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Investigating the Long-Term Influence of Atmospheric Acid Deposition and Forest Disturbance on Soil Chemistry and Cation Nutrient Supplies in a Forested Ecosystem of Southern Quebec

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Nicolas Bélanger

Ph. D. **ABSTRACT** **NRS**

Nicolas Bélanger

Investigating the Long-Term Influence of Atmospheric Acid Deposition and Forest Disturbance on Soil Chemistry and Cation Nutrient Supplies in a Forested Ecosystem of Southern Quebec

Most soils, streams, and lakes in northeastern North America have not recovered from acidification since the recent decreases in H_2SO_4 atmospheric loading as strong declines in base cation concentrations in soil solutions and surface waters have exceeded the decrease in SO_4^{2-} concentration. Furthermore, an excess of N in forest soils due to increasing NH_3 emissions in most parts of the world could mean higher levels of H^+ in the solution and further removal of base cations from the soil environment through leaching losses. In combination with intense forest harvesting, which removes base cations from the soil-plant ecosystem, acidic deposition could in the long-term result in a permanent loss of soil alkalinity and perhaps cation nutrient deficiencies. Soil chemistry and nutrition studies have not entirely succeeded in linking the decline of North American forests with acidic deposition. The objective of this thesis was to validate the dynamic model SAFE (Soil Acidification in Forested Ecosystems) in a small deciduous watershed of southern Quebec. SAFE could then be used to: 1) identify which processes are governing acidification, and 2) assess the rates of acidification according to various forest conditions.

Soil and soil solution chemistry between unburned and burned zones following fire disturbance seventy-five years ago was examined within the watershed. Results showed two major, statistically significant, differences: 1) higher base status, and 2) lower soil solution N in the burned zone. High quality leaf litter of aspen and birch (burned zone) relative to that of sugar and red maple (unburned zone) has contributed to the enrichment of base cations in the forest floor. The enrichment of the forest floor did not however impoverish the B horizon as seen in other studies. Rather, fire enriched the soil in base cations and buffered the effect of forest regrowth in the B horizon.

The MAKEDEP model was used to reconstruct the time-series input files needed to run SAFE. In MAKEDEP, the availability of N determines tree growth which in turn,

affects most of the processes involved in nutrient cycling. In that respect, we have assessed the model sensitivity to N availability at the study site for the unburned and burned conditions. The scenario that added 10 mmol_c NH_4 m^{-2} yr^{-1} through biological N fixation and dry deposition minus denitrification recreated N leaching rates with the most precision for both fire histories. Adding N to the model was necessary for: 1) trees to grow to what was measured in the field, and 2) not to underestimate canopy exchange reactions and litterfall. Regressions of measured deposition at the Hubbard Brook Experimental Forest and that of simulated deposition at the study site suggest MAKEDEP is suitable to model the deposition trends of all elements except Na.

SAFE was calibrated for the unburned and burned conditions at the study site. Fire disturbance and forest regrowth have produced different soil chemical composition within the zones as discussed above. SAFE was therefore validated at the study site as a function of its ability to reproduce soil chemistry under unburned and burned conditions. The simulated soil chemistry was in close agreement with the measured unburned soil conditions, but some processes would have to be clarified or accounted for with greater accurately, e.g., biological N fixation and N immobilization by myccorhizal fungi, to reproduce more accurately the measured burned soil chemistry. Simulated soil chemistry in the unburned zone reinforced nevertheless the conclusions of a few historical soil chemistry studies supporting the hypothesis that acid-sensitive forest sites of the United States underwent significant acidification during 1930-1980 during major input of acidity from the atmosphere. Model projections in the mineral soil suggest that a new steady-state should be reached in the 21st century assuming no harvest. Assuming harvest in 2020 creates unstable conditions which leads to further acidification and impoverishment of the soil's base cation reserve in the mineral soil. Model output suggests that cation nutrient deficiencies could occur in the long-term, but future Al phytotoxic responses are unlikely to occur due to a relatively high projected pH.

Ph. D. **RÉSUMÉ** **NRS**

Nicolas Bélanger

Influence à long terme des perturbations forestières et des dépôts atmosphériques acides sur la composition chimique du sol et la disponibilité des cations basiques d'un écosystème forestier du sud québécois

La plupart des sols, ruisseaux et lacs acidifiés du nord-est de l'Amérique du Nord n'ont pas retrouver des valeurs de pH normal depuis la réduction récente des dépôts atmosphériques de H_2SO_4 puisque les baisses de concentrations en cations basiques dans les solutions de sol et les eaux de surface dépassent encore largement les baisses de concentrations de SO_4^{2-}. De plus, un excès de N causé par l'augmentation constante des émissions de NH_3 à l'échelle de la planète favoriserait une hausse de H^+ dans les solutions de sol et, de ce fait, l'appauvrissement de la réserve de cations basiques par lessivage. En combinaison avec les pratiques forestières intensives, lesquelles exportent des cations basiques en dehors du système plante-sol, les précipitations acides résulteraient éventuellement à une perte irréversible de l'alcalinité du sol et causeraient des déficiences en Ca, Mg, et K. Les études portant sur la chimie du sol et la nutrition en forêt n'ont pas réussi entièrememt à faire le lien entre le déclin des forêts et les dépôts acides. L'objectif de cette thèse est donc de valider le model dynamique SAFE (Soil Acidification in Forested Ecosystem) dans un petit bassin versant de feuillus du Québec méridional pour qu'il serve ensuite à: 1) identifier les processus gouvernant l'acidification et 2) évaluer le taux d'acidification selon diverses conditions.

La composition chimique du sol et de la solution de sol entre une zone non-brûlée et une zone brulée a été examinée soixante-quinze années après feu dans le bassin versant. Les résultats ont démontré deux différences statistiquement significatives; 1) un statut en bases plus élevé et 2) des teneurs de N en solution plus faibles dans la couverture morte et le sol minéral de la zone brûlée. La qualité supérieure de la litière foliaire du peuplier et du bouleau (zone brûlée) relativement à celle de l'érable à sucre (zone non-brûlée) a contribué à l'enrichissement en cations basiques de la couverture morte. L'enrichissement de l'horizon organique n'a pas

appauvri l'horizon B tel qu'observé dans d'autres études. Le feu a plutôt enrichi l'horizon B en cations basiques et tamponné l'effet de la régénération.

Le modèle MAKEDEP a été utilisé afin de reconstruire les fichiers temporels nécessaires pour l'exécution de SAFE. Dans MAKEDEP, la disponibilité de N détermine la croissance de l'arbre, et de ce fait, affecte la plupart des processus du cycle des éléments nutritifs. Nous avons donc évalué la sensibilité du modèle à la disponibilité de N pour les conditions brûlée et non-brûlée. Le scénario ajoutant 10 $mmol_c$ NH_4 m^{-2} an^{-1} par la fixation biologique de N et les dépôts secs moins la dénitrification a reproduit le plus exactement les taux de lessivage mesurés sur le terrain pour les deux historiques de feu. L'ajout de N au modèle a été nécessaire pour: 1) que les arbres atteignent une masse similaire à celle mesurée sur le terrain et 2) ne pas sous-estimer la contribution du pluviolessivage et la chute de litière foliaire. Les régressions pour les dépôts atmosphériques mesurés à la forêt expérimentale de Hubbard Brook et celles pour les dépôts simulés à la station d'étude suggèrent que MAKEDEP est valable pour modéliser les tendances de dépôts de tous les éléments à l'exception de Na.

SAFE a été calibré dans la zone brûlée et la zone non-brûlée. Le feu et la régénération forestière ont créé une composition chimique du sol différente entre les zones (voire ci-haut). Le modèle fut donc validé d'après sa capacité à reproduire la chimie du sol dans les zones brûlée et non-brûlée. La chimie simulée dans la zone non-brûlée ressemblait à la chimie mesurée sur le terrain, mais il aurait fallu éclaircir ou quantifier avec plus de précision le rôle de certains processus (e.g., fixation biologique de N et immobilisation de N par les mycorhizes) pour bien reproduire les conditions dans la zone brûlée. Néanmoins, la simulation dans la zone non-brûlée appuie les études qui sous-tendent que les forêts propices à l'acidification dans l'est de l'Amérique du Nord ont subi une acidification importante par les précipitations entre les années 1930 et 1980. Tel la présomption d'aucune opération forestière, les projections suggèrent que le sol atteindrait un nouvel équilibre au cours du 21ème siècle. En présumant une coupe, l'instabilité dominerait et mènerait à une acidification et une perte d'éléments basiques dans le sol minéral. Les projections du modèle suggèrent qu'il pourrait y avoir des déficiences en Ca, Mg et K dans un avenir prochain, mais qu'une réponse à la toxicité de Al est peu probable puisque les projections de pH sont assez élevées.

AUTHORSHIP

In accordance with the regulatins of the Faculty of Graduate Studies and Research of McGill University, the following statement is included:

Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.

If this option is chosen, connecting texts that provide logical bridges between the different papers are mandotory. The thesis must be written in such a way that it is more than a mere collection of manuscripts: in other words, results of a series of papers must be integrated.

The thesis must still conform to all other requirements of the "Guidelines for Thesis Preparartion". The thesis must include: A table of content, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a comprehensive review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.

Additional material must be provided where appropriate (e.g., in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsabilities of all authors of the co-authored papers.

The candidate has been fully responsible for both conducting the original studies and for preparing the manuscripts. The first paper (Chapter 1) included in this thesis was co-authored by the candidate, his supervisor Dr. W. H. Hendershot, and a member of the supervising committee Dr. B. Côté. The next two papers (Chapters 2 and 3) were co-authored by the candidate, his supervisor, the two other members of the supervising comittee Dr. B. Côté and Dr. F. Courchesne, and Dr. P. Warfvinge from Lund University, Sweden. The last paper (Chapter 4) of the thesis is co-authored by the candidate, his supervisor, as well as Ms. H. Fyles. The study in Chapter 4 was undertaken as part of a project of Environment Canada on the toxicity of aluminum salts in the terrestrial environment (Priority Substances List II).

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CONTRIBUTION TO KNOWLEDGE

The chapters presented in this thesis contain new findings which expand further our knowledge about the effect of acidic precipitation and forest disturbance on soil chemistry and about simulating soil chemistry in deciduous forests of eastern North America using a dynamic approach. Major contributions to knowledge are as follows:

1) At the study site, regrowth of post-fire species (aspen and birch) have contributed to the enrichment of base cations in the forest floor as compared with the unburned maple-dominated stand. In studies with poorly buffered soils, a high quality leaf litter in similar post-fire forest stands has been often associated with a more intense acidification of the underlying B horizons as base cations are transferred from the mineral soil to the canopy and then to the forest floor through litterfall or foliage leaching. At the study site, however, the higher exchangeable Ca, Mg, and K content in the forest floor of the burned zone was not accompanied by an impoverishment of the B horizon. Rather, the B horizon had a greater base saturation and exchangeable Ca and K relative to unburned conditions. No significant difference in cation exchange capacity between the zones were found which suggests that the greater concentrations of exchangeable base cations in the mineral soil of the burned zone does not originate from intrinsic characteristics of the parent material. Hence, the data supports the hypothesis that the forest fire enriched the soil in base cations and buffered the effect of rapid forest regrowth in the mineral B horizon;

2) Reduced plant uptake and increased mineralization of nutrients immediately after fire disturbance increases nutrient availability in the soil system. An increase in pH and nutrient availability leads to the growth of the nitrifying bacteria community so that NO_3^- leaching in deciduous stands of eastern North America is usually enhanced after the loss of the forest cover, but the effect seldom lasts more than 5 years. At the study site, current leaching rates of NH_4^+ and NO_3^- are lower in the burned zone than in the unburned zone which suggests that mechanisms of soil N retention are associated with the development of pioneer (post-fire) and mid-successional species. Results show that higher N demand by regrowth of aspen and birch has contributed to low NH_4^+ and NO_3^- mobility than unburned sites, but low N mobility could have been also favoured directly by fire through volatilization and intense leaching in the few years following disturbance.

Based on the above, we bring forward the hypothesis that the creation of a N poor environment has triggered the phase-out of the soil bacterial community associated with the mature maple stand and a replacement with mycorrhizae. Then, the net assimilation and exudation of mineral N by mycorrhizal fungi would have resulted in a greater immobilization of mineral N than with bacteria and in further decreases in the rates of nitrification and NO_3^- leaching;

3) In the MAKEDEP model, the availability of N determines tree growth which in turn, affects most of the processes involved in nutrient cycling. Currently, this model is being used to recreate time-series input files for applications of the SAFE model. Low growth and accumulated nutrient uptake recontructed with MAKEDEP prior to the onset of industrial air pollution were shown to be poorly modelled because of a lack of available N. We demonstrated that an increase in N availability from biological N fixation and dry deposition minus denitrification was necessary for the trees to grow. In addition, we have demonstrated that underestimating forest biomass would induce large errors in the estimation of cycling processes such as plant uptake, canopy exchange and litterfall. In turn, this has a direct effect on the balance of nutrients (demonstrated here with N) calculated as the residual component of processes acting as sources and sinks of those nutrients;

4) MAKEDEP uses relative curves (0 to 100% of maximum) of European emission of major elements to reconstruct deposition history. Assuming that deposition of an element follows the same pattern as emission of that element, deposition of an element can be reconstructed by scaling into the past current values of deposition using standard curves of emission. European deposition patterns in the MAKEDEP model are however different from those of eastern North America. To verify the applicability of MAKEDEP to recreate the trends in atmospheric deposition of major ions in eastern North America, we have assembled estimates of emissions in the literature for different time periods. Simulated trends in deposition of all elements at the study site (with the exception of Na) were similar to those measured between 1963-1992 at the Hubbard Brook Experimental Forest, New Hampshire, suggesting that these standard curves are suitable for simulating deposition of most elements elsewhere in eastern North America. The standard curves of emissions for eastern North America are available via the internet

through the Biogeochemistry Research Group, Department of Chemical Engineering II, Lund University (web site: www.chemeng.lth.se);

5) Evidence from tree ring chemistry supports the hypothesis that base cation depletion and acidification in the forest soils of eastern North America occurred during approximately the period 1930-1980. Simulated soil chemistry using the SAFE model reinforces the conclusions of the tree ring research indicating that the largest changes in soil chemistry occurred between the same period and were associated with the deposition of strong acids from the atmosphere. This period of significant soil acidification corresponds exactly to the period when polluted atmospheric deposition contributed the most acidity to the forest ecosystem which is reflected in the SAFE model by the standard curves developed in Chapter 2: SO_x emissions increased by about 3-fold between 1930 and 1980, whereas NO_x and NH_x emissions more than doubled;

6) Historical base saturation data of mor layers in various eastern North American forests indicate that acidification occurred mainly between 1940 and 1970. Furthermore, significant acidification and Ca^{2+} losses in organic horizons of mixed spruce-hardwood sites in the Adirondack region of New York were observed during the time period 1930-1984. However, simulated forest floor acidity using SAFE did not exhibit a large decrease in pH as seen above. The model output therefore suggests that the soil exchange complex in the forest floor is mainly determined by: 1) organic acids which create a naturally low pH, and 2) the large flux of base cations in the soil through cycling processes such as dry deposition, throughfall, and litterfall.

7) Some researchers anticipate a decrease in base saturation and soil solution pH into the 21st century as base cation inputs from the atmosphere (because of more efficient industrial dust collectors) will decrease even more, acidifying compounds (i.e., N species) will continue to increase, and harvest operations are likely to augment in intensity. Our concern was that acidification may already have brought the cation exchange pool in the mineral soil to a low point so that it may take centuries for the system to recover. Assuming no harvest into the next century and the best-case scenario of strong acid deposition, projected soil chemistry with the SAFE model in the mineral soil suggests that the balance between acidity and alkalinity in the new century is leading towards a new steady-state as no major change is simulated. Assuming harvest in 2020 leads to further acidification because of greater cation nutrient

demands. These results show that even with the best-case scenario of deposition, southern Quebec hardwood forest soils are very acid-sensitive.

8) Values for Al concentrations in the soil solution where 10% and 50% of the studies on tree species show negative effects were 0.07 m*M* and 0.4 m*M* of Al, respectively, and values for Ca:Al molar ratios were 6 and 0.8, respectively. If we accept the assumption that the amount of total dissolved Al is controlled by the precipitation of microcrystalline gibbsite, we found that the pH values which correspond to a 50% LOAEC is 4.4 for forest soils. Based on the SAFE model pH projections, we believe it is unlikely that phytotoxic Al responses in hardwoods of southern Quebec will occur, even if harvest operations are planned.

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GENERAL INTRODUCTION
(Literature Review)

0.1 Susceptibility of Soils to Acidification

Soil acidification is a natural process that contributes to soil formation. Most soils will become acidic if they are exposed long enough to atmospheric deposition which causes leaching of base elements contained in the soil. Soils that support plant growth are acidified as well since uptake of cation nutrients by roots is accompanied with H^+ ion release. More than 2000 years ago, liming was done commonly by the Romans to improve agriculture production on acidified soils (Wild, 1994). Acid soils have therefore always existed and many regions around the globe exhibit similar conditions today.

Most of the scientific community now believes that atmospheric acid deposition increases the rate of soil and surface water acidification (Johnson et al., 1981; van Breemen et al., 1984; Reuss et al., 1987; Kirchner et al., 1992; Likens et al., 1996; Markewitz et al., 1998; Friedland and Miller, 1999). Moreover, it is believed that polluted precipitation has deleterious effects on terrestrial and aquatic ecosystems as evidence of forest decline and loss of fish stocks increases (Schindler, 1988; Joslin et al., 1992). Reuss et al. (1987) explained that regions characterized by carbonate-free and highly siliceous bedrock (e.g., granite) with thin soils were most likely to be acidified by atmospheric deposition. It is therefore not atmospheric acid deposition alone that has set off widespread acidification but rather a combination of polluted air with poorly buffered parent material. Part of northeastern Ontario, southern Quebec and the Adirondack Mountains of New York state are regions of eastern North America (ENA) with such bedrock composition and have soils exhibiting the highest sensitivity to atmospheric acid deposition. Southern Sweden and Norway are areas greatly affected in Europe. Today, throughout these sensitive regions, many forested ecosystems grow on soils with marginal fertility and thousands of lakes and hundred of thousands of kilometers of streams and rivers are at a pH level below normal (Schindler, 1988).

0.2 Concept of Soil Acidity

In forest soils, the exchangeable cations that dominate the exchange complex are Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, and H^+. On the one hand, free Al^{3+} in the soil solution behaves as a weak acid as it hydrolyses readily to form Al-OH complexes releasing H^+.

These complexes may also act to resist a decrease in pH as they react with H^+ to form H_2O and other Al-OH species or free Al^{3+} (Binkley and Richter, 1987):

$$Al(OH)_4^- + H^+ \leftrightarrow Al(OH)_3 + H^+ \leftrightarrow Al(OH)_2^+ + H^+ \leftrightarrow AlOH^{2+} + H^+ \leftrightarrow Al^{3+} \quad \text{(eq.0.1)}$$

On the other hand, Ca^{2+}, Mg^{2+}, K^+, and Na^+ do not hydrolyse readily in the soil solution so that they are often referred in soil terms as base cations (Binkley and Richter, 1987). The soil exchange complex is therefore being acidified when Ca^{2+}, Mg^{2+}, K^+, and Na^+ are replaced by H^+ and Al^{3+}. Protons will mostly exchange with base cations in organic layers, whereas Al^{3+} will displace base cations in the mineral soil. The soil environment also acidifies as a whole when base cations released to the soil solution by exchange reactions exit the system through leaching. In soils where the input of H^+ is high and the release of exchangeable base cations by weathering is low, there may be an incomplete neutralization of H^+ in the soil solution and in turn, there may be a net increase of acidity in the soil solution (van Breemen et al., 1984).

Conversely, soil alkalinization is the addition of base cations on the negatively charged soil surfaces. Adding a neutral salt such as K_2SO_4 to an acidic soil system increases K^+ activity and in turn, causes displacement of acid cations from the exchange sites as cations in solution and cations on the exchange sites reach a new equilibrium (Hendershot et al., 1991). In relatively neutral soils, only small exchanges of acidity occur. Increases in soil alkalinity are more noticeable in acid soils (pH ~4) since a larger proportion of Al^{3+} is replaced by K^+. Subsequently, acidification of the soil solution occurs as the release of Al^{3+} into the soil solution causes the activity of H^+ to increase. Base cations added to the soil system from mineral weathering and atmospheric deposition can create a similar situation where base cations are adsorbed on the soil exchange sites to replace acid cations.

0.3 Buffering Processes in Soils

In the soil environment, solution pH alone cannot describe accurately soil acidity as many processes act so that the addition of H^+ to the soil system does not always result in an increased H^+ activity in the soil solution. The most important buffer mechanisms for soil solutions are described here, except for cation exchange which was discussed previously.

The carbonate system involves a relatively weak buffering process that is a result of CO_2 dissolving in water. The H_2CO_3 that is formed has a first acid hydrolysis constant (pK_a) of 6.3 and therefore, it may be dissociated to H^+ and HCO_3^- in soils with pH values between 5.3 and 7.3 (Reuss and Johnson, 1986). The dissociation products are consumed in a reaction with $CaCO_3$:

$$CaCO_3 + H^+ + HCO_3^- \leftrightarrow Ca(HCO_3)_2 \qquad \text{(eq. 0.2)}$$

The reaction provides a buffer for the soil solution since $Ca(HCO_3)_2$ is very soluble and leaves the soil in leachate. The soil CO_2 partial pressure is typically higher than in the atmosphere because of the decomposition of organic matter by microorganisms. In soil environments with pH values close to the pK_a values of H_2CO_3, the dissociation of H_2CO_3 is generally the most significant H^+ source (Van Miegroet and Cole, 1984). The carbonate system fails, however, to create or buffer acidity at pH under 5 as H_2CO_3 does not dissociate readily (van Breemen et al., 1986).

Hydrolysis of primary, secondary, and amorphous silicate minerals consumes H^+. For example, when an orthoclase feldspar is transformed into kaolinite, two H^+ ions are consumed and two K^+ ions are released from the feldspar mineral structure (Birkeland, 1984):

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \leftrightarrow H_4Al_2Si_2O_9 + 2K^+ + 4H_4SiO_4 \qquad \text{(eq. 0.3)}$$

The amount of H^+ removed from the soil solution by hydrolysis varies among minerals (Ritchie, 1989). Aluminum is not very soluble over the normal soil pH range so that it generally precipitates near its site of release (as shown in equation 0.3). At a pH below 5.0, increased H^+ activity in the soil solution creates, however, a new equilibrium where more Al is dissolved. Consequently, any mineral containing a large proportion of Al (e.g., kaolinite) has less ability to buffer soil solution than one containing a greater proportion of base cations (e.g., feldspars). Furthermore, the buffering ability of a mineral containing base cations increases with its susceptibility to weathering. The more weatherable a mineral containing base cations, the greater is the amount of base cations released during dissolution.

In soils containing organic material, exchange sites arise from the dissociation of carboxylic (COOH) and phenolic (COH) functional groups present at the surface of humic and fulvic acids (Evans, 1994). Acidification of the soil solution is therefore often delayed since the negatively charged surfaces can be protonated after addition of H^+ to the solution:

$$>COO^- + H^+ \leftrightarrow >COOH \quad \text{(eq. 0.4)}$$

$$>CO^- + H^+ \leftrightarrow >COH \quad \text{(eq. 0.5)}$$

Models have been developed to assess the number of binding sites at different pH values. Carboxyl groups dissociate between pH 4.5 and 7, whereas phenolic hydroxyl groups dissociate at pH higher than 7. Above or below these pK_a values, functional groups would theoretically act to buffer a decrease in soil solution pH as organics would protonate (Reuss et al., 1987).

Similarly, H^+ dissociates from the surfaces of Al and Fe hydrous oxides and from the edges of clay minerals (Sposito, 1981). This gives a pH-dependent negative charge that behaves like the functional groups of organic acids, i.e., the number of negatively charged surfaces increases as pH increases. Hydrous oxides can become positively charged at low pH by adsorption of H^+ and consequently, they act as a buffer for soil solution pH:

$$>FeO^- + H^+ \leftrightarrow FeOH^0 + H^+ \leftrightarrow >FeOH_2^+ \quad \text{(eq. 0.6)}$$

Binding sites are more abundant on structurally disordered material as surfaces and edges of which pH-dependent charges arise are more abundant, e.g., imogolite and allophane.

Sulfate adsorption capacity has been considered an important parameter for assessing the effects of atmospheric acid deposition on forest soils (Fuller et al., 1985). Sulfate adsorption is a concentration-dependent process, i.e., the amount adsorbed increases with increasing SO_4^{2-} concentration in the soil solution (Reuss and Johnson, 1986). Adsorption of SO_4^{2-} can contribute to an increase in pH resulting from the auto-protolysis of water after replacement of OH^- groups on the soil surface by SO_4^{2-} (Chao et al., 1965).

0.4 Acid Neutralizing Capacity of Soils

One can determine with a charge balance if the addition of an acid or a base will affect the pH of a soil. The addition of a strong acid into the soil solution does not mean that the number of H^+ will increase proportionally. At pH values above 6, the concentration of HCO_3^- will decrease instead, and at low pH, Al concentration in solution may increase or organic functional groups may be protonated. Soil acidity is better defined by the acid neutralizing capacity (ANC) which is directly influenced by the addition or depletion of H^+. The ANC can be calculated with the simplified equation given by Warfvinge and Sverdrup (1995):

$$[ANC] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [R^-] - [H^+] - m[Al^{m+}] \qquad \text{(eq. 0.7)}$$

where R^- denotes the anion concentration of organic acids (RH). The ANC is normally around 0 at pH values between 4.6 to 5.6. Positive ANC represents alkalinity and a negative ANC represents acidity.

0.5 Sources and Sinks of Acidity in Forest Soils

A number of natural soil acidification processes have been recognized for a long time. These processes contribute H^+ to the soil system and can promote soil acidification through the leaching of base cations. On the other hand, reactions consuming H^+ may slow down the acidification of the soil as base cations adsorbed on the soil surfaces are less likely to be released to the soil solution. The soil environment has many processes that produce or consume H^+.

The net assimilation of base cations and NH_4^+ ions by plants can contribute significantly to a decrease in ANC. In this case, H^+ ions are released from the plant roots and exchanged for base cations in the soil solution (Matzner and Ulrich, 1987). The loss of ANC is temporary if the base cations taken up by vegetation are returned to the soil in litter or by the death of plants. In commercial forests, however, harvest removal is the principal process by which base cations are removed from the soil-plant ecosystem, resulting in a permanent loss of alkalinity (Federer et al., 1989). Uptake of one NO_3^- by a plant root releases about one OH^-, whereas assimilation of one NH_4^+ releases about one H^+. Since complete nitrification of one NH_4^+ produces two H^+ ions in the soil system, the assimilation of NH_4^+ by plants acidifies the soil to the same extent as if it were transformed to NO_3^- and then taken up by vegetation in exchange for OH^- (Warfvinge et al., 1998)

Oxidation of NH_4^+ to NO_3^- by chemoautotrophic bacteria is favoured by a rise in soil temperature and moisture, often triggered by the removal of forest cover (Likens et al., 1970; Dahlgren and Driscoll, 1994). Acidic soil conditions slow down the growth of microorganisms and in turn, nitrification rates (Gilmour, 1984). The reaction produces H^+ as follows:

$$NH_4^+ + 3/2O_2 \leftrightarrow NO_2^- + 2H^+ + H_2O \qquad \text{(eq. 0.8)}$$

$$NO_2^- + 1/2\ O_2 \leftrightarrow NO_3^- \qquad \text{(eq. 0.9)}$$

Similarly to the oxidation of NH_4^+, the supply of acidity is brought by fertilization with N-containing substances (Kennedy, 1992). The amount of H^+ produced by N treatments will vary according to the type of fertilizer applied:

Urea

$$(NH_2)_2CO + 4O_2 \leftrightarrow 2NO_3^- + 2H^+ + CO_2 + H_2O \qquad \text{(eq. 0.10)}$$

Ammonium sulphate

$$(NH_4)_2SO_4 + 4O_2 \leftrightarrow 2NO_3^- + SO_4^{2-} + 4H^+ + 2H_2O \qquad \text{(eq. 0.11)}$$

Nitrate is used as a terminal electron acceptor by heterotrophic bacteria growing anaerobically (Stouthamer et al., 1980). The exact reactions are not known, but the general trend of the reactions is to consume acidity as NO_3^- is transformed to NO_2^-, NO, N_2O, and then N_2. The transformation reactions can come to a stop at any stage, but N_2 and N_2O are generally lost in larger amounts, with N_2O dominating in soils that are not too low in oxygen.

Atmospheric deposition adds acidic compounds to the soil environment (Warfvinge and Sverdrup, 1995). The combustion of coal and to a lesser extent of oil has contributed to atmospheric deposition of H_2SO_4 and HNO_3. Sulphur dioxide is emitted into the atmosphere during combustion of fossil fuel. While some SO_2 is deposited directly on soils and plants, other molecules are transformed in the atmosphere to SO_3 through complex reactions with reactive hydroxyl radicals. Sulphur trioxide is later dissolved in water vapour or droplets to form H_2SO_4:

$$SO_2 + O \leftrightarrow SO_3 \qquad \text{(eq. 0.12)}$$

$$SO_3 + H_2O \leftrightarrow H_2SO_4 \qquad \text{(eq. 0.13)}$$

The main N products resulting from combustion of fossil fuels are NO and NO_2, often referred to as NO_x. These molecules are transformed in the atmosphere to HNO_3 after reacting with ozone and hydroxyl radicals:

$$NO + O_3 \leftrightarrow NO_2 + O_2 \qquad \text{(eq. 0.14)}$$

$$NO_2 + HO. \leftrightarrow HNO_3 \qquad \text{(eq. 0.15)}$$

Atmospheric deposition of NH_4^+ occurs through the volatilization of NH_3 from manure or soils treated with ammonium fertilizers. Ammonia is emitted to the atmosphere in amounts roughly equal to NO_x. Once NH_4^+ is transformed to NO_3^- in the soil environment as shown by equations 0.8 and 0.9), this source of H^+ becomes as significant as HNO_3 deposited from the atmosphere. When atmospheric deposition interacts with the canopy, it may become more acidic after the washoff of accumulated dry deposition or through the leaching of organic acids from the leaves and stems of trees, i.e., throughfall and stemflow, respectively (Reuss and Johnson, 1986). Deposition could become less acidic, however, as exchange reactions between H^+ in atmospheric deposition and base cations in the plant tissues occur.

The oxidation of some ferrous sulphide minerals, for example pyrite, releases H^+ (Binkley and Richter, 1987):

$$4FeS_2 + 15O_2 + 8H_2O \leftrightarrow 2Fe_2O_3 + 16H^+ + 8SO_4^{2-} \qquad \text{(eq. 0.16)}$$

The situation is rare in forest soils as pyrite is formed under reduced conditions such as in marine and estuarine clays, although it may be naturally present in other types of parent material. It can also be formed from coal mining. The soils that inherit such mine tailings are known as acid sulfate soils and can lead to conditions as acidic as pH 3.

Sulfate reduction to H_2S by heterotrophic bacteria is an important form of respiration in soils. Sulfate is absorbed and then activated with adenosine triphosphate (ATP) to form adenosine phosphosulphate (APS). APS can be directly reduced to H_2S with catalytic APS enzyme reductase (Thauer and Badziong, 1980). The overall effect is of an alkaline nature since the strong acid H_2SO_4 is converted to the very weak acid H_2S, but this only occurs under strongly reducing conditions.

0.6 Soil Acidification as Related to Atmospheric Acid Deposition

Over decades, changes in the acidity of forest soils can be very dynamic. Changes in soil acidity have been attributed to the alteration of the base cation reserve under the influence of species composition, forest growth and harvest operations (Alban, 1982; Brand et al., 1986; France et al., 1989; Federer et al., 1989; Binkley and Valentine., 1991). In more recent studies, however, the co-analysis of historical and recent soil samples suggest that the timing and magnitude of soil acidification in forests of ENA are better explained by increased H^+ input from atmospheric deposition. Here are a few examples:

1) Shortle and Bondietti (1992) examined the trend of exchangeable Ca^{2+} and Mg^{2+} in sensitive humus layers of ENA starting in the 1930's. The trend based on diverse studies did not permit a direct statistical analysis because of the difficulties in weighting each data set. Nevertheless, measured exchangeable Ca^{2+} and Mg^{2+} prior to 1950 were consistently 150 to 300 $mmol_c$ per kilogram of organic soil, whereas exchangeable Ca^{2+} and Mg^{2+} after 1970 were consistently below 100 $mmol_c$ per kilogram. The decrease in exchangeable cations was believed to be the result of increased atmospheric loading of strong acids as air pollution started being a concern around 1950;

2) Soil chemical changes in 48 mixed spruce-hardwood sites in the Adirondacks of New York were examined over a 50+ year period (Johnson et al., 1994). Moderately acid organic horizons ($pH>4$) showed substantial decreases in pH and extractable Ca, while extractable Ca of strongly acid organic horizons ($pH<4$) and A horizons also significantly decreased, but pH values remained unchanged. Atmospheric acid deposition was believed to be the cause of increased Ca leaching in the later part of the century. Mineral dissolution helped balance acidity addition in the B and C horizons as no acidification occurred;

3) At the Hubbard Brook experimental forest (HBEF), New Hampshire, the chemistry of bulk precipitation and stream water has been measured over the last thirty years. Likens et al. (1996) suggested that large quantities of Ca^{2+} and Mg^{2+} have been lost from the soil complex and exported by drainage water because of inputs of strong acids in precipitation beginning around 1950-1955, with H_2SO_4 contributing 55 to 75% of the measurable acidity of rain and snow. At the same time, it is believed that decreases in base cation deposition led to an accelerated acidification of the soil complex;

4) Tree ring analysis was used to establish the relationships between acidity increases in atmospheric deposition and changes in soil solution chemistry. Bondietti et al. (1989, 1990) observed anomalies in the radial concentration trends of divalent base cations in stemwood of red spruce (*Picea rubens* Sarg.) stands of New England, Tennessee and North Carolina. Tree rings of the mid 1900's showed high levels of divalent base cations, but tree rings of the later part of the century showed significantly lower concentrations. The increased levels of divalent base cations were attributed to an

increase of divalent base cations in sapwood. The changes in sap chemistry came from an accelerated release of base cations into the soil solution which were believed to be caused by increased atmospheric loading of strong acids beginning around 1950. The decrease in divalent base cation levels in more recent tree rings is explained by the reduced availability of base cations following the acceleration of leaching losses, and perhaps, by antagonistic effects of Al^{3+} on cation nutrient uptake (Cronan and Grigal, 1995).

0.7 Fate of Temperate Forest Stands on Acidified Soils

Clearly, dilute H_2SO_4 and HNO_3 solutions brought into an ecosystem by precipitation increase base cation and Al leaching. The recent decrease in the emission of S in ENA should therefore be beneficial for the recovery of acidified soils and surface waters. However, Driscoll et al. (1989) observed that changes in stream pH at HBEF were relatively small during the 1980's, regardless of the fact that the pH of precipitation increased. It is possible that the deposition of H_2SO_4 and HNO_3 may still be too high and decreased loading of these strong acids to the soil environment may only have caused a decrease in the rate of acidification. Furthermore, the considerable improvement of industrial dust collectors over the last 20 years has contributed to the decrease in deposition of base cations. Rates of decrease of base cations in precipitation have been similar to those of SO_4^{2-} as combustion is the major cause of both emissions (Hedin et al., 1994). As a consequence, supply of base cations to the soil environment, which accounts for alkalinity, has been reduced considerably. Stoddard et al. (1999) showed that most streams and lakes in both America and Europe have not shown any sign of recovery as strong declines in base cation concentrations in surface waters have exceeded the decrease in SO_4^{2-} concentration.

Moreover, NH_3 emissions are increasing in most parts of the world, particularly in developing countries (e.g., Republic of China) where emissions could rise by 3- to 4-fold within 50 years (Galloway et al., 1996). An excess of N in forest soils coupled with global warming and increased nitrification could mean higher levels of H^+ in the solution and further removal of base cations from the soil environment through leaching losses (Van Migroet et al. 1992). Over the last 30 years, northern Europe and Scandinavia have witnessed substantial increases in plant growth due to increased N availability

(Wright and van Breemen, 1995; Binkley and Högberg, 1997). Although a similar response has yet to be demonstrated throughout ENA, growth rates were shown to have increased in some forests of New England (Aber et al., 1998). Uptake of cation nutrients would be expected to increase with increasing growth rates and in turn, depletion of the soil base cation pool would occur.

Nitrogen fertilization experiments provide insights on how long-term atmospheric N deposition may affect soil acidity. In general, soil solution pH was significantly decreased (up to 1.0 unit) as a result of moderate (35 kg ha^{-1} yr^{-1}) to high (70 kg ha^{-1} yr^{-1}) inputs of N during a 10 year period (see review by Binkley and Högberg, 1997). It is safe to say that soils supporting non-commercial forests in ENA could become significantly acidified after about 100 years assuming that they receive an average of 10 kg N ha^{-1} yr^{-1} from precipitation. Commercial forests, on the other hand, could be acidified significantly well within that 100 years time period assuming that, in addition to the 10 kg N ha^{-1} yr^{-1} from precipitation, the forest ecosystem lose about half of the base cations contained in the stand biomass following stem-wood harvest within that 100 year period.

In recent years, soil chemistry and nutrition studies have not entirely succeeded in linking the decline of ENA forests with atmospheric loading of strong acids (Joslin et al., 1992). However, atmospheric acid deposition is still a concern in regions of ENA such as Quebec since they are major receptors of air pollutants transported over long distances and contain forested ecosystems in poor health on soils with marginal fertility (Ouimet and Camiré, 1995). In southern Quebec, symptoms of forest decline have been observed mainly in sugar maple (*Acer saccharum* Marsh.) stands, but also in other hardwood forests (Camiré et al., 1990). The decline of sugar maple in Quebec has led some scientists, politicians and maple producers to think that atmospheric acid deposition is jeopardizing the health of these forests. However, the majority of the scientific community has yet to be convinced. Various other stresses, such as insect attacks, frost damage and drought, are known to place a strain on the vigour of forest stands (Côté and Ouimet, 1996).

It was suggested that the present atmospheric loading of S and N may cause cation nutrient deficiencies that could lead to the decline of coniferous and deciduous stands in Ontario and southern Quebec (Arp et al., 1996; Ouimet et al., submitted). On the other hand, Binkley and Högberg (1997) suggested that the magnitude of pH changes due to atmospheric acid deposition is irrelevant for forest productivity and that any effect of soil pH on growth is overshadowed by the beneficial effect of high N availability. If this is true, then soil acidity should not be used as an indicator of soil degradation! Others would argue, however, that increased N deposition, which leads to more rapid forest growth, coupled with intense harvest operations may well bring cation nutrient availability too low for most tree species to grow well. Moreover, a combination of atmospheric acid deposition and intense harvesting is likely to create acidic soil solutions capable of dissolving Al at concentrations which become toxic to about 50% of the tree species (Cronan and Grigal, 1995).

0.8 Modelling Soil Acidification

We have seen that soil acidity is influenced by many processes. In that respect, quantifying processes individually would make it very difficult to determine, within a reasonable range of certainty, which ones are governing soil acidity (Van Oene, 1992). In this case, the use of computer simulation models, which allows us to examine acidification/buffering processes within the soil system as a whole, becomes very useful for: 1) identifying which processes are governing acidification and 2) assessing rates of acidification according to various forest conditions.

Two types of models have been used in the past 15 years to assess the effects of atmospheric acid deposition on soil and surface water acidification, i.e., static models and dynamic models. Dynamic models are built so that it becomes possible to predict the change of state variables with time, whereas static models calculate the steady-state conditions for a set of boundary conditions (Warfvinge, 1995). Much research on acidification is currently being done using dynamic models as they allow us to asses the ability of a soil to cope with changes in environmental conditions, e.g., N deposition, fire disturbance, harvesting, etc. In the past, however, static models have been widely used to calculate critical loads of acidity of forest soils (Warfvinge and Sverdrup, 1995; Sverdrup and De Vries, 1994; De Vries et al., 1994; Arp et al., 1996).

The 1991 Canada-U.S. Air Quality Agreement was written based on the predictions of these models. Similarly, the forest industry could use dynamic models to test whether current practices assure the sustainability of the forest resource. The industry could benefit from dynamic models as a tool to provide an indication of the ability of the forest soil to supply cation nutrients for optimum growth. Such models could help foresters plan the best possible long-term operational practices as a function of atmospheric acid deposition and site characteristics.

0.9 Hypothesis and Objectives

Questions still remain as to whether soil fertility in southern Quebec forests is negatively affected after harvest operations. Forest stands are currently being harvested more intensely and frequently than early in the 1900's. Also, lopping operations are now mostly performed outside the site from which the trees are actually harvested. As a consequence, more nutrients are exported from the harvest site which leads to greater rates of soil acidification relative to practices early in the century.

I hypothesize that current atmospheric loading of H_2SO_4 and HNO_3 coupled with forest management operations will lead in the long run to cation nutrient deficiencies and Al phytotoxic response in eastern Canadian deciduous forests based on the following scientific facts:

1. Dilute H_2SO_4 and HNO_3 solutions brought by atmospheric deposition increases soil acidity by directly contributing H^+ and Al ion species to the soil system;
2. Dilute HNO_3 solutions brought by atmospheric deposition (and N fertilization) treatments increase soil acidity by stimulating plant growth;
3. Clear-cutting or other intense harvest operations coupled with lopping operations outside the site of harvest accelerate soil acidification by removing from the ecosystem large amounts of base cations contained in the forest biomass;

The objective of this thesis is to calibrate and validate the dynamic model SAFE (Soil Acidification in Forested Ecosystems). This is done in a deciduous forest ecosystem of southern Quebec where fire history, harvest operations, atmospheric acid deposition and site characteristics are believed to have played key roles in soil chemistry and nutrient availability. I hypothesize that the SAFE model is capable of hindcasting (i.e., to reproduce the past), describing current, and forecasting soil chemistry and nutrient availability. If this can be demonstrated, then SAFE will be useful to estimate the extent of soil acidification in the forest stand studied and assess the net effect of forest disturbance and atmospheric acid deposition on the soil chemistry of that forest.

Scientists, foresters, politicians and the general public would all benefit if these objectives were met as they would then possess a valuable method to forecast soil chemical composition and cation nutrient availability to develop policies that will assure the sustainability of the forest resource.

One way to validate the SAFE model is to test it on sites where sufficient field data is available for: 1) model parameterization, and 2) comparison with the model output. In the site I have selected, SAFE is calibrated on a burned zone and unburned zone. Within this site, factors driving soil formation are very similar (e.g., parent material, slope, climate, etc.) but forest history is different. Therefore, I assume that pre-industrial steady-state soil chemistry yielded by the SAFE model will be similar before fire disturbance or human activities. Fire disturbance, however, should alter nutrient cycling within the system so that current soil chemistry between the burned zone and the unburned zone is reproduced accurately due to differences in site history. If the model reproduces pre-industrial steady-state soil conditions that are similar despite the site history factor and reproduces accurately current soil chemistry, then this would offer an additional indication that SAFE accounts accurately for the various cycling processes affecting soil chemistry. It would also show that it can be used with enough precision to validate the hypothesis that current atmospheric loading of H_2SO_4 and HNO_3 coupled with forest management operations will lead in the long run to cation nutrient deficiencies and Al phytotoxicity in eastern Canadian deciduous forests.

This thesis is composed of four chapters. The first three are presented under the form of scientific papers, whereas Chapter 4 is an extented literature review. The first three chapter are significant contributions and important steps to achieve the ultimate objective which was to validate SAFE for deciduous stands in ENA. The last chapter provides data which is helpful for arriving at a conclusion about the future phytotoxicity potential of Al based on the projected soil pH provided by the SAFE model:

1- In the first Chapter, I look at soil chemistry and nutrient availability in a burned zone vs unburned zone in a small deciduous watershed of southern Quebec that was disturbed by fire 75 years ago;

2- In the second Chapter, I reconstruct using the MAKEDEP model the time-series files of deposition and nutrients cycling for the burned and unburned zones. At the same time, various scenarios of N availability are used in the simulations to assess the sensitivity of the model to N;

3- In the third Chapter, I simulate soil chemistry with the SAFE model using the time-series files created under the unburned and burned conditions and forecast soil chemistry as a function of harvest operations and projected increases in N deposition.

4- The fourth chapter provides a review of the scientific literature on the chemistry of Al in forest soils and the toxicity of Al to trees. From the data gathered in this chapter, critical toxicity threshold values are identified and plotted against the solubility curve of Al (a function of pH) to assess if a phytotoxic reponse is likely to occur at pH values projected by SAFE for the study site.

0.10 References

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CHAPTER 1

Soil Chemistry and Nutrient Availability Seventy Five Years after Fire Disturbance in a Deciduous Stand of Southern Quebec

1.1 Introduction

Soil acidity generally decreases after fire events as ash deposited on the forest floor contributes base cations to the soil system (Smith, 1970; Grier, 1975; Raison, 1979; Pritchett and Fisher, 1987; Kutiel and Shaviv, 1992). Soil alkalinization occurs as increased levels of base cations in the soil solution create a new equilibrium where more H^+ and Al^{3+} are removed from the exchange sites in the organic and mineral soil, respectively (Hendershot et al., 1991). The magnitude of change in soil acidity varies with initial soil base status; the change is more pronounced in acidic soils as more H^+ and Al^{3+} are displaced (Manson and Frey, 1989).

Studies suggest that forest fire with high heat will create less acidic soils. Johnston and Elliot (1998) conducted a study on the effect of forest fire on soils as a function of fuel loadings in a boreal mixed wood stand of Ontario. They found that more base cations were released in ash with high heat through more complete consumption of forest biomass. Similarly, Marion et al. (1991) showed that levels of base cations increased in ash with increasing fire severity in a chaparral community in southern California. Furthermore, greater amounts of N and S are lost through volatilization as fire temperature increases (Knight, 1966; Marion et al., 1991). The loss of N and S can be seen as a process contributing to soil alkalinity since these elements would have produced H^+ through oxidation if they had remained in the forest ecosystem.

In a base-poor boreal forest, the leaching of SO_4^{2-} and Cl^- after fire was found to decrease the soil acid neutralizing capacity (ANC) (Bayley et al., 1992). Nitrate levels in streamwater increased more than 10-fold in the first spring following the fire but NO_3^- concentrations were maintained too low to significantly affect ANC and regained pre-fire concentrations three years after disturbance. Higher rates of nitrification and NO_3^- leaching are usually observed in hardwood forests than boreal forests (Gosz, 1981; Carlyle, 1986). Increases in soil nitrification and NO_3^- leaching after fire would generate more acidity so that NO_3^- in hardwood forests is more likely to affect soil ANC than in boreal forests.

The change in soil nutrient availability and solar radiation following forest fire favors pioneer species. When fire leads to a change in tree species composition, nutrient cycling processes (e.g., litterfall, dry deposition, canopy exchange, biological N fixation) are modified (Miles, 1985). Pioneer species usually grow faster than late successional species and that could result in accelerated rates of base cation sequestration in trees and increased input of H^+ into the soil by the roots (Binkley and Richter, 1987; Federer et al., 1989; Knoepp and Swank, 1994; Brais et al., 1995).

Tietema (1998) proposed that the N status in forest soils affects the microbial community: under N-limiting conditions, fungal biomass, including mycorrhizae, constitutes a fairly large fraction of the total microbial community, whereas at N saturation, i.e., the availability of NH_4^+ and NO_3^- is in excess of total combined plant and microbial nutritional demand (Aber et al., 1989), the fungal community declines and bacteria dominate. Nitrogen saturated forest ecosystems are common in North America and Europe (Fenn et al., 1998; Gunderson et al., 1998) and . Through volatilization of N contained in plant tissue and a high N demand by rapid pioneer plant regrowth, forest fire can create N-limiting conditions that would not be conducive to nitrification and NO_3^- leaching (Foster et al., 1997; Dow and DeWalle, 1997). Greater amounts of N brought about by atmospheric deposition would then be necessary for the ecosystem to reach N saturation. Recently, Aber et al. (1998) hypothesized that in conditions of N limitation, mycorrhizae can immobilize large amounts of mineral N that leads to inhibition of soil nitrification and NO_3^- leaching. In contrast, temperate forest soils that have not been disturbed by fire and have continued to accumulate N from atmospheric pollution would show more intense nitrification and NO_3^- leaching because of a large bacterial activity.

The objective of this study was to verify whether fire disturbance and subsequent changes in species composition and growth dynamics could have an overall long-term effect on soil fertility and acidity. More specifically, we hypothesized that fire in hardwood forests growing on sites relatively poor in base cations would acidify soils through mechanisms similar to those of boreal forests and decrease soil ANC through greater soil nitrification and NO_3^- leaching. To validate this hypothesis, we compared soil chemistry and nutrient availability of burned and unburned sections of a small deciduous forested watershed of southern Quebec that was burned 75 years ago.

1.2 Materials & Methods

1.2.1 Site Description

The study site is located in the Hermine watershed at the Station de Biologie des Laurentides de l'Université de Montréal near Saint-Hippolyte, Quebec, in the Lower Laurentians, 80 km north of Montréal (Figure 1.1). Thirty-year average precipitation at the station is 1100 mm, with 30% falling as snow. Mean annual temperature is 3.6°C. The forest has a mean basal area of 28 m^2 ha^{-1} and is dominated by sugar maple (*Acer saccharum* Marsh.) and red maple (*Acer rubrum* L.). Part of the topmost section of the southern hillslope is dominated by paper birch (*Betula paryrifera* Marsh.), yellow birch (*Betula alleghaniensis* Britt.), and largetooth aspen (*Populus grandidentata* Michx.). The bedrock is Precambrian anorthosite of the Morin series (McGerrigle, 1976). The soils at the site are sandy loam derived from well to imperfectly drained rocky glacial till with a mineral composition similar to that of the anorthosite. The forest floor is a moder humus form and the soils are classified as Orthic Humo-Ferric Podzols and Gleyed Ferro-Humic Podzols (Comité d'experts sur la prospection pédologique d'Agriculture Canada, 1987).

1.2.2 Field Study

In September of 1993, three zones that reflect the spatial variability of vegetation, soils and topography at the Hermine watershed were selected. Zone 1 along the stream and zone 2 in the uppermost section of the watershed are dominated by sugar maple, whereas zone 3 is topographically similar to zone 2 but is mainly composed of birch and aspen. More than thirty tree cores collected throughout the watershed revealed that the stand in zone 3 was about 75 years of age as compared to approximately 100 years of age in zones 1 and 2 (Côté, unpublished data). Moreover, observations revealed an abundance of charcoal in zone 3, whereas the watershed did not display traces of charcoal elsewhere. All of the above suggest that the forest stand in the uppermost section in zone 3 was initiated by fire approximately 75 years ago.

Three 300 m^2 circular plots were delimited within each zone. Samples from the surface organic (FH and Ah) and B horizons were collected in four permanent sub-plots of 5 m^2 selected randomly in each plot. Samples from the sub-plots were pooled together for each of the organic and mineral horizons for analysis. The discontinuous

Ae horizon was not sampled. In 1993, samples were collected in September, October, and November. Soil samples were collected once a month from May to November of 1994 and 1995, whereas sample collection was done three times in 1996 and 1997 (i.e., spring, summer, and fall) to decrease the impact on the plots. Zero-tension lysimeters (Hendershot and Courchesne, 1991) were installed in each plot in September of 1993 at depths of 0 cm (below the LFH layer) and 50 cm (in the lower B horizon). From 1994 to 1997, soil solutions were collected every two weeks from May to November, and every month from December to April. Foliage from five trees in each plot was also collected in August of each year from 1994 to 1998. The surface area covered by the sampling design in the Hermine watershed represents approximately 10% of the total surface of the southern hillslope.

1.2.3 Laboratory Analysis

Soil pH in water, total N, organic C, and exchangeable cations were determined on soil samples collected from 1993 to 1997. Soil pH in water was measured using a soil to water ratio of 1:2, total N was analysed on a Technicon AutoAnalyzer on digested samples (Allen, 1989), organic C content was determined on mineral soil samples using the wet oxidation method described by Nelson and Sommers (1982), and exchangeable cations were determined using an unbuffered $BaCl_2$ extraction (Hendershot et al., 1993). Levels of cations in the $BaCl_2$ extracts were determined by atomic absorption spectrophotometry (Perkin-Elmer model 2380).

Electrical conductivity and pH were measured within 24 h after collection of soil solutions on unfiltered samples. After filtration through 0.4 μm polycarbonate membranes, Ca^{2+}, Mg^{2+}, K^+, and Na^+ in both solutions were determined by atomic absorption spectrophotometry. Chloride, NO_3^-, NH_4^+, and SO_4^{2-} in soil solutions were measured by ion chromatography (Waters). Dissolved organic carbon (DOC) concentrations in the soil solutions were estimated using the linear relationship between the absorbance (ABS) at 254 nm and the DOC of over 50 samples measured at depths of 0 cm and 50 cm using the approach described by Moore (1985):

$$\text{DOC (mg L}^{-1}) = 1.01 + 24.7 * \text{ABS} \qquad \text{(eq. 1.1)}$$

with an $R^2 = 0.885$.

Shortly after collection, leaf tissue were oven-dried for 48 hours at 65°C and then weighed. The dried samples were grounded to pass through a 40-mesh screen and digested in H_2O_2-H_2SO_4 (Allen, 1989). Digests were analyzed for N using a Technicon AutoAnalyser, and Ca^{2+}, Mg^{2+}, and K^+ levels were determined by atomic absorption spectrophotometry.

1.2.4 Data Analysis

Particle size distribution, bulk density, and mineralogy of the parent material in zone 1 is clearly different from that of zones 2 and 3, whereas these properties are similar between zones 2 and 3 (Chapter 3). Further, the proximity between zones 2 and 3 (less than 100 m) and the topographical similarities between these zones (Figure 1.1) suggest that we compare zone 2 and zone 3 for determining the effect of fire and subsequent forest regrowth on soil chemistry.

All parameters were subjected to a repeated-measures ANOVA to determine if differences in soil and soil solution chemistry between the burned and unburned zones were significant. The MANCOVA function in STATISTICA 4.1 was used for this analysis, where the between-group factor was forest history (burned conditions (zone 3) vs unburned conditions (zone 2)) and the dependent variables were soil and soil solution chemical properties as a function of time. If a single observation from one of the two zones was missing within a day of sampling, then all data obtained on that day was removed for analysis. All multivariate statistics were performed at $\alpha<0.05$.

Compositional nutrient diagnosis (CND) was used to compute CND indices according to the procedures described in Parent and Dafir (1992). The total dry matter content (DM) of a leaf was considered to be made up of a mineral nutrient component (N, P, K, Ca, Mg), and another general component, represented by R, together totaling 100%.

$$DM = N + P + K + Ca + Mg + R = 100\% \qquad \text{(eq. 1.2)}$$

The fill value, R, makes up the difference to 100% and is computed as follows:

$$R = 100\,\% - (N\% + P\% + K\% + Mg\% + Ca\%) \qquad \text{(eq. 1.3)}$$

The geometric mean (G) was then used to remove the bounded sum constraint to take into account the effects of all the nutrients, and to make the data independent thus allowing for the possibility of further analysis. The geometric mean was calculated as follows:

$$G = [N * P * K * Ca * Mg * R]^{1/6} \quad \text{(eq. 1.4)}$$

The bounded sum constraint was further removed through linearization of the compositional data by calculating the log of the nitrogen dry matter content in relation to all the other components, represented by the geometric mean (V_N or CND score). The process of dividing the nitrogen content by the geometric mean serves to center the value around the mean while creating a multinutrient ratio as follows:

$$V_N = \ln (N/G) \quad \text{(eq. 1.5)}$$

Relationships between V_N scores and basal area increments of each species were assessed by linear regressions. The data set consisted of all trees sampled in the watershed between 1994 and 1998. Data used for the maple regression was from zone 1 and zone 2, whereas data for aspen and birch originated from zone 3.

1.3 Results

1.3.1 Soil chemistry

Base saturation in the mineral soil of the burned zone was significantly higher than in the unburned zone, but no significant difference was found in the forest floor (Table 1.1). The forest floor in the burned zone had significantly greater exchangeable Ca, Mg, and K than the unburned zone, and exchangeable Na, Fe and Al were not significantly different between the zones (Table 1.1). The mineral soil in the burned zone had significantly greater exchangeable Ca and K than the unburned zone, and exchangeable Mg, Na, Fe and Al were not significantly different (Table 1.1). Exchangeable Mn in both the forest floor and mineral soil was significantly lower in the burned zone relative to the unburned zone. The sum of all exchangeable cations (CEC) was significantly higher in the forest floor of the burned zone relative to the unburned zone but there was no significant difference in the mineral soil (Table 1.1). Soil pH and total N concentrations in the forest floor and mineral soil were not significantly different between the zones. Organic C in the mineral soil of both zones were statistically similar (Table 1.1).

1.3.2 Soil Solution Chemistry

Concentrations in NH_4^+, NO_3^-, and DOC between zones in the soil solutions of the forest floor but not the mineral soil differed significantly: NH_4^+ and NO_3^- levels were higher in the unburned zone and DOC concentrations were higher in the burned zone (Table 1.2). Differences between zones for pH, base cations, and SO_4^{2-} and Cl^- were generally not significant (Table 1.2).

1.3.3 *Compositional Nutrient Diagnosis*

Relationships between V_N scores and basal area increments of all maple, aspen, and birch trees sampled in the watershed are shown in Figure 1.2. Linear regressions are significant at $\alpha<0.05$ for aspen and birch but not maple. The linear regression of V_N-aspen explains 17% of the variability in basal area increment, whereas that of V_N-birch explains 14% of the variability in growth.

1.4 Discussion

The results of the comparison between the burned and unburned parts of the watershed indicate that there are two major, statistically significant, differences: namely, higher base status and lower soil solution N in the burned zone than to the unburned zone. In the discussion that follows, we will try to relate these two differences to the effects of forest fire and subsequent changes in forest composition and growth dynamics.

1.4.1 Factors Affecting Soil Base Cation Status

Both forest fire and forest regrowth will influence base cation status of the soils. Immediately after forest fire, the presence of ash on the soil surface results is a direct input of base cations to the soil system (Grier, 1975; Raison, 1979; Pritchett and Fisher, 1987). Initially, this will increase base saturation of the forest floor and then the mineral soil. The rapid regrowth of the forest following a fire removes base cations from the soil at a faster rate than the previous more mature stand and transfers them to the standing biomass in exchange for H^+ (Binkley and Richter, 1987; Federer et al., 1989; Knoepp and Swank, 1994). Analysis of leaf litter of tree species typical of sugar maple dominated forests in southern Quebec demonstrates that early successional species such as largetooth aspen, white birch and yellow birch have less acidic leaf litter and sometimes richer base cation concentrations than that of later successional species such as sugar maple and red maple (Côté and Fyles, 1994). Although the effect of the differences in leaf litter of these species have not been identified in the soil itself, we can speculate that aspen and birch have contributed to the enrichment of base cations in the forest floor as compared with the maple-dominated stand.

A high quality leaf litter is usually associated with a more intense acidification of the underlying B horizons as base cations are transferred from the mineral soil to the canopy and then to the forest floor through litterfall or foliage leaching (Alban, 1982). In the Hermine watershed, however, the higher exchangeable Ca, Mg, and K content in the forest floor of the burned zone was not accompanied by an impoverishment of the B horizon. Rather, the B horizon of the burned zone had a greater base saturation and exchangeable Ca and K than the unburned zone. Paré and Bergeron (1995) observed similar results after colonization of trembling aspen on a clay soil of the mixed boreal forest, i.e., a high quality forest floor underlain by an unacidified mineral soil. They suggested that the high base content of the clayey mineral soil provided a strong buffer against the acidifying potential of aspen. In the Hermine watershed, however, the sandy loam soil does not provide a strong buffer against acidification. There was no significant difference in the sum of cations (CEC) between the zones which suggests that the greater concentrations of exchangeable base cations in the mineral soil of the burned zone is not the result of intrinsic characteristics of the parent material in that zone. Hence, we feel that the data supports the hypothesis that the forest fire enriched the soil in base cations and buffered the effect of rapid forest regrowth in the mineral B horizon.

1.4.2 Factors Affecting Nitrification and N Leaching

Reduced plant uptake and increased mineralization of nutrients immediately after fire disturbance increases nutrient availability in the soil system (Pritchett and Fisher, 1987). An increase in pH and nutrient availability leads to the growth of the nitrifying bacteria community (Wright and Bailey, 1982). Nitrate leaching in deciduous stands of eastern North America is therefore usually enhanced after the loss of the forest cover, but the effect seldom lasts more than 5 years (Likens et al., 1970; Dahlgren and

Driscoll, 1994). Our data show that the current leaching rates of NH_4^+ and NO_3^- are lower in the burned zone than in the unburned zone (except for NH_4^+ in the mineral soil) which suggests that mechanims of soil N retention are associated with the development of pioneer and mid-successional species. It is likely that a reduced N capital after fire disturbance and increasing post-fire vegetative demand have enhance N retention as suggested by Dow and DeWalle (1997) for fires with low to moderate intensities. Low NH_4^+ and NO_3 mobility due to a higher nutrient demand by post-fire regrowth is supported at the study site by the significant relationships between V_N scores and basal area increments of aspen and birch trees. Linear regressions suggest that aspen and birch in the burned zone are growth-limited by N, whereas the lack of significance in the relationship for maple trees in the unburned parts of the watershed suggests that no growth limitation occurs (Figure 1.2).

Stark and Hart (1997) showed that gross fluxes of NO_3^- can be high in forest soils even though evidence for net nitrification and NO_3^- leaching is difficult to find so that immobilization by free-living microbes (bacteria) could be the primary cause of dissolved mineral N retention in soil organic matter. Conversely, Tietema (1998) proposed that sites with low rates of nitrification and NO_3^- leaching are associated with a soil microflora dominated by mycorrhizal fungi, but as forest succession proceeds towards later stages of forest succession and N-saturation, free-living microbes gradually replace mycorrhizae and net nitrification occurs. If the last case proves to be true, then it is possible that the creation of a N poor environment has triggered the phase-out of the soil bacterial community associated with the mature maple stand and a replacement with mycorrhizae. As hypothesized by Aber et al. (1998), the net assimilation and exudation of mineral N by mycorrhizal fungi would have then resulted in a greater immobilization of mineral N than with bacteria and in further decreases in the rates of nitrification and NO_3^- leaching. The unburned stand has been subject to continuous loading of N from the atmosphere without any significant extraction of N during the last century. As a consequence, a greater bacterial community is likely to be found in that zone and in turn, this would generate more nitrification and NO_3^- leaching than in the burned stand. Whether mycorrhizae dominate the microbial community in the burned zone and bacteria dominate in the unburned zone has yet to be demonstrated in the Hermine watershed.

The higher DOC concentrations in the forest floor of the burned zone likely explains the significantly lower solution pH in the forest floor of the burned zone relative to the unburned zone. Carbon consumption from assimilation of mineral N by mycorrhizae is lower than free-living microbial immobilization because mycorrhizal fungi use photosynthate carbon directly rather than that converted from decomposition of litter by microbes (Aber et al., 1998). Consequently, C consumption and CO_2 effluxes for immobilization of N are respectively one-third and one-tenth of the C consumption and CO_2 effluxes by free-living microbes. Again, significantly higher DOC concentrations in the forest floor of the burned zone after 75 years of disturbance is consistent with a soil microflora with a greater proportion of mycorrhizae: N availability is perhaps too low to allow free-living microbes to grow and that any addition of C to the soil solution would not stimulate an increase in metabolic rates, nor drive immobilization of carbon by free-living microbes.

1.5 Conclusion

The overall effects of fire disturbance and subsequent changes in species composition within this base poor hardwood forest have not acidified the soil. Rather, increases in exchangeable base cations in both the forest floor and mineral soil induced by the fire appear to have been large enough to buffer inputs of acidity from the leaching of strong acid anions (short term) and forest regrowth (long term). Whether soil acidification will occur after fire disturbance in a similar base-poor hardwood forest but with higher N saturation is unknown, but looking at the effects of fire disturbance in various sites offering a range of soil buffering capacities and degrees of N saturation would certainly help elucidate this question. Also, an integrated study that would look at the microflora population along the N saturation gradient of the burned stands would help to determine the role of fire on the soil's overall N status and microflora.

1.6 References

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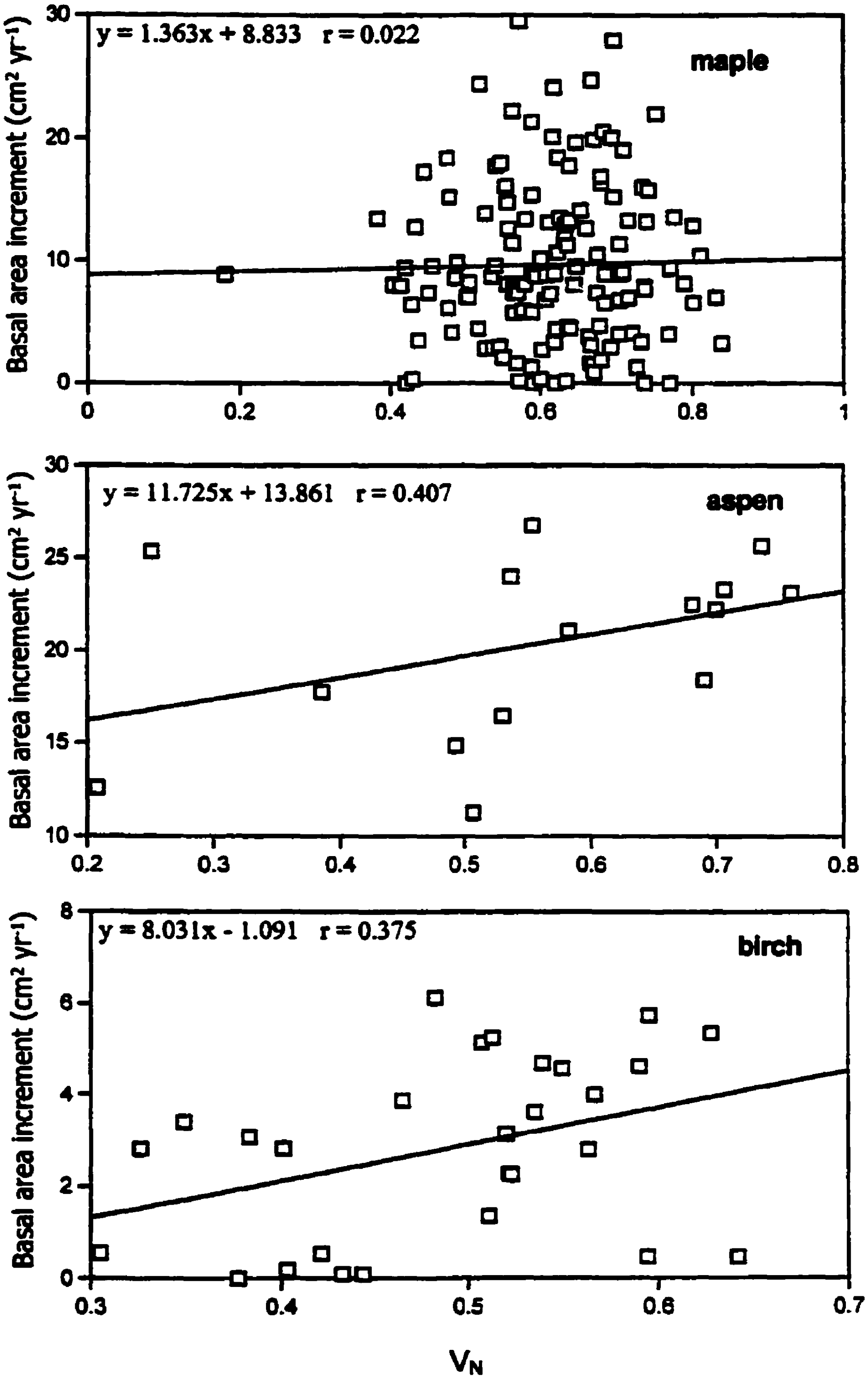

Figure 1.2. Relationship between V_N scores and basal area increments of aspen, birch and maple at the Hermine watershed.

Table 1.1. Mean concentrations of exchangeable ($_e$) cations and cation exchange capacity (CEC), concentrations of organic carbon (OC) and total nitrogen (N_{tot}), pH, and base saturation (BS) in the forest floor and mineral horizon of zone 2 (unburned) and zone 3 (burned) at the Hermine watershed.

	pH	CEC	Ca_e	Mg_e	K_e	Na_e	Al_e	Fe_e	Mn_e	BS	N_{tot}	OC
			$cmol_c\ kg^{-1}$							- % -	— $mg\ g^{-1}$ —	
Forest Floor												
Unburned	4.28a	26.8b	19.8b	2.10b	0.69b	0.13a	2.89a	0.13a	1.07a	84.1a	15.1a	n.a.
Burned	4.21a	32.7a	25.1a	2.74a	0.96a	0.14a	2.82a	0.13a	0.85b	88.0a	15.2a	n.a.
Mineral Soil												
Unburned	4.98a	4.59a	1.35b	0.13a	0.06b	0.04a	2.88a	0.10a	0.03a	34.2b	2.66a	6.11a
Burned	5.02a	5.47a	1.91a	0.19a	0.09a	0.04a	3.12a	0.10a	0.02b	40.8a	2.92a	7.77a

Table 1.2. Mean concentrations of base cations and major anions, dissolved organic carbon (DOC), and pH in the soil solutions of the forest floor and mineral soil of zone 2 (unburned) and zone 3 (burned) in St-Hippolyte.

	pH	DOC	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	NH_4^+	SO_4^{2-}	Cl^-
		– mg L^{-1} –	μmol L^{-1}							
Forest Floor										
Unburned	4.68a	26.3b	75.0a	19.5a	24.8a	9.46a	54.6a	45.6a	38.1a	21.1a
Burned	4.23b	34.0a	82.9a	9.62a	21.8a	11.3a	5.37b	8.54b	44.6a	16.3a
Mineral Soil										
Unburned	5.34a	2.22a	44.7a	12.4b	0.74a	29.2a	5.58a	2.22a	58.0a	13.8a
Burned	5.64a	2.37a	45.4a	9.91a	1.26a	24.4b	0.43b	2.22a	57.4a	9.91b

CONNECTING PARAGRAPH

In the next Chapter, I reconstruct the time-series files of atmospheric deposition and cycling processes using the MAKEDEP model for burned and unburned conditions. Some processes contributing or consuming N that we believed to be important in the Hermine watershed are omitted in the original schematic description of MAKEDEP. Because N availability is the factor limiting forest growth in MAKEDEP, I added processes of biological N fixation, dry deposition, and denitrification to the model. The objective was to assess the sensitivity of MAKEDEP to N availability and therefore, find the N availability scenario that would closely simulate current forest biomass and N leaching for unburned and burned conditions at the study site. I simulate thereafter in Chapter 3 soil chemistry with the SAFE model using the best set of time-series files created in Chapter 2.

CHAPTER 2

Simulation of Soil Chemistry and Nutrient Availability in a Forested Ecosystem of Southern Quebec. 1. Reconstruction of the Time-Series Files of Nutrient Cycling Using the MAKEDEP Model

2.1 Introduction

Evidence is accumulating that the combination of atmospheric deposition of acidic compounds and intensification of harvesting practices is leading to the degradation of the soil base cation reserves (Federer et al., 1989; Shortle and Bondietti, 1992; Keenan and Kimmins, 1993; Likens et al., 1996). Dynamic process-oriented models of soil and water acidification such as MAGIC (Cosby et al., 1985), MIDAS (Holmberg et al., 1989), SAFE (Warfvinge et al., 1993), and SMART (de Vries et al., 1989) are used as tools to assess the ability of forest soils to supply cation nutrients for optimum growth. However, these models have yet to be used to plan the best possible operational practices over the long term to maintain soil fertility as a function of atmospheric deposition and site characteristics.

Because these models account for temporal dynamics in soil acidification, they require time-series files of atmospheric deposition and other processes of nutrient cycling as key input data. Historical data from the Rothamsted Experimental station, UK (i.e., 1883, 1906, and 1964) was used to confirm that the dynamic soil model SAFE is accurate for yielding pre-industrial soil chemistry and describing current soil chemical properties (Sverdrup et al., 1995). These authors also pointed out that the uncertainties associated with the time-series files of input were diminished simply because pre-industrial soil chemistry had been assessed at the experimental station. In eastern North America, the first long-term studies of deciduous forest ecosystems were initiated in the 1960's, e.g., Hubbard Brook Experimental Forest (HBEF). In eastern Canada, most studies assessing the effects of atmospheric deposition and forest disturbance on nutrient cycling have been initiated not more than 10 years ago, e.g., Catamaran brook (New Brunswick), Duchesnay (Quebec), and Duparquet (Quebec), so historical data is not available to validate dynamic models.

The MAKEDEP model was developed to estimate historic deposition and the cycling of nutrients for sites in Europe where only present day data is available (Alveteg et al., 1998). They argued that serious errors in formulation of dynamic soil models may go unnoticed because the time-series files used to run these models could be adjusted in an unreasonable manner to obtain reasonable output. Alveteg et al. (1998) proposed that modellers use MAKEDEP so that the same set of assumptions is always applied for simulating in the long term soil and water chemistry. By doing so, it would become easier to detect invalid assumptions in the formulation of the various dynamic soil models.

In the MAKEDEP model, N availability N determines tree growth and in turn, affects most of the processes involved in nutrient cycling. In an application of the SAFE model at the Solling spruce experimental forest, Germany, Walse et al. (1998) used an unusual time-series pattern of growth/accumulated nutrient uptake which was created with MAKEDEP: no growth between 1800 and 1900 followed by sustained and rapid growth from 1900 until 2000. This was the same as assuming no standing timber between 1800 and 1900. The absence of growth was likely caused by low N availability prior to the onset of N loading from the atmosphere in the early 1900's. Two problems originate by using such an assumption about tree growth. First, forest canopy development has a large influence on the pattern of litterfall, canopy exchange, and dry deposition, whereas growth of woody components and the canopy determine nutrient uptake rates. The absence of forest growth therefore engenders an underestimation of these processes. Second, model calibration becomes more complex as pre-industrial soil chemistry is modelled incorrectly. In our previous experience with the SAFE model using time-series files created with MAKEDEP, SAFE calculated unreasonably high pre-industrial soil pH and base saturation. Further, as the forest is established very rapidly after 1900, soil acidification rates are overestimated due to the uptake of large amounts of base cations in the soil solutions in exchange for protons.

In this chapter, the time-series files of nutrient cycling in a mixed deciduous stand of southern Quebec were reconstructed using various scenarios of N availability to assess the sensitivity of the MAKEDEP model to tree growth and in turn, N cycling. There were three main objectives: 1) assess the variability of the time-series file of N leaching rates below the rooting zone (i.e., a balance between all processes included in MAKEDEP which act as sources and sinks of N) as a function of N availability and identify the scenario of N availability that agrees the most with current field N leaching rates, 2) evaluate tree growth response to the various N availability scenarios relative measured field biomass, and 3) verify the applicability of MAKEDEP to recreate the trends in atmospheric deposition of major ions in eastern North America.

2.2 Materials & Methods

2.2.1 Model Description

In forested ecosystems where nutrients are abundant, changes in tree biomass over time can be determined with the MAKEDEP model as a function of age according to a nth order Mikaelis-Menten equation (Alveteg et al., 1998):

$$w = w_{max}\,[Y^n/(Y^n+K^n)] \qquad \text{(eq. 2.1)}$$

where w is the biomass (kg m^{-2}), w_{max} is a scaling factor representing the maximum possible biomass at the site, Y is the age (years) of the stand, k is the age at which the forest reaches half of its maximum biomass, and n is the order of the equation. As the stand develops, however, the relative proportion of biomass in stems, branches, and roots increases and that in foliage decreases. The MAKEDEP model was therefore set up so that it generates half of its maximum foliage mass (i.e., twigs and leaves) three times faster than the wood mass, i.e., setting k in equation 2.1 to be a third of that for wood growth.

In the MAKEDEP model, growth rates (g m^{-2} yr^{-1}) are given by the derivative of the Mikaelis-Menten equation:

$$r_{growth} = w_{max}\,[(Y^n-1)/(Y^n+K^n) - (Y-1)^n/((Y-1)^n+K^n)] \qquad \text{(eq. 2.2)}$$

where r_{growth} is the annual growth rate. The uncertainty that tree growth may have been decreased during a certain period by N limitation is accomodated in MAKEDEP by changing Y in equation 2.2 to y, where y is the apparent age of the forest given by the Mikaelis-Menten equation:

$$y = k\,[w/(w_{max}-w)]^{1/n} \qquad \text{(eq. 2.3)}$$

The growth rate determined with y instead of Y becomes a function of forest biomass rather than stand age. Yearly uptake of Ca, Mg, K and N is calculated as the content of a nutrient in foliage (including twigs) multiplied by the total annual increment of the canopy, in addition to the weighted average of the nutrient in roots, stem wood, stem bark, and branches, multiplied by the total annual growth of these compartments combined. Pre-industrial uptake of nutrients by trees may be overestimated because current nutrient concentrations from which element mass in trees is reconstructed may actually exceed those of the pre-industrial era, particularly for N after years of air pollution from the use of fossil fuels.

Temperature and moisture conditions were likely the main factors controlling tree growth in southern Quebec. However, it is not possible to recreate these past conditions easily for site specific conditions. In the MAKEDEP model, N availability alone (provided as bulk deposition, throughfall, and litter) is used as the factor limiting forest growth. A smaller pool of nutrients in the trees than what is currently observed in the field is calculated by MAKEDEP if the amount of available N is lower than plant N uptake (i.e., a negative N balance). It then increases w_{max} until forest biomass agrees with current conditions. Several attempts are often necessary before MAKEDEP finds an appropriate w_{max} to relate atmospheric deposition and canopy biomass.

In the MAKEDEP model, it is assumed that N, Ca, Mg, and K mineralization in the forest floor is equivalent to the N, Ca, Mg, and K inputs from litterfall. The amount of N that reaches the forest floor as litterfall (twigs and foliage) is assumed to be recycled for canopy growth only and is not used for wood growth. Litterfall is reconstructed yearly by using as input the ratio between the litterfall flux of N with the uptake flux of N in the canopy (i.e., litterfall mass and canopy mass, respectively). Since only one rate of mineralization at a time can be specified in a simulation, litterfall fluxes of Ca, Mg, and K need to be corrected after each simulation as retranslocation of these elements is different from that of N.

As implemented by Alveteg et al. (1998), the MAKEDEP model uses relative curves (0 to 100% of maximum) of European emission to reconstruct deposition history. Assuming that deposition of an element follows the same pattern as emission of that element, deposition of an element can be reconstructed by scaling into the past values of deposition using standard curves of emission.

Dry deposition in MAKEDEP is the loading of elements that do not interact significantly with the canopy (i.e., Cl, SO_4, Na). Current dry deposition (DD) of non-interacting elements can be determined using the equation:

$$DD = TF - BD \qquad \text{(eq. 2.4)}$$

where TF is current throughfall deposition and BD is current bulk deposition, expressed in kg ha^{-1} yr^{-1}. For elements involved in canopy exchange, i.e., Ca, Mg, and K, a low limit value of current dry deposition can be estimated by the following equation:

$$DD = BD\,[(TF_{Na} - BD_{Na})/BD_{Na}] \qquad \text{(eq. 2.5)}$$

assuming that 1) Na is not strongly involved in canopy exchange, 2) Ca, Mg, and K are deposited by the same mechanism as Na, and 3) deposition of Na contains the same proportion of dry deposition as compared to deposition of Ca, Mg, and K. If BD_{Na} is higher than TF_{Na}, then equation 2.5 is cancelled and dry deposition of Ca, Mg, and K becomes zero. Once current dry deposition has been estimated for a particular element, the standard emission and canopy biomass curves are used to produce bulk and dry deposition for any given year, assuming that the leaf area index (LAI) is proportional to the leaf biomass:

$$DD_y = [(DD_{current}/R_{emission,current}) * W_{canopy,y} * R_{emission,y}]/\ W_{canopy,current} \qquad \text{(eq. 2.6)}$$

$$BD_y = [(BD_{current}/\ R_{emission,current}) * R_{emission,y} \qquad \text{(eq. 2.7)}$$

where $R_{emission}$ is given by the standard curve of emission, W_{canopy} is the LAI given by the canopy mass curve, *y* denotes values for year *y*, and *current* denotes values for current conditions. Canopy exchange (*CE*) is the remaining category of deposition and current interaction of elements with the canopy can be estimated for inland sites with the equation:

$$CE = TF - BD - DD \qquad \text{(eq. 2.8)}$$

Knowledge about biochemical interactions between the atmosphere and the forest canopy is still limited. Canopy exchange can be an important source or sink for NO_3^- and NH_4^+. Because of the uncertainty regarding the relationship of canopy exchange with bulk deposition and throughfall for N compounds, canopy exchange is accounted for in the MAKEDEP model only when bulk deposition of NO_3^- or NH_4^+ is greater than throughfall, i.e., when canopy acts as a net sink for N compounds. If that is the case, then equation 2.8 is modified by setting dry deposition to zero since it can not be negative and current canopy exchange is estimated as:

$$CE = TF - BD \qquad \text{(eq. 2.9)}$$

Once current canopy exchange is assessed, Ca' Mg, K, and N exchanges within the canopy for any given year is modelled according to the LAI or canopy biomass:

$$CE_y = (CE_{current} * W_{canopy,y})/\ W_{canopy,current} \qquad \text{(eq. 2.10)}$$

2.2.2 Site Description

The study site is located in the Hermine watershed at the Station de Biologie des Laurentides de l'Université de Montréal in Saint-Hippolyte, Quebec, in the Lower Laurentians, 80 km north of Montréal. See section 1.2.1 for details.

2.2.3 Field study, Laboratory Analysis and Model Parameterization

In September of 1993, three zones that reflect the spatial variability of vegetation, soils and topography in the Hermine watershed were selected (see section 1.2.2). Within each zone, three circular plots of 300 m^2 were delineated. In each zone, about 10 co-dominant and dominant trees were selected and cored in sound wood at 1.3 m aboveground. Cores were stored in the field in plastic straws and air-dried immediately in the laboratory. Ring increments were measured to a precision of 0.01 mm. The oldest sugar maple cored without heart-rot in the watershed shows a very slow growth rate during the time period 1830-1900, whereas the growth rate increased after 1900 and decreased again after about 1970 (Figure 2.1). This suggests that maple growth was suppressed prior to 1900 and that a severe perturbation resulted in its release around 1900. One commercial harvest can be documented in that area, but it is likely that operations were executed so that only large trees were harvested and small trees were left standing (now the oldest trees in the watershed). Most of the dominant sugar maples found in zones 1 and 2 are 100 years old or less, i.e., trees released by the harvest.

Tree cores collected throughout the watershed indicate that the trees of zone 3 were about 75 years of age. Moreover, observations revealed an abundance of charcoal in zone 3, whereas the watershed did not display charcoal elsewhere. This suggests that the forest stand in zone 3 was initiated by fire around 1925. Because the watershed has two distinct forest histories, reconstruction of deposition and cycling processes was performed with the MAKEDEP model using two zones representing the burned and unburned conditions, i.e., zones 2 and 3, respectively.

A funnel collector of 17.5 cm in diameter was installed at a height of 1.5 m in each plot for throughfall. In the topmost section of the southern hillslope, a tower that rises above the forest canopy (approximately 25 m) was constructed to collect bulk deposition. From 1994 to 1997, throughfall and bulk deposition were sampled every two weeks from May to November, and every month from December to April. The volume of the samples was measured in the field. Electrical conductivity and pH were measured within 24 h after collection on unfiltered samples. After filtration through 0.4 μm polycarbonate membranes, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} were determined by atomic absorption spectrophotometry (Varian), and Cl^{-}, NO_3^{-}, NH_4^{+}, and SO_4^{2-} were measured by ion chromatography (Waters). Mean concentrations of bulk deposition and throughfall samples collected from 1994 to 1997 in the Hermine watershed were used to estimate wet and dry deposition as well as canopy exchange with the MAKEDEP model (Table 2.1). Daily measurement of air temperature, humidity, wind speed and direction, and total rainfall and snowfall since 1964 was provided by the *Station de Biologie* at a location less than 2 km from the Hermine watershed.

Litterfall mass was measured within each plot using five traps of 0.25 m^2. Litterfall was collected on a monthly basis during spring and summer, and every two weeks in the fall. The material from the five traps was sorted by species. Foliage from five trees (various species) in each plot was also collected in August of each year. Shortly after collection, foliage and litter tissue were oven-dried for 48 hours at 65°C and then weighed. The dried samples were grounded to pass through a 40-mesh screen and digested in H_2O_2-H_2SO_4 (Allen, 1989). Digests were analyzed for N using a Technicon AutoAnalyser, and for Ca^{2+}, Mg^{2+}, and K^{+} by atomic absorption spectrophotometry.

Concentrations of nutrients in foliage used as inputs in MAKEDEP (Table 2.2) were those of samples collected between 1994 and 1997 in the Hermine watershed and calculated as a weighted mean according to the proportion of each species within each zone, i.e., 70% sugar maple, 25% red maple, and 5% yellow birch in the unburned zone, and 27% sugar maple, 7% red maple, 40% yellow birch and white birch, 20% largetooth aspen, and 7% American beech in the burned zone. The ratios between litterfall and nutrient uptake in foliage are presented in Table 2.3. Litterfall fluxes were calculated using measured litterfall mass and nutrient contents in litter, whereas nutrient uptake in foliage was estimated using the measured contents of nutrients in foliage and estimated foliage mass (see below for details on allometric equations used) at the study site. Average contents of nutrients in woody components used in the MAKEDEP model were calculated according to equations developed by Chatarpaul et al. (1986) for the same hardwood species (except American beech) (Table 2.2). The concentration of each element was also weighted with respect to the proportions of each species.

Equations in Chatarpaul et al. (1985) can help estimate elemental mass in tree components but not total tree mass and the mass of discrete tree components. In that respect, biomass allometric equations for sugar maple, yellow birch, and American beech created at the Duchesnay experimental forest, Quebec (Camiré et al., unpublished) were used to calculate, within each zone, current wood mass (i.e., stem wood, stem bark, and branches) and foliage mass using the 1997 DBH values in the Hermine watershed. Estimated wood biomass in Table 2.4 were used as initial inputs in the MAKEDEP model to reconstruct tree growth, nutrient cyling, and atmospheric deposition in the watershed. In the absence of allometric equations for red maple and white birch, we used equations for sugar maple and yellow birch, respectively, whereas equations for yellow birch were modified to include the difference in wood density with largetooth aspen.

Root mass in the watershed was assumed to be proportional to above-ground biomass since the variation in time of the contribution of nutrient uptake in roots is negligeable as compared to the total amount of nutrients accumulated in woody components. In a mixed northern hardwood forest at the Hubbard Brook Experimental Forest (HBEF), Whitaker et al. (1974) found that root mass was 18% of the total stand biomass. HBEF is dominated by maple, beech and birch trees and is similar to the Hermine watershed in terms of soil texture, stand age, climate and water regime. It enabled us to use the HBEF ratio of root mass to total stand mass for estimating root mass in the Hermine watershed.

2.2.4 Model Adjustments: Standard Curves of Emissions

European deposition patterns in the MAKEDEP model are different from those of eastern North America. Therefore, we assembled estimates of emissions in the literature for different time periods in North America so that standard curves in MAKEDEP would better reflect deposition in the Hermine watershed for the period being modelled (Figure 2.2). All curves are expressed in relative values, i.e., from 0 to 100% of the maximum emission. Above, each time we mention that a curve was adjusted to another curve means that emission trends were conserved rather than conserve the total amount of a compound emitted to the atmosphere. Matching emission records in terms of amounts would not be acceptable since emission estimates of compounds are not necessarily estimates for eastern North America, but could be for the United States or global estimates.

Sulphur emission estimates were assembled for the whole U.S.A. between 1700 to present day. Estimates of SO_2 emissions provided by the United States EPA (1998) were used to cover the 1985 to present day time span. Emission estimates of S by Husar (1992) helped recreate SO_4 deposition history between 1860 and 1985, whereas the S emission rate from 1700 to 1860 was assumed to be the same as in 1860.

Time series of NO_3 and NH_4 depositions were created using emission estimates coming from three sources. Emission estimates of NO_x for eastern North America provided by Husar (1992) were used between 1900-1980, whereas emission estimates of NH_x for the U.S.A. given by Galloway et al. (1996) were used between 1950 and the present day. North American emission estimates of NO_x by Galloway et al. (1996) were adjusted to Husar's estimates to cover the 1980 to present day time period. On the other hand, global emission estimates of NH_3 from 1900 to 1950 (Galloway, 1995) were adjusted to the NH_x curve. The rates of emissions of NO_x and NH_x prior to 1900 were assumed to be the same as estimated by Husar (1992) and Galloway (1995) in 1900, respectively.

For SO_2, NO_x, and NH_x emissions between 1998 to 2020, we used projections made by Galloway (1995) for the whole U.S.A..Emission projections of both NO_x and NH_x for North America made by Galloway (1995) were used to cover the 1998-2020 time period. From 2021 to 2100, emission rates were assumed to be the same as predicted in 2020. Emissions of SO_2 are predicted to decrease further until 2020 in North America and Europe, whereas NH_x and NO_x are expected to be stable. Projection models suggest that the emissions of these compounds will increase significantly in Africa, Asia, and South/Central America (Galloway, 1995). Galloway suspects that increasing S and N emissions in developing countries will increase the loading of atmospheric SO_4, NO_3, and NH_4 in North America. Whether deposition rates in North America should be scaled with global emission estimates rather than those of North America is therefore uncertain. We believe that both scenarios should be considered in order to model/forecast soil chemistry.

Many sources of Ca, Mg, and K exist, e.g., forest fires, road dust, and liming, but these are difficult to quantify. Alveteg et al. (1998) pointed out that deposition of base cations had to be executed nevertheless with precision since these elements will affect the ion-balance and in turn, the pH and acidity of forest soils. Hedin et al. (1994) showed that the decrease in SO_4 deposition in eastern North America over the last thirty years was accompanied with a decrease of Ca, Mg, and K deposition, suggesting that combustion of fossil fuel has been the main source of deposition of Ca, Mg, and K since the onset of industrial air pollution. In that respect, deposition of these base elements was modelled using the standard curve of emissions of SO_2. Chloride and Na are of less importance in an inland site such as the Hermine watershed as compared to coastal areas. Deposition of Cl was also considered to follow SO_2 emissions, whereas Na deposition was assumed to have been constant over the years.

2.2.5 Scenarios of Nitrogen Availability

Among sources of N in the forest ecosystem, biological fixation is one process that introduces uncertainty as to the amount of N available for plant growth. This process is not included in the MAKEDEP model. Forest ecosystems can acquire N through biological fixation of atmospheric N by either free-living (bacteria) or symbiotic organisms (e.g., rhizobium):

1) The net gaseous and aerosol exchange of N at HBEF was estimated from net primary biomass accumulation minus net flux (precipitation input minus stream-water output) as weathering of minerals was assumed not to contribute a significant proportion of N to the whole N cycle in forests (Likens and Bormann, 1995). The net gain in N was about 100 $mmol_c\ m^{-2}\ yr^{-1}$, most of which is likely to originate from biological N fixation. Since denitrification (another process not included in MAKEDEP) does occur at the study site at rates between about 10 $mmol_c\ m^{-2}\ yr^{-1}$ (aerobic soil) and 65 $mmol_c\ m^{-2}\ yr^{-1}$ (anaerobic soil) (Melillo et al., 1983), the actual amount of N brought to the ecosystem through biological fixation could be underestimated;

2) In a mixed hardwood forest soils of Tennessee, the total rate of non-symbiotic biological N fixation measured on twigs, branches, logs, forest floor, and mineral soil was 75 $mmol_c\ m^{-2}\ yr^{-1}$, whereas total denitrification measured in the same forests compartments was 130 $mmol_c\ m^{-2}\ yr^{-1}$ (Todd et al., 1975).

We believe denitrification is also a significant sink of N in the Hermine watershed since very little NO_3^- leaching occurs in the fall when the soils are moist and still warm enough to support an active microflora with a reducing potential. One more source of uncertainty with regards to N cycling in the MAKEDEP model is the underestimation of dry deposition. Field measurement of both canopy exchange reactions involving N ions species and dry N deposition are under improvement so that we possess very little information of measurements of the contribution of each process to the total input of N and other atmospheric elements and compounds (Parker, 1983).

The uncertainty associated with biological N fixation, denitrification, and dry deposition in the MAKEDEP model are dealt with in this paper by using various N availability scenarios. No entry/input in the MAKEDEP model allows the easy addition of a constant source of N to the system. The only way to do so is to adjust a standard curve of emission of a N compound. The standard curve should reflect the supply of N through atmospheric deposition, biological N fixation, dry deposition, and the loss of N through denitrification. From historical data provided by Bouchard (1989), it is clear that southern Quebec had productive forests prior to the onset of rapid increases of air pollution and fertilization of N through atmospheric deposition in the 20th century. With lower N deposition, it is likely that the forests had higher rates of N_2 fixation prior to the 1950's. A constant rate of biological N fixation therefore does not represent well the dynamic changes in the availability of N. In order to take care of part of this discrepancy, the standard curve of emission of NH_4 was set at one (i.e., 100% of maximum emissions) throughout the simulation period. For example, assuming that current deposition of NH_4 was 10 $mmol_c\ m^{-2}\ yr^{-1}$ and that the sum of current biological N fixation and dry deposition minus denitrification was also at 10 $mmol_c\ m^{-2}\ yr^{-1}$, then the sum of biological N fixation and dry deposition minus denitrification prior to industrial air pollution would be close to 20 $mmol_c\ m^{-2}\ yr^{-1}$. By doing so, we assume that the pre-industrial input of NH_4 from bulk deposition, dry deposition, and biological fixation minus denitrication is the same as the current input of NH_4, but only traces of the pre-industrial input of NH_4 would have been from bulk deposition itself.

To verify this hypothesis, we have made simulations with different rates of N addition. The control consisted of a simulation in which the original schematic description of the MAKEDEP model was not modified, i.e., the original standard curve of

NH_4 presented in Figure 2.2 was used and no extra N was added as the sum of biological N fixation and dry deposition minus denitrification (scenario no.1). Other scenarios covered the range of the sum of biological N fixation and dry deposition minus denitrification reported in the literature. Using the standard curve of NH_4 set at one throughout the simulation period, N was added to the system at the rates of 0 $mmol_c$ m^{-2} yr^{-1} (scenario no.2), 10 $mmol_c$ m^{-2} yr^{-1} (scenario no.3), 30 $mmol_c$ m^{-2} yr^{-1} (scenario no.4), and 60 $mmol_c$ m^{-2} yr^{-1} (scenario no.5).

All simulations were initiated in 1700 with a cleared condition (i.e., no standing timber) and were ended in 2100. The commercial harvest was simulated in 1900 in zones 2 and 3, whereas fire disturbance was simulated in 1925 in zone 3 only. The MAKEDEP model was not designed to simulate stem wood harvest (on-site lopping operations) or fire disturbance. Rather, it was design to simulate whole-tree harvest. At the turn of the 20th century, lopping was performed directly on the site during harvest. Nutrients contained in roots and branches were therefore released gradually to the soil system (stem wood harvest). Moreover, for a relatively intense fire, nutrients accumulated in the various tree components would be returned to the soil system after fire disturbance with about 30% of N lost from the system through volatilization (Knight, 1966). Prior to calculating the rates of N leaching in both zones, net mineralization created by stem wood harvest and fire in the Hermine watershed were corrected. Mass proportions calculated by Chatarpaul et al. (1985) for each element contained in the various tree components were used for simulating harvest and fire. My assumption for net mineralization was that fire released all nutrients contained in the whole tree components, whereas the stem wood harvest released nutrients in all tree components except the bole. The intensity of the fire at the Hermine watershed is not known with precision and therefore, there is uncertainty about the rates at which the burned organic materials reached the ground as charcoal or debris (particularly the bole). Thus, a single rate of nutrient release was used to simulate both the harvest and fire, i.e., 20% of the remaining pool of nutrients was mineralized each year. During fire disturbance, 30% of N was assumed to be lost from the system through volatilization as estimated by Knight (1966).

2.3 Results & Discussion

2.3.1 Nitrogen Leaching Below the Rooting Zone

Measured mean N leaching rates at 50 cm depth between 1993 and 1997 in the unburned zone are about 4 mmol$_c$ m^{-2} N yr^{-1}, whereas these rates in the burned zone are about 2 mmol$_c$ m^{-2} N yr^{-1}. These leaching rates are not volume-weighted fluxes, but estimates assuming half of the total precipitation reaches the bottom of the soil profile on a yearly basis and using mean soil solution NO_3 and NH_4 concentrations. Simulated N leaching rates in the Hermine watershed at 50 cm depth (or below the rooting zone) were calculated as the residual component of the N budget in MAKEDEP (Figure 2.3). The N budget is calculated as the balance between processes acting as sources (atmospheric deposition, canopy exchange if throughfall is greater than deposition, net litterfall, and net mineralization) and sinks (plant uptake and canopy exchange if throughfall is less than deposition). In the unburned zone, simulated N leaching in year 1997 is 4.2 mmol$_c$ m^{-2} N yr^{-1} (scenario no. 3), 48 mmol$_c$ m^{-2} N yr^{-1} (scenario no. 4), and 78 mmol$_c$ m^{-2} N yr^{-1} (scenario no. 5). In the burned zone, simulated N leaching at the year 1997 is 1.5 mmol$_c$ m^{-2} N yr^{-1} (scenario no. 3), 41 mmol$_c$ m^{-2} N yr^{-1} (scenario no. 4), and 73 mmol$_c$ m^{-2} N yr^{-1} (scenario no. 5).

The above results suggest that scenario no.3 reproduces the most accurately the field leaching rates under burned and unburned conditions in the Hermine watershed. However, three possible biases need to be considered here. First, measured N leaching rates are not volume-weighted estimates which brings uncertainty about the actual field N leaching rates that should be simulated with MAKEDEP. Second, the reconstruction method in the MAKEDEP model does not necessarily account for the individual processes involved in N cycling with accuracy. The reconstruction of these processes depends on the development of the stands. For example, foliage growth influences uptake, litterfall, and canopy exchange, whereas woody components act on nutrient uptake alone. In that sense, the simulated N budget may be similar to the field values for the wrong reasons if the stand biomass is poorly reproduced. Third, some processes known to have a significant influence on N cycling may be omitted. For example, immobilization of N from the net assimilation/exudation of mycorrhizae is suspected as one of the causes of lower soil solution N concentrations in the burned zone relative to the unburned zone (see Chapter 1). In order to validate the time-series files reconstructed with scenario no.3, an attempt to validate reconstructed tree growth and atmospheric total (wet and dry) deposition is made in the next sections.

2.3.2 Forest Growth and Nutrient Uptake

In this section, we focus on the simulated results of zone 2 only, but the same conclusions with zone 3 can be drawn. In the MAKEDEP application using scenario no.1, woody components and the canopy in the unburned zone are extremely growth-limited prior to 1900 and to lesser extents in scenarios no.2 and no.3 (Figure 2.4). Simulated woody components and canopy growth in scenarios no.4 and no.5 are not reduced prior to 1900 compared to scenarios no.1, no.2, and no.3. After 1900, simulated woody components and the canopy grow faster in scenarios no.1 and no.2, and to a greater extent in scenario no.3. Tree growth in these last scenarios are however still limited relative to scenarios no.4 and no.5 (Figure 2.4).

Low growth rates for both woody components and the canopy before 1900 in scenarios no.1, no.2, and no.3 result from low industrial air pollution/atmospheric N deposition which leads to low N availability and limited tree growth (Figure 2.5). After 1900, atmospheric deposition of N increases which increases N availability and reduces N limitation of tree growth by about 18% (scenario no.1), 27% (scenario no.2), and 42% (scenario no.3) compared to before 1900 (Figure 2.5). Nitrogen deficiencies are however so large in scenarios no.1 and no.2 that the MAKEDEP model failed (by increasing w_{max}) to match the 1997 woody components mass estimated in the Hermine watershed. As a consequence, the model output in scenarios no.1 and no.2 does not go further than the year 1996. This suggests that another source of N be included to the original description of the MAKEDEP model, otherwise the forest does not grow to values reflecting the growth conditions that prevailed in the Hermine watershed.

The simulated woody components in the unburned zone after 1900 achieves 50%, 75%, and 95% of its maximum wood mass as follows: scenario no.3 - 80, 110, and 200 years, and scenarios no.4 and no.5 - 60, 90, and 180 years, respectively (Figure 2.4). As a comparison, simulated yield tables provided by Salomon and Leak (1985) show that sugar maple stands in New England usually attain these mass values after about 55, 100, and 230 years of growth, respectively (i.e., intermediate index sites such as in the Hermine watershed). Nitrogen deficiencies occur in the simulation using scenario no.3 so that growth rates of woody components in the first stages of stand development are lower than with scenarios no.4 and no.5 (Figure 2.4). Consequently, the trees in scenarios no.4 and no.5 reach 50% and 75% of their maximum biomass more accurately than in scenario no.3 (relative to the simulated yield tables in New England). However, N availability increased significantly at the peak of industrial air pollution in the 1950's. In turn, this led to the disappearance of N limitations in scenario no.3 which brought faster growth rates in the later stages of stand development as compared to those in scenarios no.4 and no.5 (trigerred by a higher w_{max}) (Figure 2.4). As a result of faster simulated growth rates in the later stages of development, projected mass of woody components in scenario no.3 is greater than that in scenarios no.4 and no.5. Hence, the simulated growth of woody components in scenario no.3 reaches a maximum biomass after a more reasonable number of years of tenure (200 years) as compared with scenarios no.4 and no.5 (180 years).

Scenario no.3 is therefore a less severe scenario of nutrient uptake in tree components (i.e., total of the derivative of the growth curves of woody components and foliage multiplied by their respective mean nutrient concentrations) in the early stages of stand development than scenarios no.4 and no.5, but is a more severe scenario of nutrient sequestration in the later stages of growth. Aber et al. (1998) have demonstrated that growth rates in some stands of northeastern U.S.A. have increased over the last decades due to increased rates of atmospheric loading of N compounds and increased N availability for tree growth. In that sense, the simulated N deficiencies and lower growth rates in scenario no.3 prior to significant industrial air pollution, followed by more rapid tree growth in the later stages of stand development are supported if the recent increases in growth rates are true for deciduous forests of southern Quebec as well. We are unaware however of any scientific demonstration of increased growth rates in deciduous stands of eastern Canada since significant loading of N compounds from the atmosphere began in the 1900's .

Furthermore, Aber et al. (1998) have shown that N levels in foliage have increased due to increases in the rates of atmospheric loading of N compounds. It is therefore likely that foliar N concentrations in the Hermine watershed are higher relative to historic foliar N concentrations. In that respect, the accumulated net uptake of N in tree components is likely to be overestimated in scenarios no.4 and no.5, whereas limited growth (mostly woody components) in scenario no.3 may have corrected this problem to some extent. Demonstrating the increased growth rates and increased N levels in foliage would be of particular interest for modelling long-term soil chemistry and nutrient availability as dynamic models are very sensitive to the projected forest yields, nutrient uptake rates, and mineralization of the forest floor (Walse et al., 1998).

2.3.3 Total Deposition (Bulk and Dry) and Canopy Exchange

The reconstructed total deposition of elements is presented for scenario no.3 in the unburned zone only because no observable differences in deposition of elements are found between N availability scenarios within a zone and/or between the two zones but for the same scenario (Figure 2.6). No observable difference in total deposition is found for Ca, Mg, K, and Na because simulated dry deposition is a low limit value of current dry deposition (see model description). Second, the effect of the canopy on dry deposition of Cl, SO_4, and Na is hardly observable because the differences in the concentrations of these elements between bulk deposition and throughfall are relatively small and differences are likely not to be significant (Table 2.1).

Linear regressions were conducted to see whether slopes of the simulated deposition were similar to those of the measured deposition in other sites in northeastern North America. Deposition data at the nearest provincial monitoring station of the Hermine watershed is available starting in 1982, whereas deposition at HBEF has been measured since 1963 (Likens and Bormann, 1995). Therefore, measured deposition at HBEF was used to validate simulated trends in deposition at the Hermine watershed (Figure 2.7). Standard errors for the B coefficient calculated in the regression module in STATISTICA 4.1 indicate that the slopes of the regressions of measured and simulated Mg, K, SO_4, NO_3, NH_4, and Cl deposition are not different, whereas they differ for Ca and Na (Figure 2.7). This suggests that the observed decline in deposition of SO_4, Mg, and K over the last 30 years in eastern North America (Hedin et al., 1994) and N ion species can be well taken care of by the standard curves of emissions created here. The reasons behind the unsuccessful simulation of trends in Ca deposition is unclear. The attempt to simulate the trends in Ca deposition using the standard curve of emission of SO_2 was not a complete failure however as both measured and simulated Ca deposition decreased by about 10 $mmol_c\ m^{-2}\ yr^{-1}$ from 1963 until 1992.

The slopes of the regressions of simulated and measured Na deposition in HBEF did not differ, whereas those of Cl differed. On the one hand, sea-salt deposition may have something to do with total (bulk and dry) deposition of these elements at HBEF (Likens and Bormann, 1995). On the other hand, sea-salt deposition in an inland site such as in the Hermine watershed is not the dominant process of deposition of these elements. Differences in the slopes of the regressions of simulated and measured Na deposition is therefore not surprising.

Several locations of eastern North America have rates of base cation deposition similar to that in the Hermine watershed (Foster, 1974; Kramer, 1976 – in Scheider et al., 1979; Houle et al., 1997). Measured Ca, Mg, and K deposition at HBEF is lower than at the Hermine watershed (Figure 2.7). This suggests that processes other than industrial emissions contribute base cations in the atmosphere which are usually assigned to unknow continental sources (Cogbill and Likens, 1974). Therefore, standard curves of emissions of SO_2 may not be ideal for reconstructing base cation deposition. Sulphate deposition between the two sites are however very similar (Figure 2.7). Measured rates of deposition of NH_4 and NO_3 between the sites, on the other hand, are slightly different but are within rates of deposition seen elsewhere in eastern North America (Martin, 1979; Joslin et al., 1992; Houle et al., 1997). First, NH_4 deposition at the Hermine watershed is higher than at HBEF as it includes biological N fixation and dry deposition minus denitrification (i.e., 10 $mmol_c$ NH_4 m^{-2} yr^{-1}). Secondly, we speculate that some of the differences in NH_4 deposition between the sites are due to local manure management and/or fertilization treatments in agricultural fields. In that sense, NH_4 should ideally be modelled using local standard curves of NH_3 emission reconstructed as a function of the intensity of manure applications and fertilization practices in the region rather than trends of emissions for eastern North America.

The forest canopy is very effective at filtering particulates and fine droplets from the atmosphere and canopy exchange is a significant source of Ca, Mg, and K to the soil system that should not be neglected (Eaton et al., 1973; Khanna and Ulrich, 1981; Lovett et al., 1996). Therefore, low canopy density (or low LAI) in scenarios no.1, no.2, and no.3 prior to 1900 creates lower canopy exchange of Ca, Mg, and K than in scenarios no.4 and no.5 (Figure 2.8). Similarly, canopy exchange of N in scenarios no.1, no.2, and no.3 act as a very small sink but simulated canopy exchange in scenarios no.4

and no.5 is a greater sink of N (because of greater canopy mass or LAI) than scenarios no.1, no.2, and no.3 (Figure 2.8). Liechty et al. (1993) observed NH_4 absorption from incident precipitation by northern hardwood foliage at one of five sites and attributed the sink to N deficiency. Similarly, Lovett et al., (1996) reported at the HBEF net negative throughfall of NH_4 and slightly positive NO_3 net throughfall and explained that N retention in foliage is common in areas remote from atmospheric emissions of N. In the Hermine watershed, N deficiencies were found to be significant with aspen and birch trees using the compositional nutrient diagnosis (Chapter 1). However, differences in the fluxes of N between wet deposition and throughfall are probably not significant (Table 2.1).

Exchange of Ca, Mg, and K with the canopies of maple, beech, and birch trees was assessed recently at HBEF (Lovett et al., 1996). In this study, Ca deposition fluxes during the growing season increased between 4.7- and 5.3-fold after its passage through the canopy, Mg deposition fluxes increased by 6.3- to 11-fold, and K fluxes by 23- to 28-fold. In the Hermine watershed, throughfall fluxes increases are lower: Ca fluxes in throughfall are 2.4- to 2.7-fold greater than fluxes in incident precipitation, Mg fluxes in throughfall about 3.0- to 3.5-fold greater, and K fluxes are about 18-fold greater (Table 2.1). Increases of these elements in throughfall fluxes are expected to be lower in the Hermine watershed as increases are measured on a yearly basis compared to measured increases between May and August (Lovett et al., 1996). Indeed, canopy exchange is quite low during the winter months when precipitation falls as snow and leaves have fallen (Verry and Timmons, 1977). Further analysis of the Hermine watershed's bulk deposition and throughfall data is however needed to determine factors (spatial and temporal) influencing canopy exchange reactions involving Ca, Mg, K, and N.

2.4 Conclusion

Dynamic soil models could be a useful tool for forest management if an accurate and simple method to reconstruct time-series files could be developed. In this paper, we have modelled the N cycle in a forested ecosystem using MAKEDEP with some of its schematic description changed to better reflect the situation of N availability for tree growth at the Hermine watershed. A scenario that added 10 $mmol_c$ NH_4 m^{-2} yr^{-1} under burned and unburned conditions through biological N fixation and dry deposition minus denitrification seems to have recreated N leaching rates with acceptable precision. We also found that adding N to the model was necessary for the trees to grow at rates approximating field measurments. We believe however that the general approach used to calculate the various cycling processes (e.g., deposition) as well as the precision in the input parameters creates uncertainty in the model output which puts doubt as to its ability to model soil chemistry for site-specific conditions. At the present level of model development, it would be wiser to use the combination of MAKEDEP and dynamic soil models to provide a general indication of the sustainability of current forest management in a particular region rather than at a particular site. In Canada, it is therefore possible to achieve such a goal since many federal and provincial model forests offer a wide range of data that would meet the requirements of the reconstruction method presented here. Although there are uncertainties associated with the input data, the spatial resolution used for these applications would give more freedom vis-à-vis the interpretation of the model output and will help calculate critical loads of acidity as a function of anticipated forest operations. Considering the above, an indication of the applicability of the SAFE model to reproduce soil chemistry under burned and unburned conditions at the Hermine watershed is given in the next chapter using the time-series files created here.

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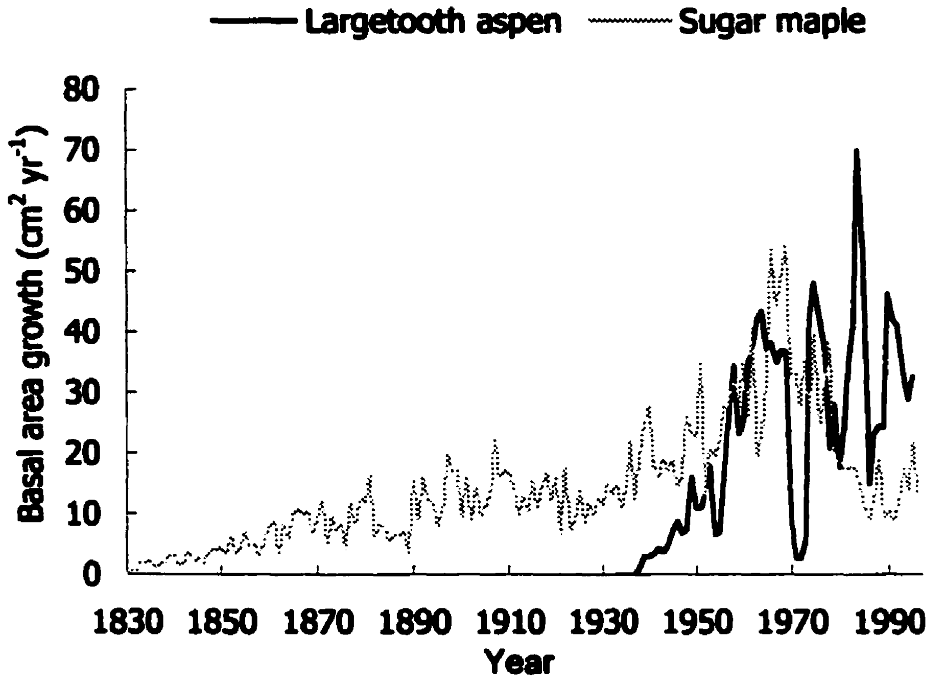

Figure 2.1. Typical growth of a sugar maple and a largetooth aspen at the Hermine watershed.

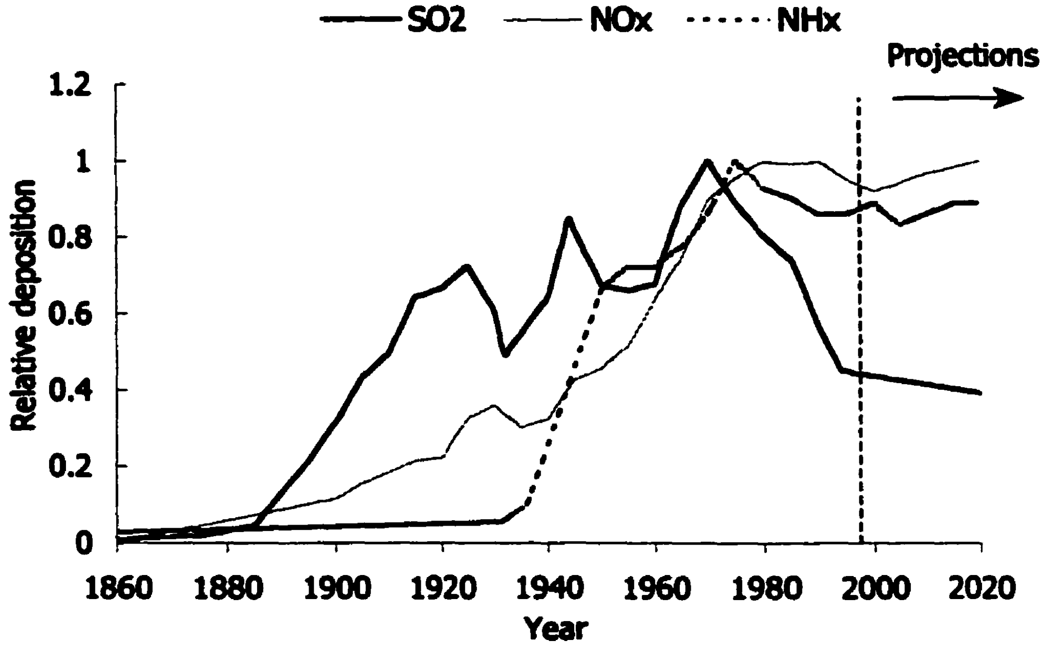

Figure 2.2. Standard curves of emissions for SO_2, NO_x and NH_x in eastern North America.

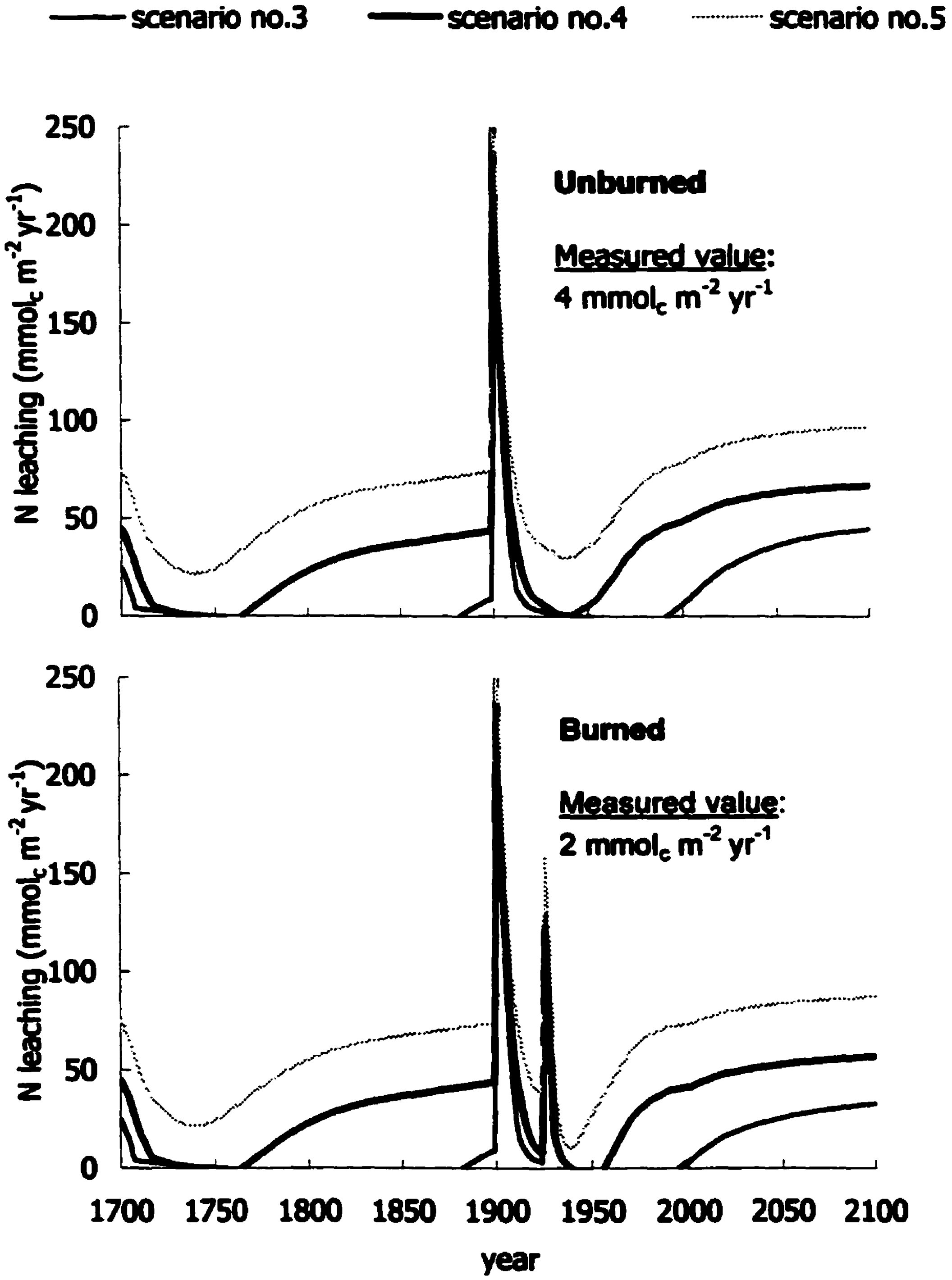

Figure 2.3. Simulated N leaching fluxes below the bottom B horizons in zone 2 (unburned) and zone 3 (burned) at the Hermine watershed.

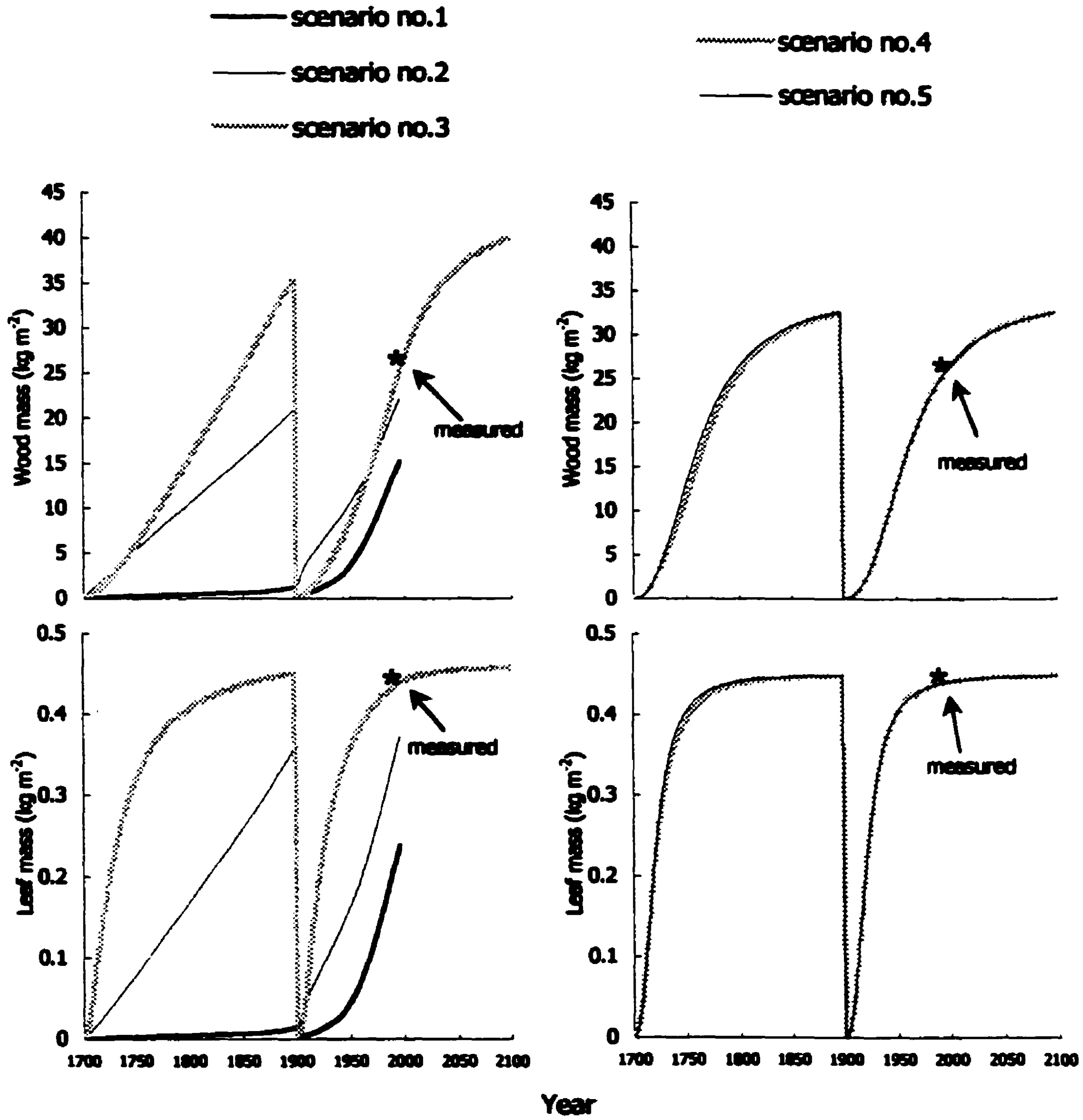

Figure 2.4. Simulated woody components and canopy growth in zone 2 (unburned) at the Hermine watershed.

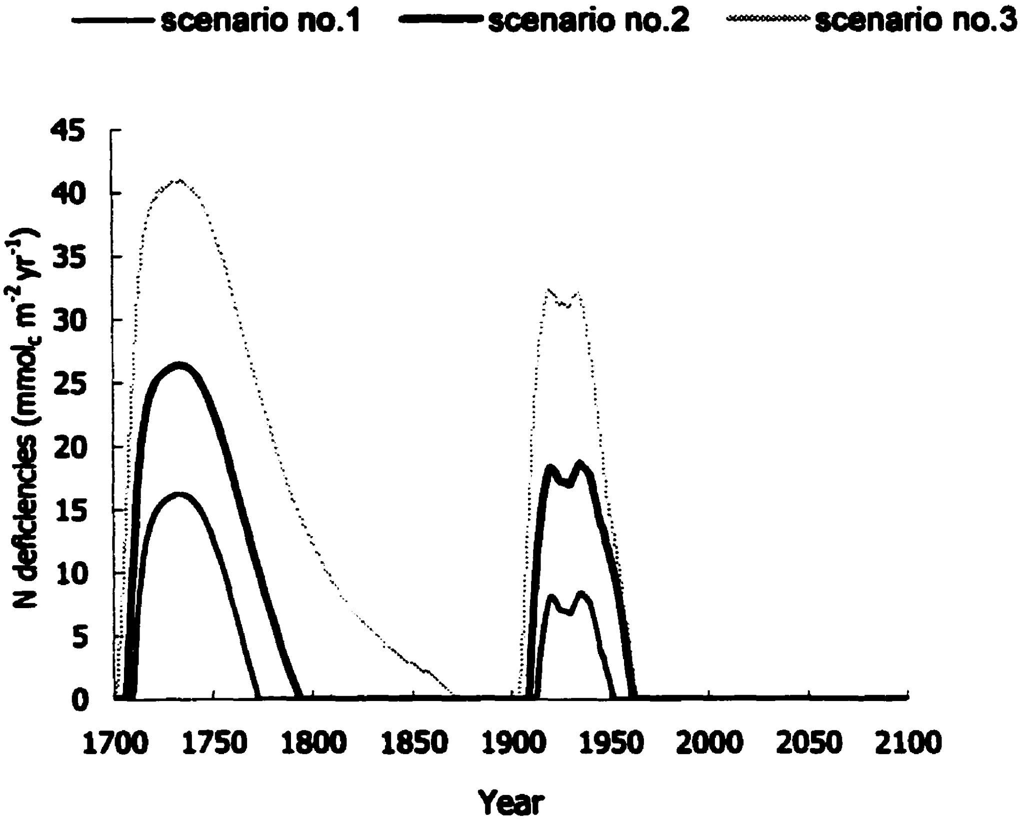

Figure 2.5. Simulated N deficiencies for optimum yearly growth in zone 2 at the Hermine watershed (deficiencies were simulated in scenarios no.1, no.2, and no.3 only).

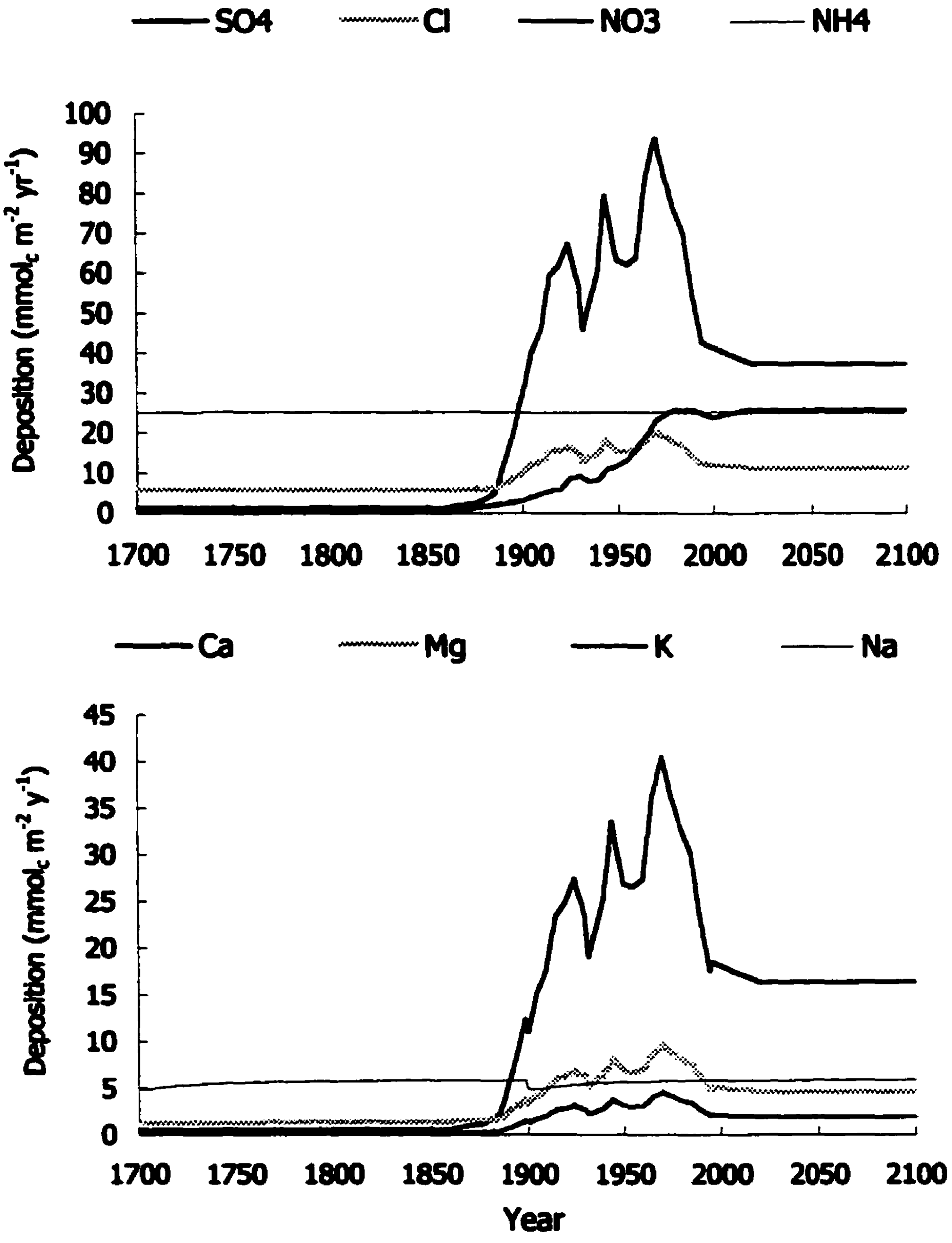

Figure 2.6. Simulated deposition in zone 2 (unburned) at the Hermine watershed with scenario no.3. NH_4 deposition includes a constant 10 mmol$_c$ m^{-2} yr^{-1} added as biological N fixation and dry deposition minus denitrification and the NH_4 standard curve was set to one throughout the reconstruction period to allocate more biological N biological fixation during periods of low N availability, i.e., prior to industrial air pollution.

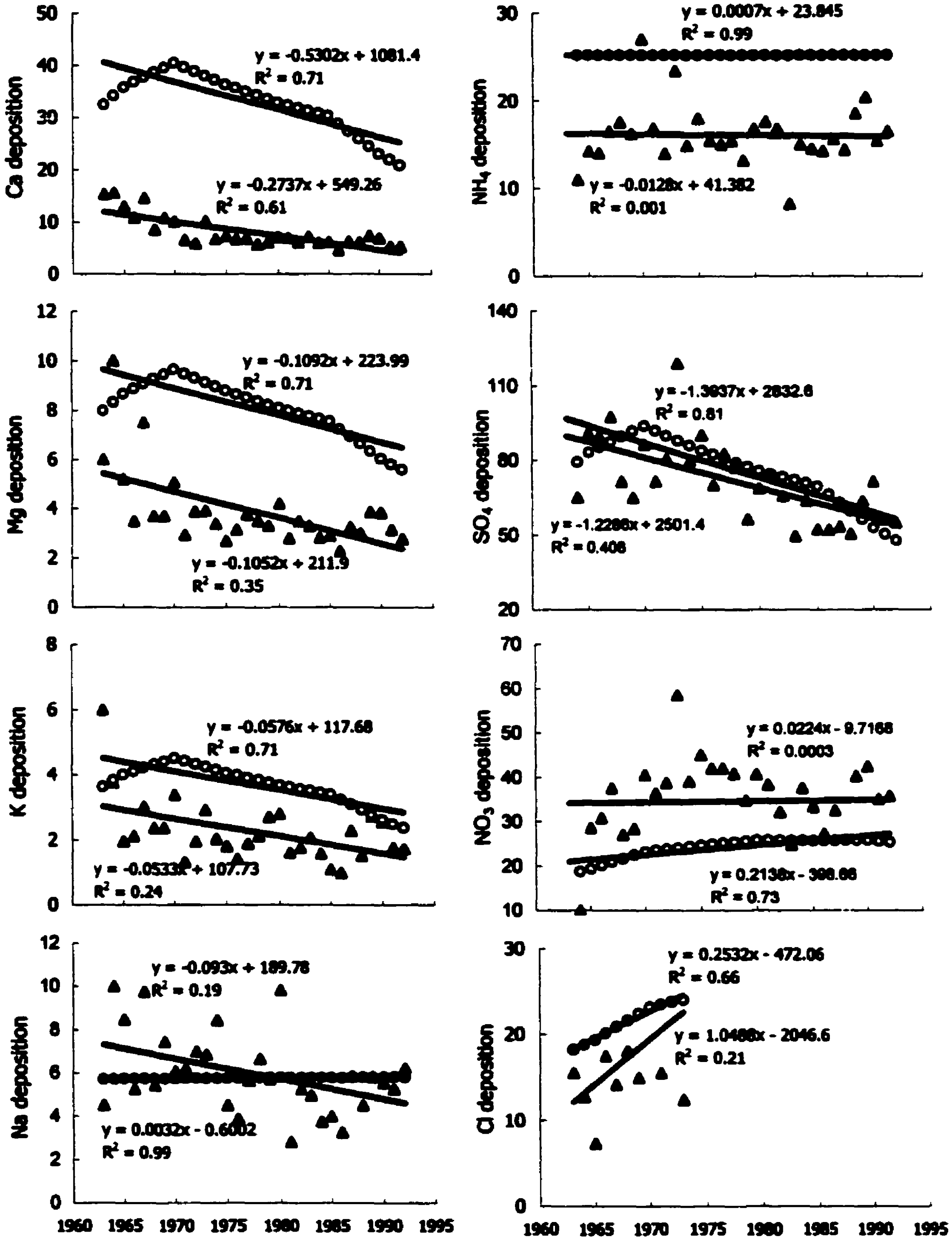

Figure 2.7. Regressions of simulated deposition (mmol$_c$ m^{-2} yr^{-1}) in zone 2 at the Hermine watershed (open circles) with scenario no.3 and that of measured deposition at the Hubbard Brook Experimental Forest (open triangles) between 1963 and 1992. Standard errors of the B coefficients indicate that the slopes of the regressions of measured (HBEF) versus simulated (Hermine watershed) deposition are different only for Ca and Na.

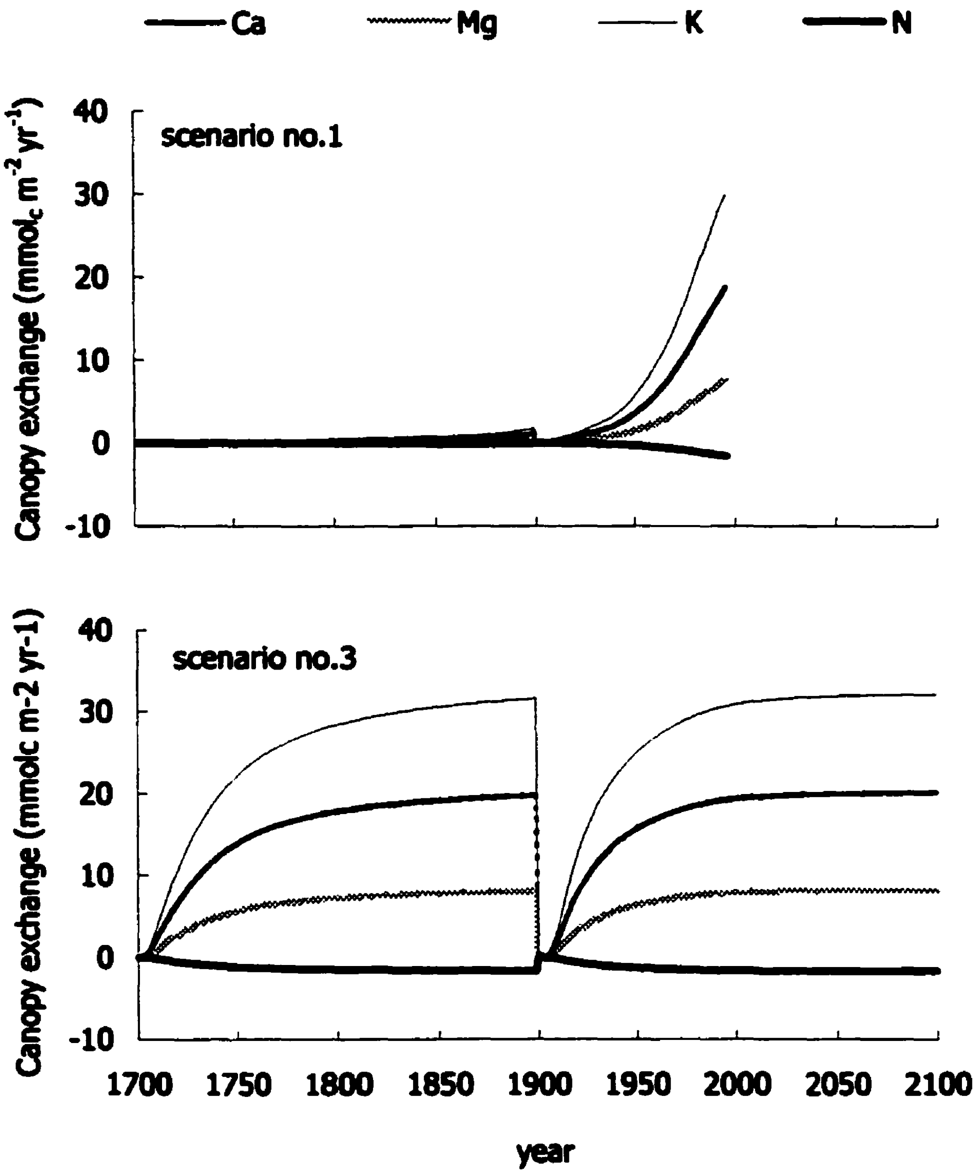

Figure 2.8. Simulated canopy exchange in zone 2 in the Hermine watershed using scenarios no.1 and no.3.

Table 2.1. Mean fluxes of dissolved substances in bulk deposition and throughfall of zone 2 (unburned) and zone 3 (burned) in the Hermine watershed between 1994 and 1997.

	——— ($\mathrm{mmol_c\ m^{-2}\ yr^{-1}}$) ———		
	Bulk deposition	**Throughfall**	
Substance		**Zone 2**	**Zone 3**
NH_4	14.8 ±10.6	15.0 ±13.3	10.7 ±11.5
Ca	15.4 ±7.35	37.6 ±23.7	42.0 ±23.7
Mg	4.25 ±4.71	12.9 ±9.32	15.0 ±10.4
K	1.76 ±4.43	32.9 ±26.7	31.0 ±22.7
Na	4.88 ±5.29	5.81 ±4.72	4.82 ±3.78
SO_4	40.9 ±24.0	42.0 ±20.2	43.0 ±19.2
NO_3	24.3 ±13.8	22.7 ±13.2	22.3 ±12.8
Cl	12.3 ±10.7	12.1 ±10.2	9.47 ±6.60

Values on the right express standard deviations.

Table 2.2. Mean nutrient concentrations measured in foliage between 1994 and 1997 and estimated in other tree components of zone 2 (unburned) and zone 3 (burned) at the Hermine watershed.

	Concentrations (g kg^{-1})			
	Unburned			
Element	**Foliage**	**Stem Wood**	**Stem Bark**	**Branches**
Ca	7.70 ±2.04	2.20 ±0.31	22.6 ±1.48	6.12 ±0.55
Mg	1.43 ±0.61	0.38 ±0.07	0.62 ±0.06	0.43 ±0.05
K	6.26 ±1.24	0.98 ±0.03	3.96 ±0.19	1.82 ±0.20
N	19.6 ±3.39	0.86 ±0.09	3.88 ±0.18	1.93 ±0.13
	Burned			
Element	**Foliage**	**Stem Wood**	**Stem Bark**	**Branches**
Ca	9.21 ±2.44	1.73 ±0.24	15.7 ±1.25	6.13 ±0.67
Mg	1.89 ±0.70	0.33 ±0.06	0.65 ±0.05	0.60 ±0.07
K	8.36 ±1.95	0.97 ±0.11	2.86 ±0.18	1.96 ±0.22
N	20.8 ±3.85	0.81 ±0.06	3.52 ±0.16	2.30 ±0.19

Nutrient concentrations in stem wood, stem bark, and branches are estimates produced from equations for estimating above-ground nutrient contents in sugar maple, red maple, yellow birch, and trembling aspen (Chatarpaul et al., 1985). Values on the right express standard deviations.

Table 2.3 Mean litterfall fluxes measured in zone 2 (unburned) and zone 3 (burned) at the Hermine watershed between 1994 and 1997 and the estimated index of nutrient retranslocation and leaching (%) from leaves.

	Litterfall (mmol$_c$ m^{-2} yr^{-1})	
Element	**Unburned**	**Burned**
Ca	175 (1.04)	168 (1.02)
Mg	38.4 (0.73)	41.6 (0.73)
K	17.6 (0.25)	24.9 (0.32)
N	167 (0.27)	146 (0.31)

Values in parentheses express the index of retranslocation and leaching calculated as the ratio between measured litterfall fluxes and estimated nutrient uptake in foliage.

Table 2.4. Estimates[1] of the component biomass of zone 2 (unburned) and zone 3 (burned) at the Hermine watershed in 1997.

	— Biomass (kg m^{-2}) —	
Tree component	**Unburned**	**Burned**
Roots[2]	3.94	3.28
Stem wood	12.2	10.4
Bark	1.38	1.11
Branches	8.33	6.71
Canopy (leaves & twigs)	0.44	0.36
Total	26.6	22.1

[1] Tree component masses are estimates based on allometric equations for sugar maple, yellow birch, and American beech (Camiré et al., 1999). [2] 18% of the sum of stem wood, bark, and branches (i.e., wood mass) according to biomass data from Whitaker (1974) in a hardwood stand of New Hampshire, USA.

CONNECTING PARAGRAPH

Assessing the sensitivity of the MAKEDEP model to N availability has helped identify the set of time-series input files of nutrient cycling that reflects the most N leaching and tree growth under the burned and unburned conditions at the Hermine watershed. In the next chapter, I use these time-series files to simulate soil chemistry under both conditions and use the differences in site history within the watershed as a tool to validate the mathematical and schematical descriptions of the SAFE model.

CHAPTER 3

Simulation of soil chemistry and nutrient availability in a forested ecosystem of southern Quebec. 2. Application of the SAFE model

3.1 Introduction

Freshwater acidification caused by the deposition of acidic compounds has been observed in eastern North America and northern Europe (Nilsson, 1985; Reuss et al., 1987; Schindler, 1988; Kirchner et al., 1992; Likens et al., 1996). In contrast, the evidence that links acidic deposition with changes in the acid-base status of the soil is not convincing: some believe that forest soils have acidified due to many decades of acid deposition (Reuss and Johnson, 1986; Johnston et al., 1986; Ulrich, 1989; Likens, 1989; Falkengren-Grerup and Eriksson, 1990; Johnson et al., 1991; Shortle and Bondietti, 1992; Johnson et al., 1994), while others suggest that acidic forest soils may have been the product of natural acidification processes, e.g., the uptake of base cations by vegetation, the dissociation of organic acids, and nitrification (Krug and Frink, 1983; Van Miegroet and Cole, 1985; Turner and Lambert, 1988).

Both natural and anthropogenic sources of H^+ to the soil solution acidify the soil as follows. In the forest floor, the H^+ will replace base cations adsorbed on the soil exchange complex. In the mineral soil, a decrease in soil solution pH can mobilize Al^{3+} which can subsequently displace base cations from exchange sites (Reuss and Johnson, 1986; Hendershot et al., 1991; Lotse, 1999). As a result, levels of base cations in the soil solution increase initially with increasing H^+ activity, and are removed from the soil in leachate. If the base cations lost through leaching are not replaced by mineral weathering or atmospheric inputs, the long-term soil response will be a decrease in base cation concentrations in the soil solution, and then a decrease in base saturation and the loss of soil fertility.

In eastern North America and Europe, soil acidification is suspected as one factor contributing to forest decline. First, a decrease in base saturation means that base cations become less available to plants and can lead to nutrient deficiencies in forest stands (Hendershot and Jones, 1989; Ulrich, 1989; Ouimet and Camiré, 1995; de Vries et al., 1995). A second problem originates from inorganic Al phytotoxicity since pH values of below 4.2 may lead to high concentrations of Al ions in the soil solution (Ulrich, 1983). Despite the uncertainty in the available data on inorganic Al toxicity to trees, a (Ca + Mg + K)/Al molar ratio less than 1.0 is usually considered to inhibit plant growth (Sverdrup and Warfvinge, 1993; Cronan and Grigal, 1995).

Although atmospheric S emissions have decreased recently in both North America and Europe and are likely to continue decreasing if goals of international agreements are reached, the latest N emission estimates for the 21st century are much less encouraging. Galloway et al. (1995) showed that N emissions increased in most parts of the world since 1950 and are expected to increase further within the next 50 years, particularly in developing countries such as China (Galloway et al., 1996). An excess of N in forest soils and increased nitrification could mean higher levels of H^+ in the solution and further removal of base cations from the soil environment through leaching losses (Van Migroet et al. 1992). Further, northern Europe has witnessed over the last 30 years substantial increases in plant growth due to increased N availability (Binkley and Högberg, 1997). Although a similar response has yet to be demonstrated throughout eastern North America, growth rates were shown to have increased in some forests of New England (Aber et al., 1998). Uptake of cation nutrients would be expected to increase with increasing growth rates and in turn, depletion of the soil base cation pool would occur. It is therefore increasingly important to assess the effects of acid deposition on soil chemistry in order to set adequate air quality standards that will assure the health and vigour of forest stands.

Identifying the processes governing soil acidity in forest soils is difficult since a forest is a highly complex interactive system in which processes act as combinations on soil chemistry. This has led scientists to develop models that allow the examination of acidification and buffering processes as a whole instead of quantifying each process individually. MAGIC (Cosby et al., 1985), SMART (de Vries et al., 1989) and SAFE (Warfvinge et al., 1993) are examples of such dynamic simulation soil models. These models require historic information of atmospheric deposition and cycling of major elements as input data. The time-series input files were assessed in Chapter 2 for burned and unburned zones at the Hermine watershed.

An approach to validate pre-industrial soil conditions i.e., prior to fire disturbance, subsequent changes in species composition, and atmospheric loading of strong acids, is to calibrate the computer simulation models for sites where factors driving soil formation, e.g., climate, parent material, and topography, are similar but forest disturbance history is different. First, we assume the pre-industrial soil conditions calculated by dynamic models will be similar between the unburned and burned zones since pre-industrial forest history used as input in this application is assumed to be the same. Second, variations in stand dynamics and species composition after fire disturbance (aspen and birch in the burned zone, and maple in the unburned zone) should have an effect on nutrient cycling which would then modify the acid-base status of the soil. We have sufficient information at the Hermine watershed to fulfill model requirements for burned and unburned sections and therefore, the data offers the possibility of validating pre-industrial soil conditions in that fashion. The objectives of this paper are 1) to evaluate the performance of the dynamic biogeochemical model SAFE to reproduce current soil and soil solution chemistry for unburned and burned sections in the Hermine watershed, 2) to test whether SAFE will reproduce similar pre-industrial soil conditions in the burned and unburned zones, 3) identify the major processes responsible for soil acidification, and 4) forecast how soil chemistry could be affected by acidic deposition and timber operations.

3.2 Materials and Methods

3.2.1 Model description

The SAFE model is a dynamic, process-oriented soil model that simulates soil and soil solution chemical composition based on a schematic description of nutrient cycling and site-specific parameters. The schematic description of the SAFE model includes: 1) atmospheric deposition of Ca, Mg, K, Na, NO_3, NH_4, SO_4, and Cl, 2) mineralization of Ca, Mg, K, and N in litter, 3) canopy exchange of Ca, Mg, K, and N, 4) plant uptake of Ca, Mg, K, and N, and 5) net mineralization of Ca, Mg, K, and N (Figure 3.1). All of these processes are specified in the SAFE model as time-series files. SAFE is a model of a forest soil that includes mathematical process-oriented descriptions of cation exchange reactions, chemical weathering of minerals, leaching and accumulation of dissolved chemical components, and solution equilibrium reactions involving CO_2, organic acids and Al-species (Figure 3.2). The soil profile can be divided into a maximum of six layers which correspond to the natural soil horizons. Each horizon is assumed to be chemically and physically homogeneous. The processes included in the SAFE model interact only via the soil solution. A full description of the SAFE model can be found in Warfvinge et al., (1993) but a brief description is given here.

Some chemical reactions were simplified or omitted. For one, cation nutrients (Ca^{2+}, Mg^{2+}, and K^+) are lumped together into one divalent cation component, i.e., BC^{2+}, whereas Na^+ is ignored as an exchangeable species as well as a nutrient since it is a conservative element. At the Hermine watershed, for example, Na occupies less than 1% of the soil's cation exchange capacity (CEC) in both the forest floor and mineral soil (Chapter 1). Second, SO_4^{2-} adsorption, which may affect the CEC of the soil is not modelled. Most young forest soils such as in the Hermine watershed (i.e., glaciated during the Quaternary) have low SO_4^{2-} adsorption capacity so that neglecting this chemical reaction should nevertheless provide acceptable simulated results.

Changes in soil acidity expressed as acid neutralizing capacity (ANC) and cation exchange capacity (CEC) are simulated by calculating the mass balance of the various processes contributing to or consuming acidity. The following differential mass balance equation constitutes the framework of the SAFE model:

$$\frac{d[ANC]}{dt} = \frac{Q}{z\ .\ \theta}([ANC])_{in} - [ANC]) + R_W - R_X - R_{BC} + R_N \quad \text{(Eq. 3.1)}$$

where no subscript refers to conditions in the soil layer as well as in the leachate of that soil layer, subscript "in" denotes concentrations in the inflow to the compartment, z is the physical height of the soil layer (m), θ is the volumetric water content ($m^3\ m^{-3}$), Q is the flow intensity through the layer ($m^3\ m^{-2}\ yr^{-1}$), R_W is silicate weathering, R_X is cation exchange, R_{BC} is base cation uptake, and R_N is nitrogen uptake (all R expressed by the rate at which they supply or withdraw ANC in $mmol_c\ m^{-3}\ yr^{-1}$). If there is variation in the hydrological conditions from year to year, changes in soil solution concentrations will occur due to dilution or concentration. Mass balances are also used to determine BC^{2+}, NO_3^- and NH_4^+ in the soil solution.

The buffering of the liquid phase is controlled by the carbonate equilibrium reactions, the dissolution-precipitation reactions of a solid gibbsite phase, producing various charged Al-OH complexes, and the acid-base reactions of a monovalent organic acid (RH):

$$[ANC] = [OH^-] + [R^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] - 3[Al^{3+}] - 2[Al(OH)^{2+}] - [Al(OH)_2^+] \quad \text{(Eq. 3.2)}$$

where NH_4^+, SO_4^{2-}, and BC^{2+} are neglected as they are not believed to be involved in the acid-base reactions in the liquid phase. In equilibrium, species from the right hand side of the equation can be estimated based on the solution H^+ concentration. In that respect, soil solution ANC is a function of pH, and vice-versa. Species of the CO_2 system are calculated with the equilibrium equations given by Henry's law for H_2CO_3 using soil P_{CO2} as input. The dissociation of RH is not modelled by the rate of mineralization of organic matter but rather specified as input data using concentrations of dissolved organic carbon (DOC) in the soil solutions. It should be noted that the complexation of Al by organic ligands is not included in the SAFE model as gibbsite ($Al(OH)_3$) is used to produce inorganic species only. The gibbsite solubility constant relates the concentration of free Al^{3+} to pH using the relationship $[Al^{3+}] = K_g [H^+]^3$.

Instead of being an input to the model, weathering rates are calculated from soil properties. The surface reactions of minerals follow kinetic rate laws. The total weathering rate (R_w) equals the sum of all dissolution rates of fourteen minerals. The dissolution of minerals can be increased by augmenting H^+ activity, organic acids concentrations, and elevated CO_2 partial pressure, but any increase in Al_t and base cations concentrations in the soil solution will decrease the rates of mineral weathering. The soil moisture content determines the exposed mineral surface in contact with water. Weathering rates are also affected by the soil temperature which is modelled using an Arrhenius equation.

The exchange reactions between H^+ and BC^{2+} are modelled as reversible chemical reactions. Cation exchange is proportional to the difference in BC^{2+} concentration between the exchange complex and the soil solution (i.e., soil solution pH does not affect mass transfer). Further, SAFE relies on input data to specify the magnitude of BC^{2+} and N uptake by vegetation in the various soil horizons. All N is assumed to be deposited as HNO_3, which means that the addition of NH_4^+ in atmospheric deposition contributes acidity through oxidation. In SAFE, uptake of BC^{2+} by plants produces acidity as plant roots release H^+ in the soil solution in exchange for base cations, whereas NO_3^- uptake contributes alkalinity from the release of OH^-.

To assure that the simulation reflects changes caused by variations in external and internal loads, the SAFE model must be started prior to industrialization so that the soil is under a steady-state, i.e., all sources of acidity and alkalinity are balanced. These steady-state conditions are calculated with the PROFILE model which includes the same chemistry as SAFE but solves the algebraic equations that result from setting all differentials to 0.

Uncertainties in the SAFE model output associated with the imprecision of the input data was assessed on most soil properties (Warfvinge and Sandén, 1992). Soil bulk density and specific surface area were found to be the most sensitive parameters on simulated ANC, followed by soil moisture content and temperature, and then by CO_2 partial pressure and CEC. As a rule of thumb, increasing mineral surface area and CEC by 25% increased soil solution acid neutralizing capacity by about 50% and 2%, respectively

3.2.2 Study Site

The study site is located in the Hermine watershed at the *Station de Biologie des Laurentides de l'Université de Montréal* near Saint-Hippolyte, Quebec, in the Lower Laurentians. See Chapter 1 for a full description.

3.2.3 Field Study and Laboratory Analysis

Sampling and analysis of soils and soil solutions were performed as described in Chapter 1. When soil profiles were dug to install the lysimeters in the plots (3 plots per zone for a total of 9 profiles), the FH-Ah horizons and the diagnostic B horizons (3 samples of B in each profile) were sampled and analysed for two physical properties: 1) particle size distribution was determined using the hydrometer method with samples treated with NaOCl and DCB (Day, 1965), and 2) bulk density was estimated using the unconfined compression method on material of 2 mm or finer (Culley, 1993). Clay mineralogical analysis of B horizons within the watershed were performed on Mg-, K- and HCl-treated clay fractions by X-ray diffraction (XRD) and contributions of each minerals found with XRD to the total soil matrix were estimated after running a total chemical analysis on these samples (McCourt, 1993). Mineralogical composition of NaOCl and DCB-treated material finer than 2 µm collected from the 9 soil profiles was also determined in this study on non-oriented slides using XRD. Soil moisture and temperature were measured periodically from 1994 to 1997 within each plot at a depth of 50 cm using time-domain reflectometry and a standard alcohol thermometer, respectively. Soil moisture was also assessed in the FH horizons using the ThetaProbe technology in zone 1 in 1996.

3.3 Model Parameterization

3.3.1 Soil properties

Means and standard deviations of soil density and texture measured in the three zones at the Hermine watershed are presented in Table 3.1. The differences suggest that the parent material in zone 2 and zone 3 is similar, whereas the material in zone 1 is different from the two other zones. Further, drainage and topographic similarities between zone 2 and zone 3 (well-drained soils in the uppermost sections of the watershed in contrast to hydromorphic conditions in zone 1 near the stream) suggest that the most suitable series of simulations between unburned and burned sections in the Hermine watershed is between zone 2 (unburned) and zone 3 (burned). Despite the fact that the XRD method only allows a semi-quantitative assessment of the proportion of each mineral to the total soil matrix, our results also support the above statement about the composition of the parent material.

The soil chemical, physical, and hydrological properties used to run the SAFE model are presented in Table 3.2. The soil profiles were divided into two layers, i.e., FH (10-0 cm) and Bhf-Bf (0-60 cm), to fit with the soil and soil solution chemistry data (1993 to 1997) we posses for the forest floor (0 cm) and the mineral soil (50 cm) in these zones (Chapter 1). These data provide base saturation, cation exchange capacity (CEC), and dissolved organic carbon (DOC) for the model.

Since each of the diagnostic B horizons had approximately the same proportion in thickness relative to the total thickness of the 3 diagnostic B horizons, the average of the 3 soil horizons for soil bulk density and specific surface area was used (Table 3.2). Specific surface area was calculated from the measured particle size distribution and soil bulk density with a simple algorithm as described by Jönsson et al. (1995):

$$A_w = (0.3\ .x\%\ \text{sand} + 2.2\ .x\%\ \text{silt} + 8.0\ .x\%\ \text{clay})\ .\ (\rho_{bulk}/1000)\ .\ x\%\ \text{of CF}$$

where A_w is the exposed mineral surface area, ρ_{bulk} is soil bulk density, CF represents coarse fragments, and the sum of clay, silt, sand, and coarse fragments equals 1 (Table 3.2). Coarse fragments were assessed in the field on all the soil profiles using the Munsell chart diagram for determining coarse fragments. Mineralogy in the mineral soil of zones 2 and 3 was assumed to be homogeneous, whereas no minerals are assumed to be present in the forest floor (Table 3.3). Mean soil moisture content measured from 1994 to 1997 at 50 cm depth and in 1996 in the FH floor were used directly as input for the B layer and the forest floor, respectively (Table 3.2). Since specific surface area and soil bulk density are inputs to calculate mineral weathering and that minerals mixed with the organic matter in the forest floor is mostly silica from the highly weathered Ae horizon. Specific surface area and soil bulk density in the forest floor were therefore set to zero (Table 3.2). Mean soil temperature measured in the mineral soil from 1994 to 1997 was 6.5° Celsius.

Soil CO_2 partial pressure calculated by Castelle and Galloway (1990) in acidic forest soils in Shenandoah National Park, Virginia, were used for the SAFE application at the Hermine watershed (Table 3.2). In SAFE, CO_2 is involved in weathering reactions and is a component of the buffering system of the soil solution. The influence of CO_2 partial pressure on simulated ANC was however small when at soil pH below 5.0 as carbonic acid fails to dissociate and Al buffering dominates (Warfvinge and Sandén, 1992). Values of pH found in the first meter of the soil profiles in the Hermine watershed are therefore too acidic for carbonic acid to dissociate and contribute significantly to mineral weathering and buffering the solution.

Bloom (1983) doubts gibbsite controls Al concentrations in the soil solution since it has very slow kinetics. Also, the wide range of gibbsite equilibrium constant found in field measurements (see review by Alveteg et al., 1995) casts doubt on the possibility of using gibbsite to predict Al^{3+} activity in the soil solution. Gibbsite has not been found in the Hermine watershed or to our knowledge elsewhere in southern Quebec. Data near the study site indicate however the presence of hydroxy-interlayered vermiculite which may control Al solubility at values close to those of $Al(OH)_3$ (Courchesne and Hendershot, 1989; Hendershot and Courchesne, 1991). Therefore, the median value of the apparent solubility constant measured in the forest floor and the B horizons just outside of the Hermine watershed (Hendershot and Courchesne, 1991) were used for the SAFE application in the Hermine watershed (Table 3.2).

On the one hand, Lajeunesse (1990) observed that about 70% of fine root mass in the Hermine watershed is located in the first 25 cm of the soil (forest floor and top of mineral soil). Au (1999) measured N induced respiration (NIR) rates in the forest floor at the Hermine watershed to be about 40 times greater than NIR rates measured in the mineral soil. Using an average depth and density for each soil compartments, we determined from Au's data that 62.5% of the total N mineralized in the soil profile occurs in the forest floor, whereas 37.5% occurs in the first 25 cm of the mineral soil. Considering the relatively tight N cycle, 60% of its total uptake was allocated in the forest floor (10 cm thick), whereas 40% of total N uptake was allocated in the mineral soil (60 cm thick) (Table 3.2). Conversely, sources of base cations are not restricted to the forest floor and can be supplied through mineral weathering along the soil profile. Therefore, cation nutrients uptake (lumped into a single divalent cation – BC^{2+}) was allocated evenly throughout the soil profile as a function of root mass and layer depth, i.e., 30% of uptake in the forest floor and 70% in the mineral soil (Table 3.2).

We possess very little data regarding the flow of water within each zone so that a simple hydrological model was used. Water fluxes within the soil profiles were assessed based on the relative capacity of the soil layers to hold water, i.e., according to its depth and rooting distribution. Biron et al. (1999) determined that about 45% of the water which entered the Hermine watershed as precipitation (1994 to 1997) exited in stream runoff. Twenty percent of the water was therefore assumed to be removed from the forest floor, whereas another 30% was assumed to be removed from the first 60 cm of mineral soil (Table 3.2). In this case, 40% of the total amount of water to be absorbed is withdrawn from the forest floor compared to 30% of the total amount of base cations to be withdrawn by vegetation is taken up in the forest floor.

3.3.2 Past deposition and nutrient cycling

Alveteg et al. (1998) developed the MAKEDEP model to estimate past, current, and future nutrient cycling for sites in Europe where only limited information is available. These authors proposed this method (as a common set of assumptions) so that it becomes easier to detect invalid assumptions in model formulation as well as in the reconstruction scheme. In that respect, the MAKEDEP model was preferred for the reconstruction step. A full description of the procedure can be found in Chapter 2.

The objective in Chapter 2 was to find the N availability scenario that would agree the most accurately with current forest biomass and N leaching in the unburned and burned zones. The simulations presented here for both zones use the estimates of nutrient cycling reproduced with the 10 $mmol_c$ N m^{-2} yr^{-1} availability scenario. Reconstructed nutrient cycling was done assuming a cleared condition back in 1700, harvest in 1900, and fire disturbance in zone 3 in 1925. Detailed information on the time-series files of input created for the unburned and burned zones in the Hermine watershed are found in Chapter 2. Base cations, SO_4, and Cl deposition was increased by 50% based on dry deposition estimates given by both Parker (1983) and Johnson et al., (1996). This was to take into consideration the underestimation of dry deposition of these elements associated with the method in MAKEDEP. The increase in deposition was done as a function of foliage growth to include the filtering effect of the canopy. All simulations presented here are initiated in 1700 to obtain stable pre-industrial conditions. Simulated results are however presented starting in 1800 when calculated soil chemistry was at a pre-industrial steady-state.

3.2.3 Precipitation

Precipitation data for St-Hippolyte is available from 1964. A linear regression was performed between Montreal and the St-Hippolyte station to produce data prior to 1964. The McGill University station was chosen for the Montreal station since it was one of the few in existence by the turn of the 20th century. Precipitation records of the McGill University station were therefore taken for the period 1900-1964 as the correlation between the St-Hippolyte and McGill University data was marginally significant at $p<0.12$ with an R^2 of 0.30. Those of St-Hippolyte were taken thereafter until present day. The precipitation data from St-Hippolyte (years 1964-1997) was used to provide the input prior to 1900 and after 1997.

Summary equations of Helvey (1971) for computing throughfall and stemflow with rainfall measurements in St-Hippolyte were used:

$$I = S[R - (0.91R - 0.015) - (0.062R - 0.005)]$$

where I is interception (mm yr^{-1}), R is rainfall (mm yr^{-1}), $0.91R - 0.015$ is throughfall, $0.062R - 0.005$ is stemflow, and S is the correction factor for snow interception as it is often greater than interception of rain by about 20% (Miller, 1967). Since the watershed receives 30% of precipitation as snow, S was set at 1.06.

3.4 Results

3.4.1 *Simulated vs Measured Soil and Soil Solution Chemistry*

Simulated mean base cation, N ions species and SO_4 concentrations in the forest floor and the mineral soil between 1994 and 1997 are all within ±15% of measured soil solution ion concentrations for that same period, except for N ion species in the forest floor of the burned zone where simulated concentrations exceed by 85% the measured concentrations (Table 3.4). The log transformation of pH values show that simulated mean H^+ concentrations between 1994 and 1997 are within ±30% of measured mean concentrations, except for simulated H^+ in the mineral soil of the burned zone where it exceeds measured mean concentrations by 50% (Table 3.4). The SAFE model is calibrated on base saturation so that the agreement between the simulated and measured mean values for the forest floor and mineral soil in both zones was expected (Table 3.4).

3.4.2 *Changes in Ion Concentrations in Soil Solution Through Time*

Concentrations of base cations in the forest floor are relatively high and stable between 1800 to 1900, decline after the harvest in 1900 in both zones, increase thereafter to reach maximum concentrations around 1970, and then decline until present day to about 80% of maximum concentrations (Figure 3.3). Patterns of base cations in the solutions of the mineral soil in both the unburned and burned zones are similar, i.e., simulated concentrations are low but stable from 1800 to 1900, increase sharply in 1900 after the harvest, fluctuate between 200 and 300 $\mu mol_c L^{-1}$ until 1970, and decrease to 80% of maximum concentrations until present day (Figure 3.4). A sharp increase in base cation concentrations in the solution of the forest floor and mineral soil is simulated after the 1925 fire in zone 3.

Simulated N concentrations in the soil solution of the forest floor is fairly stable during most of the simulation period, except that sharp increases occur for about 10 years after the harvest and 5 years after fire disturbance in zone 3 (Figure 3.3). In the mineral soil, leaching of N only occurs in the late stages of development of the first stand (starting around 1890), after the harvest (1900), in the early stages of stand development of the second stand (until about 1920), after fire disturbance in the burned zone (1925), and at present time (Figure 3.4).

Patterns are similar in both zones and at both depths, i.e., concentrations increase at the same rate as SO_4 deposition does until 1970 (see Chapter 2 for reconstructed history of SO_4 wet and dry deposition) and decrease thereafter (Figures 3.3 and 3.4). A temporary decrease in SO_4 concentrations in both the solutions of the forest floor and mineral soil occurs in the burned zone after fire disturbance.

3.4.3 Pre-industrial soil pH, Base Saturation, and Soil Solution Acid Neutralizing Capacity (ANC) and Changes Through Time

The simulated forest floor pre-industrial (at the year 1800) pH in the unburned zone is 5.21, whereas simulated forest floor pre-industrial pH in the burned zone is 4.70 (Figure 3.5). Simulated pre-industrial pH of the mineral soil is 5.92 in the unburned zone and 5.63 in the burned zone. Forest floor pH in both zones is stable from 1800 to 1900, but decreases drastically within 2 to 3 years after the harvest in 1900 (Figure 3.5). Until present day, a net increase in forest floor pH in both zones is simulated since harvest and a sharp increase for about five years occurs after fire disturbance in 1925 in zone 3. Simulated mineral soil pH is not stable throughout the simulation period in either zones: a gradual decrease of about 1.0 unit of pH occurs from 1800 to present (Figure 3.6). The simulated harvest contributes to a decreased mineral soil pH for about 10 years, whereas fire has no effect on pH.

Simulated base saturation in the forest floor is stable until 1900 in both zones, but decreases by more than 0.40 after the harvest (Figure 3.5). Simulated base saturation in the forest floor increases gradually until present day to reach 0.76 in the unburned zone and 0.80 in the burned zone. A temporary increase in base saturation in the forest floor occurs in the burned zone after fire disturbance. In contrast, simulated base saturation in the mineral soil decreases from 1800 to present day by 0.40 in the unburned zone and 0.37 in the burned zone (Figure 3.6). Small increases in simulated base saturation occur after harvest in both zones, but the most noticeable effect of simulated forest disturbance on base saturation is the increase after fire in zone 3.

Simulated pre-industrial soil solution ANC in the forest floor is 149 $\mu mol_c\ L^{-1}$ in both zones, whereas pre-industrial soil solution ANC in the mineral soil is 147 $\mu mol_c\ L^{-1}$ in the unburned zone and 43 $\mu mol_c\ L^{-1}$ in the burned zone (Figure 3.5). Declines in soil solution ANC is simulated in both zones and depths after the harvest, although the decline in soil solution ANC in the mineral soil is much lower than in the forest floor (Figures 3.5 and 3.6). A net increase in simulated soil solution ANC occurs until present day in the forest floor, whereas a net decrease in ANC is simulated in the mineral soil. A sharp increase in soil solution ANC in the forest floor can be observed in zone 3 after fire disturbance.

3.5 Discussion

3.5.1 Harvest and Fire Simulation

The forest fire in zone 3 was simulated as if it released base cations to the soil solutions as ash deposited on the soil is solubilized during rain events (Grier, 1975; Kutiel and Shaviv, 1992), whereas 30% of N in tree components was assumed to be lost through volatilization (as estimated by Knight, 1966). Simulated increases in base cation concentrations after fire disturbance created a new equilibrium between the solution and the liquid phase where more acidity was displaced from the soil complex in exchange with base cations (Hendershot et al., 1991). As a result, simulated soil solution ANC, pH, and base saturation increased in the forest floor. The net positive effect of fire on simulated soil fertility in the mineral horizons was not as large as observed in the forest floor. The simulated harvest in 1900, however, acidified the soils of both zones due to the more intense release of NO_3^- in the soil system relative to base cations. A similar effect has been observed after whole-tree clear-cutting in New Hampshire and in the boreal forest after fire (Dalhgren and Driscoll, 1994; Bailey et al., 1992). Most of the simulated acidification occurred in the forest floor rather than the mineral soil as mineral weathering provided a strong buffer against the input of acidity brought about by nitrification after the harvest. This would explain the large decrease in simulated soil solution ANC in the forest floor but not in the mineral soil. Part of the decrease in soil solution ANC after harvest can also be attributed to the decreased input of base cations from canopy exchange and dry deposition because of the lack of a canopy to filter dry particulates from the air (Lovett et al., 1996).

3.5.2 Forest Regrowth

Simulated post-fire soil pH, base saturation, and soil solution ANC in the forest floor suggest that faster growing trees in the burned zone (aspen and birch) do not acidify the soil at a greater rate than maple trees in the unburned zone. Greater uptake of base cations in the forest floor of the burned zone may have been overshadowed by a higher base cation flux (e.g., higher quality litterfall). On the other hand, post-fire simulated soil pH, base saturation, and soil solution ANC in the mineral soil are lower in the burned zone than to the unburned zone throughout the simulation period, but rates of decrease of these soil parameters through time are similar. Similarly, the model output for the mineral soil suggests that forest regrowth in the burned zone has not contributed to faster acidification through greater base cation sequestration in the tree components in exchange for H^+ (as proposed by Binkley and Richter (1987), Federer et al. (1989), and Knoepp and Swank (1994)). First, lower simulated rates of mineral weathering in the burned zone (Figure 3.7) due to lower bulk density, mineral surface area, and soil moisture content specified in SAFE is likely to explain the differences in soil solution ANC and pH between the zones in the mineral soil throughout the simulation period. It is therefore expected that the SAFE model calculates lower initial pH in the mineral soil of the burned zone as compared to the unburned zone under steady-state.

As a comparison, simulated release of base cations from weathering in the unburned zone is about 9% more than what was estimated by Courchesne (unpublished) using the mass balance approach. Estimated release of base cations by weathering using the same approach at the Hubbard Brook Experimental Forest (HBEF) (Likens and Bormann, 1995) is about 3-5% more than the simulated release of base cations using SAFE. The comparison of weathering rates between HBEF and the

Hermine watershed is appropriate because of the similarities in climate, species composition, and parent material.

3.5.3 *Pre-industrial Soil Conditions*

Pre-industrial simulated base saturation in the forest floor is higher in the unburned zone relative to the burned zone, despite the fact that simulated current base saturation in the burned zone is higher than that in the unburned zone. Also, simulated pre-industrial pH in the forest floor of the burned zone is lower than that in the unburned zone. But because pre-industrial simulated soil solution ANC in the forest is identical in the two zones until fire disturbance, we believe that the discrepancy in pre-industrial simulated base saturation as well as pH can be explained in two ways.

A first possible explanation for the discrepancy in calculated pre-indutrial steady-state conditions between the zone is the poorly simulated N concentrations in the forest floor of the burned zone. Nitrification produces two moles of H^+ for one mole of NH_4^+ nitrified. For every mole of NO_3^- and NH_4^+ absorbed by vegetation, one mole of OH^- and H^+ is released by roots into the soil solution. In that respect, assuming total nitrification in the soil would not produce more acidity if all NO_3^- was absorbed by vegetation in the forest floor. This is obviously not the case in the Hermine watershed where NH_4^+ concentrations are as high as NO_3^- concentrations in the soil solutions. As pointed out by Warfvinge et al., (1998), the significant overestimation of nitrification and NO_3^- concentrations in the forest floor of a spruce stand of southern Bavaria, Germany, creates lower soil solution ANC and pH. This also seems to be true in the forest floor in the Hermine watershed.

The cause of measured lower N concentrations in the soil solutions of the burned zone has yet to be clarified but one hypothesis was brought forward in Chapter 1. Tietema (1998) demonstrated that under N-limiting conditions, fungal biomass constitutes the largest fraction of the total microbial community, whereas at N saturation, the microbial biomass is dominated by bacteria. Furthermore, Aber et al. (1998) hypothesized that in conditions of N limitation, mycorrhizae can immobilize large amounts of mineral N that lead to inhibition of soil nitrification. In contrast, temperate forest soils that have not been disturbed by fire within the past century and have accumulated N from atmospheric pollution would show more intense nitrification and NO_3^- leaching because of a greater bacterial activity. In Chapter 1, we proposed that the relative abundance of mycorrhizae in the burned stand could have been favoured by the phase-out of the bacterial community following a significant extraction of N from the soil system either by volatilization or leaching during or after disturbance. Based on the results, it was hypothesized that mycorrhizae played an important role in the immobilization of N in the soils of the burned stand. If fungal biomass constitutes a larger fraction of the total microbial community in the burned stand, then it is possible that the activity of these microorganisms results in a efficient N immobilization and in turn, in lower N concentrations in the solutions of the forest floor (Chapter 1).

We thought that perhaps the beneficial effects of mycorrhizae on plant nutrient uptake (Rygiewicz et al., 1984) could explain the greater uptake of N in the forest floor and in turn, soil solution NO_3^- concentrations and pH in the forest floor in the burned zone. In order to calibrate soil solution N concentrations in the forest floor of the burned zone more accurately, it would have been necessary to allocate more N uptake in the forest floor: 95% of N uptake in the forest floor and 5% in the mineral soil creates about 18 μmol_c N L^{-1} in the forest floor, whereas N concentrations in the mineral soil remain the same. Simulated pH in the forest floor becomes too high (i.e., 4.50) and pH in the mineral soil remains unchanged. In the light of these results, the net immobilization/exudation of mineral N by mycorrhizae can not be successfully reproduced with a simple NO_3^- uptake - OH^- release model. Also, allocating more N uptake in the forest floor of the burned zone does not allow the comparison between simulated initial soil conditions in the two zones as a step towards model validation. In that respect, we believe there is a need for the distribution of nutrient uptake to be specified in the SAFE model as a time-series input parameter. It should also be noted that lower soil solution ANC and pH in the mineral soil of the burned zone throughout the simulation is not caused by the acidic inflow from the forest floor but rather lower mineral weathering as suggested above because no change in pH was observed after allocating 95% of N uptake in the forest floor and 5% in the mineral soil.

A second explanation for the discrepancy in pre-industrial simulated base saturation and pH may be site history. It must be understood that SAFE is calibrated on base saturation alone, and if it cannot obtain a good fit with current (measured) base saturation using the specified input, it modifies pre-industrial steady-state base saturation rather than modify the rates of change in base saturation (Walse et al., 1998). This perhaps indicates that our assumption that factors driving soil formation between the zones were similar prior to industrialization is incorrect. Past stands in the Hermine watershed may not always have been dominated by maple trees. Indeed, current aspen and birch stands (burned) were once maple-dominated stands, and in turn, current maple stands (unburned) may have been dominated in the past by aspen and birch also. If this regeneration pattern was shown to be correct at the Hermine watershed, then our approach to validate the SAFE model with pre-industrial conditions under various site history would be unacceptable.

3.5.4 Causes of Soil Acidification

The SAFE model has reproduced accurately soil solution SO_4^{2-} concentrations in both the forest floor and mineral soil of the two zones. In that respect, the assumption that SO_4^{2-} is a non-reactive element is a good and simple model to use in the Hermine watershed, despite the fact that the turnover of S compounds were observed to play a significant role in the H^+ budget in other forest ecosystems (van Breemen et al., 1983). Because of the imprecision in simulated pH and NO_3^- concentrations in the soil solution of the forest floor in the burned zone, however, only patterns of acidification in the unburned zone were used to identify the important sources of acidity in the Hermine watershed. Acidification in the mineral soil began in 1900 and accelerated during the peak of industrialization in the 1930s. Evidence from tree ring chemistry supports the hypothesis that base cation depletion and acidification in the forest soils of eastern North America occurred during approximately the same time period (Bondietti et al., 1990; Momomisha and Bondietti, 1990). External inputs of strong acids from atmospheric deposition simulated an increased in H^+ and Al^{3+} activity in the mineral soil which in turn, increased cation exchange reactions and base cation concentrations in the soil solutions.

Shortle and Bondietti (1992) found from historical base saturation data of mor layers in various eastern North American forests that acidification occurred mainly between 1940 and 1970. Further, Johnson et al. (1994) observed significant acidification and Ca^{2+} losses in organic horizons of 48 mixed spruce-hardwood sites in the Adirondack region of New York during the time period 1930-1984. This period of significant soil acidification corresponds exactly to the time period when polluted atmospheric deposition contributed the most acidity to the forest ecosystem which is reflected in the SAFE model by the standard curves developed in Chapter 2: SO_x emissions increased by about 3-fold between 1930 and 1980, whereas NO_x and NH_x more than doubled. Simulated forest floor acidity using SAFE did not exhibit a large decrease in pH as seen in the mineral soil. This suggest that the acidity and exchange complex of the forest floor is mainly determined by organic acids which create a naturally low pH, as well as the large flux of base cations in the soil through cycling processes such as dry deposition, throughfall, and litterfall (Warfvinge et al., 1998)

Despite the fact that S loading from the atmosphere has decreased since the 1980's, the mineral soil did not show any obvious sign of recovery: simulated soil solution ANC and pH in the mineral soil have stabilized in the recent years but base saturation continued to decline. In fact, the rates at which the base saturation decreased in the mineral soil in both zones did not show any significant changes as a result of SO_4^{2-} reductions over the last two decades in eastern North America. Similarly, Driscoll et al. (1989) have not observed any significant increase in streamwater pH since the decrease in S deposition. A decrease in base cation deposition over the last two decades was observed by Hedin et al. (1994) in eastern North America, suggesting that the decrease in deposition ANC was not as large as hoped since the reduction in S emissions. Moreover, it seems that simulated weathering of soil minerals in this carbonate-free siliceous bedrock in both zones was not large enough to replenish the base cations removed from the soil by leaching and sequestration in the tree components.

3.5.5 Future Nutrient Availability

Lawrence et al. (1995) and Miller et al. (1993) anticipate a decrease in base saturation and soil solution pH into the 21st century as base cation inputs from the atmosphere (because of more efficient industrial dust collectors) will decrease even more, while acidifying compounds (i.e., N species) will continue to increase. Our concern is that acidification may already have brought the cation exchange pool in the mineral soil to a low point so that it may take centuries for the system to recover. In that sense, Sverdrup et al. (1995) suggest that some of the damage already caused by acid deposition is irreversible, while Likens et al. (1996) ask that reduction plans be implemented before damage is even greater, otherwise they will fail.

Assuming no forest disturbance beyond the year 2100, projected soil chemistry in the mineral soil suggests that the balance between acidity and alkalinity in the new century is leading towards a new steady-state as no major change is simulated (Figure 3.8). In Figure 3.8, two other simulations/projections are shown assuming a stem-wood harvest in 2020 and uneven aged management where one third of the forest biomass is exported every 30 years starting in 2020 as well and regenerated naturally as sugar maple. These projections suggest that further soil acidification is to be expected if the Hermine watershed forest is harvested in the 21st century. Acidification is particularly obvious based on declines in base saturation for both harvest scenarios, but are most significant for the stem-wood harvest scenario (Figure 3.8). The projections for disturbed conditions in the 21st century suggest that the anticipated equilibrium depends largely on the assumption of steady-state cycling of nutrients with a low uptake of nutrients by trees as the stand matures. Indeed, even low-intensity harvest practices such as uneven aged management is jeopardizing this equilibrium.

At present, low Ca concentrations measured in the leaves of sugar maples in the Hermine watershed (Fyles et al., 1994) coupled with a simulated low base saturation in the mineral soil in both zones create uncertainty regarding the future availability of cation nutrients in sugar maple stands of southern Quebec where timber operations are planned for the 21st century. Sustained low base cation availability for plant growth could adversely affect forest health and vigour, particularly forests in the first or middle stages of stand development because of greater cation nutrient demands. In addition, base deficient mature trees are more vulnerable to biotic agents such as insects and root rot fungi, and more sensitive to abiotic agents such as cold and drought (Côté and Ouimet, 1996). Fortunately, simulated soil chemistry assuming forest disturbance or not suggest that soil pH will unlikely reach values low enough to render high Al levels in the soil solution that could be toxic to most tree species (see Chapter 4).

3.6 Conclusion

A few historical soil chemistry studies support the hypothesis that acid-sensitive forest sites of northeastern United States underwent a significant change that resulted in the loss of exchangeable essential base cations due to acidic inputs from the atmosphere. Simulated soil chemistry using the SAFE model however reinforces the conclusions of this work indicating that the largest changes in soil chemistry occurred between the time period 1930-1980 and were associated with the deposition of strong acids from the atmosphere. Model projections in the mineral soil suggest that a new steady-state should be reached in the 21st century.

At the present stage of model development, however, SAFE may not provide output data accurate enough to give site-specific forecasts on nutrient availability. Some processes in the forest ecosystems would have to be clarified or assessed more accurately, e.g., dry deposition, biological N fixation, and N immobilization by myccorhizal fungi. Errors associated with determining key physical and mineralogical properties may also lead to inaccurrate simulated weathering rates. Modelling the long-term effects of acidic deposition and timber operations on soils is, nevertheless, important. The application of the SAFE model to different ecosystem types in eastern North America will help determine which sites and forest types are most threatened by base cation depletion. The modelling exercise also allows foresters to specify management strategies that will lead to sustainable productivity. Governments may also be able to use this approach to determine if air-born acidifying compounds are being regulated at appropriate levels to preserve the forest resource.

3.7 References

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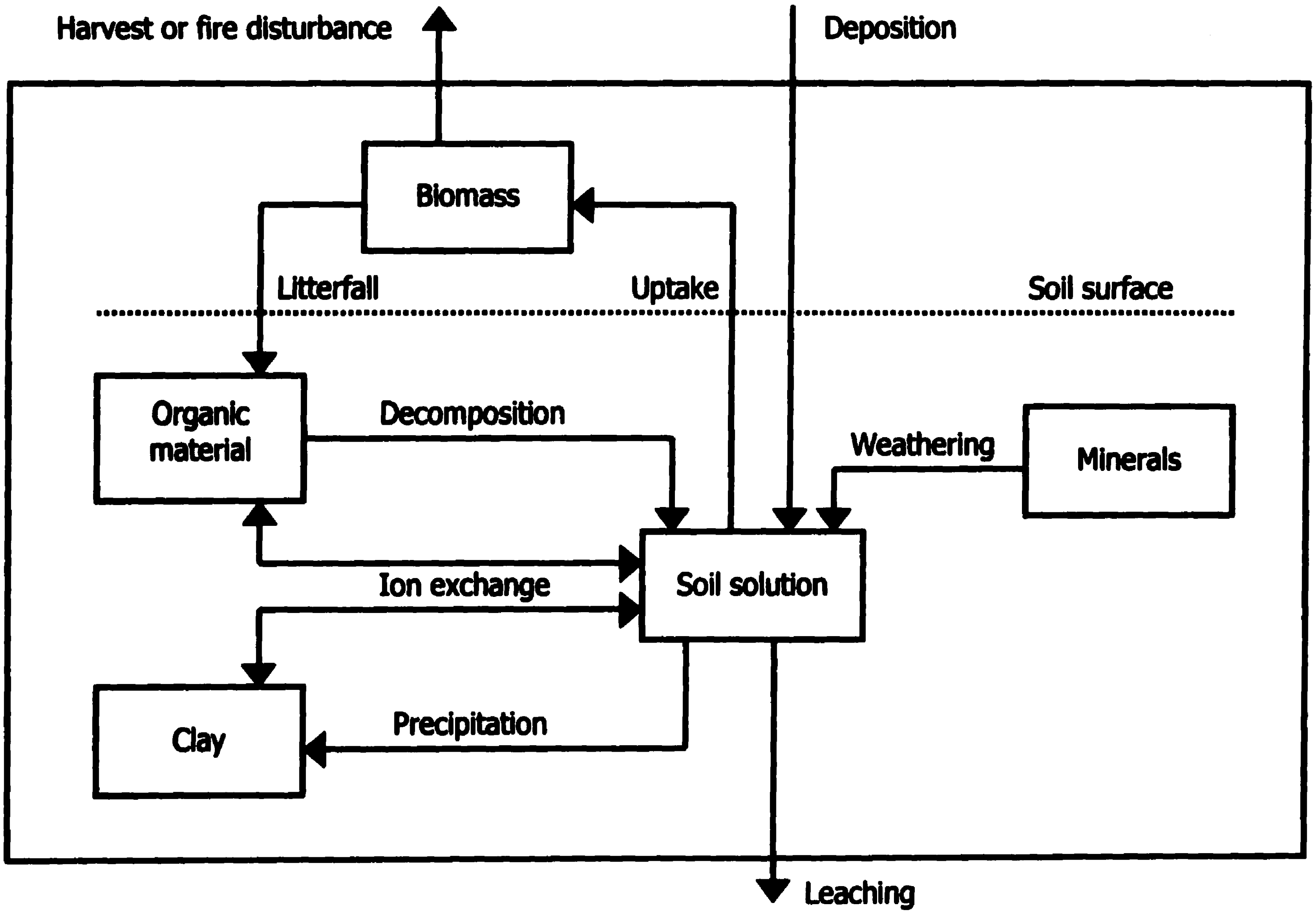

Figure 3.1. SAFE - A conceptual model of a forest soil.

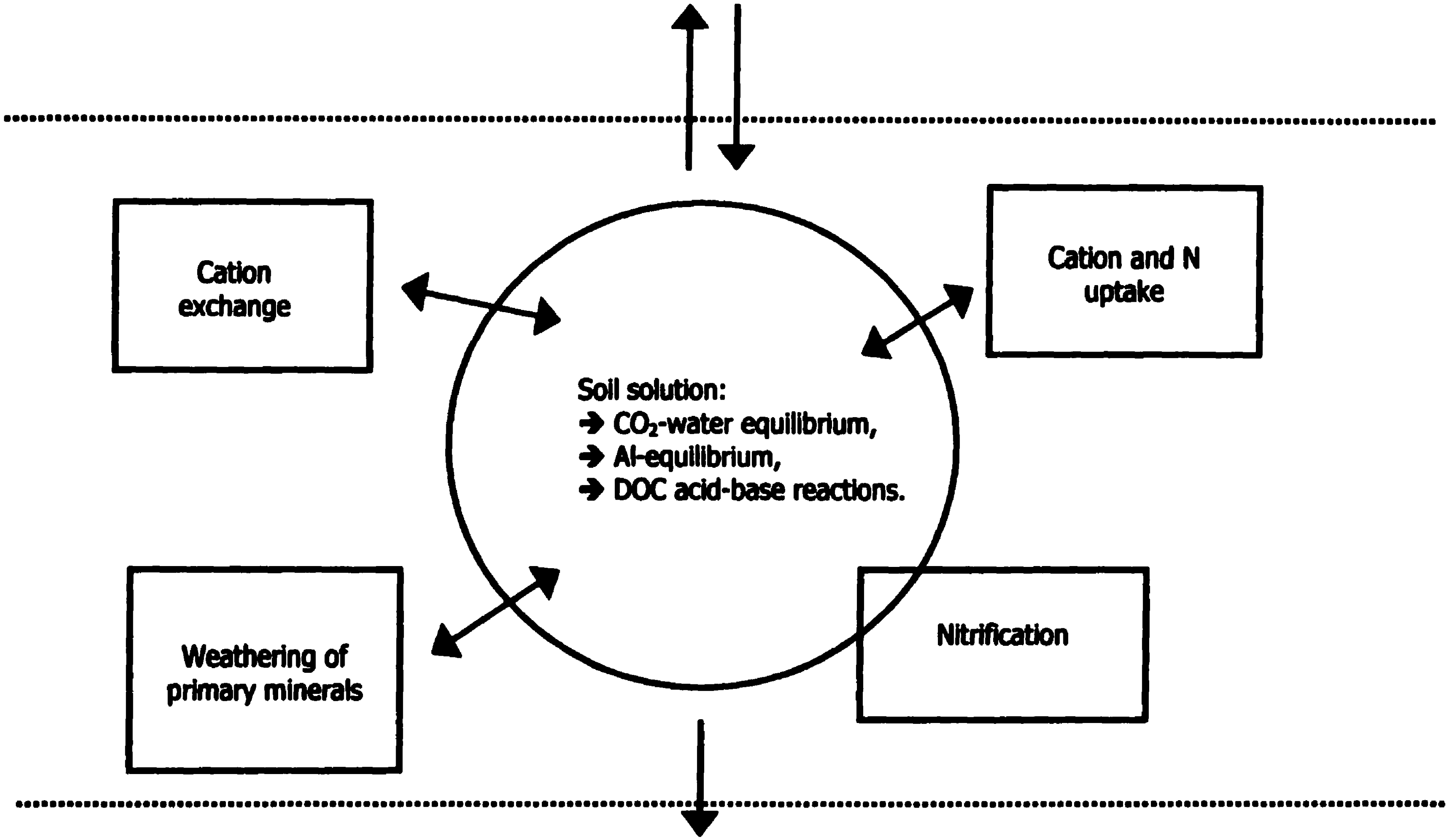

Figure 3.2 One compartment of the SAFE model.

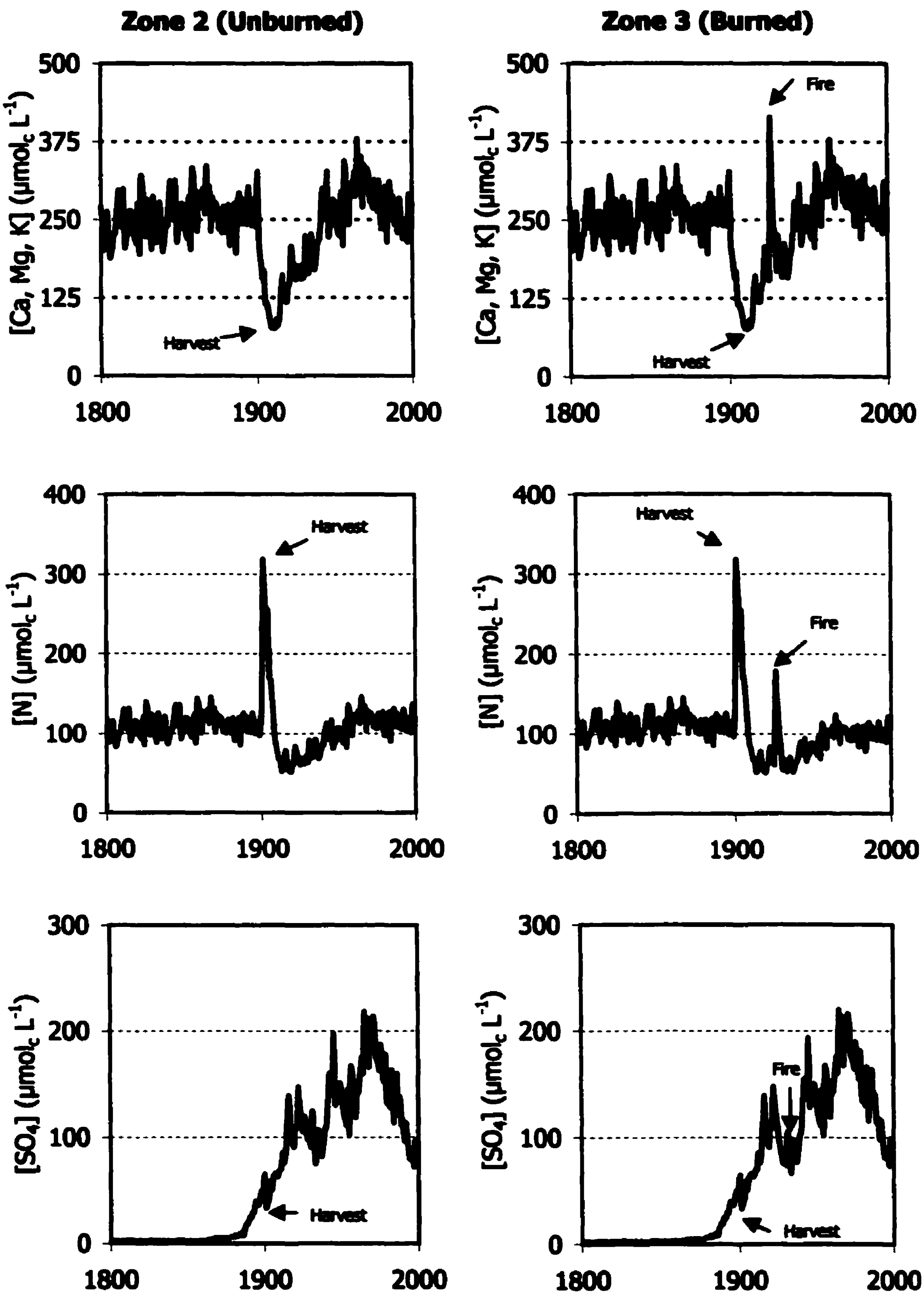

Figure 3.3. Simulated concentrations of base cations (Ca, Mg, and K), N (NO$_3$ and NH$_4$) and SO$_4$ in the soil solution of the forest floor in zones 2 and 3 at the Hermine watershed.

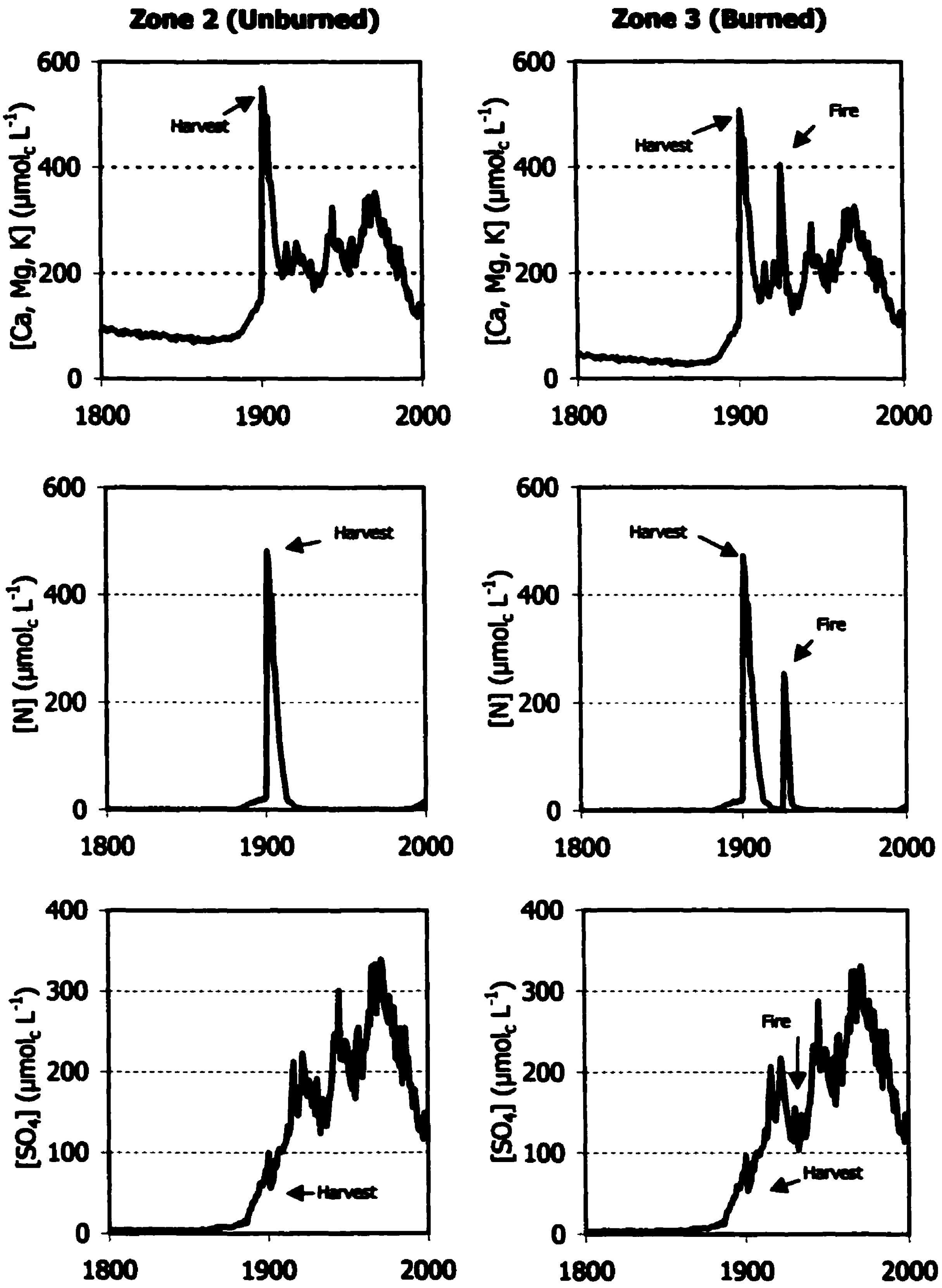

Figure 3.4. Simulated concentrations of base cations (Ca, Mg, and K), N (NO_3 and NH_4) and SO_4 in the soil solution of the mineral soil in zones 2 and 3 at the Hermine watershed.

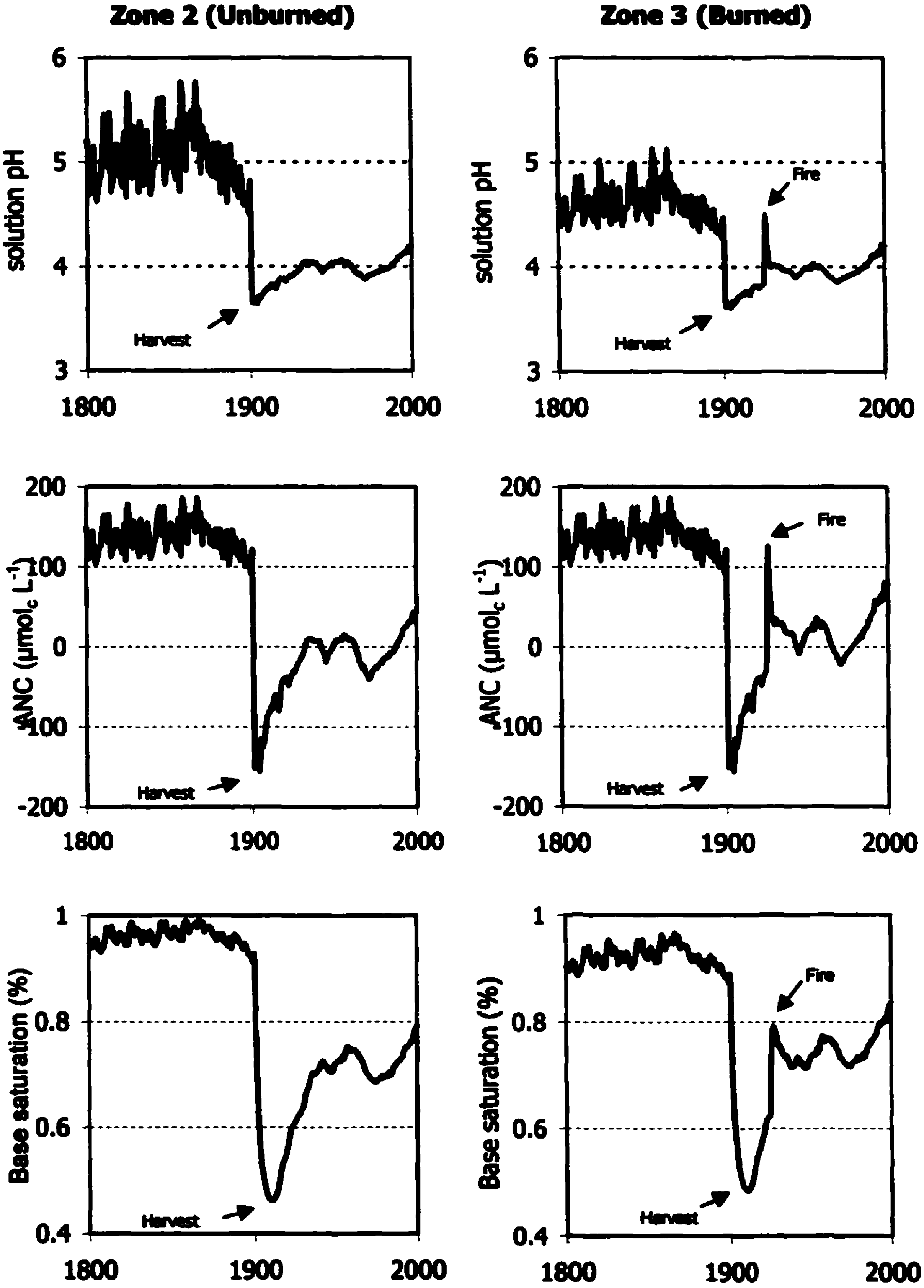

Figure 3.5. Simulated soil solution pH, acid neutralizing capacity (ANC), and base saturation in the forest floor of zones 2 and 3 at the Hermine watershed.

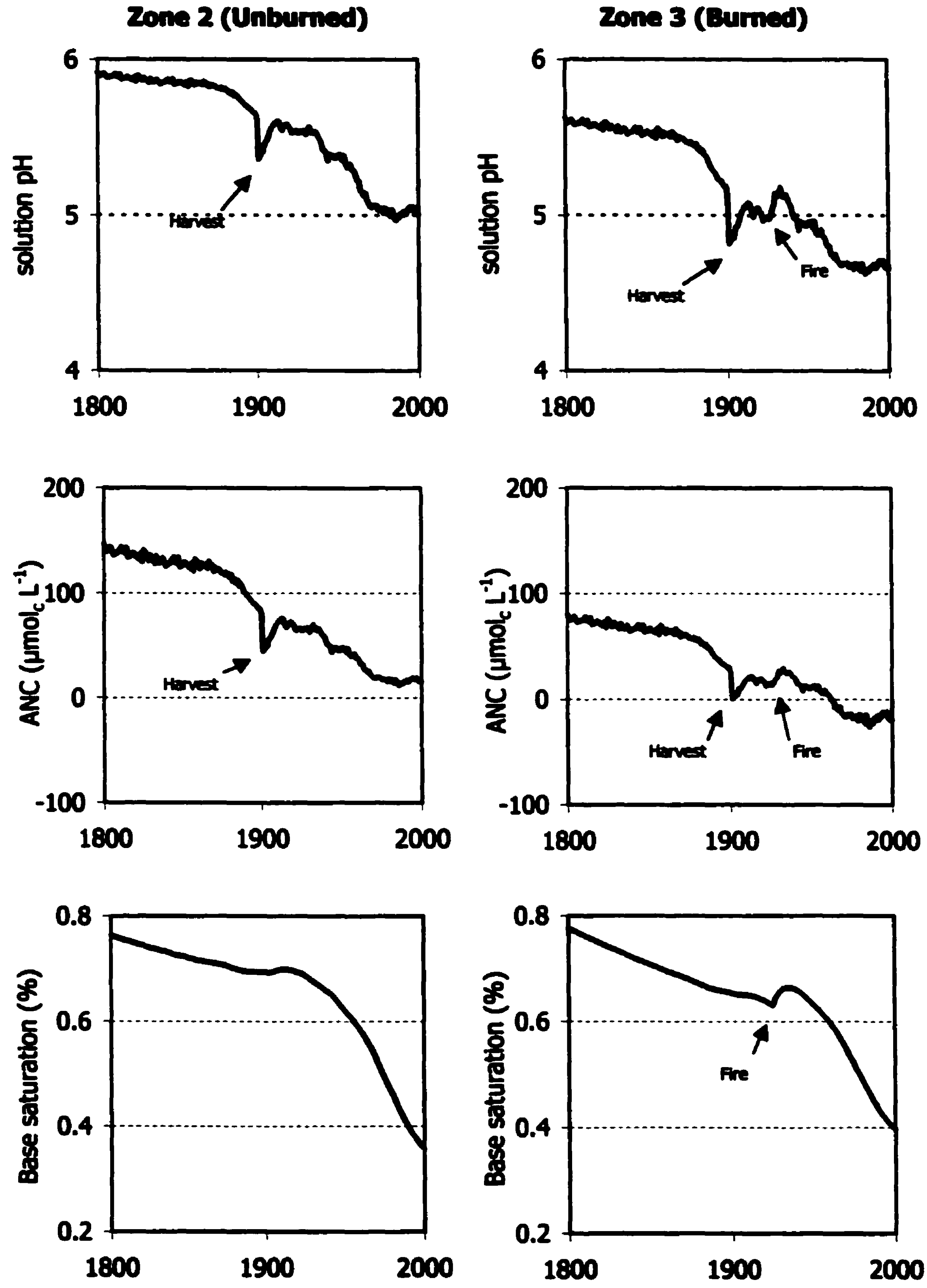

Figure 3.6. Simulated soil solution pH, acid neutralizing capacity (ANC), and base saturation in the mineral soil of zones 2 and 3 at the Hermine watershed.

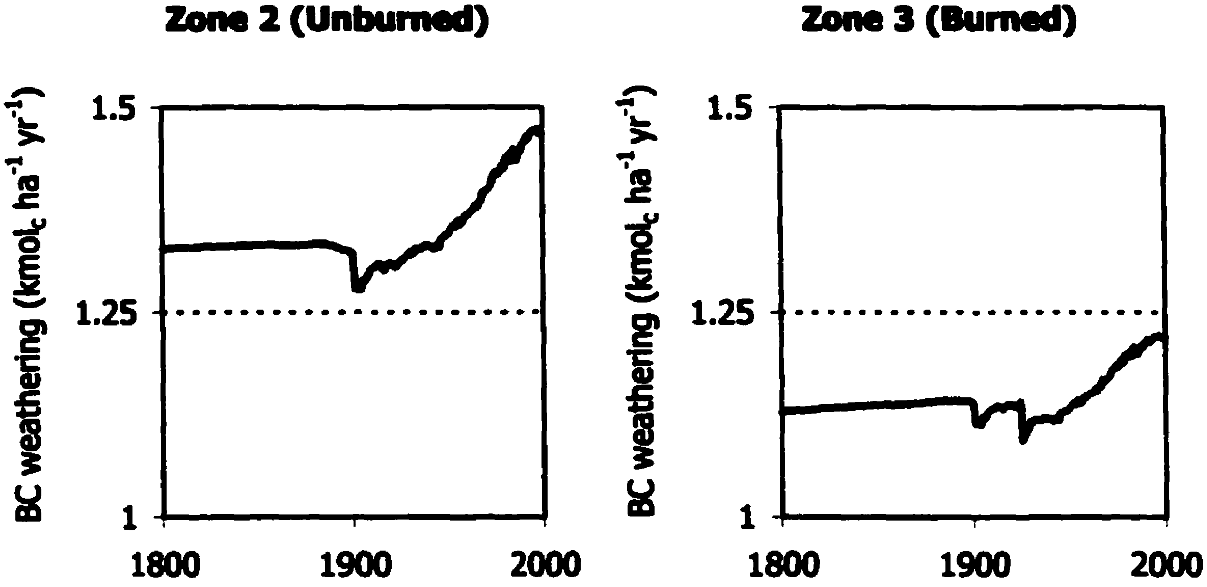

Figure 3.7. Simulated Ca, Mg, and K (BC) weathering in the mineral soil of zones 2 and 3 at the Hermine watershed.

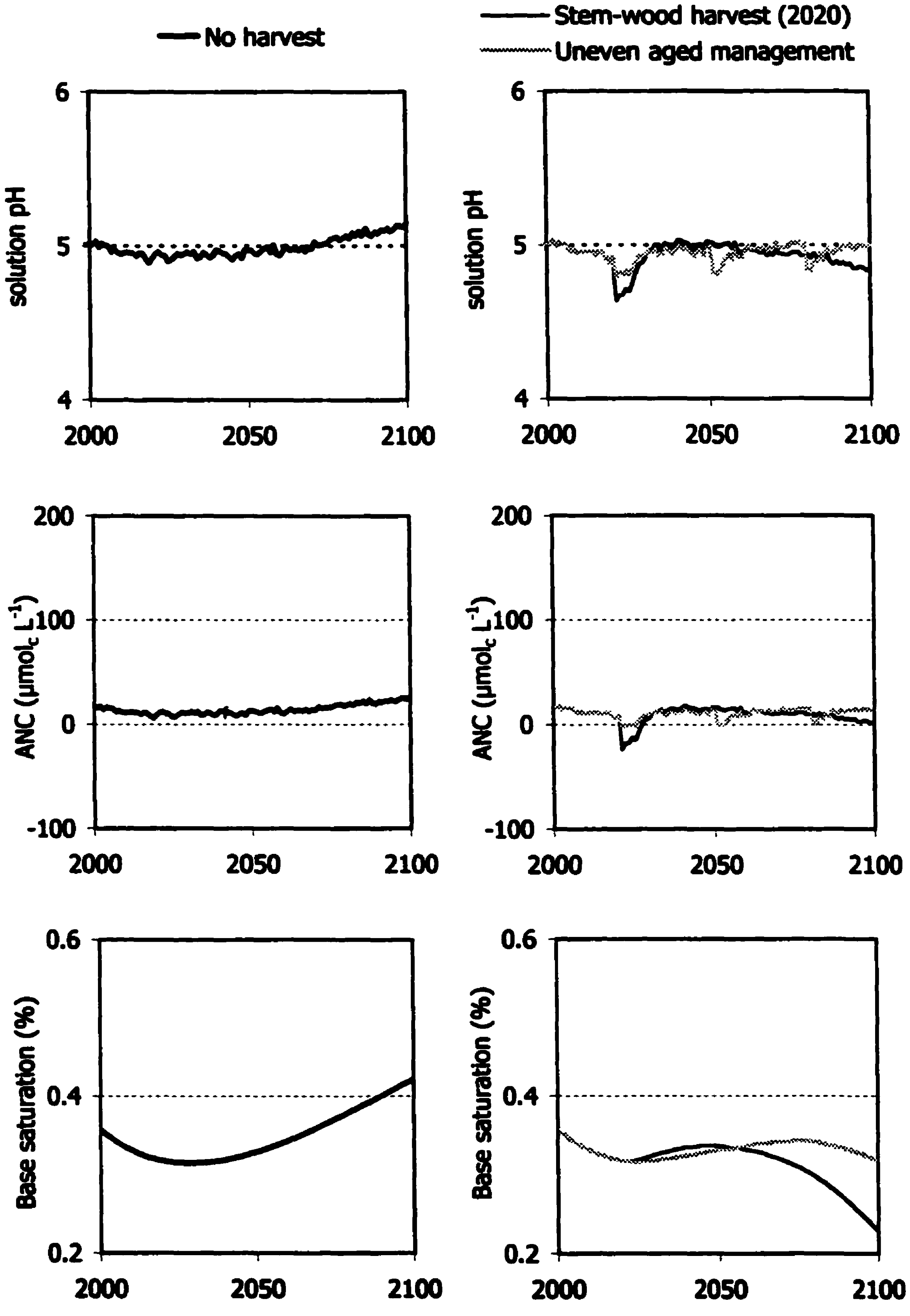

Figure 3.8. Projected soil solution pH, acid neutralizing capacity (ANC), and base saturation in the mineral soil of zone 2 at the Hermine watershed.

Table 3.1. Mean soil density and texture measured in the diagnostic B horizons of the three zones at the Hermine watershed.

			— Diagnostic B horizon —	
Zone	Soil properties	*n*	Bhf	Bf
no.1	Texture	3	12 ±1.0; 24 ±3.0; 64 ±2.1	6 ±2.0; 26 ±3.5; 68 ±4.9
	Density	3	1050 ±21	1310 ±28
no.2	Texture	3	14 ±2.0; 40 ±4.5; 46 ±4.9	11 ±1.0; 32 ±2.1; 57±5.3
	Density	3	910 ±35	1150 ±46
no.3	Texture	3	14 ±2.1; 34 ±2.1; 52 ±3.0	13 ±1.5; 34 ±2.1; 53±2.5
	Density	3	880 ±25	1060 ±42

Soil texture (clay, silt, sand) is expressed in percentage and soil density is in kg m^{-3}. Values on the right express standard deviations.

Table 3.2. Soil chemical, physical and hydrological properties used for the SAFE simulation in zone 2 (unburned) and zone 3 (burned) in the Hermine watershed.

Parameter	Unit	Unburned zone		Burned zone	
		FH-Ah	Bhf-Bf	FH-Ah	Bhf-Bf
Depth/thickness	cm	10-0	0-60	10-0	0-60
Base saturation	%	76	37	80	41
Cation exchange capacity	$kmol_c\ kg^{-1}$	2.69E-04	3.00E-05	3.26E-04	3.80E-05
Moisture content	$m^3\ m^{-3}$	0.50	0.30	0.50	0.25
Soil bulk density	$kg\ m^{-3}$	0	990	0	940
Surface area	$m^2\ m^{-3}$	0	1.70E+06	0	1.30E+06
CO_2 pressure	*x* ambient	5	20	5	20
Inflow	% of	100	80	100	80
Outflow	precipitation	80	50	80	50
Dissolved organic carbon	$mg\ L^{-1}$	26.3	2.2	34.0	2.4
Gibbsite equilibrium constant	$kmol^2\ m^{-6}$	5.5	8.5	5.5	8.5
Ca + Mg + K uptake	% of max.	30	70	30	70
N uptake	uptake	60	40	60	40

Table 3.3. Soil mineralogical properties used for the SAFE simulation in zone 2 (unburned) and zone 3 (burned) in the Hermine watershed.

Parameter	Unit	Burned and unburned zones Bhf-Bf horizons
Quartz	% of total mineral matrix	45.4
K-feldspars		0
Plagioclase		15
Albite		0
Hornblende		4
Pyroxene		0
Epidote		0
Garnet		1
Biotite		1.5
Muscovite		10
Vermiculite		4
Chlorite		19
Apatite		0.1
Gibbsite		0
Kaolinite		0

Table 3.4. Mean soil and soil solution chemistry measured in the forest floor and mineral soil of zone 2 (unburned) and zone 3 (burned) in the Hermine watershed between 1994 and 1997 and mean simulated chemistry between the same years using SAFE.

		Measured	Simulated	Measured	Simulated
Soil Parameter	**Soil Layer**	**Unburned zone**		**Burned zone**	
pH (sol'n)	Forest Floor	4.28	4.13	4.21	4.12
	Mineral Soil	4.98	5.05	5.02	4.70
Base saturation	Forest Floor	0.76	0.76	0.80	0.80
	Mineral Soil	0.38	0.38	0.41	0.41
Ca, Mg, K (sol'n)	Forest Floor	213	228	214	245
	Mineral Soil	110	124	100	108
NO_3 and NH_4 (sol'n)	Forest Floor	100	108	14	96
	Mineral Soil	7.78	7.22	2.52	2.34
SO_4 (sol'n)	Forest Floor	76	79	89	81
	Mineral Soil	116	127	115	125

Base cations, SO_4, and N concentrations are in μmol_c L^{-1}. Base saturation is in % and sol'n refers to solution chemistry.

CONNECTING PARAGRAPH

Aluminum is very soluble in acidic environments such as forest soils. Some suggested that at low pH, Al may be rendered into the soil solution at concentrations low enough to cause serious toxic responses to most tree species. The next chapter provides a review of the scientific literature on the chemistry of Al in forest soils and the toxicity of Al to trees. It is from the data gathered in this chapter and projections of pH by SAFE that the potential (i.e., into the 21st century) phytotoxic responses was assessed at the Hermine watershed in Chapter 3.

Chapter 4

Chemistry and Toxicity of Aluminum in the Forest Ecosystem
(Extended Literature Review)

4.1 Introduction

Forest decline has been observed in some parts of central Europe and eastern North America. The decline has been attributed to several environmental stresses (e.g., gaseous pollutant injury, cation nutrient deficiencies, growth altering organic chemicals, etc.) (Hinrichsen, 1986; Hendershot and Jones, 1989). Forest soils are typically acidic and relatively infertile and thus, increased atmospheric loading of acid substances could contribute to forest decline by 1) increasing cation nutrient leaching, 2) decreasing soil pH and rates of organic matter decomposition, and 3) increasing the solubility and mobility of toxic species of metals, including Al (Kelly et al., 1990). In a solution culture study, Hoyle (1971) recognised that a dissolved Al concentration of 3 m*M* resulted in decreased growth of roots and leaves of yellow birch (Table 4.1), but concluded that forest species are considered to be Al tolerant enough to withstand adverse effects in terrestrial ecosystems (refer to section 1.5 for field values). On the other hand, Ulrich et al. (1980) proposed that high levels of Al in the soil rooting zone was a possible cause of forest decline in West Germany. Hüttermann (1985) and Matzner and Ulrich (1985) showed evidence that atmospheric acid deposition, particularly H_2SO_4, had caused cation nutrient depletion and mobilisation of Al into the soil solution. Fine roots had been killed and the symptoms were comparable to those of roots killed by Al in solution culture experiments.

There are two processes by which exposure of ionic Al leads to adverse effects to plant: 1) irreversible damage to plant cells from Al interactions with sensitive biomolecules and 2) antagonistic interference with divalent cation uptake. Roots strongly adsorb Al by an exchange phenomenon or by formation of insoluble organic-Al complexes involving mucilage produced at the root tips (Horst et al., 1990). High concentrations of Al dissolved in soil solutions may inhibit root growth directly, either by inhibition of cell division or cell elongation, or a combination of both (Marschner, 1991). The direct inhibition of cell division requires high concentrations of toxic monomeric Al species to interact with DNA and RNA (Tepper et al., 1989). At lower concentrations, inhibition of cell elongation is most likely to occur. The adverse effects of Al in the cytoplasm and particularly on plasma membrane and structure are greater than the effects of Al on the apoplast, as for example, the replacement of Ca^{2+} from the middle lamella in expanding tissue (Taylor, 1988; Wagatsuma and Akiba, 1989). The replacement of Ca^{2+} by Al from the external surface of the plasma membrane may enhance Ca^{2+} influx into the cytosol and subsequently induce callose formation in the apoplast (Wissemeier et al., 1987).

The aim of this chapter is to provide a review of the scientific literature on the toxicity of Al to trees so that critical toxicity values are identified for both coniferous and deciduous tree species. This review is divided into two sections: 1) Al chemistry, speciation and bioavailability in the forest environment, and 2) Al toxicity to trees. Experiments with solution culture are a useful approach in trying to exclude factors that could not be controlled in the field. However, the plant response to Al in solution must be interpreted carefully due to the lack of agreement with the response found in forested ecosystems. This discrepancy implies that even though the main variable (Al) may have been similar, other variables that influence plant response make comparisons between field and laboratory studies very difficult. It is generally accepted that Al bioavailability (and hence toxicity or bioaccumulation) is a function of Al speciation in the soil solution. However the majority of the published research on bioaccumulation and toxicity only contain information on the amounts of total dissolved Al. This is certainly a weakness in this report, but the data do provide a sound basis for the establishment of the lowest adverse effects concentration (LOAEC) values of total dissolved Al.

4.2 Aluminum Chemistry, Speciation and Bioavailability in Forests

4.2.1 Natural Sources of Aluminum and Processes of Release

Atmospheric deposition of Al is attributed mostly to deposition of dust particles and is generally low (Driscoll et al., 1994). Aluminum is the third most abundant element in the earth's crust and makes up approximately 8% of its rocks and minerals (Skinner and Porter, 1989). Most rocks and minerals contained in the soil are in an environment that differs significantly from that where they formed. Inputs of Al into the soil solutions occur by mobilisation of Al derived from the chemical weathering of soil minerals. The most important reaction in the chemical weathering of the common silicate minerals is hydrolysis. The hydrolysis of albite (feldspar) is one example of the chemical transformation of an Al-bearing primary mineral into clay size minerals. In this case, the newly formed solid phase is kaolinite (1:1 clay mineral):

$$\underset{\text{(albite)}}{4NaAlSi_3O_8} + \underset{\text{(aq)}}{4H_2CO_3} + \underset{\text{(l)}}{18H_2O} \leftrightarrow \underset{\text{(aq)}}{4Na^+} + \underset{\text{(aq)}}{8H_4SiO_4} + \underset{\text{(kaolinite)}}{Al_4Si_4O_{10}(OH)_8} + \underset{\text{(aq)}}{4HCO_3^-} \quad \text{(eq. 4.1)}$$

Aluminum is not very soluble over the normal soil pH range and thus, it generally remains near its site of release to form clay minerals or precipitate as amorphous or crystalline oxides, hydroxides or hydrous oxides. Cations (such as Ca, Mg, K or Na) can remain in the soil solution, take part in the formation of the crystal lattice of clay minerals, adsorb to the surface of the soil's exchange sites, be absorbed by vegetation, or leach out of the soil system. Silica is much more soluble than Al at normal soil pH and is always in excess of the amount used to form most clay minerals, so that some is removed from the soil system in leachates (Birkeland, 1984).

Although the dissolution and precipitation reactions of Al-bearing minerals are often good indicators of the solubility of Al in soils, they are by no means the only pedogenic processes controlling the concentrations of Al in soil solutions. Many other processes may partly control the bioavailability of Al to plant and soil organisms. Aluminum may be 1) adsorbed on cation exchange sites, 2) incorporated into soil organic matter, 3) absorbed by vegetation, or 4) leached out of the soil system (Ritchie, 1995).

In eastern Canada, the atmospheric deposition of strong acids, such as HNO_3 and H_2SO_4, has accelerated the soil's natural acidification due to processes such as nitrification and plant uptake of cations. Acid-sensitive soils are generally underlain by siliceous bedrock (e.g., granite, granitic gneiss, quartzite) that are resistant to chemical weathering. Areas with acid-sensitive soils usually have shallow acidic soils with small pools of available base cations (Reuss et al., 1987). Cations in the soil solution exist in equilibrium with the cations that are adsorbed on the surfaces of soil colloids. In ecosystems where the soil solution is increasing in acidity due to inputs of strong acids, the equilibrium is perturbed. The increased H^+ activity (lower pH) in the soil solution creates a new equilibrium where more Al^{3+} is dissolved into the soil solution and cation nutrients (Ca^{2+}, Mg^{2+}, and K^{+}) are replaced on the soil exchange complex by Al^{3+} and the base cations are eventually leached out of the soil (Hendershot et al., 1991). The net effect of this process is to buffer H^{+} entering the soil solution. In the long term, this process may well bring the base cation pool to a point where cation nutrient availability could be low enough to seriously jeopardise the health and vigour of forested ecosystems.

There may be significant variation in Al^{3+} solubility with depth in a soil profile (Hendershot et al., 1995). In the surface horizons Al is being dissolved by the influx of solutions containing low concentrations of Al, low pH and abundant dissolved organic matter capable of complexing Al. As a result the dissolution of Al may be the rate-limiting step in obtaining equilibrium between the solid and liquid phases and the soil solutions tend to be undersaturated with respect of Al bearing minerals. In contrast, Al tends to precipitate in the lower B and C horizons that have considerably higher pH and lower dissolved organic matter contents and therefore can be expected to be near to equilibrium with some Al solids. Although the equilibrium concentration is close to that which would be expected if gibbsite were controlling equilibrium, gibbsite has generally not been found in Canadian soils. Other forms of Al, for example, hydroxy interlayered vermiculite, may control Al solubility at values close to those of gibbsite. Amorphous Al complexed with organic matter may also have a similar pH-solubility curve that is a function of the pH-dependant variation in the number of binding sites.

4.2.2 Aluminum Speciation

The fluoride and hydroxide complexes are the two strongest groups of inorganic ion associations with Al in soil solutions (Nordstrom and May, 1995). Aluminum-OH complexes vary with pH. In very acidic soils, Al in the soil solution is mainly present as free Al^{3+}. As pH increases, free Al^{3+} hydrolyses to form complexes with OH^{-} ions (e.g., $AlOH^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3^{0}$). Near pH 6.5, Al solubility is at a minimum, but increases at neutral to alkaline conditions because of the formation of $Al(OH)_4^{-}$ (Driscoll and Postek, 1995) (Figure 4.1). Fluorine is the most electronegative and one of the most reactive elements. According to Lindsay et al. (1989), it is released through the dissolution of F^- bearing minerals such as fluorapatite (and perhaps amphiboles and micas) in which the fluoride ion (F^-) replaced OH^- in the crystal lattice (F^- has the same charge and nearly the same ionic radius as the hydroxide ion (OH^-) and thus, can readily substitute for OH^- in metallic complexes). The concentration of F^- in soil solution determines the stoichiometry of Al-F complexes. In acidic soils (pH values below 5.5), the F^- concentration is generally less than that of Al^{3+}. As a result, low ligand number complexes, such as AlF^{2+}, are normally formed. In neutral to alkaline conditions, it is more difficult for F^- to compete with OH^- for Al in the soil solution because of the increased level of OH^-. Consequently, Al-OH complexes predominate over Al-F complexes in alkaline conditions (Figure 4.1). Nevertheless, the displacement of OH^- for F^- at high F^- concentrations (such as when fluorapatite is present in relatively high amounts) can result in higher-ligand-number complexes (e.g., AlF_6^{3-}). Aluminum-OH-F complexes have been reported in the literature (Couturier, 1986). However, these complexes are thought to be intermediate phases during the formation of Al-F inner-sphere complexes and therefore rather short-lived.

The complexation of Al with sulphate (SO_4^{2-}) is weaker than with F^-. However, in acidic soils where the SO_4^{2-} concentration is high, it may form Al-SO_4 complexes by competing with Al-OH complexes in the same fashion as F^- (Driscoll and Postek, 1995). At low SO_4^{2-} concentrations, $AlSO_4^+$ is the dominant aqueous form, whereas $Al(SO_4)_2^-$ is predominant in soil solutions with higher SO_4^{2-} concentrations. Generally, SO_4^{2-} concentrations are higher than those of F^-. Nevertheless, Al-SO_4 complexes become significant only at low pH values (Figure 4.1).

Aluminum may form stable complexes with various functional groups in organic matter. Vance et al. (1995) divided these into two categories: "1) well-defined biochemical compounds synthesised by micro-organisms and plants, such as simple low-molecular-mass organic acids, hydroxyphenols, and 2) a series of acidic, yellow- to black-coloured substances formed by secondary synthesis reactions, which are collectively referred to as humic and fulvic acids". It is believed that organic ligands play a dynamic and important role in the speciation of Al in the soil solution (David and

Driscoll, 1984; Driscoll et al., 1985; Ares, 1986). However, the complicated and diverse nature of dissolved organic matter makes it difficult to understand and model the chemistry of Al in soil solutions (Driscoll and Postek, 1995).

Brown and Driscoll (1992) identified and characterised several aluminosilicate complexes, which they showed to be present in various regions of the eastern U.S. and Canada. Three Al-Si complexes were described, including $AlSiO(OH)_3^{2+}$. The authors concluded that up to 95% of the total inorganic Al could be present as these complexes.

Nordstrom and May (1995) discussed the possibility of Al forming complexes with other inorganic anions in the soil solutions (e.g., HCO_3^-, Cl^-, PO_4^{3-}, or NO_3^-), but concluded that they are less significant than the complexes mentioned above.

4.2.3 Distribution of Aluminum Species in the Soil Profile

It has been shown that most dissolved Al in the soil solution of the forest floor is organically bound and that these Al-organic complexes become less abundant with increasing soil depth (Nilsson and Bergkvist, 1983; David and Driscoll, 1984; Driscoll et al., 1985). In the Adirondacks of New York, David and Driscoll (1984) found that 82 and 93% of the total dissolved Al in the organic horizons of conifer and hardwood sites, respectively, was organically complexed. The proportion of organic to inorganic Al decreased at both sites from the organic to the upper mineral horizons, and from the upper to the lower mineral horizons. In the soil solutions of the mineral horizons, Al-organic complexes represented 67 and 58% of the total Al in conifer and hardwood sites, respectively, which indicates the importance of Al-organic complexes in humus-rich forest soils of eastern North America.

At the Hubbard Brook Experimental Forest (HBEF), New Hampshire, the relative distribution of inorganic forms of Al in the soil solution suggests that Al^{3+} is the predominant form in the very acidic high elevation sites (pH 3.6-4.7), but that Al-F and Al-OH complexes become dominant in the less acidic low elevation sites (pH 4.5-5.2) (Driscoll et al., 1985). In both the hardwood (pH 4.6-4.7) and conifer (pH 4.0-4.5) sites, David and Driscoll (1984) found that Al-F complexes were the major forms of inorganic Al, ranging from 58 to 92% of total inorganic Al. Higher proportions of Al-F complexes were found in the soil solution of the organic horizons than in the mineral horizons. Free Al^{3+} concentrations were extremely low (6%) in organic horizons where Al was mostly bound with fluoride or organic carbon. In both studies, $Al\text{-}SO_4^{2-}$ complexes were generally a small percentage of total inorganic Al.

4.2.4 Concentrations of Aluminum in the Soil Solution

In Canada, one would expect to find the highest concentrations of dissolved Al in the mineral soil horizons of podzols of Ontario, Quebec and the Maritimes that have a base saturation of less than 10-15% of effective cation exchange capacity at field pH. Soil pH in water is typically 4.5 or less and soil solution sulphate is generally 50 μ*M* or greater. For example, Bélanger et al., (1997) measured peak Al concentrations of 0.012 m*M* with a pH of 4.7 in forest soils of central New Brunswick. Hendershot et al. (1995) measured a mean Al concentration of 0.024 m*M* in the soil solution of podzolic B horizons at the Hermine watershed, in the Lower Laurentians of Quebec, whereas the same authors found a mean level of 0.014 m*M* Al in the soil solutions of podzolic B horizons at Turkey Lakes, central Ontario (pH values were approximately 4.0 at the Hermine watershed and 4.5 at Turkey Lakes). Driscoll et al. (1985) found mean Al solute concentrations of 0.032 m*M* in a podzolic B soil horizon of pH 4.63 at the HBEF. Similarly, David and Driscoll (1984) found 0.041 m*M* Al in the solution of a podzolic B soil horizon of the Adirondacks at pH 4.2. Peak concentrations of 0.102 m*M* (pH 4.7) and 0.140 m*M* (pH 3.6) of dissolved Al in soil waters of surface mineral horizons have been reported at the Huntington forest (Cronan et al., 1989) and Whiteface mountain, New York (Huntington et al., 1990), respectively. This gives an indication of the highest levels of Al that could be encountered by tree roots in Canadian soils.

4.2.5 Bioavailability of Aluminum as Related to its Speciation

The toxicity of Al depends on a number of abiotic and biotic factors. Given the fact that Al is such an abundant element in soils, it is not surprising that toxicity is poorly correlated with the total Al concentration. There is general agreement that the toxicity of Al depends on its speciation in the soil solution, which in turn depends on pH, concentration (or activity) of other cations and ligands in the soil solution. The complexation of Al by natural organic substances plays a key role in the regulation of high levels of toxic Al ion species in the soil solutions as well as in surface waters. It has been shown that humic-rich soils generally have low concentrations of inorganic Al ion species, which permits better growth at otherwise toxic concentrations of dissolved Al (Taylor, 1988). The toxicity of Al is believed to be relatively low when Al is complexed with F^- or SO_4^{2-} (Kinraide and Parker, 1987; Wright et al., 1989), although AlF_2^+ and AlF^{2+} were recently found to be toxic (Kinraide, 1997). The mononuclear species Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ (Alva et al., 1986; Noble et al., 1988) and the soluble polymeric species Al_{13} (Wagatsuma and Ezoe, 1985) were shown to cause severe rhizotoxicity in solution culture experiments. However, the importance of Al_{13} in natural soil solutions has been questioned because suspended solids would readily sorb polymeric Al (Driscoll and Schecher, 1988).

4.3 Aluminum Toxicity

In this review on LOAEC values, a number of studies were eliminated if the plants were grown in solutions with less than 0.05 m*M* Ca concentrations in solution. This value is considered to be the minimum that can be expected based on studies in forest soils in eastern Canada or northeastern USA. Studies that only demonstrated a decrease in nutrient uptake were also not considered to adversely affect pant health if this was not accompanied by a decrease in growth.

4.3.1 Aluminum Toxicity Threshold Values for Hardwoods

Table 4.1 contains the lowest adverse effects concentrations for studies showing a statistically significant decrease in growth of deciduous tree species and meeting our requirements on nutrition.

McCormick and Steiner (1978) and Steiner et al. (1980) found threshold values for root elongation to be greater than 4 m*M*, and Keltjens and Van Loenen (1989) observed no seedling mortality at levels as high as 1.1 m*M*. However, the solutions used were so called optimum solutions with high N and P, a situation rarely found in forest soils. Birch species are considered to be Al-tolerant plants. This may be due to an Al tolerance mechanism in which Al is deposited in the cell walls or vacuoles where it cannot damage metabolism (Memon et al., 1981). Using P stressed plants, however, Clegg and Gobran (1995) observed that birch seedlings were sensitive to levels of Al of 0.2 m*M*. In this case, it seems that exposure to Al was enough for Al to be deposited on exchange sites of the cell walls of roots and precipitate phosphate ions, which, in turn, inhibited P uptake and lead to a decrease in the growth rate.

Thornton et al. (1989) found that ionic strength may modify Al response threshold values for European beech. In low ionic strength medium, leaf biomass declined by 40% in the presence of 0.5 m*M* of Al. A similar response was not observed in the full strength nutrient solution until Al levels of 2.0 m*M*. But because all nutrient were reduced in the one-fifth strength medium, it was not possible to determine which ion (or ions) may have limited growth compared to the full strength media. Rost-Siebert (1984) has, however, demonstrated the importance of adequate Ca nutrition for root growth of european beech. In the absence of solution Al, his studies showed a 66% increase in root elongation when Ca levels were increase from 0.1 to 0.2 m*M*. Thus, when Thornton et al. (1989) reduced the Ca concentration to 0.05 m*M* in the low ionic strength medium (compared to 0.25 m*M* Ca in the full ionic strength solution), it may have limited seedling growth due to a relative increase in the contribution of Al^{3+} to the total ionic activity of the lower strength medium. Furthermore, high levels of plant-available Ca (4.0 m*M*) in the solution culture experiment of McCormick and Steiner (1978) may explain the lack of Al sensitivity attributed to many deciduous species, but also conifers.

Similarly, Asp and Berggren (1990) showed the competitive effect of Al on Ca uptake in shoots of european beech. It was explained that Al^{3+} can compete with Ca^{2+} for negative extracellular binding sites in the cell walls and on the phospholipids and protein portions of the plasma membrane. When Al^{3+} associates with membrane phospholipids, it may change the lipid structure and indirectly disturb the structure of the transport proteins. Bengtsson et al. (1988) also found that the uptake of Ca and Mg in all parts of the plants decreased by 20% when they were exposed to 0.1 m*M* Al.

Calcium and Mg uptake in leaves and roots decreased by 50% at Al levels of 1 m*M*. The effect of Al^{3+} on Ca^{2+} uptake was immediate and primarily of a competitive nature, preventing Ca^{2+} from being adsorbed.

Bertrand et al. (1995) found that adverse effects were more pronounced in the aerial parts (shoots and leaves) than in the roots of sugar maple seedlings exposed to Al concentrations of 2 m*M*. Thornton et al. (1986a) observed a stimulation of relative root growth until 1.0 m*M*, whereas Bertrand et al. (1995) observed the same until 2 m*M* Al. This is because the solution culture medium of both experiments was very acidic ($pH \leq 4.0$). Under these acidic conditions, growth is enhanced because Al acts as a polyvalent cation and protects against H^+ ion damage to the root. However, Thornton et al. (1986a) observed adverse effects on roots exposed at levels exceeding 1.0 m*M*, suggesting that this solution culture experiment is not directly comparable with the sand culture experiment produced by Bertrand et al. (1995). Horst et al. (1990) suggested that sand culture may increase Al tolerance since Al uptake may not be as high as in solution culture. The release of exudates by plants (some as ligands) in the rhizosphere of sand cultures may increase Al tolerance by forming non-bioavailable Al complexes. Total leaf area decreased by more than 27% at Al levels of 2 m*M* in the middle of the experiment, but ended up with similar leaf area at the end of the experiment to those of the untreated seedlings (Bertrand et al., 1995). This response shows that plants can acclimate to levels of Al previously considered toxic. In this case, the exposure time was a key factor to this adaptation.

The sensitivity of honeylocust to Al was determined in a solution culture study (Thornton et al., 1986b) and two soil studies (Sucoff et al., 1990; Wolfe and Joslin, 1989). The solution culture experiment indicated that honeylocust is among the most Al-sensitive tree species. All measures of growth, except for root elongation, consistently declined as solution Al increased, 0.05 m*M* being the critical value for a 50% general decrease. The length of roots was stimulated at 0.05 m*M*, but was reduced at 0.1 m*M*. The physiological basis for the stimulation is uncertain, but may involve reallocation of assimilates from lateral roots to primary roots (Sucoff et al., 1990). On the other hand, Al inhibits root elongation in honeylocust by interfering with mitosis but cell length is not affected (Tepper et al., 1989). The sensitivity of honeylocust in the two soil studies was less pronounced than in solution culture studies since decreases in growth were witnessed at 0.1 m*M*. Although Al^{3+} and H^+ covary in soils, all three studies further indicate that high levels of either can independently reduce growth. Again, Al inhibited the accumulation of Ca and Mg to the point that the honeylocust seedlings may have become deficient in these elements (Sucoff et al., 1990).

4.3.2 Aluminum Toxicity Threshold Values for Conifers

Table 4.2 contains the lowest adverse effects concentrations for studies showing a statistically significant decrease in growth of coniferous tree species and meeting our requirements on nutrition.

With the exception of studies conducted by Schier (1985) and McQuattie and Schier (1990), growth of red spruce seedlings was inhibited at Al levels ranging from 0.185 to 0.25 m*M*. The reasons for the lack of sensitivity of red spruce to Al in the two studies mentioned above are not entirely clear. However, genetic factors may account for some of the variability in response observed in the different studies. Also, experiments using newly germinated versus 1-year-old seedlings may account for the variation in response to Al observed in red spruce. Schier (1996) observed that roots of newly germinated seedlings produced significantly less biomass when exposed to Al levels of 0.185 m*M* than roots of 1-year-old seedlings. It is well known that the major effect of Al toxicity is the inhibition of root elongation because the root meristem is the primary site of Al toxicity. With root elongation making a smaller contribution to the increase in root biomass of 1-year-old seedlings than newly germinated seedlings, Al probably had a lesser effect on the increase in root biomass of the older seedlings. Schier (1985) observed on 1-year-old seedlings significant declines in root length, while root biomass was not affected. Aluminum would have had less effect on root biomass than root elongation because reductions in root length are offset by increases in root diameter. At low pH, McCanny et al. (1995) and Schier (1996) observed stimulation of photosynthetic rate at Al levels between 0.025 and 0.1 m*M* and needle growth at 0.185

m*M* Al, respectively. This increase in growth may be explained again by alleviation of H^+ toxicity by Al^{3+} (Kinraide, 1993), but also by suppression of fungal pathogens as some Al ions are believed to be soil fungitoxins (Ko and Hora, 1972). Based on these results, McCanny et al. (1995) suggested that field conditions (*i.e.*, Al levels below 0.1 m*M*) might play a positive role on the growth of red spruce. On the other hand, Joslin and Wolfe (1992) calculated root density across a cloud water deposition gradient. Restricted root development in the mineral soil of the high cloud site was probably related to an unfavourable soil chemical environment, *i.e.*, low base cation and periodic high Al concentrations of approximately 0.2 m*M*.

In a solution culture experiment, Nosko et al. (1988) reported reductions in the elongation and biomass of roots of white spruce seedlings at 0.05 m*M* Al at pH 4.5. This level is low compared with Al concentrations found in other studies looking at the tolerance of different coniferous tree species. In hydroponics, a problem exists in the continuously changing chemical composition of the solution as plants take up and exude substances, thereby altering pH, ion concentrations, and the relative proportions of Al-complexing agents and Al species. To allow precise control of the solution, Nosko and Kershaw (1992) designed a nutrient circulation system to deliver a continuous flow. Root growth was reduced with addition of 0.01 m*M* Al. The magnitude of the decrease was more pronounced as pH decreased, possibly due to the resultant increased proportion of total Al as phytotoxic monomeric species. The Al level that inhibited root growth of white spruce seedlings was much lower than that reported for white spruce by Hutchinson et al. (1986) or other coniferous tree species. Hutchinson et al. (1986) found that the tolerance of black spruce is similar to that found for red spruce and white spruce.

In solution cultured Norway spruce seedlings, the presence of Al at concentrations found in forest soil solutions (0.1-0.2 m*M*) strongly decreases root growth (Rost-Siebert, 1984; Godbold et al., 1995). In sand culture, the phytotoxic effects of Al are often reduced as a result of increased root exudation and mucilage production (Horst *et al.*, 1990). This was demonstrated for Norway spruce by Asp et al. (1988) who found that the growth of seedlings in a sand culture was not affected until Al levels reached 1.0

m*M*. However, Hentschel et al. (1993) found that root dry weight of Norway spruce seedlings grown in sand culture colonised with mycorrhizal fungi was reduced at Al concentrations as low as 0.2 m*M*. They concluded that colonisation by mycorrhizal fungi does not significantly alter the effects of Al on root growth of Norway spruce seedlings.

Most studies on spruce species describe the effect of Al on trees growing in natural environments from solution cultures with nonmycorrhizae roots. Because mycorrhizal fungi influence the uptake of mineral elements from the soil, they may affect the response of trees to Al. Cumming and Weinstein (1990) who investigated the ability of the mycorrhizal fungus *Pisolithus tinctorius* (Pers.) to modulate Al toxicity in pitch pine concluded that mycorrhizae increase Al tolerance. Nonmycorrhizal seedlings exposed to 0.2 m*M* Al exhibited decreased growth, whereas the seedlings inoculated with *P. tinctorius* exhibited unaltered growth. The fungal symbiont evidently modulated ionic relations in the rhizosphere, reducing Al-P precipitation reactions, Al uptake, and subsequent root and shoot tissue Al exposure. Schier and McQuattie (1995; 1996) investigated the effect of Al on the growth and nutrition of ectomycorrhizal and nonmycorrhizal eastern white pine and pitch pine. For eastern white pine, Al levels of 0.46 m*M* significantly decreased shoot and root growth in both nonmycorrhizal and mycorrhizal seedlings, but had less effect on root and shoot growth in mycorrhizal seedlings. In the pitch pine experiment, Al levels of 0.37 m*M* reduced root and shoot growth in the nonmycorrhizal seedlings, but had no effect on shoot growth and only marginal significant effect on root growth of mycorrhizal seedlings. In both experiments, symptoms of Al toxicity in roots and foliage occurred at lower Al levels in nonmycorrhizal than in mycorrhizal seedlings. Schier and McQuattie (1996) found that in the nutrient-poor medium, nonmycorrhizal seedling growth was about the same as when the nutrient levels of the solution medium was higher. These authors believe that if the level of nutrients in the solution medium had been higher (i.e., optimal) in the most concentrated medium, then red spruce could have withstood exposure to higher Al concentrations without a significant decrease in seedling growth.

Paganelli et al. (1987) found that loblolly pine root regeneration was quite sensitive to Al. Aluminum concentrations as low as 0.185 m*M* reduced the number of new roots formed over the 24-day period, whereas root length declined at Al levels of 0.74 m*M*. Ilvesniemi (1992) found that when nutrition was optimal, scots pine tolerated Al levels as high as 1.85 m*M* without adverse effect, but that minimal nutrition solution medium reduced by ten times (*i.e.*, 0.185 m*M*) the tolerance of pitch pine to Al. In optimal nutrition solution medium, Hutchinson et al. (1986) and McCormick and Steiner (1978) observed high tolerance to Al of all six pine species. These results indicate that the strength of the nutrient solution must also be considered when setting critical toxicity values of Al within the same genus. Keltjens and Van Loenen (1989) observed very high tolerance of scots pine (no seedling mortality) at the highest Al treatment, *i.e.*, 1.1 m*M*, with sufficient supplies of nutrients. In the same experiment and also in a nutrient-rich medium, significant seedling mortality was witnessed for Douglas fir and larch at 0.55 m*M*, which would indicate a rather pronounced sensitivity to Al.

4.3.3 Aluminum Stress Indicators in Forests

It seems difficult to stipulate a general threshold value above which Al phytotoxicity appears since there are great differences in Al tolerance between species, and even between varieties of the same species. One approach to assess the toxicity of Al on plants is to cumulate the data available and produce a probability distribution of solution Al treatment levels at which significant effects on growth of tree species were first observed (Figure 4.2). Based on the results of this distribution analysis, we can define a value at which, for example, 10% of the studies on tree growth indicated adverse effects. In Figure 4.2, it can be observed, based on the data set of this literature review, that in 10% of the studies on growth of hardwoods there was a negative effect at a concentration of about 0.10 m*M* Al, whereas 50% of the studies on hardwood growth showed an effect at Al levels of 1.0 m*M*. For coniferous species, these values are about 0.05 m*M* and 0.30 m*M*, respectively. By lumping coniferous and harwood species together, we found that growth of 10% of tree species was negatively affected at 0.07 m*M* and 50% at 0.40 m*M*.

Ratios of Ca to Al in the soil solution change as the soil exchange complex and the soil solution react to atmospheric deposition of acidic compounds and other natural soil acidification processes. It is also known that Ca competes with Al and this gives rise to either Ca ameliorative effects on Al toxicity or Al antagonism of divalent cation uptake. Assessment of the potential plant damage from Al toxicity is therefore improved by using an indicator that integrates Al and Ca (e.g., Ca:Al molar ratio in the soil solution). Cronan and Grigal (1995) found that the Ca:Al molar ratios in the soil solution at which symptoms of toxicity appeared were in the range of 0.2 to 2.5. For example, solution culture experiments with red spruce indicated that plant growth or nutrient uptake was adversely affected at a solution Ca:Al molar ratio of 2.2 or less. Sverdrup and Warfvinge (1993) summarised data indicating the critical (Ca + Mg + K):Al molar ratio in the soil solution at which various species (trees, grass and herbs) experienced a 20% reduction in root growth and concluded that the critical (Ca + Mg + K):Al molar ratio for both coniferous and deciduous species was between 0.2 and 2.8. Based on the analysis of 36 data sets, Cronan and Grigal (1995) estimated that there is a 50% risk of adverse effects on trees when the soil solution Ca:Al molar ratio is equal or less than 1.0, whereas at 0.5 to 0.6, there is approximately 75% risk of growth declines or nutrient imbalances. At a Ca:Al molar ratio of 0.2, adverse effects are expected to manifest more than 95% of the time. The results of Ca:Al molar ratio from Cronan and Grigal (1995) are higher than our results for the same probabilities of adverse effects, probably because they included in their analysis studies which showed effects on nutrition (Figure 4.3). We found there is a 10% risk of adverse effects to occur on growth of hardwood species when the Ca:Al ratio is about 10.0, 50% risk of decrease in growth at 0.9 Ca:Al ratio, and 75% of probability if the Ca:Al ratio is close to 0.70. Adverse effects on growth of conifers is likely to occur at 1.3 Ca:Al ratio 10% of the time, 50% at 0.50, and 75% at 0.30. When conifers and hardwoods are mixed, the probabilities for adverse effects on growth are 6, 0.80, and 0.30, respectively. Adverse effects are expected to manifest 95% of the time at 0.07 Ca:Al ratio. The uncertainty associated with this probabilistic approach to assess critical solution Ca:Al molar ratios in the soil solution is that it 1) is largely based on seedling responses under controlled conditions with a mixture of more or less sensitive species studied under varying treatment conditions and 2) assumes that one can extrapolate from results with seedlings to mature trees growing under field conditions. Taking these unknowns into account and the limitations in weighting the evidence from the studies, Cronan and Grigal (1995) estimated the uncertainty to be ± 50%.

The activity of Al^{3+} can be modelled assuming equilibrium between Al in the solution and Al in the solid phase (i.e., microcrystalline gibbsite). The microcrystalline gibbsite solubility constant relates the activity of free Al^{3+} to pH using the relationship $[Al^{3+}] = K_g [H^+]^3$; where K_g is the solubility coefficient. In Figure 4.4, the LOAEC concentrations for tree species were plotted against the solubility curve of Al to assess if phytotoxic reponses are likely to occur in forest soils. If we accept the assumption that the amount of total dissolved Al is controlled by the precipitation of microcrystalline gibbsite, the pH values that correspond to the 50% LOAEC for both conifers and hardwoods is about 4.4 for forests. Most of the Al released into the soil solution by weathering of minerals would be bound to organic matter which makes dissolved Al unavailable to tree roots. We therefore conclude that Al toxicity is only likely to occur in the mineral soil when the pH is below 4.4.

4.4 Conclusion

The diversity of the methods and species used to assess the phytotoxicity of Al has led to difficulties in setting critical toxicity threshold values. The uncertainty associated with this exercise is that the database is largely seedling response studies where conditions were controlled (i.e., hydroponics). Thus, extrapolating the results from seedling studies to mature growing trees has limitations. Taking these limitations into consideration, we determined LOAEC values for Al concentrations in the soil solution where 10% and 50% of the studies on tree species show negative effects (0.07 m*M* and 0.37 m*M* of Al, respectively) as well as for Ca:Al molar ratios (5.0 and 0.82, respectively). Modelling the activity of Al in solution using microcrystalline gibbsite indicated that the 50% LOAEC for conifers and hardwoods would occur at about pH 4.4.

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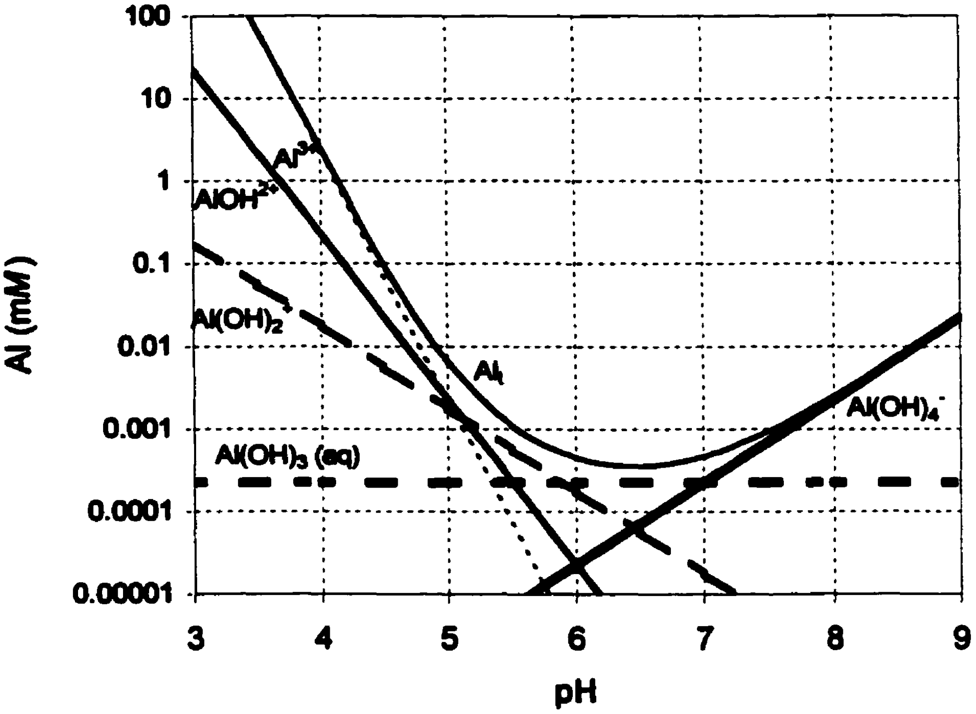

Figure 4.1 Solubility of Al species (and total Al) in relation with pH in a system in equilibrium with microcrystalline gibbsite (according to solubility constant from Lindsay, 1979).

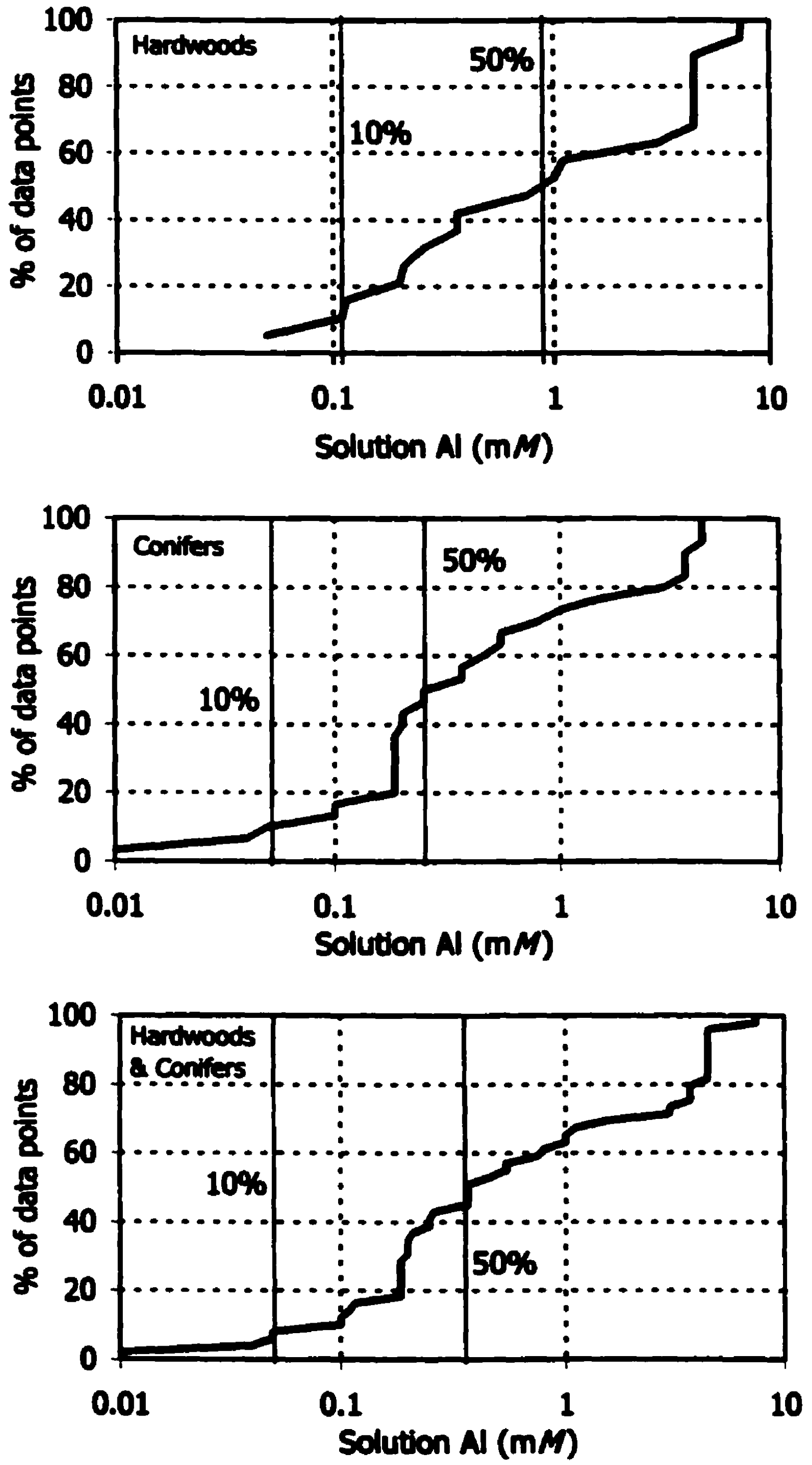

Figure 4.2. Cumulative probability distribution of solution Al treatment levels at which significant effects on growth of tree species were first observed. Data is from Tables 4.1 and 4.2.

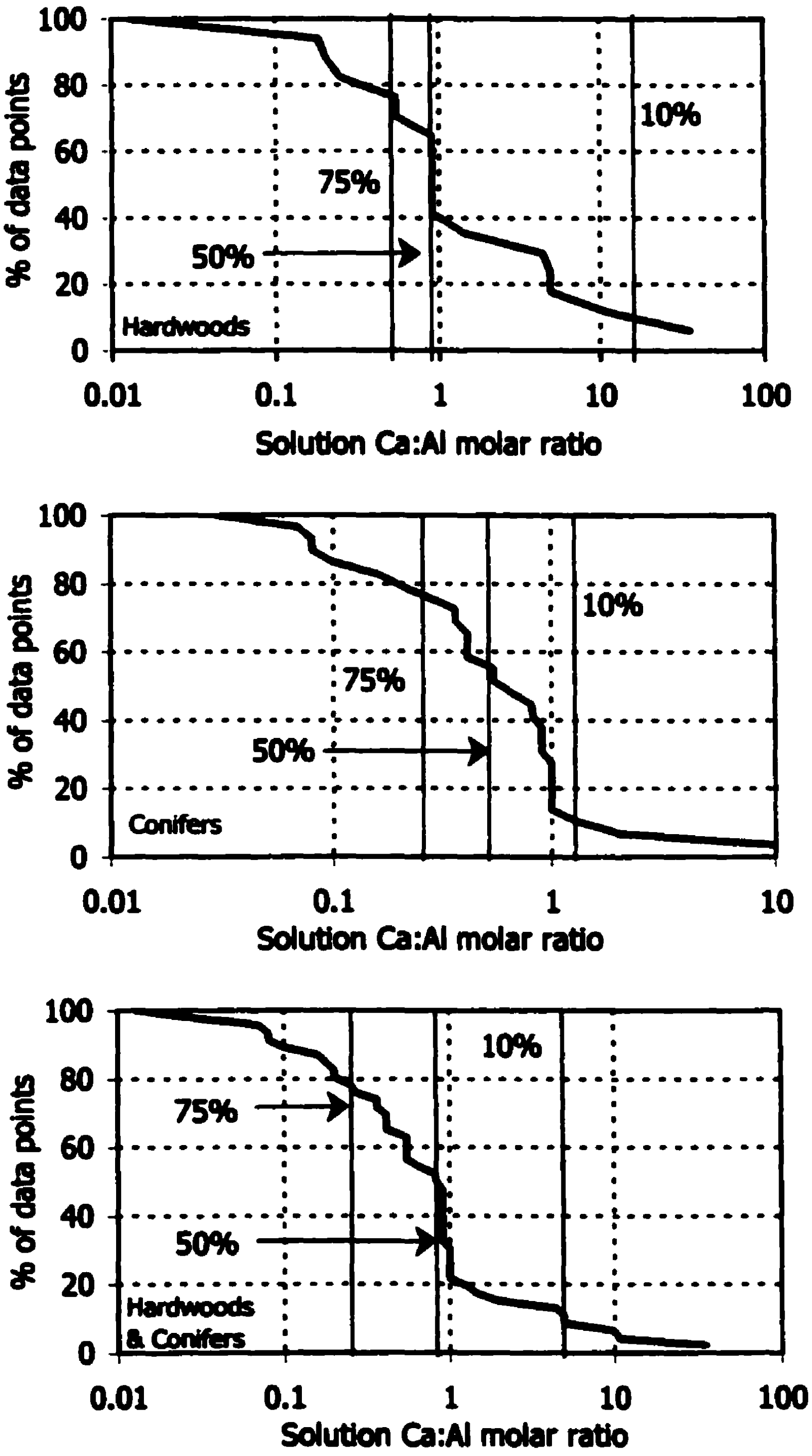

Figure 4.3. Cumulative probability distribution of solution Ca:Al ratio treatment levels at which significant effects on growth of tree species were first observed. Data is from Tables 4.1 and 4.2.

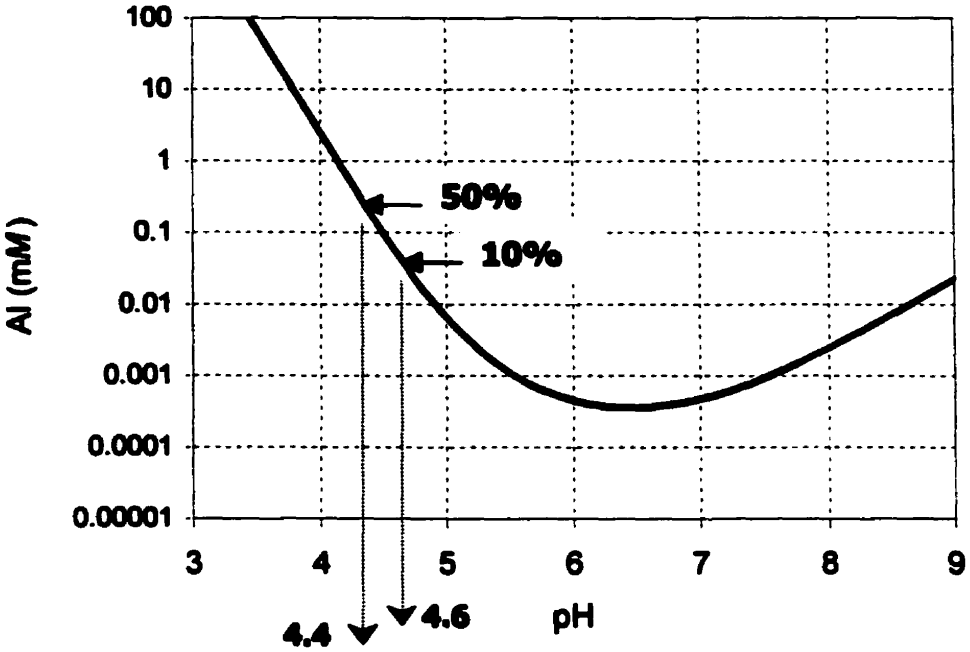

Figure 4.4 Concentrations leading to adverse growth effects in 10% and 50% of the studies on tree species plotted against the solubility curve of Al_t vs pH.

Table 4.1 Lowest statistically significant adverse effects concentrations for aluminum for hardwood species.

Species	Solution Al (m*M*)	Solution Ca:Al ratio	Effect	pH	Exposure time	Type of culture	Reference
Acer saccharum Marsh. (Sugar maple)	1.0	0.25	• Leaf and stem growth	4.0	45 days	Solution	Thornton et al., 1986a
Betula alleghaniensis Britton (Yellow birch)	3.0	Not available	• Root and leaf growth	4.5	60 days	Solution	Hoyle, 1971
	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
Betula papyrifera Marsh. (Paper birch)	4.45	0.9	• Root elongation	3.8	14 days	Solution	Steiner et al., 1980
	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
Betula populifolia Marsh. (Grey birch)	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
Betula pendula Roth. (European birch)	0.2	Not available	• Plant and root weight (under P deficiency)	4.48	15, 29 or 42 days	Sand	Clegg and Gobran, 1995
Quercus rubra L. (Red oak)	7.4	0.54	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
	0.75	0.013	• Root elongation	3.8	63 days	Solution	Kruger and Sucoff, 1989
	0.115	4.48	• Tap root and total root growth	4.5	10 weeks	Soil	DeWald et al., 1990
Quercus robur (English oak)	1.1	0.18	• No seedling mortality	3.8	150 days	Solution	Keltjens and Van Loenen, 1989
Quercus palustris Muenchh. (Pin oak)	7.4	0.54	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978

Table 4.1 (con't) Lowest statistically significant adverse effects concentrations for aluminum for hardwood species.

Species	**Solution Al (m*M*)**	**Solution Ca:Al ratio**	**Effect**	**pH**	**Exposure time**	**Type of culture**	**Reference**
Populus maximowiczii X *trichocarpa* Schreiner and Stout, clone NE-388 (Hybrid poplar)	0.37	10.8	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
10 Populus hybrid clones (e.g., NE-318, NE-19)	0.11	36	• Root elongation	3.9	7 days	Solution	Steiner et al., 1984
Gleditsia triancanthos L. (Honeylocust)	0.21	5.05	• Root elongation, branching and biomass production	4.2	37 days	Soil	Wolfe and Joslin, 1989
	0.26	1.45	• Leaf mass and number	4.2	72 days	Soil	Sucoff et al., 1989
	0.05	5.0	• Root, shoot and leaf biomass (not root elongation)	4.0	35 days	Solution	Thornton et al., 1986b
Fagus sylvatica L. (European beech)	0.37	0.2	• Root elongation	3.8	14 days	Solution	Rost-Siebert, 1984
Alnus glutinosa (European black alder)	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978

Table 4.2 Lowest statistically significant adverse effects concentrations for aluminum for coniferous species.

Species	Solution Al (m*M*)	Solution Ca:Al ratio	Effect	pH	Exposure time	Type of culture	Reference
Abies balsamea (L.) Mill. (Balsam fir)	3.7	0.41	• Root elongation	3.8	32 days	Solution	Schier, 1985
Picea rubens Sarg. (Red spruce)	0.25	0.08-0.24	• Photosynthetic rate and water-use efficiency (N deficient cultures)	3.7	6-8 weeks	Sand	McCanny et al., 1995
	0.2	1.0	• Seedling growth (High N availability, which triggered P stress)	4.0	10 weeks	Sand	Cumming and Brown, 1994
	0.185	2.0	• Newly germinated seedling growth	3.8	13 weeks	Sand	Schier, 1996
	3.7	0.41	• Root elongation	3.8	32 days	Solution	Schier, 1985
	0.25	1.0	• Root growth	4.0	35 days	Solution	Thornton et al., 1987
	0.185	0.54-2.2	• Root and shoot growth	3.8	70-98 days	Sand	Hutchinson et al., 1986
	3.7	0.41	• Root diameter	3.8	37 days	Solution	McQuattie and Schier, 1990
Picea glauca (Moench) Voss (White spruce)	0.05	0.2	• Root elongation and biomass	4.5	15 days	Solution	Nosko et al., 1988
	0.01	1.0	• Root elongation	3.5-4.5	7 days	Solution	Nosko and Kershaw, 1992
	0.185	0.54-2.2	• Root and shoot growth	3.8	70-98d	Sand	Hutchinson et al., 1986
Picea mariana (Mill.) BSP. (Black spruce)	0.37	0.27-1.1	• Root and shoot growth	3.8	70-98d	Sand	Hutchinson et al., 1986

Table 4.2 (cont.) Lowest statistically significant adverse effects concentrations for aluminum for coniferous species.

Species	Solution Al (m*M*)	Solution Ca:Al ratio	Effect	pH	Exposure time	Type of culture	Reference
Picea abies (L.) Karst. (Norway spruce)	0.04	1.0	• Root elongation	3.8	14 days	Solution	Rost-Siebert, 1984
	0.2	0.65	• Root growth	3.9	10 weeks	Sand	Hentschel et al., 1993
	0.1	1.3	• Root elongation	4.0-5.0	7 weeks	Solution	Godbold et al., 1995
	0.8	0.16	• Root elongation	3.8	35 days	Solution	Godbold et al., 1988
	1.0	0.1	• Root growth	4.2	9 weeks in sand & 3 days in solution	Sand & solution	Asp et al., 1988
	0.185	0.81	• Seedling growth	3.8	169 days	Sand	Ilvesniemi, 1992
Pinus strobus L. (White pine)	2.96	0.03-0.13	• Total growth	3.8	70-98 days	Sand	Hutchinson et al., 1986
	0.46	0.82	• Root & shoot growth	3.8	12 weeks	Sand	Schier and McQuattie, 1995
Pinus rigida Mill. (Pitch pine)	0.1	10	• Root and shoot growth	4.0	35 days	Sand	Cumming and Weinstein, 1990
	0.37	1.0	• Root & shoot growth	3.8	66 days	Sand	Schier and McQuattie, 1996
	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978

Table 4.2 (cont.) Lowest statistically significant adverse effects concentrations for aluminum for coniferous species.

Species	Solution Al (m*M*)	Solution Ca:Al ratio	Effect	pH	Exposure time	Type of culture	Reference
Pinus banksiana Lamb. (Jack pine)	1.5	0.07-0.27	• Root and shoot growth	3.8	70-98 days	Sand	Hutchinson et al., 1986
Pinus staeda L. (Loblolly pine)	0.185	Not available (no nutrient added)	• Root production	3.5	24 days	Sand	Paganelli et al., 1987
Pinus virgiana Mill. (Virginia pine)	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
Pinus sylvestris (Scots pine)	4.45	0.9	• Root elongation	3.8	7 days	Solution	McCormick and Steiner, 1978
	0.185	0.081	• Shoot growth	3.8	169 days	Sand	Ilvesniemi, 1992
Pseudotsuga menziesii (Mirb.) Franco (Douglas fir)	0.55	0.36	• Seedling mortality	3.8	150 days	Solution	Keltjens and Van Loenen, 1989
Larix decidua (Larch)	0.55	0.36	• Seedling mortality	3.8	150 days	Solution	Keltjens and Van Loenen, 1989

GENERAL CONCLUSIONS AND FUTURE RESEARCH

Dilute H_2SO_4 and HNO_3 solutions brought into ecosystems by precipitation have acidified forest soil environments since the onset of industrialization. Recent decreases in H_2SO_4 loading from the atmosphere in northeastern North America did not have the expected beneficial effect on the acid-base status of forest soils. In fact, many soils, streams, and lakes in northeastern North America have not recovered from acidification as strong declines in base cation concentrations in soil solutions and surface waters have exceeded the decrease in SO_4^{2-} concentrations. Moreover, NH_3 emissions are increasing in most parts of the world. An excess of N in forest soils could mean higher levels of H^+ in the solution and further removal of base cations from the soil environment through leaching losses. In commercial forests, harvest removes permanently base cations from the soil-plant ecosystem, resulting in a permanent loss of soil alkalinity. Therefore, the combination of acidic deposition and intensification of forest operations (whole-tree harvest vs. stem wood harvest) may cause cation nutrient deficiencies that could lead to the decline of coniferous and deciduous stands in northeastern North America. In recent years, soil chemistry and nutrition studies have not entirely succeeded in linking the decline of forests of northeastern North America with atmospheric loading of strong acids. The objective of this thesis was to validate the dynamic model SAFE (Soil Acidification in Forested Ecosystems) in a small deciduous forest of southern Quebec so that the model could be used to: 1) identify which processes are governing acidification, and 2) assess the rates of acidification according to various forest conditions. This thesis was composed of four chapters which were all necessary steps leading to the validation of SAFE and determining the fate of deciduous forests in northeastern North America:

Chapter 1 - Soil and soil solution chemistry between burned and unburned zones following fire disturbance seventy-five years ago was examined within the stand. The forest floor and mineral soil of the burned and unburned sections and soil solutions were sampled periodically from 1993 to 1997 and analysed for basic chemistry. Results show two major, statistically significant, differences: 1) higher base status, and 2) lower soil solution N in the burned zone. High quality leaf litter of aspen and birch (burned zone) relative to that of maple (unburned zone) has contributed to the enrichment of base cations in the forest floor. The enrichment of the forest floor did not impoverish the B horizon as seen in other studies. Rather, fire enriched the soil in base cations and buffered the effect of forest regrowth in the B horizon. It is hypothesized that lower N mobility in the burned zone is caused by greater mycorrhizal fungi activity.

Chapter 2 - The MAKEDEP model was used to reconstruct the time-series input files needed to run the SAFE model. In MAKEDEP, the availability of N determines tree growth which in turn, affects most of the processes involved in nutrient cycling. In that respect, we have assessed the model sensitivity (i.e., reconstructed tree growth and cycling processes) to N availability at the study site under burned and unburned conditions and in turn, calculated the N leaching rates as the residual component of all processes acting as sources and sinks of N. The scenario that added 10 $mmol_c$ NH_4 m^{-2} yr^{-1} through biological N fixation and dry deposition minus denitrification recreated N leaching rates at the study site with the most precision. Adding N to the model was also necessary for: 1) the trees to grow to what was measured in the unburned and burned zones, and 2) not to underestimate cycling processes such as canopy exchange and litterfall. Further, the slopes of the regressions of measured deposition at the Hubbard Brook Experimental Forest, New Hampshire, and simulated deposition at the study site suggest that MAKEDEP is a suitable approach to model the deposition trends of major elements with the exception of Na. We needed however to modify the standard curves of emissions in MAKEDEP (originally european curves of emissions) so that they would reflect the northeastern North American scenario to obtain a better fit with the measured trends.

Chapter 3 - The SAFE model was calibrated under burned and unburned conditions at the study site. Within the site, factors driving soil formation are very similar (e.g., parent material, slope, climate, etc.). Fire disturbance and forest regrowth have however produced a different soil chemical composition which was used to validate SAFE. One way we have validated SAFE was to see whether it could reproduce the current differences in soil chemistry between the zones due to differences in site history, i.e., fire disturbance. A second approach for model validation was to verify if SAFE could reproduce similar pre-industrial steady-state soil chemistry between the zones as the site history was assumed to be the same prior to fire disturbance. The simulated soil chemistry was in close agreement with the measured unburned soil conditions, but some processes would have to be clarified or accounted for with greater accurately, e.g., biological N fixation and N immobilization by myccorhizal fungi, to reproduce more accurately the measured burned soil chemistry. Further, the assumption that pre-industrial soil chemistry yielded by SAFE would be similar could not be validated since some processes in the burned zone were poorly modelled and/or pre-industrial soil forming factors may have not been similar as believed. Simulated soil chemistry using the SAFE model reinforced the conclusions of a few historical soil chemistry studies which support the hypothesis that acid-sensitive forest sites of northeastern United States underwent a significant change during 1930-1980. Most of the loss of exchangeable base cations was believed to be caused by inputs of strong acids from the atmosphere. Model projections in the mineral soil suggest that a new steady-state should be reached in the 21st century using the best-case scenario of N deposition and assuming no harvest into the next century. A harvest in 2020 (unevenaged management or a clear-cut with on-site lopping) could create unstable conditions which leads to further acidification and impoverishment of the soil's base cation reserve in the mineral soil.

Chapter 4 - The aim of this chapter was to provide a review of the scientific literature on the toxicity of Al to trees so that critical toxicity values are identified for both coniferous and deciduous tree species. In this review on LOAEC values, a number of studies were eliminated if the plants were grown in solutions with less than 0.05 m*M* Ca concentrations in solution. This value is considered to be the minimum that can be expected based on studies in forest soils in eastern Canada or northeastern USA. Studies that only demonstrated a decrease in nutrient uptake were also not considered to show an adverse effect if this was not accompanied by a decrease in growth. We found in 10% of the studies on coniferous and deciduous tree species that there was a negative effect at a concentration of 0.07 m*M* Al, whereas 50% of the studies showed an effect at Al levels of 0.4 m*M*. Also, we found that there was a 10% risk of adverse effects to occur on tree species when the Ca:Al ratio was 4.0 and a 50% risk of decrease in nutrition or growth at 0.8. If we accept the assumption that the amount of total dissolved Al is controlled by the precipitation of microcrystalline gibbsite, the pH values that correspond to the 50% LOAEC is about 4.4 for forests. Most of the Al released into the soil solution by weathering of minerals would be bound to organic matter which makes dissolved Al unavailable to tree roots. We therefore conclude that Al toxicity is only likely to occur in the mineral soil when the pH is below 4.4, but projections of pH into the 21st century using SAFE suggests that Al phytotoxicity is unlikely to occur in the future.

It seems that at the present stage of model development, the combination of MAKEDEP and SAFE to simulate soil chemistry does not provide output data accurate enough to give site-specific forecasts on nutrient availability. Some processes are either simplified or poorly assessed. For example, there are errors associated with determining key physical and mineralogical properties which may lead to inaccurracies in simulated weathering rates. Similarly, methods for determining dry deposition are still being improved which creates uncertainties about the rates of input we have used in this SAFE application. Also, the microbial community could influence N mobility in the soil profile which, in turn, affects the acid-base status of the soil, but this is not included in any way in MAKEDEP or SAFE.

The simplified approach used to calculate the various cycling processes as well as the lack of precision in the input parameters therefore created uncertainty about simulating soil chemistry for site-specific conditions. However, if this is the goal of a modeller, we suggest the following for future research:

1- A study that would look at the microflora population along the N saturation gradient of burned stands vs unburned stands would help to determine the role of fire on the soil's overall N status and microflora. Once the contribution of the microbial community to N immobilization as been assessed, then the modeller can provide changes in the schematic description of SAFE so that simulated soil chemistry will likely be in better agreement with the measured soil data;

2- Most of the scientific literature on dry deposition is either for coniferous tree species often at high elevation sites or other hardwoods than maple, birch, and aspen. Dry deposition is a function of leaf surface area, but this parameter varies significantly among tree species (coniferous vs deciduous and within hardwoods). If the goal of the modeller is to simulate soil chemistry between maple, birch, and aspen, we therefore suggests to improve the knowledge about dry deposition for these specific tree species using the currently available techniques.

We strongly believe that MAKEDEP and SAFE would be more useful if they were applied at the regional scale rather than for specific sites. SAFE could give a generalized forecast of soil chemistry and nutrient availability. This could be done for various forest sites in Quebec where species composition, stand age, parent material, soil fertility, and future harvest operations vary. By doing so, SAFE would offer an indication of the ability of a forest soil to supply cation nutrient for optimum growth, e.g., applications of SAFE for fast growing tree species (Norway spruce or Japanese larch) and slower growing species (black spruce and balsam fir). This would be an improvement to all the critical loads simulation work (steady-state models) that was conducted recently in the sense that the dynamic modelling approach would provide valuable forecasts to foresters including projected harvest operations. But before doing so, we suggest the following approach to fulfil model parameterization:

1- Use the provincial or state deposition monitoring programs as a basis for fluxes of major elements in deposition;

2- Develop a method for estimating throughfall fluxes for the various tree genera based on deposition data;

3- Assemble general equations to assess growth, nutrient contents, and uptake rates for the different tree components including roots;

4- Provide ranges of fluxes for litterfall, mineralization in the forest floor and mineral soil, and net mineralization during and after forest disturbance;

5- Establish a method to determine the distribution of nutrient uptake along the soil profile based on rooting distribution and mineralization rates.

Assessing cycling processes in such fashion is important for the application of SAFE at the regional scale as the same set of assumptions will always be applied for simulating the long term changes in soil chemistry. This will help avoid serious errors in model output which may go unnoticed if the time-series files used to run SAFE is adjusted unreasonably to obtain reasonable output.