

A Novel Environmental Quality Criterion for Acidification in Swedish Lakes – An Application of Studies on the Relationship Between Biota and Water Chemistry

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Received: 12 June 2005 / Accepted: 3 April 2006 / Published online: 27 January 2007
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Abstract The recovery from acidification has led to the demand for more precise criteria for classification of acidification. The Swedish Environmental Protection Agency has revised Sweden's Ecological Quality Criteria for acidification to improve the correlation between the chemical acidification criteria and bio-

logical effects. This paper summarises the most relevant findings from several of the studies commissioned for this revision. The studies included data on water chemistry in 74 reference lakes in southern Sweden with data on fish in 61 of the lakes, as well as data on littoral fauna in 48 lakes. We found that the acidity variable most strongly correlated to the biota was the median pH from the current year. Our results probably do not reflect the mechanisms behind the negative effects of acidity on the biota, but are fully relevant for evaluation of monitoring data. The biogeochemical models used for predicting acidification reference conditions generate a pre-industrial buffering capacity. In order to get an ecologically more relevant criteria for acidification based on pH, we transferred the estimated change in buffering capacity into a corresponding change in pH. A change of 0.4 units was defined as the threshold for acidification. With this criterion a considerably lower number of Swedish lakes were classified as acidified when compared with the present Ecological Quality Criteria.

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Keywords fish · monitoring · littoral fauna ·
water chemistry

1 Introduction

In Sweden, a set of official Environmental Quality Criteria for surface waters (EQC) have been used for

evaluation of monitoring data since 1990. In the EQC, anthropogenic impact is assessed using the ratio between an observed value and a modelled value of pre-industrial reference conditions (Swedish Environmental Protection Agency, 2000). This ratio is referred to as an Ecological Quality Ratio, EQR. As acid deposition declines, the demand for accuracy in the criteria for classification of acidification has increased. This is because as surface waters recover and approach pre-industrial reference condition chemistry, we need to know whether acidification is still an environmental problem of a magnitude that motivates further expensive actions to reduce emissions. When acidification was higher, it was not as important to know exactly what degree of acidification existed.

Another reason for the EQC revision is that implementation of the EU Water Framework Directive calls for more ecological relevance in the application of chemical EQC for water chemistry. In Sweden, where 20 million Euros are spent annually to mitigate acidification by liming, it is also important to assess when liming can be reduced, without risk of ecological damage from reacidification. In response to these demands, the Swedish Environmental Protection Agency (SEPA) initiated a number of research projects to give a basis for new EQC for acidification with a better correlation of the chemical acidification criteria to biological effects than the present EQC.

In the current EQC for acidification, anthropogenic impact is measured as a decrease in alkalinity (Alk), and the EQR is calculated as Alk/Alk_0 , where Alk_0 is a reference value modelled with an F-factor model proposed by Bernes (1991). When the EQR is <0.75 , the water is classified as acidified. The EQC for acidification has been disputed for two reasons. Firstly, the correlation of the ratio Alk/Alk_0 to biological effects is poor. In very alkaline waters, the biological effects of an EQR of 0.75 is negligible. For weakly buffered waters, on the other hand, biological effects may occur at smaller changes in the alkalinity. Secondly, the F-factor model has been shown to give systematic errors during recovery from acidification (Rapp, 1998). The present paper reports the work on finding an ecologically relevant criterion for acidification impact. The work with improved prediction of reference values will be reported elsewhere.

An alternative to an EQR threshold for anthropogenic impact is to use critical values of an acidity parameter. In calculations of Critical Loads for acid

deposition, for example, a critical value of Acid Neutralising Capacity (ANC), $\text{ANC}_{\text{limit}}$ of 20 $\mu\text{eq/l}$ is used (Henriksen, Kämäri, Posch, & Wilander, 1992; Lien, Raddum, Fjellheim, & Henriksen, 1996). The $\text{ANC}_{\text{limit}}$ was based on studies of relationships between biology and water chemistry in Norwegian lakes and streams. However, these waters are less humic than many of those in Sweden. The maximum concentration of Total Organic Carbon (TOC) in Lien's et al. (1996) study of Norwegian waters was less than 4 mg/l, while the median concentration of TOC in Swedish lakes was 9.8 mg/l (Wilander, Johnson, & Goedkoop, 2003). It has thus been questioned whether an $\text{ANC}_{\text{limit}}$ of 20 $\mu\text{eq/l}$ is relevant as a threshold for biological damage in Swedish waters. In an initial study on the relationship between presence of roach and acidity in Swedish lakes, an $\text{ANC}_{\text{limit}}$ several times higher was suggested (Andersson, Appelberg, & Wilander, 2001). In this study the presence of roach was more closely correlated to pH than to either ANC or Alk. The appropriateness of ANC was also questioned by Lydersen, Larssen, and Fjeld (2004) who suggested a modified ANC where a fraction of the organic anions were regarded as strong acids.

It is well established that fish toxicity in acidic systems can be related to both low pH and elevated inorganic aluminium, Al (e.g. Cronan & Schofield, 1979). Mechanisms for aluminium toxicity have been proposed (Exley, Chappell, & Birchall, 1991). Other indicators such as ANC/H^+ and Ca/Al have also been found to give a good correlation to fish mortality (Laudon, Poleo, Vollestad, & Bishop, 2005).

This paper summarises the most relevant findings from the studies initiated by SEPA where different acidity indicators were evaluated with respect to the relevance for littoral fauna and fish in lakes (Cory & Andrén, 2004; Holmgren & Buffam, 2005; Johnson, Goedkoop, & Wilander, 2004). Based on these results, we suggest a new criterion of acidification impact for the EQC related to changes in pH.

2 Materials and Methods

The study included 74 lakes which are part of national and regional monitoring programs. They are relatively small, with forest dominated catchments and they are not influenced by point source pollution. The study

lakes are representative of the range of lakes in Sweden with the exception that eutrophic and dystrophic lakes are underrepresented (Johnson, 1999). In our study we restricted the data to lakes in southern Sweden (Fig. 1). The reason for this was that the statistical analysis was compromised by a number of lakes in northern Sweden that lacked fish due to reasons other than acidity. This restriction is also relevant for our study since lake acidification is predominantly a problem in southern Sweden.

Littoral fauna samples were collected in 48 of the 74 study lakes. The samples were taken in autumn from stony habitats using standardized kick-sampling with a handnet of mesh size 0.5 mm. Organisms were identified to the lowest taxonomic unit possible, generally to the species level. The littoral fauna was represented both as the first axis of a Correspondence analysis (CA) and by an acidity index (Swedish Environmental Protection Agency, 2000).

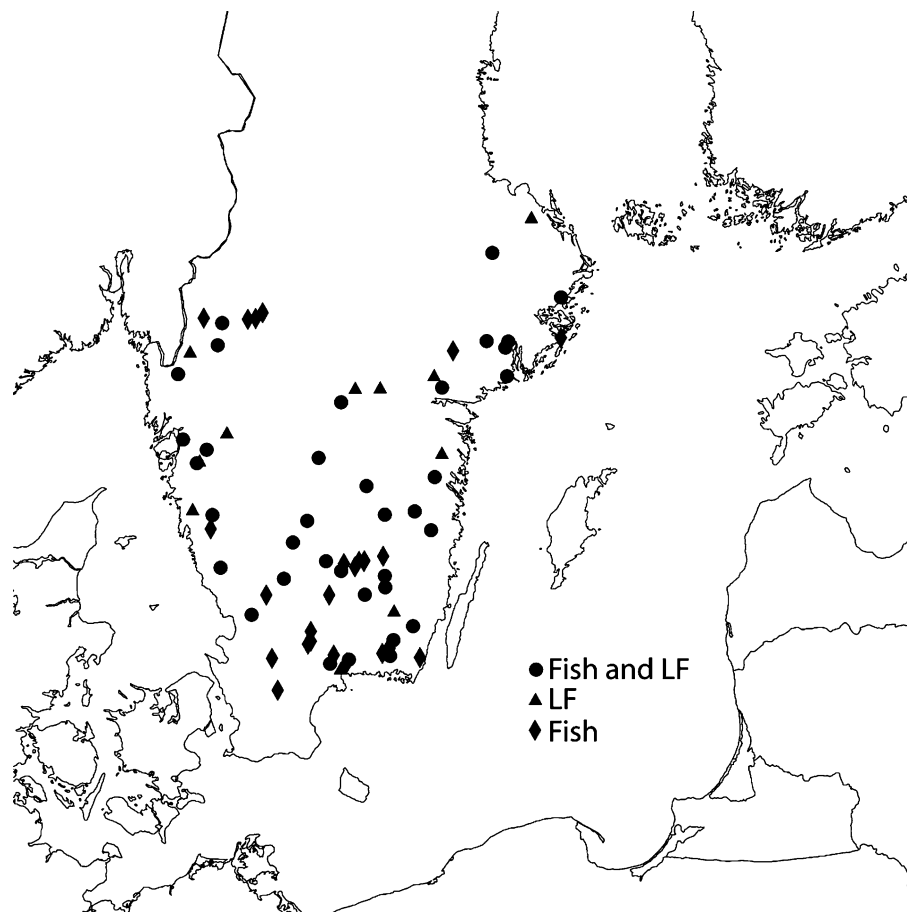
Fish were sampled in 64 of the study lakes with multi-mesh gillnets following standard protocols.

Fish were represented as presence/absence of acid sensitive species or size classes (Holmgren & Buffam, 2005). In southern Sweden, presence of small roach (<100 mm) is most often a good indicator of acidification.

Lake water chemistry was sampled at least four times a year. All water chemistry determinations were made according to ISO standards. The method used for alkalinity (Alk) in the Swedish monitoring programs, (ISO 9963-2) includes a titration down to pH 5.6 while the sample is purged with N₂ to remove CO₂. The method gives an alkalinity close to the carbonate alkalinity since only a small amount of organic acids are titrated at such a high titration end point. In samples where pH was less than 5.6, the acidity was measured by titration with a base up to the same pH.

An alternative estimate of buffering capacity is ANC which is calculated as the difference between base cations (BC) and strong acid anions (SAA). A modified ANC (ANC_{mod}) was also calculated to

Fig. 1 Southern Sweden showing locations of the 74 lakes included in this study



account for the fact that up to ca 2/3 of the organic anions are strong acid anions, i.e. not buffering within the pH range of natural waters. This ANC_{mod} was defined as Eq. 1:

$$ANC_{mod} = \text{Alkalinity}(\text{meq/l}) + \beta\text{TOC}(\text{mg/l}) \quad (1)$$

with β -values between 0 and 6.3, where 6.3 is the charge density at pH 5.6 (Köhler, Laudon, Wilander, & Bishop, 2000). The different modified ANC-values correspond to fractions between 0 and c. 2/3 of the organic anions being strong acid anions.

Inorganic Aluminium, Al_i , is routinely determined within Swedish acidification and liming monitoring using the cation exchange method (Driscoll, 1984), as described in Andrén (1995). In the data used in this study, laboratory fractionation is not comprehensive. Instead we used Al_i modelled with the chemical equilibrium model WHAM (Tipping, Berggren, Mulder, & Woof, 1995), after calibration of the model to Swedish waters (Cory & Andrén, 2004).

Besides these common acidity indicators, a range of alternative chemical acidity indicators were also tested: ANC/H^+ , BC/SAA , Al^{3+} , $H^+ + Al^{3+}$ and Ca^{2+}/Al_i .

Calculation of pH from ANC and TOC was done using the charge balance Eq. 2:

$$ANC = (\text{OH}^- + \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{RCOO}^- - \text{H}^+ - n\text{Al}^{n+}) \quad (2)$$

HCO_3^- and CO_3^{2-} were calculated with the equilibrium equations for the carbonate system by setting the $p\text{CO}_2$ to four times the background partial pressure in the atmosphere. Organic acids, RCOO^- , were calculated using the triprotic model proposed by Köhler et al. (2000).

3 Results and Discussion

3.1 Selecting Acidity Indicator

For both littoral fauna and fish, pH was generally the most strongly correlated acidity variable. The correlation of Alk, and Al_i with the biota was either similar or weaker than for pH (Figs. 2 and 3). ANC was more poorly correlated to biota than Alk. The performance of ANC_{mod} was intermediate between

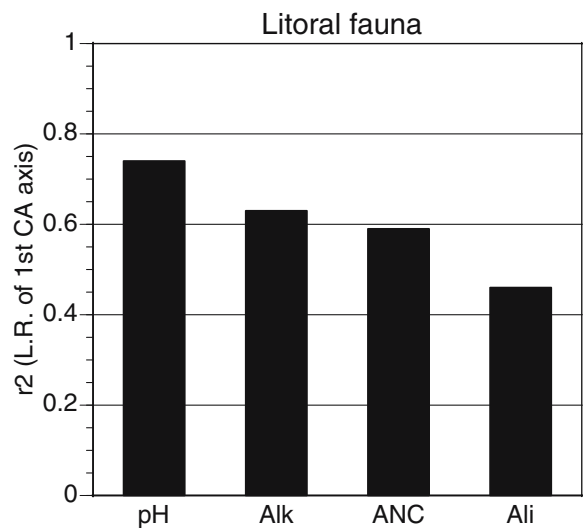


Fig. 2 The r^2 for linear regression of the first CA axis of littoral fauna against medians for pH, Alk, ANC and Al_i in lakes in southern Sweden

those of ANC and Alk (data not shown). Similar results were found for the less common acidity indicators. The results are in accordance with the study on roach by Andersson et al. (2001), although that study did not include Al_i . The toxicity of Al_i is well established. Therefore a better correlation with Al_i could have been expected, however, it is noted that most studies have concerned the effects of Al_i on salmonids in streams.

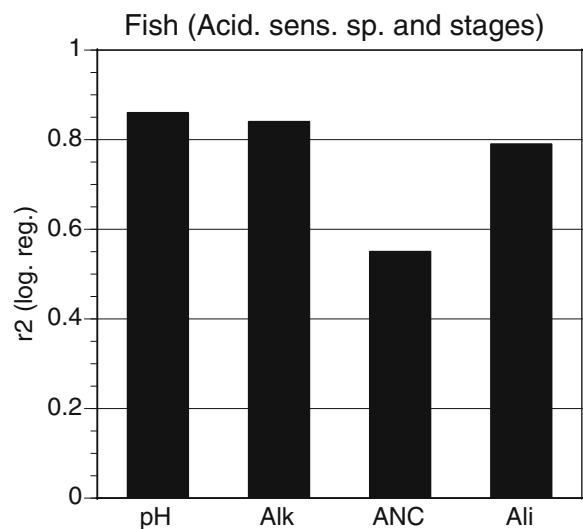


Fig. 3 Nagelkerke r^2 for logistic regression of presence/absence of acid sensitive stages of fish in relation to median pH, Alk, ANC and Al_i of lakes in southern Sweden

The relatively poor correlation of biota to Al_i in our studies could be due to the lack of sampling at critical periods such as spring snow melt. Additional errors could also be introduced by using modelled data on Al_i , instead of measured concentrations, as well as the analytical error of the Al_i values used to calibrate the model.

Lake water chemistry varies over time with more acid conditions after periods of high precipitation and more well buffered chemistry during dry periods. The magnitude of the variation and the response time to the change in hydrology depends on catchment area and lake turnover times. Several studies in streams have shown that the biota is controlled by the extreme acidic situations during high flow periods (Baker et al., 1996; Laudon et al., 2005). We expected to find a similar relationship in lakes, although with lower variability. This was, however, not the case in our data. The regressions between pH and biota did not improve significantly when the minimum pH was used instead of the median pH. A complicating factor is that the extreme situations during, for example, spring snow melt, are seldom represented by water samples taken only four times a year. The annual minimum values will then have a large variation and include both extreme and more stable conditions. To test this, water chemistry during years with unusually acid conditions were compared with observations of biota. Still, the extreme value was not better correlated to biota than the median value. One reason for this might be that the extreme situation does not always correspond to the season when biota are most sensitive to acidity (McCormick & Leino, 1999). For littoral fauna, there is also a possibility of recolonisation between the extreme situation and the autumn sampling. From our results, we cannot conclude whether the extreme or the average situation controls biota. Since the median chemistry and extreme chemistry are well correlated in many regards, it is expected that the median chemistry correlates to the biota even if the critical values would occur at peak flow. Due to the difficulty in consistently observing critical but transient situations during routine monitoring, the use of median values would seem preferable in the evaluation of monitoring data.

The current annual median gave generally as good or better correlations to both littoral fauna and fish as the 1-year lag or 3 year median. Our results contrast

partly with what we envisaged for the relationship between water chemistry and biota. We expected that extreme values should be better correlated to biota than the median or mean values, and that there would be a “memory” effect from earlier acid conditions captured by time-lags or long-term means of the data. For fish at least we considered Al to be a more important predictor than demonstrated in our results. For fish we also expected a better correlation of water chemistry with a lag time of 1 year than for the current year since the most sensitive stages occur at least 1 year before the fish are caught in the gill nets. Instead it was the median pH of the current year that was the best acidity variable for both fish and littoral fauna. The large variety of lake size, turnover time, and humic content in the data set may help explain this. Furthermore, the sampling frequency for many lakes was too low to cover the inter-annual variation. It is possible that with a more homogeneous dataset or with a higher sampling frequency, the findings would better reflect expected correlations. However, the data provide good coverage of the range of lakes and sampling frequency that EQC are meant to be applied to. Thus the results are fully relevant for our purpose.

3.2 How Shall Acidification be Assessed?

Our studies suggested that pH is the preferred acidity index. The use of measured pH is however problematic, since it is sensitive to changes in TOC and CO_2 pressure, pCO_2 . pH can also change during sample handling due to degassing of CO_2 , and the risk for analytical error is large in waters with low ionic strength. In this study, the high correlation of pH to biota was found for median values of at least four samples from 1 year where sample handling and determination were well standardised. This cannot be taken for granted in all monitoring programs. Also due to the labile nature of pH, most biogeochemical models calculate reference conditions in terms of buffering capacity.

Our solution to this problem is to translate the change in buffering capacity between the present and the predicted pre-industrial reference value, into a change in pH (ΔpH). In other words, present and pre-industrial pH values are calculated from the present and pre-industrial ANC values. This is done using chemical equilibrium equations and includes the

assumption that TOC has remained constant since pre-industrial conditions. The pCO_2 is also assumed to be constant over time and was set to four times the background value in air, which was the average pCO_2 in the lakes included in the study. In reality both TOC and pCO_2 are likely to have changed due to climate variability and changes in land use (Clair et al., 2002; Pastor et al., 2003). By fixing the TOC and pCO_2 we do not estimate the actual change in pH, but rather how much deposition of strong acids has depressed pH under the current climate and land use. In a recent paper, it was suggested that acidification might depress TOC concentrations (Evans, Monteith, & Cooper, 2005) which would give us an overestimation of the pH change caused by acid deposition. Until this effect has been quantified, however, we assume it to be negligible.

One source of error in the calculation of ΔpH is that Al was not included in the chemical equilibrium model. At low pH, when the concentration of cationic Al and its pH buffering can be substantial, the model will underestimate the pH. This is not seen as a problem for the application of the EQR, since it will give an overestimation of the ΔpH when cationic Al is present. The calculated ΔpH will then be an approximation of the increase in total acidity.

In the proposal for new EQC, a change in pH of 0.4 units was set as the limit for acidification. This corresponds approximately to a change of one unit in the biological acidification index used in the EQC for

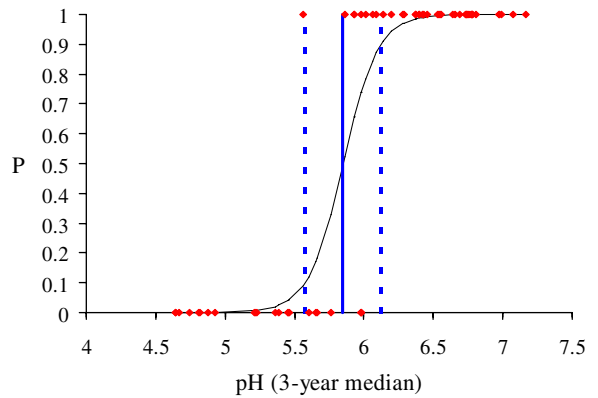


Fig. 5 Logistic regression of presence of acid sensitive species and stages of fish against pH of lakes in southern Sweden

littoral fauna (Fig. 4). The 0.4 unit pH decline is also slightly more than the difference between the 10 and 90% levels in the logistic regression of acid sensitive fish in southern Sweden (Fig. 5). Due to the logarithmic scale of pH, an absolute change is more appropriate than a pH ratio. A ΔpH of 0.4 is equal to a hydrogen ion ratio (H_0^+/H_t^+) of 0.398.

When we compare ΔpH as the criterion for acidification with the presently used ratio Alk/Alk_0 , we find that the former gives a lower number of acidified lakes in Sweden. In the national lake survey 2000 (Wilander et al., 2003), only 2.6% of 3,464 lakes were acidified, according to the criteria $\Delta pH > 0.4$. With the criteria of $Alk/Alk_0 < 0.75$, 8.9% were considered

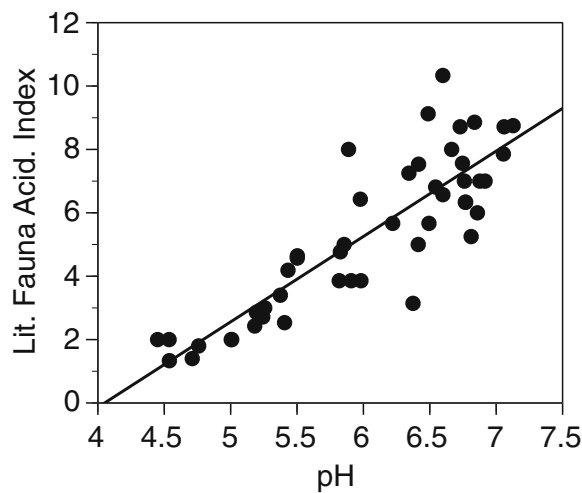


Fig. 4 Medin’s acidity index against mean pH for lakes in southern Sweden

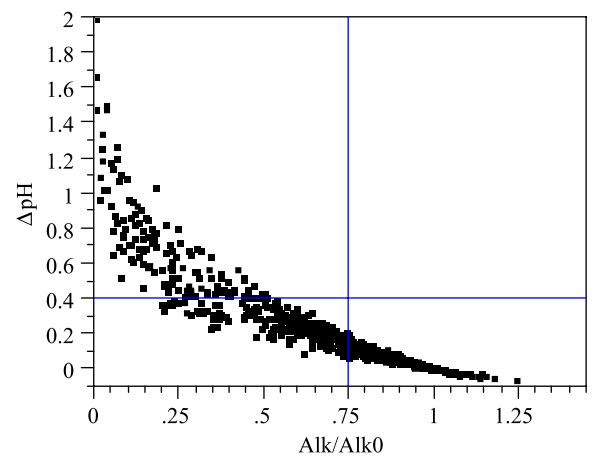


Fig. 6 Comparison of two criteria for acidification for the national lake survey 2000 in Sweden. For ΔpH , the limit for acidification was set to 0.4, and for Alk/Alk_0 , the limit was 0.75

acidified. In both cases the reference value was calculated with the F-factor model used in the Swedish EQC. A comparison of the two criteria shows that there are a large number of lakes in the lake survey that were classified as acidified with the present EQC, where the corresponding change in pH was too small to have had a significant effect on the biota (Fig. 6).

4 Conclusions

We found that median pH from the current year was the acidity variable most consistently and strongly correlated to the biota. Our results probably do not reflect the mechanisms behind the negative effects of acidity on the biota, where Al_i and extreme situations are likely to be more important. However, our results are fully relevant for evaluation of monitoring data where extreme situations are not likely to be sampled.

The biogeochemical models used for predicting acidification reference conditions generate a pre-industrial ANC. In order to obtain an ecologically relevant criteria for acidification, we transferred the estimated change in ANC into a corresponding change in pH, where a change of 0.4 units was defined as the limit for acidification. With this criterion a considerably lower number of Swedish lakes were classified as acidified compared to the present EQC.

Compared to the present Swedish EQC, the suggested new chemical criterion for acidification is better correlated to biological effects. Therefore it will be more reliable for setting targets for reductions in emissions and adapting the liming policy to the decreasing levels of acid deposition.

Acknowledgements This report is based on data from monitoring programs funded by the Swedish Environmental Protection Agency.

References

- Andersson, H. C., Appelberg, M., & Wilander, A. (2001). Gränsvärden för försurning ur svenska fiskars perspektiv. (Engl. summary: Critical chemical values based on Swedish condition). In: Sötvatten. Årsskrift för miljöövervakningen 2001. ISBN 91-620-5149-0, 24–27.
- Andrén, C. (1995). Aluminium speciation; effects of sample storage. *Water, Air and Soil Pollution*, 85, 811–816.
- Baker, J. P., VanSickle, J., Gagen, C. J., DeWalle, D. R., Sharpe, W. E., Carline, R. F., et al. (1996). Episodic acidification of small streams in the northeastern United States: Effects on fish populations. *Ecological Applications*, 6, 422–437.
- Bernes, C. (1991). Acidification and liming of Swedish freshwaters. ISBN 91-620-1109-X. Swedish Environmental Protection Agency, Solna.
- Clair, T. A., Ehrman, J. M., Ouellet, A. J., Brun, G., Lockerbie, D., & Ro, C. U. (2002). Changes in freshwater acidification trends in Canada's Atlantic Provinces: 1983–1997. *Water, Air and Soil Pollution*, 135, 335–354.
- Cory, N., & Andrén, C. (2004). *Modelling of aluminium speciation as a complement to laboratory-based analysis*. Uppsala, Dep. of Environ. Assess., Swedish University of Agricultural Sciences. Report 2004:12. ISSN 1403–977X.
- Cronan, C. S., & Schofield, C. L. (1979). Aluminium leaching response to acid precipitation: Effects on high-elevation watersheds in the northeast. *Science*, 204, 304–306.
- Driscoll, C. T. (1984). A procedure for the fractionation of aqueous aluminium in dilute acidic water. *International Journal of Environmental Analytical Chemistry*, 16, 267–284.
- Evans, C. D., Monteith, D. T., & Cooper, D. M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, 137(1), 55–71.
- Exley, C., Chappell, J. S., & Birchall, J. D. (1991). A mechanism for acute aluminum toxicity in fish. *Journal of Theoretical Biology*, 151, 417–428.
- Henriksen, A., Kämäri, J., Posch, M., & Wilander, A. (1992). Critical loads of acidity: Nordic surface water. *Ambio*, 21, 356–363.
- Holmgren, K., & Buffam, I. (2005). Critical values of different acidity indices – as shown by fish communities in Swedish lakes. *Verhandlungen der Internationalen Vereinigung für Theoretische und Angewandte Limnologie*, 29, 654–660.
- Johnson, R. K. (1999). Regional representativeness of Swedish reference lakes. *Environment and Man*, 23, 115–124.
- Johnson, R. K., Goedkoop, W., & Wilander, A. (2004). *Relationships between macroinvertebrate communities of stony littoral habitats and water chemistry variables indicative of acid-stress*. Report 2004:6, pp. 35, Dep. of Environ. Assess., Swedish Univ. of Agr. Sci.
- Köhler, S., Laudon, H., Wilander, A., & Bishop, K. (2000). Estimating organic acid dissociation in natural surface waters using total alkalinity and TOC. *Water Research*, 34, 1425–1434.
- Laudon, H., Poleo, A. B. S., Vollestad, L. A., & Bishop, K. (2005). Survival of brown trout during spring flood in DOC-rich streams in northern Sweden: the effect of present acid deposition and modelled pre-industrial water quality. *Environmental Pollution*, 135, 121–130.
- Lien, L., Raddum, G. G., Fjellheim, A., & Henriksen, A. (1996). A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. *Science of the Total Environment*, 177, 173.

- Lydersen, E., Larssen, T., & Fjeld, E. (2004). The influence of total organic carbon (TOC) on the relationship between acid neutralizing capacity (ANC) and fish status in Norwegian lakes. *Science of the Total Environment*, 326 (1–3), 63–69.
- McCormick, J. H., & Leino, R. L. (1999). Factors contributing to first-year recruitment failure of fishes in acidified waters with some implications for environmental research. *Transactions of the American Fisheries Society*, 128, 265–277.
- Pastor, J., Solin, J., Bridgham, S. D., Updegraff, K., Harth, C., Weishampel, P., et al. (2003). Global warming and the export of dissolved organic carbon from boreal peatlands. *Oikos*, 100, 380–386.
- Rapp, L. (1998). Critical loads for surface waters: Validation and challenges. Licentiate Thesis, pp. 23, Swedish University of Agricultural Sciences, Umeå.
- Swedish Environmental Protection Agency (2000). *Environmental quality criteria – lakes and watercourses*. Report 5050. ISBN 91-620-5050-8. Kalmar.
- Tipping, E., Berggren, D., Mulder, J., & Woof, C. (1995). Modeling the solid-solution distributions of protons, aluminum, base cations and humic substances in acid soils. *European Journal of Soil Science*, 46, 77–79.
- Wilander, A., Johnson, R. K., & Goedkoop, W. (2003). Riksinventering 2000, Institutionen för Miljöanalys, SLU. Rapport 2003:1. ISSN 1403-977X.