Modelling Chemical Weathering in Different Scales

by

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Doctoral Thesis

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To Anna,
Herman & Hanna
THE ONLY GOAL IS IN THE PROCESS, THE PROCESS IS THE THING........

from JEFF BUCKLEY
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Appendices

This thesis is based on the following papers which are referred to by their Roman numerals.


Related papers

The author has also been involved in the following papers and reports, which are only briefly mentioned and not included in this thesis.


1 Prologue

This thesis is the result of more than five years of interdisciplinary research on chemical weathering. I have studied the importance and some use of chemical weathering in forest and agricultural management assessments. Another important aim was to show how chemical weathering can be used for assessing sustainability in forestry and for calculating sustainable biomass production. At the same time I have endeavoured to identify the pitfalls associated with the various techniques used and to highlight the uncertainties connected with these kinds of estimations. The aim was not only to provide answers to scientific questions or to test hypotheses, it was also to put forward new questions and identify new interesting research areas for the future. An important aspect of adapting a systems view to the necessity of synthesizing information from different sciences. A significant part of this research was to collect information from relevant disciplines and use this information in a new context. To do this work successfully, collaboration with scientists from different universities, faculties and institutions was a prerequisite. Another important part of this thesis is a discussion about the concept of biogeochemical models and the model framework. The work was carried out with the aim of benefiting both model development and managers of forest- and agro- ecosystems. The measure of success is if the model and related data have the ability to capture the characteristics of whole system in a field situation in a way that is applicable and reliable.

The target audience was first and foremost forest and agricultural managers, and researchers working with questions related to elemental balance and circulation in soil, spatial distribution of geochemical properties and sustainable biomass production.

Johan Holmqvist

Lund, October 16th 2001
2 Why chemical weathering?

That one might read the book of fate
And see the revolution of the times
Make mountains level, and the Continent,
Weary of solid firmness, melt itself
Into the sea.

William Shakespeare
(Henry IV Part 2, Act III, Scene I)

Chemical weathering\(^1\) is one of the most important processes supporting life on Earth. Together with solar radiation and the hydrological cycle, weathering is fundamental to most biological production system. Chemical weathering continuously contributes macronutrients such as Ca, K, Mg and P, as well as micronutrients such as B, Cu, Fe and Cr, to the soil solution. These recycling, essential elements are used as building blocks for all organic living matter.

Chemical weathering is a vital factor in the analysis and understanding of a large number of important environmental issues, acidification and nutrient cycling in managed forests and agro-ecosystems. Chemical weathering of soils and rocks is also the only self-repair mechanism for acidified ecosystems. Furthermore, weathering of parent material and the bedrock also strongly influences soil formation (Jenny 1941) and groundwater quality. Chemical weathering is important on a global scale for the geochemical carbon cycle which, on a time scale of \(10^5\) years, influences atmospheric CO\(_2\) concentration, and thus has a profound effect on the climate on Earth (Volk 1987, Berner 1992, Berner 1995).

However, our knowledge and understanding of the weathering processes appears incomplete compared to our knowledge of other scientific disciplines concerning ecosystem productivity. There are still a wide range of different issues and problems regarding chemical weathering of which the scientific community has limited knowledge and these need to be further investigated. Examples are the spatial variability of chemical weathering in a defined area and kinetic reaction coefficients of some soil minerals. Some of the important questions regarding weathering rate concern how to interpret and use the results from experimental studies in different environmental contexts and in the management of forest and agricultural systems. However, the quantification of the weathering rate in the laboratory cannot be used directly in calculating the weathering rate on a local, catchment or regional scale due to: 1) the heterogeneity and the complexity of the natural systems and 2) the complex task of converting a rate under laboratory conditions to another corresponding rate under only partly known field conditions.

\(^1\)Chemical weathering is defined as the release of elements due to chemical dissolution and transformation of specific minerals in the soil matrix and the bedrock, and the changes in the alkalinity or acidity in the soil solution connected to this process.
One way to put into practice the results from dissolution experiments in estimating and quantifying weathering rates is by using process-orientated and statistical mathematical models.
3 Objectives and scope of this thesis

The main thread in this thesis is to give the readers a background and an understanding of how chemical weathering can be an important process in nutrient budgets and sustainable biomass production.

The thesis work did not focus on developing new hypotheses about the theory behind the kinetics of mineral dissolution, nor did it aim to develop new principles about dissolution mechanisms for those minerals included in the investigation.

The work is a part of a broader research theme where the objective is to provide recommendations and guidelines towards a sustainable forestry in southern Sweden. This work forms a vital link in the process of making a useful model that could be distributed and used by foresters, landowners and authorities to estimate the sustainable yield in a defined forested area.

The main research objectives forming the basis of this thesis were to:

1. Improve the numerical estimations of the reaction coefficients in the mathematical biogeochemical soil model PROFILE (Warfvinge and Sverdrup 1992, Warfvinge and Sverdrup 1995, Sverdrup and Warfvinge 1995) by dissolution experiments of epidote and clay-size soil minerals,

2. Use the PROFILE model to estimate the potential potassium weathering rate in agricultural soils/systems and to assess the contribution of potassium weathering to mass balances and field budgets in agricultural systems and forest ecosystems

3. Investigate if and how the chemical weathering rate can be spatially distributed in a local scale (1000-5000 ha), and finally,

4. Develop a technique to estimate the weathering-related limits for regional sustainable biomass production in a forested area in southern Sweden.
4 Developing a model framework

The main objectives behind the development and uses of models are often to:

1. Organize, structure, summarize and interpret knowledge about a given system in such a way that it become useful for an audience that has interests about the system,

2. Be able to reconstruct the past, explain the present and test the hypothesis and

3. Predict future scenarios of defined systems and develop new designs.

4.1 Model development with a system dynamic perspective

The model development performed in this work should not be regarded as an isolated activity. The development of the model should be seen as a development of a whole model framework in which testing and validation of the model are only one part in a interrelated and linked process. It is important for the learning process of understanding the model system and for further research in chemical weathering that laboratory experiments are connected to model development. If the intention is to improve the estimates of chemical weathering rates in the field, results from experiments in laboratory and field can be merged with the results from model scenarios and model development. How this could be accomplished and implemented is visualized in a causal loop diagram (CLD) in Figure 1.

This causal loop diagram starts with Define problem (1) and an understanding of which questions should be answered. The next step in the development process is to propose a strategy to develop a model. From Define problem the work with developing the model framework moves on to Model development (2). Between the Model development and Test the model (3) stages is the mathematical computer model, in this case the biogeochemical model PROFILE. It is important to stress that PROFILE is only one part of the model system. PROFILE is only a result of the functions and the reaction coefficients and constants of these functions.

The refinement and testing of the model result in an increased understanding and a acquisition of knowledge, Test the model (3) to Learn (4) in Figure 1. New experiences and knowledge result in the design of new experiments which produce more data. The process of model development moves from Design experiments (5) to Data from experiments (6) and Data (7). New Data (7) makes it possible to Test the model (8) with new experiences and new data which gives more experience for Learn (9). The use of the model results in increased understanding and subsequently in modifying and enhancing of the model system. This reinforced loop, Model development to Test the model to Learn can continue for several laps before conclusions of the results are drawn, Conclude and report. The final step is the use of the developed model in the model framework and its testing in practice by an end-user, Practical / Operational use of the system. Eventually, the use of
4.2 The complexity of modelling

One of the most intriguing parts of model development is finding the right balance between simplicity and complexity in model design (Figure 2). A simplistic model
4.3 Validation process or “Test the model”

An important aspect regarding modelling of field scale weathering is the validation process. The validation process, as it is used in this work, is testing the model on another independent data set, to establish procedures for the comprehensive evaluation of the modelled results and to evaluate the quality of the model. The validation used in our studies can be divided into different levels shown in Figure 3. The first level in the validation process is to test the model on individual sites with high resolution. If data with high precision and quality produce reliable results in the field then one can assume that the model is of sufficient quality to become useful for an end-user. The next level is to use or test the model on different geographical scales and to apply the model with regional data sets. The usefulness of the model on this scale is often determined by the precision and accuracy of the input data. The final level, the quality control and audit, is to validate the performance of the model on regionally predicted parameters that can be surveyed. Such field parameters could be soil pH, runoff ANC and the availability and storage of K, Ca and Mg in soil.

4.4 A road map to the thesis

The main final specific questions that were the driving force for developing the model system were two-fold, and are related to the main objectives on page 4.
1. Estimate mineral nutrient budgets and mass balances in agricultural and forest ecosystems,

2. Estimate sustainable biomass production in forest ecosystems.

To work on these questions and to find reasonable solutions to them, a road map was set up where the important parts were identified (Figure 4). Developing a model framework was an important step in the work of solving the problems defined. The next important step was the choice of model platform, where Use of PROFILE system was a natural choice. The biogeochemical soil model calculates Field weathering estimates. Determination of the field weathering rate in Forest ecosystem and in Agricultural system was chosen as a solution to tackle and solve the questions above. The Define problems and the work with estimating field weathering rates within the model framework resulted in dissolution experiments being conducted to find important missing kinetic information about epidote and clay-size soil minerals (Paper I and III). This step can be seen as an application of the model framework in CLD (Figure 1), and is described by the route Define problem to Model development to Test the model to Learn to Design experiments and Data from experiments. This route resulted in a test of the model in eight different agricultural systems in northern Europe (Paper IV) which could be seen as movement from Test the model to Test the model to Learn to Conclude and report (Paper IV) in the CLD in Figure 1. The work can be seen as a result of the questions defined. The results from the work with the model and the associated model framework also highlight gaps in understanding and the demand for external knowledge and further improvement of the model.

Earlier work and development of the model system (Conclude and report in the CLD, Figure 1, Barkman et al. (1999) and Barkman and Alveteg (2001))
4.4 A road map to the thesis

Figure 4: Road map showing the principle working path of the thesis work and the connections between the different parts included in the thesis.

have resulted in new questions about using spatially distributed input data and the possibility of distributing the calculated weathering rate spatially in a defined forested area in Asa, southern Sweden (Paper V). This work with handling regional data and the results obtained made it possible to define a new problem, "Estimate sustainable biomass production" and develop a new model system to solve this question (Paper VI).
5 Modelling field weathering rate

The processes that control chemical weathering in a natural soil system are regulated and affected by several biotic and abiotic factors (Casey and Sposito 1992, Brady and Carrol 1994, White and Brantley 1995, White et al. 1999). These factors in turn depend on geology, climate, vegetation, topography and human activity (Figure 5). This complexity explains why modelling has become such an important tool in estimating weathering rates.

![Diagram showing factors affecting chemical weathering rate]

Figure 5: A simplified diagram showing a part of the complexity behind the constituents and factors that control and regulate the chemical weathering rate.

Chemical weathering is an important concept in e.g. the understanding and quantification of nutrient budgets and mass balances in different ecosystems. The complexity of the ecosystems and the chemical weathering processes is the reason why use of conceptual and mathematical models can be an important tool if a quantification of the chemical weathering is to be possible.

There are several important feedbacks between major constituents such as topography, climate, geology, human activities and nature (vegetation and micro-organism activity), in the chemical weathering process (Figure 5). Several of these constituents are dynamic, change with time, have different distributions in
time and space, and have different impacts on the chemical weathering rate. The variability and interactions between these constituents result in a complexity that is difficult to structure without a systematic tool that has the capability to organize the constituents in the chemical weathering processes and the feedbacks between them. Furthermore, if the aim is to quantify interrelated chemical weathering processes to a chemical weathering rate, then a mathematical model would be an useful tool to achieve this aim.

5.1 The biogeochemical steady state model PROFILE

PROFILE is a process-oriented steady state model originally designed to calculate the effect of soil acidification caused by acid rain and to calculate weathering rates of base cations and steady state soil conditions for a given set of input parameters (Warfvinge and Sverdrup 1995, Sverdrup and Warfvinge 1995). The definition of steady state\(^2\) implies no change in the composition of the ion exchange complex or any other variable with time. In the biogeochemical soil model PROFILE

![Diagram](image)

Figure 6: A schematic figure of the components and biogeochemical cycles that are built into the PROFILE model.

\(^2\)A description and definition of the concept steady state and how it is used in this thesis is shown in the definition box on page 15.
(Figure 6) the soil is stratified in a series of mixed compartments, where each compartment represents different soil layers. Each soil layer has an individual character and is assumed to be well mixed and with no internal chemical gradients. Soil stratification in PROFILE enhances structural reliability but involves increased data needs.

The main subsystems can be summarized as;

- Atmospheric deposition, fertilization, leaching and accumulation of dissolved chemical components
- Chemical weathering reactions of soil minerals
- Internal cycling of nitrogen and base cations in the vegetation, such as uptake by crop or tree, canopy exchange, litter fall and mineralization
- Solution equilibrium reactions involving the carbonate system, organic acids and speciation of aluminium

5.1.1 The chemical weathering submodel in PROFILE

The model PROFILE is designed to calculate the weathering rate on the basis of the data input and calculated steady state soil conditions. The temperature dependency is included in the modelling of nitrification, denitrification and weathering. The chemical weathering of soil minerals is a function of the soil environment, for example different chemical variables such as hydrogen and cation concentration, and organic acids.

The conceptual model of the total weathering process that was used consistently in this work is presented by a causal loop diagram (Figure 7). The dissolution rate in Figure 7 is determined by the chemical hydrogen (H$^+$); water (H$_2$O); hydroxide (OH$^-$); carbon dioxide (CO$_2$) and organic acid (DOC) reaction at the mineral surface. All these reactions have a positive feedback on the dissolution rate for all primary silicate minerals. The breakdown of the mineral structure generates dissolution products, which consume hydrogen ions and thereby decrease the hydrogen concentration and the dissolution rate. The dissolution products, such as cations, also decrease the available activated surface complex and thereby act as a negative feedback on the dissolution rate. The principal equation that describes the feedback mechanisms above is detailed in Section 6. Another important component for all chemical reactions is the temperature, which has a direct positive feedback on the dissolution rate through the chemical reactions and by increasing the soil micro-organism activity. The temperature dependency is described by the apparent activation energy for all individual chemical reactions (Sverdrup 1990). Soil micro-organisms also have positive feedback on the dissolved organic carbon (DOC) and hydrogen concentrations. The mineral surface area has also a direct positive feedback on the dissolution rate. The active surface area, i.e. the surface area where the chemical reactions is active, is governed by the soil wetness (Equation 1).
Figure 7: Causal loop diagram of the chemical weathering process including the reactions and feedbacks. The dotted lines and the components written in italics represent processes that are not included or used in PROFILE. Plus signs indicate that the action reinforce the loop whereas minus signs indicate a balancing action.

As stated before, PROFILE is a multi-layer model and can thus be parameterised for all individual soil horizons (all the specific input data are presented in Paper IV). Therefore, PROFILE is regarded as quite parameter demanding and needs an extensive set of input data.

The input data for PROFILE may be subdivided into 6 groups and comprise in short:

Climatic parameters  Mean soil temperature, mean precipitation, mean runoff and percolation.
Atmospheric deposition Anions: $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{Cl}^-$. Cations $\text{NH}_4^+$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and $\text{K}^+$.
Stand characteristics  Base cations and nitrogen uptake, base cations and nitrogen in litter fall.
Mineral composition  Mineralogy.
Soil properties Exposed mineral surface area, moisture, bulk density and soil layer thickness.
Solution chemical parameters Carbon dioxide pressure, soil solution DOC, Al solubility.
The output, the chemical weathering rate, from the model is presented in various ways. The model presents the total release rate of base cations $\text{K}^+$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$. However, it also has the ability to calculate how much each mineral in the soil contributes of these base cations, and how much the different chemical reactions contribute to the weathering rate. These abilities and the performance of the PROFILE model provide the model user with the potential to understand and interpret the results in more detail. They also provide an opportunity to gain knowledge about quantitative controls of the chemical weathering rate.
The concept steady state

Steady state is a crucial and important concept, relevant to the kinetic studies and the theory behind the modelling discussed in this thesis. The term steady state is defined as a situation when no state variables of a system change with time. Such state variables include solute concentrations in a soil solution or in an aqueous dissolution system.

In closed systems, steady state often implies that the chemical reactions in that system have reached an equilibrium. In an open system, steady state does not necessarily imply chemical equilibrium, but rather that the sources of a species perfectly balance the sinks of that species.

One example of an open system is the flow-through experimental system (Figure 8) that was used in dissolution experiments with epidote (Paper I) and in several other water-rock studies, as introduced by Chou and Wollast (1984). This experimental design leads to the establishment, not of equilibrium, but of steady state for the solution composition (Lasaga 1998). The steady state mass balance equation for a species $i$ in an open system with a dissolution reaction can be expressed as:

$$0 = \frac{dN}{dt} = Q \cdot (C_{in} - C_{out}) + A \sum_{j} \nu_j x_j R_j$$

where $N$ is the number of moles of $i$ in the system (moles), $Q$ is the volumetric flow rate ($m^3 s^{-1}$), $C$ are concentrations (moles $m^{-3}$), $A$ is the surface area ($m^2 m^{-3}$), $x_i$ is the fraction of the surface area that can be attributed to a certain mineral, $\nu_j$ is the stoichiometric coefficient of $i$ in mineral $j$, and $R_j$ is the dissolution rate of mineral $j$ (moles $m^{-2} s^{-1}$). The magnitude of $R_j$ may be a function of the solute concentrations, such as pH and base cation concentrations.

The PROFILE model assumes steady state. Hence, the derivatives of all state variables with respect to time are zero. This also means that irreversible reactions such as chemical weathering proceed at constant rate, while the rate of reversible reactions, such as cation exchange is zero.

In field situations, a true steady state will never occur. For example, the temperature will vary, the water flux will not be absolutely constant. Furthermore, one assumption is that the composition of the weatherable matrix is constant. While this is almost true for short time scales, it is not true over periods of thousands of years. For a model user, the validity of the steady state assumption thus depends on the time scale of the question addressed with the model. For a real system, the output of the PROFILE model should be interpreted as the state towards which the system is drifting, and would reach only after infinite time has passed. The steady state will implicitly be related to a certain time perspective. This perspective is defined by the user of the model and the questions that should be answered by the model system.

![Figure 8: A schematic illustration of the flow-through set-up in the dissolution experiments.](image)
6 Experimental kinetics

One cornerstone of the weathering module inside the PROFILE model is the kinetic coefficients for the dissolution of different soil minerals. These kinetic coefficients have been estimated for all major silicate mineral groups e.g. (Sverdrup 1990, Sverdrup and Warvinge 1995) using both experiments and literature data. Later further compilations of reaction values have been made (Schott and Berner 1985, Blum and Stillings 1995, Brantley and Chen 1995, Pokrovsky and Schott 2000, Rosso and Rimstidt 2000, Acker and Bricker 1992, Nagy 1995, Kalinowski and Schweda 1996, Kalinowski et al. 1996, Taylor et al. 2000)\(^4\). However, the determined specific kinetic coefficients for each mineral are only valid in the specific environment where they were studied and therefore there are a lot of gaps in the kinetic coefficient list for each mineral.

6.1 Determination of the rate coefficients in PROFILE

The engine behind the calculations of the weathering rate in forest ecosystems and in agro-ecosystems, which is an extension of the theoretical expression (Sverdrup 1990, Sverdrup and Warvinge 1995) to field conditions, is the equation:

\[
R_W = \sum_{j=1}^{\text{minerals}} r_j \cdot A_W \cdot x_j \cdot \Theta \cdot Z
\]

where \(R_W\) is the weathering rate; \(A_W\) the exposed surface area of soil minerals \((\text{m}^2 \text{ m}^{-3})\); \(x_j\) the surface area fraction of soil mineral \(j\); \(r_j\) the reaction rate of mineral \(j\) \((\text{keq m}^{-2} \text{s}^{-1})\); \(\Theta\) the soil moisture saturation; and \(Z\) soil layer thickness \((\text{m})\) and where the total rate for the soil horizon is obtained by repeating the calculation for all minerals present.

In equation 1 \(r_j\) is the dissolution rate of the mineral. This \(r_j\) can be divided into five simultaneous reaction systems: The reaction with the hydrogen ion; water and with the hydroxide ion. The reaction with carbon dioxide; and the reaction with strongly complexing organic acids.

The total elemental release rate by the dissolution of the mineral is the sum of the rate of all parallel simultaneous reactions;

\[
r_j = r_{j, H^+} + r_{j, H_2O} + r_{j, OH^-} + r_{j, CO_2} + r_{j, Org}
\]

For each reaction included in equation 2, an expression based on transition state theory (Eyring 1935, Lasaga 1998) and modified to be used for evaluation of available laboratory experiments could be worked out (Sverdrup 1990, Sverdrup

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\(^4\)A comprehensive review of kinetic coefficients can be found in Sverdrup (1990) and White and Blum (1995)
6.1 Determination of the rate coefficients in PROFILE

and Warvigne 1995):

\[ r_j = k_{H^+}^E \cdot \frac{[H^+]^n}{([BC^{2+}] + C_{BC,H^+})^{2BC} \cdot (\Al^{3+}] + C_{Al,H^+})^{\nu Al} + \] (3)

\[ k_{H_2O}^E \cdot \frac{1}{([BC^{2+}] + C_{BC,H_2O})^{2BC} \cdot (\Al^{3+}] + C_{Al,H_2O})^{\nu Al} + \]

\[ k_{OH^-}^{E,org,acids} \cdot \frac{[OH^-]^n}{([BC^{2+}] + C_{BC,OH^-})^{\nu BC} \cdot (\Al^{3+}] + C_{Al,OH^-})^{\nu Al} + \]

\[ \sum_{i=1}^{n} k_{org}^E \cdot \frac{[R_i]^n}{(1 + K_{org}, [R_i]^n)} + k_{CO_2} \cdot f_{CO_2} \]

\(C\) in equation 3 is the concentration of base cations and aluminium ions at the surface of the mineral and is in theory variable with \(r_j\) and \([BC^{2+}],[\Al^{3+}]\) are the respective concentration of \(BC^{2+}\) and \(Al^{3+}\) in the bulk solution. \(k^E\) is the experimentally determined rate coefficient for the specific mineral, determined from the dissolution experiments (Paper I).

The expression that is used in the PROFILE model, based on concentrations instead of activities, is a simplification and modification of equation 3 due to historical reasons and for reasons of calculation stability (Sverdrup and Warvinge 1995):

\[ r_j = k_{H^+}^{PROFILE} \cdot \frac{[H^+]^n}{f_{H^+}} + k_{H_2O}^{PROFILE} \cdot \frac{k_{H_2O}^{PROFILE}}{f_{H_2O}} + k_{CO_2}^{PROFILE} \cdot \frac{[CO_2]^n}{f_{CO_2}} \] (4)

\[ k_{org}^{PROFILE} \cdot \frac{[R_i]^n}{f_{org}} \]

The retardation factors \(f\), as they are used and incorporated in PROFILE, are given by (Sverdrup and Warvinge 1995):

\[ f_H = (1 + \frac{[BC]}{C_{BC,H}})^{2BC} \cdot (1 + \frac{[Al^{3+}]}{C_{Al,H}})^{\nu Al}, \] (5)

\[ f_{OH} = (1 + \frac{[BC]}{C_{BC,OH}})^{2BC} \cdot (1 + \frac{[Al^{3+}]}{C_{Al,OH}})^{\nu Al}, \] (6)

\[ f_{H_2O} = (1 + \frac{[BC]}{C_{BC,H_2O}})^{2BC} \cdot (1 + \frac{[Al^{3+}]}{C_{Al,H_2O}})^{\nu Al}, \] (7)
\[ f_{\text{org}} = (1 + \frac{[R^-]}{C_R})^{0.5} \cdot (1 + \frac{[\text{Al}^{3+}]}{C_{\text{Al,H}}} )^{y_{\text{Al}}} \text{ and} \]

\[ f_{\text{CO}_2} = 1. \]  

To determine the kinetic coefficient for the different reactions that should be used in the PROFILE model the rate expression:

\[ r_{H^+} = k_{H^+}^{\text{PROFILE}} \cdot \frac{[\text{H}^+]^n}{(1 + \frac{[\text{BC}^{2+}]}{C_{BC}})^x \cdot (1 + \frac{[\text{Al}^{3+}]}{C_{\text{Al}}} )^y} \]  

is multiplied by \( C_{BC}^{x} \cdot C_{\text{Al}}^{y} \) to get:

\[ r_{H^+} = k_{H^+}^{\text{PROFILE}} \cdot \frac{[\text{H}^+]^n \cdot C_{BC}^{x} \cdot C_{\text{Al}}^{y}}{([\text{BC}] + C_{BC})^x \cdot ([\text{Al}^{3+}] + C_{\text{Al}})^y} \]  

by combining the hydrogen reaction in equation 3 with equation 11, the coefficient used in PROFILE can be derived by:

\[ k_{H^+}^{\text{PROFILE}} \cdot C_{BC}^{x} \cdot C_{\text{Al}}^{y} = k_{H^+}^{E} \]  

\[ k_{H^+}^{\text{PROFILE}} = k_{H^+}^{E} \cdot C_{BC}^{x-} \cdot C_{\text{Al}}^{y-} \]  

\[ -\log k_{H^+}^{\text{PROFILE}} = -\log k_{H^+}^{E} + x \cdot \log C_{BC} + y \cdot \log C_{\text{Al}} \]  

The notations of the equations are listed at the end of the thesis (Page 66).
6.2 Dissolution rate of epidote

Epidote is a mineral with a relatively high dissolution rate (Sverdrup 1990, Rose 1991) and it is also a mineral that can be found frequently in boreal and northern temporal forest soils. Epidote and other dark minerals are therefore among the main contributors to the flux of base cations (BC) such as Ca²⁺, Mg²⁺ and trace elements to the soil solution. An accurate estimation of the weathering rate of epidote is important for calculations of the resistance of soils to acid deposition (The critical load) (Nilsson and Grennfelt 1988, Holmqvist 1994). Therefore one goal was to determine the kinetic coefficient, for epidote in aqueous solutions (Paper I). This experimental study on epidote was motivated by the lack of studies regarding the retarding effect by base cation and aluminium concentrations on the dissolution rate.

The rate coefficients for epidote dissolution for the early versions of PROFILE were derived from literature data and experiments by Sverdrup (1990). However, the rate coefficients are uncertain and additional experiments are needed in order to improve the coefficient data base required by the weathering module inside PROFILE.

Heavy minerals normally only constitute 5-15% of the total mineral content in boreal and northern temporal forest soils. Nevertheless, some of the less investigated minerals are easily weathered and contribute significantly to the total amount of weathering products in low latitude forest soils (Sverdrup and Warfvinge 1988, Sverdrup 1990). Sverdrup and Warfvinge (1995) conclude that plagioclase, K-feldspar, hornblende and epidote account for 85% of the weathering observed in most soils of granitic origin. In the geochemical survey in Asa, South Sweden approximately 13% (equivalent to 1.3 Ca eq ha⁻¹ year⁻¹) of the total contribution of Ca could be attributed to epidote.
6.2.1 Methods

The experimental set-up used in the dissolution experiments was an in-house modification of the Chou and Wollast (1984) fluidized bed flow-through reactor (Figure 9). In addition, a batch technique was used in the experiments for determining the activation energy of epidote. The rate coefficients and the activation energy were determined from diagrams constructed from the experimental data.

Four batch experiments were carried out at pH 2 and at different temperatures. Fourteen flow-through experiments at different pH, temperature, Al\(^{3+}\) and Ca\(^{2+}\) concentration were performed to determine the reaction coefficients and reaction orders of the dissolution reaction of epidote (Table 1). The dissolution rate for all individual experiments was determined from diagrams at a time when the dissolution had reached an apparent steady state, after approximately 500 to 1500 hours. The techniques and methods used are described in Paper I.

![Fluidized bed flow-through reactor assembly](image)

Figure 9: Experimental set-up used for the dissolution experiments with epidote.

<table>
<thead>
<tr>
<th>pH</th>
<th>([H^+])</th>
<th>([Ca^{2+}]) (mol l(^{-1}))</th>
<th>([Al^{3+}]) (mol l(^{-1}))</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10(^{-6}) 10(^{-5}) 10(^{-4}) 10(^{-3}) 10(^{-2})</td>
<td>10(^{-4}) 10(^{-2})</td>
<td>23 33 63 83</td>
</tr>
<tr>
<td>2</td>
<td>2173</td>
<td>1248 1248 1294 1270 2041</td>
<td>1294 1053</td>
<td>1148 741 482 1063</td>
</tr>
<tr>
<td>3</td>
<td>355</td>
<td>2661 2235 2636</td>
<td>2249</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>337</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2 Dissolution rate of epidote

6.2.2 Results

The results from the dissolution experiments on epidote in aqueous solution, using batch and flow-through reactors, regarding rate coefficients for the hydrogen reaction were comparable and consistent with previous results (Nickel 1973, Rose 1991, Kalinowski et al. 1998) (Figure 10).

![Diagram showing stoichiometric dissolution of epidote at 23°C, in aqueous solution at pH 4. The diagram shows that time required to steady state in this experiment was ≈1200 hrs.](image)

The rate coefficients for the hydrogen, water and hydrogen reaction were determined from diagrams constructed from both original experimental data and other published dissolution rate data on epidote (Nickel 1973, Rose 1991, Kalinowski et al. 1998). The results are shown in Figure 11, which shows how the rate coefficients were determined. The modelled rate, which is the sum of the hydrogen, water and hydroxide reactions shown as the solid line was adapted to go through the experimental data. It is important to note that the coefficients can only be determined by constructing a modelled rates not by the individual straight line that represents only one reaction. However, this is something that never or seldom occurs in geochemical literature.

Dissolution experiments on feldspars (Chou and Wollast 1985, Schweda 1990, Sverdrup 1990) have shown that aluminium and base cation concentration have a retarding effect, $x_{BC}\approx0.4$ and $y_{Al}\approx0.2$ respectively, according to equation 5. In contrast to those studies, the present investigation could not establish significant effects on the dissolution rate by aluminum and base cation concentration (Paper 1).

Potential inhibitors are important as regards the dissolution rate of epidote and all other aluminium silicate minerals, and as regards the comparison between modelled catchment weathering rate studies and mass balance budget studies (Blum and Stillings 1995). If modelled weathering rate studies regarding flows of base cations in groundwater applications or in regional catchment studies are to be comparable with mass balance studies, inhibitors must be built-in to the
mathematical biogeochemical weathering rate models. It is most likely that some ions or bi- or multinuclear complexes or surface films act as inhibitors on the dissolution rate of epidote (Stumm and Morgan 1996). Further studies on ion strength, base cation and aluminium concentration and complexes that affect the dissolution rates are necessary to identify the role of possible inhibitors.

By using approximate estimates of $\chi_{BC}$ and $y_{Al^{3+}}$ in the H$^+$ reaction in Equation 15 it is possible to translate the experimentally determined rate coefficient for epidote to the rate coefficients used in PROFILE. The rate coefficients for the dissolution of epidote estimated and approximated by this work (Paper I) are shown in Table 2. $pk^{PROFILE}$ was estimated through field validation of PROFILE (Sverdrup et al. 1992) and was used in calculating the residual:

$$-\log k_{H^+}^{PROFILE} = -\log k_{H^+}^{E} + x \cdot \log C_{BC} + y \cdot \log C_{Al}$$

Thus, if any term is missing, this will show up as a residual:

$$Residual = pk_{H^+}^{PROFILE} - (x \cdot \log C_{BC} + y \cdot \log C_{Al})$$

By filling in the actual kinetic coefficients determined from diagrams in Paper I:

$$0.84 = 14.0 - (6.0 \cdot 0.01 + 5.5 \cdot 3.7)$$

$p k^E$, $n$, $p C_{Al}$ and $y_{Al}$ were experimentally determined in this study. $p C_{BC}$ and $\chi_{BC}$ were approximates from other studies on similar minerals (Sverdrup 1990) and from interpretation of the experimental data. Epidote is a mineral containing iron(II) and this ion may be involved in backward reaction.

The magnitude of the residual could be due to several factors such as: inhibition by iron; experimental errors in this study; long-term surface effects; and errors or misinterpretation in the field experiments.

### 6.2.3 Temperature dependence of rate constant

In any situation where reaction coefficients are used to calculate reaction rates, temperature is one of the most important variables. For example, rate constant is approximately changed by a factor of 2 for epidote, as the temperature is varied by 10°C. This implies that determination of the activation energy for the dissolution reaction of the minerals is important in estimating the weathering rates in different geographical regions with different temperatures.

The activation energy ($E_a = 64 kJ mol^{-1}$) determined in this study was slightly lower compared with the results ($E_a = 64 kJ mol^{-1}$) presented by Rose (1991) and the investigations on epidote at pH 1.4 (Figure 12). One possible explanation could be that our experiment was conducted at pH 2. This is consistent with our experiments at pH 4 and pH 6 which indicated that the activation energies changed with
6.2 Dissolution rate of epidote

Table 2: Experimental rate coefficients \( (k^E) \) and the rate coefficient \( (k^{PROFILE}) \) as used in PROFILE for the dissolution of epidote expressed as the flux of calcium. The weathering rate is expressed as \( k \) \( \text{eg} \) \( \text{m}^{-2} \text{s}^{-1} \) at 8°C and C is expressed as \( k \) \( \text{eg} \) \( \text{m}^{-3} \).

<table>
<thead>
<tr>
<th></th>
<th>( \rho ) ( k^{PROFILE} )</th>
<th>( \rho ) ( k^E )</th>
<th>( n )</th>
<th>( \rho C_{BC} )</th>
<th>( x_{BC} )</th>
<th>( \rho C_{AI} )</th>
<th>( y_{AI} )</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>14(4)</td>
<td>10.9(1)</td>
<td>0.62(1)</td>
<td>6.0(2)</td>
<td>0.01(2)</td>
<td>5.5(1)</td>
<td>0.4(1)</td>
<td>0,84(3)</td>
</tr>
<tr>
<td>PROFILE</td>
<td></td>
<td>11.75(5)</td>
<td>5.7(5)</td>
<td>0.2(5)</td>
<td>5.5(5)</td>
<td>3.7(5)</td>
<td>0.3(5)</td>
<td>0</td>
</tr>
</tbody>
</table>

1) Rate coefficients estimated by the experimental study presented in Paper I
2) Rate coefficients approximated by experimental study presented in Paper I
3) The residual is the difference between \( \rho \) \( k^{PROFILE} \) and the product of Equation 15 using the experimentally estimated rate coefficients
4) Present rate coefficients in the PROFILE model
5) Rate coefficient calculated by Equation 15 on page 22

pH. There were no significant differences in the activation energy with regard to the release rate of Si and Al at different temperatures (Paper I). This supports the theory that it is the same chemical reaction that governs the release of different base cations, independent of their position in the crystal lattice, even if different mechanisms may be involved for the different cations (Sverdrup 1990, Kalinowski et al. 1998). The different activation energies at different pH are to be expected according to Equation 2 and are caused by a shift in stoichiometry and in the reaction order of the rate-determining reaction (Sverdrup 1990, Sverdrup and Warvvinge 1995). At low pH the hydrogen reaction has a stronger impact, higher degree of protonation, on the overall dissolution reaction than the water and hydroxide reactions, whereas the opposite is true at pH 6.

The determined apparent activation energy values strengthen the hypothesis that the dissolution of epidote is surface controlled and not diffusion controlled. According to Lasaga (1984) and Glasstone et al. (1941), the activation energy for the dissolution rates controlled by diffusion ranges from 17 to 34 kJ mol\(^{-1}\).

6.2.4 Depleted mineral zones

The preliminary results from the dissolution experiments on epidote show incongruent dissolution when pH is changed in the experimental reactor (Figure 13). This incongruent dissolution is interpreted as formation of a leached layer or depletion of base cations at the mineral surface. Leached layer formation was recognized to be an important part of understanding earth-surface geochemical processes. Chou and Wollast (1985), Casey et al. (1988), Casey et al. (1989), Casey et al. (1993), Rimstidt (1993), Kalinowski et al. (1998), Weissbart and Rimstidt (2000) among others report formation of leached layers for different mineral groups. The observed initial incongruent dissolution is probably related to the differences in
the strength of the bonding in the mineral structure.

Weakly bonded cations are released to solution relatively quickly before it has reached a “new” steady-state. Leached layer formation has been put forward as one of the most important explanations for incongruent dissolution. Our findings according to dissolution experiments at different pH (Figure 13) suggest that the development of a mineral surface with a basic alumina-silicate structure goes through different steps before it reaches steady state conditions. These steps can take such a long time that evolution of depleted zones under natural conditions cannot always be neglected. The steps involve evolution of different zones (Figure 14) with different ratios of base cations/alumina-silicate.

In highly acid environments (solutions) the depleted zones or layers are more depleted of base cations and thicker than in more neutral environments. These depleted zones have a significant effect on the base cation release when the chemical environment is changing. If the surrounding environment changes from less to more acidic, the adjustment is comparatively fast (Figure 15). The reason for this is that the hydrogen ions, now in higher concentration, will attack the available base cation sites that were not exposed to such an extension before. The highly acidic solution has developed thick depleted mineral surface zones and when the environment is changing to less acidic, it will take a considerable amount of time before the depleted zones have been dissolved, and reached a new state. When the former “thick” depleted zones have been dissolved, the new steady state between the less acidic conditions and a thinner depleted zone is established and a new steady rate will be achieved. This mechanism at the mineral surface makes the system more inert to changes in the soil chemistry. The results suggest that the time is in the the order of 1,000-3,000 hours depending on direction of change and where in the pH range the change takes place.

The weathering mechanisms described above can have important implications for dynamic soil chemistry. The soil solution will only seldom reach a true steady state, but will change towards new final states as the conditions change through the seasons, years and decades. In this respect the soil solution composition reflects the outer environment and affects the reaction at the mineral surface. Therefore, this approach to chemical dissolution of alumina-silicate minerals can have an impact on the interpretation of how the release rate of base cations is affected by changes in the soil environment.
Figure 11: Test of the model against data. The straight dotted lines represent different models for the dissolution rate of epidote calculated from the release rate of Si (plot A) and Ca (plot B) for the ($H^+$), ($H_2O$) and ($OH^-$) reactions, at 23°C. The graph also shows a modelled rate, the solid line, which is the sum of the hydrogen, water and hydroxide reaction rates. Experimental data from this study are represented by •, previous studies are represented by (△) Kalinowski et al. (1998), (square) Rose (1991) and (◇) Nickel (1973) respectively (Paper I).
2.7 2.8 2.9 3 3.1 3.2 3.3 3.4

$-\ln \text{Rate (moles m}^{-2}\text{s}^{-1})$

$1/T(\text{K}) \times 1000$

$E_a (\text{pH 2, Si}) = 64.9 \text{kJ mol}^{-1}$

$E_a (\text{pH 4, Si}) = 63.8 \text{kJ mol}^{-1}$

$E_a (\text{pH 1.4, Rose}) = 83.7 \text{kJ mol}^{-1}$

Figure 12: $\ln$ dissolution rate of epidote as a function of reciprocal temperature ($^\circ\text{K}$), calculated from the Si and Al release. The data points span the temperature range 23$^\circ\text{C}$ to 83$^\circ\text{C}$ at pH 2, corresponding to 3.38 and 2.81 $1/T(\text{K}) \times 1000$. Dotted and solid lines represent regression calculations based on the data to yield the indicated apparent activation energies ($E_a$). Results from Rose (1991) on epidote dissolution experiments at different temperature at pH 1.4 are shown as ●.

Figure 13: The diagram shows dissolution of epidote, where the solution pH changed from pH 2 to pH 4. The base cation release rate decreases, but the release of silica continues. This shows that the transient phenomena described in the text consume the base cations internally in the material, at the same time as the structural lattice continues to decompose as a result of dissolution reactions. It may take several months before the mineral starts to approach the new steady state dissolution rate.
6.2 Dissolution rate of epidote

During dissolution, a steady-state situation builds up at the surface with an outer layer depleted of base cations, an intermediate layer partially leached, and the inner unchanged mineral core. The thicknesses of these layers are then controlled by the outer chemical conditions. Moving from acid solution to less acid, the completely leached layer decreases and the partly leached layer expands into the leached layer. These adjustments can only occur very slowly, and may for periods of time decrease the net base cation release most significantly.

---

Figure 14: During dissolution, a steady-state situation builds up at the surface with an outer layer depleted of base cations, an intermediate layer partially leached, and the inner unchanged mineral core. The thicknesses of these layers are then controlled by the outer chemical conditions. Moving from acid solution to less acid, the completely leached layer decreases and the partly leached layer expands into the leached layer. These adjustments can only occur very slowly, and may for periods of time decrease the net base cation release most significantly.

---

Figure 15: Moving from less acidic to more acidic solutions, the system usually adjusts to the new conditions relatively fast (A). The adjustment when the conditions move from acidic to less acidic conditions differs very much from the scenario described above and takes a considerably longer time before it has come to a new steady state (B).
Present agricultural management in western and northern Europe is based on optimisation of fertilizer management. Therefore understanding of nutrient budgets and circulation of nutrients in agro-ecosystems becomes a priority issue for agricultural managers and environmental authorities. The need for models with the ability to estimate the different pools in budget calculations has increased. The objective here was to develop a model that could estimate the base cation supply to the soil solution by chemical weathering of clay-size soil minerals and set it in relation to nutrient budgets and balances.

Agricultural soils normally imply clay minerals and altered primary sheet silicates, and any assessment models for such soils must attempt to calculate clay weathering rates. However, kinetic information on clay-size soil minerals so far is incomplete and partly of very low accuracy. Therefore more experimental studies on dissolution of clay-size soil minerals are needed to strengthen choice of coefficient values.

Using field experimental data to calibrate the weathering kinetic coefficient data base inside the PROFILE model could be a plausible strategy to enhance the accuracy and precision of estimating the weathering rate in agricultural soils. This should be done in an iterative process according to Figure 1 where the model is continuously developed and improved through experiences from field and laboratory experiments. According to the causal loop diagram (Figure 1) a model should be developed through several iterative cycles before it becomes applicable to an end-user of the model, i.e. a farmer or agricultural manager.

The strategy for continuing this iterative process for evolving a chemical clay weathering model was to identify the tasks that should be accomplished:

1. For an applied purpose a pragmatic simplification of clay mineral weathering should be developed where the model contains the most important features such as
   - main reactants and reactions
   - a simple product inhibition
   - dependence on wetting and mineral surface area
   - dependence on temperature

   but where details of less importance for field performance and overall accuracy are left out.

2. The weathering kinetics of clays must be brought into the context of other minerals and all the other chemically active processes in the soil.
3. The characterization of clay minerals needs to be adapted for weathering purposes. If the objective is release of cations, then this will be the parameter for creating new functional groups of clays, and this characterization scheme may differ totally from earlier schemes.

This procedure will involve simplification of existing knowledge and a selective choice of the most important features. The objective of selecting features that enhance the field performance of the model is a pre-requisite for the overall success of the model.

<table>
<thead>
<tr>
<th>Initial mineral</th>
<th>Pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotite</td>
<td>Triocahedral vermiculite/Intergrade vermiculite-chlorite</td>
</tr>
<tr>
<td>Muscovite</td>
<td>Illite1, Illite2, Illite3</td>
</tr>
<tr>
<td></td>
<td>Dioctahedral vermiculite, Diocahedral smectite, Kaolinite Halloysite</td>
</tr>
<tr>
<td>Feldspars</td>
<td>Sericite, Saussurite, Noncrystalline aluminosilicates</td>
</tr>
</tbody>
</table>

Figure 16: A simplified summary of the weathering pathways for the micas and the feldspars. We suggest that there are at least three major pathways determined by whether the starting point is 1) a trioctahedral biotite mica, 2) a dioctahedral muscovite type of mica or 3) a feldspar. The literature is not internally consistent with the definition of sericite, but we define it as the first alteration product of feldspar weathering.

7.1.1 Proposed mechanisms for dissolution of clay minerals

The most common minerals of Northern Europe that exist as precursors for the most abundant pedogenic clay minerals in soils can in principle be divided into four types, and hence four basic mineral lattice destruction rates can be calculated, based on (1) muscovite lattice going to illite, (2) biotite going to vermiculite, (3) feldspars going to sericite and (4) chlorite going to vermiculite (Figure 16). The base cation release rate is determined by the mineral lattice destruction rate and the stoichiometric content of base cations in the lattice. The kinetic coefficients can be determined by working with the alteration series, and empirical clay stoichiometries (Paper II). It is obvious that Figure 16 is a simplification of what...
is going on, but a large simplification was a necessity for arriving at an operable model concept.

The base cation release from clay minerals in soils is assumed to be controlled mainly by two factors. First, it is assumed that the weathering kinetics is determined by the basic alumina-silicate structure of the clay mineral; secondly, that the base cation release rate is determined by the amount of base cation released per unit basic lattice destroyed per unit time.

\[
BC \text{ release rate} = (Lattice \text{ destruction rate}) \times (Mineral \ BC \ content)
\]

We define the “lattice destruction rate” as the long-term decomposition rate of the most resistant lattice structure and we define “stoichiometry” as the elemental composition of the lattice. The lattice structure will be the same for many clays and will be based on the top member of the clay genesis series. Thus we will have a series of illites starting with muscovite, a serie of vermiculites and chlorites starting with biotite and a series of sericite and saussuritization starting with feldspars.

This initial work to develop a strategy for estimating weathering rate in agricultural soils in mid- and low-latitude regions should be seen as a first step in the learning process (Figure 1 on page 6). More work should be focused on how the dissolution rate of the primary sheet silicates is affected by a gradual alteration of clay minerals and how this can be formulated mathematically in existing chemical weathering models such as PROFILE. Differences in the physical and chemical soil properties of forest soils with low clay contents compared with fertilized agricultural soils with high clay contents should also be further investigated. The results from Paper II can be summarized as:

1. The PROFILE model framework and model structure described in Section 4 and 5 can be used as a platform for investigating different modelling strategies concerning the calculation of base cation release rate in clay-rich agricultural soils and

2. There is a need for practically applicable methods for characterizing clays in regional soil sampling, as well as a simple model for transforming survey data to quantitative soil primary and clay mineralogy.
7.2 Dissolution rate of clay size minerals

The knowledge about rate coefficients of secondary silicate minerals or altered sheet silicates and how the rate coefficients for several soil minerals are affected by high concentration of cations and different ligands is very limited (Huang and Keller 1972, Sverdrup and Warfvinge 1995, Nagy 1995, Kalinowski and Schweda 1996, Kalinowski et al. 1996). According to several studies in which the model PROFILE has been evaluated, there is a retarding/inhibition effect from base cations on the weathering rate. This phenomenon has also been shown in different laboratory experiments with feldspars (Chou 1985, Schweda 1990, Gautier et al. 1994, Oelkers et al. 1994, Stillings and Brantley 1995). The effect on the dissolution rate of sheet silicates of aluminium, silicon and cation concentration in laboratory experiments is difficult to interpret clearly (Nagy 1995). Different sheet silicate minerals show different responses in different environments and it is therefore impossible to draw any general conclusions regarding how sheet silicate weathering rate is affected by various ions in a soil solution. There are also technical difficulties that restrict the possibilities to determine the inhibition effect in aqueous solutions at natural pH in laboratory experiments due to the precision of the analytical instruments, water and buffer/gas quality.

In Paper III the specific objectives were to:

- Determine the dissolution rate for a clay-size soil mineral with a high content of illite,
- Estimate the influence of pH and base cation concentration on the dissolution rate and
- Estimate the activation energy for the dissolution reaction of clay-size mineral at pH 1.0 and 4.4.

7.2.1 Materials and methods

The material used in the dissolution experiments was fractionated from a bulk soil sample collected from a soil profile in an agricultural long-term field experiment, Kungsängen, located 70 km north of Stockholm, Sweden. The Kungsängen soil is developed on a postglacial sediment characterized by relatively high clay content (40-60%).

The procedure to estimate the mineralogical composition for the clay-size soil material (0.5-2 μm) was to:

1. Determine the elemental composition,
2. Qualitatively and semi-quantitatively determine the mineralogical composition by XRD and
3. Estimate the elemental composition and the quantitative mineralogical composition by a normalization model, and in addition determine the mineralogical composition by XRD.
The experimental series was conducted in a fluidized bed flow-through reactor similar to that used in the dissolution experiment of epidote (Figure 9). The experimental conditions and the duration of each experiment is shown in Table 3.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Soil horizon</th>
<th>Eluent (M)</th>
<th>pH out min</th>
<th>pH out max</th>
<th>Duration (h)</th>
<th>Temp. (°C)</th>
<th>BET Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kung11a</td>
<td>C</td>
<td>10⁻⁵ HCl</td>
<td>4.29</td>
<td>4.87</td>
<td>4460</td>
<td>23</td>
<td>10.5</td>
</tr>
<tr>
<td>Kung11b</td>
<td>C</td>
<td>10⁻² HCl</td>
<td>2.13</td>
<td>2.79</td>
<td>4010</td>
<td>23</td>
<td>10.5</td>
</tr>
<tr>
<td>Kung15a</td>
<td>C</td>
<td>10⁻⁴ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>2521</td>
<td>23</td>
<td>26.9</td>
</tr>
<tr>
<td>Kung15b</td>
<td>C</td>
<td>10⁻⁴ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>6387</td>
<td>6.5</td>
<td>26.9</td>
</tr>
<tr>
<td>Kung16a</td>
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<td>10⁻⁶ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>2521</td>
<td>23</td>
<td>13.4</td>
</tr>
<tr>
<td>Kung16b</td>
<td>C</td>
<td>10⁻¹ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>6387</td>
<td>6.5</td>
<td>13.4</td>
</tr>
<tr>
<td>Kung17a</td>
<td>C</td>
<td>10⁻⁵ HCl</td>
<td>1.34</td>
<td>1.96</td>
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<td>1.34</td>
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<td>3003</td>
<td>23</td>
<td>26.6</td>
</tr>
<tr>
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<td>C</td>
<td>10⁻¹ KCl</td>
<td>1.34</td>
<td>1.96</td>
<td>5515</td>
<td>23</td>
<td>26.5</td>
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<tr>
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<td>1.34</td>
<td>1.96</td>
<td>3199</td>
<td>23</td>
<td>26.5</td>
</tr>
<tr>
<td>Kung20</td>
<td>B</td>
<td>10⁻⁴ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>6118</td>
<td>23</td>
<td>17.4</td>
</tr>
<tr>
<td>Kung21a</td>
<td>B</td>
<td>10⁻³ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>4552</td>
<td>23</td>
<td>16.8</td>
</tr>
<tr>
<td>Kung22</td>
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<td>10⁻⁶ HCl</td>
<td>1.34</td>
<td>1.96</td>
<td>2946</td>
<td>23</td>
<td>16.8</td>
</tr>
</tbody>
</table>

The method used to calculate the dissolution rate of the Kungsängen illite, with specific assumptions and limitations, started from the experimental total release ($R_{exp.}$) rate from the soil material. The modelled dissolution rate ($R_i$) of K-feldspar, albite, hornblende and chlorite ($\sum_{i=\text{Mineral excl. illite}} R_i$), i.e. all the base cation containing minerals in the sample, excluding the illite release rate was subtracted from the experimental release rate ($R_{exp.}$) see equation 19. The residual will consequently be the calculated release rate for illite ($R_{\text{Kungsängen illite}}$), based on experimental results and release rate data from literature.

$$R_{\text{Kungsängen illite}} = R_{\text{exp.}} - \sum_{i=\text{Mineral excl. illite}} R_i$$

The estimated contribution to the release rate of Si and K from the investigated illite is varies depending on the pH, element concentration and horizon (Table ??). In the interval pH 3 to pH 5, illite contributes more than 75% of the release rate of Si.
7.2 Dissolution rate of clay size minerals

7.2.2 Results

The results from the dissolution of the clay-size soil minerals are shown in Figure 17. The rate coefficients were determined as \( k_{\text{H}^+}^E = 12.35 \) and \( k_{\text{H}^+}^E = 10.8 \) with respect to K for the B- and C-horizons respectively according to Equation 3. The reaction order \( (n_{\text{H}^+}) \) was determined to 0.85 and 0.25 for material from the B- and C-horizon respectively.

According to the results from the experiments presented in Paper III, the retarding factor \( x_{\text{BC}} \) was estimated to be \( \approx 0.29 \) at pH 1.0 and \( \approx 0.17 \) at pH 4.5.

The activation energy at pH 1.0 and pH 4.4 was calculated to be 71.3 kJ mol\(^{-1}\) and 79.5 kJ mol\(^{-1}\) respectively for Si. This indicates that the dissolution of the silica structure for this clay-size soil material is surface controlled and not diffusion controlled.

The conclusions from the dissolution experiments on clay-size soil material are:

1. It is possible to perform experimental dissolution experiments on clay-size material (0.5-2.0\( \mu \)m),
2. Dissolution of clay-size soil material shows a clear pH dependency, which indicates that it is the hydrogen reaction that governs the dissolution rate at pH 1 to pH 5 and
3. There is a negative correlation between dissolution rate and \( K^+ \) concentration, suggesting product inhibition.

7.2.3 Determined kinetic coefficient to field weathering calculation

In order to use experimentally determined rate coefficients in PROFILE, they must be transformed according to Equation 15 on page 22. Note that even if some coefficients such as the retarding coefficient have not been experimentally determined, it is possible to estimate them from experiments carried out on minerals that have the same or similar structure. For PROFILE to be able to generate a field weathering rate from rate coefficients, the model must be complete regardless of how they were actually determined For the rate to be reasonable then the coefficient values must be realistic. This is also the reason why it is important that the process of increasing the precision and accuracy in this matrix continuous.

Table 4 shows the rate coefficients of clay minerals determined in this work and by other experimental dissolution studies.

---

\(^4\) The high reaction order \( n = 0.85 \) for the C-horizon was determined only by one observation at pH 1 and can therefore be regarded as uncertain (Paper III).
Table 4: Experimental rate coefficients ($k^E$) and the rate coefficient ($k^{PROFILE}$) as used in PROFILE for the dissolution of clay-size illite expressed as the flux of potassium (K) and silica (Si). The weathering rate is expressed as mol m⁻² s⁻¹ at 25°Celsius and C is expressed as kmol m⁻³

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Experimental kinetic coefficients</th>
<th>$pk^E_{H^+}$</th>
<th>$n_{H^+}$</th>
<th>$pk_w$</th>
<th>$x_{BC}$</th>
<th>$y_{Al}$</th>
<th>$pC_{BC}$</th>
<th>$pC_{Al}$</th>
<th>$pk^{PROFILE}_{H^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kungsängen illite</td>
<td></td>
<td>12.4¹</td>
<td>0.25¹</td>
<td>14.5¹</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
<td>13.7</td>
</tr>
<tr>
<td>B-horizon (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kungsängen illite</td>
<td></td>
<td>11.6¹</td>
<td>0.50¹</td>
<td>14.0¹</td>
<td>0.23¹</td>
<td>0.4²</td>
<td>2.15³</td>
<td>≈4²</td>
<td></td>
</tr>
<tr>
<td>C-horizon (Si)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-horizon (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fithian Illite</td>
<td></td>
<td>-</td>
<td>0.39⁵</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td></td>
<td>12.2⁶</td>
<td>0.13⁶</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td></td>
<td>12.4⁷</td>
<td>0.14⁷</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

¹) Rate coefficients estimated by the experimental study presented in Paper III
²) Rate coefficients determined or estimated by Sverdrup (1990)
³) Rate coefficients estimated from field experiment in combination with literature (Sverdrup 1990) and experimental study presented in Paper III
⁴) Rate coefficient calculated by Equation 15 on page 22
⁵) Rate coefficients determined by Feigenbaum and Shainberg (1975)
⁶) Rate coefficients determined by Nickel (1973)
⁷) Rate coefficients determined by Stumm et al. (1987)
7.2 Dissolution rate of clay size minerals

Figure 17: Modelled dissolution rate for the illite in the B- and C-horizon, plot A and B respectively. The dotted lines represent different models for the dissolution rate based on the release rate for K for the (H$^+$), (H$_2$O) and (OH$^-$) reactions, at 23°C. The graph also shows a modelled rate, the solid line, which is the sum of the hydrogen, water and hydroxide reaction rates (a simplification of Equation 3). Experimental data from this study are represented by o, the error bars represent the variation in the experimental data in the steady state range.
7.3 Field weathering rate in agricultural systems

Chemical weathering of soil minerals can contribute significant quantities of potassium (K) to the soil exchange complex and therefore ultimately to plant uptake. Quantifying the release rates of K and other nutrients by chemical weathering in different types of agricultural soil systems is important in order to better predict optimal fertilization rates and hence to contribute to the increased sustainability of the system. Inaccurate assessment of the K supply from this weathering source may in the long-term result in nutrient imbalances.

In Paper IV, an attempt to estimate the potassium release from chemical weathering in different Northern European agricultural systems was carried out. The chemical weathering rate was calculated using PROFILE and long-term field experiments. This also tests the validity of the adaptions of PROFILE to clay-rich soils. In this study, an annual input-output balance for K was also calculated for one Swedish site, Kungsångens outside Uppsala, and one Scottish site, Countesswells, in Aberdeen NE Scotland. The inputs taken into account were chemical weathering ($Weathering_K$) atmospheric deposition ($Dep_K$), and the outputs included were K removed by harvest products ($Crop_K$) and leaching ($Leach_K$). A K-surplus indicates a net accumulation of K in the soil pool ($Soil_K$), whereas a K-deficit means that $Soil_K$ is decreasing.

$$Weathering_K + Dep_K - Crop_K - Leach_K = Soil_K$$

(20)

At the Scottish site with its relatively low weathering rate, due to coarse texture, the deficit and most probably the plant-available K pool decrease rapidly (Figure 18), if one assumes that there is a relationship between soil K and plant K (Springob et al. 1995, Barber 1995). The high deficit at the beginning of the experiment (Year 1) was probably due to a large exchangeable K pool in the soil caused by K fertilization before the experiment was established. If the calculated weathering rate is included, then the K-deficit about 20 kg K ha$^{-1} yr^{-1}$ (Figure 18A). The reason for the discrepancy between the K-deficit and the estimated weathering in the Countesswells soil can be explained by: 1) Decrease in the exchangeable K-pool has not reached a steady state level; and 2) Important parameters that govern the weathering rate such as specific active surface area and mineralogy are difficult to determine. This decrease in the plant available K-pool cannot be seen for the Swedish site. At the Kungsångens long-term field experiments, the K mass balances are almost in equilibrium $Soil_K \approx 0$ in the mass balance calculation if the weathering rate is included in the mass-balance calculation. This means that the deficit is shown in Figure 18B is in the same range as the calculated weathering rate.

The conclusions from this study in estimating the weathering rate for K in agricultural soils/systems are:

- Chemical weathering is important in estimating the K budgets in agricultural systems,
• PROFILE can be used for calculating reasonable estimates for the weathering rate of K in different agricultural soils if the inputs to the model are accurate and reliable. Thus the performance of the new model is satisfying, producing values that are reasonable and appear to have sufficient accuracy for this purpose.

• More experimental studies on mass balances in agricultural systems are necessary in validating the PROFILE model and in the continuing process of model development.

Figure 18: Deficit of K (kg ha\(^{-1}\) year\(^{-1}\)) without including the weathering rate of K, between 1970 and 1997 for Countesswells (A) and between the years 1963 - 1996 for the Kungsängen site (B). The black dotted lines show the best estimated weathering rate and the gray area represents the range of the minimum and maximum weathering rate. The gray solid line represents the average K deficit the last 4-5 years of the two grass periods (years 9-12; 24-29) for the Scottish site and between years 1 to 35 for the Swedish site. The area between the vertical dotted lines in (A) represents the years of the cereal period with basal fertilization with nitrogen, phosphorus and potassium.
8 Chemical weathering on a spatial scale

Once a map is drawn people tend to accept it as reality.

Bert Friesen

The description and analysis of spatial variation over the land surface of phenomena are central in Earth science and other geographical disciplines. Soil scientists, forest ecologists and forest managers as well as others working with spatially distributed data have therefore devoted much attention to defining regional patterns in the natural landscape. Several natural geographical properties vary continuously and randomly in space and time, but the pattern and scale of their variation is not readily apparent. The key issue for many practitioners working with spatially distributed data is to determine the scale and pattern of variation of continuous spatial variables, and to estimate or interpolate not investigated values optimally.

The focus of the geochemical investigation in Asa a forested area in Southern Sweden, has been to provide forest managers, land owners and decision makers with an understanding and knowledge of how different geochemical properties such as chemical weathering rate and sustainable biomass production are spatially distributed\(^5\). It has also been the intention to show the spatial uncertainty that is associated with biogeochemical surveys like the one performed in Asa.

The main specific objectives for the geochemical investigation in Asa were to:

- Investigate the geostatistical properties of important soil parameters regarding chemical weathering rate,
- Investigate the possibility of spatially distributing the calculated chemical weathering rate and
- Suggest a time and cost effective sampling strategy and design a spatial survey to estimate the weathering rate in a 3,200 ha large forested area in southern Sweden.

To visualize the distributed results from the chemical weathering rate calculations and the sustainable biomass production geostatistical tools and methods (Appendix A) were used.

8.1 Survey optimization and spatial heterogeneity

In spatial surveys the geostatistical methods are goal-orientated (Chilès and Delfiner 1999) and this also includes geochemical surveys. One of the most important questions regarding general and regionalized mapping of soil properties is whether more sampled and processed data justify the extra cost and delay.

Regarding biogeochemical modelling such as that performed at Asa (Paper V and VI) there is another dimension of these aspects. More or less all input data to

\(^5\)The original data from the geochemical investigation in Asa is presented in Appendix B
PROFILE have a spatial component, but the spatial homogeneity/heterogeneity varies between the different data inputs. A spatial survey that is aiming at producing an interpolated map from geographically distributed model outputs should focus on minimizing the spatial uncertainty for those model inputs that have strongest influences on the outputs. The sampling density or the spatial density for the different inputs could or should therefore vary.

8.2 The geochemical investigation in Asa, South Sweden

The field studies and the biogeochemical studies were primarily focused on a 3.200 ha forested area in Southern Sweden (Figure 19).

![Figure 19: Location map of the investigation area i Asa, southern Sweden.](image)

The studied area is located in the interior of Southern Sweden 40 km north of Växjö in the county of Kronoberg (57°10’N, 14°47’E). A thorough description of Asa is given in Paper V.

8.2.1 Interpretation of variograms

Geostatistical techniques were used as tools to understand the geographic distribution of *regionalized variables*\(^6\) which are input parameters in the modelling work. Unlike random variables, regionalized variables have continuity from point to point, but the changes in the variable are so complex that they cannot be described by any controllable deterministic function (Davis 1986). In this study

\(^6\)A regionalized variable has properties intermediate between a truly random variable and one completely deterministic (Davis 1986).
variograms were used (a short theoretical description can be read in Appendix A) as a basic statistical method to describe the semivariance, which is used to express the rate of change of a regionalized variable along a specific orientation.

The results from the geostatistical study for some of the most of important data input parameters are shown in Figure 20. The regionalized variograms (defined as theoretical variogram in Appendix A) of plagioclase, K-feldspar, biotite and surface area show that the range of spatial dependence for these minerals are ≈300 m. The regionalized variogram for the surface area has no upper limit for the sill variance (Appendix A) probably due to a to small numbers of sampling sites. From the variograms of the spatially distributed data (Figure 20) from the most

Figure 20: Experimental and modelled omnidirectional semivariograms of the geochemical survey in Asa for plagioclase, K-feldspar, biotite and surface area.

important minerals, with regard to chemical weathering, the range (the distance at which the sites have no relation to each other) was calculated to approximately 300-400 metres. This distance defines a neighbourhood within which all sampling points are geostatistically related to one another. One conclusion that can be drawn is that if the intention is to produce a map that describes the spatial distribution of the minerals, then sampling distance must be less than 300 m. One of the major problems with the geostatistically interpretation of the data set from the survey is the homogeneity and the low variability of the parameters investigated in the area.
8.2 The geochemical investigation in Asa, South Sweden

The microscale variation, which is due to the variance at distances shorter than the measured distance, and the uncertainties associated with the data set are large in comparison to the maximum semi-variance ($\gamma$). This is shown by the proportion $\sqrt{\text{nugget} / \text{var}}$ which is 55% for Plagioclase and 66% for K-feldspar. This indicates that the variation in the measurement is large compared to the spatial variability. This homogeneity is reflected in the underlying bedrock (Figure 21). To further illustrate the spatial variability, a comparison between the distribution of the calcium content in Asa (355 sites) and in the geochemical database for southern Sweden (Geological Survey of Sweden) was made. The national survey, with a sampling density of 0.15 samples per square kilometre, shows a poor spatial dependency in the range 0 - 10,000 m due to low sampling density in relation to the microscale variation. However, an obvious spatial dependency can be shown for the entire investigated area (Figure 22). It is important to know the spatial scale of variation within the area of interest in order to produce a map of the variable. A conclusion regarding the spatial scale of variation and the use of variograms is that a reconnaissance variogram could enhance the understanding of the spatial properties and the effectiveness of the sampling design. It is also important to stress that for kriging or any kind of interpolation, neighbouring samples should be spatially correlated.

![Image](image_url)

Figure 21: Bedrock map from the investigated area in Asa, south Sweden. From Bedrock map 5E Växjö NO, SGU series Af no. 201, Geological Survey of Sweden (SGU). Admission: 00-1039/2001.
Figure 22: Experimental and modelled omnidirectional semivariograms of the 355 sites in the geochemical survey in Asa and 9606 sites of the geochemical mapping by the Geological Survey for CaO content in the C-horizon.
8.2 The geochemical investigation in Asa, South Sweden

8.2.2 Kriging interpolation

Interpolation of the output parameters from the biogeochemical soil model PROFILE, i.e. calcium weathering rate, potassium weathering rate and magnesium weathering rate, was done on basis of the detrended, isotropic and omnidirectional variogram presented in Paper V.

The resulting maps of the weathering rate and the standard error of the kriging (See Appendix A) prediction are shown in Figures 23 and 24. The omnidirectional variograms modelled at different maximum lag distances are also shown. The regionalized variograms show that it is possible to carry out kriging interpolation on the weathering rate with the sampling density used in this geochemical study. The relative homogeneity regarding the weathering rate is shown by the maps of the corresponding standard deviation (Figure 23 and 24).

Figure 23: Maps of Ca-weathering (keq ha\(^{-1}\) year\(^{-1}\)) and the standard error obtained by ordinary kriging and the corresponding standard deviation and the omnidirectional experimental and modelled variogram used.
Figure 24: Maps of K-weathering (B) and Mg-weathering (C) (kg ha$^{-1}$ year$^{-1}$) and the standard error obtained by ordinary kriging and the corresponding standard deviation and the omnidirectional experimental and modelled variogram used.
8.2.3 Distance and density analyses

A novel approach was used to study how the distance to the sampling sites, i.e. the distribution and the sampling interval between the sampling sites, influences the variogram and the kriging prediction. Two different scenarios were evaluated with regard to the sampling density. In the first scenario 150 sampling sites were spread evenly over the investigated area with a sampling density of 6-15 samples per square kilometre (Figure 25).

In the second scenario the 96 sampling sites from the nested survey were used with an additional 54 sampling sites, to make both scenarios comparable. The sampling density of the second scenario is 50-60 samples per square kilometre (Figure 25). The results from this study show that an evenly spatially distributed sampling scheme with a sampling interval of ≈300 metres and 150 sampling sites is not sufficient with respect to kriging prediction. There is no spatial dependency between the sampling points which can be seen by the “Pure Nugget” of the experimental variogram (Figure 25).

One of the key findings in this investigation was the identification of the relationship between the homogeneity of the soil parameters in Asa and the performance of the model variograms due to a limited distributed data set. An evenly distributed data set with 150 locations and a sampling density of 6-15 samples per km² yields no reliable variogram and therefore by kriging prediction becomes impossible. However, if one uses a nested sampling scheme (Figure 26) with 150 locations and with a sampling density of 50-60 samples per km² it is possible to make a modelled variogram that resembles the modelled variogram, which was calculated from the entire data set of 355 locations. The feasibility of using a modelled variogram to extrapolate a kriging prediction based on a limited data set in space and in number is questionable.
Figure 25: Maps showing the distance to the sampling sites in Asa Royal Park with an even (A) and nested (B) distributed sampling scheme with a total of 150 sampling sites each and the omnidirectional-directional experimental variograms for the potassium weathering rate at these 150 sites. An additional experimental and modelled variogram, for the K-weathering rate for all 355 sampling sites, was incorporated in sub-figure B for comparison, shown as ○.
Figure 26: *The sampling scheme for the nested sampling (A) and spatial configuration of a set of sampling points (B), a so-called “spider”, showing the principle of nested sampling. Each point at every stage has a fixed distance to its related point, but the direction is chosen randomly.*

The most important conclusions and overall suggestions regarding designing geostatistical surveys that can be drawn from our geochemical spatial survey at Asa can be summarized as follows:

- Design the spatial survey on the basis of the questions that one would like to be answered,
- Gather and use all available information concerning the parameters that could be used in the spatial investigation,
- If possible perform a preinvestigation on the study area,
- Use a sampling design that can detect the spatial variability with a limited number of sampling sites,
- Determine what the acceptable limit is regarding the precision and the uncertainty concerning the spatial survey and
- Use the final result from the geostatistical study in conjunction with the spatial standard deviation.
9 Sustainability in managed forest ecosystems

Forest sustainability, in the perspective of sustainable forestry, can be defined by natural, social and economic sustainability (Sverdrup and Svensson 2001). The importance of these criteria depends on the context in which forest sustainability is defined. Natural sustainability defines the maximum long-term\(^7\) use of natural resources as sources of raw material and energy without decreasing or limiting the forests natural capacity. The natural capacity is given by the long term use of the ecosystem, optimised to the intensity where the resource base, structure or function of the ecosystem is not unacceptably degraded or changed (Sverdrup and Svensson 2001). This definition includes biodiversity, forest health, soil water quality and natural resource conservation or maintenance of nutrient concentrations in the soil solution.

Some of these sustainability limitations have precedence over others. The parameters of social and economic sustainability must stay within the boundaries set by the physical and thermodynamical sustainability criteria of the natural system in order to be relevant (Sverdrup and Svensson 2001).

If forest management is to be carried out in such a way that it fulfils the criteria of the The Brundtland Commission definition of sustainability,\(^8\) then is it important to work out natural and economic boundaries of forest sustainability.

9.1 Sustainable yield

In this thesis the focus has been on natural sustainability, the long-term supply of base cations. The consequence and importance of the definition of sustainable forestry, in this context, is that harvest of forest is limited by the base cation with the slowest supply rate. The relationship between field weathering rate and yield is demonstrated in Figure 29 as a causal loop diagram (CLD). The CLD show the relationship between chemical weathering rate and long-term sustainable yield. Increasing Field weathering rate increases Available BC and thereby leads to an increased BC uptake by the trees (Kimmins 1997, Waring and Running 1998). This base cation (BC) increases the Biomass growth rate if the base cations are a limited source or if BC\(_i\) : N where \(i=\text{Ca, Mg, K}\) is low compared to an optimum level mineral nutrient concentration in the soil (Larcher 1995, Lambers et al. 1998). The growth rate increases the standing biomass and Yield can thereby increase. The size of the available base cation pool is also dependent on the BC Deposition, nutrient supply by e.g. Ash recycling and by leaching. By increasing the Rooting depth the total soil volume that is available by the tree-roots increases and therefore this increases the available base cations that originate from Field weathering rate. Deciduous trees such as beech and oak have a larger amount

---

\(^7\)Long-term is here defined as several forest rotation periods, i.e. more than 400 years.

\(^8\)Humanity has the ability to make development sustainable - to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs (World Commission on Environment and Development 1987).
of root biomass in deeper soil horizons than spruce in a similar environment (Eichhorn 1992, Zoth and Block 1992, Jackson and M. 1996, Südhaus 1999). The connection between the fractions of different tree species in a forest stand and yield is thus illustrated. Another important factor is the Rooting efficiency, where a high rooting efficiency increases the BC uptake. However, the rooting efficiency is difficult to determine because the mineral uptake in a situation where the trees are affected by natural and anthropogenic acidification and nutrient deficiency is poorly investigated and understood.

If the available BC is in balance with the field weathering rate, leaching, total deposition and BC uptake, the yield becomes a long-term sustainable yield. An objection to the described co-variation and relevance of the CLD in Figure 29 is the lack of a relationship between growth rate and available base cations in the soil solution in present managed forest ecosystems. This non-relationship can be explained by the time-frame chosen. The time-frame that is chosen for the scenario described by the CLD is several tree-rotation periods, 400-500 years. Figure 27 is a schematic diagram showing how the available BC and growth rate decline according to the CLD if the yield is larger than the sustainable yield seen in a time perspective of 400-500 years. If the available BC is less than desirable BC uptake for a longer time period the uptake will consequently decrease and the growth rate will also decrease which could finally result in decreased yield.

9.1.1 Calculation flowchart

The strategy that was used to calculate nutrient mass balance and sustainable yield in forest ecosystems is shown in Figure 28. The assessment to estimate the sustainable yield could be summarized by the steps:

1. Gather information using analytical results from the geochemical study in Asa, such as determination of the elemental composition and grain-size analysis, generic data from other sources on factors such as temperature (Asa Forest Station) and deposition (IVL, Swedish Environmental Research Institute) and also for example root depth and efficiency

2. Convert the data-sets to a readable input data file for the PROFILE model.

3. Calculate the weathering rate for calcium, potassium and magnesium by the PROFILE model
4. Determine site specific weathering rate where spatially distributed by kriging interpolation

5. Estimate weathering rate, deposition, uptake and leaching for use in calculating the mass balance

6. On the basis of the mass balance calculation, estimate the sustainable yield in Asa.

9.1.2 Nutrient mass balances in forest ecosystem

In order to determine the supply rate of base cations to the soil solution a biogeochemical mass balance must be set up for each base cation. The study presented in Paper VI, the focus was on calcium, magnesium and potassium. Atmospheric deposition and weathering are the sources of base cations, uptake and leaching are the sinks. The mass balance for each base cation ($BC_i$) can be described as:

$$
\Delta_{BC_i} = W_i + D_i - U_i - L_i
$$

(21)
where $U$ is uptake and depends on the amounts removed by harvest from the system; $D$ is deposition; including fertilization, which partly depends on human activities; $W$ is the contribution of base cations from chemical weathering and $L$ is leaching, which depends on water flux.

In this thesis sustainable yield is defined as the maximum yield that can be harvested based on the available nutrients in the system, without causing long-term imbalance or deficiency of base cations in the soil solution. The sustainable yield is calculated according to the Liebig “Law of the Minimum”, it is the element present in the least relative amount that sets the limit for growth and yield von (von Liebig 1862). In principle, this limitation applies to any nutrient and to water. A mass balance can be assessed for any bulk or trace nutrient. Sustainability prevails when the long-term average value of $\Delta_i$ is $\geq 0$. In this first estimate, sustainability with respect to Ca, Mg and K was calculated using the equation:

$$Y_{BC} = \min_i \left( \frac{U_{BC, crit}}{\rho \cdot x_i} \right) \tag{22}$$

where $Y_{BC}$ is the sustainable yield with respect to base cations; $U_{BC, crit}$ is the critical...
Figure 30: Frequency plot of the number of stands that have a sustainable yield ($m^3 \text{ ha}^{-1} \text{yr}^{-1}$) at Asa, based on the long-term availability of Ca, Mg and K for a Norway spruce and a mixed conifer-birch forest. The traditional yield of 9.1 $m^3 \text{ ha}^{-1} \text{yr}^{-1}$ overestimate the possible long term production for Norway spruce in the area.

uptake of element $i$ = Ca, Mg, K; $E_i$ is the equivalent weight of element $i$; $\rho$ is the density of the harvested biomass; and $x_i$ is the content in the harvested biomass of element $i$. In most cases Mg was the element setting limitations, but for some cases Ca was also limiting. The critical uptake is limited by the available nutrient;

$$
U^{crit}_{BC_i} = W_i + D_i - L_{min}
$$

where $W_i$ is the weathering release of element $i$; $D_i$ is the atmospheric deposition of element $i$; and $L_{min}$ the minimum leaching from the system.

The results of the sustainable production estimates are shown in Figures 30, 31 and 32 (see also Paper VI). The total maximum sustainable production is found by taking the minimum production from each of these maps. This is shown in Figure 33 where a comparison with the stand quality (Swe. Bonitet) map estimated according to the traditional method (Karlsson and Westman 1991) was carried out. One conclusion of this comparison is that traditional yield is not always a good predictor of long-term sustainable yield and that the method presented in this study should be used.

The maps of the sustainable production estimates in Asa are based on available base cations in the soil, converted to stemwood biomass, or if distributed among different tree species also converted to SPE (Spruce Pulpwood Equivalents) (Sverdrup and Stienquist 2001).

The calculated differences in forest yield between Norway spruce in monoculture and a mixed conifer-birch forest are due to the root system base cation capturing efficiency. For Norway spruce the estimated rooting depth was estimated at 0.3-0.4 m and the mixed forest has a uptake efficiency of 80-85% with an estimated rooting depth of 0.55 m (Sverdrup and Stienquist 2001). However, the measured physical root depth does not necessarily imply that the nutrients are
Figure 31: *Sustainable yield in m³ ha⁻¹ yr⁻¹ based on potassium for Norway spruce in monoculture (left) and in a mixed stand (right).*

Acidification of soils can change the physiological efficiencies drastically to the degree where uptake to the tree can become severely restricted. A more detailed description of the nutrient uptake by the trees is given in Paper VI.

It can be seen that even if the stand quality map and sustainable yields maps (Figure 33) were estimated with totally different data, the two maps qualitatively show approximately the same pattern. The quality stand map has its high and low values in the same places as the sustainability maps, but the quality stand map is consistently higher. A conclusion could be that the stand quality map is a qualitative map, where as the sustainability map is both qualitative and quantitative. If whole tree harvest is practised within the sustainability limits according to the definition used in this work, wood production efficiency will be substantially reduced. One other way to view this is that the stand quality map illustrates the maximum growth management, whereas the sustainability map shows how much of the production capacity that is sustainable to use.

### 9.2 Forest sustainability

Biogeochemical mass balance is a useful instrument to calculate a sustainable yield in forest management, different techniques and methods must be developed and introduced in forest and soil surveys (Thelin 2000, Thelin *et al.* 2001, Sverdrup
Table 5: Summary of the weathering rate calculations. The large number is the average, the lower case the maximum and the upper case the minimum. Below, comparable numbers for atmospheric deposition and leaching are shown, units are mEq m⁻² yr⁻¹.

<table>
<thead>
<tr>
<th>Forest type</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norway Spruce</td>
<td>5.01/5.9</td>
<td>0.95/1.9</td>
<td>2.86/2.9</td>
</tr>
<tr>
<td>Spruce-Beech; 50:50</td>
<td>15.3/4.3</td>
<td>4.89/2.8</td>
<td>7.72/1.3</td>
</tr>
<tr>
<td>Beech</td>
<td>20.1/5.9</td>
<td>6.7/2.9</td>
<td>9.72/1.7</td>
</tr>
<tr>
<td>Deposition</td>
<td>328.2/50</td>
<td>17.55/27</td>
<td>13.52/22</td>
</tr>
<tr>
<td>Leaching</td>
<td>181.8/2</td>
<td>15.2/26</td>
<td>1.01/1.6</td>
</tr>
</tbody>
</table>

and Svensson 2001). This study has shown that existing traditional techniques for calculating the long-term yield of forest with no long-term depletion of adsorbed stores of base cations, are insufficient. According to our results of nutrient sustainability in the Asa Forest Research Park more attention must be given to the reservoir of essential elements in the soil, especially in a temporal aspect. If the intention is to have a modern commercially sustainable forestry, dynamic mathematical forest yield models must be used together with frequently spatially distributed soil surveys.

This assessment to calculate sustainable biomass production and estimate biogeochemical nutrient mass balances in forest soils is important knowledge for the problem of declining base saturations in long-term managed forest soils (Falkengren-Grerup 1986, Tamm and Hallbäck 1988, Eriksson et al. 1992, Gustafsson et al. 1993, Wesselink et al. 1995, Adamson et al. 1996, Karlton 1998, Anderson and Sonesson 2000, Thelin 2000). The understanding of mass balance and nutrient budgets is one of the many steps needed in taking appropriate measurements to increase the soil quality in intensive managed forests.

The technique of using biogeochemical mass balance in prediction of sustainable biomass production gives forest managers, land owners, biomass energy and paper mill companies, state governments and authorities an opportunity to calculate the true costs of the harvested biomass. Simple economic calculations (Paper VI) showed that the resulting nutrient deficiency in the soil caused by over-exploitation and too high biomass harvest in Asa Research Park costs 5-20%
of the profit as nutrient addition. Restoring over-exploited forest soil and maintaining of the soil quality should be as natural as it is in other areas of forest management, for example ensuring regeneration of harvested forested areas.

In a scenario where the forest is used intensively, as an energy resource for example, a more active forest management is required. A system for auditing the available nutrient pools and establishing a method to make nutrient budgets for the forest ecosystem will be essential. Bookkeeping of the flows and pools of nutrients in the soil is necessary if the continuous processes of depletion of exchangeable cations and decline of the base saturation in a intensively managed forest are to be avoided. If the exchangeable base cations in the upper horizons of the forest soil are regarded as a natural resource, then the harvest of essential elements and the natural leaching must not exceed the sum of weathering, atmospheric deposition and fertilization (eq. 21). If this criterion is violated, the present ecosystem will change and degrade as a natural resource.
Figure 32: Sustainable yield in m³ ha⁻¹ yr⁻¹ based on calcium for Norway spruce in monoculture (left) and a mixed stand (top). Below is the same for magnesium. The sustainable yield is based on the assumption that Norway spruce has an average rooting depth of 0.35 metre. Yield express in m³ ha⁻¹ yr⁻¹.
10 Uncertainty in modelling chemical weathering

Estimation of the uncertainty is as important as the calculation of the chemical weathering rate itself. An understanding and quantification of the uncertainty in the calculated results is important for the user to assess the usefulness of the results.

The uncertainty assessment of the chemical weathering rate in Asa Forest Research Park was carried out in collaboration with Mattias Alveteg and Daniel Kurz and by reviewing work done by Barkman (1998) and Alveteg et al. (2000). It is important to note that only the uncertainty in the mineralogy content has been stress. There are also other uncertainties in the other input parameters but these have not been considered in this study. Issues related to uncertainties in modelling have been discussed thoroughly by Barkman (1998) and Barkman and Alveteg (2001).

The importance of discussing uncertainties associated with a data set, such as technical uncertainties and random errors in a geostatistical context, has been stressed by Ramsey and Argyraki (1996) and Goovaerts (2000). Ramsey and Argyraki (1996) argue that in a geochemical survey, consideration should be given to geochemical variance \( (s^2_{\text{geochem}}) \), which is the between-location variance, the sampling uncertainty \( (s^2_{\text{samp}}) \), or within-location variance, and the analytical uncertainty \( (s^2_{\text{analytical}}) \) (Equation 24).

\[
s^2_{\text{total}} = s^2_{\text{geochem}} + s^2_{\text{samp}} + s^2_{\text{analytical}}
\]

10.1 Mineralogical sensitivity analysis

A sensitivity analysis was assessed to investigate how the weathering rate depends on the quantitative mineralogy. Two different elemental compositions, one with a high and one with a low content of Ca, were used to generate 15,000 to 18,000 different mineralogical compositions by a normalization model, described in detail by Kurz et al. (1998). The restriction or boundaries for the normalization modelling was the mineral assemblage, determined by the qualitative mineralogical analyses such as XRD- and SEM-EDX analysis, and with a fixed stoichiometry.

The results from the normalization show that the distribution of the dark minerals is very wide (Figure 34A) and normally distributed. The standard deviations of the pyroxene and amphibole were 0.88% and 1.55% respectively for the elemental composition with high Ca content and 0.50% and 0.86% respectively for the elemental compositions with low Ca content. The range of the pyroxene content, for example, in the 18,000 mineralogical composition was from 0% to 4.2% for the scenario with high Ca elemental content and 0 to 2.5% for the scenario with low Ca elemental content.

This wide distribution for the different minerals also resulted in a wide variation in the calculated Ca weathering rate (Figure 34B). The total range for Ca weathering rate was calculated to be 7.1-16.5 keq ha\(^{-1}\) year\(^{-1}\) and 8.7-15.5 keq
10.1 Mineralogical sensitivity analysis

Figure 34: The histogram (Figure A) shows the mineralogical distribution, from the normalization modelling, for the two different scenarios with a high and low Ca content in the original elemental composition. The error bars in the histogram shows the total range of the mineral content for each mineral. The probability graph (Figure B) show the calculated Ca weathering rate by PROFILE using 18,000 different mineralogical compositions for each scenario.

ha\(^{-1}\) year\(^{-1}\), for the elemental composition with high and low Ca content, respectively (Table 6). This implies that there is no significant drift between high and low Ca content.

Table 6: Results of the uncertainty analysis on chemical weathering rate using different mineralogies. High and Low Ca content represent scenarios with 15,000 - 18,000 normalized mineralogy from two different elemental compositions, with high and low Ca content.

<table>
<thead>
<tr>
<th></th>
<th>Weathering rate (keq ha(^{-1}) year(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>High Ca content</td>
<td>10.6</td>
</tr>
<tr>
<td>Low Ca content</td>
<td>10.9</td>
</tr>
</tbody>
</table>

The results of this mineralogical uncertainty analysis showed that the pyroxene content determines the Ca weathering rate when all input parameters were fixed except for the mineralogy. One important conclusion from this novel mineralogical sensitivity analysis is that the mineralogy has a large impact on the weathering rate. Therefore the qualitative and quantitative determination of the mineralogical composition, at site level as well as regional scale, is important when assessing field weathering rates. It is especially important to recognize and quantify the
dark minerals (amphiboles, pyroxenes and epidotes etc.) with high dissolution rate even if they only contribute 2 - 10% of the mineralogical content.

Figure 35: The pyroxene content shows a strong relationship with Ca weathering rate. The samples with high and low percentage of elemental Ca has a distribution of pyroxene from 0 to 4.2% and 0 to 2.5%, respectively. This correspond to a Ca weathering rate of 7.0 to 16.5 keq ha\(^{-1}\) year\(^{-1}\) and 8.5 to 15.5 keq ha\(^{-1}\) year\(^{-1}\), respectively. The probability diagram of the pyroxene distribution shows that 90% of the 18,000 different mineralogical composition from the two different scenarios had < 2.7% pyroxene and < 1.4% pyroxene, respectively.

10.2 Uncertainty in spatial modelling

To understand the effect of the uncertainty and variance of the spatially distributed data on the assessments in this work, it is important to measure and interpret the uncertainty. This limited and simple study on uncertainty calculation does not result in any definitive answers. However, it could help to interpret the results from the geochemical survey and highlight the weak links in this study thus improving the next generation geochemical field studies.

Four replicates regarding the elemental composition at two different sites were analyzed to calculate the analytical uncertainty \(\sigma_{\text{analytical}}^2\). The same normalization procedure as for the whole data set was then applied for these samples to obtain the mineralogy. To estimate the effect of the uncertainty on the calculated weathering rate these mineralogies were then used in a second modelling of the weathering rate.

The total estimated uncertainty can be regarded as a model output uncertainty. This output uncertainty is a combination of the sampling,\(^9\) analytical and the

\(^9\)The sampling variance was analysed at one site but was not interpreted in this study.
model variance, giving the output variance \( s^2_{\text{output}} \) as:

\[
s^2_{\text{output}} = s^2_{\text{sample}} + s^2_{\text{analytical}} + s^2_{\text{model}}
\]  

(25)

To determine if the uncertainty in the weathering rate could be regarded as acceptable, the output variance \( s^2_{\text{output}} \) was compared with the total variance \( s^2_{\text{total}} \), including the spatial variation.

Ramsey and Argyraki (1996) have suggested an acceptable limit for measured variance, concerning identification of “hot spots” on contaminated land, which is given by the equation:

\[
\frac{s^2_{\text{output}}}{s^2_{\text{total}}} < 20\% 
\]  

(26)

where \( s^2_{\text{output}} \) is the estimated variance of the modelled output and \( s^2_{\text{total}} \) is the total variance (Equation 24). It is however important to stress that there is no universal limit to the acceptable level of uncertainty.

The ratio \( s^2_{\text{output}}/s^2_{\text{total}} \) was calculated to 14%, 6.8% and 14% respectively for the Ca, K and Mg weathering rate which is below the acceptable level of uncertainty according to Ramsey and Argyraki (1996) of the limit for measurement of variance.

Another method could be to use the proportion of \( \frac{\text{nugget}}{\text{still}} \) of the modelled variogram (Jönsson 1999). A more comparable estimate than the proportion of \( s^2_{\text{output}} \) and \( s^2_{\text{total}} \) in equation 26 could be to use the relationship \( \frac{\text{nugget}}{\text{still}} \), where the nugget (see Appendix) is the microscale variation and could be referred to as \( s^2_{\text{output}} \) and where the still is the total variation. The relationship \( \frac{\text{nugget}}{\text{still}} \) was calculated to be 62%, 38% and 52% for the Ca, K and Mg weathering rate respectively.

One problem with this approach is to determine the nugget. The modelled variogram is dependent on several properties, e.g. max lag distance, but also on the distance considered to be the most important. Normally, one tries to get a best fit to the experimental variogram at short lag distances but this is not always the case when the modelled variogram is computed to have a best fit for the whole experimental variogram, to maximum lag distance (Figure ??).

It is difficult to draw any definitive conclusions about the results from this study on uncertainty in spatial modelling. However, the uncertainty in the analytical measurements and in the determination of the mineralogical composition together with the high homogeneity in the area studied, gives an indication that the weathering rate values should be interpreted with some caution.

### 10.3 Sustainability assessment at Asa

The current calculation of the mineral nutrient sustainability in the Asa Forest Research Park should be regarded as an attempt to introduce a newly developed
assessment method rather than as a measure of sustainable biomass production in this area. At present there are several items in the mass balance calculation that are uncertain. The highest uncertainty in the mass balance calculation is the calculation of the weathering rate and the availability of nutrients to the trees from the weathering pool, $\dot{U}$ in the mass balance equation 21. However, the average rooting depth of the trees is critical because it determines the “available” weathering rate, which consistently increases with depth.
11 The Bottom Line

The chemical weathering rate in natural soils is determined by numerous different abiotic and biotic factors and several of these are interconnected. These factors and their interactions all affect the actual weathering rate. The conclusion that can be drawn from this thesis is that the only reasonable way to determine or more correctly, estimate, the chemical weathering rate for field conditions is to use mathematical models that consider the biogeochemical soil environment.

I have shown that mathematical process-orientated models like PROFILE can be used to calculate field weathering rates for various environmental systems and on different scales. However, the precision of the results is wholly dependent on the quality of the data inputs and the kinetic coefficients for the dissolution reactions incorporated in the model.

For successful modelling, it is important to have a holistic approach to model development of ecosystems due to the complexity of the model system. Therefore there must be a close connection and feedback between: 1) model use and development, 2) experimental studies, and 3) practical use and field experiments, according to our experience of modelling events in different ecosystems (Figure 1).

Field chemical weathering rate is a central concept when calculating nutrient budgets for forest and agricultural systems, in estimating critical loads of acidifying substances and in estimating sustainable biomass production in a defined production system. Therefore, it is important and critical that the work of developing and enhancing the chemical processes and rate coefficients in the PROFILE model system continues. It is also important to continue a two-track approach of experimental and field studies in future model development. Finally, there is also a need and a demand for results to be continuously validated through experimental laboratory work and field studies representative of different environments and ecosystems.

The conclusions from the thesis work can be summarized as:

1. Estimating kinetic coefficients in aqueous solution
   - Kinetic processes must be seen as a whole system. It requires a holistic view for the system of simultaneous chemical reactions and all chemical participants in promoting and retarding effects.
   - Difficulties in determining the inhibiting kinetic coefficients for epidote because several different inhibiting factors are acting simultaneously in each reaction.
   - It is possible to estimate reasonable kinetic coefficients for clay-size illite with a pedological origin from Kungsängen western Sweden with a fluidized bed flow-through reactor.
   - Dissolution experiments on clay-size minerals require significantly more than 1000 h to reach steady state.
2. Calculating mass balances in agricultural and forest ecosystems.
   - PROFILE could be adapted to calculate the weathering rate in agricultural soil system Countesswells, Scotland and Kungsängen, Sweden with reasonable accuracy.
   - It is feasible to calculate spatially distributed mass balances for mineral nutrients in a 3,500 ha large forested area in southern Sweden.

3. Spatial distribution of soil parameters.
   - Regionalized variograms can be made of mineralogical compositions and physical soil characteristics with 350 sampling sites in a 3,500 ha large forested area.
   - To spatially distribute the weathering rate in a relative homogenous 3,500 ha large forested area the sampling distance should not exceed \( \approx 300 \) m.
   - Spatial distribution of weathering rate is possible using kriging interpolation with a nested sampling strategy in the same forested area.

4. Sustainability assessment in a forested area in southern Sweden
   - By using the Liebig “Law of the Minimum” is possible to estimate the long-term sustainable biomass production in a 3,500 ha large forested area in southern Sweden, based on mineral nutrient mass balances.
   - Forestry is not always sustainable with respect to Ca and Mg in the investigated area.
   - The stand quality (Swedish; Bonitet) is not a good predictor of long-term sustainable yield.
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Notation

\[ r = \text{Reaction rate} \quad \text{kmol m}^{-2} \text{s}^{-1} \]
\[ k_{H^+} = \text{Rate coefficient in the H}^+ \text{ reaction} \]
\[ k_{OH^-} = \text{Rate coefficient in the OH}^- \text{ reaction} \]
\[ k_{H_2O} = \text{Rate coefficient in the H}_2\text{O reaction} \]
\[ k_{CO_2} = \text{Rate coefficient in the CO}_2 \text{ reaction} \]
\[ k_{org} = \text{Rate coefficient in organic acid reaction} \]
\[ C_{Al} = \text{Aluminium saturation constant} \quad \mu\text{m l}^{-1} \]
\[ C_{BC} = \text{Base cation saturation constant} \quad \mu\text{m l}^{-1} \]
\[ C_R = \text{Organic complex saturation constant} \quad \mu\text{m l}^{-1} \]
\[ n = \text{Reaction order in the H}^+ \text{ reaction} \]
\[ m = \text{Reaction order in the OH}^- \text{ reaction} \]
\[ q = \text{Reaction order in the CO}_2 \text{ reaction} \]
\[ t = \text{Reaction order in the organic acid R reaction} \]
\[ x = \text{Base cation reaction order in the H}^+ \text{ reaction} \]
\[ y = \text{Aluminium reaction order in the H}^+ \text{ reaction} \]
\[ w = \text{Base cation reaction order in the OH}^- \text{ reaction} \]
\[ v = \text{Aluminium reaction order in the OH}^- \text{ reaction} \]
\[ z = \text{Base cation reaction order in the H}_2\text{O reaction} \]
\[ u = \text{Aluminium reaction order in the H}_2\text{O reaction} \]
\[ s_{org} = \text{Organic acid reaction order in organic acid reaction} \]
\[ [H^+] = \text{Hydrogen ion concentration} \quad \text{kmol m}^{-3} \]
\[ [OH^-] = \text{Hydroxide ion concentration} \quad \text{kmol m}^{-3} \]
\[ [BC] = \text{Hydroxide ion concentration} \quad \text{kmol m}^{-3} \]
\[ [R] = \text{Free dissociated organic ligand concentration} \quad \text{kmol m}^{-3} \]
\[ P_{CO_2} = \text{Partial CO}_2 \text{ pressure in the soil solution} \quad \text{atm} \]
References


REFERENCES


Oliver, M. A. and Webster, R.: 1999, Geostatistics for environmental scientists, Course notes, Department of Soil Science, The University of Reading.


Volk, T.: 1987, Feedbacks between weathering and atmospheric CO2 over the past 100 million years, Amer. J. Science 287, 763–779.


REFERENCES 73


A Appendix

A.1 Geostatistical methods

A.1.1 Variogram

The variogram is a measure of how fast things change on average on a spatial scale and the single most important tool in geostatistical applications of geographic properties. An experimental variogram estimates the theoretical variogram, i.e., variogram of the particular realization of the property in the sampled region. The theoretical variogram is continuous and can be described as a continuous function, whereas the experimental variogram is discontinuous. To obtain an approximation of the theoretical variogram, one must adjust a smooth curve or surface through the experimental points, and treat the point-to-point fluctuation as sampling effects.

The theoretical variogram function, \( \gamma(h) \), can be considered as a random function \( Z(x) \) to determine the variation in space. \( Z(x) \) can be described by taking the differences between values at pairs of points \( x \) and \( x + h \):

\[
Z(x + h) - Z(x), \tag{27}
\]

The difference between \( Z(x + h) \) and \( Z(x) \), separated by the lag or distance \( h \), is called the increment of the random function, which describes the variation in space (Wackernagel 1998).

“The theoretical variogram \( \gamma(h) \) is defined by the intrinsic hypothesis, which is a short form for a hypothesis of intrinsic stationarity of order two”. This hypothesis, which is merely a statement about the type of stationarity characterizing the random function, is formed by two assumptions about the increments:

- the mean \( m(h) \) of increments, called the drift, is invariant for any translation of a given vector \( h \) within the domain (D).

- the variance of the increments has a finite value \( 2\gamma(h) \), but not on the position of \( h \) in the domain.

That is to say, for any pair of points \( x, x+h \in D \) we have

\[
E[Z(x + h) - Z(x)] = m(h) = 0, \tag{28}
\]

\[
\text{var} [Z(x + h) - Z(x)] = 2\gamma(h) \tag{29}
\]

These two properties of an intrinsically stationary random function yield the definition for the theoretical variogram
A.1 Geostatistical methods

\[ \gamma(h) = \frac{1}{2} E \left[ (Z(x + h) - Z(x))^2 \right] \]

(Direct quote from Wackernagel 1998, page 49)

Variograms can usually be defined by three properties sill, range and nugget (Figure 36). The sill is where the variogram (\(\gamma\)) increases to a maximum and where the value shows the maximum dissimilarity for the region. The range indicates at which lag distance (h) the dissimilarity stops increasing: it marks the limit of spatial dependence. Places separated by distances greater than this are spatially independent. The semivariance should theoretically be zero at lag zero. Usually, the adjusted smooth curve has a positive intercept on the ordinate. This feature is well known in mining and is called the "nugget variance" or the nugget-effect. The nugget-effect arises due to erratic behavior of the regionalized variable at a very small scale, i.e. the variogram goes from zero to the nugget over a smaller distance than the sampling distance. The nugget is sometimes referred to as white noise (Cressie 1991).

![Variogram diagram](image)

**Figure 36:** Variogram showing the general characteristics: sill variance, range and nugget variance. These parameters describe the variation of the theoretical variogram.

One of the main purposes with a theoretical variogram is to set up a kriging system and thereby be able to perform a kriging interpolation. Creating an experimental variogram from the data set and then replacing it with a theoretical variogram can do this.
A.2 Kriging

One of the main goals with the geochemical investigation of Asa Forest Park has been to measure and estimate the values of regionalized variables like soil properties and different modelled output. The procedure embodied in geostatistics for distributing spatial variables are known generally as *kriging* (Oliver and Webster 1999). Kriging is a geostatistical estimation technique and an unbiased optimal spatial prediction or estimation. Detailed description and the theoretical concepts regarding kriging can be found in e.g. Goovaerts (1997), Wackernagel (1998) and Chilès and Delfiner (1999).

**Geostatistical software**

In the geostatistical analyses of the data input and output data two different software programmes were used. Genstat 5 Release 4.1, 4th edition, was used for the statistical summary of the data set and for calculating the variogram model for the different soil parameters and for the weathering rate. Surfer 7 was used to construct the experimental and model variograms and the kriged interpolated maps.
B  Appendix

B.1  Original data from the geochemical investigation at Asa
B.1 Original data from the geochemical investigation at Asa
B.2 Methods

The pH and exchangeable cations (mg g⁻¹) was determined by talking 10 g humus or 20 g mineral soil sample into 200 ml bottle and adding 100 ml of 0.1 M BaCl₂ solution. The mixture was shaken for 2 hours and filtered. The filtrate was analyzed by ICP-AES (Perkin Elmer, Connecticut, USA) with regard to the base cations Ba, K, Ca, Mg, and Na together with acid cations such as Al, Fe, and Mn. The amount of hydrogen per gram soil was determined by:

\[ H^+(\text{μe}g^{-1}) = -\frac{\log_{10} p\text{BaCl}_2 \cdot V_{0.1\text{MBaCl}_2}}{m_{\text{fine earth}}} \]  (31)

The CEC was calculated by making the sum of all exchangeable cations and the base saturation was calculated as (32):

\[ \text{Base saturation(%) } = \frac{\text{Sum base cations}}{\text{CEC}} \cdot 100 \]  (32)

The exchangeable metal (mg g⁻¹) ions were determined with extraction with an acid 0.02 M EDTA solution. The extraction of the metal ions followed the same procedure as for extraction with BaCl₂.

Nitrogen was analysed by the Kjeldahl method. The carbon content was determined by LECO, at 550°C and the soil organic carbon content was determined through loss-of-ignition LOI (Bengtsson and Enell 1986).

The elemental composition of the minerals in the C-horizon the sample was determined by using Li₂B₄O₇ with a following dissolution of the fused melt. The soil-sample was preheated to 550°C for 2 h. 0.1 g of the ash was then mixed with 0.5 g of the flux Li₂B₄O₇. The mixture was fused to 1000°C for 15 min to a homogenous melt. The melt was dissolved in heated 5dissolved Li₂B₄O₇ melt was analyzed with ICP-AES with regard to the elements Si, Al, Fe, Ba, K, Na, Ca, Mg, Mn, P, Zn, Zr and Ti.

The weathering rate (Ca-Weath., K-Weath. and Mg-Weath) are expressed as keq ha⁻¹ yr⁻¹.