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Recovery from episodic acidification delayed by drought and high sea salt deposition

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Abstract

For the prediction of episodic acidification large uncertainties are connected to climatic variability and its effect on drought conditions and sea-salt episodes. In this study data on 342 hydrological episodes in 25 Swedish streams, sampled over 10 years, have been analyzed using a recently developed episode model. The results demonstrate that drought is the most important factor modulating the magnitude of the anthropogenic influence on pH and ANC during episodes. These modulating effects are especially pronounced in southern and central Sweden, where the historically high acid deposition has resulted in significant S pools in catchment soils. The results also suggest that the effects of episodic acidification are becoming less severe in many streams, but this amelioration is less clear in coastal streams subject to high levels of sea-salt deposition. Concurrently with the amelioration of the effects of episodic acidification, regional climate models predict that temperatures will increase in Sweden during the coming decades, accompanied by reductions in summer precipitation and more frequent storms during fall and winter in large areas of the country. If these predictions are realized delays in streams' recovery from episodic acidification events can be expected.

1 Introduction

A steady but slow recovery from acidification is occurring in many surface waters in Europe and North America due to reduction in anthropogenic acid deposition (Skjelkvåle et al., 2001; Stoddard et al., 1999). These findings have been based on assessments that have focused mainly on changes in annual mean values of pH and Acid Neutralization Capacity (ANC). Although the documented improvements are important, the ecological significance of these trends has been difficult to assess in many places because the aquatic biodiversity is as much or more affected by transient declines in pH and ANC associated with snow melt and rain episodes than long-term mean values of

stream water chemistry (Baker et al., 1996; Kowalik and Ormerod, 2006; Lepori et al., 2003). While surface waters in Europe and North America are recovering from chronic acidification (Raddum et al., 2001; Yan et al., 2004), severe episodic acidification may continue to threaten sensitive biota in many regions.

Although much work has focused on identifying the causes and effects of episodic acidification in recent decades, the role of confounding factors is less well understood. In order to predict the effects of future transient acidification events some of the most important uncertainties that need to be addressed are those mediated by drought and sea-salt episodes, which may in turn be strongly affected by climatic change. Summer droughts in humid glaciated regions are known to lower the water table of wetlands, thereby causing conditions suitable for the re-oxidation of previously reduced compounds. In areas with historically high levels of acid deposition, hydrological events following these dry periods can result in pulses of acidic, SO_4^{2-}-rich water entering streams (Christophersen et al., 1983; Devito et al., 1999; Eimers et al., 2004a). Sea-salt episodes occur due to cation exchange processes in the soil, mainly involving exchange of Na^+ with acidifying H^+ and Al-cations, while Cl^- acts as a mobile anion and passes through the soil relatively unaltered (Heath et al., 1992; Neal and Kirchner, 2000). Sea-salt deposition associated with severe storm conditions therefore can transiently increase the acidification effects by mobilizing acid cations that are subsequently transported to streams. Predictions of climate-change effects in Europe suggest that future conditions will be drier in some regions, and storm frequencies will increase in others (Kjellström, 2004). Thus, anticipated climatic changes may have significant effects on sea-salt episodes, drought conditions, and associated responses of stream water chemistry, but the magnitude of these likely effects, and their interactions with the ongoing decline in the effects of anthropogenic acidification, warrants further investigation.

Because of the stochastic and transient nature of episodic acidification events, they have not received the same attention as chronic acidification. With a few exceptions (Laudon et al., 2002; Laudon and Hemond, 2002; Lawrence, 2002) long-term assess-

ments of episodic stream water chemistry trends have been constrained by data availability. Most previous work on episodic acidification has focused on short-term time series lasting only a few years (Wigington et al., 1996). Therefore it has often been difficult to assess whether the long-term decline in acid depositions has resulted solely in improvements in annual average values, or whether it has also ameliorated the effects of episodic acidification. The lack of long-term studies also makes it difficult to discern if temporal changes observed in the intensity of episodic pH and ANC declines are caused by inherent variability in the episodic responses, changes in rates of acid deposition or natural climatic variability.

The objective of this study was to assess whether the long-term decline in acid deposition has ameliorated the effects of episodic acidification in a number of small streams in Sweden monitored over 10 years. In total, data related to 342 hydrological episodes from 25 streams have been analyzed in an attempt to separate the responses to anthropogenic acidification in surface water chemistry from natural variability during summer and fall episodes using the Boreal Dilution Model (BDM; Bishop et al., 2000; Laudon et al., 2001).

2 Study region and data

The data analyzed in the study consist of measurements acquired during the course of 342 hydrological episodes in 25 Swedish streams (Fig. 1; Table 1). The catchments of these streams are located along a climate and deposition gradient, across which mean annual temperatures and precipitation vary from +7 and >1000 mm, respectively, in the southern parts of the country, to –3°C and 600 mm in the northern parts of the country. Of the 25 streams, 16 are located in southern Sweden, four in central Sweden and five in northern Sweden. The separation of the catchments into regions is based on both geography and acid deposition history. Open-field rates of deposition of sulfur and nitrogen compounds in Sweden ranged from 2 to 15 kg S ha^{-1} $year^{-1}$ and 2 to 10 kg N ha^{-1} $year^{-1}$, respectively, during the late 1990's (Kindbom et al., 1998),

decreasing from both west to east and from south to north. Hence, the highest deposition loads of acidifying compounds occurred in southern Sweden (>7 kg S ha^{-1} year^{-1}) followed by central Sweden (3–5 kg S a^{-1} year^{-1}) and northern Sweden (<3 kg S ha^{-1} year^{-1}) (Table 1). Sulfur deposition has been decreasing at a steady rate since 1970 (Mylona, 1996), while nitrogen deposition has remained constant since the beginning of the 1990's (Warfvinge and Bertills, 2000).

The streams, all drain forested catchments varying from 2 to 1090 ha in size, and have been included in two national sampling programs: the PMK network program funded by the Swedish EPA, and the Skokal network program funded by the Swedish Forest Agency. No major forestry activities have been undertaken in any of the catchments in recent decades (Folster and Wilander, 2002).

All the streams have been sampled weekly to monthly, with varying sampling frequency over time. The samples obtained have been analyzed at the Department of Environmental Assessment, Swedish University of Agricultural Sciences, Sweden. All streams have been sampled during at least a 10-year period, starting between 1985 and 1990. Rather than analyzing the same time period for all streams, the time series were kept as long as possible to enable trend assessments of episodic acidification in the individual streams. Chemical analyses were performed by certified laboratories according to EN or ISO standards where applicable (Wilander et al., 1998). Un-aerated samples were used for the pH measurements, immediately after sampling. Analyses of Ca, Mg, Na and K were measured using inductively coupled plasma-optical emission spectrometry (ICP–OES), while Cl^- and SO_4^{2-} were measured using ion chromatography. NO_3 was analyzed using the cadmium reduction method with a segmented flow analyzer.

3 Data analysis

An episode is defined here as a 10-fold (or more) increase in discharge rate. Thus, the definition is based entirely on hydrology. Each hydrological episode was analyzed

using the Boreal Dilution Model (BDM; (Bishop et al., 2000; Laudon et al., 2001). This model has been used to quantitatively distinguish between natural and anthropogenic mechanisms underlying episodic declines of acid neutralising capacity (ANC) during both snow melt-driven hydrological episodes (Laudon and Hemond, 2002) and rain-driven episodes (Laudon and Bishop, 2002) in northern Sweden and during rain events in Canada (Laudon et al., 2002; Laudon et al., 2004). The BDM identifies the anthropogenic component of episodic ANC decline ($\Delta ANC_{(poll)}$) from relative differences in the runoff dynamics of base cations and anthropogenic acid anions during hydrological events.

The BDM is based on the concept that the natural, pre-industrial acid-base chemistry dynamics during episodes result primarily from dilution of the buffering capacity by low ionic strength precipitation (Bishop et al., 2000). The BDM is driven by the observed ANC ($ANC_{(obs,t)}$) at any time "t" during the flow event (Eq. 1) and a dilution index ($DI_{(t)}$; Eq. 2), which is an estimate of the natural dilution of both BC and the anthropogenically significant anions of strong mineral acids ($ANSA = (SO_4^{2-}) + (NO_3^-)$). The sum of base cations ($BC = (Ca^{2+}) + (Mg^{2+}) + (Na^+) + (K^+)$) is used in the determination of the DI (Eq. 2). The natural, pre-industrial ANC ($ANC_{(preind,t)}$) is calculated from the dilution of baseflow ANC ($ANC_{(base)}$, Eq. 3). The difference between $ANC_{(preind,t)}$ and the observed $ANC_{(obs,t)}$ represents the human influence on the ANC ($\Delta ANC_{(poll,t)}$, Eq. 4) during the episode. All concentrations are in μeq L^{-1} of charge.

$$ANC_{(obs,t)} = (Ca^{2+})_{(t)} + (Mg^{2+})_{(t)} + (Na^{2+})_{(t)} + (K^+)_{(t)} - (SO_4^{2-})_{(t)} - (NO_3^-)_{(t)} - (Cl^-)_{(t)}$$
$$= BC_{(t)} - ANSA_{(t)} - (Cl^-)_{(t)} \quad (1)$$

$$DI_{(t)} = BC_{(t)}/BC_{(base)} \quad (2)$$

$$ANC_{(preind,t)} = DI_{(t)} * (BC_{(base)} - ANSA_{(base)}) - (Cl^-)_{(t)} \quad (3)$$

$$\Delta ANC_{(poll,t)} = ANC_{(preind,t)} - ANC_{(obs,t)} \quad (4)$$

Organic acidity is not included in the ANC calculation as DOC has not been analyzed during the entire sampling period used in this study. The exclusion of the strong organic acid component from the ANC expression is the common procedure in international negotiation work in Europe (Posch et al., 1997). Furthermore, as the analyses of $\Delta ANC_{(poll,t)}$ is based on the relative difference between $ANC_{(preind,t)}$ and $ANC_{(obs,t)}$ (Eq. 4) this simplification should not bias the results.

The assumptions and sensitivity of the model have been tested by Bishop, et al. (2000) and Laudon, et al. (2001). Since the purpose of modeling in this study was limited to determining the changes in $\Delta ANC_{(poll,t)}$ during runoff episodes, it was not necessary to satisfy all of the assumptions made when modeling natural pH declines in the original BDM (Bishop et al., 2000). However, one assumption that must be fulfilled in this use of BDM is that the sum of base cations can be used as a surrogate for the natural dilution of ANC, as discussed in more detail by Laudon et al. (2001).

Trends in the anthropogenic component of episodic ANC declines were analysed using the non-parametric Kendall tau (Systat version 14) to identify monotonic long-term trends (Yue et al., 2002). The significance level of the statistical analyses was set to be significant when the p-value was <0.05.

4 Results

In total 342 episodes were identified using the hydrological definition of a 10-fold increase in discharge from baseflow to peak flow. The number of identified episodes affecting each stream varied between ten and 28. Of the 25 sampled streams, ten displayed a decreasing trend in $\Delta ANC_{(poll)}$ ($p<0.05$) over the study period (Table 1), hereafter termed "recovering" streams. Nine of these ten recovering streams are located in southern Sweden and one in central Sweden; no stream in northern Sweden showed a decreasing trend. Of the recovering streams in southern Sweden most were located relatively far from the Atlantic coast. The mean annual Cl^- stream water concentration (average 185 $\mu eq\,L^{-1}$; standard deviation 66 $\mu eq\,L^{-1}$) was also signifi-

cantly lower ($p<0.01$; one way ANOVA) than in the non-recovering streams (average 271 μeq L^{-1}; standard deviation 43 μeq L^{-1} Table 2, Fig. 2). No correlation ($p>0.1$; one way ANOVA) was found between recovering streams and any other stream chemical parameter tested including all other major an- and base cations. Furthermore, no correlations ($p>0.1$; one way ANOVA) were found between the recovering streams and either sulfur or nitrogen deposition in any of the regions.

Most streams displayed a clear relationship between episodic response and antecedent runoff (Fig. 3). In southern Sweden $\Delta ANC_{(poll)}$ was logarithmically correlated ($p<0.05$) to antecedent discharge in 11 of the 16 studied streams (Table 1). The lowest antecedent discharge resulted in ANC declines of over 500 μeq L^{-1} in some instances driven mainly by increases in SO_4^{2-} concentration. In central Sweden all of the studied streams showed a significant relationship, but the two variables were significantly correlated for only one of the five studied streams in northern Sweden. In all streams SO_4^{2-} was the most important driving variable for changes in $\Delta ANC_{(poll)}$ although both BC dilution and NO_3^- influenced the ANC decline during occasional episodes. The role of SO_4^{2-} concentration driving the ANC decline was especially prominent when drought conditions where preceding the episode. At wetter conditions BC dilution played a larger role in depressing ANC, whereas NO_3^- showed a more stochastic influence on the ANC decline during episodes.

5 Discussion

Generally most surface waters in Sweden have shown a significant decline in stream water SO_4^{2-} concentrations, associated with the long-term decline in anthropogenic acid deposition, during the last decades (Fölster et al., 2003; Fölster and Wilander, 2002). However, these reductions in stream water SO_4^{2-} concentrations are often offset during high runoff by pulses of SO_4^{2-} from episodically activated flow pathways. Such offsets are especially pronounced during high sea-salt episodes and by preced-

ing drought conditions, which cause transient increases in anthropogenically derived H^+ and labile inorganic aluminum (Al_i) concentrations, with associated effects on the stream water ANC and pH.

Deposition of marine base cations can cause transient sea-salt related acidification episodes (Heath et al., 1992). Such episodes have been reported to cause severe fish kills in coastal rivers (Hindar et al., 1994). The clear difference in recovery of $\Delta ANC_{(poll)}$ found in this study between inland and coastal streams (with low Cl^- and high Cl^- concentrations, respectively) in southern Sweden indicates that sea-salt deposition has an influence not only on the effects of individual episodes, but also on the cumulative effects of episodic acidification in the longer-term. Sea-salt deposition is generally regarded as being highly stochastic, primarily occurring in short, intense events that cause transient, episodic declines in both and pH and ANC. However, the deposition of marine ions in coastal sites can also be described as a continuum of high sea-salt deposition that continuously affect soil and stream water chemistry in some regions (Evans et al., 2001). This suggests that sea-salt does not solely have transient, short-term influences, but could also have more long-term effects on surface water chemistry due to the continuous addition of marine base cations in some coastal regions.

The main influence of sea-salt on stream water ANC is due to the exchange of marine base cations, primarily sodium (Na^+), with adsorbed acid cations, hydrogen (H^+) and labile inorganic aluminum (Al_i), in the soil. Hence, continuous low doses of marine base cations, spiked with occasional high doses, could retard the episodic recovery. Sea-salt induced hydrochemical episodes have also been linked to decadal cycles of storm intensities driven by the North Atlantic Oscillation (NAO) (Hindar et al., 2004). This pattern of short-term variability in sea-salt deposition superimposed on more long-term cycles makes it difficult to disentangle trends in episodic response from natural variability. Indeed, the strong but intermittent marine influence in many coastal regions could explain why coastal catchments with relatively high stream water Cl^- concentrations are not recovering to the same degree as streams further inland.

The strong correlation between episodic responses and antecedent runoff (which

may be considered a surrogate for soil wetness) suggests that re-oxidation of sulfur in catchment soils is an important factor affecting hydrochemical responses during episodes. Reports from acidified regions in both Europe and North America have shown that re-oxidation of previously water-logged organic soil leads to pulses of acidic, SO_4^{2-}-rich water that may have a dramatic influence on stream ANC and pH during episodes (Schiff et al., 2005; Laudon et al., 2004). The strong correlation between $\Delta ANC_{(poll)}$ and antecedent discharge found for most of the streams included in this study also suggests that the largest anthropogenic component of the episodic acidification is associated with preceding drought conditions. These results have important implications for predictions of acidification recovery in the future, especially in regions where climate scenarios forecast that conditions are likely to become warmer and drier.

The rapid release of sulfate associated with drought is clearly not primarily caused by the most recent deposition of atmospheric sulfur. Recent trend analyses in Canada have demonstrated that long-term or multi-season drought-induced SO_4 mobilization retards general recovery from acidification (Eimers et al., 2004b; Jeffries et al., 2002). Hence, a possible explanation for the strong correlation between low antecedent runoff and the anthropogenically driven $\Delta ANC_{(poll)}$ found in this study is that a temporary lowering of the ground water level can result in a transformation of immobile sulfides to readily mobile sulfates that can be washed out during subsequent hydrological episodes. In support of this hypothesis, it has been found that mineralization of organic sulfur compounds in organic soils can be an important mechanism in generating sulfate-rich pulses which, temporarily at least, transform some catchments from sinks to sources of stream water sulfate (Alewell et al., 1999). In a recent study by Laudon et al. (2004) in central Canada the areal coverage of wetlands also showed to be a good predictor of the size of the anthropogenic acidity pulse following drought. However, no information of the amount of organic soils or wetland coverage is available for the streams reported on here.

In many of the streams included in this study, especially those in the inland sites, the negative effects of episodic acidification events on ANC are correlated with stream

water sulfate concentrations in the region (Fölster et al., 2003; Fölster and Wilander, 2002), indicating that the magnitude of sulfate pulses during droughts depend on the size and lability of the sulfur pools remaining in the catchments' soils. This suggests that the magnitude of drought-induced sulfate pulses in the future will primarily be determined by the source depletion rate together with the rate of sulfate pool reloading by future deposition. Therefore, despite a likely continuation of emission reductions in Europe drought-induced sulfate episodes may continue to cause extreme values of $\Delta ANC_{(poll)}$ in some streams in the future.

Regional climate models predict that further increases in temperature will occur in Sweden during the coming decades, accompanied by reductions in summer precipitation and more frequent storms during the fall and winter in large areas of the country (Kjellström, 2004). If these predictions are realized, the effects of episodic acidification in many Swedish streams may be prolonged and aggravated by increases in the frequency and intensity of droughts and sea-salt episodes.

In summary, the anthropogenic contribution to the declines in ANC observed during rain episodes in Sweden often follow periods of drought. This phenomenon is especially prominent in southern and central Sweden; regions that have been subject to high levels of acid deposition historically. However, these streams are generally found in inland regions, where the long-term effects of the decline in anthropogenic acidification are ameliorating the effects. In coastal areas, high deposition of sea-salt appears to be retarding the episodic recovery in many streams.

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Table 1. Summary of catchment characteristics.

Stream	Year	Catchment size (ha)	N Episodes	Deposition (Kg S ha^{-1} yr^{-1})	$\Delta ANC_{(poll)}$ vs Q (p-value)	$\Delta ANC_{(poll)}$ vs year (p-value)
Southern Sweden						
G1 (4)	1991–2001	275	13	5–7	0.001	0.04
G2 (4)	1991–2001	125	13	5–7	0.04	0.05
G2 (4R)	1991–2001	179	14	5–7	0.01	0.04
K2 (4)	1991–2001	157	11	5–7	0.02	N.S.
L1 (4)	1990–2000	41	12	8–9	0.02	0.05
L2 (4)	1990–2000	92	11	5–7	N.S.	0.03
O2 (4)	1990–2000	16	10	5–7	N.S.	N.S.
N1 (4)	1990–1999	12	10	10–15	0.0007	N.S.
P1 (4)	1991–2000	14	16	10–15	0.0001	N.S.
P2 (4)	1991–2001	20	16	7–9	N.S.	0.05
P3 (4A)	1991–2000	2.2	10	10–15	0.002	0.05
P3 (4B)	1991–2000	4.0	11	10–15	0.0008	0.02
R2 (4)	1991–2000	32	12	5–7	N.S.	0.03
Berg (Pipbäcken N)	1986–1995	90	8	10–15	N.S.	N.S.
Berg (Pipbäcken Ö)	1986–1995	73	13	10–15	0.04	N.S.
Tostarp	1985–2000	170	13	10–15	0.02	N.S.
Central Sweden						
Tresticklan	1985–2002	140	25	3–5	0.002	N.S.
Tiveden (Bråtäng)	1985–2002	750	23	3–5	0.01	0.02
Tiveden (Lomma N)	1985–2002	100	28	3-5	0.03	N.S.
Tiveden (Lomma Ö)	1985–1996	30	13	3-5	0.08	N.S.
Northern Sweden						
Tandövalen	1986–2000	580	17	2–3	N.S.	N.S.
Stormyran	1986–2002	320	13	2-3	0.03	N.S.
Sandnäset	1985–2002	50	10	1-2	N.S.	N.S.
Ammarnäs	1985–2002	220	9	1-2	N.S.	N.S.
Reivo	1985–2002	1090	11	1-2	N.S.	N.S.

Table 2. Summary of average stream chemistry.

Stream	pH	SO4 μeq/l	Cl μeq/l	NO3 μeq/l	Ca μeq/l	Mg μeq/l	Na μeq/l	K μeq/l
Southern Sweden								
G1 (4)	4.99	170	169	1	151	101	200	10
G2 (4)	4.70	175	176	0	166	106	189	7
G2 (4R)	4.48	176	179	1	103	88	196	9
K2 (4)	4.44	354	205	12	272	124	246	23
L1 (4)	4.74	320	346	7	202	155	385	15
L2 (4)	4.32	350	264	5	169	105	271	7
O2 (4)	4.35	157	302	3	60	77	295	8
N1 (4)	5.18	214	312	11	181	128	286	13
P1 (4)	4.99	166	275	4	122	73	266	7
P2 (4)	4.99	163	202	2	113	80	210	7
P3 (4A)	4.61	229	146	41	88	62	123	28
P3 (4B)	4.73	191	167	25	158	62	141	24
R2 (4)	5.40	182	208	2	269	101	225	11
Berg (Pipbäcken N)	4.58	158	294	1	87	98	274	8
Berg (Pipbäcken Ö)	4.42	132	286	1	67	83	259	8
Tostarp	6.00	374	295	14	352	213	322	17
Central Sweden								
Tresticklan	4.44	89	161	1	50	45	163	9
Tiveden (Bråtäng)	4.60	124	96	1	90	51	117	9
Tiveden (Lomma N)	4.30	124	89	0	56	41	111	7
Tiveden (Lomma Ö)	4.28	156	98	1	69	50	118	7
Northern Sweden								
Tandövalen	4.67	52	18	1	28	15	39	4
Stormyran	6.31	36	21	2	120	116	48	7
Sandnäset	6.64	293	81	2	175	53	83	9
Ammarnäs	6.92	49	42	1	284	67	58	25
Reivo	6.78	29	14	2	112	34	58	8

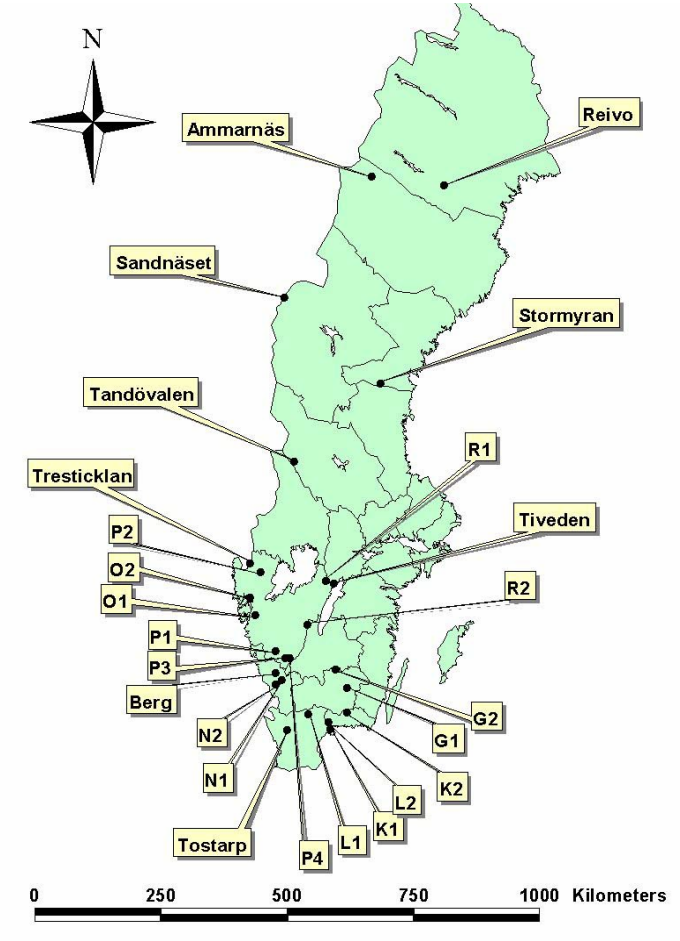

Fig. 1. Map showing the locations of the studied streams in Sweden.

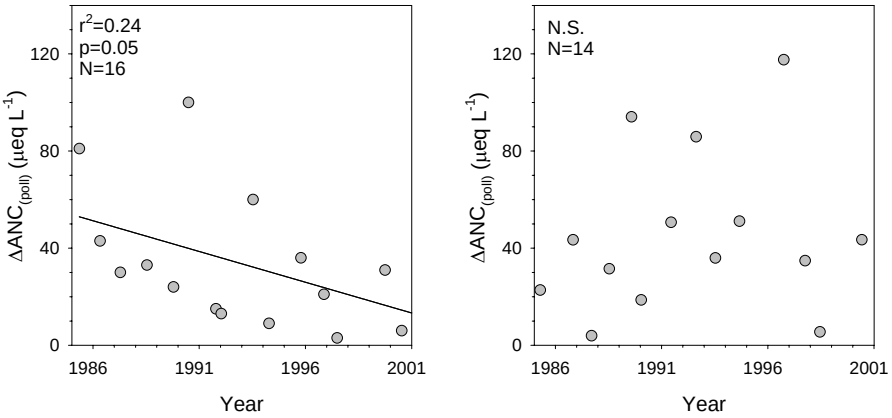

Fig. 2. Trend in anthropogenic response $\Delta ANC_{(poll)}$ during episodes in one inland stream (Bråtäng) with declining $\Delta ANC_{(poll)}$ (left) and one coastal stream (Tostarp) with no trend in $ANC_{(poll)}$ over time (right).

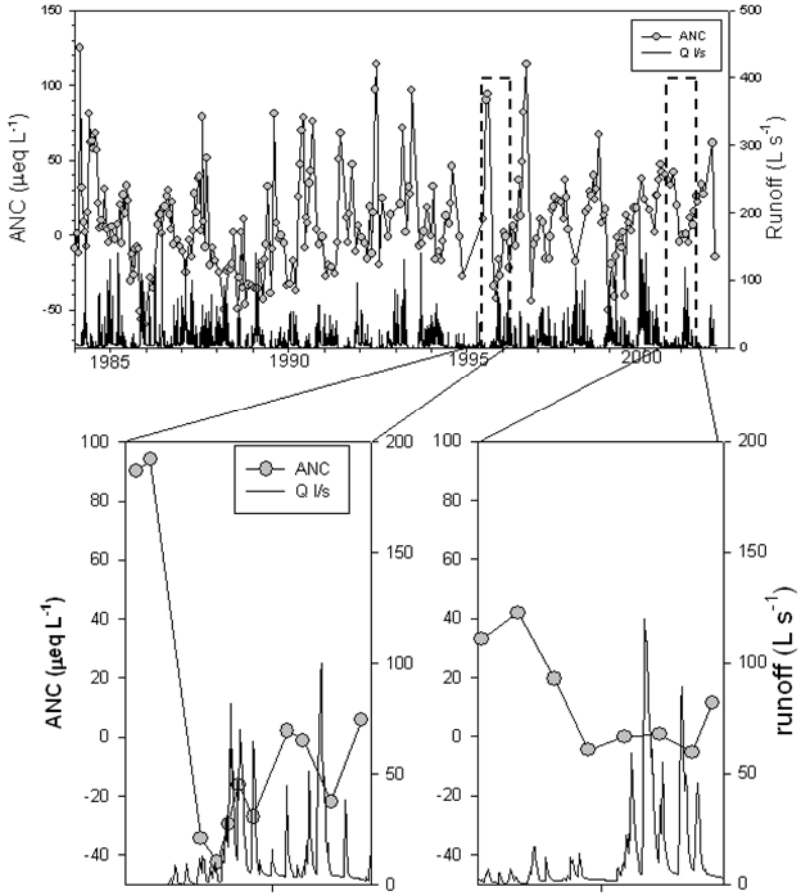

Fig. 3a. Time series of ANC variability from 1985–2002 in Tresticlan (above) with examples of episodic ANC response with dry antecedent conditions (below left) and wet antecedent conditions (below right).

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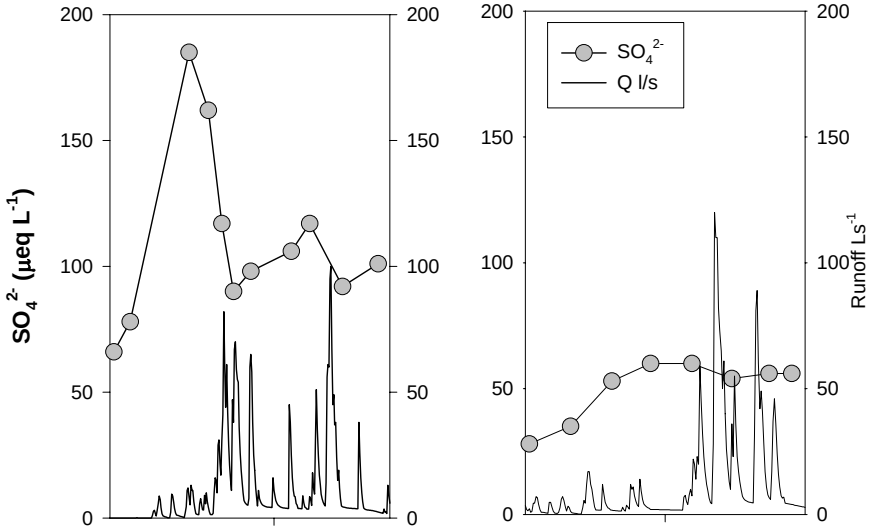

Fig. 3b. The accompanied SO4 response to the dry antecedent conditions (left) and wet antecedent conditions (right).

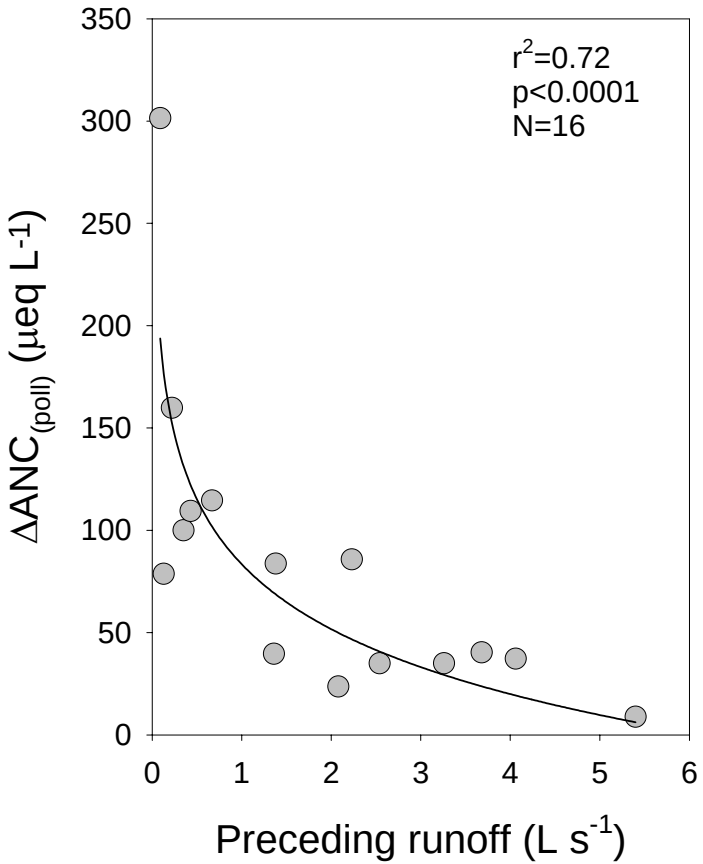

Fig. 4. Correlation between antecedent runoff and anthropogenic response ($\Delta ANC_{(poll)}$) during episodes in one of the study streams (P1 (4)). The remaining p-values of the correlation are given in Table 1.