

REPORT SNO 4567-2002

# **C**ritical Load of Acidity to Surface Waters in South- central Ontario, Canada

II. Application of the First-order  
Acidity Balance (FAB) Model

***Acid  
Rain  
Research***

REPORT 55/02




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Title Tentative Critical Load of Acidity to Surface Waters in South-central Ontario, Canada II. Application of the First-order Acidity Balance (FAB) Model	Serial No. 4567-2002	Date 2002.06.07
	Report No. Sub-No. O-20138	Pages Price 29
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	Geographical area Canada	Printed NIVA

Client(s) Trent University, Ontario, Canada URL: <a href="http://www.trentu.ca/biogeochemistry">http://www.trentu.ca/biogeochemistry</a>	Client ref.
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**Abstract**  
The First-order Acidity Balance (FAB) model was applied to 291 lakes in the Muskoka river catchment in Ontario, Canada. Critical loads and exceedances calculated for the region indicate that the portion of the lakes with exceedances dropped from approximately 90% 20 years ago to approximately 40% in the late 1990s.

4 keywords, Norwegian 1. Innsjøer 2. Vannkjemi 3. Tålegrenser 4. Modeller	4 keywords, English 1. Lakes 2. Water chemistry 3. Critical loads 4. Models
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**Critical Load of Acidity to Surface Waters  
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## 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 in the negotiations for the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone signed in Gothenburg, Sweden, in December 1999.

The Norwegian Institute for Water Research (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.

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# Contents

<b>Summary</b>	<b>5</b>
<b>1. Introduction</b>	<b>6</b>
a. Background	6
b. Site description	7
c. Data collection	9
<b>2. The First-order Acidity Balance (FAB) model</b>	<b>10</b>
<b>3. Data requirements</b>	<b>11</b>
a. Critical load of acidity	11
b. Mass transfer coefficients	11
c. Denitrification	12
d. Nitrogen immobilisation	13
e. Nitrogen uptake	13
<b>4. Critical loads and exceedances for Ontario lakes</b>	<b>13</b>
a. Deposition of sulphate and nitrogen	13
b. Critical loads for the eight long-term study lakes	14
c. Critical loads for the Muskoka river catchment lakes	18
d. Uncertainties in critical load and exceedance estimates	21
<b>5. Conclusions and recommendations</b>	<b>22</b>
<b>6. References</b>	<b>24</b>
<b>Appendix A.</b>	<b>26</b>
The First-order Acidity Balance (FAB) model	26

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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 currently accepted 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 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 sulphur (S) and nitrogen (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 S and N 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, critical loads for S and N obtained using the FAB model are described. Critical loads of acidity, using the SSWC model, have also been recently investigated and are described in a companion report (Henriksen and Dillon 2001).

The sensitivity of freshwaters in Ontario to acid deposition is defined in general terms by their location relative to the boundary of the 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. These waters are believed to be more sensitive to acid deposition than the ones located south of the Precambrian Shield. The climate of the study area is north temperate, with long-term average precipitation ranging between about 80–110 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. Critical loads for S and N have been estimated for 291 lakes in the Muskoka river catchment, south-central Ontario. The Muskoka river catchment extends into four districts (Muskoka, Haliburton, Nipissing and Parry Sound) and is entirely located on the Precambrian Shield. Critical load exceedances have been estimated using S and N deposition data for the period 1976–1999. Sulphur deposition in Muskoka shows a clear downward trend during the study period. The decrease of more than 50% is consistent with decreases in S emissions in eastern Canada and the north-eastern USA. There has been no significant trend or change in N deposition over the study period. As a result of the declining deposition, the portion of lakes with critical load exceedances has dropped substantially, from approximately 90% in the late 1970s to 40% in the late 1990s.

In addition to the information collected on the Muskoka river catchment lakes via chemical surveys, eight lakes have been sampled regularly since 1980. Deposition of S and N on Heney and Plastic lakes exceeded their critical load over the entire study period. Similarly, Chub and Crosson lakes exceeded their critical load over the entire period except for the 1997–1998 hydrological year, which had unusually low S and N deposition due to low rainfall volume. In contrast, Blue Chalk Lake did not exceed critical load after 1982. Under current depositions of S and N, four of the eight lakes exceed their critical load. Differences between the SSWC and FAB model results are expected as the FAB model takes into account N retention in the lake and in the terrestrial catchment. As such, the decrease in acid sensitivity for Plastic and Blue Chalk is explained by their high lake:catchment ratios and more importantly their high N mass transfer coefficients. This is clearly seen in the fraction of N deposition retained in Blue Chalk (> 70%) and Plastic (> 60%) lakes compared to the other lakes (40–50%).

# 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 United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) established an International Collaborative Programme on Modelling and Mapping Critical Levels and Loads under the Working Group on Effects to develop and agree upon methods for calculating and mapping critical loads. Critical load 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 currently accepted 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 (S) deposition, used in the negotiations of the Second Sulphur Protocol, signed in Oslo in 1994 (UNECE 1994). To prepare the scientific support for the negotiations of a revised protocol on the reduction of nitrogen (N) emissions, a new methodology was developed to take into account multiple effects (i.e. acidification and eutrophication) of multiple pollutants (S and N). Since both S and N 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 methodology was used in the negotiations for the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone signed in Gothenburg, Sweden, in December 1999 (UNECE 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 neutralising capacity (ANC). The present value for the (ANC) is based on the response of fish (brown trout) to the ANC of the lake-water.

In the FAB model (Posch et al. 1997, Henriksen and Posch 2001) 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 forest soil critical loads (UBA 1996, Posch and de Vries 1999). In addition to processes in the terrestrial catchment soils, such as uptake, immobilisation, and denitrification, the FAB model also takes into account the in-lake retention of S and N. Furthermore, the acidity critical load, CL(A), estimated by the SSWC model is used as an input to the FAB 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 S emission reductions, and in particular, on the interactions of acid deposition and climate phenomena, including long-term climate change. One of the projects that has been undertaken is designed to evaluate the critical S and N 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. The Norwegian Institute for Water Research (NIVA) was approached to assist in applying these critical load models to lakes in this region of Ontario, Canada. Using the FAB model, critical loads for S and N have been estimated for: (a) the Muskoka river catchment south-central Ontario (291 lakes); and (b) eight long-term study lakes in south-central Ontario, which have been sampled intensively since at least 1980. The overall objective of this report is to investigate the exceedance of critical loads of S and N, using the FAB model, for lakes in south-central Ontario. Critical loads of acidity, using the SSWC model, have also been recently investigated and are described in a companion report (Henriksen and Dillon 2001).

## 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 the Precambrian Shield (Figure 1). Those waters that are on the Shield are situated in a region of predominately silicate bedrock, which is overlain by thin glacial tills. There are many localised 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  $\mu\text{S}$  and 40  $\mu\text{S}$ ) 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.



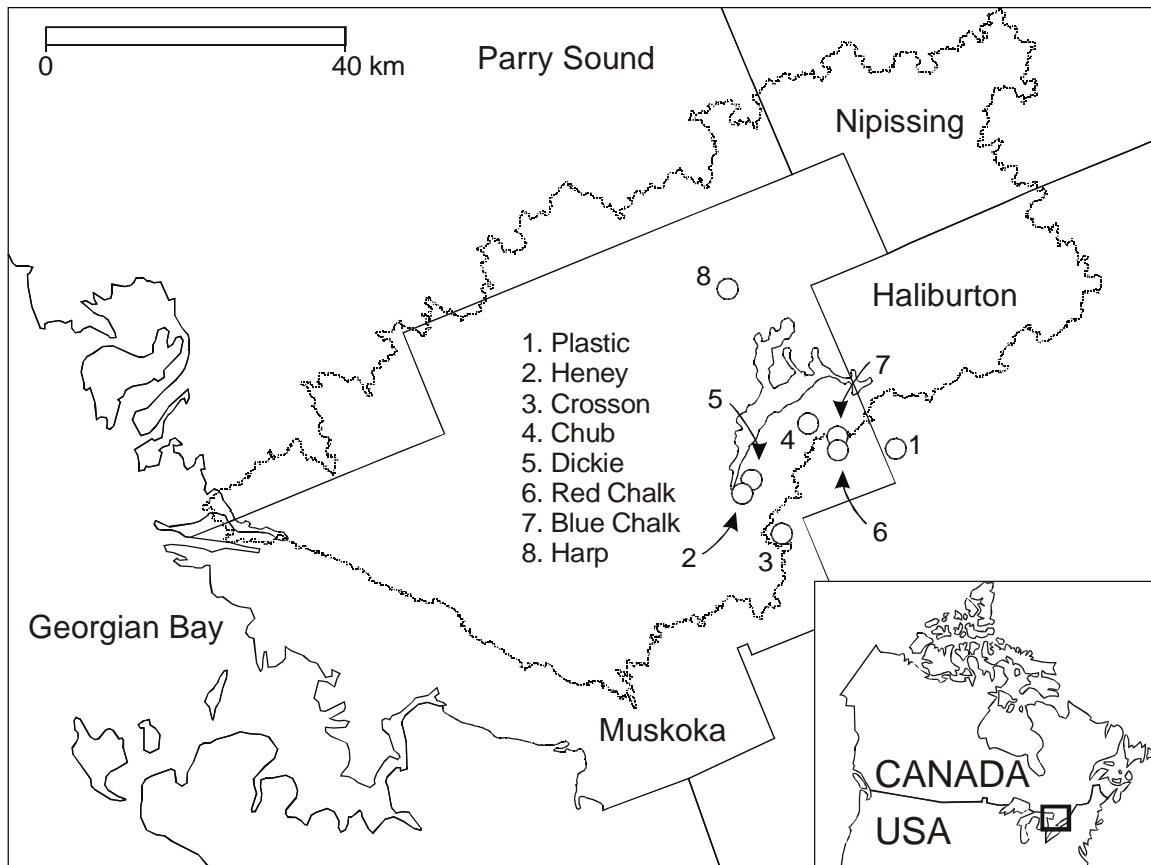
**Figure 1.** Map of Ontario with the Precambrian Shield shaded. Areas to the south (the St. Lawrence Lowlands) and the north (the Hudson Bay Lowlands) have calcareous bedrock and soils, and lakes and streams in these regions are generally insensitive to acid deposition.



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

On the Precambrian 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 Muskoka river catchment extends into four districts (Muskoka, Haliburton, Nipissing, and Parry Sound) in south-central Ontario (Figure 2). However, the majority of the catchment is located in the district of Muskoka. Similarly, seven of the eight long-term study lakes are situated in the Muskoka district, with the remaining lake situated in Haliburton (Figure 2). All lakes in the current study are located on the Precambrian Shield. Further details for the regional data-set and the eight long-term study lakes are given in Henriksen and Dillon (2001).



**Figure 2.** Location of the study area (Muskoka river catchment: dotted line) and the eight long-term study lakes in south-central Ontario.

### c. Data collection

Chemical data for the lakes in the Muskoka river catchment have been collected during the course of a number of different research projects and lake surveys over the period 1981–1995, with most of the data collected between 1983 and 1988. In cases where data from more than one year were available for any lake, the average value was used for that lake. 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. For the eight lakes that have been studied extensively for over 20 years (Dillon and Molot 1997), data collected throughout the year as whole-lake, morphometrically weighted samples (Dillon et al. 1997) were available for each year (see Table 1 for selected chemical variables). Depending on the year, between 8 and 26 samples were collected per lake 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).

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. Earlier data using different methods, e.g. colourimetric 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 (1983).

In addition to chemical data, the FAB model requires measured or estimated runoff within each catchment. Runoff coefficients ( $\text{m yr}^{-1}$ ) were interpolated from measured 30-year average runoff at all long-term hydrologic gauging stations throughout Ontario to produce a provincial runoff map (Cumming Cockburn Ltd., unpublished map). Measured catchment runoff is available for the eight long-term study lakes (Table 1). The catchment and lake sizes as well as the fraction of forest, wetland and open land (Table 1), required by the FAB model, have been derived from digitised maps (Ontario Base Maps 1:50,000 scale).

**Table 1.** Average runoff, selected chemistry, lake and catchment sizes, and the fraction of forest and wetland for the eight long-term study lakes and the Muskoka river catchment ( $n = 291$  lakes).

Lake	Runoff mm	Ca <sup>2+</sup> µeq L <sup>-1</sup>	Mg <sup>2+</sup> µeq L <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> µeq L <sup>-1</sup>	Lake ha	Terrestrial ha	Forest %	Peat %
Blue Chalk Lake	0.514	126.45	59.72	128.91	52.35	105.92	98.6	0.0
Chub Lake	0.485	113.74	52.53	145.71	34.41	271.84	94.0	4.4
Crosson Lake	0.558	104.13	47.89	138.37	56.74	521.75	86.4	7.4
Dickie Lake	0.511	125.53	51.11	133.22	93.60	406.42	86.1	13.9
Harp Lake	0.543	143.90	72.99	149.71	71.38	470.66	92.6	6.3
Heney Lake	0.515	92.21	42.77	128.37	21.37	71.66	96.0	3.6
Plastic Lake	0.512	91.78	36.56	129.62	32.14	95.50	93.7	4.2
Red Chalk Lake	0.548	126.50	63.99	136.44	57.13	374.09	91.0	3.4
Muskoka catchment <sup>†</sup>	0.509	140.02	60.75	148.60	120.66	686.73	89.2	4.0

<sup>†</sup> Average lake and catchment values for 291 lakes.

## 2. The First-order Acidity Balance (FAB) model

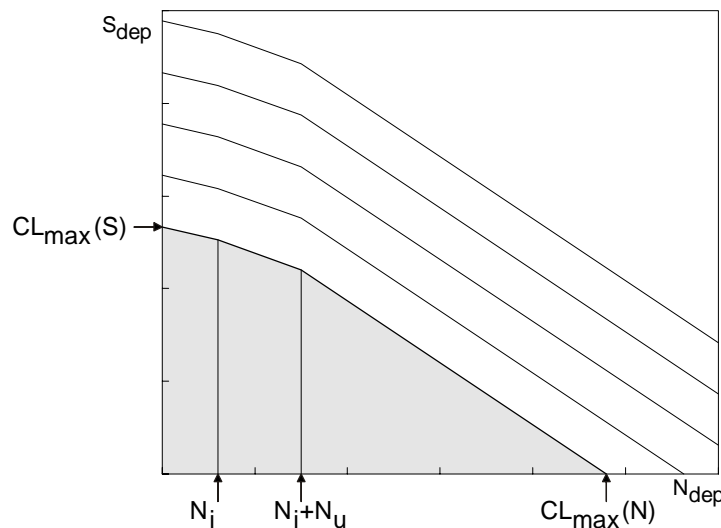
The FAB model accounts for the sources and sinks of S and N in a simple, but explicit way, both in the terrestrial catchment (uptake, immobilisation and denitrification) as well as in the lake/sediment (retention). The FAB model is described in detail in Appendix A following the most recent published descriptions of the model (Hindar et al. 2000, Henriksen and Posch 2001). In brief, the FAB model is made “compatible” with the SSWC model by inserting its acidity critical load,  $CL(A)$ , for the base cation and  $ANC_{limit}$  runoff, i.e.,  $L_{crit} = CL(A)$  (see Equation 9, Appendix A). There is no unique critical load, but every pair of N and S deposition,  $(N_{dep}, S_{dep})$ , satisfying the following equation is called a critical load:

$$(1 - \rho_S) \cdot S_{dep} + (1 - \rho_N) \cdot b_N \cdot N_{dep} = (1 - \rho_N) \cdot M_N + CL(A) \quad (1)$$

where  $b_N$  and  $M_N$  depend on the denitrification fraction in soils, the net uptake of N and the net immobilisation of N and are a fraction of  $N_{dep}$  (see Appendix A). The in-lake retention coefficients ( $\rho_S$  and  $\rho_N$  for S and N, respectively) are modelled by a kinetic equation (Kelly et al. 1987, Dillon and Molot 1990):

$$\rho_N = \frac{s_N}{s_N + \frac{Q}{r}} \quad (2)$$

where  $Q$  is catchment runoff,  $s_N$  is the net mass transfer coefficient for N ( $m \text{ yr}^{-1}$ ) and  $r$  is the lake: catchment ratio. An analogous equation holds for  $\rho_S$  with mass transfer coefficient  $s_S$  (Baker and Brezonik 1988). Equation 1 defines the so-called Critical Load Function (CLF) of a lake (Figure 3). The intercepts of the CLF on the  $S_{dep}$  and  $N_{dep}$  axes define the “maximum” critical loads of S and N, i.e. the critical load for either S or N alone. All combinations of  $S_{dep}$  and  $N_{dep}$  lying below the CLF (grey-shaded area) do not exceed critical loads (see Appendix A).



**Figure 3.** Critical Load Function (CLF) for S and acidifying N as defined by catchment properties. The thin lines parallel to the CLF are isolines of excess acidity leaching (Henriksen and Posch 2001).

### 3. Data requirements

For the calculation of the critical load of S and N for a lake using the FAB model, the following data are required (see Appendix A):

- SSWC critical load of acidity (lake chemistry and annual average catchment runoff)
- Catchment and lake sizes as well as the fraction of forest, wetland and open land
- Net mass transfer coefficients for S and N
- Denitrification rates within the catchment soils
- Net N immobilisation rates within the catchment soils
- Net N uptake rates by forests within the catchment

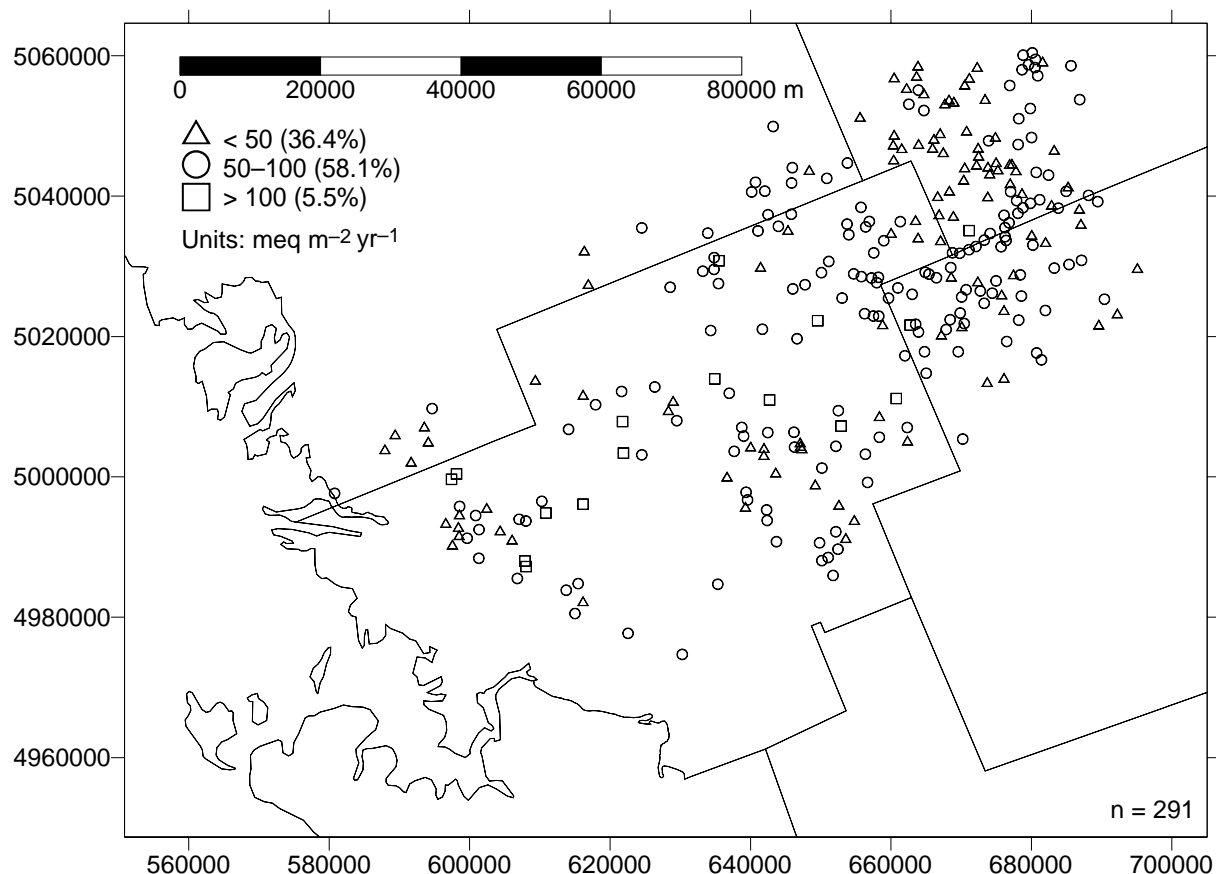
The successful application of the FAB model requires the estimation of the net mass transfer coefficients for S and N in lakes, and N immobilisation, N uptake and denitrification fraction within the terrestrial catchments. These parameters are notoriously difficult to estimate and FAB model applications typically rely on default values that are generally applied across large regions. The values selected for each parameter in the current study are discussed in more detail below. Further background information can be found in Grennfelt and Thörnelöf (1992), Hornung et al. (1995), Rihm 1996 and UBA (1996).

#### a. Critical load of acidity

The SSWC critical loads of acidity, CL(A), 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. The buffer required to protect selected biota is represented by the  $ANC_{limit}$ . SSWC critical loads have previously been estimated for south-central Ontario (Henriksen and Dillon 2001, see Figure 4). Critical ANC values for biodiversity have been developed for Ontario lakes. Based on zooplankton species composition and species richness models, Holt et al. (2002) estimated that the critical pH value fell between 5.98 and 6.07, and that the critical alkalinity was between  $19 \mu\text{eq L}^{-1}$  and  $33 \mu\text{eq L}^{-1}$ . A value of  $40 \mu\text{eq L}^{-1}$  was selected to provide a margin of safety (Henriksen and Dillon 2001). For further details on the SSWC model and its application to south-central Ontario see Henriksen and Dillon (2001).

#### b. Mass transfer coefficients

The mass transfer coefficients describe the net loss of the substance (S or N) from the water column by all mechanisms other than flushing via the lake outflow (Kaste and Dillon 2002). The N mass transfer coefficients ( $s_N$ ) are typically based on nitrate ( $\text{NO}_3^-$ ) mass balance data. Due to a lack of observation data, a default value for  $s_N$  of  $5 \text{ m yr}^{-1}$  is generally applied (Henriksen and Posch 2001), which is based on the range  $2\text{--}8 \text{ m yr}^{-1}$  given by Dillon and Molot (1990). However, Kaste and Dillon (2002) suggested that it is more appropriate to use the mass transfer coefficients for total inorganic nitrogen (TIN) rather than  $\text{NO}_3^-$ . Estimates for  $s_N$ , based on TIN, have been used in the current study. Values for the eight long-term study lakes range between  $5.9\text{--}11.4 \text{ m yr}^{-1}$  (Table 2, Kaste and Dillon 2002), the average value ( $7 \text{ m yr}^{-1}$ ) has been selected for the lakes in the Muskoka river catchment. A default value of  $0.5 \text{ m yr}^{-1}$  has been selected for the S mass transfer coefficient ( $s_S$ ) for the eight long-term study lakes and the Muskoka river catchment lakes. This is based on the range  $0.2\text{--}0.8 \text{ m yr}^{-1}$  given by Baker and Brezonik (1988).



**Figure 4.** Spatial distribution of the SSWC critical loads of acidity, CL(A), for lakes ( $n = 291$ ) in the Muskoka river catchment. Details on lake chemistry and the application of the SSWC model are given in Henriksen and Dillon (2001). Note: co-ordinate projection is World Geodetic System 1984, Universal Transverse Mercator Zone 17N.

### c. Denitrification

Denitrification is the process in which N is lost to the atmosphere under anaerobic soil conditions. Based on a compilation of denitrification rates, Ineson (1992) demonstrated that denitrification rate increases linearly with N deposition. In Europe, denitrification has been modelled by using fixed values based on soil type (e.g., see Hall et al., 1997 for United Kingdom values) or as a fraction of available N, i.e., a denitrification fraction,  $f_{de}$ . The denitrification fraction depends on soil type and its moisture status; Posch et al. (1997) suggested a model based on the fraction of peat soils in a catchment, which has been used in the current study:

$$f_{de} = 0.1 + 0.7 \cdot f_{peat} \quad (3)$$

where  $f_{peat}$  is the proportion of peat soils within the catchment. This equation is based on the assumption that in peat soils, denitrification of net nitrogen inputs could reach a maximum of 80%, while the minimum denitrification fraction for other soil types would be around 10% (Posch et al. 1997).

#### **d. Nitrogen immobilisation**

For critical load calculations N immobilisation,  $N_i$ , refers to the long-term storage of N in soil organic matter. It may be reasonable to assume that ‘long-term’ refers to at least 50–200 years. Chronosequence studies, where the total N content of soil profiles is divided by the age of the profile (assumed to be 10,000 years since the last glaciation) indicate long-term immobilisation rates in the range of 3.6–7.1  $\text{meq m}^{-2} \text{yr}^{-1}$  (UBA 1996). However, under current conditions with increased N cycling due to increased N deposition, this range may be higher. Hornung et al. (1995) suggest a range of 7.1–21.4  $\text{meq m}^{-2} \text{yr}^{-1}$  depending on warm–cold climate for coniferous and deciduous forests. Based on this, a default value of 14.3  $\text{meq m}^{-2} \text{yr}^{-1}$  has been used in the current study. This is in agreement with recent studies on critical load for forest soils in the region (Watmough and Dillon, 2002).

#### **e. Nitrogen uptake**

Nitrogen uptake,  $N_u$ , refers to the net removal of N in biomass from catchments through harvesting of forests. Estimates of harvesting removal vary depending on forest type, harvesting practice (e.g., whole-tree or stem-only harvest) and forest age. Hornung et al. (1995) suggest a range of 15–70  $\text{meq m}^{-2} \text{yr}^{-1}$  for coniferous forests and a range of 35–100  $\text{meq m}^{-2} \text{yr}^{-1}$  for deciduous forests depending on low–high vegetation growth. In the current study,  $N_u$  has been set to zero, i.e., no harvesting or removal of biomass is accounted for. However, it is known that harvesting is a common occurrence in south-central Ontario (Watmough and Dillon, 2002) and more research is needed to adequately quantify the removal of biomass through harvesting and the impacts on critical load estimates.

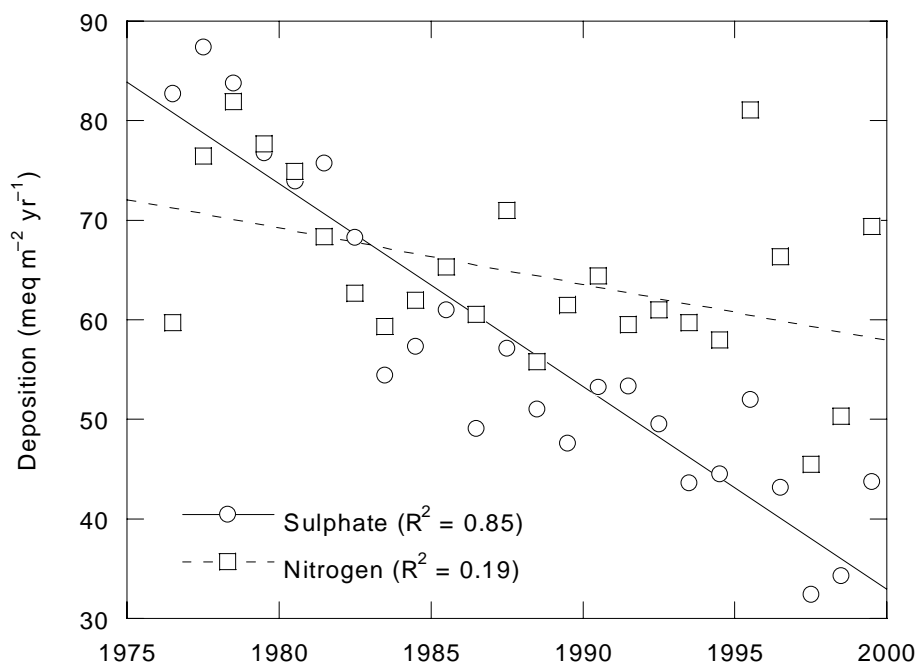
## **4. Critical loads and exceedances for Ontario lakes**

### **a. Deposition of sulphate and nitrogen**

Deposition of S and N are required for exceedance calculations. Deposition has been measured in Muskoka as part of the research program conducted on the eight long-term study lakes since 1976 (Dillon et al. 1988). Either four (1976–1989) or three (1990–present) stations located in this region were used to generate a single daily value for deposition for the Muskoka catchment; daily values were summed to give annual deposition. All measurements were made as bulk deposition using Teflon-coated, 0.25  $\text{m}^2$ , continuously open collectors (Dillon et al. 1988). Independent measurements of wet-only S deposition combined with estimates of dry S deposition based on measured  $\text{SO}_2$  and particulate  $\text{SO}_4^{2-}$  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 deposition at these sites are representative of deposition to the region. Deposition of N and S is given in Figure 5; data are presented as hydrological years, June 1 to May 31, e.g., 1976 represents the average deposition from June 1976 to May 1977.

Sulphur deposition in Muskoka shows a clear downward trend during the study period ( $R^2 = 0.85$ ). The decrease of more than 50% in deposition is consistent with decreases in S emissions in eastern Canada where a 50–55% decline has occurred over the past two decades (Clair et al. 1995), and decreases in the north-eastern USA where emissions have dropped by about 30% between 1980 and 1995 (Stoddard et al. 1999). There has been no significant trend or change in N deposition over the course of the study, which is consistent with the fact that estimates of emissions suggest no changes. Nitrate deposition is currently equivalent to S deposition (approximately 40  $\text{meq m}^{-2} \text{yr}^{-1}$ ). Total

nitrogen ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) is therefore quite considerable, making N the parameter of most concern since both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can lead to acidification of soils and waters. In addition, emissions are unlikely to decrease for some time. The annual average depositions (1995–1999) for S and N are  $41.1 \text{ meq m}^{-2} \text{ yr}^{-1}$  and  $62.5 \text{ meq m}^{-2} \text{ yr}^{-1}$ , respectively.



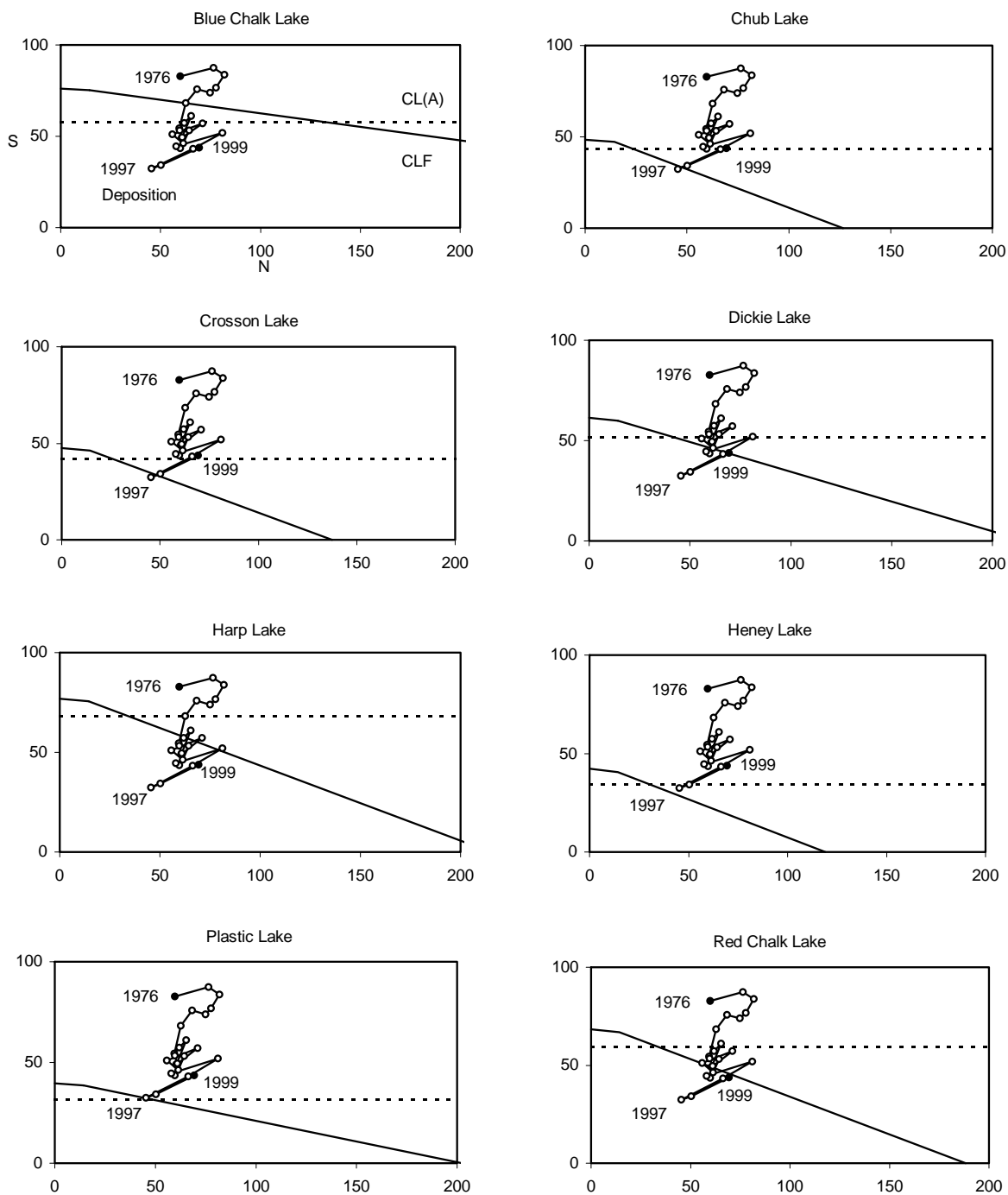
**Figure 5.** Sulphur (circles) and nitrogen (squares) deposition ( $\text{meq m}^{-2} \text{ yr}^{-1}$ ) at Dorset, Ontario, for the hydrological years (June 1–May 31) for the period June 1976 – May 2000.

## b. Critical loads for the eight long-term study lakes

The critical load functions (CLFs) have been computed for the eight long-term study lakes (Table 2 and Figure 6). The intercepts of the CLF on the  $S_{\text{dep}}$  and  $N_{\text{dep}}$  axes define the ‘maximum’ critical loads of S and N, i.e., the critical load for either S or N alone (Table 2). All combinations of  $S_{\text{dep}}$  and  $N_{\text{dep}}$  lying below the CLF do not exceed critical loads (see Section 2 or Appendix A). In Figure 6 the CLFs for the eight lakes are plotted along with the SSWC critical loads, CL(A), and the temporal development of S and N deposition (1976–1999). Deposition of S and N on Heney and Plastic lakes exceeded their critical load during all years. Similarly, Chub and Crosson lakes exceeded their critical load over the entire period except for the 1997–1998 hydrological year, which had unusually low S and N deposition due to low rainfall volume. In contrast, Blue Chalk Lake did not exceed critical load after 1982. Four of the eight lakes currently exceed critical load for S and N based on the FAB model.

For every pair of deposition ( $N_{\text{dep}}$ ,  $S_{\text{dep}}$ ) lying on or below the CLF neither critical loads of N nor S are exceeded. Since it is impossible to define unique critical loads of N and S, it is also impossible to define a unique exceedance in the sense of quantifying the amount of S and N to be reduced. However, it is possible to define an exceedance function via the charge balance which describes the excess leaching, i.e., the leaching above the limit set by the critical ANC (see Equation 18 Appendix A). The exceedance leaching,  $\text{Ex}_{\text{le}}$ , is the excess acidity (or ANC) leached from the soil after all

transformations have taken place, as opposed to the amount of N and S deposition to be reduced to reach non-exceedance.



**Figure 6.** Critical load functions (CLFs) for the long-term study lakes ( $\text{meq m}^{-2} \text{ yr}^{-1}$ ). Also shown, as a dashed horizontal line, is the critical load of acidity, CL(A), estimated with the SSWC model (Henriksen and Dillon 2001) and the temporal development of S and N deposition (1976–1999; filled circles represent first and last years).



**Table 2.** Lake to catchment ratio, N mass transfer coefficients, SSWC critical loads of acidity, maximum critical loads for S and N, and the fraction of N retained in the terrestrial catchment and the lake.

Lake	r	$s_N$ m yr <sup>-1</sup>	CL(A)	CLmax(S)	CLmax(N)	$N_{terr}^\dagger$	$N_{lake}^\dagger$
			meq m <sup>-2</sup> yr <sup>-1</sup>			%	%
Blue Chalk	0.33	11.4	57.56	76.08	522.80	20.17	70.25
Chub	0.11	5.9	43.41	48.44	126.60	27.26	42.01
Crosson	0.11	6.1	41.83	47.60	137.47	26.63	46.03
Dickie	0.19	6.8	51.83	61.32	216.25	25.66	53.04
Harp	0.13	6.5	68.15	76.85	215.06	26.95	45.58
Heney	0.23	4.2	34.54	42.24	119.06	23.71	49.74
Plastic	0.26	9.1	31.76	39.71	202.55	22.62	63.45
Red Chalk	0.14	5.7	59.37	68.24	188.32	25.39	47.01

<sup>†</sup> Presented as a fraction of annual average N deposition, 62.5 meq m<sup>-2</sup> yr<sup>-1</sup> (1995–1999).

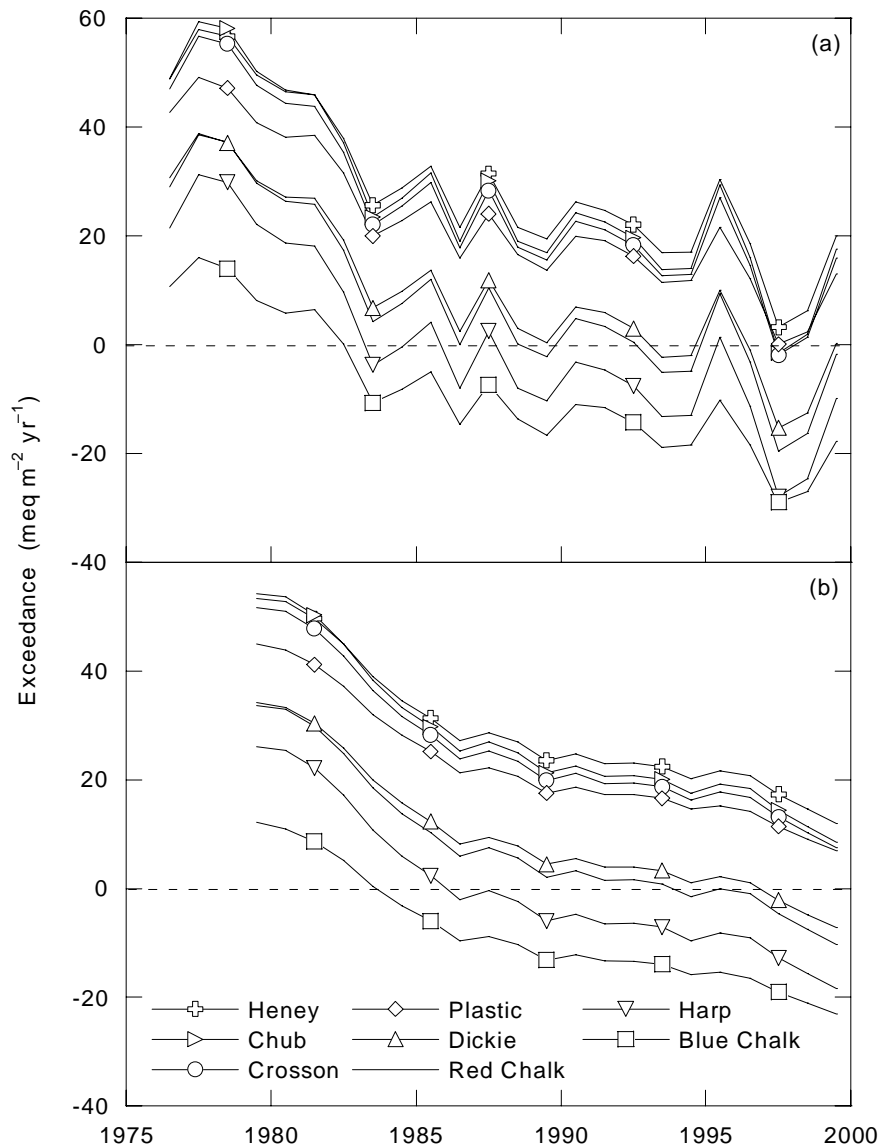
The temporal development of  $Ex_{le}$  has been estimated for the entire deposition period (Table 3 and Figure 7). In Figure 7, lakes have been arranged in decreasing order of sensitivity. There is a clear divide between four more-sensitive and four less-sensitive lakes. However, due to the considerable year-to-year variation in deposition, it is more reasonable to use the four-year moving average  $Ex_{le}$  (Figure 7b).

**Table 3.** Exceedance leaching for the eight long-term study lakes (see Equation 18 Appendix A).

Year <sup>†</sup>	Blue Chalk	Chub	Crosson	Dickie	Harp	Heney	Plastic	Red Chalk
	meq m <sup>-2</sup> yr <sup>-1</sup>							
1976	10.73	48.93	47.08	30.74	21.49	48.85	42.69	28.97
1977	16.09	59.36	56.63	38.81	31.15	57.91	49.12	38.56
1978	13.96	58.18	55.26	37.13	29.77	56.69	47.13	37.25
1979	8.18	50.30	47.70	30.14	22.14	49.61	40.82	29.73
1980	5.78	46.77	44.35	27.10	18.75	46.47	38.15	26.39
1981	6.40	45.89	43.76	26.97	18.15	45.85	38.50	25.75
1982	0.10	37.06	35.32	19.24	9.63	37.95	31.59	17.36
1983	-10.71	23.42	22.08	6.73	-3.73	25.59	20.00	4.22
1984	-8.27	26.95	25.44	9.78	-0.34	28.74	22.70	7.56
1985	-5.08	31.57	29.83	13.78	4.09	32.86	26.23	11.94
1986	-14.63	19.07	17.77	2.50	-8.08	21.59	15.91	-0.04
1987	-7.39	30.21	28.27	11.90	2.53	31.47	24.05	10.44
1988	-13.73	18.99	17.88	2.92	-7.98	21.64	16.65	0.03
1989	-16.69	16.87	15.57	0.32	-10.30	19.55	13.78	-2.21
1990	-11.09	24.21	22.66	6.94	-3.15	26.18	19.83	4.83
1991	-11.55	22.49	21.16	5.82	-4.67	24.73	19.12	3.30
1992	-14.27	19.61	18.28	2.96	-7.57	22.07	16.31	0.47
1993	-18.89	13.85	12.68	-2.35	-13.22	16.85	11.38	-5.09
1994	-18.40	13.99	12.89	-2.03	-13.01	17.02	11.81	-4.90
1995	-10.19	29.36	27.03	10.04	1.29	30.42	21.55	9.29
1996	-18.44	16.00	14.52	-1.02	-11.36	18.63	12.15	-3.21
1997	-28.93	-1.56	-1.85	-15.36	-27.90	3.18	0.10	-19.59
1998	-27.00	1.91	1.36	-12.60	-24.66	6.21	2.36	-16.37
1999	-17.73	17.58	15.95	0.15	-9.91	19.99	13.04	-1.78

<sup>†</sup> Hydrological year (June 1–May 31).

From the four-year moving average, the divide between lakes is more distinct; Heney, Chub, Crosson and Plastic are the most sensitive lakes and exceed critical load over the entire period. According to the SSWC model, Plastic Lake has the lowest critical load (Table 2 and Figure 6) and as such the greatest exceedance. However, based on the FAB model, Plastic has the lowest  $Ex_{I_e}$  of the four most sensitive lakes. Similarly, based on the FAB model Blue Chalk Lake is the least sensitive lake (Figure 7) as opposed to Harp Lake according to the SSWC model (Table 2).

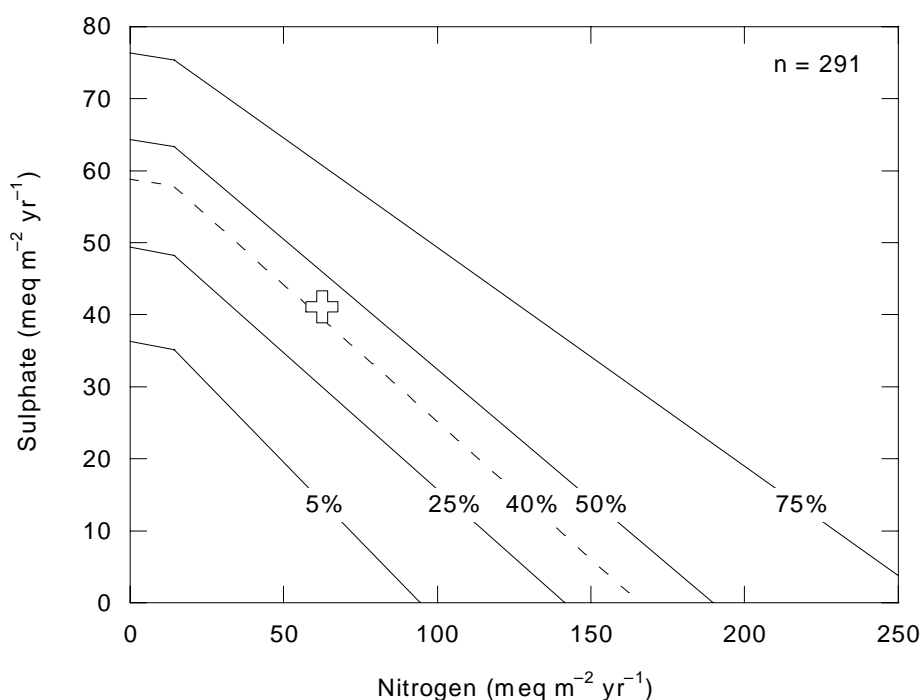


**Figure 7.** (a) Exceedance,  $Ex_{I_e}$ , for the eight long-term study lakes arranged by decreasing order of sensitivity ( $\text{meq m}^{-2} \text{yr}^{-1}$ ); (b) Four-year moving averages for exceedance for the eight long-term study lakes ( $\text{meq m}^{-2} \text{yr}^{-1}$ ).

The difference between the two models is expected as the FAB model takes into account N retention in the lake and in the terrestrial catchment. As such, the decrease in sensitivity for Plastic and Blue Chalk is explained by their high lake:catchment ratios and more importantly their high N mass transfer coefficients (Table 2). This is clearly seen in the fraction of N deposition retained in Blue Chalk (> 70%) and Plastic (> 60%) lakes (Table 2) compared to the other lakes (40–50%). Higher in-lake inorganic N retention typically increases critical load in lakes by making them less susceptible to acid deposition (Hindar et al. 2001). Most of the N deposited is retained in the lake system and a smaller fraction is retained in the terrestrial system for the eight long-term study lakes (Table 2).

### c. Critical loads for the Muskoka river catchment lakes

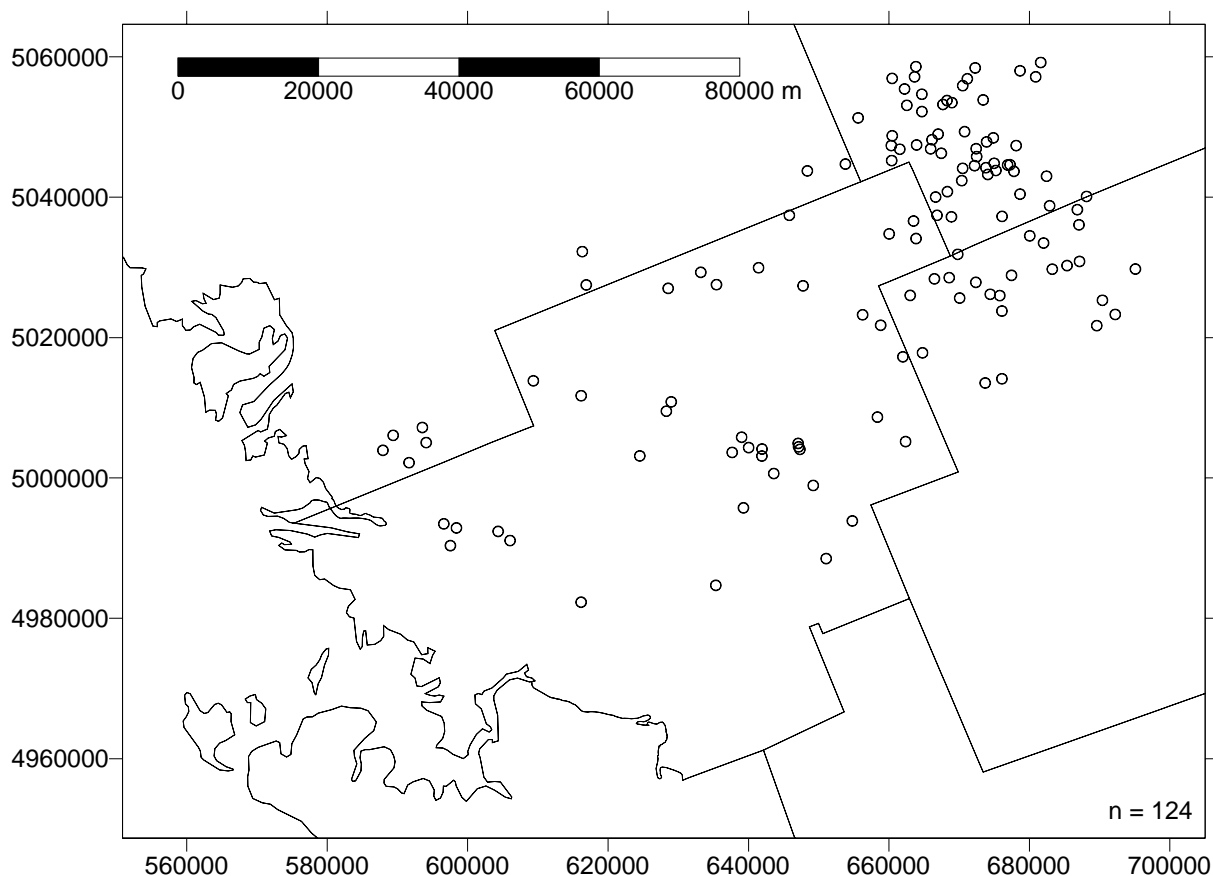
Similar to the eight long-term study lakes, CLFs have been estimated for each of the 291 lakes in the Muskoka river catchment. The large number of CLFs have been aggregated using percentiles (Figure 8). The simultaneous treatment of S and N does not allow the calculation of a single critical load value, and thus the concept of a percentile has to be generalised. The 5<sup>th</sup>, 25<sup>th</sup>, 40<sup>th</sup>, 50<sup>th</sup> and 75<sup>th</sup> percentile functions for the Muskoka river catchment are shown in Figure 8. All combinations of  $N_{\text{dep}}$  and  $S_{\text{dep}}$  lying below the p-th percentile function protect 100-p percent of the lakes. Approximately 40% of the lakes exceed critical load (60 % are protected) based on S and N deposition (41.1 meq m<sup>-2</sup> yr<sup>-1</sup> and 62.5 meq m<sup>-2</sup> yr<sup>-1</sup>, respectively) for the period 1995–1999 (see cross in Figure 8).



**Figure 8.** Percentile distributions of the CLFs for the Muskoka river catchment lakes (meq m<sup>-2</sup> yr<sup>-1</sup>). Also shown is the annual average deposition of S and N (41.1 meq m<sup>-2</sup> yr<sup>-1</sup> and 62.5 meq m<sup>-2</sup> yr<sup>-1</sup>, respectively) for the period 1995–1999 (cross).

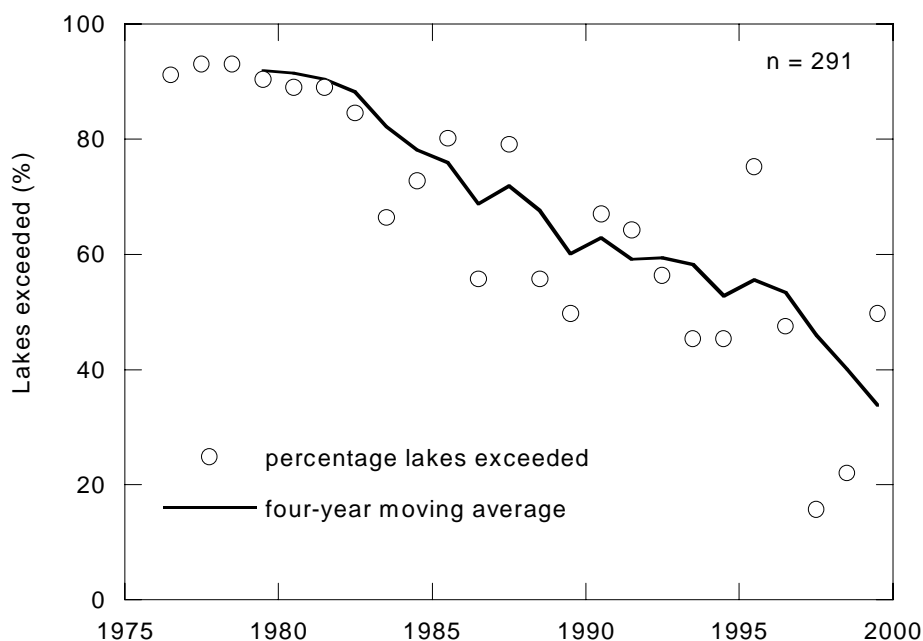
The spatial distribution of lakes in the Muskoka river catchment with exceedance of critical load is shown in Figure 9. In total, 124 lakes (42.6%) exceed critical load; the majority of lakes are located at the intersection of the four districts (Muskoka, Haliburton, Nipissing, and Parry Sound; see Figure 2),

with the greatest proportion of exceeded lakes in Nipissing (Figure 9). Nipissing also has the lowest SSWC critical loads of acidity (see Figure 4).

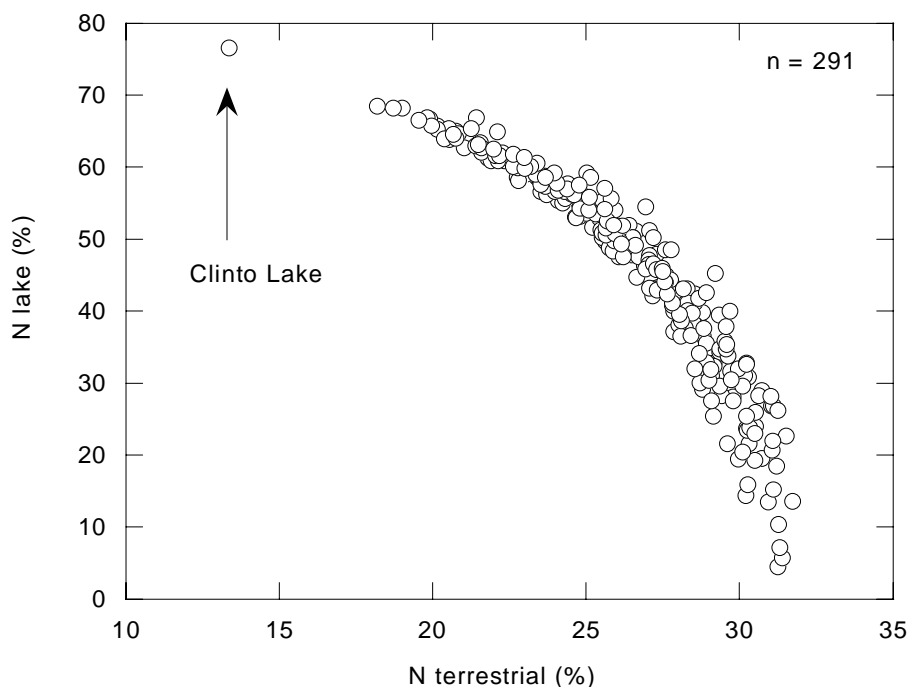


**Figure 9.** Lakes in Muskoka river catchment with acid deposition greater than their critical load, i.e., lakes with exceedance of critical load (42.6%). Exceedance is based on the annual average deposition of S and N ( $41.1 \text{ meq m}^{-2} \text{ yr}^{-1}$  and  $62.5 \text{ meq m}^{-2} \text{ yr}^{-1}$ , respectively) for the period 1995–1999. Note: co-ordinate projection is World Geodetic System 1984, Universal Transverse Mercator Zone 17N.

The proportion of lakes that exceed critical load each year have been estimated for the entire deposition period (Figure 10). As a result of the declining deposition, the portion of lakes with critical load exceedances has dropped substantially, from approximately 90% in the late 1970s to 60% in the late 1990s. However, due to the considerable year-to-year variation in deposition, it is more reasonable to use the four-year moving average. Using the four-year moving average, the decline is such that approximately 40% of the lakes still have exceedances. The fractions of N retained in each lake and its terrestrial catchment are shown in Figure 11. Retention is expressed as a fraction of annual average N deposition for the period 1994–1999 ( $62.5 \text{ meq m}^{-2} \text{ yr}^{-1}$ ). The in-lake N retention ranges from approximately 10–70% compared to the terrestrial catchment, which ranges from 20–30%. N retention is highly dependent on the lake:catchment ratio, this is clearly seen for Clinto Lake which has the highest lake:catchment ratio ( $r = 0.6$ ) and consequently the highest in-lake N retention (Figure 11). Retention of N in the terrestrial catchment is considerably more static as it depends on a constant N immobilisation plus a denitrification fraction based on the proportion of wetlands in the catchment. As such, lakes with a high in-lake N retention have a lower sensitivity to acidity, while those with a low in-lake retention may be more susceptible to acidity (Hindar et al., 2001).



**Figure 10.** Proportion (%) of lakes in the Muskoka river catchment ( $n = 291$ ) with exceedance of critical load over the period 1976–1999 (circles). Also shown is the four-year moving average of the proportion of lakes exceeded in the Muskoka river catchment.



**Figure 11.** Retention of N in the terrestrial catchment versus retention in the lake for the 291 lakes in the Muskoka river catchment (circles). Retention is expressed as a fraction of annual average N deposition for the period 1994–1999 ( $62.5 \text{ meq m}^{-2} \text{ yr}^{-1}$ ).

#### d. Uncertainties in critical load and exceedance estimates

The provision of some estimate of uncertainty is important and necessary for the subsequent interpretation of critical loads and their exceedances. Uncertainty arises from two sources: model structure and input data. Uncertainty in model structure refers to the importance that parameter values have on model output. The current application of the FAB model was based on a number of default parameter values, namely for the mass transfer coefficients (S and N) and N immobilisation. To investigate the importance of these parameters in the calculation of critical load for lakes in Muskoka river catchment, the number (and percentage) of lakes that exceed critical load have been estimated for different values of the S and N mass transfer coefficients and N immobilisation (Table 4). Uncertainty in input data is beyond the scope of this report. However, in general terms, data uncertainty is derived from two sources: chemical and physical lake data and deposition data. Both data-sets have undergone rigorous quality control and have been the focus of many peer-reviewed publications. As such, confidence in the data quality is high. For further descriptions on the data-sets see Clair et al. (1995), Dillon and Molot (1990, 1997), Dillon et al. (1988, 1997) and Henriksen and Dillon (2001).

The suggested default value for the S mass transfer coefficient is  $0.5 \text{ m yr}^{-1}$  (Henriksen and Posch, 2001), which is the mid-point of the range  $0.2\text{--}0.8 \text{ m yr}^{-1}$  given by Baker and Brezonik (1988). Varying the value from  $0.2$  to  $0.8 \text{ m yr}^{-1}$  had a slight effect on the number of exceeded lakes, with an 11% increase in exceeded lakes across the range applied (Table 4). Current research on the eight long-term study lakes suggests that the S mass transfer coefficients are nearer the lower end of the range reported by Baker and Brezonik (1988). This would cause only a slight increase in exceedance compared to the current study.

**Table 4.** Mass transfer coefficients ( $s_N$  and  $s_S$ ), nitrogen immobilisation ( $N_i$ ) and their effect on the number of lakes with exceedance of critical load in the Muskoka river catchment. Exceedance is based on the annual average deposition of S and N ( $41.1 \text{ meq m}^{-2} \text{ yr}^{-1}$  and  $62.5 \text{ meq m}^{-2} \text{ yr}^{-1}$ , respectively) for the period 1995–1999.

Parameter	Value	Units	Exceeded lakes	
			n	%
1. Sulphate mass transfer coefficient ( $s_S$ )	0.2	$\text{m yr}^{-1}$	143	49.1
	$0.5^\dagger$	$\text{m yr}^{-1}$	124	42.6
	0.8	$\text{m yr}^{-1}$	112	38.5
2. Nitrogen mass transfer coefficient ( $s_N$ )	4.0	$\text{m yr}^{-1}$	158	54.3
	$7.0^\dagger$	$\text{m yr}^{-1}$	124	42.6
	10.0	$\text{m yr}^{-1}$	107	36.8
3. Nitrogen immobilisation ( $N_i$ )	7.1	$\text{meq m}^{-2} \text{ yr}^{-1}$	134	46.0
	$14.3^\dagger$	$\text{meq m}^{-2} \text{ yr}^{-1}$	124	42.6
	21.4	$\text{meq m}^{-2} \text{ yr}^{-1}$	112	38.5

<sup>†</sup> Default values used in regional application

The default value used for the N mass transfer coefficient was  $7.0 \text{ m yr}^{-1}$ , which is the average of the range  $5.9\text{--}11.4 \text{ m yr}^{-1}$  given by Kaste and Dillon (2002) for the eight long-term study lakes. The generally applied default value is  $5 \text{ m yr}^{-1}$  (Henriksen and Posch 2001), which is based on the mid-point of the range  $2\text{--}8 \text{ m yr}^{-1}$  given by Dillon and Molot (1990). A range of  $4.0\text{--}10.0 \text{ m yr}^{-1}$  was used in the current uncertainty analysis to cover the majority of the ranges discussed above. Varying the N mass transfer coefficient from  $4.0$  to  $10.0 \text{ m yr}^{-1}$  had a noticeable effect on the number of exceeded lakes, with an 18% increase in exceeded lakes across the range applied (Table 4). However, current research

on the eight long-term study lakes suggests that the value of  $7.0 \text{ m yr}^{-1}$ , used in the current study, is towards the higher end of the range and a lower value may be more appropriate (e.g.,  $6.0 \text{ m yr}^{-1}$ ). This would cause only a slight increase in exceedance compared to the current study.

The default value used for N immobilisation was  $14.3 \text{ meq m}^{-2} \text{ yr}^{-1}$ , which is the mid-point of the range  $7.1\text{--}21.4 \text{ meq m}^{-2} \text{ yr}^{-1}$  given by Hornung et al. (1995). Varying the value from 7.1 to  $21.4 \text{ meq m}^{-2} \text{ yr}^{-1}$  had little effect on the number of exceeded lakes, with a  $< 9\%$  increase in exceeded lakes across the range applied (Table 4). The proportion of lakes that exceeded critical load decreases with higher mass transfer coefficients (S and N) and higher N immobilisation. This is expected, as higher values for these parameters result in higher S and N retention in the lake and N retention in the terrestrial catchment. Higher retention typically increases critical load making the lake less susceptible to acid deposition. Despite the potential uncertainties associated with using default parameter values, or a single value for the entire region, the critical loads appear to be quite stable as the number of lakes that exceed critical load were not greatly affected when the S and N mass transfer coefficients and N immobilisation were varied (Table 4). In general, the uncertainty analysis indicates that approximately 40–50% of the lakes exceed their critical load based on annual average deposition for the period 1995–1999.

## 5. Conclusions and recommendations

The work described here, which 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, is designed to evaluate the critical S and N 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, critical loads for S and N obtained using the FAB model are described. Critical loads have been estimated for 291 lakes in the Muskoka river catchment and eight long-term study lakes, which have been sampled regularly since 1980.

The sensitivity of freshwaters in Ontario to acid deposition is defined in general terms by their location relative to the boundary of the 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, and are more sensitive to acid deposition. Sulphur deposition in the study area shows a clear downward trend over the 1976–1999 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 USA. Over the same time period, there has been no significant trend or change in N deposition. However,  $\text{NO}_3^-$  deposition is currently equivalent to S deposition, making total N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) quite considerable and the parameter of most concern since both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can lead to acidification of soils and waters.

The critical load of S and N was exceeded for all eight long-term study lakes until 1983–1984. Deposition of S and N on Heney and Plastic lakes exceeded their critical load during all years. Similarly, Chub and Crosson lakes exceeded their critical load over the entire period except for the 1997–1998 hydrological year, which had unusually low S and N deposition due to low rainfall volume. In contrast, Blue Chalk Lake did not exceed critical load after 1982. Four of the eight lakes currently exceed critical loads for S and N based on the FAB model. There is a clear divide between four more-sensitive and four less-sensitive lakes; Heney, Chub, Crosson and Plastic are the most sensitive lakes. According to the SSWC model, Plastic Lake has the lowest critical load and as such the greatest exceedance. However, based on the FAB model, Plastic is the least sensitive of the four most sensitive lakes. Similarly, based on the FAB model Blue Chalk Lake is the least sensitive lake, as

opposed to Harp Lake according to the SSWC model. The difference between the two models is expected as the FAB model takes into account N retention in the lake and in the terrestrial catchment. As such, the decrease in sensitivity for Plastic and Blue Chalk is explained by their high lake:catchment ratios and more importantly their high N mass transfer coefficients. This is clearly seen in the fraction of N deposition retained in Blue Chalk (> 70%) and Plastic (> 60%) lakes compared to the other lakes (40–50%). Higher in-lake inorganic N retention typically increases critical load in lakes by making them less susceptible to acid deposition.

Approximately 40% of the lakes in the Muskoka river catchment exceed critical load (60 % are protected) based on S and N deposition for the period 1995–1999. In total, 124 lakes exceed critical load; the majority of lakes are located at the intersection of the four districts (Muskoka, Haliburton, Nipissing, and Parry Sound), with the greatest proportion of exceeded lakes in Nipissing. Nipissing also has the lowest SSWC critical loads of acidity. As a result of the declining deposition, the portion of lakes with critical load exceedances has dropped substantially, from approximately 90% in the late 1970s to 40% in the late 1990s. The provision of some estimate of uncertainty is important and necessary for subsequent interpretation of critical load and exceedance. Despite the potential uncertainties associated with using default parameter values or a single value for the entire region, the critical loads appear to be quite stable as the number of lakes that exceed critical load were not greatly affected when the S and N mass transfer coefficients and N immobilisation were varied. In general, the uncertainty analysis indicates that approximately 40–50% of the lakes exceed their critical load based on annual average deposition for the period 1995–1999.

The current application of the FAB model to the Muskoka river catchment assumed that all 291 lakes were headwater lakes (only 146 lakes are headwater lakes). Further evaluation on the effects of this assumption should be carried out. Hindar et al. (2001) modified the FAB model to deal with the many lakes connected by streams in the Killarney Park, Ontario, Canada. They found that lakes located downstream from other lakes were generally favoured by the in-lake retention of a larger fraction of deposited N than headwater lakes by increasing their critical loads and making them less sensitive to acid deposition. As such, the current study may have overestimated the extent of exceedance. Furthermore, the FAB model is based on expected steady-state conditions, and while it yields an estimate of the ultimate exceedance for any lake, it does not allow evaluation of when this state will be reached. Dynamic acidification models, such as MAGIC (Cosby et al. 2001), are required to estimate the time involved in attaining a certain lake chemical state in response to deposition changes. These more complex models may present a less optimistic picture.

## **Acknowledgements**

This work was supported by grants from Ontario Power Generation Inc. and Natural Sciences and Engineering Research Council of Canada to P.J. Dillon, and by the Ontario Ministry of the Environment. The authors would like to thank Caryn Perry (Ministry of Natural Resources, Peterborough, Canada) for generating the area-specific catchment data from the Ontario Base Maps.



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## Appendix A.

### The First-order Acidity Balance (FAB) model

Here we derive the so-called First-order Acidity Balance model (FAB model) for calculating critical loads of sulphur (S) and nitrogen (N) for a lake taking into account sources and sinks within the lake and its terrestrial catchment. The lake and its catchment are assumed small enough to be properly characterised by average soil and lake water properties. With  $A$  we denote the total catchment area (lake + terrestrial catchment),  $A_l$  is the lake area,  $A_f$  the forested area and  $A_g$  the area covered with grass/heath land; we have  $A_l + A_f + A_g \leq A$ , and a non-zero difference represents a land area on which no transformations of the deposited ions take place (“bare rocks”).

Starting point for the derivation of the FAB model is the charge balance (“acidity balance”) in the lake water running off the catchment:

$$(1) \quad S_{runoff} + N_{runoff} = BC_{runoff} - ANC_{runoff}$$

where BC stand for the sum of (non-marine) base cations and ANC is the acid neutralisation capacity. In the above equation we assume that the quantities are total amounts per time (e.g., eq yr<sup>-1</sup>). In order to derive critical loads we have to link the ions in the lake water to their depositions, taking into account also their sources and sinks in the terrestrial catchment and in the lake.

For  $X = S, N$  and BC the mass balance in the lake is given by:

$$(2) \quad X_{runoff} = X_{in} - X_{ret}, \quad X = S, N, BC$$

where  $X_{in}$  is the total amount of ion X entering the lake and  $X_{ret}$  the amount of X retained in the lake. The in-lake retention of S and N is assumed to be proportional to the input of the respective ion into the lake:

$$(3) \quad X_{ret} = \rho_X \cdot X_{in}, \quad X = S, N$$

where  $0 \leq \rho_X \leq 1$  is a dimensionless retention factor. Thus the mass balances for the lake become:

$$(4) \quad X_{runoff} = (1 - \rho_X) \cdot X_{in}, \quad X = S, N$$

The total amount of sulphur entering the lake is given by:

$$(5) \quad S_{in} = A \cdot S_{dep}$$

where  $S_{dep}$  is the total deposition of S per unit area. Immobilisation, reduction and uptake of sulphate in the terrestrial catchment are assumed negligible, and sulphate ad/desorption is not considered since we model steady-state processes only. Equation 5 states that all sulphur deposited onto the catchment enters the lake, and no sources or sinks are considered in the terrestrial catchment.

In the case of nitrogen we assume that immobilisation and denitrification occur both in forest and grass/heath land soils, whereas net uptake occurs in forests only (equalling the annual average amount

of N removed by harvesting); the deposition onto the remaining area (lake + “bare rocks”) enters the lake unchanged. Thus the amount of N entering the lake is:

$$(6) \quad N_{in} = (A - A_f - A_g) \cdot N_{dep} + A_f \cdot (N_{dep} - N_i - N_u - N_{de})_+ + A_g \cdot (N_{dep} - N_i - N_{de})_+$$

where  $N_{dep}$  is the total N deposition,  $N_i$  is the long-term net immobilisation of N (including fixation),  $N_{de}$  is N lost by denitrification, and  $N_u$  the net growth uptake of N, all per unit area. The symbol  $(x)_+$  or  $x_+$  is a short-hand notation for  $\max\{x, 0\}$ , i.e.,  $x_+ = x$  for  $x > 0$  and  $x_+ = 0$  for  $x \leq 0$ . The effects of nutrient cycling are ignored and the leaching of ammonium is considered negligible, implying its complete uptake and/or nitrification in the terrestrial catchment.

While immobilisation and net growth uptake are assumed independent of the N deposition, denitrification is modelled as fraction of the available N:

$$(7) \quad N_{de} = \begin{cases} f_{de} \cdot (N_{dep} - N_i - N_u)_+ & \text{on } A_f \\ f_{de} \cdot (N_{dep} - N_i)_+ & \text{on } A_g \end{cases}$$

where  $0 \leq f_{de} \leq 1$  is the (soil-dependent) denitrification fraction. The above equation is based on the assumption that denitrification is a slower process than immobilisation and growth uptake. Inserting Equation 7 into Equation 6 one obtains:

$$(8) \quad N_{in} = (A - A_f - A_g) \cdot N_{dep} + A_f \cdot (1 - f_{de}) \cdot (N_{dep} - N_i - N_u)_+ + A_g \cdot (1 - f_{de}) \cdot (N_{dep} - N_i)_+$$

If sufficient data for quantifying the sources and sinks of base cations in the catchment, such as deposition, weathering and uptake, are available, the runoff of base cations ( $BC_{runoff}$ ) could be described in the same way as S and N. This would be in analogy to the so-called SMB critical load model for (forest) soils. Alternatively, water quality data can be used to quantify the runoff of base cations and ANC, as is done in the SSWC model.

To arrive at an equation for critical loads, i.e., depositions of S and N which should not be exceeded, a link has to be established between a chemical variable and effects on aquatic biota. The most commonly used criterion is the so-called  $ANC_{limit}$ , i.e. a minimum concentration of ANC derived to avoid “harmful effects” on fish:  $ANC_{runoff,crit} = A \cdot Q \cdot [ANC]_{limit}$ .

Defining  $L_{crit} = (BC_{runoff} - ANC_{runoff,crit})/A$ , inserting Equations 5 and 8 into Equation 4 and Equation 1 and dividing by  $A$  yields the following equation to be fulfilled by critical depositions (loads) of S and N:

$$(9) \quad (1 - \rho_S) \cdot S_{dep} + (1 - \rho_N) \cdot \left\{ (1 - f - g) \cdot N_{dep} + f \cdot (1 - f_{de}) \cdot (N_{dep} - N_i - N_u)_+ + g \cdot (1 - f_{de}) \cdot (N_{dep} - N_i)_+ \right\} = L_{crit}$$

where we have defined:

$$(10) \quad f = A_f / A, \quad g = A_g / A \Rightarrow 1 - f - g \geq r \quad \text{with} \quad r = A_l / A$$

Equation 9 defines a function in the  $(N_{dep}, S_{dep})$  plane, the so-called critical load function, and in the following we will look at this function in more detail. The general form of the critical load function is:

$$(11) \quad a_S \cdot S_{dep} + a_N \cdot N_{dep} = L_N + L_{crit}$$

with

$$(12) \quad a_S = 1 - \rho_S, \quad a_N = (1 - \rho_N) \cdot b_N, \quad L_N = (1 - \rho_N) \cdot M_N$$

The quantity  $M_N$  and the dimensionless coefficient  $b_N$  depend on  $N_{dep}$ :

(a)  $N_{dep} \leq N_i$ : In this case  $(N_{dep} - N_i)_+ = 0$  and  $(N_{dep} - N_i - N_u)_+ = 0$ , which means that all N falling onto forests and grassland is immobilised and only the N deposition falling directly onto the lake and “bare rocks” contributes to the leaching of N:

$$(13) \quad b_N = b_1 = 1 - f - g, \quad M_N = M_1 = 0$$

(b)  $N_i < N_{dep} \leq N_i + N_u$ : In this case  $(N_{dep} - N_i)_+ = N_{dep} - N_i$ , but  $(N_{dep} - N_i - N_u)_+ = 0$ , meaning that all N deposition falling onto forests is immobilised or taken up, but N falling onto the other areas is (partially) leached:

$$(14) \quad b_N = b_2 = 1 - f - g \cdot f_{de}, \quad M_N = M_2 = (1 - f_{de}) \cdot g \cdot N_i$$

(c)  $N_{dep} > N_i + N_u$ : Some N deposition is leached from all areas:

$$(15) \quad b_N = b_3 = 1 - (f + g) \cdot f_{de}, \quad M_N = M_3 = (1 - f_{de}) \cdot [(f + g) \cdot N_i + f \cdot N_u]$$

The maximum critical load of sulphur is obtained by setting  $N_{dep} = 0$  in Equation 9:

$$(16) \quad CL_{max}(S) = L_{crit} / a_S$$

Setting  $S_{dep} = 0$  and considering the 3 different cases for  $N_{dep}$ , gives the following expression for the maximum critical load for nitrogen:

$$(17) \quad CL_{max}(N) = \min\{(L_{crit} / (1 - \rho_N) + M_i) / b_i, i = 1, 2, 3\}$$

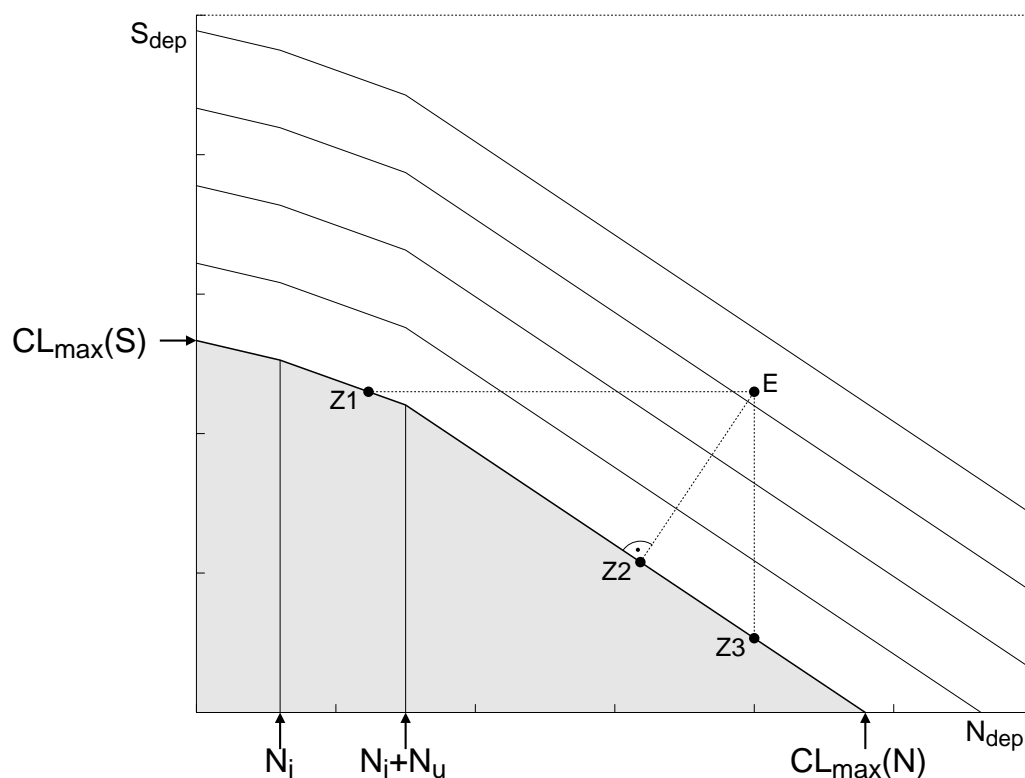
For arbitrary  $N_{dep}$  and  $S_{dep}$  we can compute the excess leaching as:

$$(18) \quad Ex_{le}(N_{dep}, S_{dep}) = a_S \cdot S_{dep} + a_N \cdot N_{dep} - L_N - L_{crit}$$

where  $a_N$  and  $L_N$  have to be chosen depending on the range in which  $N_{dep}$  lies (see above).

If  $Ex_{le}(N_{dep}, S_{dep}) = 0$ , N and S deposition fulfil Equation 11 and are critical loads, lying on the critical load function (thick line in Figure A1). If  $Ex_{le}(N_{dep}, S_{dep}) > 0$ , we say critical loads are exceeded, and isolines of positive excess leaching are shown in Figure A1 as thin lines parallel to the critical load function. The grey-shaded area indicates all pairs of  $(N_{dep}, S_{dep})$  for which  $Ex_{le} < 0$ , i.e. for which there is no exceedance. It is important to note that a (positive)  $Ex_{le}$  is *not* the amount of S and N to be reduced to reach non-exceedance; in fact, there is no such unique amount of N and S. This is illustrated in Figure A1. Let point E denote the current deposition of N and S: Reducing  $N_{dep}$  substantially, one reaches the point Z1 and therefore non-exceedance without reducing S; on the other hand one can attain non-exceedance also by only reducing  $S_{dep}$  (by a smaller amount) until reaching Z3; finally, by a reduction in both  $N_{dep}$  and  $S_{dep}$  one can reach non-exceedance as well (e.g., point Z2). In practice

external factors, such as costs of emission reduction measures, will determine which path will be followed to reach non-exceedance.



**Figure A1.** Piece-wise linear critical load function for S and acidifying N as defined by catchment properties (thick line). The grey-shaded area below the critical load function defines deposition pairs  $(N_{dep}, S_{dep})$  for which there is no exceedance. The thin lines parallel to the critical load function are isolines of excess acidity leaching. The points E and Z1–Z3 are explained in the text.