

**Assessing the Suitability of the MAGIC Model for Analysis of  
Acidification Potential in the Oil Sands Region of  
Northeastern Alberta**

**By**

**Benjamin M. Kampala**

**B.Sc., University of Calgary, 2001**

**A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF**

**MASTER OF APPLIED SCIENCE**

**in**

**THE FACULTY OF GRADUATE STUDIES**

**(Civil Engineering)**

**THE UNIVERSITY OF BRITISH COLUMBIA**

**April 2006**

**© Benjamin M. Kampala, 2006**

## **ABSTRACT**

This thesis is an evaluation of the suitability of the Model of Acidification of Groundwater in Catchments (MAGIC) for estimating acidification potential in lakes in the oil sands producing region of Northeastern Alberta. Parameterization of the model is undertaken for two study lakes representing cases with differing acidification potential. Applications of MAGIC for these cases demonstrate that the model is robust for explaining the behavior of these different natural systems. Additional applications of the model demonstrate how it may be used to predict the impact of various projections of oil sands emissions on the future status of lakes affected by acidifying emissions. Under all cases, it is shown that oil sands production may occur without resulting in harmful effects on these two study lakes. Improvements in the parameterization of the model are also identified, and these include gathering more soil data and information regarding nitrogen immobilization. Extensions of this work that would lead to a greater understanding of acidification in the Oil Sands Region include: regionalizing MAGIC for Northeastern Alberta, including climate change considerations, and incorporating this or other predictive models as part of a greater management system to assess the potential acidification of lakes.

# TABLE OF CONTENTS

ABSTRACT.....	ii
LIST OF TABLES .....	iv
LIST OF FIGURES .....	v
ACKNOWLEDGEMENTS .....	vi
CO-AUTHORSHIP STATEMENT .....	vii
<b>1 INTRODUCTION.....</b>	<b>1</b>
<b>1.1 SUSTAINABLE OIL SANDS DEVELOPMENT: A SYSTEMS APPROACH.....</b>	<b>1</b>
<b>1.2 THE OIL SANDS INDUSTRY OF NORTHEASTERN ALBERTA.....</b>	<b>3</b>
<b>1.3 ACIDIFICATION OF LAKES .....</b>	<b>4</b>
1.3.1 History of our Understanding of Acidification .....	4
1.3.2 Acid-Base Chemistry .....	5
1.3.3 Major Reactions.....	6
1.3.4 Acid Neutralizing Capacity .....	8
1.3.5 Sulfur Deposition .....	9
1.3.6 Nitrogen Deposition .....	11
1.3.7 Aluminum Mobilization.....	12
1.3.8 Organic Acids .....	13
1.3.9 Climate Change .....	14
1.3.10 Critical Loads .....	14
1.3.11 Modelling Acidification Numerically .....	16
1.4 SCOPE OF THESIS .....	22
1.5 CHAPTER 1 REFERENCES .....	23
<b>2 MODELLING ACIDIFICATION IN OIL SANDS REGION LAKES USING THE MAGIC MODEL.....</b>	<b>27</b>
2.1 INTRODUCTION.....	27
2.2 APPLICATION TO TWO STUDY LAKES IN NORTHEASTERN ALBERTA .....	31
2.2.1 Representing Catchments in MAGIC.....	31
2.2.2 Calibration.....	37
2.2.3 Sensitivity Analysis of Estimated Parameters.....	42
2.2.4 Uncertainty Analysis .....	44
2.2.5 Development Scenarios .....	46
2.3 DISCUSSION AND CONCLUSIONS .....	50
2.4 ACKNOWLEDGEMENTS .....	52
2.5 CHAPTER 2 REFERENCES .....	53
<b>3 FUTURE DIRECTIONS AND INSIGHTS.....</b>	<b>57</b>
3.1 SHORTCOMINGS AND IMPROVEMENTS.....	57
3.2 EXTENTIONS AND APPLICATIONS .....	58
3.3 CHAPTER 3 REFERENCES .....	60

## LIST OF TABLES

Table 1-1	Assumptions of the SSWC Model.....	16
Table 2-1	Air monitoring sites in and around the Oil Sands Region used to estimate deposition into study catchments .....	33
Table 2-2	Values of Fixed Parameters Used for Lake 270 and 354 .....	36
Table 2-3	Calibrated values of adjustable parameters for Lakes 270 and 354.....	38
Table 2-4	Greatest positive and negative effect on modelled outputs based on perturbations of uncertain parameters.....	43
Table 2-5	Water quality concentration and fixed parameter ranges in uncertainty analysis.....	45

## LIST OF FIGURES

Figure 1-1	Soil processes moderating soil acidification.....	6
Figure 1-2	Soil processes occurring when sulfur deposition occurs and binding sites for sulfate are available .....	10
Figure 1-3	Soil processes occurring when sulfur deposition occurs and no binding sites for sulfate are available.....	11
Figure 1-4	Soil processes moderating nitrogen cycling and the potential for nitrogen to contribute to acidification of soil water.....	12
Figure 2-1	The Oil Sands Producing Region of Northeastern Alberta .....	28
Figure 2-2	General flow chart of MAGIC.....	30
Figure 2-3	Data used to relate recorded sulfur deposition data to recorded emissions data .....	35
Figure 2-4	Sulfur deposition profile used as input to MAGIC (1864-2004).....	35
Figure 2-5	Results of Calibration of Lake 270 .....	39
Figure 2-6	Results of Calibration of Lake 354 .....	40
Figure 2-7	Deposition profiles for development scenarios.....	47
Figure 2-8	Impacts of development scenarios on Lake 270.....	48
Figure 2-9	Impacts of development scenarios on Lake 354.....	49

## ACKNOWLEDGEMENTS

I would like to express my thanks to my supervisor Dr. B.J. Lence whose suggestions, ideas and support continually provided me with insights and interesting challenges.

I am very grateful to all those who helped me complete this thesis, including Dr. Les Lavkulich for reviewing the draft and providing comments, Dr. Hans Schrier and Dr. Jack Cosby for their assistance in running the MAGIC model, Dr. Preston McEachern, Dale Doram, Tammy Rosner, Erin Bush, Zsolt Kovats, Dr. Mike Wang, Justin McPhearson, Wayne Speller and Golder Associates Ltd. for the various contributions they made throughout my studies. I am also very grateful for the support I received from my family and friends throughout this endeavour.

Finally, I would also like to express my deep thanks to Mr. Ian Mackenzie and Dr. Andrews Takyi of Golder Associates Ltd. for their helpful assistance, dedication to this work and for supporting my studies from the very beginning.

## **CO-AUTHORSHIP STATEMENT**

The paper presented in Chapter 2 will be re-written with Dr. B.J. Lence for publication.

# **1 INTRODUCTION**

## **1.1 SUSTAINABLE OIL SANDS DEVELOPMENT: A SYSTEMS APPROACH**

Sustainable development is the stated objective of large industrial oils sands projects. Examples of this include the vision of Suncor, which is to become a sustainable energy company, and Syncrude Canada Ltd., which requires that its goals are met in an environmentally and socially responsible manner (Suncor Energy 2005; Syncrude Canada Ltd. 2004). Also, Clive Mather, CEO of Shell Canada, sees their focus on sustainable development as integral to future growth and profitability (Shell Canada Limited 2004). Each of these prominent oil sands producers views sustainable business practices as vital to their concept of social corporate responsibility. Thus the actions of the company are bound to have certain limits and obligations. These include limitations on water abstractions, limits to land disturbance near rivers and limits to releases of acidifying air emissions. This thesis evaluates the suitability of a modelling approach for estimating acidification potential in lakes in Northern Alberta. The focus of the modelling approach is on adequately capturing the processes responsible for nitrogen and sulfur retention in soils. It may also be used to determine sustainable levels of emissions that may be released from regional oil sands production.

Industrial projects are subject to constraints, each of which may bound the outcome of operations (de Neufville 1990). The novel approach of analyses of sustainable development is that non-technical constraints are included in the analysis of the project system. Industry has recognized that non-technical approaches for solving engineering problems can result in economic as well as social and environmental gains at a minimal additional cost (Hartshorn et al. 2005). An example of considerations of non-technical constraints occurs when oil sands production companies apply for new permits and choose to engage in and respond to a certain level of public consultation.

They do this because they recognize the value of stakeholder acceptance of projects in an effort to minimize the downstream mitigation and legal costs.

The environmental limit on acidifying pollution is an example of a constraint which may enhance sustainable development. Prediction of the water quality response of Oil Sands Region lakes to acid input requires the use of predictive models. These models may be applied for investigating options for reducing risks of acidification (Fitzpatrick et al. 2001). The Oil Sands Region of Northeastern Alberta, Canada is a major petroleum producing region where several projects already reside, and other large oil sands ventures are planned (Imperial Oil Resources Ventures Limited (Imperial Oil) 2005).

This document explores methods for predicting the effects of acidifying emissions on aquatic ecosystems in this region, specifically numerical modelling using the Model of Acidification of Groundwater in Catchments (MAGIC), and the efficacy of these methods as environmental assessment tools. The MAGIC model is based on soil and water process-level information that governs acidification processes in a catchment (Cosby et al. 2001). The model is applied to two lakes, representative of average lakes in the region, to evaluate the robustness of the model for simulating a range of acid neutralizing conditions in the region.

In order to identify oil sands production practices that meet the goals that constitute sustainable business practices one must have access to effective predictive tools and decision support systems (Fitzpatrick et al. 2001). Such tools include numerical models that predict the impacts of ecosystem use and are used to identify management practices that limit or prevent harmful effects of operations. Chapter 1 of this document presents an introduction to the topic of acidification in Northeastern Alberta and a review of key literature related to acidification. Chapter 2 develops and compares applications of the MAGIC model for predicting acidification effects in Northeastern Alberta lakes under current and potential development and is presented as a stand

alone paper which will be submitted for publication. Concluding remarks and recommendations for future study of modelling acidification are presented in the third chapter.

## **1.2 THE OIL SANDS INDUSTRY OF NORTHEASTERN ALBERTA**

Oil sands production in Northeastern Alberta is a unique form of heavy oil production that exists no other place in the world (see Figure 2-1 in Chapter 2). Here, bituminous sands are mined and processed to yield synthetic crude oil. With deposits exceeding 300 billion barrels, and a strong demand from the United States and China, this type of industrial development has rapidly expanded since the late 1990s (Sutherland 2006). Potential of the oil sands to meet crude oil demands was developed through the 20<sup>th</sup> century with several research programs involving publicly traded companies, universities, government and privately owned companies (Ferguson 1985).

Oil sands are mined using conventional, large scale earth moving methods and are brought to central processing facilities where extraction and upgrading occur. Bitumen in the oil sands is extracted by chemically breaking the bonds between the sand and the bitumen. The bitumen is then upgraded to a synthetic oil using large cokers (Ferguson 1985). The air emissions from the mine fleet, and chemical processes which are used to extract and upgrade the bitumen generate air emissions that lead to acidification of lakes. Oil sands production is the main industry in Northeastern Alberta. The scope and scale of such projects require that adequate environmental and social assessments of the impacts of developments occur (AEPEA 2000; Suncor Energy 2005).

Various stakeholders maintain an active interest in the practices of oil sands development and its associated effects (Imperial Oil 2005). These include aboriginal communities, non-governmental organizations, the Alberta Energy and Utilities Board and the numerous labour unions in the

region. Water abstraction excesses, water quality impairment, species at risk issues, air quality degradation and human health issues are the most important environmental concerns of oil sands production. The potential acidification of lakes from increased acidifying air emissions is an example of a water quality impairment issue.

### **1.3 ACIDIFICATION OF LAKES**

Surface water acidification is a phenomenon that has the potential to change the water quality of freshwater lakes throughout the world (Gorham 1998). The current scientific understanding of the problem of surface water acidification is reviewed herein. While surface water acidification may also affect riverine systems, this literature review is primarily focused on lake systems. A discussion of the potential effects of the changing global climate on acidification processes is also included.

#### **1.3.1 History of our Understanding of Acidification**

Gorham (1998) notes that the scientific study of acid deposition has been occurring since the mid-eighteen hundreds. Although the study of acidification was initially focused on precipitation, focus shifted to acidified surface water bodies in the mid-nineteen hundreds. Psenner (1994) reviews the history of freshwater lake acidification which has resulted from anthropogenic air pollution. Acidification of lakes was not thought of as a major environmental problem until the 1970s. Since then there have been numerous instances of acidification effects throughout the world, including the English Lake District in the U.K., Northern Ontario, Canada and throughout Norway (Gorham 1998; Hill et al. 2002; Larssen et al. 1999; Neary and Dillon 1988; Wright 2001). Until recently, experts only expected to observe acidification resulting from the activities of developed nations. However, cases have been documented in developing nations as well, for example China (e.g., Larssen et al. 1999). In the coming decades acidifying emissions in Asia are expected to increase, surpassing those of Europe and North America (Gorham 1998; Larssen et

al. 1999).

### 1.3.2 Acid-Base Chemistry

Snoeyink and Jenkins (1980) give an overview of acid-base chemistry. An acid is a substance which can donate a hydrogen ion ( $H^+$ ), and a base is a substance which can accept a proton ( $B^-$ ). An exchange of a proton is referred to as an acid-base reaction. Acids and bases are able to act as bases and acids, respectively, when the acid-base reaction is reversed. Thus each acid and base substance has a conjugate acid or base pairing. On the left side of Equation (1) below HA is the acid and  $B^-$  is the base. On the right side of Equation (1) BH is the conjugate acid to  $B^-$ ;  $A^-$  is the conjugate base to HA. A proton ( $H^+$ ) is transferred to a base when the reaction goes from left to right, and the proton is transferred from the conjugate acid to the conjugate base when the reaction proceeds from right to left.



The progression of an acid-base reaction is governed by a dimensionless rate constant,  $K$ . The rate constant of reaction,  $K$ , is regulated by the amount of free energy in the aqueous system. Rates of reaction in an acid-base aqueous system can be described as either  $K_a$ , the rate at which an acid donates a proton, or  $K_b$ , the rate at which a base accepts a proton. By taking the negative logarithm of the concentration of the proton ions, a standard measure of the acidity of a solution may be expressed. This is called the pH. A low pH indicates a high concentration of acidity; a high pH indicates a low concentration of acidity.

A key feature of acid-base chemistry is that the ionic charges of the solution must always be zero. A larger concentration of an acid or a base in water causes ionization of other molecules present in order to balance the charges.

### 1.3.3 Major Reactions

A decreased pH and diminished ability to neutralize acid, referred to as acid neutralizing capacity (ANC), are the most important chemical effects of acidification (Cosby et al. 2001). ANC is measured in  $\text{meq}/\text{m}^3$ . A general overview of the soil processes occurring which moderate surface water acidification is given in Cosby et al. (2001). Figure 1-1 shows the conceptualized processes which moderate surface water acidification. Note that when  $\text{Al}^{3+}$  ions come in contact with soil matrix that is already bound to an  $\text{Al}^{3+}$  ion, they may displace the current ion or continue to 'search' for a base cation to replace. When  $\text{Al}^{3+}$  ions react with water it produces hydrogen ions that contribute to acidification.

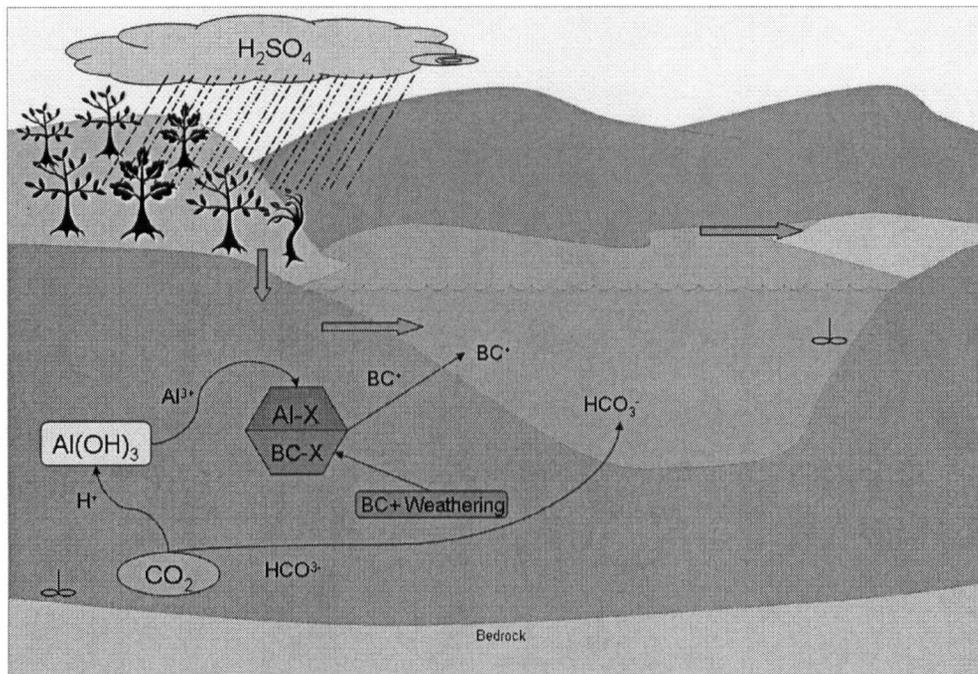


Figure 1-1 Soil processes moderating soil acidification. (Cosby 2003; Cosby et al. 2001)

These reactions occur naturally, independent of anthropogenic acid deposition. If no acid deposition is taking place, the equilibrium conditions in Figure 1-1 exist.

Cosby et al. (2001) observe that carbon dioxide ( $\text{CO}_2$ ) is a by-product of biological processes in

soil. The difference between the partial pressure of  $\text{CO}_2$  in the soil pore spaces and in the soil solution drives the dissolution of  $\text{CO}_2$  in the soil solution. Dissociation of carbonic acid ensues (see Equations 2 and 3).



The dissociation of carbonic acid ( $\text{H}_2\text{CO}_3$ ) releases small amounts of protons to the soil solution. The bicarbonate ion ( $\text{HCO}_3^-$ ) is stable and flows to receiving waters in runoff and leaching. The  $\text{H}^+$  ions in the soil solution, including those which result from the dissociation of  $\text{H}_2\text{CO}_3$ , preferentially react with aluminum tri-hydroxide ( $\text{Al}(\text{OH})_3$ ), common in the soil matrix, thus mobilizing  $\text{Al}^{3+}$ . In soils rich in base cations, the mobilized aluminum ion ( $\text{Al}^{3+}$ ) binds to the soil matrix and frees a sufficient amount of base cations ( $\text{BC}^+$ ) (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) so that the net difference in the ionic charge of the soil matrix is zero. The release of these strong base cations from the soil matrix allows them to be transported to surface water via runoff or to groundwater via leaching. The rate of base cation removal can be measured in a catchment input-output mass balance (Langan et al. 1996). The net effect of these reactions is that the charge being introduced to surface waters by the inflow of bicarbonate is balanced by the introduction of base cations concurrently.

Cosby et al. (2001) describe situations where there are few base cations and where long time series of natural (background) acid deposition have depleted the base cations. This situation has occurred frequently in Scandinavian catchments (Mylona 1996; Wright 2001). In such cases, the mobilized  $\text{Al}^{3+}$  is unable to bind to the soil solution and flows into the surface water body. In the surface water the aluminum reacts preferentially with the hydroxide ions ( $\text{OH}^-$ ) in water, and forms the stable molecule  $\text{Al}(\text{OH})_3$  and three  $\text{H}^+$ . The  $\text{H}^+$  binds to the  $\text{HCO}_3^-$  molecules which are

able to form CO<sub>2</sub> and water, H<sub>2</sub>O. This effectively balances the charges. In higher rates of Al<sup>3+</sup> mobilization, acidification of the water body occurs.

The introduction of acidifying emissions such as sulfur or nitrogen compounds to a system changes the acid-base reaction rates. The introduction of anthropogenic acid emissions to a soil system is discussed in the Sections 1.3.5 and 1.3.6 of this thesis.

### 1.3.4 Acid Neutralizing Capacity

The concept of acid neutralizing capacity (ANC) is used to grade the sensitivity of surface water to acidification (Driscoll et al. 1994). While alkalinity may also be used to measure the ability of a water body to buffer against acidification, ANC is a more exact and widely applied measure (Henriksen and Posch 2001). ANC, in meq/m<sup>3</sup>, represents the difference between the concentration (in moles per litre) of base cations and the concentration of strong acid proton donors in a given solution (Cosby et al. 2001). It is determined based on Equation (4).

$$\text{ANC} = 2(\text{Ca}^{2+}) + 2(\text{Mg}^{2+}) + (\text{Na}^{+}) + (\text{K}^{+}) + (\text{NH}_4^{+}) - 2(\text{SO}_4^{2-}) - (\text{Cl}^{-}) - (\text{NO}_3^{-}) \quad (4)$$

This equilibrium exists in the soil solution. Cosby et al. (2001) make several observations about ANC and suggest that processes that produce strong base cations increase the ANC of the soil solution. An increase in strong acid anions consequently decreases the ANC of a solution. A decrease in the ANC indicates a decrease in the pH and an increase in the amount of inorganic aluminum in solution. A large pool of strong base cations in the soil buffers against a change in ANC.

ANC can be used as a measure against which harmful effects to aquatic organisms are gauged (Henriksen and Posch 2001). Comparing ANC with aquatic affects in cases of lake acidification aids in the establishment of limits of acceptable deposition levels (Cosby et al. 1985). Cosby et al. (1985) develop a numerical model capable of calculating ANC throughout the time scale of

lake acidification. Henriksen and Posch (2001) show that equivalent ANC limits may affect the same fish differently in different water bodies. Therefore, ANC limits should be calculated for each water body being studied and not simply assigned based on the aquatic organisms present. There may be situations where it is impractical to calculate the ANC for each lake in a study as a given study may include hundreds of lakes (Moldan et al. 2004; Neary and Dillon 1988). In these situations a generalized estimate of the ANC can be obtained for lakes exhibiting similar catchment and underlying geological characteristics.

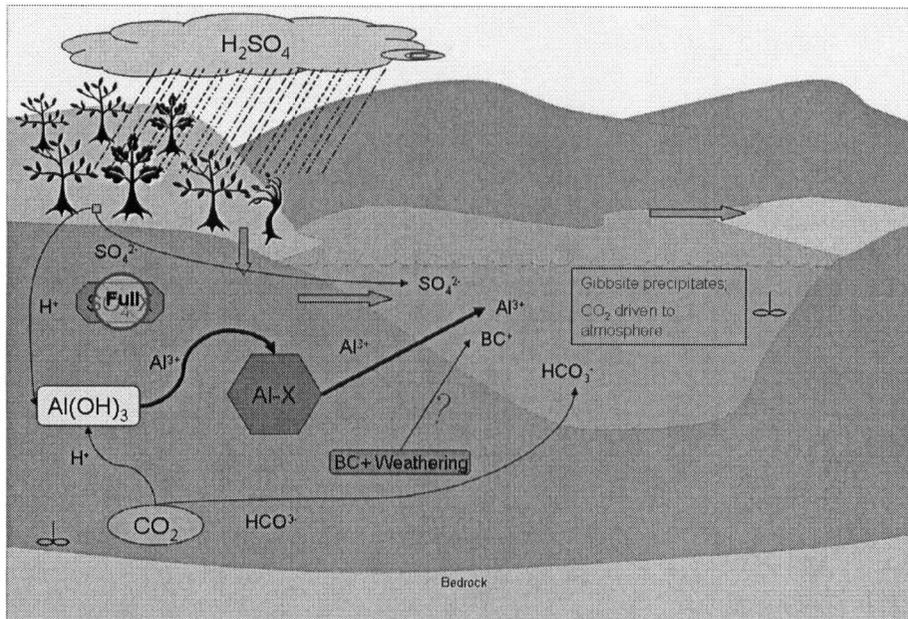
ANC is typically an output of surface water acidification models (Cosby et al. 2001; Driscoll et al. 1994; Henriksen and Posch 2001). As such it may be used as a measure to interpret results and trends of experiments.

### **1.3.5 Sulfur Deposition**

Levels of sulfur deposition have been increasing since the industrial revolution (Jenkins et al. 1997; Mylona). It is generally understood that the most important cause of acidification is the introduction of sulfur to the ecosystems via anthropogenically produced deposition (Jenkins et al. 1997; Psenner 1994). This includes the wet, dry or occult (cloud) deposition of oxidized forms of sulfur compounds (Mylona 1996). An input of sulfur dioxide is an increase in the concentration of strong acid in a catchment (Cosby et al. 2001). The acidifying effect of sulfur is dependant on the mobility and retention of sulfate anions ( $\text{SO}_4^{2-}$ ) in the soil ecosystem (Jenkins et al. 1997). In some situations sulfate is not retained via adsorption in the ecosystem and thus input concentrations to the ecosystem closely equal output (Jenkins et al. 1997).

The effect of the introduction of sulfur to an ecosystem over time is described in detail by Cosby et al. (2001). Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) dissociates to two protons ( $\text{H}^+$ ) and the sulfate ion ( $\text{SO}_4^{2-}$ ) when it impinges in the soil solution.  $\text{SO}_4^{2-}$  may either adsorb onto the soil matrix (see Figure 1-2), or if there are no binding sites in the soil matrix it is not retained (see Figure 1-3). When



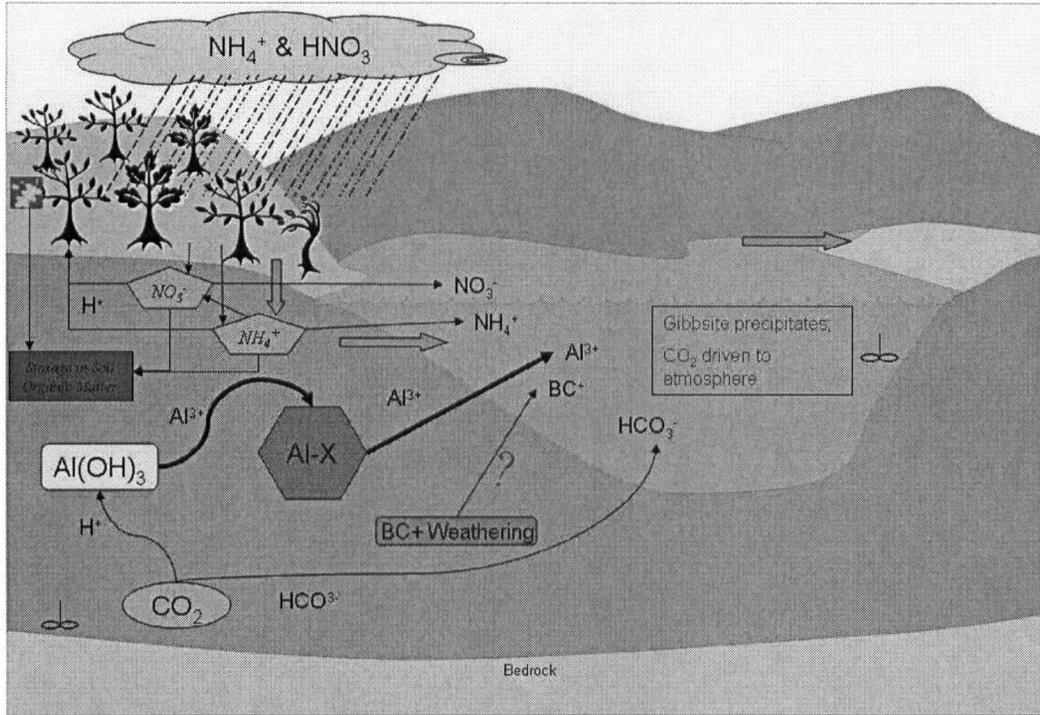


**Figure 1-3 Soil processes occurring when sulfur deposition occurs and no binding sites for sulfate are available (Cosby 2003; Cosby et al. 2001)**

### 1.3.6 Nitrogen Deposition

Atmospheric nitrogen deposition has increased since the industrial revolution (Jenkins et al. 1997). An input of nitrogen is also an increase in the concentration of strong acid in a catchment (Cosby et al. 2001). However, unlike sulfur emissions which are expected to decrease, global nitrogen emissions are generally expected to remain constant or to rise in the next 50 years (Aber et al. 1998; Wright 2001). Nitrogen is deposited via wet, dry or occult deposition of oxidized or reduced forms of nitrogen compounds. The acidifying effect of nitrogen is dependant on the mobility and retention of nitrate anions in the soil ecosystem (Jenkins et al. 1997). Nitrogen is generally retained and consumed within terrestrial systems until all biological needs in the soil have been met, e.g., a saturation level has been reached (Cosby et al. 2001; Jenkins et al. 1997). An excess of unassimilated nitrogen in the soil may lead to eutrophication, acidification of soils and/or nitrate leaching (Jenkins et al. 1997). The in-soil processes of nitrification, denitrification and mineralization determine the amount of nitrogen immobilized in the soil and how much is

available to contribute to acidification (Jenkins et al. 1997). The manner in which unassimilated nitrogen contributes to acidification is analogous to that of sulfur and is summarized in Figure 1-4.



**Figure 1-4** Soil processes moderating nitrogen cycling and the potential for nitrogen to contribute to acidification of soil water (Cosby 2003; Cosby et al. 2001)

### 1.3.7 Aluminum Mobilization

Sullivan and Cosby (1998) cite aluminum mobilization as an important ecological effect of acidification. They note that the contribution to acid neutralization by aluminum as well as the toxic effects of aluminum in surface water make aluminum an important chemical parameter in evaluating the effects of acidic deposition. The authors assert that the processes which govern aluminum mobilization, solubility and speciation are not well understood. Neal (1995) studied

aluminum speciation in acidic streams and observed that most modelling studies do not account for the formation of aluminum with organic complexes, and that usually only hydroxide, fluoride and sulfate are examined (Cosby et al. 2001; Neal 1995; Sullivan and Cosby 1998). Neal (1995) concludes that the characterization of aluminum in surface waters is not adequately described by current models. He suggests that silica complexes be included in the analysis of aluminum chemistry.

### **1.3.8 Organic Acids**

Driscoll et al. (1994) discuss the importance of organic acids in regulating the acidification of lakes. Until recently, it was assumed that organic acids are of limited importance in the acidification of lakes (Cosby et al. 1985; Driscoll et al. 1994; Sullivan and Cosby 1998). Sullivan et al. (1998) conclude that organic acids are important in regulating the acidity of surface waters. Organic acids originate from the decomposition of biomass in ecosystems. The presence of organic acids may contribute to or buffer acid-base reactions occurring in a catchment (Driscoll et al. 1994; Sullivan and Cosby 1998). The manner in which organic acids contribute to or buffer acidification of lakes is not well understood (Driscoll et al. 1994; Sullivan and Cosby 1998). Gorham (1998) suggests that organic acid concentrations are expected to decline in acidified lakes as a result of decreased biological productivity. Driscoll et al. (1994) conclude that reliable predictions of pH and ANC must include an adequate calculation of organic acids. Sullivan et al. (1998) find good agreement between diatom inferred historical pH values and modelled pH values which include an acid analogue containing three H<sup>+</sup> ions to represent organic acids. They conclude that pH and ANC values are better estimated when this theoretical acid analogue, which behaves in the numerical model like an acid, is used to represent the effect of organic acids on surface waters. Cosby et al. (2001) make a similar conclusion in a study of two lakes in Norway.

### 1.3.9 Climate Change

A change in the global climate would likely change lake acidification rates (Cruise et al. 1999; Murdoch et al. 2000). Murdoch et al. (2000) observe that potential changes in temperature may affect soil productivity and biogeochemical cycling. These changes could significantly affect the runoff water quality and pH of surface waters. Also, reductions of surface water flows may lengthen time scales of acid recovery. Alternatively, a wetter climate may increase the rate of base cation depletion in soils. Schindler (2001) and Cruise et al. (1999) suggest that surface water bodies can expect to experience pH values beyond their normal range as a result of re-oxidation of sulfur deposits as wetlands and littoral areas are subjected to warmer climates.

### 1.3.10 Critical Loads

UNECE (2004) defines critical loads as 'the atmospheric concentrations of pollutants in the atmosphere above which adverse effects in ecosystems may occur, according to present knowledge'. In order to prevent the acidification of lakes, a measure is needed to determine the critical acid loading. Each critical load is specific for a given catchment. If acid deposition is below a target load, then no damage to the lake should occur (Gorham 1998). The critical load of acidity is represented in the Steady-State Water Chemistry (SSWC) Model as:

$$[critical\_load] = [BC]_w + [BC^*]_{dep} - [BC]_u - [ANC]_{lim} \quad (5)$$

Where  $[BC]_w$  is the average weathering flux of base cations in the soil,  $[BC^*]_{dep}$  is the non-anthropogenic, non-marine atmospheric deposition of base cations,  $[BC]_u$  is the net uptake of base cations by biological processes and  $[ANC]_{lim}$  is the lowest acid neutralizing capacity flux in the ecosystem that does not cause harm to fish species present (UNECE 2004). Here, the units of all the parameters are  $keq \cdot ha^{-1} \cdot year^{-1}$ . The terms in Equation (5) cannot all be determined experimentally (Henriksen and Posch 2001). Therefore the simplified form of the SSWC Model

is derived as:

$$[critical\_load] = Q \times ([BC^*]_0 - [ANC]_{lim}) \quad (6)$$

Where  $Q$  is annual catchment runoff and  $[BC^*]_0$  is calculated as:

$$[BC^*]_0 = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] \quad (7)$$

Molar concentrations are measured in mg/l. As such, field data is used to experimentally determine  $[BC^*]_0$  in  $keq \cdot ha^{-1} \cdot year^{-1}$  for any lake. The  $[ANC]_{lim}$  value used in the SSWC Model can be taken from experimental data (UNECE 2004). The acid neutralizing capacity is correlated to fish health. A typical value of  $[ANC]_{lim}$  is  $75 \cdot 10^{-9} keq \cdot ha^{-1} \cdot year^{-1}$ . This equation can be used to estimate the critical load in terms of the annual average catchment runoff. This formulation of the SSWC Model is based on several conservative assumptions (Henriksen and Posch 2001). They are listed in Table 1-1 below.

**Table 1-1 Assumptions of the SSWC Model**

Assumptions include:

---

1. The system being studied is at steady-state;
2. Water quality data represent annual averages;
3. Pre-industrial development base cation concentration are estimated by current base cation concentrations;
4. Bicarbonate ( $\text{H}_2\text{CO}_3$ ) is the primary source of buffering in the lake;
5. Runoff from the catchment is the only source of alkalinity; and
6. All nitrates in deposition are acidifying (no nitrogen storage in soil).

Gorham (1998) cites examples where calculations for the critical loads have aimed to limit sulfur, nitrogen or both. In a study of weathering rates in soils, Langan et al. (1996) concludes that a good estimate of weathering rates is needed to accurately measure critical loads. Langan et al. (1996) found that for the study of acidification there are several good methods for calculating weathering rates accurately. Several researchers have used steady-state models to calculate weathering and critical loads.

### **1.3.11 Modelling Acidification Numerically**

Mitigating or preventing acidification requires an in-depth understanding of the socio-economic and environmental features of the region as well as the history of events leading to the current state (Fitzpatrick et al. 2001; Wetzel 2001). It is important to develop a thorough understanding of the potential for lakes to acidify in an industrial region. The potential acidification of lakes has been identified as an important potential issue arising out of oil sands production (Imperial Oil 2005; Western Resource Solutions (WRS)).

Numerical models are useful for making predictions of the acid status of lakes based on a set of specified assumptions and conditions. These models may be either steady-state or dynamic through time. Field experiments cannot be used to explain and predict the likelihood of lake acidification because the processes occurring in natural systems are highly variable, and processes cannot be separated and isolated (Reuss and Walthall 1989). Cosby et al. (1985) demonstrate that a relatively small number of soil processes and equilibrium can be used to predict the response of an aquatic system subjected to acidifying inputs.

Steady-state models calculate the critical load using assumptions about the interactions occurring in catchment soils at one point in time (Henriksen and Posch 2001). If the atmospheric deposition exceeds the estimated critical load, then the outcome of the model is that acidification is likely to occur. Henriksen and Posch (2001) give a synopsis of three steady-state models which have been used to calculate critical loads in surface waters. They are the (modified) SSWC model, the Empirical Diatom model and the First-order Acidity Balance (FAB) model. The authors describe the differing calculations and assumptions in each model, but conclude that they all may be appropriate in calculating critical loads.

Henriksen et al. (2001) and Canadian Natural Resources Ltd. (2002) demonstrate an effective use of the SSWC model to determine critical loads in Canada. The drawback to steady-state models is that they are unable to estimate when and to what extent acidification occurs (Cosby et al. 1985). Dynamic models offer an effective solution to this shortcoming (Cosby et al. 1985).

The ability to predict acidification using a dynamic model is an improvement over steady-state assessment techniques because the system may be examined with greater rigour. In such models, the responses of numerous chemical species are modelled in discrete time increments. Dynamic modelling of acidification can account for the influence of groundwater flows and may be used to predict in-soil nitrogen dynamics. Dynamic models may also be used to estimate the time needed

for a catchment to recover from acidification upon cessation or reduction of acid inputs (Wright 2001) and to predict acidification effects when deposition is ongoing for protracted periods of time (Jenkins et al. 1997). The dynamic model that has been most widely applied is MAGIC.

MAGIC is a lumped-parameter, physically based, process oriented model developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al. 2001; Cosby et al. 1985). It assumes that soil processes are solely responsible for observed surface water acidification effects and predicts leaching of base cations based on inputs of strong acid anions such as  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$ . In separate compartments meant to represent the soil and lake components of a catchment, these processes are simulated by a series of sequential acid-base equilibrium equations (Cosby et al. 1985). Evaluating the model outcomes allows one to predict time series of acidification. The soil processes and equilibrium used in the MAGIC model are described by Reuss and Johnson (1985), and form the conceptual basis of the model. Cosby et al. (2001; 1986; 1985) fully describe the mechanisms of the model, conceptual formulation, representation of sulfate and nitrogen retention in soil and dynamic equilibrium equations. Comprehensive discussions of the uncertainty in the model predictions have been explored by Page et al. (2003) and Larssen et al. (2004).

MAGIC is built upon three groups of equations that utilize a set of equilibrium equations to describe soil processes, a set of mass balance equations to describe catchment input-output budgets and a series of equations to describe nitrogen immobilization in the soil. These reactions are able to account for adsorption and acid/base reactions in soil solution subsequent surface water (Cosby et al. 1985; Cosby et al. 1985; Reuss and Johnson 1985). Since its first application to a small stream in Shenandoah National Park in Virginia, USA, the model has been refined several times and used throughout the world (Cosby et al. 2001). Refinements have been incorporated to address shortcomings that have been revealed in application of the model. These additions include changes to the assumptions controlling aluminum solubility, organic acid

buffering and distributed nitrogen dynamics (Cosby et al. 2001). The discussion of the model provided here focuses on the seventh version of the model.

There are two main assumptions that are central to the model. The first is that concentrations of major ions are governed by simultaneous reactions of sulfate adsorption, nitrogen retention and cation exchange (Cosby et al. 1995; Reuss and Johnson 1985). Furthermore, simulated dissolution, precipitation and speciation of aluminum and inorganic carbon are important reactions in this model. The second main assumption is that the flux of major ions coming into and out of the soil is controlled by atmospheric inputs, chemical weathering, biomass uptake and losses to runoff. The flux rates controlling these processes are key to the ability of MAGIC to balance inputs and outputs from the pool of exchangeable ions in the soil, and thus predict a soil's response to acidifying emissions. The equations that control selectivity of cations in the soil are specific for each of the base cations and for aluminum (Cosby et al. 1985). Changes occurring in the equilibria in the soil are interpreted as changes in the acid response of surface water. The model is dynamic and can be used to predict a lake's acid status in monthly or annual time steps to reconstruct historical acidification and predict future time series of acidification potential (Cosby et al. 1985).

The sizes of the exchangeable pools in the model are influenced by the input of sulfur and nitrogen to the soil compartment. Furthermore, the sulfur and nitrogen are controlled by assumptions which simulate the behavior of these chemicals in catchments (Cosby et al. 2001; Cosby et al. 1986). The model assumes that there is no biological transformation or uptake of sulfur. Also, adsorption rates are held constant over the range of pH and soil organic matter concentration entered in the model. This is in contrast to the assumptions for nitrogen in the model. Biological mechanisms assumed to be occurring in the soil retain nitrogen.

The retention of nitrogen is predicated on carbon:nitrogen ratios. The result of these assumptions

is that the outlet concentration is a function of the retention time and amount of nitrogen and sulfur adsorbed or retained in the soil (Cosby et al. 2001; Cosby et al. 1986). If a high carbon:nitrogen ratio is predicted, then nitrogen is retained in the soil. Conversely, a low carbon:nitrogen simulates the release of nitrogen from the soil compartment to the surface water body.

Lake water pH is governed by three processes (Jenkins et al. 1997). First, when water leaves the soil compartment and enters the lake compartment, CO<sub>2</sub> degassing occurs. Also, a specified amount of strong acid anions are deposited directly into the lake and finally, organic anions are assumed to dissociate according the rate constants specified in the model set up. Dissociation mediates the organic anion buffering.

The model can make use of one or two soil compartments which can be arranged vertically to simulate soil horizons or horizontally to simulate runoff through two soil types (see Figure 2-2 in Chapter 2). A wetlands compartment may also be used, and has implications for nitrogen cycling in the catchment. Deposition and precipitation are applied to the soil compartment, with a specified fraction of flow diverting directly to the lake compartment via overland flow. Runoff is calculated as the volume of water leaving the catchment from the lake. Input precipitation and runoff from the lake are assumed to be equal.

There is a great deal of research that addresses the question of appropriately describing the effects of aluminum and organic acids in MAGIC. The processes governing aluminum and effects of aluminum in acidification are discussed by Neal (1995) and Sullivan and Cosby (1995). The effects organic acids on acidification of lakes are well discussed by Sullivan et al. (1996), Wright (1989), Köhler et al. (1999), Cosby et al. (1995), Driscoll et al. (1994).

The MAGIC model has been used in numerous studies and has been shown to simply and

effectively provide a tool to test assumptions and controls of acidification (Cosby et al. 1985).

Some of the best examples of its use include:

- studying the effects of acidic deposition in the Adirondack Mountain region of New York (Sullivan 2000);
- investigating the effects of re-forestation in the United Kingdom (UK) (Jenkins et al. 1997); and
- studying effects of sulfur deposition in Ontario, Canada (Neary and Dillon 1988).

The Adirondacks Region of New York has been intensively studied for the effects of acidification on lakes. Here the MAGIC model was used in scientific studies of the role of organic acids in regulating lake water pH and alkalinity.

In the United Kingdom, future re-forestation policy and its effects on acidification recovery of lakes in the Acid Monitoring Network was investigated with the aid of the MAGIC model. Here MAGIC was applied to 21 lakes in order to determine the role of re-forestation in the future acidification status, the required deposition reductions required to alleviate acidification effects and the response of lakes to current acid reduction strategies.

Clear links between acid deposition and changes in lake chemistry were reported for the first time in North America with the application of MAGIC to Central Canada. In this study decreasing pH and alkalinity in Ontario lakes were attributed to the deposition of strong acids.

Studies such as these have shown MAGIC to be robust, reliable and useful in scientific analysis, in establishing management practices and as a policy making tool. Its use in this project is predicated upon a recommendation by CEMA to the provincial regulator, Alberta Environment (AENV), that dynamic modelling be applied in the Oil Sands Region.

## 1.4 SCOPE OF THESIS

The purpose of this thesis is to assess the applicability of MAGIC for a collection of lakes in the Oil Sands Region of Northeastern Alberta. The ability of MAGIC to facilitate ecosystem protection, thus allowing oil sands production to occur while preventing harmful effects to the region's lakes is examined. Whether or not this model is capable of explaining the behavior of the natural systems is assessed. Effective prediction, based on current understanding of the sensitive elements in that ecosystem, helps keep pollutants below harmful levels.

Effective numerical models require calibration and validation (Ford 1999). A calibration of MAGIC is conducted with data collected in the Oil Sands Region and is discussed in Chapter 2. Additionally, a discussion of the validity of the calibration of the model is given. Future development scenarios are analyzed with the calibrated model and detailed results are presented.

In Chapter 3, comments are provided regarding shortcomings of the MAGIC model application and suggested improvements are given. Also extensions of this study and novel applications of the MAGIC model are discussed. Throughout this thesis the intention is to examine the applicability of MAGIC as an assessment tool, not to draw conclusions about the establishment of limits for development. No specific recommendations are made regarding the allowable levels of pollutants from oil sands developments. Setting levels of pollutants requires more factors and information than is available for this study, such as detailed emission predictions, deposition modelling, agreements among emitters and stakeholder preferences.

No new field data have been collected in order to perform this study and the work is not intended to expand upon the scientific understanding of acidification processes. This thesis explores the analysis of acidification based on the current understanding of the issue, and examines a selection of factors needed for the methodology that influence the application of the MAGIC model to the Oil Sands Region of Northeastern Alberta.

## 1.5 CHAPTER 1 REFERENCES

- Aber, J. D., McDowell, W. H., Nadelhoffer, K. J., Magill, A., Berntson, G., Kamakea, M., McNulty, S. G., Currie, W., Rustad, L., and Fernandez, I. (1998). "Nitrogen saturation in temperate forest ecosystems: hypotheses revisited." *BioScience*, 48, 921-934.
- AEPEA. (2000). "Alberta Environmental Protection and Enhancement Act." Chapter E-12.
- Canadian Natural Resources Limited. (2002). "Horizon Oil Sands Project - Application for Approval." Submitted to Alberta Energy and Utilities Board and Alberta Environment, Calgary, A.B.
- Cosby, B. J., Ferrier, R. C., Jenkins, A., and Wright, R. F. (2001). "Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model." *Hydrology and Earth System Sciences*, 5(3), 499-517.
- Cosby, B. J., Hornberger, G. M., Galloway, J. N., and Wright, R. F. (1985). "Time scales of catchment acidification; A quantitative model for estimating freshwater acidification." *Environmental Science and Technology: Features*, 19, 1144-1149.
- Cosby, B. J., Hornberger, G. M., Wright, R. F., and Galloway, J. N. (1986). "Modeling the Effects of Acid Deposition: Control of Long-Term Sulphate Dynamics by Soil Sulfate Adsorption." *Water Resources Research*, 22(8), 1283-1291.
- Cosby, B. J., Wright, R. F., and Gjessing, E. (1995). "An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway." *Journal of Hydrology*, 170, 101-122.
- Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N. (1985). "Modelling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment." *Water Resources Research*, 21(11), 1591-1601.
- Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N. (1985). "Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry." *Water Resources Research*, 21(1), 51-63.
- Cruise, J. F., Limaye, A. S., and Al-Abed, N. (1999). "Assessment of impacts of climate change on water quality in the southeastern united states." *Journal of the American Water Resources Association*, 35(6), 1539-1550.
- de Neufville, R. (1990). *Applied Systems Analysis; Engineering Planning and Technology Management*, McGraw-Hill Inc.
- Driscoll, C. T., Lehtinen, M. D., and Sullivan, T. J. (1994). "Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes." *Water Resources Research*, 30(2), 297-306.
- Ferguson, B. G. (1985). *Athabasca Oil Sands*, Alberta Culture, Alberta.
- Fitzpatrick, J., Imhoff, J., Burgess, E., and Brashear, R. (2001). "Water Quality Models: A Survey and Assessment." Project 99-WSM-5, Water Environment Research

Foundation, Alexandria, VA.

- Ford, A. (1999). *Modeling the Environment*, Island Press, Covelo, California.
- Gorham, E. (1998). "Acid deposition and its ecological effects: a brief history of research." *Environmental Science and Policy*, 1, 153-166.
- Hartshorn, J., Maher, M., Crooks, J., Stahl, R., and Bond, Z. (2005). "Creative destruction: building toward sustainability." *Canadian Journal of Civil Engineering*, 32, 170-180.
- Henriksen, A., and Posch, M. (2001). "Steady-state models for calculating critical loads for acidity for surface waters." *Water, Air and Soil Pollution: Focus*, 1, 375-398.
- Hill, T. J., Skeffinton, R. A., and Whitehead, P. G. (2002). "Recovery from acidification in the Tillingbourne catchment, southern England: catchment description and preliminary results." *The Science of the Total Environment*, 282-283, 81-97.
- Imperial Oil Resources Ventures Limited (Imperial Oil). (2005). "Kearl Oil Sands Project - Mine Development. Volumes 1 to 9. Submitted to Alberta Energy and Utilities Board and Alberta Environment. Prepared by Imperial Oil Resources Ventures Limited in association with Golder Associates Ltd., AXYS Environmental Consulting Ltd., Komex International Inc. and Nichols Applied Management." Calgary, Alberta.
- Imperial Oil. (2005). "Kearl Oil Sands Project - Mine Development. Volumes 1 to 9. Submitted to Alberta Energy and Utilities Board and Alberta Environment. Prepared by Imperial Oil Resources Ventures Limited in association with Golder Associates Ltd., AXYS Environmental Consulting Ltd., Komex International Inc. and Nichols Applied Management." Calgary, Alberta.
- Jenkins, A., Ferrier, R., and Cosby, B. J. (1997). "A dynamic model for assessing the impact of coupled sulphur and nitrogen deposition scenarios on surface water acidification." *Journal of Hydrology*, 197, 111-127.
- Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C., Ferrier, R., and Swingewood, P. (1997). "Modelling surface water in the UK; Application of the MAGIC model to the Acid Water Monitoring Network." IH Report No. 131, Natural Environmental Research Council.
- Köhler, S., Hruška, J., and Bishop, K. (1999). "Influence of organic acid site density on pH modelling of Swedish lakes." *Canadian Journal of Fisheries and Aquatic Science*, 56, 1461-1470.
- Langan, S. J., Reynolds, B., and Bain, D. C. (1996). "The calculation of base cation release from mineal weathering in soils derived from Palaeozoic greywackes and shales in upland UK." *Geoderma*, 69, 275-285.
- Larssen, T., Cosby, B. J., and Hogasen, T. (2004). "Uncertainties in predictions of surface water acidity using the MAGIC model." *Water, Air and Soil Pollution: Focus*, 4, 125-137.
- Larssen, T., Seip, H. M., Semb, A., Mulder, J., Muniz, I. P., Vogt, R. D., Lydersen, E., Angell, V., Dagang, T., and Eilersen, O. (1999). "Acid deposition and its effects

- in China: an overview." *Environmental Science and Policy*, 2, 9-24.
- Moldan, F., Kronnas, V., Wilander, A., Karlton, E., and Cosby, B. J. (2004). "Modelling acidification and recovery of swedish lakes." *Water, Air and Soil Pollution: Focus*, 4, 139-160.
- Murdoch, P. S., Brown, J. S., and Miller, T. L. (2000). "Potential effects of climate change on surface-water quality in North America." *Journal of the American Water Resources Association*, 36(2), 347-366.
- Mylona, S. (1996). "Sulphur dioxide emissions in Europe 1880-1991 and their effect on sulphur concentrations and depositions." *Tellus*, 48B(5), 662-689.
- Neal, C. (1995). "Aluminium speciation variations in an acidic upland stream draining the Hafren spruce forest, Plynlimon, Mid-Wales." *Journal of Hydrology*, 164, 39-51.
- Neary, B. P., and Dillon, P. J. (1988). "Effects of sulphur deposition on lake-water chemistry in Ontario, Canada." *Nature*, 333, 340-343.
- Page, T., Beven, K. J., Freer, J., and Jenkins, A. (2003). "Investigating the uncertainty in predicting responses to atmospheric deposition using of acidification of groundwater in catchments (MAGIC) within a generalized likelihood uncertainty estimation framework." *Water, Air and Soil Pollution*, 142, 71-94.
- Psenner, R. (1994). "Environmental impacts on freshwaters: acidification as a global problem." *The Science of the Total Environment*, 143, 53-61.
- Reuss, J. O., and Johnson, D. W. (1985). "Effect of Soil Processes on the Acidification of Water by Acid Deposition." *Journal of Environmental Quality*, 14(1), 26-31.
- Reuss, J. O., and Walthall, P. M. (1989). *Soil reaction and acidic deposition in Soils, Aquatic Processes and Lake Acidification* (S.A. Norton, S.E. Lindberg & A.L. Page, eds.), Springer-Verlag; New York.
- Schindler, D. W. (2001). "The cumulative effects of climate warming and other human stresses on Canadian freshwaters in teh new millennium." *Canadian Journal of Fisheries and Aquatic Science*, 58, 18-29.
- Shell Canada Limited. (2004). "Progress Toward Sustainable Development." Calgary.
- Snoeyink, V. L., and Jenkins, D. (1980). *Water Chemistry*, John Wiley & Sons, Toronto.
- Sullivan, T. J. (2000). *Aquatic Effects of Acidic Deposition*, CRC Press LLC, Boco Raton.
- Sullivan, T. J., and Cosby, B. J. (1998). "Modeling the concentration of aluminium in surface waters." *Water, Air and Soil Pollution*, 105, 643-659.
- Sullivan, T. J., Cosby, B. J., Driscoll, C. T., Charles, D. F., and Hemond, H. F. (1996). "Influence of organic acids on model projections of lake acidification." *Water, Air and Soil Pollution*, 91, 271-282.
- Suncor Energy. (2005). "2005 Report on Sustainability." Suncor Energy, Calgary, AB.
- Suncor Energy. (2005). "Voyageur Project Application and Environmental Impact

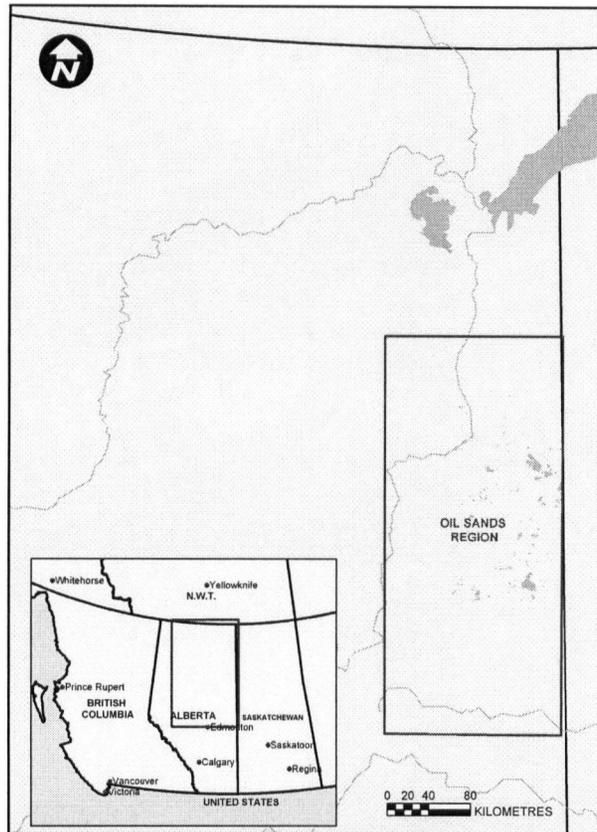
- Assessment. Volumes 1A, 1B, 2, 3, 4, 5 and 6. Submitted to Alberta Energy and Utilities Board and Alberta Environment. Prepared by Suncor Energy Inc. Oil Sands in Association with Golder Associates Ltd. And Nichols Applied Management." Fort McMurray, Alberta.
- Sutherland, S. (2006). "Building a Sustainable Future." Alberta Venture.
- Syncrude Canada Ltd. (2004). "2004 Sustainability Report." Fort McMurray, AB.
- UNECE. (2004). "Manual on methodologies and criteria for modelling and mapping critical levels and air pollution effects, risks and trends." UNECE Convention on Long-Range Transboundary Air Pollution.
- Western Resource Solutions (WRS). (2004). "Calculation of Critical Loads of Acidity to Lakes in the Athabasca Oil Sands Region." NOX-SOX Committee of Cumulative Environmental Management Association, Calgary, AB.
- Wetzel, R. G. (2001). *Limnology; Lake and River Ecosystems*, Third Edition, Academic Press, San Diego.
- Wright, R. F. (1989). "RAIN Project: Role of Organic Acids in Moderating pH Change Following Reduction in Acid Deposition." *Water, Air and Soil Pollution*, 46, 251-259.
- Wright, R. F. (2001). "Use of the dynamic model 'MAGIC' to predict recovery following implementation of the Gothenburg Protocol." *Water, Air and Soil Pollution: Focus*, 1, 455-482.

## **2           MODELLING ACIDIFICATION IN OIL SANDS           REGION LAKES USING THE MAGIC MODEL**

### **2.1       INTRODUCTION**

In order for any new oil sands project to be approved in the oil sands producing region of Northeastern Alberta proponents must demonstrate that there will be no effects on regional ecosystems. This includes effects of acidifying air emissions from mine fleets and extraction plants on aquatic ecosystems, as mandated by provincial environmental regulators (Imperial Oil 2005). Acidification of lakes has been identified as an issue of concern arising from oil sands production (Imperial Oil 2005; WRS 2004) and the Cumulative Environmental Management Association, CEMA, an industry supported policy institution charged with addressing environmental issues related to oil sands production, has recommended that environmental assessments of new projects include analyses of lake acidification potential using the Model of Acidification of Groundwater In Catchments, MAGIC (personal communication, P. McEachern, May, 2005).

This work develops a version of the MAGIC model for acidification studies in Northeastern Alberta including identification of fixed and estimated adjustable parameter values and their sensitivities. The robustness of the model for assessing the impacts of acidifying emissions on the ecosystems of Northeastern Alberta is also demonstrated. Acidification potential of two study lakes, typical of the petroleum producing Athabasca Oil Sands Region, but with different neutralizing capacities, is estimated using the MAGIC model and future development scenarios are investigated in order to examine the risk of acidification as a result of possible oil sands development. The methods developed in this study can be applied to other acid sensitive lakes in the region (see Figure 2-1).



**Figure 2-1 The Oil Sands Producing Region of Northeastern Alberta (GeoBase.ca 2006)**

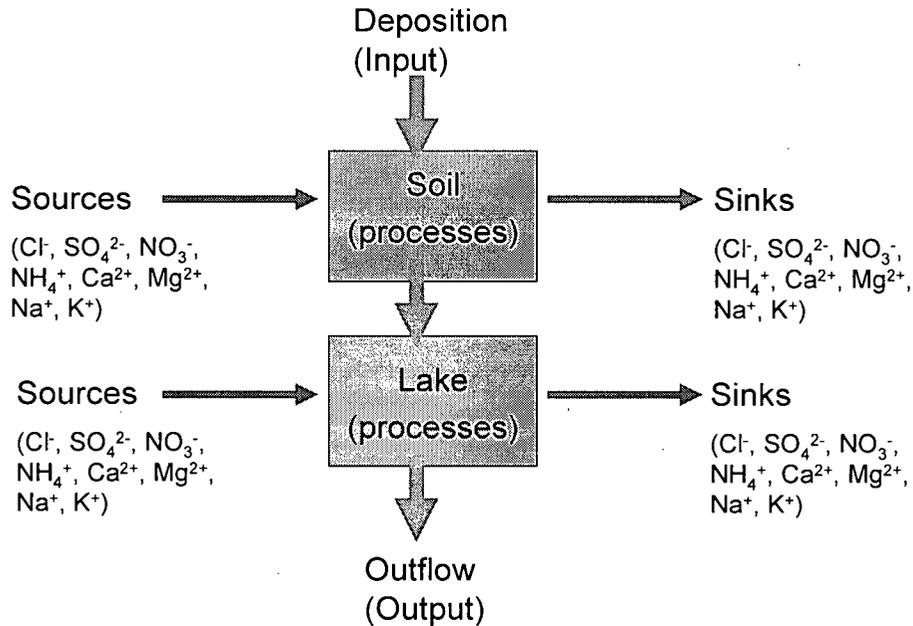
The Athabasca Oil Sands Region is home to several existing large-scale oil sands projects that extract oil from the vast oil deposits in the region, with more development planned. The concern over the potential for lakes to acidify arises because oxides of sulfur and nitrogen,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  respectively, are produced as by-products of the methods used to mine oil sands and to extract oil from these bituminous sands. Wet and dry air transport and deposition processes transfer these compounds to remote catchments that are otherwise unaffected by oil sands development. This could lead to acidification of surface water bodies as has been observed in other parts of the world (Larsen et al. 1999; Neary and Dillon 1988; Sullivan 2000). Acidification of lakes is indicated when the atmospheric addition of pollutants ( $\text{SO}_x/\text{NO}_x$ ) exceeds the acid neutralizing capacity (ANC) of a standing surface waterbody, measured in  $\text{meq}/\text{m}^3$  (Sullivan 2000).

ANC represents the difference between the concentration of base cations and the concentration of strong acid anions in a given solution, and is used to indicate the sensitivity of surface water to acidification (Cosby et al. 2001; Driscoll et al. 1994). Cosby et al. (2001) make several observations about ANC and suggest that soil processes which produce strong base cations increase the ANC of a catchment; and conversely, an introduction of strong acid anions to a catchment decreases the ANC. A large pool of strong base cations in the soil buffers against a change in ANC. In order to prevent the acidification of lakes, levels of acidifying deposition should be kept below concentrations that are defined as critical loads (typical critical loads for the region are reported in the Regional Aquatics Monitoring Program (RAMP) (Hatfield Consultants Ltd 2005)). If acid deposition is below the critical load, then no damage to the lake is likely to occur (Gorham 1998).

Currently, the Steady-State Water Chemistry (SSWC) model is used in the Alberta Oil Sands Region to determine if critical loads are being exceeded. Henriksen et al. (2001) and the Canadian Natural Resources Ltd. (2002), among others, demonstrate an effective use of the SSWC model to determine critical loads in Canada. However, there are certain drawbacks to this steady-state model. Cosby et al. (Cosby et al.) identify these drawbacks as the inability to 1) estimate when and to what extent acidification occurs; 2) account for buffering by sub-surface flows; and 3) account for retention of acid anions in soil. The effect of these shortcomings is inflated projections of the potential for acidification of subject lakes. Dynamic models such as MAGIC offer an effective alternative to these models (Cosby et al. 1985).

The MAGIC model predicts the long term ANC estimates for lakes based on acidifying air emissions and lumped soil and water parameters that characterize the acid neutralizing potential of the catchment. It simulates sulfate adsorption, nitrogen retention, and cation exchange, as well as organic and carbonic acid, and aluminum equilibrium reactions occurring in the soil in response to deposition, weathering, biological uptake of ions and related chemical equilibria. It is

applied in discrete time increments, such as on a yearly basis, to predict acidification potential for many years in the future (typically on the order of 100 years) and has been shown to be an effective tool in the analysis and management of acid sensitive lakes (Jenkins et al. 1997; National Park Service 2003; Sullivan 2000). The model may be represented by the flow chart in Figure 2-2 and is discussed in detail in Cosby et al. (2001; 1985; 1986; 1990; 1985).



**Figure 2-2 General flow chart of MAGIC**

In this paper, the MAGIC model is developed for predicting ANC values in the boreal forest of Northeastern Alberta and the robustness of the model for predicting acidification trends for lakes with different neutralizing capacities is assessed. The model is applied to the Oil Sands Region for the first time in this study. It may also be used as part of an integrated management and planning program for analyzing the impacts of different oil sands production scenarios and an approach for investigating the potential impacts of future oil sands growth on regional lakes is demonstrated herein.

## **2.2 APPLICATION TO TWO STUDY LAKES IN NORTHEASTERN ALBERTA**

Two study lakes, Lake 270 and Lake 354, are selected for application of the model because they have similar sizes and hydrology, yet different neutralizing capacities, and exhibit typical characteristics of regional lakes (Hatfield Consultants Ltd 2005). Lake 270 has a high neutralizing capacity and Lake 354 has a medium capacity. Other lakes closer to the oil sands developments, with different acid neutralizing capacities are not used because they are considered to be politically sensitive at this time. While the period of record for the surface water quality data, i.e., the pH, ionic concentrations and temperature, for these lakes is limited to three years, corresponding to the three annual averages of water quality constituent values reported, the methods being developed in this study may be applied to a wide variety of lakes in the region now and as more data become available.

Calibration and scenario analyses are undertaken for each study lake. The scenario analyses are undertaken to estimate the effects of different future deposition sequences for the time period 2005-2104. Though validation of the model using an independent data set is not possible given that the model estimates acidification in the distant future, a discussion of the validity of the data and parameters is provided. Additionally, an uncertainty analysis which provides potential bounds of model predictions based on perturbations of fixed and adjustable parameters of the model, and on variable water quality concentrations in the lakes, is used to identify the range of potential model outcomes (Cosby et al. 1995).

### **2.2.1 Representing Catchments in MAGIC**

Each lake studied requires a set of fixed input parameters and a set of calibrated adjustable parameters to account for regional characteristics. The calibration process begins with the application of a hindcast of historical deposition rates to predict current water quality conditions,

and these estimates are compared with known water quality levels at the present to determine the best choice of adjustable parameters. The hindcast years of 1864 to 2004 are used in this study.

Though there is the option to represent the study catchments as having up to two soil layers and to account for wetlands, for simplicity sake, this study represents the region as having only one soil layer and no wetlands. The various different soil types are represented in the soil layer as an aggregate based on relative proportions of soils in the catchment. The wetlands module provides an additional mechanism, other than the soil compartment, which can account for the immobilization of nitrogen. Not using the wetlands module may result in overestimates of nitrogen in the lake and conservative estimates of ANC. The data available permitted the use of annual time steps, which have been successfully used in a number of model applications (Cosby et al. 1990; Jenkins et al. 1997; Wright et al. 1988).

Winter conditions, defined by snow cover in the catchment and ice on the lake, exist in the study area for five months of the year, in November to March (Mitchell and Prepas 1990). Precipitation that falls as snow runs overland during melting and leaves the catchment without infiltrating into the soil (Kikuchi 2004). Though this would serve to lower the acidification potential in the winter months, the amount of infiltration in the catchment simulated is not altered to account for snow and ice cover due to a lack of hydrologic and snow-pack data from the catchment. This is a conservative approach.

The MAGIC model has the ability to predict the dynamics of nitrogen cycling when using the distributed nitrogen module (Cosby et al. 2001). Retention and loss of nitrogen from the soil compartment is based on the carbon to nitrogen ratio (i.e., carbon:nitrogen) calculated in that compartment.

Deposition into the catchment is key input for this model. Catchment-specific deposition data are not available for the study lakes analyzed herein and thus deposition estimates from five other

sites in the region are used, all of them near cities or towns in the Oil Sands Region (see Table 2-1 for a description of these sites). Precipitation chemistry data for annual average wet deposition of sulfate, nitrate, ammonia, calcium, sodium, magnesium and potassium (in kg/ha/yr) are taken from the National Atmospheric Chemistry (NATChem) Database. Deposition data are averaged annually and deposition profiles for sulfur and nitrogen compounds are estimated separately. Ions other than  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  are held at background levels as they are not significantly influenced by oil sands activities.

**Table 2-1 Air monitoring sites in and around the Oil Sands Region used to estimate deposition into study catchments**

Location	Data Available for Years (NATChem 2005)	Assumed to be Subject to Oil Sands Emissions
Beaverlodge (AB)	1999, 2000, 2001, 2003, 2004	No
Fort McMurray B (AB)	1999, 2000, 2001, 2004	Yes
Fort Vermillion (AB)	1999, 2004	No
Cold Lake (AB)	1999, 2000, 2001, 2002, 2003, 2004	Yes
Fort Chipewyan (AB)	1999	No

The composition of deposition at the measured sites is likely to be somewhat different from that in the study catchments, because the study area is remote and not populated. For this reason the estimates of the deposition data are developed as described in the following paragraphs.

First sulfur and nitrogen emission profiles for the entire period of oil sands development are obtained from a study of historical and projected future oil sands production (CEMA 2004). Figure 2-3i shows the historical total sulfur emissions from oil sands production, in tonnes/calendar day. Next, the nearest sites with observed deposition measurements are obtained and sorted into two categories: those sites affected by oil sands deposition and those not affected

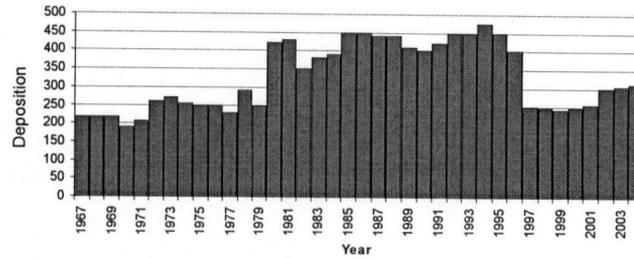
by oil sands deposition (see Table 2-3). The assumption that Fort Vermillion, Fort Chipewyan and Beaverlodge are not significantly affected by oil sands deposition is based on the observation that these areas are far from the oil sands production areas. These areas are also less populated than Fort McMurray and Cold Lake.

The five-year average annual deposition observed at Fort Vermillion, Fort Chipewyan and Beaverlodge is taken as the background deposition. The five-year average annual amount of additional deposition that Fort McMurray and Cold Lake receive above this background deposition is assumed to be the average annual deposition influenced by industrial emissions for that period, and sulfur and nitrogen deposition estimates are calculated separately (see Figure 2-3ii for the five-year average annual sulfur deposition rates at the background and industrially influenced sites).

The ratio of the five-year average annual deposition due to industrial emissions and the five-year average annual emission level for the period 1999-2004 is 0.582 (unitless). This ratio is then used to estimate the deposition due to industrial emissions for the period 1967-2004, based on the product of known annual emission levels in that period and the ratio of 0.582. The five-year average annual background deposition is considered to be the background deposition for the post-war years 1950-2004, a time in which increased vehicle use and other industrialization took place.

The model formulation of MAGIC requires that deposition levels be expressed in terms of their relative magnitude compared with the total deposition for a reference year. In this project the reference year selected is 2004 and all deposition levels are expressed in terms of a scaling factor that is equivalent to the ratio of deposition in a given year to the total deposition in 2004. For the period 1864-1950, this scaling factor, which represents the background deposition only, is assumed to increase gradually from a value of 0.1. These deposition levels are represented in terms of the scaling factor in Figure 2-4. This approach has been used in other studies and

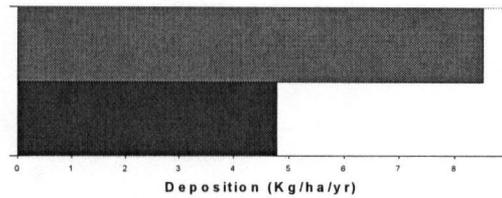
provides a complete deposition profile for the entire hindcast period (Jenkins et al. 1997).



- i) Sulfur emissions for period of oil sands development (tonnes/calender day) (Source: CEMA 2004)

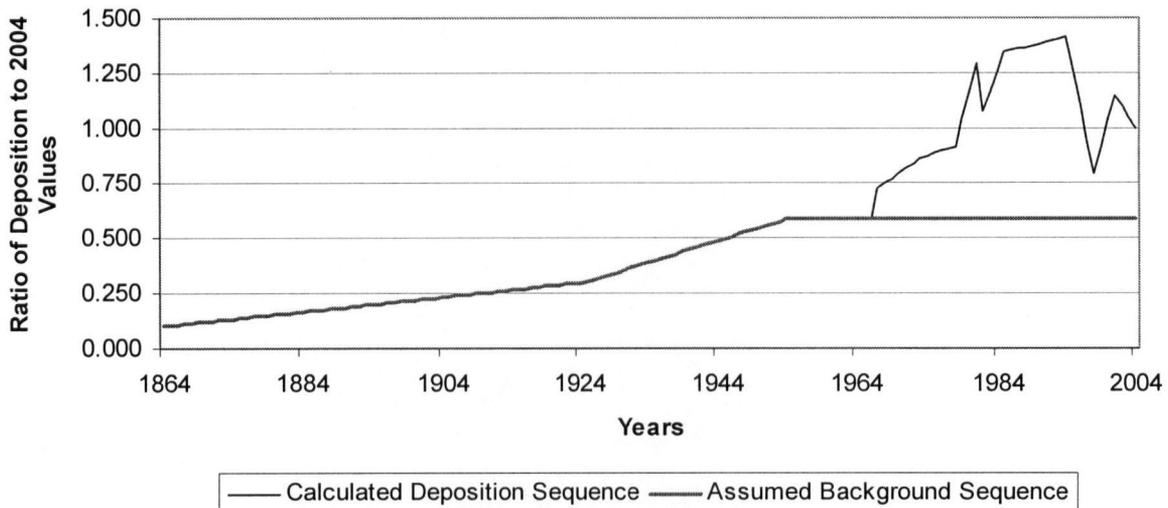
Influenced Sites

Not Influenced Sites



- ii) Comparison of mean annual sulfur deposition measured at sites influenced and not influenced by oil sands deposition (Source: NATChem 2004)

**Figure 2-3 Data regarding sulfur deposition and emissions data**



**Figure 2-4 Sulfur deposition profile used as input to MAGIC (1864-2004)**

Surface water data requirements include size of lake, retention time, depth, concentrations of

major ions, annual runoff and mean lake temperature (for estimates of these and their sources see Table 2-2). The two lakes have been regularly sampled in the RAMP program since 2001 and will continue to be sampled indefinitely.

**Table 2-2 Values of Fixed Parameters Used for Lake 270 and 354**

	Units	Lake 270	Lake 354	Source of Data
<b>Fixed Soil Parameters</b>				
<i>Depth</i>	<i>M</i>	1.07	0.75	Soil surveys undertaken as part of regulatory applications from 2000 to 2005 (Imperial Oil 2005; OPTI Canada Inc. 2000; Petro-Canada 2001)
<i>Porosity</i>		0.5	0.5	No direct measurements available. (Estimated from Cosby et al. 1995; Hornberger et al. 1989; Larssen et al. 2004)
<i>Bulk Density</i>	<i>kg·m<sup>-3</sup></i>	700	712.20	No direct measurements available. (Estimated from Miller and Gardiner 2001).
<i>Cation Exchange Capacity</i>	<i>meq·kg<sup>-1</sup></i>	157.96	138.00	(Turchenek and Lindsay 1982)
<i>SO<sub>4</sub> Half Saturation</i>	<i>meq·kg<sup>-1</sup></i>	1.0	1.0	(UNECE 2004)
<i>SO<sub>4</sub> Maximum Saturation</i>	<i>meq·kg<sup>-1</sup></i>	5.94	5.66	No direct measurements available. (Estimated from Turchenek and Lindsay 1982; UNECE 2004)
<i>Soil Temperature</i>	<i>°C</i>	0.7	0.7	(Environment Canada 2005)
<i>Organic Matter Content</i>	<i>Mmol·m<sup>3</sup></i>	7.0	7.0	(Turchenek and Lindsay 1982)
<i>pK1 Dissolved Organic Carbon (DOC)</i>	<i>(log<sub>10</sub>)</i>	3.04	3.04	(Moldan et al. 2004)
<i>pK2 DOC</i>	<i>(log<sub>10</sub>)</i>	4.51	4.51	(Moldan et al. 2004)
<i>pK3 DOC</i>	<i>(log<sub>10</sub>)</i>	6.46	6.46	(Moldan et al. 2004)

<i>Annual Precipitation Volume</i>	$m \cdot yr^{-1}$	0.460	0.460	(Environment Canada 2005)
<b>Fixed Surface Water Parameters</b>				
<i>Runoff</i>	$m \cdot year^{-1}$	0.206	0.387	(WRS 2004)
<i>Lake Al(OH)<sub>3</sub> Solubility</i>	$(log_{10})$	8.04	8.04	No direct measurements available. (Estimated from Reuss and Walthall 1989)
<i>Organic Matter Content</i>	$Mmol \cdot m^3$	38.4	23.7	No direct measurements available. (Estimated from Hatfield Consultants Ltd 2005)
<i>Relative Area</i>	%	12.90	18.00	(AGRASID 2005)
<i>Retention Time</i>	<i>Years</i>	1.25	0.95	No direct measurements available. (Estimated from WRS 2004)
<i>Annual Average Temperature</i>	$^{\circ}C$	9.0	9.0	No direct measurements available. (Estimated from Mitchell and Prepas 1990)

Data requirements for soil characteristics include size of catchment, bulk density, cation exchange capacity, maximum sulfate saturation capacity, cation exchange capacity, depth, porosity and temperature (for estimates of these and their sources, see Table 2-2). The exchangeable base cations available in the soil and the selectivity coefficients that determine the equilibrium of cations between soil and soil water are adjustable parameters and are determined during the calibration process.

### 2.2.2 Calibration

The calibration of the MAGIC model is used to estimate the adjustable parameters shown in Table 2-3 based on comparisons of simulated and measured concentrations of constituents. The parameter estimates are conducted in sequence whereby the concentration of Cl<sup>-</sup> is simulated first and compared with known values, and these comparisons are used to estimate all parameters relevant to chlorine deposition, weathering, and biological uptake. The process is repeated for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, base cation concentrations and pH in this order as described in Cosby et al.

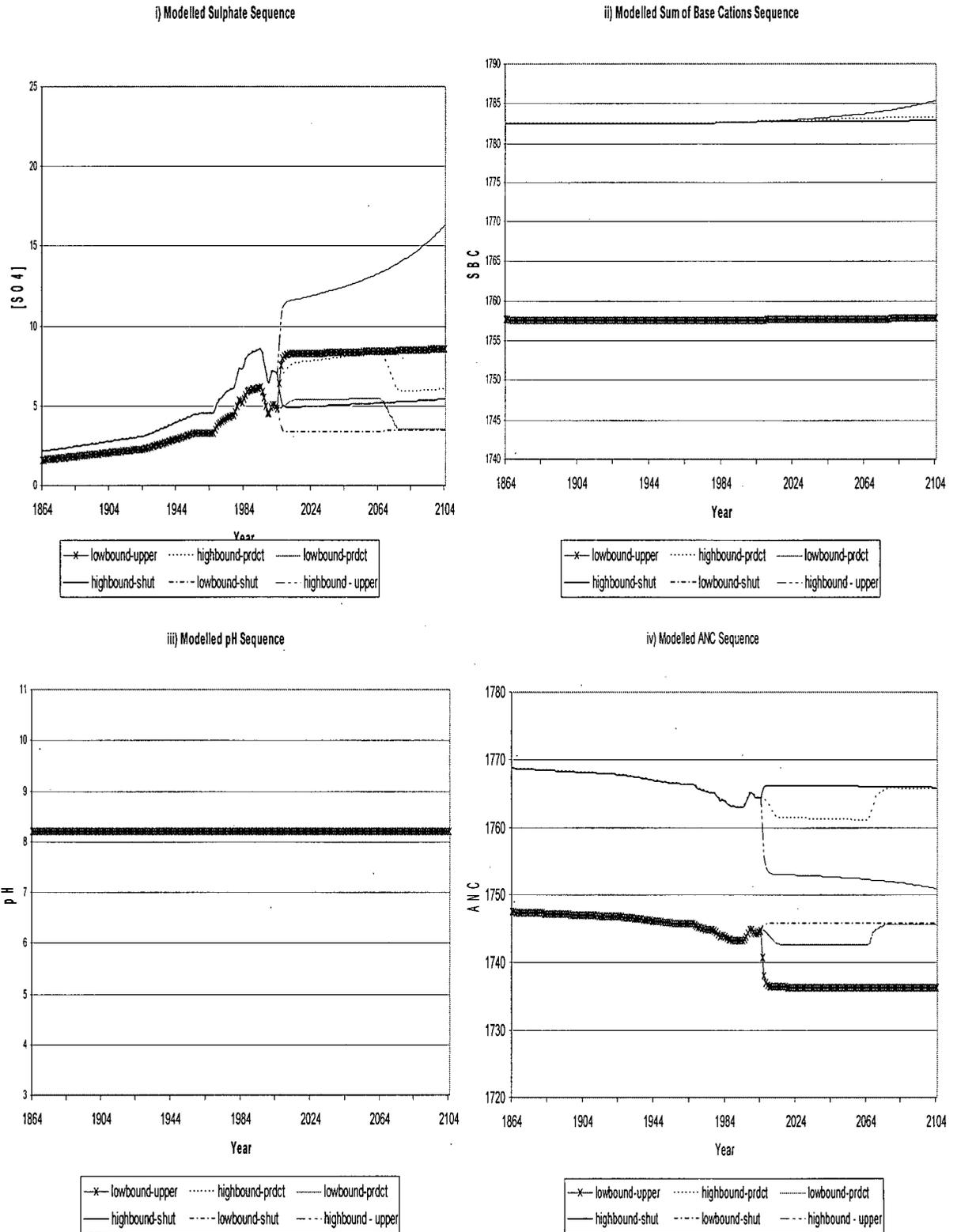
(1995), Jenkins et al. (1997) and Wright (1988). This procedure establishes the sulfate and nitrogen retention processes in the soil matrix that are central to making predictions of the acidification potential of the catchment, specifically by simulating the propensity of these compounds to leach to surface waters. Once all the constituents are estimated the simulated and measured ANC are compared and used to adjust the aluminum solubility. In this work, the measured and modelled data are compared and selected parameter values are determined based on the minimization of the sum of squared errors of the comparisons.

**Table 2-3 Calibrated values of adjustable parameters for Lakes 270 and 354**

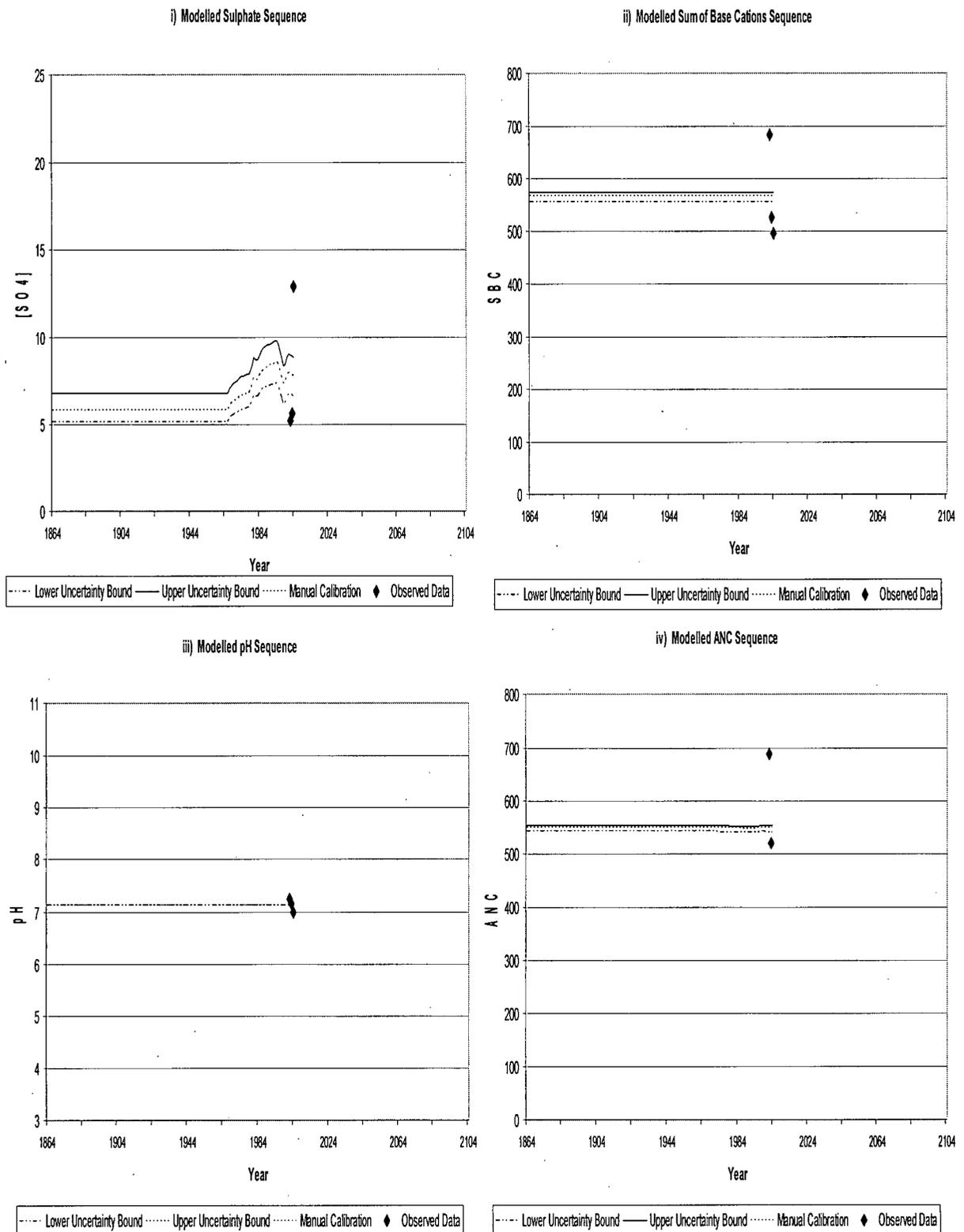
<b>Adjusted Parameters</b>	<i>Units</i>	<b>Lake 270</b>	<b>Lake 354</b>
<i>Soil Al(OH)<sub>3</sub> Solubility</i>	<i>(log<sub>10</sub>)</i>	6.73	7.36
<i>NO<sub>3</sub><sup>-</sup> Sink in Lake</i>	<i>meq/m<sup>2</sup>/yr</i>	10.0	10.5
<i>Ca Weathering</i>	<i>meq/m<sup>2</sup>/yr</i>	247.0	139.0
<i>Mg Weathering</i>	<i>meq/m<sup>2</sup>/yr</i>	143.0	82.0
<i>Na Weathering</i>	<i>meq/m<sup>2</sup>/yr</i>	19.0	29.0
<i>K Weathering</i>	<i>meq/m<sup>2</sup>/yr</i>	1.1	9.8
<i>Cl- Dry Deposition Factor</i>	<i>(-)</i>	6.63	4.10

Calibration results for estimates of SO<sub>4</sub><sup>2-</sup>, the sum of base cation concentrations, pH and ANC are provided in Figures 2-5 and 2-6, for Lakes 270 and 354, respectively. Although based on limited known field data these results show agreement between observed water quality constituents and the modelled concentrations and that the model output provides an apt representation of the conditions in the study lakes.

**Figure 2-5 Results of Calibration of Lake 270**



**Figure 2-6 Results of Calibration of Lake 354**



Lake 270 is well buffered against acidification. Although the period of oil sands development (1967 to 2004) shows an increase in acidifying emissions, there is no observable effect on the ANC or pH in this lake. Lake 354 is not as well buffered as Lake 270 and the ANC is not as high as that for Lake 270. Regardless both systems appear to be sufficiently buffered through the period of oil sands development.

The resulting weathering rates and cation exchange selectivity coefficients are higher in these catchments than in previously studied systems (Cosby et al. 1990; Hornberger et al. 1989; Wright 1989). Weathering is the mechanism that accounts for the addition of base cations in the lake and cation exchange selectivity coefficients act as rate constants in the exchange of cations between soil solution and soil matrix. In order to have greater confidence that these values are appropriately capturing processes occurring in the soil, improved soil parameter data should be gathered. Currently, data are limited to a select number of studies and soil survey programs conducted during EIA baseline studies.

### **2.2.3 Sensitivity Analysis of Estimated Parameters**

Sources of information for lake retention time, porosity, bulk density, maximum sulfate saturation capacity and the dissolved organic carbon (DOC) concentration in soil are limited (see Table 2-2) and data for these parameters are estimated based on other studies. In order to determine the importance of these parameters in the model, a sensitivity analysis of them is conducted. This procedure offers insight into where sampling efforts should be focused should the RAMP program choose to collect additional data for this model. No sensitivity analysis was performed on parameters for which detailed information was available, because this thesis focuses on those parameters related to acidification of lakes. The objective was not to remove uncertainty but to establish a model working model based on currently available data. To remove uncertainty from measured parameters was not included in the scope.

The model is evaluated for parameter increases of as much as 155% of the original value and decreases of as much as 70% of the original value, to determine the effect of such a perturbations on model outcome. The effects of the greatest positive (155%) and negative perturbation (70%) on the outcome of modelled sulfate, chloride and sum of base cation concentrations, as well as the pH, ANC are provided in Table 2-4.

**Table 2-4 Greatest positive and negative effect on modelled outputs based on perturbations of uncertain parameters**

	Modelled Output									
	SO <sub>4</sub> <sup>2-</sup>		Cl <sup>-</sup>		pH		ANC		SBC	
	High	Low	High	Low	High	Low	High	Low	High	Low
Water Temperature	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Retention Time	8%	0%	0%	0%	0%	0%	-1%	24%	5%	0%
Soil Depth	28%	-6%	0%	0%	0%	0%	-1%	11%	1%	-1%
Porosity	0%	0%	0%	0%	0%	0%	-1%	2%	1%	0%
Bulk Density	26%	-5%	0%	0%	0%	0%	-3%	12%	0%	-1%
Maximum Sulfate Saturation Capacity	393%	-8%	0%	0%	0%	-1%	-2%	82%	24%	0%
DOC in Soil	0%	0%	0%	0%	0%	-1%	13%	96%	-4%	-33%
SO <sub>4</sub> <sup>2-</sup> Half Saturation	31%	5%	0%	0%	0%	0%	1%	6%	2%	0%

The most sensitive parameter affecting modelled sulfate concentration is the maximum sulfate saturation capacity in the soil. The soil depth, bulk density and half-saturation capacity of sulfate are also important for modelling sulfate concentrations. Chloride concentrations are insensitive to these parameters. The pH is also largely unaffected by these parameters. The ANC is strongly influenced by the concentration of DOC in the soil. Retention time, maximum sulfate adsorptivity, bulk density and soil depth also have an effect on the ANC. The sum of base cations is influenced by the concentration of DOC in the soil and the maximum sulfate saturation capacity. These results suggest that the maximum sulfate adsorptivity and the DOC in the soils are the most important parameters for which there is limited information.

A reasonable calibration of measured water quality parameters is obtained despite limited DOC and maximum sulfate adsorptivity data, suggesting that proper model function has not been impeded. This partial sensitivity analysis shows that more data gathering should be focused on the soil parameters of DOC in soil solution and the sulfate adsorptivity coefficients.

## 2.2.4 Uncertainty Analysis

The fixed parameters in the model are subject to measurement uncertainty as well as uncertainty associated with lumping parameters in the soil compartment (Cosby et al. 1990; Jenkins et al. 1997) and this may lead to uncertainty in the model outcomes. An uncertainty analysis is conducted to obtain the potential range of uncertainty in the calibrated model (Cosby et al. 1990; Jenkins et al. 1997). The analysis yields the range of results for the calibrated model under assumptions regarding the distribution of the fixed parameters and the water quality concentrations in the lake. The potential range of uncertainty is bounded by the maximum and minimum results of ten simulations of the model, each based on randomly selected fixed parameters and water quality concentrations (Cosby et al. 1990). The range of the possible water quality concentrations is taken as the larger of 10% or 5 meq/m<sup>3</sup>, and the range of the soil base saturation parameters is taken as 0.5% or as the observed variability of the data as suggested by Cosby (1990). Parameters used to obtain the range of model outcomes are given in Table 2-5.

The potential range of uncertainty produced by this method is provided in Figures 2-5 and 2-6. The maximum and minimum bounds for each of the study lakes present the same results as the manually calibrated model in each lake; the systems are well buffered against acidification.

**Table 2-5 Water quality concentration and fixed parameter ranges in uncertainty analysis**

	Variable	Units	Lake 270		Lake 354	
			Upper	Lower	Upper	Lower
Target Variables	Total Nitrogen Concentration in Lake	meq/m <sup>3</sup>	7.68	0.00	8.50	0.00
	Sulfate Concentration in Lake	meq/m <sup>3</sup>	10.83	0.83	12.91	2.91
	Calcium Concentration in Lake	meq/m <sup>3</sup>	1180.20	965.62	335.76	274.72
	Magnesium Concentration in Lake	meq/m <sup>3</sup>	675.85	552.97	195.51	159.97
	Sodium Concentration in Lake	meq/m <sup>3</sup>	94.41	77.27	70.50	57.68
	Potassium Concentration In Lake	meq/m <sup>3</sup>	10.97	0.97	26.38	16.38
	Exchangeable Calcium in Soil	%	25.13	24.88	7.84	7.76
	Exchangeable Magnesium in Soil	%	24.12	23.88	5.53	5.47
	Exchangeable Sodium in Soil	%	13.07	12.94	2.31	2.29
	Exchangeable Potassium in Soil	%	7.04	6.97	1.71	1.69
pH	(log10)	9.5	7.5	9.5	7.5	
Optimized Parameters	Calcium Weathering	meq/m <sup>2</sup> /yr	271.70	222.30	152.90	125.10
	Magnesium Weathering	meq/m <sup>2</sup> /yr	157.30	128.70	90.20	73.80
	Sodium Weathering	meq/m <sup>2</sup> /yr	20.90	17.10	31.90	26.10
	Potassium Weathering	meq/m <sup>2</sup> /yr	1.21	0.99	10.78	8.82
	Exchangeable Calcium in Soil	%	25.13	24.88	7.84	7.76
	Exchangeable Magnesium in Soil	%	24.12	23.88	5.53	5.47
	Exchangeable Sodium in Soil	%	13.07	12.94	2.31	2.29
	Exchangeable Potassium in Soil	%	7.04	6.97	1.71	1.69
Fixed Parameters	Lake Runoff	m·year <sup>-1</sup>	0.23	0.18	0.43	0.35
	Precipitation	m·year <sup>-1</sup>	0.50	0.42	0.51	0.42
	Retention Time	year	1.38	1.13	1.05	0.86
	Soil Depth	m	2	0.4	2.00	0.75
	Bulk Density	frac.	1500.00	500.00	1500.00	500.00
	Cation Exchange Capacity	meq·kg <sup>-1</sup>	219.00	60.50	176.00	84.87
	Soil Al(OH) <sub>3</sub> Solub.	(log10)	8.00	6.00	8.00	6.00

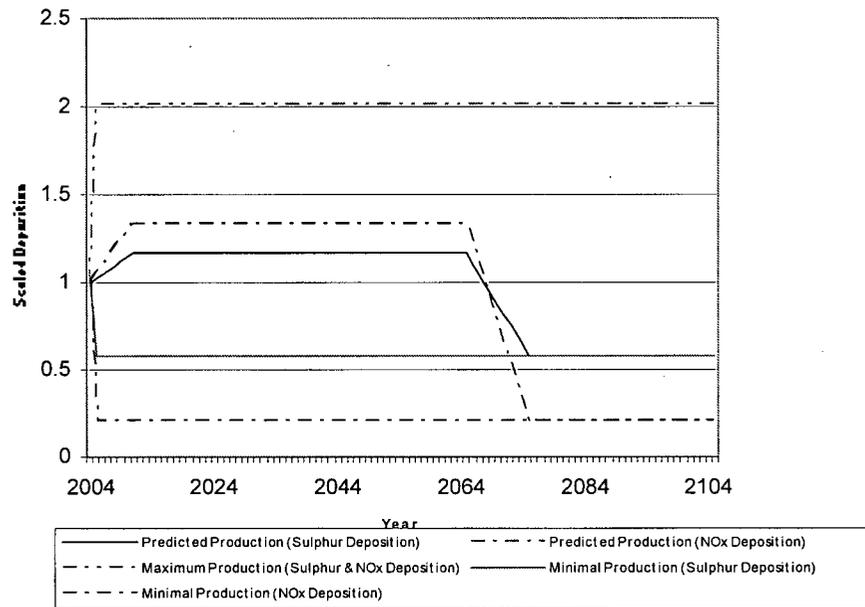
## 2.2.5 Development Scenarios

Provided the shortcomings of the calibrated model are acknowledged, it may be used to estimate the effects of various future development schemes. Various deposition rates that represent different development scenarios are used herein and ANC values for the years 2005 to 2104 are estimated for these. A 100 year forecast is selected to ensure that the timescale is long enough to represent the full extent of the dynamics of acidification.

Three development scenarios are investigated (see Figure 2-7). These scenarios are the:

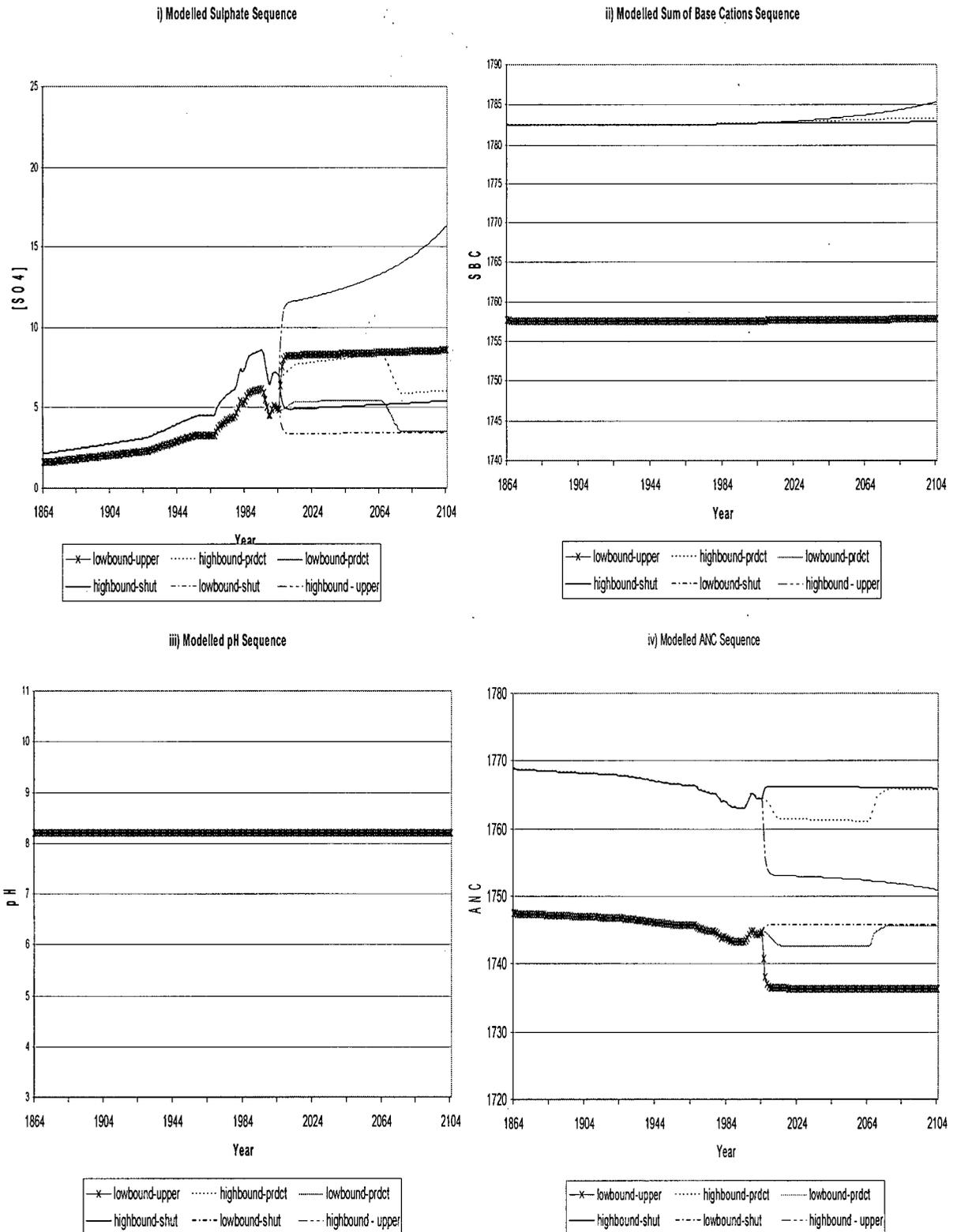
- '*predicted production*' scenario which is the most likely future trend of acidifying emissions in the region as calculated by CEMA (2004) and is used to assess the most likely effects of acidification on the study lakes.
- '*miminal production*' scenario which examines the impact of closing all oil sands projects as of 2005 and assumes that emissions fall immediately to background levels. This is considered the lower bound of the problem space.
- '*maximum production*' scenario which assumes that oil sands emissions double between the years 2004 and 2005. Although this level of emission is unlikely even in the long term, this case serves as a potential upper bound of the problem space.

The potential range of uncertainty for the impacts of each of these scenarios is determined based on an uncertainty analysis described in Section 2.2.4. The range of outcomes for these development scenarios are shown in Figures 2-8 and 2-9, for Lake 270 and 354, respectively.

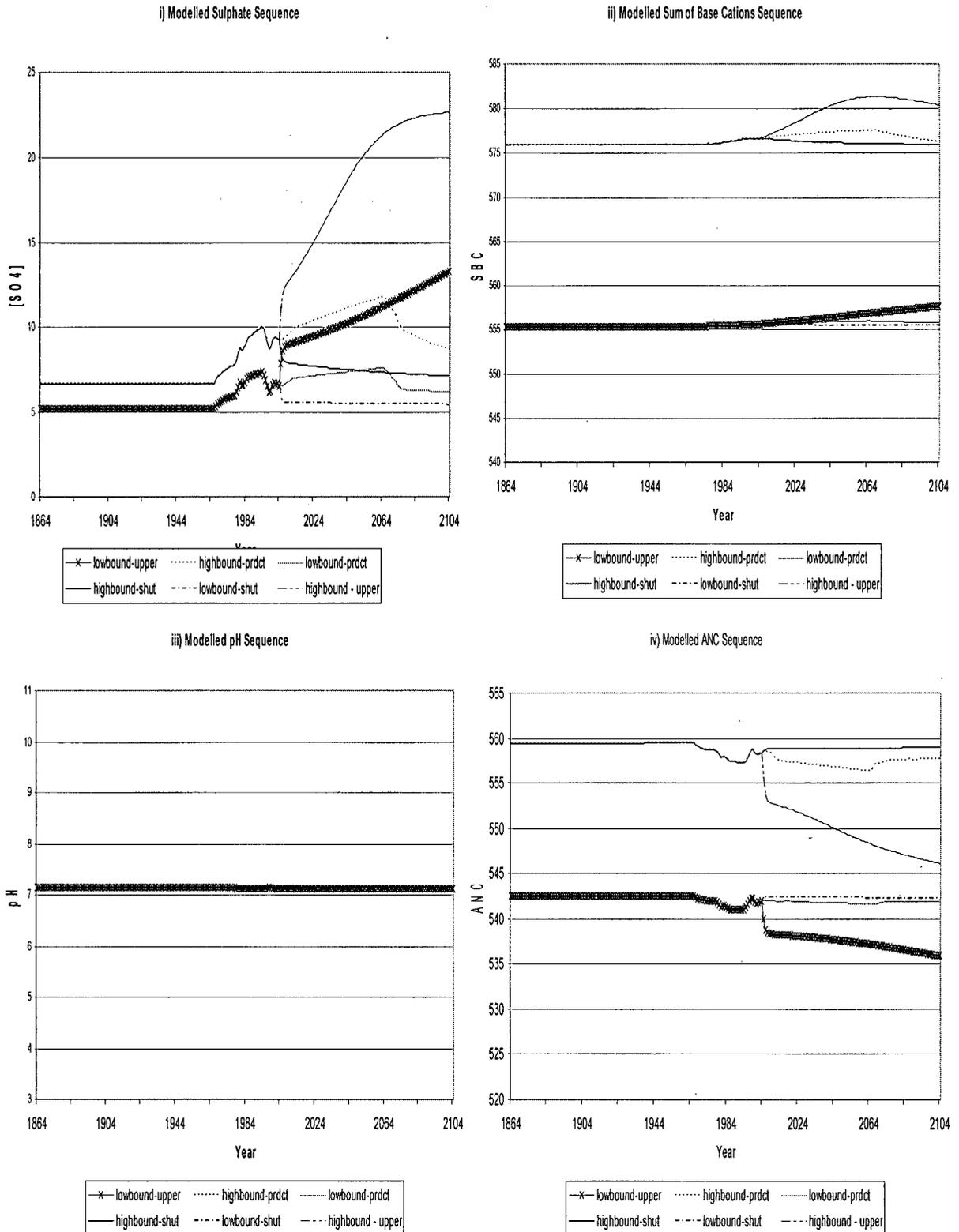


**Figure 2-7 Deposition profiles for development scenarios**

**Figure 2-8 Impacts of development scenarios on Lake 270**



**Figure 2-9 Impacts of development scenarios on Lake 354**



The impacts of the development scenarios on acidification in the years 2005 to 2104 indicate a low risk of acidification for these cases. Small increases in the concentration of sulfate and nitrate in the lake are observed, and these are likely due to direct deposition and a marginal decrease in the ANC. However, the ANCs of the lakes under these modelled scenarios are still well above the critical threshold of zero. Concentrations of sulfate, nitrate and ammonia in each lake followed the trend of deposition with a short lag time. Corresponding changes in ANC show a marginal decrease for the same years. Base cation and chloride concentrations and pH remain unchanged. Only the maximum production scenario results in a slight increase in base cation leaching (see Figure 2-8ii and 2-9ii). The main difference between the two study lakes is the level of base cations in the water. There is a lower concentration of base cations in Lake 354 than in Lake 270, which contributes to the lower ANC and pH observed for Lake 354.

## **2.3 DISCUSSION AND CONCLUSIONS**

Levels of sulfur and nitrogen deposition, which have been increasing since the industrial revolution, lead to the addition of strong acid anions in the catchments of lakes. The acidification of surface water is of concern to environmental scientists and managers because this phenomenon may change the water quality of freshwater lakes.

The validity of a model for evaluating the acidification of surface waters, such as MAGIC, must be demonstrated prior to using it in industrial management (Ford 1999). Model validation is typically undertaken by comparing simulated results from the calibrated model with some different set of environmental conditions, or some subset of historical data (Oreskes et al. 1994). Given a sufficiently large dataset, this would be the preferred approach for investigating the validity of a model. Unfortunately this approach cannot be applied in verification of the MAGIC model due to the paucity of data available for the study lakes or for the acidification process in general. Ford (1999) identifies this shortcoming and suggests other means of validating the

MAGIC model, which are applied herein to validate the models of two study lakes. The calibration of the deposition and the parameters in the lake compartment of the model are within accepted ranges. Calibrated parameter values in the soil compartment are similarly suitable, with two noteworthy exceptions. Weathering rates and soil selectivity coefficients are higher than previously reported studies and need to be confirmed.

The main shortcoming of the modelling exercise undertaken herein is the absence of soil data against which soil compartment parameters may be compared. However, the partial sensitivity analysis shows that in spite of this shortcoming, the model results are only meaningfully sensitive to the concentration of DOC and the maximum adsorptivity of sulfate in the soil. Improved deposition data, longer time series of water data, and better soil data are required before this model may be considered an effective tool to be used in making management decisions for oil sands production.

Improvements in data collection could be incorporated in the course of regular environmental impact assessment baseline studies, which are required for each regulatory application (Imperial Oil 2005). While there would be benefits to gathering data for each of the model parameters, efforts should be focused on improving the information about soil DOC concentrations and maximum sulfate saturation capacity.

The modelling results show that the sum of acid ions do not exceed the sum of base cations in either lake. The base cations buffer the effects of acid ions, and thus the ability of acid ions to affect the pH in the lake is mitigated. If no change in the leaching of base cations occurs this indicates that the sulfate pool in the soil has not reached its capacity and there is no leaching of sulfate to the lake.

The structure of the model has been demonstrated to be valid in this and as found in other studies and the observed lake chemistry is well explained by the principles of acidification captured in

the model. The performance of the model relative to pre-1999 conditions cannot be determined given the lack of data. This is not an uncommon limitation for studies of acidification in remote areas and should not preclude modellers from building continued confidence in the model (Ford 1999; National Park Service 2003). The trend of the results of the models applied herein is not unrealistic. Further validation of these models may be undertaken by examining diatom records of the sediments of lakes to evaluate the assumptions made about the acid neutralizing status of a given lake in the past. Also, the two study lakes considered herein may be further analyzed to determine the adequacy of the model as more data are gathered.

Mitigating acidification requires an in-depth understanding of the socio-economic and environmental features of the region as well as the history of events leading to the current state (Fitzpatrick et al. 2001; Wetzel 2001). Using a model to predict the response of acidifying emissions is only one part of the impact analysis. Other relevant issues include establishment of regional critical loads, air emissions modelling to more accurately predict deposition, and analysis of fish health and aquatic ecosystem integrity. These topics are all related and should be given due consideration prior to drawing conclusions about the effects of acid emissions on lakes.

Scientific and engineering research has made significant advances in understanding the phenomenon of surface water acidification in the last 20 years. The current understanding of surface water acidification, coupled with the technical ability to simulate system responses, constitute valuable tools for developing sound public policy to address this problem.

## **2.4 ACKNOWLEDGEMENTS**

Gratitude is expressed to all those who helped with this paper, including Dr. Les Lavkulich for reviewing the draft and providing comments as well as the contributions of Dr. Hans Schrier. The assistance and support of Mr. Ian Mackenzie and Dr. Andrews Takyi of Golder Associates Ltd. contributed greatly to this project. The assistance by Dr. Jack Cosby of the University of

Virginia and Dr. Richard Wright of the Norwegian Institute for Water Research with the MAGIC Model is greatly appreciated. This work was carried out with the financial support of an Industrial Post-Graduate Research Grant from the Natural Science and Engineering Research Council of Canada with partial support from Golder Associates Ltd.

## 2.5 CHAPTER 2 REFERENCES

- AGRASID. (2005). "Agricultural Region of Alberta Soil Inventory Database; Version 3.0." Provided by Alberta Agriculture, Food and
- Canadian Natural Resources Limited. (2002). "Horizon Oil Sands Project - Application for Approval." Submitted to Alberta Energy and Utilities Board and Alberta Environment, Calgary, A.B.
- CEMA. (2004). "Recommendation for the Acid Deposition Management Framework for the Oil Sands Region of Northeastern Alberta." Cumulative Environmental Management Association, Fort McMurray.
- Cosby, B. J., Ferrier, R. C., Jenkins, A., and Wright, R. F. (2001). "Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model." *Hydrology and Earth System Sciences*, 5(3), 499-517.
- Cosby, B. J., Hornberger, G. M., Galloway, J. N., and Wright, R. F. (1985). "Time scales of catchment acidification; A quantitative model for estimating freshwater acidification." *Environmental Science and Technology: Features*, 19, 1144-1149.
- Cosby, B. J., Hornberger, G. M., Wright, R. F., and Galloway, J. N. (1986). "Modeling the Effects of Acid Deposition: Control of Long-Term Sulphate Dynamics by Soil Sulfate Adsorption." *Water Resources Research*, 22(8), 1283-1291.
- Cosby, B. J., Jenkins, A., Ferrier, R., Miller, J. D., and Walker, T. A. B. (1990). "Modelling Stream Acidification in Afforested Catchments: Long Term Reconstruction at two sites in Central Scotland." *Journal of Hydrology*, 120.
- Cosby, B. J., Wright, R. F., and Gjessing, E. (1995). "An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway." *Journal of Hydrology*, 170, 101-122.
- Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N. (1985). "Modelling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment." *Water Resources Research*, 21(11), 1591-1601.
- Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N. (1985). "Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry." *Water Resources Research*, 21(1), 51-63.
- Driscoll, C. T., Lehtinen, M. D., and Sullivan, T. J. (1994). "Modeling the acid-base

- chemistry of organic solutes in Adirondack, New York, lakes." *Water Resources Research*, 30(2), 297-306.
- Environment Canada. (2005). "Canadian Climate Normals."  
[http://www.climate.weatheroffice.ec.gc.ca/climate\\_normals/index\\_e.html](http://www.climate.weatheroffice.ec.gc.ca/climate_normals/index_e.html).
- Fitzpatrick, J., Imhoff, J., Burgess, E., and Brashear, R. (2001). "Water Quality Models: A Survey and Assessment." Project 99-WSM-5, Water Environment Research Foundation, Alexandria, VA.
- Ford, A. (1999). *Modeling the Environment*, Island Press, Covelo, California.
- GeoBase.ca. (2006). "Geospacial Information." Canadian Council on Geomatics.  
Accessed online: March 28, 2006.
- Gorham, E. (1998). "Acid deposition and its ecological effects: a brief history of research." *Environmental Science and Policy*, 1, 153-166.
- Hatfield Consultants Ltd. (2005). "Regional Aquatics Monitoring Program (RAMP); Technical Report." RAMP Steering Committee.
- Henriksen, A., and Posch, M. (2001). "Steady-state models for calculating critical loads for acidity for surface waters." *Water, Air and Soil Pollution: Focus*, 1, 375-398.
- Hornberger, G. M., Cosby, B. J., and Wright, R. F. (1989). "Historical Reconstructions and Future Forecasts of Regional Surface Water Acidification in Southernmost Norway." *Water Resources Research*, 25(9), 2009-2018.
- Imperial Oil. (2005). "Kearl Oil Sands Project - Mine Development. Volumes 1 to 9. Submitted to Alberta Energy and Utilities Board and Alberta Environment. Prepared by Imperial Oil Resources Ventures Limited in association with Golder Associates Ltd., AXYS Environmental Consulting Ltd., Komex International Inc. and Nichols Applied Management." Calgary, Alberta.
- Jenkins, A., Ferrier, R., and Cosby, B. J. (1997). "A dynamic model for assesing the impact of coupled sulphur and nitrogen deposition scenarios on surface water acidification." *Journal of Hydrology*, 197, 111-127.
- Jenkins, A., Renshaw, M., Helliwell, R., Sefton, C., Ferrier, R., and Swingewood, P. (1997). "Modelling surface water in the UK; Application of the MAGIC model to the Acid Water Monitoring Network." IH Report No. 131, Natural Environmental Research Council.
- Kikuchi, R. (2004). "Deacidification effect of the litter layer on forest soil during snowmelt runoff - laboratory experiment and its basic formularization for simulation modelling." *Chemosphere*, 54, 1163-1169.
- Larssen, T., Cosby, B. J., and Hogasen, T. (2004). "Uncertainties in predictions of surface water acidity using the MAGIC model." *Water, Air and Soil Pollution: Focus*, 4, 125-137.
- Larssen, T., Seip, H. M., Semb, A., Mulder, J., Muniz, I. P., Vogt, R. D., Lydersen, E., Angell, V., Dagang, T., and Eilersen, O. (1999). "Acid deposition and its effects in China: an overview." *Environmental Science and Policy*, 2, 9-24.

- McEachern, P., 2005. Personal Communication with Dr. P. McEachern on May 20th, 2005. Edmonton, AB.
- Miller, R., and Gardiner, D. (2001). *Soils in our Environment*, Prentice Hall, Toronto.
- Moldan, F., Kronnas, V., Wilander, A., Karlton, E., and Cosby, B. J. (2004). "Modelling acidification and recovery of swedish lakes." *Water, Air and Soil Pollution: Focus*, 4, 139-160.
- NATChem. (2005). "Canadian National Atmospheric Chemistry Precipitation Database, Summary Statistics of Precipitation Chemistry Data." Environment Canada, Meteorological Service of Canada, 4905 Dufferin Street, Toronto, Ontario, Canada M3H 5T4.
- National Park Service. (2003). "Assessment of Air Quality and Related Values in Shenandoah National Park; Technical Report NPS/NERCHAL/NRTR-03/090, Appendix F." U.S. Department of the Interior, Northeast Region.
- Neary, B. P., and Dillon, P. J. (1988). "Effects of sulphur deposition on lake-water chemistry in Ontario, Canada." *Nature*, 333, 340-343.
- OPTI Canada Inc. (2000). "Long Lake Project Application for Approval to Alberta Energy and Utilities Board and to Alberta Environment." Fort McMurray, AB.
- Oreskes, N., Shrader-frechette, K., and Belitz, K. (1994). "Verification, Validation, and Confirmation of Numerical Models on the Earth Sciences." *Science*, 263, 641-646.
- Patricia Mitchell, and Prepas, E. E. (1990). *Atlas of Alberta Lakes*, The University of Alberta Press, Edmonton, AB.
- Petro-Canada. (2001). "(Petro-Canada Oil and Gas) Application for the Approval of the Meadow Creek Project (Environmental Impact Assessment)." Calgary, AB.
- Reuss, J. O., and Walthall, P. M. (1989). *Soil reaction and acidic deposition in Soils, Aquatic Processes and Lake Acidification* (S.A. Norton, S.E. Lindberg & A.L. Page, eds.), Springer-Verlag; New York.
- Rural Development, used under license.
- Sullivan, T. J. (2000). *Aquatic Effects of Acidic Deposition*, CRC Press LLC, Boca Raton.
- Turchenek, L. W., and Lindsay, J. D. (1982). "Soils Inventory of the Athabasca Oil Sands Environmental Research Program Appendix - 9.4; Soil Survey Report No. 42." Alberta Research Council Soils Department.
- UNECE. (2004). "Manual on methodologies and criteria for modelling and mapping critical levels and air pollution effects, risks and trends." UNECE Convention on Long-Range Transboundary Air Pollution.
- Wetzel, R. G. (2001). *Limnology; Lake and River Ecosystems*, Third Edition, Academic Press, San Diego.
- Wright, R. F. (1989). "RAIN Project: Role of Organic Acids in Moderating pH Change Following Reduction in Acid Deposition." *Water, Air and Soil Pollution*, 46, 251-

259.

Wright, R. F., Emmett, B. A., and Jenkins, A. (1988). "Acid Deposition, land use change and global change: MAGIC 7 model applied to Aber, UK (NITREX project) and Risdalsheia, Norway (RAIN and CLIMEX projects)." *Hydrology and Earth System Sciences*, 2(4).

WRS. (2004). "Calculation of Critical Loads of Acidity to Lakes in the Athabasca Oil Sands Region." NOX-SOX Committee of Cumulative Environmental Management Association, Calgary, AB.

### **3 FUTURE DIRECTIONS AND INSIGHTS**

This chapter is a discussion of the shortcomings and future improvements of the modelling exercise, as well as the extensions and applications related to this project. First the shortcomings of the models developed are addressed and suggestions for future improvements to the work presented in Chapter 2 are made. Areas with the greatest uncertainty are discussed and the means of alleviating such issues are explored. Supplemental work that could be carried out to enhance the certainty of the projections of Chapter 2 is also highlighted. In Section 3.2, supplemental work which extends the usefulness of the model beyond the scope of the thesis project is discussed. These concluding recommendations and areas for future work are considered from the perspective of interested parties in the oil sands industry who would most likely benefit from the recommended work. The interests of practitioners (i.e., consultants) who conduct EIAs of oil sands projects, the provincial regulator (AENV), oil sands producers and stakeholders (including aboriginal groups and community groups) are considered.

#### **3.1 SHORTCOMINGS AND IMPROVEMENTS**

The main shortcoming of the modelling exercise is the high levels of soil selectivity coefficients which are related to the high weathering rates that are determined internally within the model, but are affected by the choice of the proportion of exchangeable base cations in the calibration procedure. The appropriate range of soil selectivity coefficient values is roughly between -3 and +3 (personal communication, B.J. Cosby, Dec. 2005), but the values determined as a result of the calibrated model are an order of magnitude higher than this range. The reason for the high selectivity coefficients is the elevated weathering rates. Lower valued weathering rates do not result in selectivity coefficients beyond suggested ranges. Without better field data it is difficult to say if this problem is significant. The contribution of a soil scientist should be sought in order to verify the parameterization of the soil compartment. Such work could help to validate

weathering rates, thus improve the understanding of the selectivity coefficients.

The second shortcoming of the modelling exercise is the limited availability of nitrogen immobilization data. A study into the relationship between carbon:nitrogen ratios and nitrogen release rates from regional soils would provide insights into how best to represent nitrogen retention processes in the oil sands region. Gathering data in this area could be included in the EIA field programs undertaken in baseline studies prior to the preparation of an EIA.

A shortage of observed soil conditions in the catchments prevents the model from adequately representing aluminum and dissolved organic carbon. Improved soil solution chemistry data and estimates of cation-aluminum exchange coefficients would contribute to a better representation of the processes responsible for aluminum and DOC dynamics in MAGIC. This concern points to one of the key issues regarding the application of the MAGIC model in this region. Many of the parameters needed to set up this model are not currently collected in any of the sampling programs published for the region. These include soil porosity, maximum sulfate adsorptivity, DOC concentration in the soil, retention time in the lake, lake temperature and lake depth. Fortunately, the lack of data for some of these parameters may be addressed by the use of information from related data sources (see Table 2-2).

### **3.2 EXTENSIONS AND APPLICATIONS**

A number of studies could be undertaken to enhance current understanding of acidification. These projects represent extensions of the MAGIC model or of the applications described in Chapter 2.

'Regionalizing' the model for Northeastern Alberta, in which one model parameterization is used to represent a number of lakes, may support planning by reducing the number of lakes that require analysis. This method has been successfully demonstrated by Hornberger et al. (1989)

and Sefton and Jenkins (1998). In this approach, the acidifying emission contributions from all regional sources are assessed. Then lakes in the region are classified based on similar parameter values. Uncertainty analysis is used to assess the impacts of the range of observed values of key parameters and the range of uncertainty produced represents the range of possible results for the lakes of the subject region. This approach has the benefit of assessing the risk of acidification for entire sub-regions within the Oil Sands Region, and thus reducing the need to demonstrate such conclusions for each lake in an EIA study area. Similar studies have been conducted in Ontario by Neary and Dillon (1988). This work would best be undertaken as a regional study by AENV or as a CEMA directed project.

Another extension of the MAGIC model could be to include climate change considerations in the assessment. Accounting for dynamic climate conditions in future sequences is a task ideally suited to MAGIC, given the model structure. The challenge in such a study would be to determine the relationships between variables in the model and changes in climate. Climate change scenarios have already been analyzed in oil sands EIAs (Imperial Oil 2005) and altered hydrologic conditions and temperature changes have been shown to be the anticipated main effects of climate change (Psenner 1994). Current research suggests that surface water bodies may experience pH values beyond their normal range when subjected to changing climatic temperatures (Psenner 1994). Also, reductions of surface water flows may lengthen time scales of acid recovery (Murdoch et al. 2000).

Additional scenarios of change in the region and their affects on acidification may also be analyzed with MAGIC. Example of such changes include: land use changes, changes in forest cover, and varied deposition schemes (Ferrier et al. 1995; Jenkins et al. 1990). These dynamic conditions are represented by altering the model parameterization, climate related variables, inputs and source/sink/weathering rates as required.

The MAGIC model can also be used by oil sands producers to investigate the affects of systematic decisions regarding resource development in the region. Though acidification issues are not central to the decision making process when planning a new project or operating an existing operation, consideration of acidification may be accommodated at little cost to the objectives of oil sands producers. Incorporating choices in a systems approach could serve to limit harm to highly sensitive lakes in the region, of which there are approximately ten (Canadian Natural Resources Limited 2002), without affecting the performance of oil sands producers. Production decisions regarding the level of pollution control options, location of monitoring equipment, timing of pollution release decisions and possibly even facility location or stack height considerations could be supported by such an analysis. Additionally, AENV could use such an approach to improve policy criteria for operating permits and regulatory applications.

The deposition of acidifying emissions will continue for many years to come. As such the topic of acidification in Northeastern Alberta warrants further study. There is a great deal of effort already underway on this topic and this study contributes to that effort. Improvements in our understanding of acidification processes and modelling will contribute to the preservation of oil sands lakes and continued use of these lakes for stakeholders in the region.

### **3.3 CHAPTER 3 REFERENCES**

- Canadian Natural Resources Limited. (2002). "Horizon Oil Sands Project - Application for Approval." Submitted to Alberta Energy and Utilitles Board and Alberta Environment, Calgary, A.B.
- Cosby, B.J., 2005. Personal Communication with Dr. J. Cosby in December, 2005 via telephone from Vancouver, BC.
- Ferrier, R., Wright, R. F., Cosby, B. J., and Jenkins, A. (1995). "Application of the MAGIC Model to the Norway Spruce Stant at Stolling, Germany." *Ecological Modelling*, 83, 77-84.
- Ford, A. (1999). *Modeling the Environment*, Island Press, Covelo, California.
- Hindar, A., Posch, M., and Henriksen, A. (2001). "Effects of In-Lake Retention of Nitrogen on Critical Load Calculations." *Water, Air and Soil Pollution*, 130,

1403-1408.

Hornberger, G. M., Cosby, B. J., and Wright, R. F. (1989). "Historical Reconstructions and Future Forecasts of Regional Surface Water Acidification in Southernmost Norway." *Water Resources Research*, 25(9), 2009-2018.

Imperial Oil. (2005). "Kearl Oil Sands Project - Mine Development. Volumes 1 to 9. Submitted to Alberta Energy and Utilities Board and Alberta Environment. Prepared by Imperial Oil Resources Ventures Limited in association with Golder Associates Ltd., AXYS Environmental Consulting Ltd., Komex International Inc. and Nichols Applied Management." Calgary, Alberta.

Jenkins, A., Cosby, B. J., Ferrier, R., Walker, T. A. B., and Miller, J. D. (1990). "Modelling Stream Acidification on Afforested Catchments: An Assessment of the Relative Effects of Acid Deposition and Afforestation." *Journal of Hydrology*, 120, 163-181.

Murdoch, P. S., Brown, J. S., and Miller, T. L. (2000). "Potential effects of climate change on surface-water quality in North America." *Journal of the American Water Resources Association*, 36(2), 347-366.

Neary, B. P., and Dillon, P. J. (1988). "Effects of sulphur deposition on lake-water chemistry in Ontario, Canada." *Nature*, 333, 340-343.

Psenner, R. (1994). "Environmental impacts on freshwaters: acidification as a global problem." *The Science of the Total Environment*, 143, 53-61.

Sefton, C. E. M., and Jenkins, A. (1998). "A regional application of the MAGIC model in Wales: calibration and assessment of future recovery using a Monte-Carlo approach." *Hydrology and Earth System Sciences*, 2(4), 521-531.