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Critical Load of Acidity to Surface Waters in South- central Ontario, Canada

I. Application of the Steady State
Water Chemistry (SSWC) Model

***Acid
Rain
Research***

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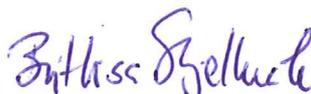
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Abstract

The Steady-State Water Chemistry Model was applied to lakes in 5 regions in Ontario, Canada. Critical loads and exceedances calculated for the regions indicate that the portion of the lakes with exceedances dropped from 65-70% 20 years ago to 8-18% in the late 1990's. Detailed long-term information collected for 8 lakes was used to assess a number of the assumptions in the model.

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Critical Load of Acidity to Surface Waters

in South-central Ontario, Canada

I. Application of the Steady State Water Chemistry (SSWC) Model

Preface

The concept of critical loads has been widely accepted in Europe as a basis for designing control strategies to reduce regional and transboundary air pollution. Until 1994 the international work focused on the development of methodologies and the collection of national data to produce European maps of critical sulphur deposition, used in the negotiations of the second Sulphur Protocol that was signed in Oslo, Norway in 1994. To prepare the scientific support for the negotiations of a revised protocol on the reduction of nitrogen emissions, a new methodology was developed to take into account multiple effects of multiple pollutants (sulphur and nitrogen). This methodology was used as a basis in the negotiations for the new multi-pollutant, multi-effect protocol signed in Gothenburg, Sweden, in December 1999.

NIVA has been active in developing and applying methodologies for calculating critical loads of acidity for surface waters. Therefore, NIVA was contacted by P. Dillon for assistance in estimating critical loads for lakes in Ontario, Canada. The Ontario studies are being conducted as part of an evaluation of the adequacy of existing sulphur emission control programmes in eastern North America. An assessment of the current status of lakes in acid-sensitive areas with respect to their critical loads will assist in determining whether additional reductions in sulphur emissions are warranted. This information will be used in the next national assessment and reporting process.

Oslo, September, 2001

Arne Henriksen

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Summary

The concept of critical loads has been widely accepted in Europe as a basis for designing control strategies to reduce regional and transboundary air pollution. The working definition of a critical load is “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” (Nilsson and Grennfelt 1988). Two models – one empirical and one process-oriented – are presently in use for calculating critical loads of acidifying deposition (S and N) for surface waters on a regional scale (Henriksen and Posch 2001). The Steady-State Water Chemistry (SSWC) model allows the calculation of critical loads of acidity and their *present* exceedances. The First-order Acidity Balance (FAB) model allows the simultaneous calculation of critical loads of acidifying S- and N-deposition and their exceedances. The work described here is part of a research programme initiated at Trent University, Ontario with the collaboration of the National Science and Engineering Research Council, the power-producing industry (Ontario Power Generation Inc.) and the Ontario Ministry of the Environment. One of the projects is designed to evaluate the critical sulphur and nitrogen loads to lakes in south-central Ontario using both steady-state and dynamic models, with the intent of determining whether emission reductions of the past 15 years are adequate. In this report, results obtained using the SSWC model are described. In addition to evaluating, in general, the current status of lakes in this part of Ontario, we have used intensive, detailed data sets collected for a small number of lakes over many years to evaluate several of the assumptions inherent in the SSWC model.

The sensitivity of freshwaters in Ontario to acid deposition is defined in general terms by their location relative to the boundary of Precambrian Shield. Those waters that are north of the southern boundary of the Shield are situated in a region of predominately silicate bedrock, which is overlain by thin glacial tills. The climate of the study area is north temperate, with long-term annual average precipitation ranging between about 80 and 110 cm, about one quarter to one third of which falls as snow. On the Shield, the land cover is largely mixed forest, with deciduous forests dominating where the soil is thicker, e.g. outwash plains, deeper glacial tills, and conifers dominating where the soils are thin. We have chosen for study lakes in 5 regions in south-central Ontario. These regions include the District of Muskoka, and the counties of Haliburton, Nipissing, and Parry Sound. Information was also gathered for a fifth set of lakes, the Southern lakes, which includes lakes along the southern boundary of the Shield where the geology is a mixture of carbonate and silicate bedrock. Single measurements for 1469 lakes in the 5 regions were used to calculate critical loads and their exceedances using S deposition data for the period 1977-1998. Sulphur deposition in the study area shows a clear downward trend over this time period, with the decrease of more than 50% in S deposition being consistent with decreases in S emissions in eastern Canada and the north-eastern U.S.A. Over the same time period, there has been no significant trend or change in N-deposition. As a result of the declining S deposition, the portion of lakes with critical load exceedances has dropped substantially, from 65-70% in the 4 sensitive regions in 1977 to 8-18% in the late 1990's.

In addition to the information collected on many lakes via chemical surveys, eight lakes have been sampled regularly since 1980. The critical sulphur load was exceeded for all 8 of these lakes until 1982-83, whereas none of them were exceeded in 1997-98. The most sensitive lakes, Plastic, Heney and Crosson, were exceeded until 1996-97. The two last years reported here had particularly low S deposition (see Table 8), and unless this continues, we expect improvements in water quality in the subsequent years may be somewhat less pronounced than indicated by the 1997-98 data. The intensive data were also used to demonstrate that a single sample taken shortly after spring circulation gives a reasonable estimate of the critical load for a lake and its catchment.

1. Introduction

a. Background

The concept of critical loads has been widely accepted in Europe as a basis for designing control strategies to reduce regional and transboundary air pollution. In 1990 the Executive Body of the UN/ECE Convention on Long-range Transboundary Air Pollution (LRTAP) established an International Collaborative Programme on Mapping Critical Levels and Loads under the Working Group on Effects to develop and agree upon methods for calculating and mapping critical loads. Critical loads data from individual countries are collated, mapped and reported by the Mapping Programme's Coordination Center for Effects (e.g., Posch et al. 1999).

The working definition of a critical load is "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt 1988). Thus, critical loads can be directly compared to deposition estimates; this makes them usable and useful in integrated assessment models, linking emission abatement strategies to the capacity of ecosystems to withstand and buffer the effects of acid deposition.

Until 1994 the international work focused on the development of methodologies and the collection of national data to produce European maps of critical sulphur deposition, used in the negotiations of the second Sulphur Protocol, signed in Oslo in 1994 (UN/ECE 1994). To prepare the scientific support for the negotiations of a revised protocol on the reduction of nitrogen emissions, a new methodology was developed to take into account multiple effects (i.e. acidification and eutrophication) of multiple pollutants (sulphur and nitrogen). Since both sulphur and nitrogen contribute to acidification, the critical loads of S- and N-acidity are interrelated and a single critical load for one pollutant cannot be defined without making assumptions about the other. This new methodology was used as a basis in the negotiations for the new multi-pollutant, multi-effect protocol signed in Gothenburg (Sweden) in December 1999 (UN/ECE 1999).

Two models – one empirical and one process-oriented – are presently in use for calculating critical loads of acidifying deposition (S and N) for surface waters (Henriksen and Posch 2001). The Steady-State Water Chemistry (SSWC) model allows the calculation of critical loads of acidity and their *present* exceedances. The First-order Acidity Balance (FAB) model allows the simultaneous calculation of critical loads of acidifying S- and N-deposition and their exceedances.

The Steady-State Water Chemistry (SSWC) model estimates the weathering rate from the present-day base cation flux and uses the so-called F-factor to account for the part of present base cation leaching due to ion exchange processes in the catchment soils. The buffer required to protect selected biota is represented by the acid neutralizing capacity (ANC_{limit}). The present value used in Norway for the ANC_{limit} is based on the response of fish (brown trout) to the ANC of the lake-water, and will, in general, be a function of catchment characteristics.

In the FAB model (Posch et al. 1997) critical loads of S- and N-acidity for freshwaters are derived in the same way as in the Simple Mass Balance (SMB) model, widely used for computing soil critical loads (UBA 1996, Posch and de Vries 1999). In addition to processes in the catchment soils, the FAB-model also takes into account the in-lake retention of N and S. The base cation and ANC components of the model are taken from the SSWC model.

The work described in this report is part of a research programme initiated at Trent University, Ontario with the collaboration of the National Science and Engineering Research Council, the power-producing industry (Ontario Power Generation Inc.) and the Ontario Ministry of the Environment. This research programme focuses on recovery of ecosystems following sulphur emission reductions, and in particular, on the interactions of acid deposition and climate phenomena, including long-term climate

change. One of the projects that have been undertaken is designed to evaluate the critical sulphur and nitrogen loads to lakes in south-central Ontario using both steady-state and dynamic models, with the intent of determining whether emission reductions of the past 15 years are adequate. NIVA was approached to assist in applying these critical load models for surface waters to lakes in this region of Ontario, Canada. In this report, results obtained using the SSWC model are described. In addition to evaluating, in general, the current status of lakes in this part of Ontario, we have used intensive, detailed data sets collected for a small number of lakes over many years to evaluate several of the assumptions inherent in the SSWC model.

b. Site description

The sensitivity of freshwaters in Ontario to acid deposition is defined in general terms by their location relative to the boundary of Precambrian Shield (Figure 1). Those waters that are north of the southern boundary of the Shield are situated in a region of predominately silicate bedrock, which is overlain by thin glacial tills. There are many localized exceptions, of course, but the bedrock and surficial geology of this region results in lakes and streams that contain soft waters (conductivity typically ranges between 15 and 40 uS) that are low in nutrients as well as major ions. Many contain appreciable levels of dissolved organic carbon (DOC) and organic anions often form a major component of the charge balance. Lakes on or below the Shield boundary typically contain water of high ionic strength because the southern area of the province is underlain by sedimentary bedrock (largely limestone) which is overlain by thick soil high in carbonate content. The south-eastern portion of the province has mixed geology with great variability between lakes in terms of water chemistry.



Figure 1. Map of Ontario with the Precambrian Shield shaded. Areas to the south (the St. Lawrence Lowlands) and the north (the Hudson Bay Lowlands) have calcareous bedrock and soils, and lakes and streams in these regions are generally insensitive to acid deposition.

The climate of the study area is north temperate, with long-term average precipitation ranging between about 80 and 110 cm, about one quarter to one third of which falls as snow. The mean monthly temperature range between -5 and -10°C in the coldest winter months, and 22 to 25°C in the summer. About half of the precipitation produces runoff, while about half is evapotranspired.

On the Shield, the land cover is largely mixed forest, with deciduous forests dominating where the soil is thicker, e.g. outwash plains, deeper glacial tills, and conifers dominating where the soils are thin. Small wetlands are ubiquitous throughout the entire region, covering an estimated 10% of the total area. It is extremely unusual to find a catchment with no wetland within its boundary. The southernmost and eastern regions where the soil is thick and contains carbonates have an appreciable portion of their land area used for agriculture, typically forage, grain or row crops, and the raising of livestock.

We have chosen for study the lakes in 5 regions in south-central Ontario. Our expectation is that the majority of the lakes in 4 of the regions are sensitive to the deposition of strong acids because of their geological setting. These regions include the District of Muskoka, and the counties of Haliburton, Nipissing, and Parry Sound (Figure 2). We have also gathered information for a fifth set of lakes, the Southern lakes, which includes lakes along the southern boundary of the Shield where the geology is a mixture of carbonate and silicate. We expect that the lakes in this set will be much less sensitive to acid deposition.

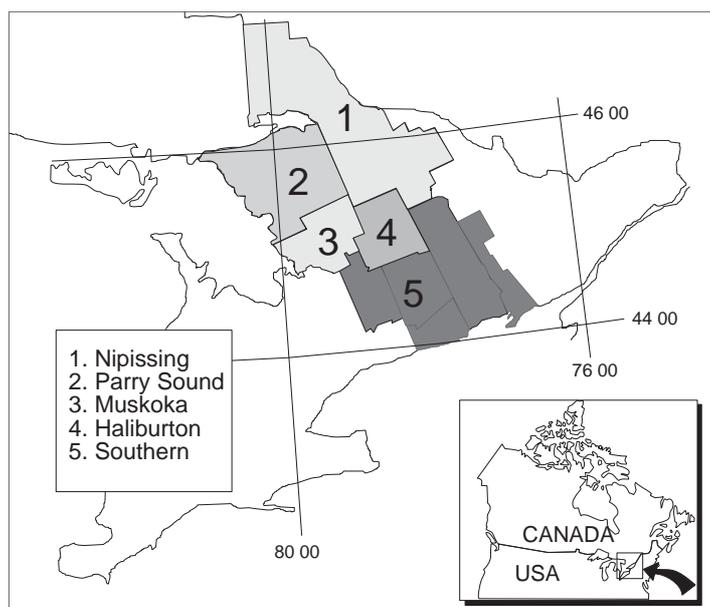


Figure 2. Location of study area, and of the 5 lake regions.

c. Data collection

To calculate critical loads using the SSWC model, we require base cation (Ca, Mg, Na and K) and SO_4 measurements for each lake as a minimum, with Cl data being a useful addition. Although the study area is remote from influences of marine sea salts, road salt (NaCl) is used as a de-icing agent on paved roads in winter; as this may result in excess Na levels in some lakes. Cl concentration is a useful means of correcting for this phenomenon.

All available chemical data were gathered for lakes in each of the 5 regions. These data had been collected during the course of a number of different research projects and lake surveys over the period 1981-95, with most of the data collected between 1983 and 1988. In cases where data from more than one year were available for any lake, we used the average value for that lake. Preference was given to integrated, whole-lake samples when available. The exception was a set of 8 lakes that have been studied extensively for over 20 years (Dillon and Molot 1997); for these lakes, data collected throughout the year as whole-lake, morphometrically weighted samples (Dillon et al. 1997) were available for each year. Depending on the year, between 8 and 26 samples were collected per lake. We used these 8 lakes to evaluate long-term trends in estimates of critical loads by calculating critical loads based on data from each individual year. We also used these data to determine whether a single sample collected at spring overturn provided adequate information for estimating critical loads by comparing results based on single samples with results based on annual average chemistry.

There was some variation in the within-year timing of the sampling of the surveyed lakes. Most lakes were sampled during spring overturn (April, May), although several surveys were conducted during fall overturn. Data collected during the period of thermal stratification in the summer or during the winter under ice cover were used only when no other data were available for that lake.

All chemical analyses were carried out at Ontario Ministry of the Environment laboratories, either at Dorset or Toronto. Analytical methods were identical at the two sites, and remained consistent for the duration of these studies. Earlier data using different methods, e.g. colorimetric measurement of sulphate, were excluded from this analysis because of systematic differences in results. Methods are described in detail in Ontario Ministry of the Environment (1993).

In addition to chemical data, the SSWC-model requires measured or estimated runoff within each lake's catchment. We calculated runoff coefficients (m/yr) by interpolating a runoff map of Ontario (provided by Cumming Cockburn Ltd.) that was created using measured 30-year average runoff at all long-term hydrologic gauging stations throughout the province.

2. Data requirements

For the calculation of the critical for a lake using the SSWC model, the following data are required (see Appendix A):

- *base cation (Ca, Mg, Na and K) concentrations.*
- *chloride (Cl) and sulphate (SO₄) concentrations.*
- *yearly average runoff from the catchment.*

On the basis of these data, the required variables in the critical load equations (see Appendix A) can be calculated.

The Ontario data have been evaluated with respect to certain assumptions made in formulating the model.

a. Sea salt correction

The SSWC model assumes that all chloride in runoff originates from sea salts transported and deposited with the precipitation. The chloride concentrations are then used to correct the base cation and sulphate concentrations to remove the sea salt influence on lake chemistry. As the study area is located over two thousand km from the sea, the sea salt influence must be very low. A significant number of lakes have, however, rather high concentrations of Na and Cl; however, this is due to extensive road salting of paved roads during the winter months. In more remote areas, the Cl concentrations are low, averaging about 10 $\mu\text{eq/l}$. The Na in these lakes is also low, with an average value of about 20 $\mu\text{eq/l}$. Generally it is assumed that only the non-marine sodium concentration results from weathering. Thus, the sea salt correction was not used on these data, and the contribution of Na to the base cation concentrations is considered either negligible, or in those cases where road salt use is apparent, is not considered in the model calculations. Generally potassium (K) is not considered as an important weathering product, since it participates in the nutrient cycle. In any case, K levels in lakes in the study area are very low.

b. Background sulphate

The sulphate concentration in a lake reflects the magnitude of the anthropogenic sulphur deposition. In addition it is assumed that the pre-acidification sulphate concentration $[\text{SO}_4^*]_0$ is assumed to consist of an atmospheric pre-acidification contribution and a geologic contribution proportional to the concentration of base cations (Brakke et al. 1989; see also Appendix A). The equation used for Norway is:

$$[\text{SO}_4^*]_0 = 8 + 0.16 [\text{BC}^*]_t \quad (1)$$

We have considered this equation to be applicable to the Ontario study lakes.

c. The F-factor

This is defined as the ratio of change in non-marine base cation concentrations to changes in strong acid anion concentrations (Henriksen 1984, Brakke et al. 1990; see also Appendix A). If $F=1$, all incoming protons are neutralized in the catchment (only soil acidification); if $F=0$, none of the incoming protons are neutralized in the catchment (only water acidification).

The presently used formulation is:

$$F = \sin((\pi/2)Q[\text{BC}^*]_t/S) \quad (2)$$

where Q is the annual runoff (m yr^{-1}) and S is the base cation flux at which $F=1$. For Norway S has been estimated to be $400 \text{ meq m}^{-2} \text{ yr}^{-1}$. If $Q[\text{BC}^*]_t > S$, F is set to 1.

We consider the F function given above to be valid for the Ontario lakes.

d. Weathering

Chemical weathering releases base cations from minerals to solution, to an exchange site, or to the biota. Chemical weathering comprises a major process by which acids are neutralised in the terrestrial environment. A good estimate of the present-day weathering rate is necessary to determine the long-term resistance of ecosystems to soil acidification in areas exposed to acid deposition, that is, to calculate the critical load.

The total net flux of base cations from the catchment is the sum of weathering plus cations from cation exchange minus inputs from atmospheric deposition. The partitioning between weathering and cation exchange can be estimated using the F -factor (defined above). This estimate assumes that the catchment soils were at steady-state prior to the onset of acid deposition, i.e. that the biomass of the

terrestrial biota is at steady-state and that the cation exchange capacity and base saturation of the soil/till are not changing. The weathering rate for a site can thus be calculated with yearly flow-weighted average chemistry and yearly average runoff (see Appendix A). Such values are not generally available for large numbers of lakes. Weathering rates can, however, be estimated on the basis of a single sample considered representative of yearly flow-weighted averages. A sample collected shortly after the fall circulation of a lake has been claimed to fulfil this purpose (Henriksen et al. 1992). Henriksen and Posch (2001) checked this claim by comparing weathering rates calculated from yearly flow-weighted average concentrations with weathering rates calculated from a single fall value for sites for which long-term data series are available. Such data were available from the calibrated catchments in the Norwegian monitoring program for long-range transported air pollutants (SFT 1999). Results for seven catchments indicated clearly that the single fall value is representative of the annual average chemistry.

For Ontario, samples have been collected during the spring circulation period more frequently than during the fall circulation period. The yearly weighed average value could not be calculated for these lakes, since fall samples were not collected with the same regularity as for the remainder of the year. Thus, we have explored the spring data (collected shortly after spring overturn) for the Ontario lakes with an estimate of the yearly average value for all samples.

e. ANC-limit

Critical loads of acidity for surface waters are based on the principle that the acid load should not exceed the non-marine, non-anthropogenic base cation input and sources and sinks in the catchment minus a buffer to protect selected biota from being damaged:

$$CL(A) = BC_w + BC_{dep}^* - BC_u - ANC_{limit} \quad (3)$$

where $CL(A)$ is the critical load of acidity, BC_w is the average weathering flux, BC_{dep}^* is the non-marine, non-anthropogenic deposition of base cations, BC_u the net long-term average uptake of base cations in the biomass (i.e. the annual average removal of base cations due to harvesting), and ANC_{limit} the lowest ANC-flux that does not damage selected biota. Lien et al. (1996) analyzed the status of fish and invertebrate populations in the context of surface water acidification and loss of acid neutralizing capacity (ANC) in Norwegian lakes and streams. The critical level of ANC varied among fish species, with Atlantic salmon being the most sensitive, followed by brown trout. They concluded that Atlantic salmon appeared to be a good indicator of acidification of rivers, and trout seemed to be a useful indicator for acidification of lakes. Based on an evaluation of fish and invertebrate populations, a critical lower limit of ANC of $20 \mu\text{eq l}^{-1}$ was suggested as the tolerance level for Norwegian surface waters (Lien et al. 1996). In the United Kingdom a value of zero has been chosen, accepting a 50% probability of damage to fish populations (CLAG 1995). Later, Henriksen and Posch (2001) formulated a catchment-dependent ANC_{limit} , which is derived from experience in the Nordic countries and reflects the geology, deposition history and biological diversity (fish species) of that region. This formula (see Appendix A) results in a “variable” ANC_{limit} , depending on the sensitivity of the lake. Lakes with high sensitivity will have low ANC_{limit} , while non-sensitive lakes will have higher ANC-limits, with up to $50 \mu\text{eq/l}$ as an upper limit. The equation developed does not allow any lake to have zero critical load. Such values caused practical problems in the modelling process for the 1994 Oslo protocol (UN/ECE 1994) and the 1999 Gothenburg protocol (UN/ECE 1999) because of the impossibility of achieving zero deposition.

The catchment-dependent ANC_{limit} was derived for lakes in the Nordic countries exhibiting a large gradient in lake sensitivity (weathering rate) and in runoff. For the Ontario lakes both gradients are smaller. Further, we have explicitly chosen to accept critical loads of zero for this area if the model indicated this.

It is possible to establish a critical threshold for ANC for Ontario lakes that is specifically based on biological data from Ontario. Critical ANC-values for biodiversity have been developed for Ontario lakes. Based on zooplankton species composition and species richness models, Holt et al. (2000) estimated that the critical pH value fell between 5.98 and 6.07, and that the critical alkalinity was between 19 and 33 ueq/L. This is consistent with critical values estimated earlier for a number of native fish species (Hutchinson et al. 1990), and those proposed for several species of benthic organisms, including molluscs, crayfish, etc. In general, a critical or threshold pH of 6.0 is generally accepted; this can correspond to alkalinities of between 20 and 40 ueq/L (in part, depending on the contribution of organic anions to the measured alkalinity). We have chosen 40 ueq/L as our standard ANC_{limit} to provide a margin of safety. This value will lead to generally lower critical loads for the most sensitive lakes than using the catchment dependent ANC_{limit} . We have also, for one set of lakes (Haliburton), evaluated critical load exceedances based on a range of values for ANC_{limit} including the variable limit.

f. Runoff

A value for the yearly average runoff from the lake and catchment is required. A preferable value is an average based on runoff measurements for a longer period (i.e. 30 years). Such values are available for the study area and these values have been used in this study.

3. Water chemistry data

From the above considerations, the essential data for calculating critical loads for the Ontario lakes are Ca, Mg, runoff and SO_4 . Since we assume no significant seasalt influence to the lakes, data for Cl are not necessary. In our calculations we have sorted the data sets to include only those with the required data referred to above. Table 1 shows the total number of data sets for each district, those containing the required variables, and the number of single lakes with adequate data within each district.

The average values for each district for a selection of the variables analysed are given in Table 2. A corresponding table derived from the Nordic lake survey carried out in 1995 (Henriksen et al.1998) allow for comparison of the Canadian data with the European lake water quality (Table 3).

Table 1. Lake data sorted for CL calculations.

District	No. of data sets	No. of accepted sets	No. of individual lakes
Muskoka	631	588	217
Haliburton	666	567	302
Parry Sound	371	299	255
Nipissing	732	674	609
Southern Lakes	118	97	86
Total	2518	2225	1469

Table 2. Average values for some chemical variables of lakes in the Ontario regions (BC = Ca+Mg).

County	n	Runoff mm/yr	pH	Ca µeq/l	Mg µeq/l	BC µeq/l	Na µeq/l	Cl µeq/l	K µeq/l	SO ₄ µeq/l	DOC mgC/l	NH ₄ µeq/l	NO ₃ µeq/l	TotN µmol/l
Muskoka	217	500	6.35	172.8	69.7	243.5	86.9	81.7	12.9	142.8	4.75	37	83	337
Haliburton	302	456	6.33	235.9	84.6	320.5	42.9	34.5	13.5	166.2	4.04	29	82	267
Parry Sound	255	507	5.99	154.7	58.3	213	52.6	33.2	11.6	147.1	4.80	33	54	310
Nipissing	609	477	6.32	157.8	81.6	239.4	47.9	40.9	12.8	156.5	4.92	46	56	310
Southern	86	404	7.16	888.1	201.1	1089	69.6	62.4	21.8	186.6	5.63	78	34	402

The lakes in the three Nordic countries, Finland, Norway and Sweden, and the Kola Peninsula exhibit rather similar water chemistry, whereas Denmark shows entirely different water chemistry largely due to different geology and more polluted lakes. Thus, we have excluded Denmark in the further discussion.

Norway shows the highest average runoff value in the Nordic countries due to a large gradient from west to east, whereas the other countries have average runoff values generally less than 400 mm/yr, somewhat lower than those for the Ontario lakes. In the other Nordic countries the precipitation gradient is much smaller than the one for Norway. The average base cation concentrations (BC) in the study area (except for the Eastern lakes) are rather similar to the 50% values for Finland, Sweden and Russian Kola, whereas Norway show a lower average value, partly due to generally higher runoff values.

Table 3. The Nordic Lake Survey 1995. 50-percentile values (weighted) for a selection of the variables (BC* and SO₄* are sea salt corrected concentrations).

Country	Runoff mm/yr	pH	BC* µeq/l	Cl µeq/l	Alk µeq/l	SO ₄ * µeq/l	NO ₃ µeq/l	Tot-N µmol/l	TOC mgC/l
Finland	315	6.58	240	28	111	57	0.8	28.6	7.6
Norway	1590	6.36	79	47	36	26	.07	9.9	1.9
Sweden	300	6.75	226	24	119	41	0.7	28.7	6.1
Denmark	284	7.87	3096	1086	2222	614	36.8	93.6	7.40
Russian Kola	381	6.45	172	60	79	36	0.1	14.4	7.62

4. Critical loads for Ontario lakes

a. Study lakes

As described above, eight lakes have been sampled intensively since at least 1980. They have been sampled 8-26 times per year, with all samples collected as either whole-lake, volume-weighted samples, or, during summer stratification, as volume-weighted, integrated samples for each thermal region (epi-, meta-, hypolimnion).

Runoff estimated from the runoff map based on long-term data collected for the entire provincial hydrological monitoring network gives slightly different values of the runoff coefficient for each of the 8 lakes compared with the runoff values measured for these catchments over our study period. The measured annual runoff values are different for each year, and those between-year differences greatly

exceed the differences either between sites or between the measured and map-based values. The average measured value for the period 1980-1998 is 0.537 m/yr, while the yearly runoff values read from map are given in Table 4. The average value of 0.505 m/yr does not differ significantly from the measured value of 0.537. Thus, it appears safe to apply the runoff values read from maps for all CL calculations, especially since such values are available for all lakes, whereas measured values are available for only the few study lakes.

Table 4. Yearly runoff values read from a runoff map for Ontario, and average measured runoff between 1980-98.

Lake	Runoff from map	Measured runoff
Plastic	0.458	0.550
Heney	0.511	0.546
Crosson	0.468	0.552
Chub	0.518	0.470
Dickie	0.510	0.546
Red Chalk	0.488	0.527
Blue Chalk	0.496	0.527
Harp	0.589	0.575
Average	0.505	0.537

We have calculated the critical loads based on the yearly average chemical data for each of the 8 lakes as well as for a yearly selected spring value for the same lakes (Figure 3). In both sets of calculations we have used the runoff value taken from the provincial map. Both sets of data show similar patterns and similar values for the critical loads. The mean values (Table 5) are similar and the standard deviations are small and are of about the same size for all lakes. Thus, it can be concluded that using a single spring sample taken shortly after spring circulation will give a reasonable estimate of the critical load for a lake and its catchment.

Table 5. Mean values of critical loads for yearly spring values and for annual averages for study lakes together with their respective standard deviations. Runoff values read from map; NO₃⁻ concentrations and NO₃N runoff are also given. Lakes are arranged in the order of decreasing sensitivity (critical load). Note that the concentrations are not yearly weighed concentrations, since values for the fall are not as frequent as for the rest of the year.

Lake	CL-spring meq/m ² /yr	Std-spring meq/m ² /yr	CL-yr meq/m ² /yr	Std-yr meq/m ² /yr	NO ₃ µeq/l	Runoff-map m/yr	NO ₃ -flux meq/m ² /yr
Plastic	34.1	5.1	32.5	4.3	4.0	0.458	1.9
Heney	39.8	5.5	39.2	5.5	7.1	0.511	3.6
Crosson	44.0	5.6	42.3	5.7	9.2	0.468	4.3
Chub	52.3	6.0	52.8	6.2	8.1	0.518	4.2
Dickie	57.5	5.6	58.1	5.9	9.0	0.510	4.6
Blue Chalk	61.6	4.0	61.3	4.8	5.0	0.496	2.5
Red Chalk Main	61.8	5.2	61.3	4.4	9.9	0.488	4.8
Harp	83.0	4.4	86.1	4.8	10.9	0.589	6.4
Average	54.3	5.2	54.2	5.2	7.9	0.505	4.0



Figure 3. Comparison of critical load (CL) based on spring chemistry measurements (thick line) with CL based on annual average values (thin line). An ANC_{limit} of 40 ueq/L was used in these calculations.

b. Critical loads for study lakes

Deposition

Deposition of sulphur (SO_4) and nitrogen (NO_3 and NH_4) has been measured in Muskoka and Haliburton as part of the research programme conducted on the 8 long-term study lakes since 1976 (Dillon et al. 1988). Either 4 (1976-1995) or 3 (1996-present) stations located in this region were used to generate a single daily value for deposition for the Muskoka-Haliburton region; daily values were summed to give annual deposition. All measurements were made as bulk deposition using Teflon-coated, 0.25 m^2 , continuously open collectors (Dillon et al. 1988). Independent measurements of wet-only S deposition combined with estimates of dry S deposition based on measured SO_2 and particulate SO_4 concentrations suggest that dry deposition contributed 15-20% of the total S deposition and that bulk deposition corresponded reasonably well to wet plus dry deposition (Dillon et al. 1988). It is assumed that the deposition at this site is representative for all districts considered here as they are close to the deposition stations in Muskoka and Haliburton. Annual deposition values for the Muskoka-Haliburton region are given in Table 6 and plotted in Figure 4.

Table 6. Sulphur and nitrogen deposition ($\text{meq m}^{-2} \text{ yr}^{-1}$) in Muskoka-Haliburton, Ontario, Canada for hydrological years (June 1 – May 31) for the period June 1, 1977 – May 31, 1998

Hydr. Year	76-77	77-78	78-79	79-80	80-81	81-82	82-83	83-84	84-85	85-86	86-87
S-dep	82.8	87.4	83.8	76.7	74.0	75.8	68.3	54.5	57.3	61.0	49.1
N-dep	59.8	76.4	81.9	77.7	74.9	68.3	62.7	59.3	61.9	65.3	60.5

Hydr. Year	87-88	88-89	89-90	90-91	91-92	92-93	93-94	94-95	95-96	96-97	97-98
S-dep	57.1	51.0	46.3	53.2	53.3	49.5	43.6	44.5	51.9	43.2	30.1
N-dep	71.0	55.8	61.5	64.4	59.6	61.0	59.8	58.0	81.1	66.4	42.7

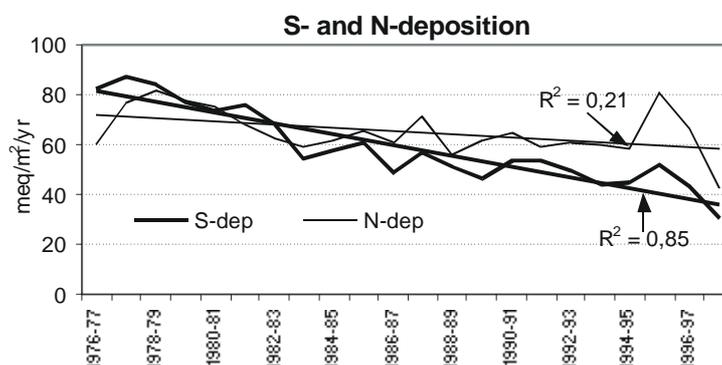


Figure 4. Sulphur and nitrogen deposition in Muskoka-Haliburton, Ontario, Canada for hydrological years (June 1 – May 31) for the period June 1, 1977 – May 31, 1998.

Sulphur deposition in Muskoka-Haliburton shows a clear downward trend during the study period ($R^2 = 0.85$), although most of this decrease occurred in the first 10 years (1976-86). The decrease of more than 50% in deposition is consistent with decreases in S emissions in eastern Canada where a 50-55% decline in emissions has occurred over the past two decades (Clair et al. 1995), and decreases in the north-eastern U.S.A. where emissions have dropped by about 30% between 1980 and 1995 (Stoddard et al. 1999, Shannon 1995). There has been no significant trend or change in N-deposition over the course of the study, which is, again, consistent with the fact that estimates of emissions suggest no changes.

Critical load exceedances of the study lakes

The critical load and the critical load exceedances are calculated from equations (7) and (8):

$$CL(A) = Q([BC^*]_0 - [ANC]_{limit}) \quad (7)$$

$$CL(Ex) = -CL(A) + S\text{-dep} + NO_3\text{-flux} \quad (8)$$

Annual exceedances are shown in Table 7, and exceedances plus the 4-year moving average of exceedances are plotted in Figures 5 and 6.

Table 7. Critical load exceedance calculations for the study lakes using equation (8). The critical load values are taken from table 5 (spring value), the S-dep is given in the first column and the NO₃-flux is given in table 5. Non-exceedance is given by negative number. ANC_{limit} of 40 ueq/L was used in the calculations. Units: meq/m²/yr.

Hydr. yr	Plastic	Heney	Crosson	Chub	Dickie	Red Chalk Main	Blue Chalk	Harp
76-77	50.6	46.6	43.1	34.7	29.9	25.8	23.7	6.2
77-78	55.2	51.2	47.7	39.3	34.5	30.4	28.3	10.8
78-79	51.6	47.6	44.1	35.7	30.9	26.8	24.7	7.2
79-80	44.5	40.5	37.0	28.6	23.8	19.7	17.6	0.1
80-81	41.8	37.8	34.3	25.9	21.1	17.0	14.9	-2.6
81-82	43.6	39.6	36.1	27.7	22.9	18.8	16.7	-0.8
82-83	36.1	32.1	28.6	20.2	15.4	11.3	9.2	-8.3
83-84	22.3	18.3	14.8	6.4	1.6	-2.5	-4.6	-22.1
84-85	25.1	21.1	17.6	9.2	4.4	0.3	-1.8	-19.3
85-86	28.8	24.8	21.3	12.9	8.1	4.0	1.9	-15.6
86-87	16.9	12.9	9.4	1.0	-3.8	-7.9	-10.0	-27.5
87-88	24.9	20.9	17.4	9.0	4.2	0.1	-2.0	-19.5
88-89	18.8	14.8	11.3	2.9	-1.9	-6.0	-8.1	-25.6
89-90	14.1	10.1	6.6	-1.8	-6.6	-10.7	-12.8	-30.3
90-91	21.0	17.0	13.5	5.1	0.3	-3.8	-5.9	-23.4
91-92	21.1	17.1	13.6	5.2	0.4	-3.7	-5.8	-23.3
92-93	17.3	13.3	9.8	1.4	-3.4	-7.5	-9.6	-27.1
93-94	11.4	7.4	3.9	-4.5	-9.3	-13.4	-15.5	-33.0
94-95	12.3	8.3	4.8	-3.6	-8.4	-12.5	-14.6	-32.1
95-96	19.7	15.7	12.2	3.8	-1.0	-5.1	-7.2	-24.7
96-97	11.0	7.0	3.5	-4.9	-9.7	-13.8	-15.9	-33.4
97-98	-2.1	-6.1	-9.6	-18.0	-22.8	-26.9	-29.0	-46.5

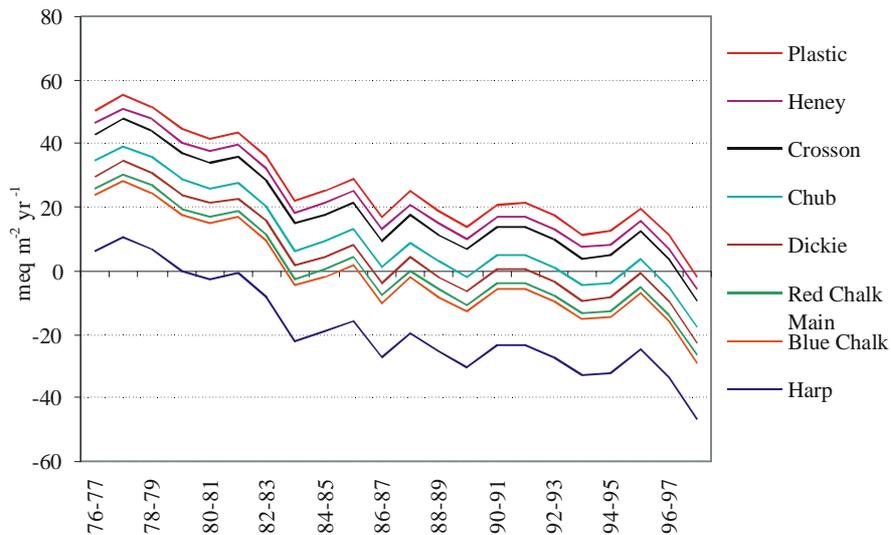


Figure 5. The exceedance data from Table 7 plotted according to decreasing sensitivity of lakes.

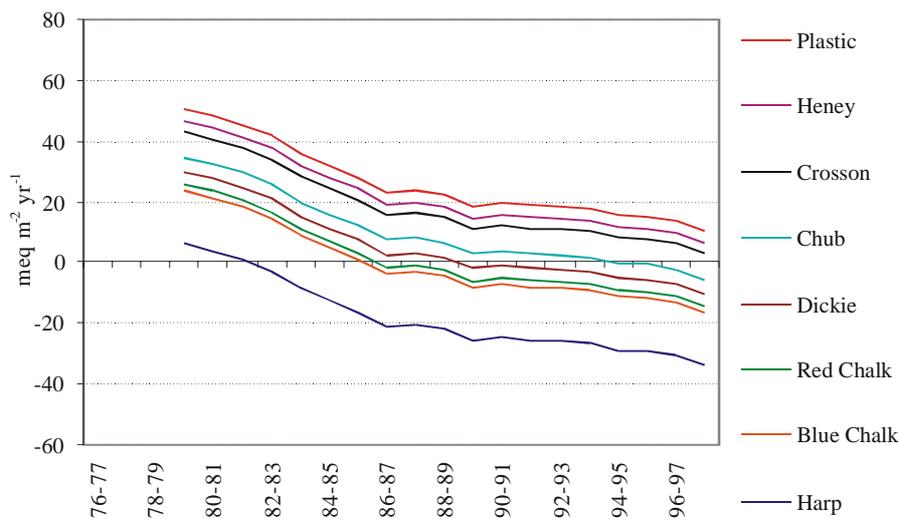


Figure 6. Four-year moving averages of exceedance for study-lakes.

Sulphur deposition in the study area has decreased by about 50% from 1977 to 1998 (Figure 4). Consequently, the critical load exceedance has also decreased accordingly. In Figures 5 and 6 we have arranged the study lakes in decreasing order of sensitivity (increasing critical load) and calculated their exceedances for each year. We have here included the NO_3 -leaching (see Table 6) in the exceedance calculations, based on the average NO_3 -leaching during the period (from $1.9 \text{ meq m}^{-2} \text{ yr}^{-1}$ for Plastic Lake to $6.4 \text{ meq m}^{-2} \text{ yr}^{-1}$ for Harp lake). All lakes were exceeded until 1982-83, whereas no lakes are exceeded in 1997-98. The most sensitive lakes, Plastic, Heney and Crosson, had critical load exceedances until 1996-97. The two last years have the lowest S-deposition (see Table 7), and if this continues, we expect a significant improvement in water quality in the years to come. As pointed out above, the S-deposition has decreased by about 50% since the late 70's, which has resulted in a long-

term decrease of 18–40% in SO_4 -concentrations in the study lakes. The 4-year moving averages (Figure 6) indicate a steady decrease in exceedance, showing that Plastic, Heney and Crosson still are slightly exceeded today.

There are, however, a number of factors that influence the linkage between changes in S deposition and the changes in the chemistry of a catchment, and that therefore will influence recovery rates of catchments. One such factor affecting these calculations is the biogeochemical redox-controlled S cycle within the catchments. For example, in the principal study lakes, the response to the decreases in S deposition has been much less than expected based on simple models of S flux, and it has been demonstrated (Dillon et al, 1997, Dillon and Evans 2001) that climate-controlled redox processes that occur in wetlands in the catchments are delaying recovery through re-release of previously-stored S. As a consequence, the current lake chemistry, including SO_4 and base cation concentrations, may not reflect adequately the fact that CL exceedances for some of the lakes such as Plastic and Heney have dropped to almost 0.

c. Critical loads for all lakes

The data for the study-lakes strongly indicate that a single sample taken shortly after spring overturn, can give a good estimate of the critical load of a lake. We have used the data for the 5 districts (Table 2) to calculate the critical loads for each of the 1469 lakes; these are categorized and plotted in Figure 7. The critical loads are lowest in the central and western parts of the studied area, whereas the highest critical loads are found in the southern lakes. This is consistent with the geological conditions for these areas, with the southern region having a mixture of silicate and carbonate bedrock and surficial deposits, and the central and eastern portions of the other 4 regions having the thinnest soil/till and the most frequent occurrences of exposed bedrock.

We have further calculated the critical load exceedances for each lake in each district in the same way as for the principal study-lakes. (Table 9, Figures 8 and 9), but instead of calculating the amount of exceedance, the percent of the lake population that is exceeded is plotted.

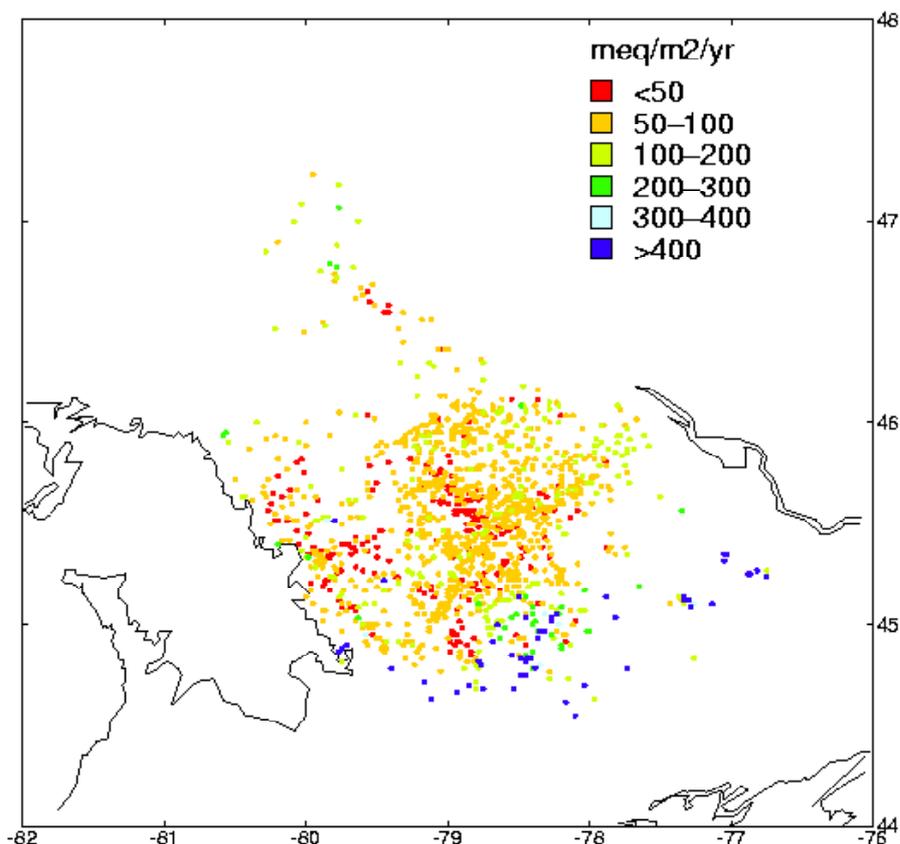


Figure 7. The critical loads (using $ANC_{\text{limit}} = 40 \mu\text{eq L}^{-1}$) for the 1469 lakes in the study region.

Table 9. Percent of lakes exceeded for each year of deposition.

Year	Parry Sound	Muskoka	Haliburton	Nipissing	Southern	All lakes
<i>No of lakes</i>	255	217	302	609	86	1469
77	73.7	72.4	69.5	65.5	25.6	66.4
78	78.8	76.5	71.5	71.3	25.6	70.7
79	74.1	73.3	70.2	66.8	25.6	67.4
80	68.2	64.1	66.2	55.7	23.3	59.4
81	67.1	60.4	62.9	52.9	23.3	56.7
82	67.8	63.6	65.6	54.2	23.3	58.2
83	62.0	52.1	54.0	43.5	20.9	48.7
84	36.5	18.9	26.8	23.3	14.0	25.0
85	42.0	25.3	31.5	26.9	17.4	29.6
86	47.5	36.9	40.1	32.8	18.6	36.7
87	25.5	12.0	17.5	15.1	8.1	16.3
88	41.6	25.3	31.1	26.8	17.4	29.4
89	29.0	13.4	20.9	17.7	10.5	19.1
90	20.8	9.2	13.2	11.2	3.5	12.5
91	32.9	16.1	24.2	20.7	11.6	22.3
92	33.3	17.5	23.8	20.7	12.8	22.5
93	25.9	12.0	16.9	15.9	9.3	17.0
94	16.9	7.8	8.9	8.4	1.2	9.5
95	18.8	8.8	10.3	9.0	1.2	10.5
96	29.4	14.7	22.5	19.9	11.6	20.6
97	16.5	6.9	7.9	8.0	0.0	8.8
98	4.7	1.8	0.7	1.6	0.0	1.9

The general trend in the data is a clear and steady decrease in critical load exceedances in all regions for the period 1976-98. In the 4 acid sensitive regions (Parry Sound, Haliburton, Muskoka, Nipissing), the number of lakes experiencing exceedances dropped from 65-74% to 1-5%. However, the last year (1997-98) had anomalously low S deposition, almost certainly because the amount of precipitation was exceptionally low (ca. 40% below the long-term average). Because of this, it is more reasonable to use the 4-year moving average exceedances. Furthermore, sulphur deposition varied substantially from year to year, but the 4-year averages (Figure 8) reduce the effect of this year-to-year variability. Using the 4-year average, the decline is such that approximately 8-18% of the lakes still have exceedances, which still represents a major decrease from the initial 65-74%. In the southern region, only 26% of the lakes initially had exceedances; this dropped to a few % by the end of the study period. The low initial value reflects the fact that many of the catchments in this region are influenced by carbonates in their bedrock and/or surficial deposits, and the lakes are insensitive to acid deposition. Virtually all of the remaining lakes in this region that were sensitive have now recovered chemically.

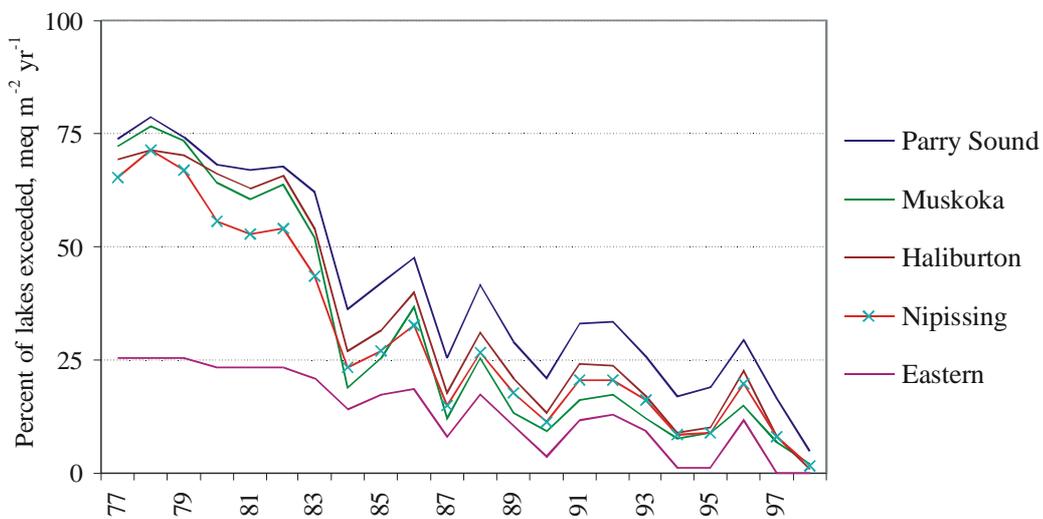


Figure 8. Critical load exceedances for lakes in the five districts.

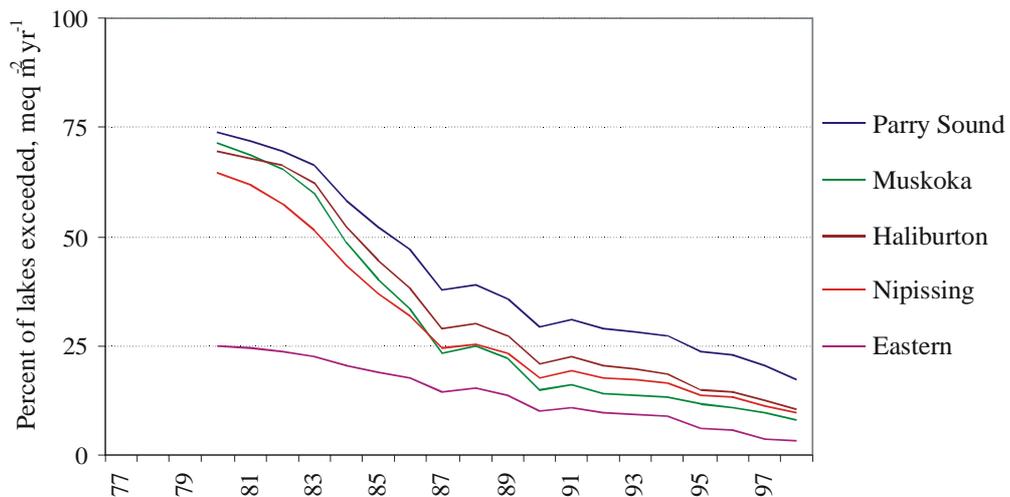


Figure 9. 4-year moving averages of exceedance for lakes in the five districts.

The exceedances in all regions decreased faster during the first ten years than during the last ten years (Figures 8 and 9), almost certainly because the S deposition decreases occurred largely in these first 10 years. Another factor that influences the linkage between changing deposition and the timing of the changes in exceedance is the delay in response of the S flux from catchments to changes in S deposition that are caused by biogeochemical processes within the catchment. For example, in the principal study lakes discussed in this report, the response to the decreases in S deposition has been much less than expected based on simple models relating deposition to S flux, and it has been demonstrated (Dillon et al, 1997, Dillon and Evans 2001) that climate-controlled redox processes that occur in wetlands in the catchments are delaying recovery through re-release of previously-stored S. As a consequence, the current chemistry of some lakes may not adequately reflect the fact that CL exceedances are small.

d. Effects of choice of ANC_{limit} on CL

In many ways, the most subjective part of the SSWC critical load model is the choice of the ANC threshold (ANC_{limit}), or the lowest flux that doesn't damage selected biota. This choice of ANC_{limit} is subjective, in part, because there is little or no information available about the suitable thresholds for most of the species in these or other lakes, and what little information exists is typically focused on a few species of economic importance, e.g. brown trout, Atlantic salmon. In this study, we have chosen 40 ueq/L as the critical lower limit for ANC based on knowledge that this will provide a small margin of safety for the zooplankton communities in the lakes in this area. For example, Holt (2001) found that zooplankton diversity in lakes in our study area was adversely affected at $ANC < 30-33$ ueq/L. Some of the fish species present in these lakes are likely less sensitive, but there are probably other biota including crayfish, molluscs and some benthos that are more sensitive; however, there are no quantitative data that will allow such a determination.

To assess the effect of the choice of ANC_{limit} on the calculation of CL and CL exceedances, and thus on extent of recovery, we picked one of the sensitive areas (Haliburton) and recalculated CL using different values for ANC_{limit} . We chose 20, 30, 40 and 50 ueq/L, and the variable ANC_{limit} used in the Norwegian analysis of CL (see Appendix A). The results are shown in Figure 10. The number of lakes with their critical load exceeded is greatest with the highest ANC_{limit} chosen (50 ueq/L) as expected, and the numbers exceeded each year decreases as the ANC_{limit} chosen decreases. The results obtained using the variable threshold are very similar to those obtained with 20 ueq/L. The range in the portion of Haliburton lakes with CL exceeded based on the different choices for ANC_{limit} is ca. 20%, with this shrinking in recent years as the number exceeded drops. With ANC_{limit} of 20 ueq/L or using the variable limit, there are almost no lakes where the CL is exceeded.

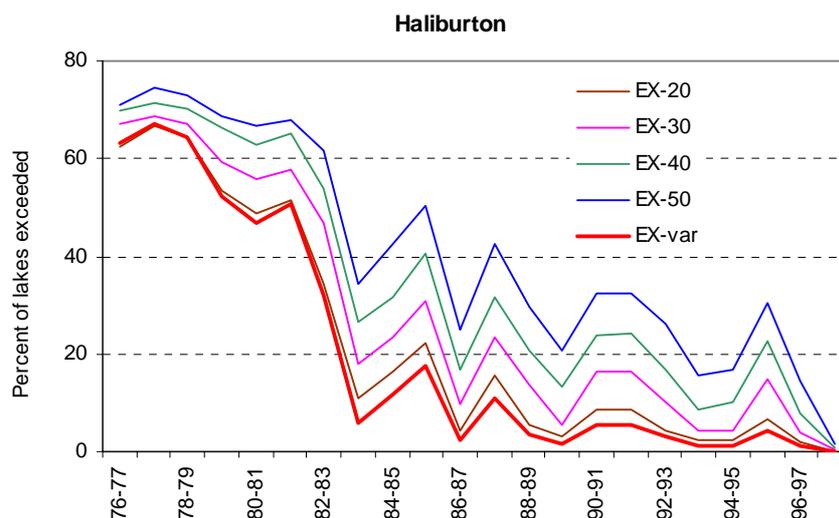


Figure 10. Per centage of lakes in the Haliburton region where the critical load is exceeded based on ANC_{limit} of 20, 30, 40 and 50 $\mu\text{eq/L}$, and on the variable ANC_{limit} calculated for Norwegian lakes (see Appendix A) that takes into consideration the geology, deposition history and the biota's (principally fish) ability to respond to these factors.

These results indicate that the calculation of critical load is strongly dependent on the choice of ANC_{limit} , and that it is imperative to obtain suitable data on the sensitivity of the appropriate species for the specific region and/or lake.

5. Conclusions and recommendations

The concept of critical loads that has been widely accepted in Europe as a basis for designing control strategies to reduce regional and transboundary air pollution was applied to lakes in south-central Ontario, Canada. The work described here, part of a research programme initiated at Trent University, Ontario with the collaboration of the Natural Sciences and Engineering Research Council (NSERC), the power-producing industry (Ontario Power Generation Inc.) and the Ontario Ministry of the Environment, is designed to evaluate the critical sulphur and nitrogen loads to lakes in south-central Ontario using both steady-state and dynamic models, with the intent of determining whether emission reductions of the past 15 years are adequate. In this report, results obtained using the Steady-State Water Chemistry (SSWC) model, which allows the calculation of critical loads of acidity and their present exceedances, are described. In addition to evaluating the current status of lakes in this part of Ontario in general, we have used intensive, detailed data sets collected for a small number of lakes over many years to evaluate several of the assumptions inherent in the SSWC model.

The sensitivity of freshwaters in Ontario to acid deposition is defined in general terms by their location relative to the boundary of Precambrian Shield. Those waters that are north of the southern boundary of the Shield are situated in a region of predominately silicate bedrock, which is overlain by thin glacial tills. We have chosen for study lakes in 5 regions in south-central Ontario. These regions include the District of Muskoka, and the counties of Haliburton, Nipissing, and Parry Sound. Information was also gathered for a fifth set of lakes, the Southern lakes, which includes lakes along the southern boundary of the Shield where the geology is a mixture of carbonate and silicate bedrock. Single measurements for 1469 lakes in the 5 regions were used to calculate critical loads and their exceedances using S deposition data for the period 1977-1998. Sulphur deposition in the study area shows a clear downward trend over this time period, with the decrease of more than 50% in S deposition being consistent with decreases in S emissions in eastern Canada and the north-eastern

U.S.A. Over the same time period, there has been no significant trend or change in N-deposition. As a result of the declining S deposition, the portion of lakes with critical load exceedances has dropped substantially, from 65-70% in the 4 sensitive regions in 1977 to 1-5% in 1998. Because 1998 had anomalous precipitation and S deposition (40% less precipitation than the long-term average), we also used the 4-year moving average values; in this case, the portion of the lakes where their CL was exceeded was 8-18%.

In addition to the information collected on many lakes via chemical surveys, eight lakes have been sampled regularly since 1980. The critical sulphur load was exceeded for all 8 of these lakes until 1982-83, whereas none of them were exceeded in 1997-98. The most sensitive lakes, Plastic, Heney and Crosson, were exceeded until 1996-97. The two last years reported here had particularly low S deposition (see Table 8), and unless this continues, we expect improvements in water quality in the subsequent years may be somewhat less pronounced than indicated by the 1997-98 data. The intensive data were also used to demonstrate that a single sample taken shortly after spring circulation gives a reasonable estimate of the critical load for a lake and its catchment, and that the critical load calculated based on each year's data did not change from year to year.

We evaluated the effect of the choice of ANC_{limit} on the calculated exceedances for lakes in 1 region (Haliburton). The portion of lakes with CL exceeded varied by 20% (in absolute rather than relative terms) across a range of ANC_{limit} from 20 to 50 ueq/L, with the variable ANC_{limit} method providing results similar to those obtained using 20 ueq/L. Thus, it is important to choose a value for ANC_{limit} that is relevant to the specific lakes and their biota.

In summary, the SSWC model indicates that most lakes in south-central Ontario that had critical loads that were exceeded in the 1970's and early 1980's now experience deposition at or near their CL. Further evaluation using the FAB model, which explicitly considers N dynamics, and MAGIC, a dynamic critical load model, is essential. These more complex models may present a less optimistic picture, in that their inclusion of additional processes will result in lower estimates of critical load for many lakes and greater exceedances.

Acknowledgement

The authors would like to thank Maximilian Posch (RIVM, The Netherlands) for fruitful discussions and for preparing the map in Figure 7

Appendix A.

The steady state water chemistry (SSWC) model

Here, the SSWC critical load model is described in some details: For full description and evaluation see Henriksen and Posch (2001).

Preliminaries

With the Steady-State Water Chemistry (SSWC) model the critical load of a lake can be derived from present day water chemistry, if weighted annual mean values, or estimates thereof, are available. It assumes that all sulphate in runoff originates from sea salt spray and anthropogenic deposition (no adsorption or retention). The model uses Acid Neutralizing Capacity (ANC) (Reuss and Johnsson 1986) as the chemical criterion for sensitive indicator organisms in surface waters. ANC is defined as the difference between base cations (BC) and strong acid anions (AN):

$$[\text{ANC}] = [\text{BC}] - [\text{AN}] = [\text{HCO}_3^-] + [\text{A}^-] - [\text{H}^+] - [\text{Al}^{n+}] \quad (1)$$

where $[\text{HCO}_3^-]$ is the bicarbonate concentration, $[\text{A}^-]$ the concentration of organic anions, $[\text{H}^+]$ is the hydrogen ion concentration, and $[\text{Al}^{n+}]$ is the sum of all positively charged aluminum concentrations. The second identity in equation 1 follows from the charge balance.

To estimate changes in surface water chemistry due to anthropogenic atmospheric deposition, it is necessary to account for the ions originating from sea salt spray. Assuming that all chloride in the water comes from sea salt spray and that all sea salt components are transported and deposited in the same ratio as found in seawater, sea salt corrected concentrations (marked with an asterisk) are calculated as (in $\mu\text{eq l}^{-1}$):

$$[\text{Ca}^*] = [\text{Ca}] - 0.037 [\text{Cl}] \quad (2)$$

$$[\text{Mg}^*] = [\text{Mg}] - 0.198 [\text{Cl}] \quad (3)$$

$$[\text{K}^*] = [\text{K}] - 0.018 [\text{Cl}] \quad (4)$$

$$[\text{Na}^*] = [\text{Na}] - 0.858 [\text{Cl}] \quad (5)$$

$$[\text{SO}_4^*] = [\text{SO}_4] - 0.103 [\text{Cl}] \quad (6)$$

$$[\text{Cl}^*] = 0 \quad (7)$$

Derivation of a critical load

Critical loads of acidity for surface waters are based on the principle that the acid load should not exceed the non-marine, non-anthropogenic base cation input and sources and sinks in the catchment minus a buffer to protect selected biota from being damaged:

$$\text{CL(A)} = \text{BC}_w + \text{BC}^*_{\text{dep}} - \text{BC}_u - \text{ANC}_{\text{limit}} \quad (8)$$

where BC_w is the average weathering flux, BC^*_{dep} the non-marine, non-anthropogenic deposition of base cations, BC_u the net long-term average uptake of base cations in the biomass (i.e. the annual average removal of base cations due to harvesting), and $\text{ANC}_{\text{limit}}$ the lowest ANC-flux that does not damage selected biota. Since the average amount of base cations weathered in a catchment and reaching the lake is difficult to measure or compute from available information, a critical load equation that uses water quality data alone has been derived. In pre-acidification times the non-marine flux of base cations from the lake, BC^*_0 , is given by (all parameters are expressed as annual fluxes, e.g. in $\text{meq m}^{-2} \text{yr}^{-1}$):

$$BC^*_0 = BC_w + BC^*_{dep} - BC_u \quad (9)$$

Thus we have for the critical load from equation 8:

$$CL(A) = BC^*_0 - ANC_{limit} = Q([BC^*]_0 - [ANC]_{limit}) \quad (10)$$

where the second identity expresses the critical load in terms of the catchment runoff Q (in $m\ yr^{-1}$) and concentrations ($[X]=X/Q$). To estimate the pre-acidification flux of base cations we start by calculating the present flux of base cations, BC^*_t , given by

$$BC^*_t = BC_w + BC^*_{dep} - BC_u + BC_i \quad (11)$$

where BC_i is the release of base cations due to ion-exchange processes. Assuming that weathering rate, deposition and net uptake have not changed over time, we obtain by subtracting equation 9 from equation 11:

$$BC_i = BC^*_t - BC^*_0 \quad (12)$$

This present-day excess production of base cations in the catchment is related to the long-term changes in inputs of non-marine acid anions (ΔAN^*) by the so-called F-factor (see below):

$$BC_i - BC_u = F \cdot \Delta AN^* = F \cdot (\Delta SO_4^* + \Delta NO_3) \quad (13)$$

For the pre-acidification base cation flux we thus get from equation 12 ($\Delta X = X_t - X_0$):

$$BC^*_0 = BC^*_t - F \cdot (SO_4^*_t - SO_4^*_0 + NO_{3,t} - NO_{3,0}) \quad (14)$$

Finally, the so-called present exceedance of the critical load of acidity is defined as:

$$Ex(A) = S^*_{dep} + N_{leach} - CL(A) \quad (15)$$

While sulphate is assumed to be a mobile anion ($S_{leach}=S^*_{dep}$) (Seip 1980) nitrogen is to a large extent retained in the catchment by various processes and therefore N_{dep} cannot be used directly in the exceedance calculation. Therefore, only present-day exceedance can be calculated from the leaching of N, N_{leach} , which is determined from the sum of the measured concentrations of nitrate and ammonia in the runoff. No N-deposition data are required for exceedance calculations; however, $Ex(A)$ quantifies only the exceedance at present rates of retention of N in the catchment. Only in the FAB-model (see below) are nitrogen processes modeled explicitly, and thus only that model can be used for comparing the effects of different N-deposition scenarios. In the above derivation we assumed that base cation deposition and net uptake did not change over time. If there is increased base cation deposition due to human activities or a change in the net uptake due to changes in management practices, this has to be taken into account in the exceedance calculations by subtracting that anthropogenic ($BC^*_{dep}-BC_u$) from $S^*_{dep}+N_{leach}$.

In the following we will describe how to calculate the F-factor, the pre-acidification sulphate concentration ($NO_{3,0}$ is generally set to zero), and the ANC_{limit} .

The F-factor

According to equations 12 and 13, using concentrations instead of fluxes, the F-factor is defined as the ratio of change in non-marine base cation concentrations due to changes in strong acid anion concentrations (Henriksen 1984, Brakke et al. 1990):

$$F = ([BC^*]_t - [BC^*]_0) / ([SO_4^*]_t - [SO_4^*]_0 + [NO_3]_t - [NO_3]_0) \quad (16)$$

where the subscripts t and 0 refer to present and pre-acidification concentrations, respectively. If $F=1$, all incoming protons are neutralized in the catchment (only soil acidification), at $F=0$ none of the incoming protons are neutralized in the catchment (only water acidification). The F-factor was estimated empirically to be in the range 0.2–0.4, based on comparisons of historical data from Norway, Sweden, U.S.A. and Canada (Henriksen 1984). Brakke et al. (1990) suggested later that the F-factor should be a function of the base cation concentration:

$$F = \sin((\pi/2)[BC^*]_t/[S]) \quad (17)$$

where [S] is the base cation concentration at which F=1; and for $[BC^*]_t > [S]$ F is set to 1. For Norway [S] has been set to $400 \mu\text{eq l}^{-1}$ (ca. 8 mg Ca l^{-1}) (Brakke et al. 1990).

In equation 17 the present base cation concentration is used for practical reasons. To render the F-factor independent from the present base cation concentration. Posch et al. (1993) suggested a relationship between F and the pre-acidification base cation concentration $[BC^*]_0$:

$$F = 1 - \exp(-[BC^*]_0/[B]) \quad (18)$$

where [B] is a scaling concentration estimated to be $131 \mu\text{eq l}^{-1}$ from paleolimnological data from Finland (Posch et al. 1993). Inserting this expression into equation 16 gives a non-linear equation for $[BC^*]_0$ which has to be solved by an iterative procedure.

The two expressions for the F-factor give similar results when used to calculate critical loads for surface waters in Norway.

The use of the F-factor, defined as a function of the base cation concentration (Henriksen 1984) was originally derived from Norwegian lake-data. In Norway the range of runoff is wide ($0.3\text{-}5 \text{ m yr}^{-1}$), with an average of 1 m yr^{-1} . In other countries, like Sweden and Finland, the runoff is low compared to most of Norway (see Henriksen et al. 1998). The weathering rate of a catchment is largely dependent on the bedrock and overburden and not on runoff itself. Thus, catchments with similar bedrock and overburden characteristics should have similar weathering rates. If one catchment has a high runoff, say 2 m yr^{-1} , and another one has a low runoff, e.g. 0.3 m yr^{-1} , their base cation fluxes will be similar, but their concentrations will differ considerably. Thus, in the F-factor the BC^* -value should be a flux instead of a concentration:

$$F = \sin((\pi/2)Q[BC^*]_t/S) \quad (19)$$

where Q is the annual runoff (m yr^{-1}) and S is the base cation flux at which F=1. For Norway S has been estimated to be $400 \text{ meq m}^{-2} \text{ yr}^{-1}$. If $Q[BC^*]_t > S$, F is set to 1.

The non-anthropogenic sulphate concentration

Pre-acidification sulphate concentrations, $[SO_4^*]_0$ in lakes are assumed to consist of an atmospheric pre-acidification contribution and a geologic contribution proportional to the concentration of base cations (Brakke et al. 1989):

$$[SO_4^*]_0 = a + b [BC^*]_t \quad (20)$$

The coefficients in this equation have been estimated for different areas and by different authors. Table I summarizes values of a (in $\mu\text{eq l}^{-1}$), b and correlation coefficient r as found in the literature

Table A. Constants in equation 20 estimated from empirical data from Norway, Sweden and Finland.

a	b	r	N	Reference
15	0.16	0.38	143	Lakes, Norway (Brakke et al. 1989)
8	0.17	0.78	289	Lakes, Norway (Henriksen. unpubl.)
5	0.05	n.g.	n.g.	Groundwater, Sweden (Wilander 1994)
14	0.10	0.29	61	Lakes, Finland (Posch et al. 1993)
19	0.08	0.66	251	Lakes, Norway+Finland+Sweden (Posch et al. 1997)

Brakke et al. (1989) estimated their relationship from 143 lakes little affected by acid deposition, sampled in 1986 in Norway. Pre-acidification sulphate was recalculated based on a survey of statistically selected lakes in Norway carried out in 1995 (see Skjelkvåle et al. 1998), comprising lakes

located above 100 m above sea level and receiving S-deposition less than $0.25 \text{ g S m}^{-2} \text{ yr}^{-1}$ ($N=289$) (Henriksen *unpubl.*). The second lake survey gave a value of $8 \mu\text{eq l}^{-1}$ for a. about half the value obtained from the 1986 lake survey. Monitoring data indicate that the sulphate deposition has decreased also in the low pollution areas in Norway (SFT 1999), suggesting that most of it could be due to anthropogenic S-emissions in the first place.

Wilander (1994) analyzed concentrations in precipitation, geo-chemical ratios of groundwater chemistry and historical data on denudation in Sweden. Posch et al. (1993) obtained their equation from 61 Finnish lakes located in unpolluted areas, whereas Posch et al. (1997) combined data for 251 lakes located in the northern regions of Finland, Norway and Sweden receiving low acidic deposition.

To assess the influence of the non-anthropogenic sulphate, Henriksen and Posch (2001) compared the area of critical load exceedances using the five equations given in Table I and the average sulphur and nitrogen deposition in Norway for the period 1992-1996 (Tørseth and Semb 1997). The results showed that the five different estimates of the non-anthropogenic sulphate did not influence the estimated exceeded area significantly, although the Wilander equation results in a somewhat larger exceeded area. Thus, it is largely a matter of taste which equation to use.

The ANC-limit

Lien et al. (1996) analyzed the status of fish and invertebrate populations in the context of surface water acidification and loss of acid neutralizing capacity (ANC) in Norwegian lakes and streams. The data for fish came from populations in 1095 lakes, mostly from the regional lake survey carried out in 1986 (Henriksen et al. 1988, 1989). The critical level of ANC varied among fish species, with Atlantic salmon being the most sensitive, followed by brown trout. They concluded that Atlantic salmon appeared to be a good indicator of acidification of rivers, and trout seemed to be a useful indicator for acidification of lakes. Based on an evaluation of fish and invertebrate populations, a critical lower limit of $[\text{ANC}] = 20 \mu\text{eq l}^{-1}$ was suggested as the tolerance level for Norwegian surface waters (Lien et al. 1996), and zero in the United Kingdom (CLAG 1995) (see Figure 1).

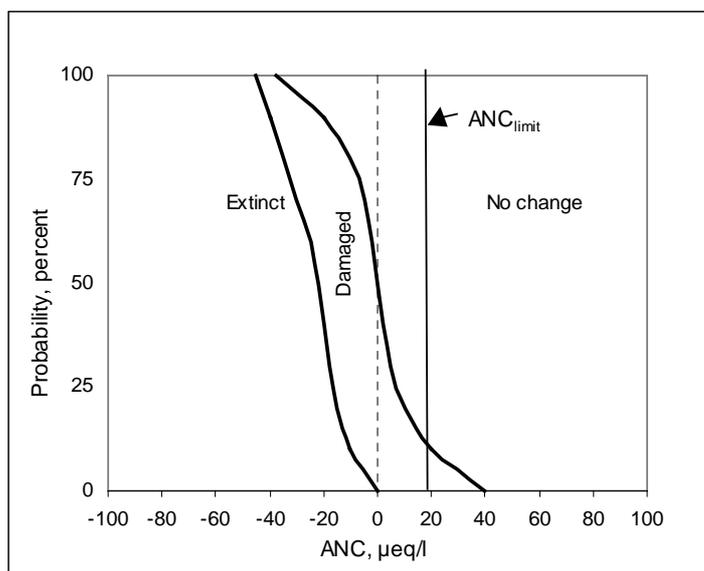


Figure 1. Relationship between the ANC concentrations in lakes and damage to fish populations (from Lien et al. 1996).

Figure 1 indicates that in the range $0-50 \mu\text{eq l}^{-1}$ ANC there is a decreasing probability from about 50% to 0% for fish populations to be damaged. The lakes studied receive depositions from very low to very high (for Norway), thus including a wide range of affected lakes. This implies that for a given ANC-

value there exist lakes of varying sensitivity, receiving varying amounts of deposition. This could reflect that fish have responded to the same ANC differently in different lakes, indicating that a catchment-dependent ANC-limit would be more appropriate than a fixed value for all lakes. In other words, every lake has its own characteristic ANC-limit (in the range shown in Figure 1). Less sensitive lakes, i.e. lakes with higher critical loads, should have a higher ANC-limit, since less sensitive ecosystems will have a higher biological variety/diversity and thus require a higher $[\text{ANC}]_{\text{limit}}$ to keep that diversity intact. The simplest functional relationship with this feature is a linear relationship between $[\text{ANC}]_{\text{limit}}$ and CL:

$$[\text{ANC}]_{\text{limit}} = k \cdot \text{CL} \quad (21)$$

This yields the following implicit equation for calculating the critical load:

$$\text{CL} = Q \cdot ([\text{BC}^*]_0 - k \cdot \text{CL}) \quad (22)$$

Or, solving for CL:

$$\text{CL} = Q \cdot [\text{BC}^*]_0 / (1 + k \cdot Q) \quad (23)$$

and thus from equation 21 also:

$$[\text{ANC}]_{\text{limit}} = k \cdot Q \cdot [\text{BC}^*]_0 / (1 + k \cdot Q) \quad (24)$$

This is a special case of a more general expression derived earlier using somewhat different arguments (Henriksen et al. 1995). As for the constant $[\text{ANC}]_{\text{limit}}$ earlier, the proportionality constant k has to be derived from data. First, for $\text{CL}=0$, we assume $[\text{ANC}]_{\text{limit}}=0$. If we further assume that for a critical load of $200 \text{ meq m}^{-2} \text{ yr}^{-1}$ the $[\text{ANC}]_{\text{limit}}$ should not exceed $50 \mu\text{eq l}^{-1}$ ($=50 \text{ meq m}^{-3}$), as has been assumed in Sweden, we arrive at a k -value of $50/200 = 0.25 \text{ yr m}^{-1}$. In addition, for CL values above $200 \text{ meq m}^{-2} \text{ yr}^{-1}$ we set the $[\text{ANC}]_{\text{limit}}$ to the constant value of $50 \mu\text{eq l}^{-1}$. This means that equation 21 should actually be written as:

$$[\text{ANC}]_{\text{limit}} = \min\{k \cdot \text{CL}, 50\} \quad (25)$$

The value of k is derived from experience in the Nordic countries and reflects thus the geology, deposition history and biological diversity (fish species) of that region. For other regions other k -values could be more appropriate.

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