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Spatiotemporal patterns of drivers of episodic acidification in Swedish streams and their relationships to hydrometeorological factors

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ABSTRACT

This study examined the spatiotemporal patterns of episodic acidification in 87 weakly buffered streams in Sweden at a monthly sampling frequency during a ten-year study period (1998–2007). Time series of pre-industrial pH (pH_0) were reconstructed from the acidification model $Meta_{MAGIC}$, and the acidification impact was defined by the difference between the pH_0 and the contemporary pH (*i.e.*, $\Delta pH = pH_0 - pH_t$). Acidification episodes were defined as observations for which the pH_t was at least 0.4 units lower than average, in combination with a ΔpH at least 0.2 units higher than average. Thus, only occasions in which the stream water was both more *acidic* and more *acidified* than average were characterized as acidification episodes. For each observed episode, the primary cause was identified from one of the following five possible drivers: dilution, increase in sulfate, nitrate or organic acids, or sea salt deposition. In total, 258 episodes were observed during the study period. The study showed that streams that were acidified during baseflow ($\Delta pH > 0.4$), but not chronically acidic ($pH > 5.2$), were subjected to regular episodic acidification. Dilution was the single most important cause and the main driver for 58% of the identified episodes. Increases in sulfate concentrations were also relatively common (26% of episodes), whereas increases in nitrate and organic acids as well as sea salt deposition were of minor importance. The total number of dilution-related acidification episodes within a year had a significant ($p = 0.005$) positive correlation ($r = +0.83$) with the average annual precipitation. Occurrences of sulfate episodes were related to droughts during the preceding summers. While the number of streams that are susceptible to episodic acidification will decrease as a consequence of recovery from acidification, the hydrological and meteorological consequences of future climate change may make episodic acidification more common.

1. Introduction

After the successful implementation of commitments to reduce sulfate emissions through the Geneva Convention on Long Range Transboundary Air Pollution and its associated protocols (in 1985, 1994 and 1999), the deposition of sulfate is approaching natural background levels in Europe and North America. In addition, recovery of surface and ground water chemistry from acidification has been documented since then in these regions (Evans et al., 2001; Skjelkvåle et al., 2001; Stoddard et al., 1999) and model projections predict a steady recovery of the water chemistry (Moldan et al., 2004; Wright and Cosby, 2003). As the recovery progresses, and acidity moves closer to natural levels, accurate acidification assessments are needed because of their policy implications (Fölster et al., 2007). For example, the national environmental goals in Sweden (Miljömålsrådet, 2008) and stipulations in the European Union's "Water Framework Directive" (2000) require all surface waters within the Union's jurisdiction to have "good ecological status" by 2015. In practice, this means that there should be no significant ecological differences in the waters and associated ecosystems compared to pre-industrial conditions. Furthermore, the annual cost for liming lakes in Sweden is currently about 23 000 000 EUR/year (SEPA, 2007). To evaluate whether these legislative demands have been met and to determine when liming treatments are no longer needed, precise assessment of acidification is required.

Acidification assessments in current environmental quality criteria (EQC) in Sweden are based on the parameter ΔpH, calculated as the difference between the pre-industrial and contemporary pH (*i.e.*, $\Delta pH = pH_0 - pH_t$), with $\Delta pH \geq 0.4$ defining significant acidification (Fölster et al., 2007). The EQC also states that assessments should be based on long-term water chemistry variables. Assessments of streams are based on flow-weighted annual means, whereas assessments of lakes are based on annual medians. However, during events such as storm floods, the pH may be more affected in the current, acidified state (pH_t) than it would have been in the pristine, pre-industrial state (pH_0).

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If so, there will be temporary increases in ΔpH, indicating a greater anthropogenic impact on acidification.

Episodic acidification may be one reason for the apparently modest responses of sensitive biota to the chemical recovery observed by various authors (Monteith et al., 2005; Stendera and Johnson, 2008; Tipping et al., 2002) because acid episodes have been found to prevent re-colonization of biota in previously acidified systems (Bradley and Ormerod, 2002; Kowalik et al., 2007). Studies that have examined chemical recovery after episodic acidification have shown that sulfate-driven episodes have become less severe in both intensity and frequency (Laudon and Hemond, 2002), but weather-driven episodes (due to high flow and sea salt deposition during storm events) persist (Laudon, 2008; Wright, 2008). Since the recovery of base saturation of acidified soils is predicted to be slow (Aherne et al., 2003; Beier et al., 2003), many recovering freshwaters will probably remain vulnerable to storm-related episodic acidification for several decades (Evans, 2005).

A number of factors can influence episodic acidification. Many episodes are associated with high runoff, for example during spring snowmelt and heavy rains. Such events will cause dilution of the Acid Neutralizing Capacity (ANC), provided that ANC>0, and hence decrease pH. The effect is furthermore enhanced if the melt water or rain contains more acid anions than base cations, relative to baseflow (Bishop et al., 2000; Eshleman et al., 1995). This effect on pH may also be enhanced by elevated concentrations of organic acids that are flushed out during high runoff (Laudon et al., 1999; Wellington and Driscoll, 2004), and by nitrate if the fluxes exceed the uptake by vegetation in the catchment during periods of biological dormancy (Lepori et al., 2003; Stoddard, 1995). Furthermore, in coastal areas, sea salt deposition during storms may cause a decrease in pH, especially in areas with low base saturation in the soil (Hindar et al., 1995; Langan, 1989). Acid episodes are also affected by the prevailing weather conditions. For instance, drought can result in the oxidation of sulfur to sulfate as the water table drops, and the sulfate may be subsequently washed out when the water table rises again (Devito et al., 1999; Laudon et al., 2004).

Episodes caused by elevated concentrations of sulfate or nitrate can generally be attributed to anthropogenic pollution, except in areas with naturally acidic sulfate soils (Ivarsson and Jansson, 1995). Soil acidification is also regarded as a prerequisite for the occurrence of sea salt episodes (Heath et al., 1992). In contrast, the dilution of base cations and temporary increases in organic acids are natural phenomena that can depress pH by several units, even in areas with low levels of anthropogenic deposition (Laudon et al., 2000).

The objectives of this study were to examine the occurrence of episodic acidification on several temporal (inter-annual and seasonal) as well as spatial scales and to compare the importance of the five driving mechanisms of episodic acidification, which are dilution (indicated by a decrease in base cations) and temporary increases in sulfate, nitrate, sea salt (indicated by an increase in chloride) and organic acids. The anthropogenic acidification (ΔpH) was calculated over a 10-year period (1998–2007) for both individual occasions and for the 5-year running medians in monthly time series from 87 acid-sensitive streams in Sweden. We then defined acidification episodes as occasions in which the pH declined by 0.4 units or more from its base level (the running 5-year median), with a concurrent decline in pH_0 by *less* than 0.2 units (the latter criterion being equivalent with an increase in ΔpH of at least 0.2 units). This criterion was biologically relevant because biota respond more strongly to changes in pH than to changes in buffering capacity, and was also focused on anthropogenic acidification, in contrast to natural acid episodes. The criterion also enabled us to identify episodes in which naturally occurring phenomena, such as dilution or flushing of organic acids, added to anthropogenic acidification.

A common problem for the assessment of episodic acidification is that most monitoring programs do not provide high frequency data on stream water chemistry. To overcome this challenge, most previous studies focused on a small number of streams with high temporal sampling resolution. An alternative approach, which was applied in this study, was to use more commonly available long-term datasets generated from less frequent sampling programs to obtain statistical estimates of the frequency and nature of episodic acidification. While many episodes will be missed using this approach (Brewin et al., 1996), more streams can be included to give greater regional representation.

2. Materials and methods

2.1. Water chemistry data

All water chemistry data were taken from the Swedish national and regional acidification monitoring programs. The material was limited to acid-sensitive streams with mean alkalinity <300 μeq/l for which monthly time series of data for the 10-year period between 1998 and 2007 were available, giving in total 120 samples for each stream with a complete dataset. Up to 45 missing samples were allowed for each stream included in the study. The streams could be divided between two geographical regions, north and south of the *limes norrlandicus*, which separates the nemoral and boreal zones in Scandinavia. The northern streams had a hydrological regime dominated by high discharge during spring snowmelt, whereas southern streams had a more irregular runoff pattern, although their discharge was usually highest during the winter season. In total, 87 streams (34 southern and

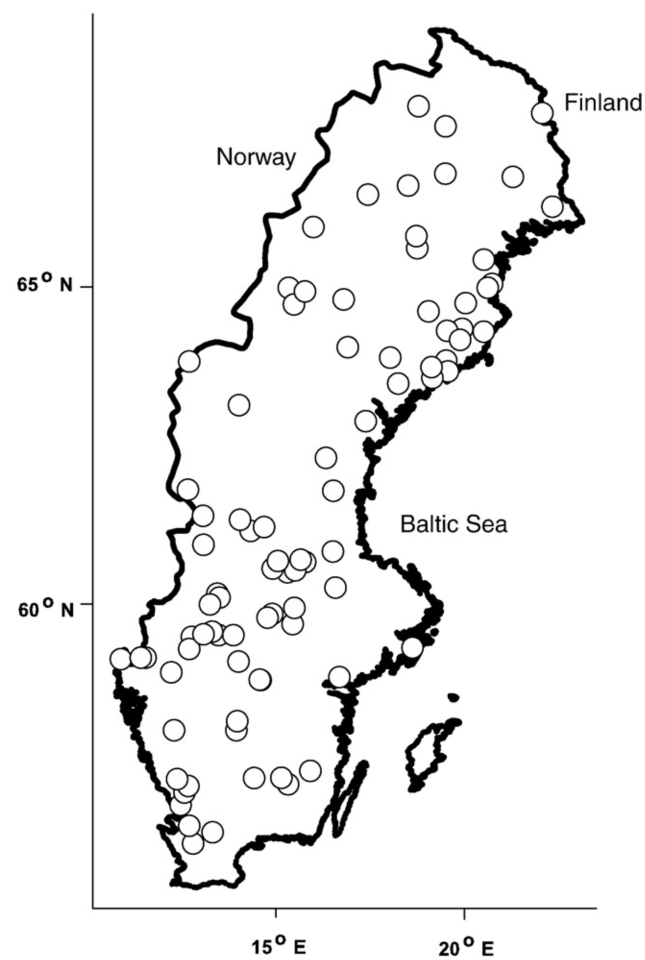

Fig. 1. Map of Sweden showing the locations of the 87 study streams.