in the base cation concentration is a good estimate of the natural dilution of ANC during hydrological events.
2. Baseflow chemistry is not affected by acid deposition, or can be corrected for.
3. DOC has not changed due to human activity since the pre-industrial period.

The BDM accounts for two natural sources of acidity associated with hydrological events. One is the dilution of runoff ANC and the other is organic acidity. The data requirement for the model is a time series of 10-15 water chemistry samples collected before and during an episode. This sample resolution is limited enough for regional water quality monitoring programs that aim to assess the variation of the anthropogenic impact on runoff chemistry in time and space.

Paper II

Results from the stream water chemistry part of the Episode Project are presented. The paper provides an overview of the project and presents spatial and temporal variability of spring flood hydrochemistry during 1997 and 1998 in a dozen streams in northern Sweden. Sources and driving mechanisms of the pH decline are also quantified.

There was a large variation in both baseflow and chemical response to snow melt in the streams included in this study. The 0.5 to 2.5 pH unit decline during the spring flood recorded for the streams was accompanied by a substantial increase in TOC and a decrease in most mineral constituents. During the 1997 spring flood, organic acids contributed more than 80% of the acidity in most of the locations in this study. In three of the streams, the anthropogenic contribution was closer to, but still lower than, that from organic acidity. During the 1998 spring flood, with a larger SO_4^{2-} deposition in the region, the anthropogenic contribution of protons was in general higher than during the previous year. In three of the streams, the contribution from anthropogenic sources was similar to, or somewhat larger than, that from the natural organic acids.

Paper III

In this paper modeling results of pre-industrial pH using BDM on the spring flood data from the Episode Project are presented. The anthropogenic component of the pH decline was in general 0.1 to 0.3 pH units. The study further demonstrated that pH under certain circumstances can decline to close to pH 4.5 as a result of natural processes alone (Fig. 4). The most important factor influencing the pH was the combined effect of natural processes, caused by an increase in TOC, and dilution of ANC.

While the results from this study suggest that the anthropogenic acidity was generally limited in the 22 spring flood episodes with applicable data from the episode project, the results also suggest that the weakly buffered catchments in the coastal area with the highest SO_4^{2-} deposition were the sites most affected by acid deposition. These catchments were also the sites most sensitive to model assumptions.

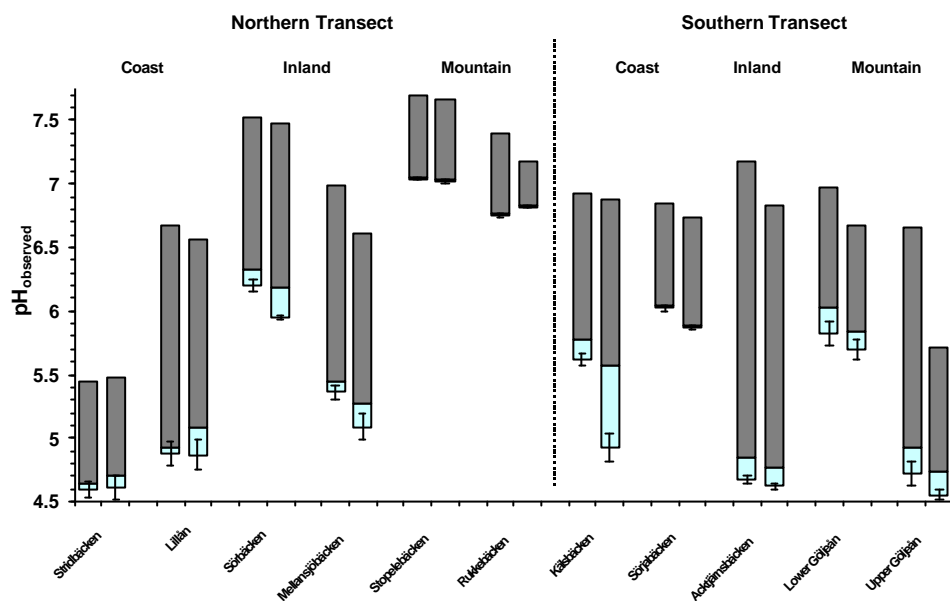


Fig. 4. Variation in baseflow/peakflow pH. The first column for each stream is the 1997 spring flood, the second column is the 1998 flood. The dark gray area is the natural pH decline. The white area is the anthropogenic pH decline (DpH_{poll}). The error bars denote the standard deviation in the DpH_{poll} of the peak flow phase.

Paper IV

This paper is based on the consistent relationship between the S content in the snow and the anthropogenic component of ANC decline found in the spring flood in northern Sweden (Fig. 5). The correlation is used for a regional prediction of the severity of episodic acidification in northern Sweden using SO_4^{2-} winter deposition data together with hydrochemical data from 1240 lakes selected to be geographically representative of the region.

The regional assessment provided in this paper suggests that the anthropogenic influence on spring flood ANC decline in northern Sweden currently is limited (Fig. 6). While the results have major implications for the future liming strategy in northern Sweden, the results also indicate that the rate at which emissions are reduced in Europe is of great importance for the rate of improvement in the acidification status of surface waters in the region.

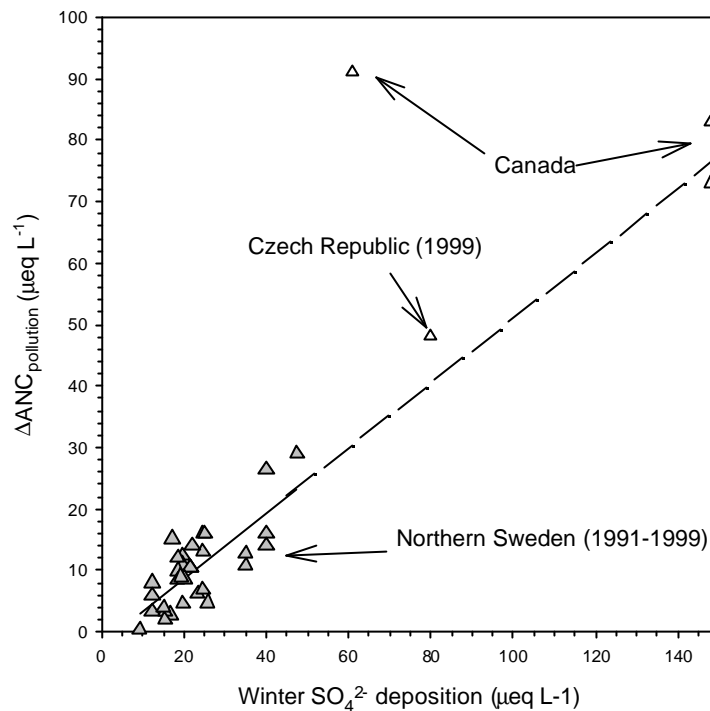


Fig. 5. The correlation between SO_4^{2-} concentration in snow and $\Delta\text{ANC}_{\text{poll}}$ during spring flood in 34 spring floods from 24 sites with baseflow ANC below $250 \mu\text{eq L}^{-1}$ ($r^2 = 0.60$; $p < 0.001$). Spring flood data with much higher deposition from an artificially acidified catchments in Canada (Allan, 1995) and a heavily acidified catchment in the Czech Republic are also shown (unpublished data). These results generally fall on the regression derived from the data from northern Sweden.

Paper V

The controversy over the ca one billion Swedish crowns spent on liming in northern Sweden during the last decade has led to several scientific advances in understanding the role of natural and anthropogenic acidity. These improvements include tools for both detailed quantification of acidity sources during hydrological episodes as well as regional predictions of the anthropogenic contribution to episodic acidification in northern Sweden.

In this last paper, scientific advances and the development of liming policy during the last decade are compared. Despite the active role of policy makers in supporting the scientific advances in understanding the role of natural acidity, recent policy proposals for the liming of northern Sweden during the coming decade have yet to take account of relevant scientific findings.

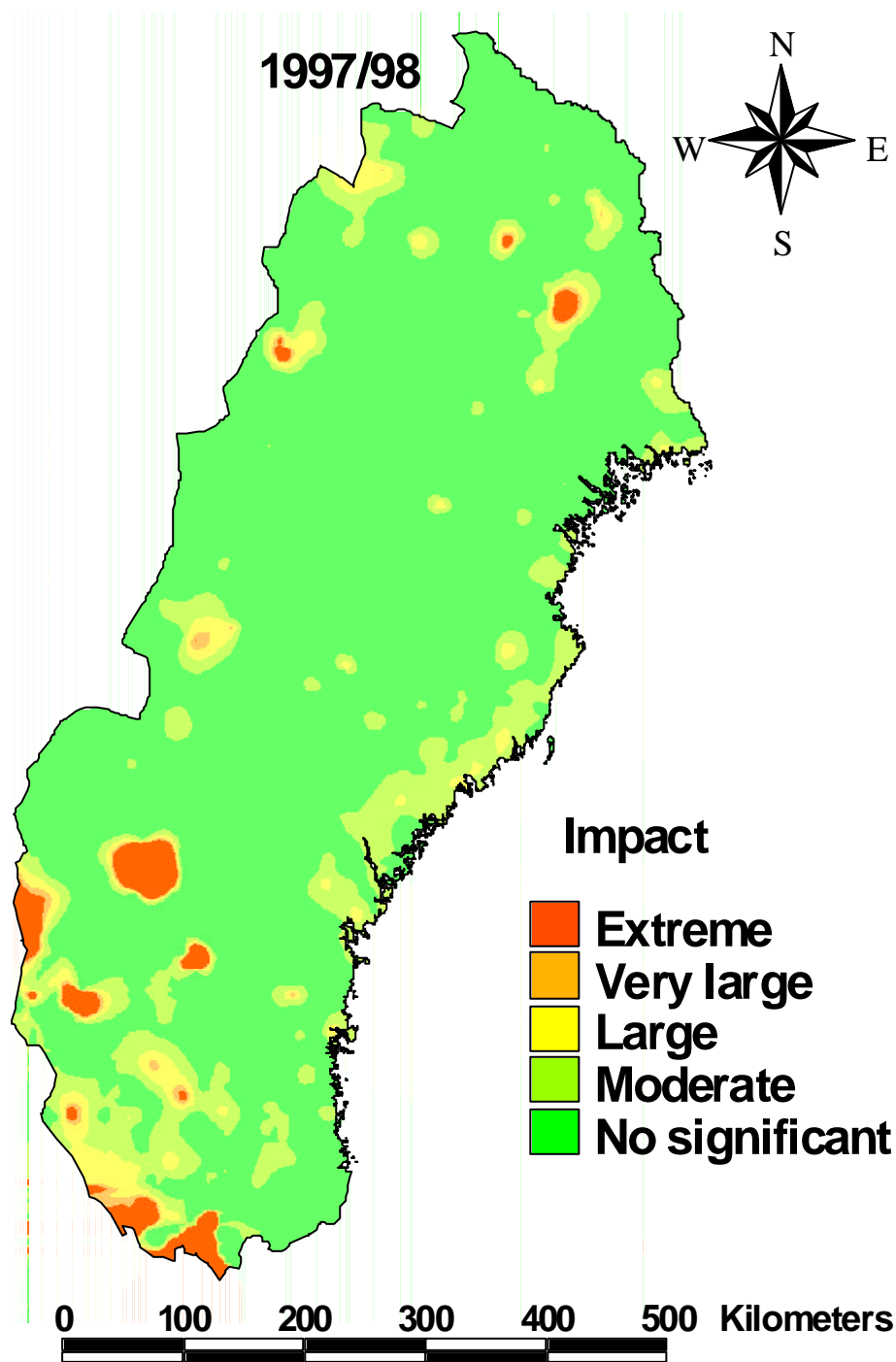


Fig. 6. Areas affected by different levels of anthropogenic episodic acidification during the 1998 spring flood.

Assumptions in the BDM

Most of the results, discussions and conclusions in this thesis rest on the foundation of the BDM. Critical tests and validation of important assumptions in the model are therefore necessary for the plausibility and relevance of the findings in this thesis.

Validity of BC as the Dilution Index

The most important of the assumptions in the BDM is that the base cation dilution index (BC-DI) is a reliable measure of ANC dilution under natural pre-industrial conditions. An erroneous dilution quantification will not only provide an inaccurate buffering capacity dilution but also give an incorrect estimate of the anthropogenic contribution during the episode.

When quantifying the pre-industrial dilution of ANC, the sum of base cations are used to separate the natural dilution of ANC from the contemporary dilution. While it is tempting to conceive this ANC dilution separation in the BDM in terms of a two-component mixing where the natural dilution would be a product of unpolluted dilute snowmelt water diluting a well buffered “pre-event” baseflow component, this concept is not applicable in the model. Instead, the use of contemporary BC dilution is taken as a surrogate for the pre-industrial dilution quantification in the BDM which is not necessarily the same as hydrograph separation.

While conservative hydrological tracers such as oxygen-18 (e.g. Rodhe, 1987; Mast et al., 1995) are excellent for separating between “event” and “pre-event” water during spring flood episodes (if the specific criteria for the tracers are fulfilled, see Rodhe, 1998), the advantage of BC lies in its non-conservative nature (Fig. 7). While oxygen-18 is not affected by its flow pathway, BC is affected by both exchange reactions and neutralization processes on its way to the stream. “Self-compensating” effects of BC-DI is one important reason for using BC in the BDM.

Two “self-compensating” effects are conceivable (and quantified in paper I). The first being neutralization of anthropogenic acidity in the soil (or by anthropogenic BC in the precipitation). This will result in extra inputs of BC during the episode, and less than the natural BC dilution. This underestimate of the dilution will compensate for the neutralized fraction of anthropogenic acid anions in the runoff when calculating $\Delta\text{ANC}_{(\text{poll})}$, thus giving a correct assessment of the anthropogenic influence during the episode. The other “self-compensating” response in the BC-DI is when more superficial soil layers are depleted in BC by soil acidification. During episodes, when flowpaths rise into more acidified and therefore more BC-depleted soil horizons, the flux of BC will decline relative to pre-industrial levels. This will yield an over-estimate of the natural ANC dilution and increase the BDM prediction of the anthropogenic component of ANC/pH decline. This is appropriate when it is not only the presence of anthropogenic sulfate, but also a depletion of BC which makes up the anthropogenic contribution to episodic acidification.

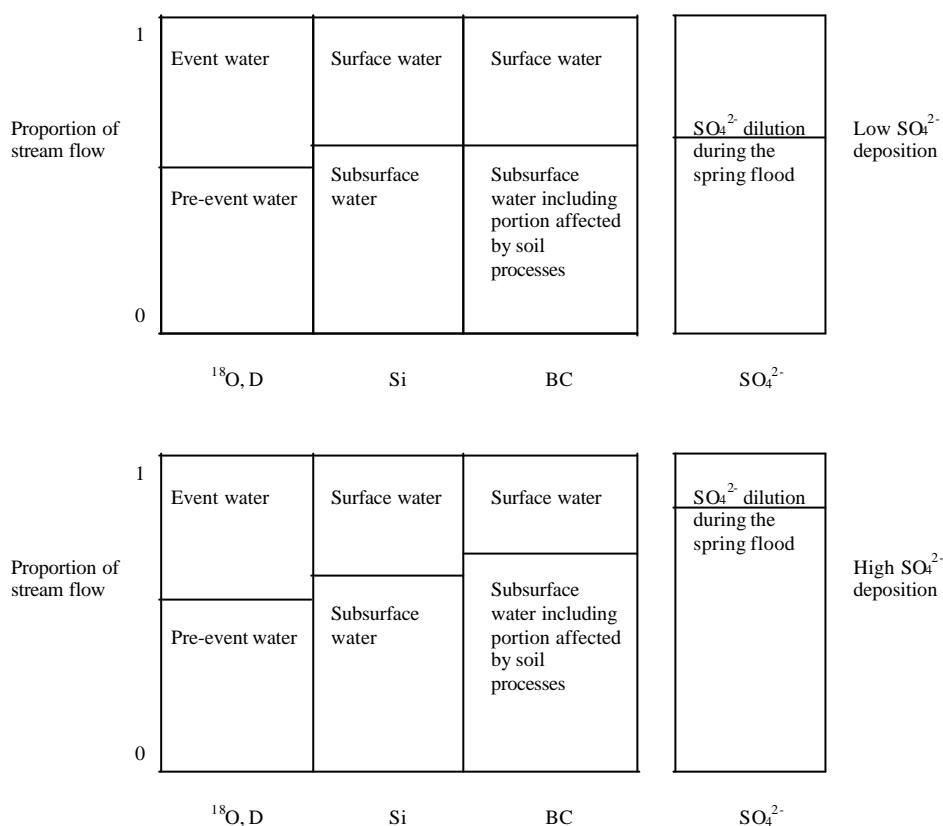


Fig. 7. A conceptual diagram of potential tracers for quantifying dilution. The upper panel depicts a situation of low anthropogenic SO_4^{2-} deposition. The lower panel depicts a situation of high anthropogenic SO_4^{2-} deposition (note the difference in the dilution of Si, BC and SO_4^{2-} between the two panels).

In paper **I** and **III** it is argued that the largest potential errors using BC-DI in boreal regions are associated with the large relative increase in organic anions (compared to the BC flux) during the spring flood. An error in the BC-DI measure would arise if a significant amount of BC were co-transported by organic anions to the stream since this would prevent BC from diluting proportionally to the natural ANC dilution. An error caused by a co-transport of BC and organic anions would therefore tend to underestimate the natural dilution of ANC and hence the anthropogenic component in the BDM.

Despite the limitation in using two-component mixing models for estimating the natural ANC dilution, comparisons of the dilution pattern between BC and more traditional hydrological tracers, such as oxygen-18 and silica, can be used to estimate potential errors associated with the BC-DI. In paper **I-III** the discrepancy between silica and BC dilution was used to quantify the potential co-transport of BC and organic anions. The maximum potential error associated with the co-transport was in general less than 0.10 pH units. This limited effect could possibly be explained by the spatial independence of BC and TOC sources during high

flow events. It is also possible that the discrepancy between silica and BC dilution is due to the non-conservative behavior of silica which has been shown for some Canadian wetland dominated catchments (Wels et al., 1991). Similar results were found by Cory (1999) when comparing silica and BC dilution with separations using oxygen-18 as a hydrological tracer during spring flood. In Cory's study, BC and oxygen-18 gave almost identical results, while silica overestimated the melt water component (Fig. 8). The results from Wels et al. (1991) and Cory (1999) are supported by the results in paper **II** and **III** where the discrepancy between BC and Si dilution were well correlated with the areal extent of wetlands in the different catchments.

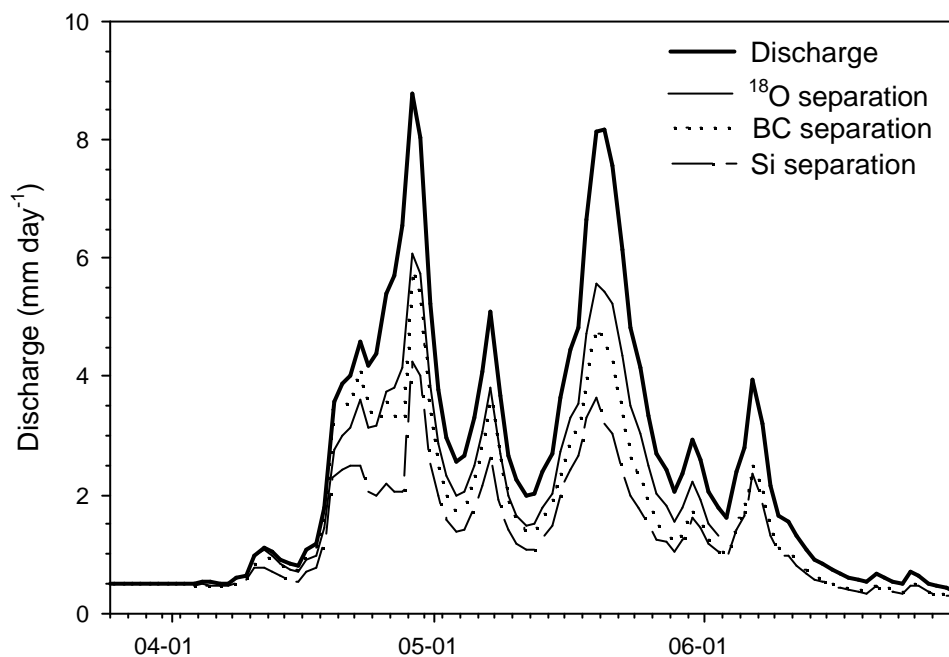


Fig. 8. Hydrograph separation using O^{18} , Si and BC in a small catchment in northern Sweden.

The sum of base cations has also previously been used to separate sources of episodic acidification during high flow events (Campbell et al., 1992; Kahl et al., 1992). The ANC separation approach for episodic acidification that was first presented by Molot et al. (1989), and later used by numerous episode studies (DeWalle and Swistock, 1994; Evans et al., 1995; Hyer et al., 1995; Wigington et al., 1996) also indirectly used base cations as a separation tracer of dilution and acid contribution.

Baseflow as a Benchmark in BDM

The baseflow chemistry constitutes the starting point in the BDM for separating the transient changes driving the pH and ANC decline during hydrological episodes. An important assumption in the modeling of natural ANC and pH using BDM during spring flood events is therefore that the baseflow ANC and pH has not been affected by anthropogenic deposition, or alternatively that the change in baseflow chemistry can be quantified.

In paleolimnological studies already cited (Korsman, 1993; 1999) large scale chronic acidification has not occurred in the two most northerly counties of northern Sweden (Västerbotten and Norrbotten). In the paleolimnological work by Korsman over 120 geographically representative lakes demonstrated a lack of regional pH and alkalinity decline over the last 200 years. The only area with a substantial pH decrease was the coastal area close to the city of Umeå (Renberg et al., 1993). However, in the more recent study by Korsman (1999), he found that not even acid sensitive, poorly buffered lakes in the SE part of Västerbotten, where the acid deposition has been significantly higher than in the inland, show any signs of recent atmospheric anthropogenic acidification. The acidified, coastal lakes in the Renberg et al. (1993), study are therefore believed to be acidified by changes in land-use or ditching of sulfur-rich marine sediments which are common along the coast, lying below the highest post-glacial coast line in northern Sweden (Korsman, 1999). In one of the lakes, Abbotträsket, included in the paleolimnological work by Korsman (1999), the lumped-parameter acidification model known as MAGIC (Model of Acidification of Groundwater in Catchments (Cosby et al., 1985)) was used within the Episode Project (Kram et al., in review). The acid sensitive lake, situated in an area of the highest level of acid deposition in the region, was partly deforested during the 1970's. The results from the MAGIC simulation showed that the lake has experienced a 0.2 pH decline (Fig. 9) due to acid deposition and forestry since 1850 (Kram et al., in review) which is similar to the findings of Korsman (1999). Furthermore soil chemical studies, in the region, comparing recent analyses with work carried out at the beginning of the century on the same location, have confirmed the paleolimnological findings (Tamm och Hallbäcken, 1988; Jacks, 1991). The base saturation of the soil in this region has also not been significantly altered (Eriksson et al., 1992) which suggests that most of the acid buffering potential remains in the forest soils.

In the southern part of northern Sweden, Renberg and Ek (1998) showed that pH has remained constant around 4.8 in three weakly buffered headwater lakes in Borlänge township, despite a history of extreme SO_4^{2-} deposition from the 1000 year mining activity in the area. In another study by Ek and Renberg (1998) in the same region, 14 lakes were studied. Of these, five lakes had been acidified 200 to 300 years ago, while one lake had been acidified after 1950. In two lakes, pH had increased due to changes in land use during the same time period. In the most southeastern county of the northern Sweden region, one soil study has shown a significant decline in pH down to 0.6 meters soil depth during the last decades

(Stegman, 1990). The base saturation in this southern region has also decreased marginally (Eriksson et al., 1992). Despite the changes related to acidification found by Stegman (1990) and Eriksson et al. (1992), a very intensive soil chemical study in Värmland (just south of the border to northern Sweden) showed that it was only the southern part of that county that was affected by acid deposition (Lundström et al., 1998). The northern parts of Värmland, which are similar in both physical characteristics and acid deposition load to areas of northern Sweden, showed limited soil chemical alteration due to anthropogenic deposition.

Even though the conclusion from studying previous acidification work in the region must be that ANC and pH of baseflow in northern Sweden not has been significantly affected by acid deposition (possibly exempting the southeastern corner of the region), the SSWC model as implemented by Wilander et al. (1998) has been used in this work to test the sensitivity of that assumption (paper I, III and IV). Despite the criticism concerning the validity of the SSWC model (and the empirical F-factor on which it is based) in surface waters of northern Sweden (e.g. Rapp et al., 1998; Andersson et al., 1999), SSWC is still the model used for critical load estimates in Sweden (Henriksen et al., 1992). The SSWC can therefore serve as a first approximation when the BDM is used in regions where baseflow may have been affected by anthropogenic deposition. The results using the SSWC model for correcting the baseflow ANC and pH in this work was that a correction was of limited importance on the regional scale (paper IV) but had some effect in very low buffering catchments (paper III).

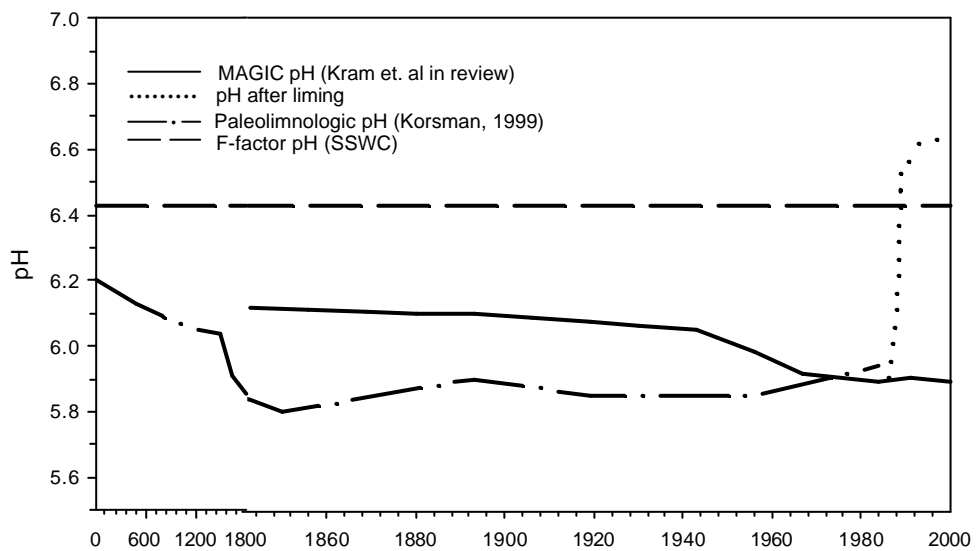


Fig. 9. The pH development in Abborträsket in southwestern Västerbotten estimated using MAGIC and paleolimnological studies. In the figure the pH development after liming (estimated using MAGIC) and the pH using SSWC are also shown.

Natural DOC in northern Sweden

Since the DOC flux associated with hydrological episodes in northern Sweden is important as a driving mechanism of the transient pH decline, an important assumption in the BDM is that the concentrations and acid functionality of DOC have not been influenced by human activity.

Forestry practices in Sweden can lead to changes in hydrology and hydrochemistry since both the runoff and the groundwater level can be affected (Grip, 1982; Lundin, 1995). The increase in runoff from clear-cut areas can be up to 100% (Grip, 1982). The practice of clear-cutting can also lead to increased degradation and mineralization of organic material which can enhance the leakage of DOC and solutes. Studying the effects of clear-cuts, constituting 2%-6% of the catchment area, Juto and Temnerud (1999) demonstrated that no significant effects could be observed during the spring flood in any hydrochemical parameter. The result that DOC is not affected by upstream clear-cuts has been confirmed by paleolimnological studies showing that the color of surface waters in Norrbotten and Västerbotten has not changed significantly during the last 200 years (Korsman, 1993). Larger water-courses in Sweden sampled since the 1960's also do not show any significant trends due to forestry practice or other human activity (Löfgren, 1991; Löfgren and Fölster, 1998), but rather a precipitation-related variation.

Studies of DOC dynamics following ditching of wetlands have demonstrated that DOC decreases in concentration following an initial DOC flush (Magnusson, 1982). By channeling the water away from wetlands with deep ditches down to the underlying mineral soil, the contact zone between water and organic material is reduced. Thus changes in the hydrological pathways in wetlands in northern Sweden associated with forest drainage could potentially lead to decreased concentrations of DOC in surface waters in the region.

One last aspect of the BDM plausibility for separating sources of pH decline related to organic acidity is the modeling of pH from ANC and DOC. Work to better understand the acid functionality of organic acids and the relationship between DOC and buffering capacity in the region has recently been published (Köhler, 1999; Köhler et al., 2000). Great efforts have also been made to study the spatial and temporal aspects of the acid-base character of DOC in northern Sweden (Köhler et al., 1999; Hruška et al., in press). The results from these studies suggest that the variation in time and space in the acid functionality of DOC is limited, which is also confirmed in this thesis (paper II).

Implications of the Episode Project

Even if the BDM succeeds in separating natural from anthropogenic influences on episodic acidification in boreal Sweden, our understanding of the behavior of these surface waters is not only a function of the extent and timing of the anthropogenic component. While acidification of surface waters is caused by chemical

pollution, it is the negative effects on the biota that are of concern when trying to remediate the human impact. This difficulty in the nature of cause and effect can sometimes be difficult to solve due to both shortcomings in the understanding of chemical-biological interaction as well as the often limited information about the past biology (and chemistry) of individual waters. In Norway detailed annual catch volumes of salmon have been recorded since the mid 1800's (Hesthagen, 1997). In such cases, direct effects of human activity (i.e. acid deposition) on salmon can be inferred. These data can lay the foundation for effective and appropriate remediation programs (such as liming) in order to restore the fish population. A more difficult task is to use the oral information from older, recreational fishermen in northern Sweden to unravel the causes of a possible fish decline. The task is made even more difficult since habitat destruction (from straightening streams and rivers and removing larger boulders during the great log-driving era in the region between 1800-1970), migration barriers (from the many thousands of forest road culverts and log-driving dams), overfishing and introduction of new species can diminish fish stocks and reproduction in northern Sweden.

The understanding of toxicity to aquatic organisms caused by surface water acidification has improved greatly during the last two decades (e.g. Driscoll et al., 1980; Excley et al., 1991; Poléo, 1995). The toxicity of surface waters is mainly caused by the speciation and polymerization of the toxic labile inorganic aluminum species (Al_i) which is to a large extent controlled by pH (although high levels of calcium can mitigate this effect). Transient changes in pH associated with hydrological events can therefore lead to an increased toxicity of the water which can cause episodic fish kills under certain circumstances (e.g. Baker et al., 1996). See Gensemer and Playle (1999) for an extensive review of aluminum toxicity and effects to aquatic organisms.

In Norway much work has been carried out to try to determine critical levels of Al_i and Ca/Al_i ratios for different fish species (Lydersen et al., 1994; Poléo, 1995; Poléo and Bjerkely, 2000). Since those studies have focused on clear water systems, the results can not directly be translated to the conditions in northern Sweden, as organic complexation significantly decreases the concentration of toxic aluminum species (Driscoll et al., 1980; Witters et al., 1990). Furthermore, in the Episode Project, a comparison between different aluminum speciation analyses using the Clarke-method (Clarke et al., 1992) and the Barnes/Driscoll method (Barnes, 1975; Driscoll, 1984) in laboratory and field, showed large discrepancies (Fig. 10; Laudon et al., in press). The main conclusion from that comparison was that Al_i cannot be measured accurately in surface waters with high levels of organic acidity and relatively low levels of Al_i (even if these levels are still high with respect to fish toxicity). Since Al_i , with the Barnes/Driscoll method, is not measured directly, but calculated from the difference between the total labile Al fraction (Al_a) and the labile organic Al fraction (Al_o), the precision of the Al_i estimate is a function of the analysis precision and the relative difference between Al_a and Al_o . Since Al_o in surface waters with high levels of organic acidity is often of the same magnitude as Al_a , a small uncertainty in the measurements leads to a large uncertainty in the

Al_i estimate. The results show that it is difficult with the methods used in Sweden (and the lack of a standardized method makes it even more difficult) to say anything about the speciation of aluminum and its toxicity in high DOC surface waters in northern Sweden (Laudon et al., in press).

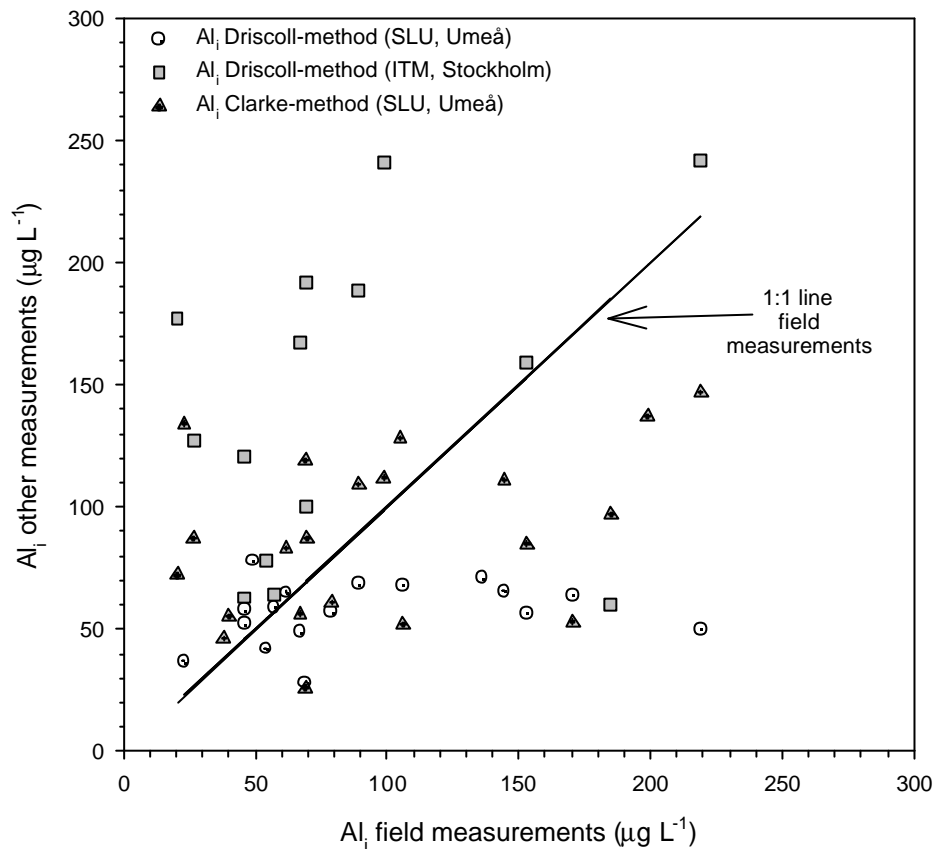


Fig. 10. Comparison between Al_i analyzed in the field and with different techniques. FIA is a Flow Injection method (Clarke-method; Clarke et al., 1992) while the other measurements are done with the Driscoll-method (Driscoll, 1984).

Within the framework of the episode project, the fish physiological response of Brown trout (*Salmo trutta*) was studied in cage experiments during six spring flood episodes in northern Sweden (Karlsson and Wallin, 1999; Sedin, 1999). Physiological stress ranging from no clear response to significant mortality was observed (Laudon et al., in press). The study showed that although the physiological response of the fish during spring flood was clearly caused by toxic levels of Al_i , it was not possible to correlate the fish response with either the Al_i measurement or the Ca/Al_i ratios (Laudon et al., in press). Since the Al_i measurements could not explain the critical levels for Brown trout in the cage experiment, other chemical parameters were used to separate the four classes of fish response: 1) no significant

response, 2) significant response without mortality, 3) significant response with some mortality, and 4) significant mortality. The measure that could best explain the response classes was the ratio between ANC and H^+ (Fig. 11). Further support for the finding that the ANC/ H^+ ratio is an appropriate measure of toxic Al_i rich water is that ANC/ H^+ correlates well with the Ca/ Al_i ratio (which does not correlate with the fish response pattern due to the large measurement uncertainty of Al_i). Furthermore, the entire discrepancy in the ANC/ H^+ and Ca/ Al_i correlation can be explained by the large uncertainty in the Al_i measurement found in the Episode Project (Laudon et al., in press).

An advantage with the ANC/ H^+ ratio is that it derives from standard chemical analyses, which makes it useful for both national and regional environmental monitoring programs. Another advantage with the ANC/ H^+ ratio is that pre-industrial conditions, calculated with BDM, can easily be used to analyze how the toxicity has changed due to anthropogenic deposition (Fig. 12). In streams from northern Sweden that currently have water chemistry falling into the mortality classes (class 3 and 4), removal of the anthropogenic acidification component would generally move the stream chemistry above the level of toxicity (Fig. 12). These results indicate that the anthropogenic acidification of 0.1 to 0.3 pH units superimposed on the natural pH decline in very acid sensitive systems can be enough to cause fish mortality. Stridbäcken (and partly Lillån) is an exception in this respect (Fig. 12). This may either result from baseflow having been affected by anthropogenic acidification, or that toxic episodes have always occurred. Natural populations of Brown trout have been shown to survive toxic levels of the ANC/ H^+ ratio that have persisted for several weeks (and pH below 4.6) in Acktjärnsbäcken where vigorous and reproducing populations have been found for several years (Fiskeriverket, 2000). The fact that vigorous fish populations can survive toxic episodes can be due to spatial variability in the water chemistry caused by groundwater discharge where fish can find temporal refuges (Baker et al., 1996). These results show that it can be difficult to draw direct parallels between toxicity studies in cage experiments to natural stream conditions. The results from the cage studies do, however, provide a critical limit of when the conditions start becoming toxic for individuals that can not find temporal refuges during spring flood.

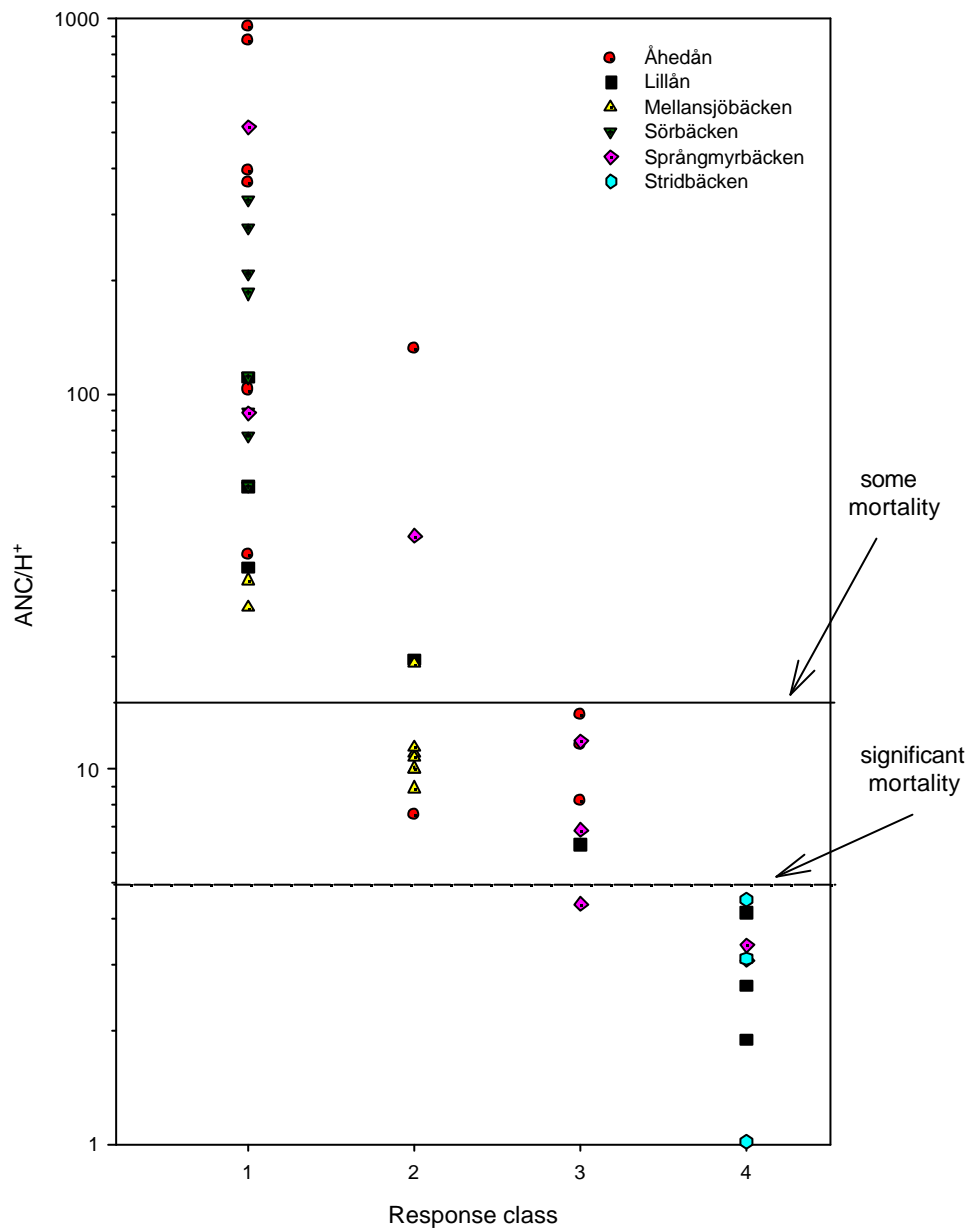


Fig. 11. Relationship between the response pattern of the experimental fish and the ANC/H⁺ ratio during spring flood. The response is divided into 1) no significant response; 2) significant response without mortality; 3) significant response with some mortality and 4) significant mortality. The thresholds for some mortality and significant mortality is provided in the figure.

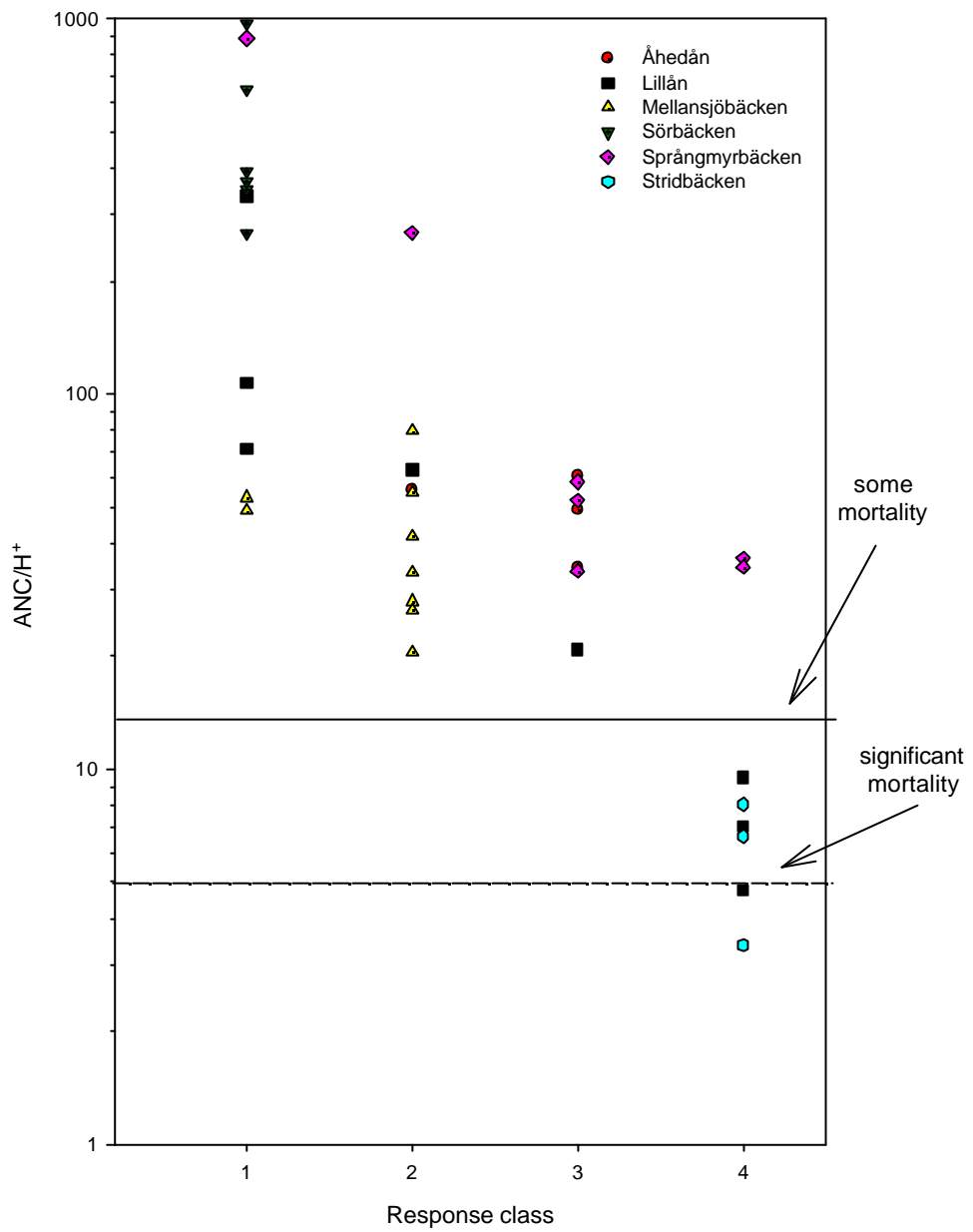


Fig. 12. Fish Response pattern in relation to the pre-industrial ANC/H⁺ ratio during spring flood. See further explanation in legend of Fig. 11.

Spring flood episodes – past and future – what can we expect?

The most important result from the Episode Project is that the extent of episodic acidification in northern Sweden is currently limited. Although the anthropogenic component superimposed on the natural pH decline in some very acid sensitive surface waters can create conditions that are toxic to the natural biota, these cases are probably now few and decreasing due to the low and generally still declining SO_4^{2-} deposition load in northern Sweden.

The findings in the Episode Project do, to a large extent, confirm the concern raised earlier by several researcher (e.g. Jansson et al., 1992; Bishop, 1997) that liming is not appropriate in most surface waters in northern Sweden. Although these results question the need for a large scale liming program in northern Sweden they do not entirely invalidate the biological indications presented by Ahlström and Isaksson (1990). Instead the new insights from the project help us to better interpret the different temporal aspects of a fast chemical and slow biological response to changes in acid deposition, as well as the effects associated with hydrological episodes in northern Sweden.

Another major finding of the Episode Project has been the strong correlation between winter SO_4^{2-} deposition and the anthropogenic component of acidification associated with spring flood episodes. This strong correlation clearly indicates that increasing or decreasing SO_4^{2-} deposition load will lead to an immediate response in the spring flood ANC and pH decline (see Fig. 5). While the hydro-chemical response is immediate, the biological response is slow. Reestablishment in previously acidified waters can be particularly difficult and slow in headwater streams where there are other impacts on fish habitat (e.g. migration barriers, damaged spawning grounds, channel alteration).

The new focus in the Swedish liming plan for the next ten years (SEPA, 1999) is on protecting and reestablishing the natural biodiversity. This could potentially provide a better basis for preserving naturally acid ecosystems. There is, however, a risk that this new biodiversity focus may instead accelerate the inappropriate liming in northern Sweden. In the new plan, the presence of a high biodiversity value is needed to give a liming object the highest priority. The effect of this is that many heavily acidified surface waters in southwestern Sweden will not be given priority, since they lost much of their biodiversity and hence could lose their liming subsidies for the benefit of “protecting” previously unlimed surface waters in northern Sweden by redirecting liming to those waters (SLU, 1999). In the light of the rapid chemical response to changes in acid deposition, and the fact that the biodiversity of these high priority surface waters survived the several times higher acid deposition during the 1970’ and 1980’s, liming now to protect against acid episodes caused by contemporary acid deposition levels is evidently inappropriate.

Liming in northern Sweden is inappropriate because current biological status can not be understood solely from the current chemical status of the stream (which is

all that liming affects). This is the great fallacy of the reliance on biological indicators which have been relied on heavily in Sweden to guide liming. A full understanding of the current biological status still requires advances in ecological understanding. What this thesis can provide is a reconstruction of the chemical history, which is an important step on the way to a more complete understanding of the situation in northern Sweden. In a number of companion reports, past and future deposition scenarios have been used to make assessments of the development of spring flood hydrochemistry (Laudon et al., manuscript; Laudon and Bishop, in review B; Laudon et al., in press). Using deposition scenarios Laudon and Bishop (in review B) made regional assessments of how the anthropogenic acidification have been or will be affecting surface waters from 1970 to 2010 following the new Gothenburg Protocol signed in December 1999. The results from that study showed that the recovery from the maximum SO_4^{2-} deposition load in 1970 has been extensive and that this regional recovery will continue until 2010 if the commitments made in the Gothenburg Protocol are honored.

Conclusions

In this thesis, the operational model BDM (Boreal Dilution Model) for separating episodic acidification associated with spring flood episodes into natural and anthropogenic components is presented. The result from applying the model to over 20 spring flood episodes in northern Sweden is that the major driving mechanisms of episodic acidity during spring flood events are the combination of natural organic acidity and dilution. The results from this study further demonstrate that the current regional extent of anthropogenic acidification during spring flood in northern Sweden is limited.

In the Episode Project it was discovered that there is a close correlation between the SO_4^{2-} winter deposition and the anthropogenic component driving ANC and pH decline during spring flood in northern Sweden. While this correlation greatly improves our ability to make regional assessments of the severity of episodic acidification, it also demonstrates that a decreasing acid deposition load will lead to a direct improvement of any anthropogenic acidification associated with snow melt. The results from this study therefore indicate that the large decline in SO_4^{2-} deposition during the last two decades have led to a great improvement in the hydrochemistry of the spring flood in northern Sweden.

The modeling tool and sampling strategy developed by the Episode Project provide a systematic methodology to evaluate the anthropogenic component during hydrological episodes. The BDM is already in use by several regional environmental monitoring programs in the country where it previously has been difficult to justify special sampling programs to evaluate hydrochemical variations during spring flood and rain storm events despite their influence on biodiversity. Despite the

generally limited role of anthropogenic acidification in northern Sweden, toxic conditions due to acid deposition superimposed on the natural pH decline can still occur in some very acid sensitive catchments during the spring flood. The identification of these toxic episodes for remediation will be an important future task for the BDM.

Thoughts about the future!

The overall purpose of the Episode Project has been to develop a scientific basis for understanding the problem of episodic acidification in northern Sweden in order to improve the national liming policy. The results from this study show that the anthropogenic component associated with spring flood episodes is limited in northern Sweden. Furthermore, this anthropogenic component is not adequately quantified in either the old liming guidelines (SEPA, 1988), or the new guidelines that were recently proposed by the Swedish Environmental Protection Agency (SEPA, in review). It is now time for the policy makers to take their responsibility for developing a more appropriate liming strategy in northern Sweden based on what has been learned from a decade of concerted research.

The Episode Project is the largest scientifically based acidification research program focused on the specific conditions in northern Sweden since liming started in the region. In spite of the relatively large size of the program, its annual budget has been less than 1% of the annual liming budget in the region. The better awareness of natural acidity, as well as the possibility for quantifying the role of anthropogenic deposition associated with spring flood, has greatly improved the understanding of acidity sources in northern Sweden. Despite the many scientific advances that have been made within the Episode Project, the results have also posed many new questions about the ecological situation in the region. Most significantly, by showing that current levels of anthropogenic acidity do not explain the perceived problems with biodiversity in the region, the need for other explanations has been highlighted.

References

* References from the Episode Project

- Ahlström, J. 1994. Svavelsyradepositionens betydelse för pH-värdet under vårfloden i Stridbäcken, ett mindre vattendrag i södra Västerbottens kustområde. *Västerbotten County Administration Board, Report*. Umeå. (In Swedish.)
- Ahlström, J. 1999. Försurningens betydelse för vattendrag i Västerbottens län under vårfloden 1995. *Västerbotten County Administration Board, Report*. Umeå. (In Swedish.)
- Ahlström, J., E. Degerman, L. Lindgren and P. E. Lingdell. 1995. Försurning av små vattendrag i Norrland. *Swedish Environmental Protection Agency, Report 4343*. Stockholm. (In Swedish.)
- Ahlström, J. and K. E. Isaksson. 1990. Försurningsläget i norrlands inland och fjälltrakter - Kalkning. *Swedish Environmental Protections Agency, Report 3781*. Stockholm. (In Swedish.)
- Akselsson, C. 2000. Övervakning av luftföroreningar i norra Sverige. Resultat till och med september 1999. *Swedish Environmental Research Institute, IVL report B1378*. Aneboda. (In Swedish.)
- Allan, C. J. 1995. Hydrochemical response of upland Precambrian Shield catchments to additions of H₂SO₄ and NH₄NO₃ during snowmelt. *Canadian Journal of Fisheries and Aquatic Sciences* 52, 2213-2228.
- Andersson, T., H. Ivarsson, A. Bergqvist and L. Brydsten. 1999. Sulfatkällor för ytvatten i norra Sverige. *Umeå University, Dept. of Physical Geography, Report*. (In Swedish.)
- Baker, J. P., J. VanSickle, C. J. Gagen, D. R. DeWalle, W. E. Sharpe, R. F. Carline, B. P. Baldigo, P. S. Murdoch, D. W. Bath, W. A. Kretser, H. A. Simonin and P. J. Wigington. 1996. Episodic acidification of small streams in the northeastern United States: Effects on fish populations. *Ecological Application* 6, 422-437.
- Barnes, R. 1975. The determination of specific forms of aluminum in natural water. *Chemical Geology* 15, 177-191.
- Bernes, C. 1991. Försurning och kalkning av svenska vatten. *Swedish Environmental Protection Agency, Monitor 12*. Stockholm. (In Swedish.)
- Bertills, U. and T. Näsholm. 2000. Effekter av kvävenedfall på skogsekosystem. *Swedish Environmental Protection Agency, Report 5066*. Stockholm. (In Swedish.)
- Binkley, D. and P. Högberg. 1997. Does atmospheric deposition of nitrogen threaten Swedish forests. *Forest Ecology and Management* 92, 119-152.
- Bishop, K. H. 1991. *Episodic Increases in Stream Acidity, Catchment Flow Pathways and Hydrograph Separation*. Ph.D. Thesis. Cambridge University.
- Bishop, K. H. 1997. Liming of acid surface waters in northern Sweden: Questions of geographical variation and the precautionary principle. *Transactions of the Institute of British Geographers* 22, 49-60.
- Bishop, K., H. Grip and A. O'Neill. 1990. The origin of acid runoff in a hillslope during storm events. *Journal of Hydrology* 116, 35-61.
- *Bishop, K., H. Laudon, J. Hruška, P. Kram, S. Köhler and S. Löfgren. Does acidification policy follow research in northern Sweden? The case of natural acidity during the 1990's. (In review.)
- *Bishop, K., H. Laudon and S. Köhler. 2000. Separating the natural and anthropogenic components of spring flood pH decline: A method for areas that are not chronically acidified. *Water Resources Research* 31, 1873-1889.
- Bishop, K. and C. Pettersson. 1996. Organic carbon in the boreal spring flood from adjacent subcatchments. *Environmental International* 22, 535-540.
- Björnberg, B. 1983. Dilution and acidification effects during the spring flood of four Swedish mountain brooks. *Hydrobiologia* 101, 19-26.
- Blomqvist, P., R. T. Bell, H. Olofsson, U. Stensdotter and K. Vrede. 1995. Plankton and water chemistry in lake Njupfatet before and after liming. *Canadian Journal of Fisheries and Aquatic Sciences* 52, 551-565.

- Campbell, P. G. C., H. J. Hansen, B. Dubreuil and W. O. Nelson. 1992. Geochemistry of Quebec North Shore salmon rivers during snowmelt - organic-acid pulse and aluminum mobilization. *Canadian Journal of Fisheries and Aquatic Sciences* 49, 1938-1952.
- Clarke, N., L.-G. Danielsson and A. Sparen. 1992. The Determination of Quickly Reacting Aluminium in Natural Waters by Kinetic Discrimination in a Flow System. *International Journal of Environmental Analytical Chemistry* 48, 77-100.
- *Cory, N. 1999. *Hydrograph Separation: The application of ancillary data*. M.Sc. Thesis. Umeå University, Dept. of Physical Geography.
- Cosby, B. J., R. F. Hornberger, J. N. Galloway and R. F. Wright. 1985. Modeling the effects of acid deposition: Estimation of long term water quality responses in small forested catchments. *Water Resources Research* 21, 1591-1601.
- Dahlström, N. and H.-E. Johansson. 1997. *Sulfat i sjöar i Västerbottens och Norrbottens län*. M.Sc. Thesis. Umeå University, Dept. of Physical Geography. (In Swedish.)
- Davies, T. D., M. Tranter, P. J. Wigington and K. N. Eshleman. 1992. Acidic episodes in surface waters in Europe. *Journal of Hydrology* 132, 25-69.
- DeVito, K. J. and A. R. Hill. 1997. Sulphate dynamics in relation to groundwater - surface water interactions in headwater wetlands of the southern Canadian Shield. *Hydrological Processes* 11, 485-500.
- DeWalle, D. R. and B. R. Swistock. 1994. Causes of episodic acidification in 5 Pennsylvania streams on the Northern Appalachian Plateau. *Water Resources Research* 30, 1955-1963.
- Dise, N. B., E. Matzner and P. Gundersen. 1998. Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water, Air and Soil Pollution* 105, 143-154.
- Driscoll, C. 1984. A procedure for the fractionation of aqueous aluminium in dilute acidic water. *International Journal of Environmental and Analytical Chemistry* 16, 267-283.
- Driscoll, C. T., J. P. Baker, J. J. Bisogni and C. L. Schofield. 1980. Effect of aluminium speciation on fish in dilute acidified waters. *Nature* 284, 161-164.
- Ek, A. and I. Renberg. 1998. *Förurning återhämtning och kritisk belastning*. Swedish Environmental Protection Agency, Report. Stockholm. (In Swedish.)
- Eriksson, E., E. Karlton and J. E. Lundmark. 1992. Acidification of forest soils in Sweden. *Ambio* 21, 150-154.
- Eshleman, K. N., T. D. Davies, M. Tranter and P. J. Wigington. 1995. A 2-Component mixing model for predicting regional episodic acidification of surface waters during spring snowmelt periods. *Water Resources Research* 31, 1011-1021.
- Eshleman, K. N. and H. F. Hemond. 1985. The role of organic acids in the acid-base status of surface waters at Bickford Watershed, Massachusetts. *Water Resources Research* 21, 1503-1510.
- Eshleman, K. N., P. J. Wigington Jr., T. D. Davies and M. Tranter. 1992. Modelling episodic acidification of surface waters: the state of the science. *Environmental Pollution* 77, 287-295.
- Evans, C. D., T. D. Davies and P. J. Wigington. 1995. Assessing the contribution of individual dissolved ions to depressions in acid neutralising capacity of streams in the Adirondack and Catskill Mountains, New York. *Water, Air and Soil Pollution* 85, 425-432.
- Exley, C., J. S. Chappell and J. D. Birchall 1991. A mechanism for acute aluminium toxicity in fish. *Journal of Theoretical Biology* 151, 417-428.
- Fiskeriverket. 2000. *Elfiskeregistret*. <http://www.fiskeriverket.se>
- *Forsgren, F. 1999. *Jämförande studie av hydrografsepareringsmetoder under vårfloden*. M.Sc. Thesis. Umeå University, Dept. of Physical Geography. (In Swedish.)
- Frink, C. R. 1996. Acid rain revisited? *Science* 273, 293-293.
- Galloway, J. N., G. R. Hendrey, C. L. Schofield, N. E. Peters and A. H. Johannes. 1987. Processes and causes of lake acidification during spring snowmelt in the West-Central Adirondack Mountains, New York. *Canadian Journal of Fisheries and Aquatic Sciences* 44, 1595-1602.
- Gensemer, R.W. and R. C. Playle. 1999. The bioavailability and toxicity of aluminium in aquatic environments. *Critical Reviews in Environmental Sciences and Technology* 29, 315-450.

- Granlund, E. 1943. Beskrivning till jordartskarta över Västerbottens län nedanför odlingsgräns. *Swedish Geological Survey, Map description Ca 26*. Uppsala. (In Swedish.)
- Grip, H. 1982. Water chemistry and runoff in forest streams at Kloten. Ph.D. Thesis. *Uppsala Universitet, UNGI report No. 58*.
- Heath, R. H., J. S. Kahl, S. A. Norton and I. J. Fernandez. 1992. Episodic stream acidification caused by atmospheric deposition of sea salts at Acadia National Park, Maine, United States. *Water Resources Research* 28, 1081-1088.
- Henriksen, A. 1979. A simple approach for identifying and measuring acidification of freshwater. *Nature* 278, 542-545.
- Henriksen, A., J. Kämäri, M. Posch and A. Wilander. 1992. Critical loads of acidity: Nordic surface waters. *Ambio* 21, 356-363.
- Hesthagen, T. 1997. *Population response of Arctic charr (Salvelinus alpinus (L.)) and brown trout (Salmo trutta L.) to acidification in Norwegian inland waters*. Ph. D. Thesis. Norwegian University of Science and Technology, Dept. of Zoology. Trondheim.
- Hindar, A., A. Henriksen, K. Torseth and A. Semb. 1994. Acid water and fish death. *Nature* 372, 327-328.
- Hope, D., T. K. Kratz and J. L. Riera. 1996. Relationship between pCO₂ and dissolved organic carbon in Northern Wisconsin Lakes. *Journal of Environmental Quality* 25, 1442-1445.
- *Hruška, J., H. Laudon, C. E. Johnson, S. Köhler and K. Bishop. Acid/base character of organic acids in boreal stream during snowmelt. *Water Resources Research*. (In press.)
- Hyer, K. E., J. R. Webb and K. N. Eshleman. 1995. Episodic acidification of three streams in Shenandoah National Park, Virginia, USA. *Water, Air and Soil Pollution* 85, 523-528.
- Ivarsson, H. and M. Jansson. 1995. Sources of acidity in running waters in central Northern Sweden. *Water, Air and Soil Pollution* 84, 233-251.
- Jacks, G. 1991. Soil Acidification and its relation to surface water quality. *Vatten* 47, 339-341. (In Swedish.)
- Jacks, G., E. Olofsson and G. Werme. 1986. An acid surge in a well-buffered stream. *Ambio* 15, 282-285.
- Jansson, M., A. K. Bergström, P. Blomqvist, A. Isaksson and A. Jonsson. 1999. Impact of allochthonous organic carbon on microbial food web carbon dynamics and structure in Lake Örträsket. *Archiv für Hydrobiologie* 144, 409-428.
- Jansson, M. and H. Ivarsson. 1994. Causes of acidity in the River Lillån in the coastal zone of central Northern Sweden. *Journal of Hydrology* 160, 71-87.
- Jansson, M., H. Ivarsson, K. Bishop and H. Grip. 1992. Kalka inte naturligt sura sjöar. *Miljö-aktuellt*, April 29. (In Swedish.)
- Johannessen, M. and A. Henriksen. 1978. Chemistry of snow meltwater: Changes in concentration during melting. *Water Resources Research* 14, 615-619.
- *Juto, U. and J. Temnerud. 1999. *Undersökning av skyddszoners effekter på vattenkemin under vårfloden 1998 i fyra bäckar i östra Jämtland*. M.Sc. Thesis. Umeå University, Dept. of Physical Geography. (In Swedish.)
- Kahl, J. S., S. A. Norton, T. A. Haines, E. A. Rochette, R. H. Heath and S. C. Nodvin. 1992. Mechanisms of episodic acidification in low-order streams in Maine, USA. *Environmental Pollution* 78, 37-44.
- Karlton, E. 1995. *Sulphate adsorption on variable-charge minerals in podzolised soils in relation to sulphur deposition and soil acidity*. Ph.D. Thesis. Swedish University of Agricultural Sciences.
- *Karlsson, J. and R. Wallin. 1999. Responser hos öring (*Salmo trutta*) under vårfloden. Kan hög TOC-halt reducera surstötens effekter på öring? M.Sc. Thesis. *Swedish University of Agricultural Sciences, Dept. of Forest Ecology, Stencilserie No. 53*. Umeå. (In Swedish.)
- Kindbom, K., K. Sjöberg and G. Pihl-Karlsson. Trends in air concentrations and deposition in background areas in Sweden - major inorganic compounds, heavy metals and ozone. *Swedish Environmental Research Institute, Report*. (In press.)
- Köhler, S. 1999. Quantifying the role of natural organic acids on pH and buffering in Swedish surface waters. Ph.D. Thesis. *Swedish University of Agricultural Sciences, Acta Universitatis Agriculturae Sueciae, Silvestria* 92. Umeå.

- Köhler, S., J. Hruška and K. Bishop. 1999. Influence of organic acid site density on pH modeling of Swedish lakes. *Canadian Journal of Fish Aquatic Sciences* 56, 1461-1470.
- *Köhler, S., H. Laudon, A. Wilander and K. Bishop. 2000. Estimating organic acids dissociation in natural surface water using total alkalinity and TOC. *Water Research* 34, 1425-1434.
- Korsman, T. 1993. *Acidification trends in Swedish lakes: An assessment of past water chemistry conditions using lake sediments*. Ph.D. Thesis. Umeå University, Dept. of Ecological Botany.
- Korsman, T. 1999. Temporal and spatial trends of lake acidity in Northern Sweden. *Journal of Paleolimnology* 22, 1-15.
- Kortelainen, P. and S. Saukkonen. 1995. Organic vs. minerogenic acidity in headwater streams in Finland. *Water, Air and Soil Pollution* 85, 559-564.
- *Kram, P., H. Laudon, K. Bishop, L. Rapp and J. Hruška. Magic modeling of long-term lake water and soil chemistry at Abborrträsket, Northern Sweden. (In review.)
- Kullberg, A., K. H. Bishop, A. Hargeby, M. Jansson and R. Petersen. 1993. The ecological significance of dissolved organic-carbon in acidified waters. *Ambio* 22, 331-337.
- *Laudon, H. 1999. Spring Flood pH Decline in Northern Sweden: Towards an Operational Model for Separating Natural Acidity from Anthropogenic Acidification. Licentiate Thesis. *Swedish University of Agricultural Sciences, Dept. of Forest Ecology, Stencilserie No. 49*. Umeå.
- *Laudon, H and K. Bishop. 1997. Identification of sources leading to episodic stream acidification in northern Sweden. In the *proceedings of the conference Acid Rain and Snow, Niigata, Japan, October 1997*, pages 575-582.
- *Laudon, H and K. Bishop. 1999a. Quantifying sources of ANC depression during spring flood in northern Sweden. *Environmental Pollution* 105, 427-455.
- *Laudon, H and K. Bishop. 1999b. *SLU, Miljötrender Nr 3*, 1999.
- *Laudon, H. and K. Bishop. 2000. Verktyg för att bedöma den antropogena försurningspåverkan på ANC och pH i vattendrag under högfloöden. *Swedish Environmental Protection Agency, Liming Program Report*. Stockholm. (In Swedish.)
- *Laudon, H. and K. Bishop. In review A. Episodic pH decline in small streams in Northern Sweden during autumn storms.
- *Laudon, H. and K. Bishop. In review B. The Rapid and Extensive Recovery from Episodic Acidification in Northern Sweden Due to Declines in SO₄²⁻ Deposition.
- *Laudon, H., J. Hruška and K. Bishop. Predicting episodic acidification in the recovery from chronic acidification. (Manuscript.)
- *Laudon, H., S. Köhler and K. Bishop. 1999. Natural Acidity or Anthropogenic Acidification in Spring Flood of Northern Sweden. *Science of the Total Environment* 234, 63-73.
- *Laudon, H., O. Westling, A. Bergquist and K. Bishop. Episodic acidification in northern Sweden: A regional assessment of the anthropogenic component. (Manuscript.)
- *Laudon, H., O. Westling and K. Bishop. 2000. Variability of spring flood hydrochemistry in Northern Sweden. *Canadian Journal of Fisheries and Aquatic Sciences* 57, 1888-1900.
- *Laudon, H., O. Westling, S. Löfgren and K. Bishop. Modeling preindustrial ANC and pH during the spring flood in Northern Sweden. (In review.)
- *Laudon, H., O. Westling, A. B. S. Poléo and L. A. Vøllestad. Naturligt sura och försurade vatten i Norrland. *Swedish Environmental Protection Agency, Report*. Stockholm. (In press; in Swedish.)
- Likens, G. E., C. T. Driscoll and D. C. Buso. 1996. Long-term effects of acid rain: Response and recovery of forested ecosystem. *Science* 272, 244-245.
- Löfgren, S. 1991. Naturliga och antropogena källors betydelse för de ökade halterna av kväve och organiskt material i Västerdalälven och klarälven 1965-89. *Swedish Environmental Protection Agency, Report 3902*. Stockholm. (In Swedish.)
- Löfgren, S. 1996. Naturlig surstöt i Dalavattendrag. In *Sjöar och vattendrag - årsskrift från miljöövervakningen 1995* (eds. G. Persson and T. Wiederholm). (In Swedish.)
- Löfgren, S. 2000. Environmental status of Swedish forest ecosystems - integrated monitoring. *Swedish Environmental Protection Agency, Report 5071*. Stockholm. (In Swedish with English summary.)

- Löfgren, S. and U. Bertills. 1995. Naturligt surt eller antropogent försurat ytvatten i Norrland? *Swedish Environmental Protection Agency, Report*. Stockholm. (In Swedish.)
- Löfgren, S. and S. Fölster. 1998. Trender och samband för pH, alkalinitet och andra försurningsparametrar i svenska vattendrag. *Swedish Environmental Protection Agency, Report*. Stockholm. (In Swedish.)
- Lövblad G., K. Kindbom, P. Grennfelt, H. Hultberg and O. Westling. 1995. Deposition of acidifying substances in Sweden. *Ecological Bullentins* 44, 17-34.
- Lundgren, L. J. 1991. Försurningen på dagordningen: En bild av ett händelseförlopp 1966-1968. *Swedish Environmental Protection Agency, Report 3886*. Stockholm. (In Swedish.)
- Lundin, L. 1995. Vattnet i skogsmarken; skogsbrukets effekter på hydrologi och vattenkemi. *Skogen* 4, 8-16. (In Swedish.)
- Lundström U. S., L. Nyberg, R. Danielsson, P. A. W. van Hees and M. Andersson. 1998. Forest Soil Acidification: Monitoring on the regional scale, Värmland, Sweden. *Ambio* 27, 551-556.
- Lydersen, E., E. Fjeld and T. Andersen. 1994. Fiskestatus og vannkjemi i norske innsjøer. *NIVA, NIVA rapport - O - 93172, LNR:3002-94*. Oslo. (In Norwegian.)
- Lydersen, E. and A. Henriksen. 1995. Seasalt effects on the acid neutralizing capacity of streamwaters in southern Norway. *Nordic Hydrology* 26, 4-5.
- Magnusson, T. 1982. Skogs- och myrdikningens inverkan på försurningen av ytvatten; en litteraturstudie. *Swedish Environmental Protection Agency, Report 1626*. Stockholm. (In Swedish.)
- Mason, B. J. 1990. *The surface waters acidification programme*. Cambridge University Press, Cambridge.
- Mast, A. M., C. Kendall, D. H. Campbell, D. W. Clow and J. Back. 1995. Determination of hydrological pathways in an alpine-subalpine basin using isotopic and chemical tracers, Loch Vale Watershed, Colorado, USA. *IAHS*, 263-270.
- Mitchell, M. J., C. T. Driscoll, J. S. Kahl, G. E. Likens, P. S. Murdoch and L. H. Pardo. 1996. Climatic control of nitrate loss from forested watersheds in the northeast United States. *Environmental Science and Technology* 30, 2609-2612.
- Molot L. A., P. J. Dillon and B. D. LaZerte. 1989. Factors affecting alkalinity concentration of streamwater during snowmelt in Central Ontario. *Canadian Journal of Fisheries and Aquatic Sciences* 46, 1658-1666.
- Mörth, C.-M., P. Torssander, M. Kusakabe and H. Hultberg. 1999. Sulfur isotope values in a forested catchment over four years: Evidence for oxidation and reduction processes. *Biogeochemistry* 44, 51-71.
- Munson, R. K. and S. A. Gherini. 1993. Influence of organic-acids on the pH and acid-neutralizing capacity of Adirondack lakes. *Water Resources Research* 29, 891-899.
- Mylona, S. 1996. Sulphur dioxide emissions in Europe 1880-1991 and their effect on sulphur concentrations and depositions. *Tellus B48*, 662-689.
- Nyberg, L., M. Stähli, P.-E. Mellander and K. H. Bishop. Soil frost effects on soil water and runoff dynamics along a boreal forest transect. 1. Field investigations. *Hydrological Processes*. (In press.)
- Odén, S. 1967. Nederbördens försurning. In *Dagens Nyheter October, 24*. Stockholm. (In Swedish.)
- Odén, S. 1968. Nederbördens och luftens försurning - dess orsaker förlopp och verkan i olika miljöer. *NFR, Ekologikommittén, Bulletin nr. 1*. (In Swedish.)
- Oliver, B. G., E. M. Thurman and R. Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochemica Cosmochemica Acta* 47, 2031-2035.
- Poléo, A. B. S. 1995. Aluminium polymerization - a mechanism of acute toxicity of aqueous aluminium to fish. *Aquatic Toxicology* 31, 347-356.
- Poléo, A. B. S. 1998. Forsurning - kalkning - og hva som er best for fisken? *Biolog* 16, 22-27. (In Norwegian.)
- Poléo, A. B. S. and F. Bjerkely. 2000. Effect of unstable aluminium chemistry in Arctic char (*Salvelinus alpinus*). *Canadian Journal of Fisheries and Aquatic Sciences* 57, 1423-1433.
- Posch, M., J.-P. Hettelingh, P. A. M. de Smet and R. T. Downing. 1997. Calculation and mapping of critical thresholds in Europe: Status Report 1997. *CCE, RIVM, Report No. 259101007*.

- Rapp, L. 1998. Critical loads for surface waters: Validation and challenges. Licentiate Thesis. *Swedish University of Agricultural Sciences, Dept. of Forest Ecology, Stencilserie No. 36.* Umeå.
- Renberg, I. and A. Ek. 1998. Försurat eller naturligt surt? En undersökning av den historiska pH utvecklingen i tre sjöar i Gyllbergen. *Dalarna County Administration Board, Report 1998:7.* Falun. (In Swedish.)
- Renberg, I., T. Korsman and N. J. Anderson. 1993. A temporal perspective of lake acidification in Sweden. *Ambio* 22, 264-271.
- Rodhe, A. 1987. The origin of streamwater traced by oxygen-18. Ph.D. Thesis. *Uppsala University, UNGI Report Series A no. 41.*
- Rodhe, A. 1998. Snowmelt - dominated systems. In *Isotope tracers in catchment hydrology* (eds. C. Kendall and J. J. McDonnell), pp. 391-433. Elsevier Sciences.
- Rodhe, H., P. Grennfelt, J. Wisniewski, C. Agren, G. Bengtsson, K. Johansson, P. Kauppi, V. Kucera, L. Rasmussen, B. Rosseland, L. Schotte and G Sellén. 1995. Acid Reign '95? - Conference summary statement. *Water, Air and Soil Pollution* 85, 1-14.
- Rosenqvist, I. 1978. Alternative sources of acidification of river water in Norway. *Science of the Total Environment* 10, 39-49.
- Reuss, J. O. and D. W. Johnson. 1986. Acid deposition and the acidification of soils and waters. *Ecological studies* 59. Springer-Verlag, New York.
- SEPA (Swedish Environmental Protection Agency). 1988. Allmänna råd för kalkning av sjöar och vattendrag. *Swedish Environmental Protection Agency, Report 88:3.* Stockholm. (In Swedish.)
- SEPA (Swedish Environmental Protection Agency). 1999. Nationell plan för kalkning av sjöar och vattendrag 2000-2009: Redovisning av ett regeringsuppdrag. *Swedish Environmental Protection Agency, Report.* Stockholm. (In Swedish.)
- SEPA (Swedish Environmental Protection Agency). *Handbok för kalkning av sjöar och vattendrag.* Swedish Environmental Protection Agency, Stockholm. (In review; In Swedish.)
- SLU (Swedish University of Agricultural Sciences). 1999. *Evaluation of the Swedish Environmental Protection Agency's "Nationell plan för kalkning av sjöar och vattendrag 2000-2009"*. Swedish University of Agricultural Sciences. Uppsala. (In Swedish.)
- Schaefer, D. A., C. T. Driscoll, R. Van Dreason, and C. P. Yatsko. 1990. The episodic acidification of Adirondack lakes during snowmelt. *Water Resources Research* 26, 1639-1647.
- *Sedin, A. 1999. *Fysiologisk respons hos havsöring (Salmo Trutta) under vårfloden, i humösa vattendrag i centrala norra Sverige.* M.Sc. Thesis. Umeå University, Dept. of Physical Geography. (In Swedish.)
- Simonin, H.A., W. A. Kretser, D. W. Bath, M. Olson and J. Gallagher. 1993. In situ bioassays of brook trout (*Salvelinus fontinalis*) and blacknose dace (*Rhinichthys atratulus*) in Adirondack streams affected by episodic acidification. *Canadian Journal of Fisheries and Aquatic Sciences* 50, 902-912.
- Stähli, M., L. Nyberg, P.-E. Mellander, P.-E. Jansson and K. H. Bishop. Soil frost effects on soil water and runoff dynamics along a boreal forest transect. 2. Simulations. *Hydrological Processes.* (In press.)
- Steele, D. W. and J. M. Buttle. 1994. Sulfate Dynamics in a Northern Wetland Catchment During Snowmelt. *Biogeochemistry* 27, 187-211.
- Stegman, B. 1990. Försurat skogsmark i Gävleborgs län 1949-1989. *Gävleborg County Administration Board, Report 1990:2.* Gävle. (In Swedish.)
- *Stepanouskas, R., H. Laudon and N. Jørgensen. 2000. High DON bioavailability in boreal rivers during spring flood. *Limnology and Oceanography* 45, 1298-1307.
- Stumm, W. and J. J. Morgan. 1981. *Aquatic chemistry. An introduction emphasizing chemical equilibria natural waters.* John Wiley and Sons, Inc. New York.
- Tamm, C. O. and L. Hallbäcken. 1988. Changes in soil acidity in two forest areas with different acid deposition: 1920s to 1980s. *Ambio* 17, 56-61.
- Tranter, M., T. D. Davies, P. J. Wigington and K. N. Eshleman. 1994. Episodic acidification of fresh-water systems in Canada - physical and geochemical processes. *Water, Air and Soil Pollution* 72, 19-39.

- Vanoffelen, H. K., C. C. Kreuger, C. L. Schofield and C. Kelehier. 1994. Survival, distribution, and ion composition in 2 strains of brook trout (*Salvelinus fontinalis*) fry after exposure to episodic pH depression in an Adirondack lake. *Canadian Journal of Fisheries and Aquatic Sciences* 51, 792-799.
- Warfvinge, P., G. Jacks and B. Allard. 1998. Försurningssituationen på Gyllberget - bedömning av vattenkvaliteten i Hyttingsån. *Swedish Environmental Protection Agency, Report 4943*. Stockholm. (In Swedish.)
- Warfvinge, P., S. Löfgren and U. Lundström. 1995. Implications of natural acidification for mitigation strategies in northern Sweden. *Water, Air and Soil Pollution* 85, 499-504.
- Wels, C., R. J. Cornett and B. D. LaZerte. 1991. Hydrograph separation: A comparison of geochemical and isotopic tracers. *Journal of Hydrology* 122, 253-274.
- Wigington Jr., P. J., T. D. Davies, M. Tranter and K. N. Eshleman. 1990. Episodic acidification of surface waters due to acidic deposition. *State of Science and Technology, National Acid Precipitation Assessment Program, NAPAP Report 12 Acidic Deposition*. Washington, D. C.
- Wigington, P. J., T. D. Davies, M. Tranter and K. N. Eshleman. 1992. Comparison of episodic acidification in Canada, Europe and the United-States. *Environmental Pollution* 78, 29-35.
- Wigington, P. J., D. R. DeWalle, P. S. Murdoch, W. A. Kretser, H. A. Simonin, J. VanSickle and J. P. Baker. 1996. Episodic acidification of small streams in the northeastern United States: Ionic controls of episodes. *Ecological Applications* 6, 389-407.
- Wilander, A. Surhet/försurning. 1999. In *Bedömningsgrunder för miljö kvalitet: Sjöar och vattendrag* (ed. T. Wiederholm). *Swedish Environmental Protection Agency, Report 4920*. Stockholm. (In Swedish.)
- Wilander, A., R. K. Johnson, W. Goedkoop and L. Lundin. 1998. Riksinventeringen 1995. *Swedish Environmental Protection Agency, Report 4813*. Stockholm. (In Swedish.)
- Witters, H., S. Van Puymbroeck, J. Vangenechten and O. Vanderborcht. 1990. The effect of humic substances on the toxicity of aluminium to adult rainbow trout, *Oncorhynchus mykiss* (Walbaum). *Journal of Fish biology* 37, 43-53.

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