Thesis for the degree
of Candidatus Scientiarum

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Acidification in China

—Model simulation of soil acidification in the Tie Shan Ping catchment, Chongquin.

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Preface

> *"The essence of the whole Sermon on the Mount is given here in a few words to show that God has not been partial in blessing only a single nation with high moral teachings. Even an Ethiopian could preach the meekness and humility of which the most materially advanced nations of the day may well feel proud."*
>
> ***Luqman Al-Hakim***

The thought of taking environmental chemistry as my subject for my Cand. scient. grew out of my first contact three years ago with Dr Rolf David Vogt. He was then an associate professor and was lecturing in analytical chemistry. I was then greatly moved and made my historical and lifetime choice, which I feel no regret at all. It would not be an overstatement to say that it was Dr Vogt who enlightened me and guided me into the field of environmental chemistry.

Curious, yet still innocent I, together with Dr Thorjørn, Dr Rolf and other experts, took a field trip to China. There I experienced in person the splendid culture that evolved in the long river of history, and the sense of responsibility of the people. Humanity is on one hand creating civilizations, but is on the other hand ruining the well being.

I was happy that I could participate in the joint Sino-Norway project IMPACTS (Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems) and did my share, no matter how little it was. It occurred to me that I could benefit a lot by gaining expertise from the collective exploration to the nature of this problem, and maybe serve in the future for my native country Somalia, which shares some similarities with China.

Thanks to the Model of Acidification of Groundwater In Catchments (MAGIC), I got a better understanding of the dynamic processes between soil, water and gas in soil chemistry, and applied it to the Chinese sites. The simulation and prediction results were consistent with some other previous scientific findings. This made me feel relieved as two and half years of hard work finally paid off.

From introduction to conclusion, there are six chapters, which is the basis of this thesis. I tried to cover essential areas within discussed topics and present it in a simple and understandable way with standard quality language to the readers. I wish to strongly acknowledge in this regard the continual assistance, the extensive help and advice in term of linguistic corrections that I have received from my supervisors during the writing period.

It’s approaching an end of an epoch, time to celebrate, time to think a head of what the new academic life will bring in the future. But time for big celebration is still not ripe yet. At its best this thesis represents the enclosure of my journey, but more importantly, it represents the beginning of the journey for me in the years to come.

I thank to Allah the Lord of the universe by completing this work without serious difficulties.
Special thanks go to my principal supervisor, Professor Hans Martin Seip. He is the very man of deep insight and full knowledge. The spirit of this thesis was nurtured in many ways by his wisdom and generosity. He especially wet-nursed it in its infancy through some difficult times.

I am very grateful to my co-supervisors, associate professor Rolf David Vogt and Dr. Thorjørn Larssen, for their elaborate instruction and inspiring encouragement. I really appreciate Dr. Thorjørn’s tolerance and patience whenever there was a need to go to minute details of some questions, especially problems in the MAGIC model.

My colleagues in our environmental group contributed to this thesis in the ways probably they didn’t realize. We shared the congenial academic atmosphere in which I benefited by many means, such as the open or personal discussions. For this, I’m heartily indebted.

Taking environmental chemistry as my subject was truly challenging. There were much more feelings of hardship than that of joy during “the gestation period”. Whenever I was depressed and frustrated, my closest friend, Hassan Ali Khaire, was always there, ready to help me. Thanks to his sincere spiritual support, I can be Abdi Dahir Osman as it stands here today.

The final acknowledgement is to my wife, Fahma Ali Shire. Through her wish from deep in her mind, her love from the bottom of her heart, and her unmatched patience, my dear wife, Fahma Ali, has created conditions that made this thesis possible.

Oslo, Norway Abdi Dahir Osman
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Abstract

Acid rain is becoming an increasing environmental problem in China. Coal accounts for about 63 % of the energy consumption in China, leading to a high emission of sulfur. Chongqing is the largest city in southwest of China. The energy production of the city is dominated by combustion of high-sulfur and high ash coal. The average sulfur content of the coal consumed is 2.8%. The annual average concentration of SO_2 in ambient air was $0.2 mg/m^3$ in 1999, and the corresponding median pH in precipitation was far below 5. The low base saturation and high aluminum saturation (average AlS is 80.5 % in the deeper soil) suggest that the soil is sensitive to acid deposition.

In Tie Shan Ping (TSP), SO_4^{2-} is the dominant anion in soil water. The median value of SO_4^{2-} for four plots is 1432μeq/L. Al^{3+} is the dominant cation and the contribution from this element is considerable. The median concentration of Al^{3+} in soil water is 728μg/L and 836μg/L in the upper and deeper soil respectively. Although heavy vegetation damage was not observed, moderate harmful levels of aluminum when compared to other base cations have been occurring.

As the Lei Gong Shan (LGS) is located far away from large emission source, the sulfate concentration in precipitation is relatively low. However the concentration levels of light hydrocarbons show that the Lei Gong Shan area is also influenced by pollution sources on the regional scale.

In order to understand the future effect of acid deposition on soils and soil waters in Tie Shan Ping area, the MAGIC model was selected as a methodic tool to investigate long-term changes in soils and soil waters due to acid deposition for four different plots in the catchment. The MAGIC model is also applied to predict possible soil responses to assumed future deposition scenarios.

The model simulations clearly indicate that long-term acid deposition has resulted in soil acidification in both upper and deeper soils of four different plots (B, C, K and L) in the catchment. Despite this fact, vegetations and topography and the parameters such as pH, base saturation and cation exchange capacity show substantial differences resulting in large variations in sensitivity to acidification even within this small catchment. The results from model output depend on values selected for dry deposition factors for major ions, the solubility constant for $Al(OH)_3$, weathering rates of minerals, Dissolved Organic Carbon (DOC), H-power, sulfate adsorption, CEC and ion concentration in precipitation.

The model predictions show that soil acidification will continue if deposition of base cations decreases or deposition of SO_4^{2-} increases by 30%. According to these modeling results, soil conditions will improve if a 30% reduction in sulfur deposition is achieved in the future. The model results also predict that soil acidification will continue slowly, similar to the present situation in the catchment, if acid deposition continues at the present level.

1. Introduction

1.1. Environment in general

The environment has been defined and explained by scientist and philosophers in different ways. But the common dictionary meaning is "surrounding objects, regions or conditions specially circumstances of live society"[1]. The meaning of surroundings has been confined by some to mean physical or material conditions only, but others have incorporated in it both material and moral aspects of our existence. The following definitions of environment seem appropriate in our case

a. External conditions as affecting plant and animal life[2].

b. The totality of the physical conditions on the earth or a part of it, especially as affected by human activity[3].

1.2. Background

1.2.1. Environmental problems in China

China with its about 1.3 billion people (≈21% of the world population) is one of the world's rapidly developing countries. Coal is the primary energy source (63% in 2000) for power plants, industrial boilers and domestic heating. The result is high levels of urban air pollution especially particulates and sulfur dioxide (SO_2), and widespread acid deposition. This developing country follows the same historic pattern today as many now developed countries once did. The industrial countries' extensive economic development for the past decades with coal as a prime resource of energy pays the expense of human health and material damage in the country. The energy consumption in China increased 5.1 %

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[1] Cambridge dictionary

[2] Oxford concise dictionary

[3] Oxford concise dictionary

annually over the period 1980-1995 (Seip et al 1999) and, probably temporarily, declined during the last five years (figure 1.1) (Byrne *et al.*, 1996; BP-Amoco, 2001). The average sulfur content of the coal consumed is 1.2%, but in the Sichuan and Guizhou provinces sulfur content is 2.8% and 3.2%, respectively. This sulfur rich coal accounts for about 63 % of the energy consumption in China, (figure 1.2) *(BP-Amoco, 2001)* leading to a high emission of sulfur. Since air concentrations of alkaline dust in the southern and southwest part of the China are low, this sulfur emission leads to acid deposition, which has become one of the large environmental problems in this part of the country. The nitrogen emissions in the country are dominated by NH_3 from fertilizer and domestic animal waste (Zhao and Wang, 1994; Galloway et al., 1996). Commercial fertilizer accounts for about 80% of the country's total 25 million tones per year of nitrogen mobilization to the atmosphere.

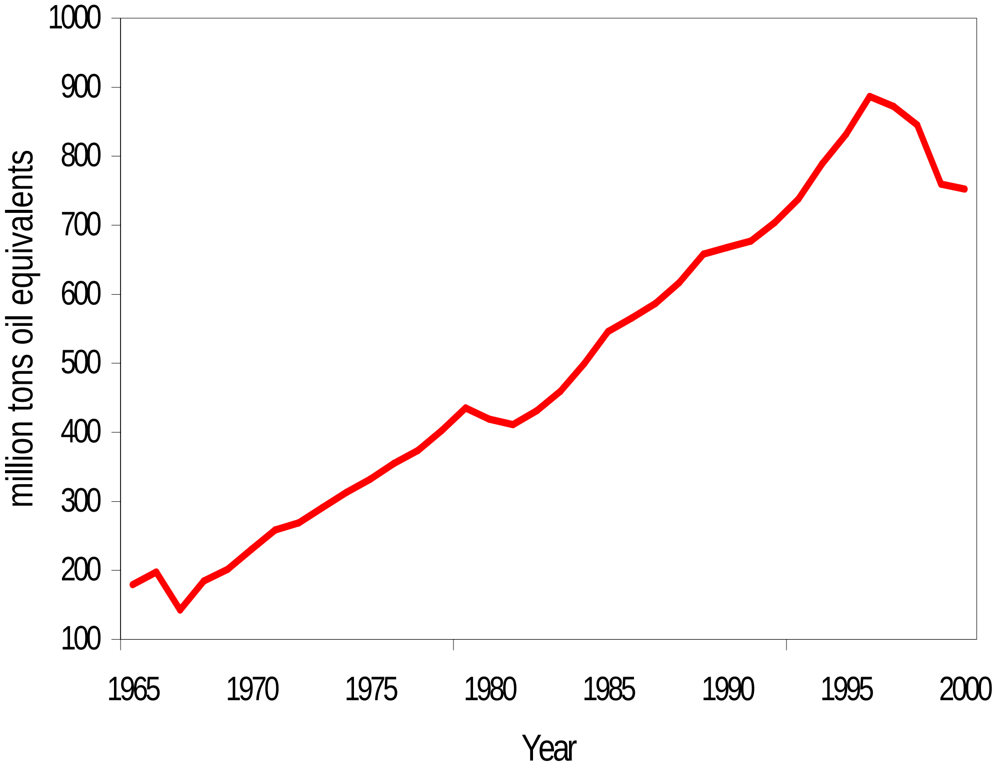

Figure 1.1 *Energy consumption in China (BP-Amoco, 2001)*

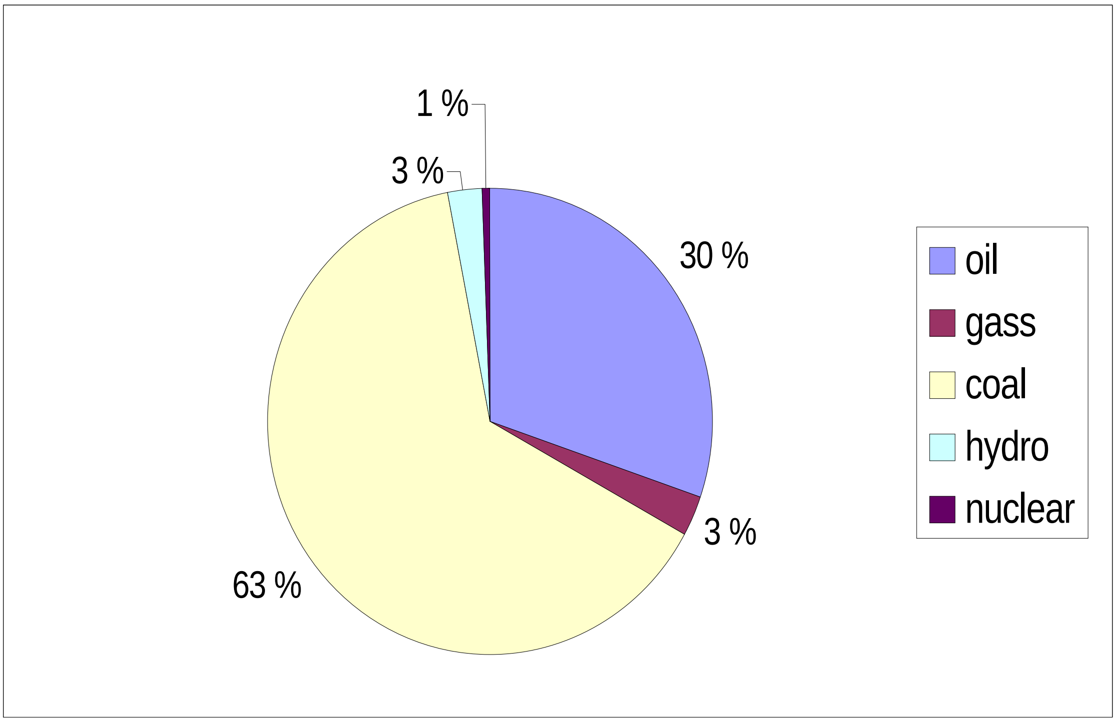

Figure 1.2 *Primary energy carriers in China in 2000 (BP-Amoco, 2001)*

1.3. Acid rain in China

Acid rain has become a serious environmental problem in large parts of China. The southern and southwest cities in China are among the heaviest exposed to acid rain (Lei et al 1997). Acid rain is observed in most cities and provinces in this part of the country. In Chongqing the average concentration of SO_2 in air was as high as $177 \mu g/m^3$ in 1999. Acid rain was also found in small regional areas in northern China. The annual average pH of rains in cities across China ranged between 4.15 to 7.69 in 1999 and 40.1% of the cities had acid rain with annual average pH less than 5.6 (Ding et al., 2001).

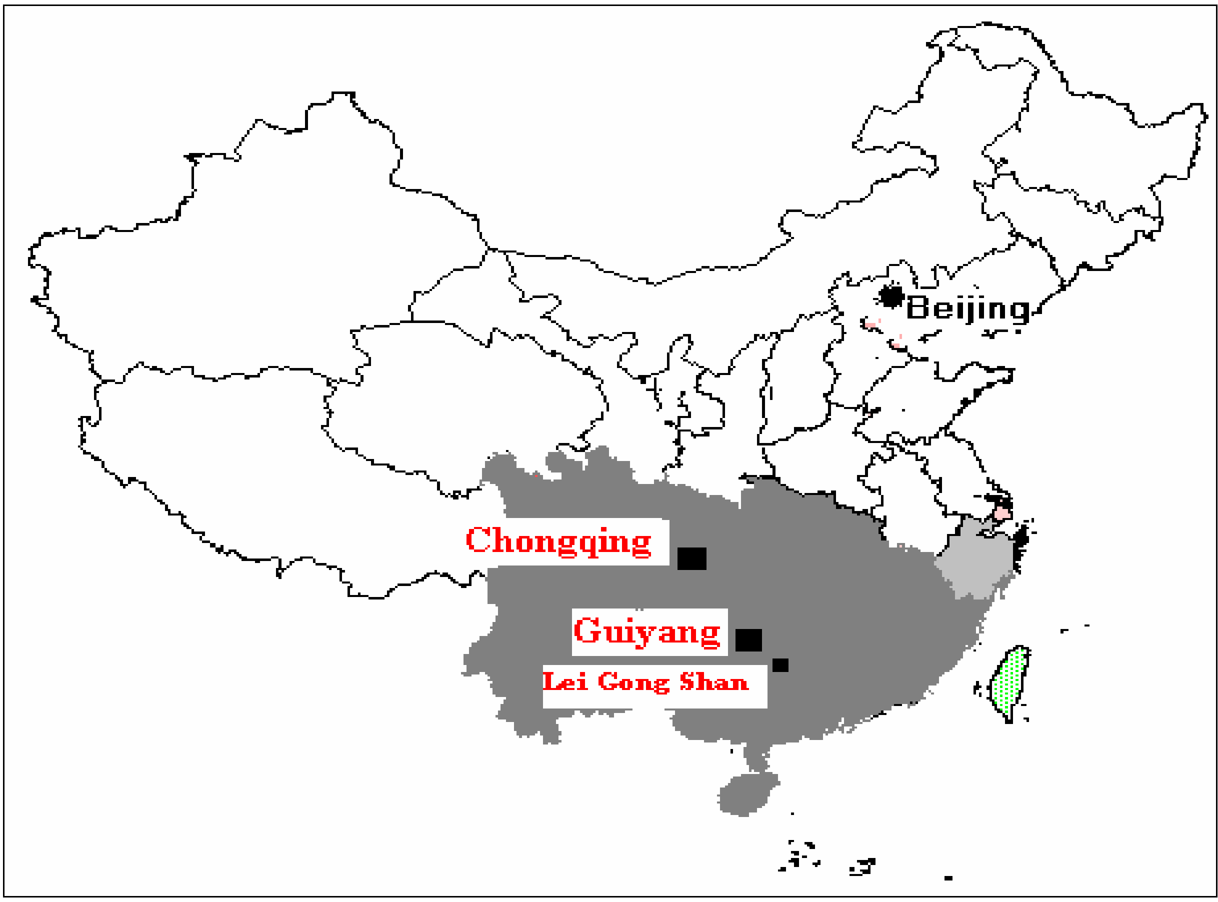

Figure 1.3 *Map of China showing the area most effected by acid deposition including Chongqing (Sichuan province) and Lei Gong Shan (Guizhou province)*

1.4. Modeling

1.4.1. Motivation

Models can be as simple as a verbal statement about a subject or two objects connected by an arrow to represent some relationship. Alternatively, models can be extremely complex and detailed. Modeling has become an important tool in the study of chemical processes in soils and soil waters, as a scan of the table of contents of any major chemical journal makes abundantly clear. A number of models have been constructed to increase understanding of acidification and related environmental problems (e.g., MAGIC, Profile, RAINS-ASIA, Nu CM, Soil-N and EMMA). Modeling offers exciting possibilities for the exploration of hypotheses that are not easily pursued through field experimentation or laboratory studies.

Models provide an opportunity to describe processes and understand how ecosystem is functioning; they may be used for prediction and scenario analysis and to calculate chemical concentrations and determining critical load (Schnoor, 1996). Furthermore, simulation of systems with models helps identify data needs and knowledge gaps.

1.4.2. MAGIC model applications in China

MAGIC (Model of Acidification of Groundwater In Catchments) is a dynamic acidification model that was originally developed to assess long-term changes in surface waters. The model has been widely used in North America and Europe (Cosby et al., 1985). Zhao and Seip used MAGIC for Chinese conditions; they applied the model to predict soil acidification and to estimate critical loads of acidity in some Chinese soils (Zhao and Seip, 1991). In later work the MAGIC model has been applied to specific plots from Liu Chong Guan, LCG, and Tie Shan Ping, TSP, at the Guiyang and Chongqing respectively for prediction of soils, soil water and surface water acidification (Liao, et al., 1998 and Larsen, et al., 1998).

1.5. The IMPACTS project and the aims of this thesis

The Environmental Chemistry Group at the University of Oslo (UIO) has had a close cooperation with Chinese scientists since 1988. The cooperation with Chongqing Institute of Environmental Science and Monitoring (CIESM) was initiated in 1992. The motive for this cooperation was to exchange ideas and experience between Norwegian and Chinese scientists within the research field of acid rain, and to establish new monitoring catchment sites in China.

In cooperation with five Norwegian research institutes NIVA[4], NILU[5], NISK[6], NUPI[7],

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[4] Norwegian Institute for Water Research

[5] Norwegian Institute for Air Research

[6] Norwegian Forest Research Institute

[7] Norwegian Institute of International Affairs

NINA[8], and support with the Word Bank and NORAD[9], the Environmental Chemistry Group at UiO completed a pilot project with the acronym PIAC (Planning of an Integrated Acidification Study on Survey on Acid Rain Impacts in China). PIAC became the basis of the ongoing project Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems (IMPACTS), which involves many Chinese research institutions and authorities.

The key objective of the IMPACTS project is to transfer experience on acid rain research and thereby enhance the ability of Chinese research institutes and environment institutions in monitoring acidification and its environmental effects in China. Furthermore the project intended to form the basis for Chinese participation in international co-operation on acid rain. As part of this project the Tie Shan Ping site outside the city of Chonqing, had been chosen as an experimental field study. Lund (2001) has described the Tie Shan Ping site and discussed general problems related to soil and soil water acidification for specific plots in this catchment.

The aim of this study may be summarized as follows:

1. To study the role of calcium and sulfate in soil acidification and acid deposition in Tie Shan Ping and to assess possible historical deposition sequences for these elements by applying a model

2. To model long-term changes in soil and soil water chemistry processes in the Tie Shan Ping catchment due to acid deposition, and to predict possible future trends in soil acidification at this site, by using the MAGIC model

3. To systemize existing data for Tie Shan Ping, supplement with new data when necessary, and to ensure the quality of these data.

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[8] Norwegian Institute for Nature Research

[9] Norwegian Agency for Development Cooperation

2. Theory

2.1. Soil composition

There are three different phases, the gas, the liquid and the solid phases, which are important for the most soils.

The Gas phase: The CO_2 pressure of today's atmosphere is $10^{-3.44}$ atm. Because the CO_2 is generated in soils by decay of organic material and by root respiration, the concentration of CO_2 may be much higher in soils than atmosphere (Seip, 1993).

The Liquid phase: Ions and molecules in the soil water are moving through the soil by different processes. Ion and molecule transportation is mainly in the liquid phase of the soil. The composition of the soil water is dependent on the water origin and the type of soils or rocks through which the water flows.

The Solid phase: The solid phase of the soils consists of organic and inorganic parts.
The organic parts in soils are largely derived from plants. It may originate directly from plants grown in the soil or indirectly from plants grown elsewhere when manure or sewage or other organic products is applied. The topsoil layers will naturally have higher amount of organic matter than the sub soils.
The inorganic part mainly contains oxides/hydroxides, clay minerals, silicates and different salts, and its origin is weathered rocks. Soil composition is determined by the particles in which the soil is consisting. Sands and silt-sized particles are e.g. composed mainly of either quartz (silica) or other rock minerals from which the soil was formed.

2.2. Soil organic matter

Organic matter has many important effects on soil properties, such as soil structure, particularly its stability, soil water reserves, soil color, nutrient supply, particularly nitrogen, phosphorus and sulfur, and leaching of nutrients. The organic matter in soils is largely derived from plants; but microorganisms and animals also contribute.

In soil solution the organic matter is the product of biomass degradation and is called natural organic matter (NOM). The organic compounds that pass through a 0.45µm membrane filter is called dissolved organic carbon (DOC).

The total concentration including larger particles and colloids is called total organic matter (TOC). The organic matter in soil solution has generally a weak negative charge because of some protolyzed carboxylic and phenolic groups.

2.3. Sorption and ion exchange

Appelo and Postma (199) describe sorption as the change in concentration of a chemical compound in the solid matter as a result of mass transfer between solution and solid. The sorption processes as illustrated in figure 2.0 may be divided into the following subdivisions:

Adsorption occurs between the solid surface and ions/complexes or molecules. The molecules are held at the surface by weak van der Waals forces, or chemical bonds. Complex formation on the surfaces of metal oxides and hydroxides is a typical example of adsorption. The surface atoms will be partly hydrated in aquatic environment, the hydrolysis products will then cover the oxide surfaces. The surface atoms can react with ions in the diffuse double layer around the solid surface. The adsorption between an active cation M^{n+} and a solid with surface of hydroxyl groups may be written as follows,

$$\text{SOLID-OH} + M^{n+} \Leftrightarrow \text{SOLID-OM}^{(n-1)+} + H^{+} \qquad \text{(eq. 2.1)}$$

The adsorption of a ligand L^{n-} on a solid with surface of hydroxyl groups may be written as,

$$\text{SOLID-OH} + L^{n-} \Leftrightarrow \text{SOLID-L}^{(n-1)-} + OH^{-} \qquad \text{(eq. 2.2)}$$

Sulfate is also assumed to have an adsorbed phase and to follow a Langmuir[10] isotherm.

Absorption is a process in which the chemical species is taken up or transmitted into the solid. See figure 2.0

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[10] Method for classic adsorption isotherm, which is used for description of adsorptions.

Ion exchange involves replacement of one ion for another one at the solid surface. A major difference between sorption (adsorption and absorption) and ion exchange is that the ion exchange reactions do explicitly account for all ions and always balance the surface charge. The sorption reactions use the concentration of one chemical only which could lead to a net change in surface charge.

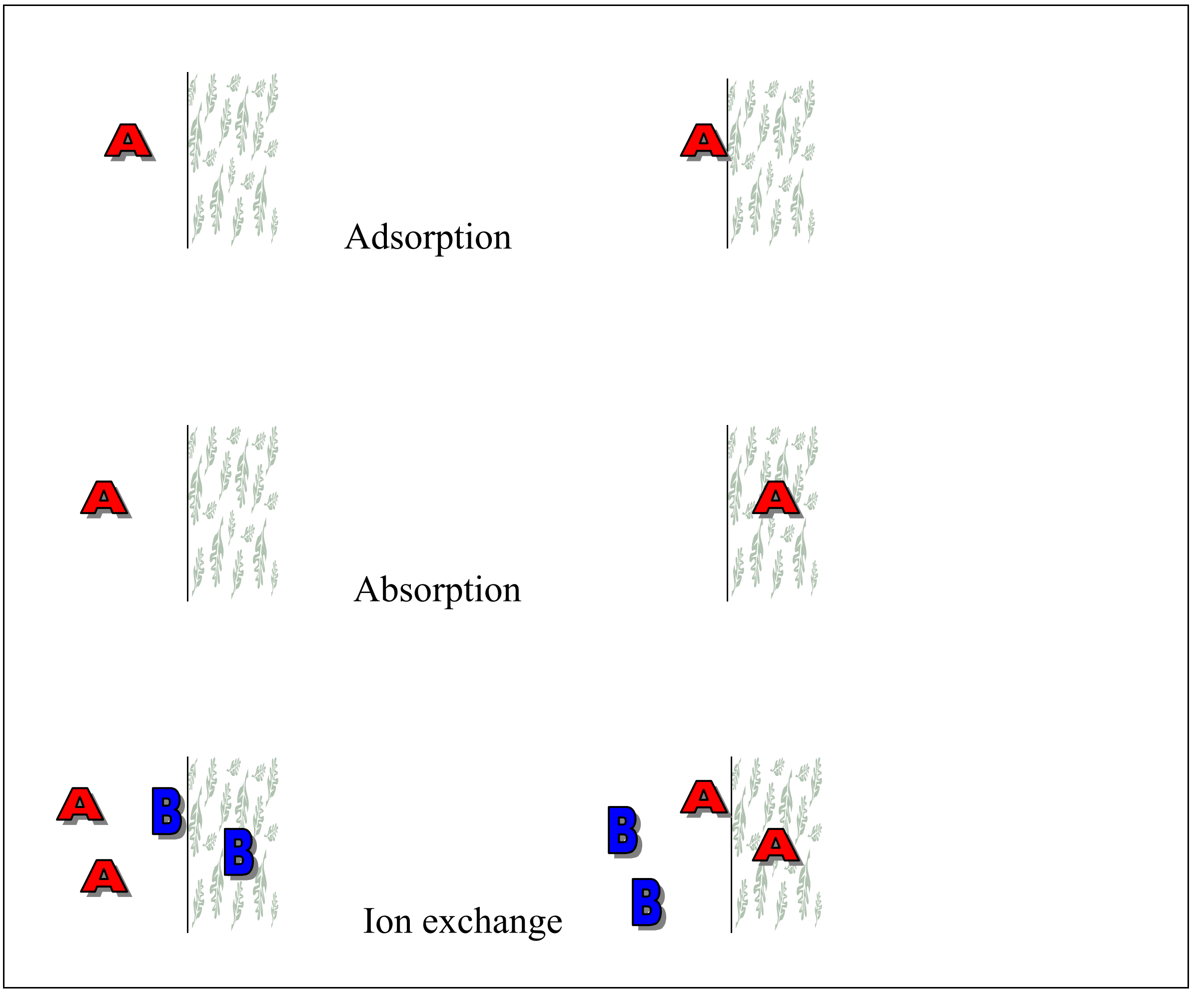


Figure 2.0. *The figure shows schematically the different sorption processes. The figure is taken from Appelo and Postma, 1999.*

2.4. Soil cation exchange reactions

In mineral soils clay minerals are very important cation exchangers (Scheffer/Schachtschabel, 1992). The exchange process between two monovalent ions A and B in figure 2.0 may be expressed as an equilibrium reaction:

$A^+ + \text{soil-}B^+ \Leftrightarrow B^+ + \text{Soil-}A^+ \qquad K = [B^+][\text{Soil-}A^+] / ([A^+][\text{Soil-}B^+])$ (eq. 2.3)

Different descriptions of the sites on the surface have been suggested and different equations describing the ion exchange exist (e.g. Gaines Thomas, Vanselow and Gapon). For homovalent exchange it makes no different what convention is used, while for hetrovalent exchange the effect is quite notable. The equilibrium constant for the exchange process between hetrovalent ions (e.g Na^+ and Ca^{2+}) may be expressed after Gaines-Thomas equation as:

$$K^{GT}_{Na/Ca} = \frac{\beta_{Ca}\,[Na^+]}{\beta_{Na}\,[Ca^{2+}]^{\frac{1}{2}}} \qquad (eq.2.4)$$

Where as β_{Ca} and β_{Na} are the relative amounts of Ca^{2+} and Na^+ on the ion exchange complex. The theory of Debye-Hückel may be used for calculations between concentrations and activities.

2.5. Important elements in soil acidification

The distinction between base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and acid cations (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^+_2$, Fe^{2+} and H^+) is important when considering soil acidification. Thus, Reuss and Johnson (1986) emphasizes that soil acidity is determined by the relationship between the amount of the basic cations and the acid aluminum species on the exchange complex. One must distinguish between capacity and intensity terms (Reuss and Johnson, 1986). Capacity refers to the total storage in a system, e.g. CEC or the sum of exchangeable base ctions. Intensity refers to the concentration in solution at a given time, e.g. to solution pH.

In an acid environment base cations on soil surfaces (e.g. Ion exchanger) will be displaced by H^+ or Al^{3+} ions in solution, and the base metal ions will then enter the aquatic phase. Depletion of base cations on the cation exchanger will eventually lead to elevated activity of aluminum and mobilization of toxic heavy metals. High concentration of aluminum in the soil solution may have toxic effects on both vegetation and microorganisms in the surrounding environment (Nilsson and Grennfelt, 1988).

2.5.1. Base saturation (BS)

McFee (1980) consider BS as one of four important parameters in estimating soil sensitivity to acid precipitation.

Reuss and Johnson (1986) support the theory of McFee and agree there is a general relationship between pH and base saturation, but pointed out that the estimation of base saturation by pH is questionable because pH depends on several other parameters as well. Both Wiklander, 1980 and Johnson, 1981 pointed out that decrease of base saturation results in a decrease of $\Delta M/\Delta H$ (ΔM is the cation removal and ΔH the H^+ input), so that base cation leaching will decrease at low base saturation (i.e. less than 20%). Reuss and Johnson (1986) conclude that the soils having moderate to high base saturation (i.e. more than 20%) in general will lose more base cations than soils having very low base saturation. Again they emphasized the important of base saturation and conclude that the low base saturation soils will tend to be sensitive to aluminum mobilization.

2.5.2. Sulfur

A large part of SO_2 (about 30%) emitted to the atmosphere is produced in natural processes by volcanoes and by the oxidation of sulfur gasses produced by the decomposition of plants. SO_2 the marine biosphere accounts for about 50% of the natural sulfur (Harrison 1999). Main anthropogenic sources are SO_2 combustion of coal and oil containing sulfur and metal production. SO_2 will rapidly oxidize to SO_3 and, therefore, be equivalent to H_2SO_4 in precipitation. Equations 2.5a-c show an important route oxidation for SO_3. Sulfate enters the soil as wet deposition with the rainwater as SO_4^{2-} in precipitation. Sulfate may also enter in the soil as dry deposition either directly or through the canopy.

$$HO\bullet\ SO_2 + M \rightarrow HOSO_2\bullet + M^* \qquad \text{(eq. 2.5a)}$$

$$HOSO_2\bullet + O_2 \rightarrow HOO\bullet + SO_3 \qquad \text{(eq. 2.5a)}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad \text{(eq. 2.5c)}$$

2.5.3. Nitrogen

Apart from sulfuric acid the dominant acid in acid rain is nitric acid. Thus nitrogen chemistry and its associated processes are important for soil acidification. The most important source of anthropogenic nitrogen oxide (nitrogen monoxide NO) is the NO formed in combustion processes.

$$N_2 + O_2 \rightarrow 2NO \qquad \text{(eq. 2.6)}$$

NO oxidized with air and give NO_2:

$2NO + O_2 \Leftrightarrow 2NO_2$ (eq. 2.7)

Direct oxidation with oxygen air is a slow process. Nitrogen dioxide and water give nitric acid after this reaction:

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (eq. 2.8)

Nitrogen enters soils as nitrate (NO_3^-) and ammonium (NH_4^+). The NO_3^- may cause leaching out of equivalent amounts of base cations. It may cause soil acidification if not taken up by plants or microorganisms. If plant or microorganism assimilates NO_3^- there will be no soil acidification, because OH^- is released in the uptake process and naturalize the input acid.

Plants or microorganisms would rather take up NH_4^+. NH_4^+ can also be oxidized to NO_3^-. Soil acidification will especially occur if NH_4^+ is oxidized to NO_3^- in the soil, because $2H^+$ are released in the oxidation process. The following reaction describes the nitrification process of ammonium in the soil,

$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ (eq. 2.9)

The concentration of NO_x in Chinese cities is relatively low. The average concentrations at National Air Monitoring System (NAMS) in year 2000 are below 0.05 mg/m^3 (Ding et al., 2001). However, considering the strong development in southern cities in combination with the growing number of motor vehicles, the concentration of NO_x emission is expected to increase in the future. This may result in a worsening environmental condition in China for the coming decades.

2.5.4. Aluminum

Aluminum is present in acid soil water as $Al(H_2O)_6^{3+}$ (written as Al^{3+} in this text), $Al(OH)_n^{(3-n)+}$ or as complexes with sulfate, fluoride, silicates and organic matter. Al^{3+} dominates at pH less than 5.0, while hydroxide complexes are dominating in solutions with pH higher than 5.0 (dependent on temperature). The chemical equations describing the formation of the different aluminum complexes are shown in table 2.0

Table 2.0.*The stability of dissolved aluminum hydroxide complexes at 25^{0}C (Ball et al., 1980)*

Reaction	**logK**	
$Al^{3+}_{(aq)} + H_2O \Leftrightarrow Al(OH)^{2+}_{(aq)} + H^+_{(aq)}$	-4.99	(eq. 2.10)
$Al^{3+}_{(aq} + 2H_2O \Leftrightarrow Al(OH)_2{}^+_{(aq)} + 2H^+_{(aq)}$	-10.13	(eq. 2.11)
$Al^{3+}_{(aq} + 4H_2O \Leftrightarrow Al(OH)_4{}^-_{(aq)} + 4H^+_{(aq)}$	-22.05	(eq. 2.12)

Aluminum also forms complexes with fluoride and sulfate. Significant amounts of $Al(SO_4)^+$, may be formed when acid rain (i.e. rich in sulfate) falls in acid soils. The reaction is,

$$Al^{3+} + SO_4^{2-} \Leftrightarrow Al(SO_4)^+ \quad \Rightarrow \quad K = [Al(SO_4)^+]/([Al^{3+}][SO_4^{2-}]) \qquad \text{(eq. 2.13)}$$

Lindsay (1979) has determined the equilibrium constant $K=10^{3.20}$, for this reaction.

The gibbsite constant

The expression commonly used to predict the concentrations of Al^{3+} in solution is equilibrium with gibbsite:

$$Al(OH)_3\,(s) + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O \qquad K_{Gibbsite} = \{Al^{3+}\}/\{H^+\}^3 \qquad \text{(eq. 2.14)}$$

$$\text{Log}\,\{Al^{3+}\} = \log K_{Gibbsite} + 3\text{Log}\{H^+\} \Rightarrow pAl = pK_{Gibbsite} + 3pH \qquad \text{(eq. 2.15)}$$

The MAGIC model (previous versions) uses the relationship of $pAl = pK_{Gibbsite} + 3pH$ for the solubility of aluminum. This is a linear relationship between pAl and pH with slope of 3. Crystalline gibbsite has $pK_{Gibbsite}$ value of -8.11 and amorphous $Al(OH)_3$ has a -10.8 (Stumm and Morgan, 1996). However, Larssen et al (1998) used $pK_{Gibbsite}$ in the interval {-7.70, -8.94} in an application of MAGIC to the Tie Shan Ping catchment.

2.5.5. Fluoride

Coal burning and emission from metal production are the main sources for fluoride in the atmosphere. Fluoride is strongly bound by aluminum giving complexes as AlF^{2+} and possibly some AlF_2^+ and $Al(OH)F^+$. High aluminum concentrations dominate in acidic environment, and most of the F^- in such system is complexed by aluminum. The chemical equation for the formation of AlF^{2+} may be written:

$Al^{3+} + F^- \Leftrightarrow AlF^{2+} \Rightarrow K = [AlF^{2+}]/[Al^{3+}][F^-]$ (eq. 2.16)

The equilibrium constant for this reaction is $10^{6.98}$ (Lindsay, 1979).

2.6. Acid deposition

2.6.1. Wet deposition

One of the most serious environmental problems facing many regions of the world today is acid rain. Ecological damages caused by acid rain are increasing. The acid particles in air probably also have direct effects on human health (Baird 1998). The pH of unpolluted rainwater is about 5,6. Rainwater with a pH of less than about 5 is considered to be acid rain. The two common wet deposited acids in acid rain are sulfuric acid and nitric acid. *Wet deposition* is the transfer of the substance from the atmosphere within, or at the surface of hydrometeor (rain, snow, hail etc) (Fowler, 1980). Acid rain can precipitate far downwind from the source of the pollutants due to transportation of air masses that contain SO_2 and NO_x. Acid rain is a pollution problem that does not respect national boundaries. For example, most acid rain that falls in Norway, Sweden and the Netherlands originates from sources of SO_2 and NO_x in other countries in Europe.

2.6.2. Dry deposition

Dry deposition is the direct transfer to and absorption of particulate aerosols and gases by surfaces (Fowler, 1980). Direct measurement of dry deposition is extremely difficult, as the processes involved include both gas absorption and particle impaction on all kinds of surfaces (Overrein et al, 1980). Indirect methods must therefore be used, e.g. Schoeller (1960), Ericsson (1960) and Lerner et al., (1990) have used Cl^- to estimate the contribution of dry deposition to atmospheric deposition. Such methods are less suitable in non-marine area (i.e. > 200km from the sea). The calculation for dry deposition from chemical balances can be compared with results from a physical model of deposition velocity. The dry deposition may be estimated from,

$D = \Phi . v_d . C$

Where D is dry deposition ($\mu g/m^2.yr$) Φ is a constant, v_d is the dry deposition velocity (cm/s) and C is concentration in ($\mu g/m^3$) of the depositing substance. With the above units $\Phi = 3.15.10^5$.

2.7. Critical load (CL)

The critical load of acidity (CL) is defined:

" The maximum input of acid deposition to an ecosystem which will not cause long-term damage to ecosystem structure and function " (Nilsson and Grennfelt, 1988)

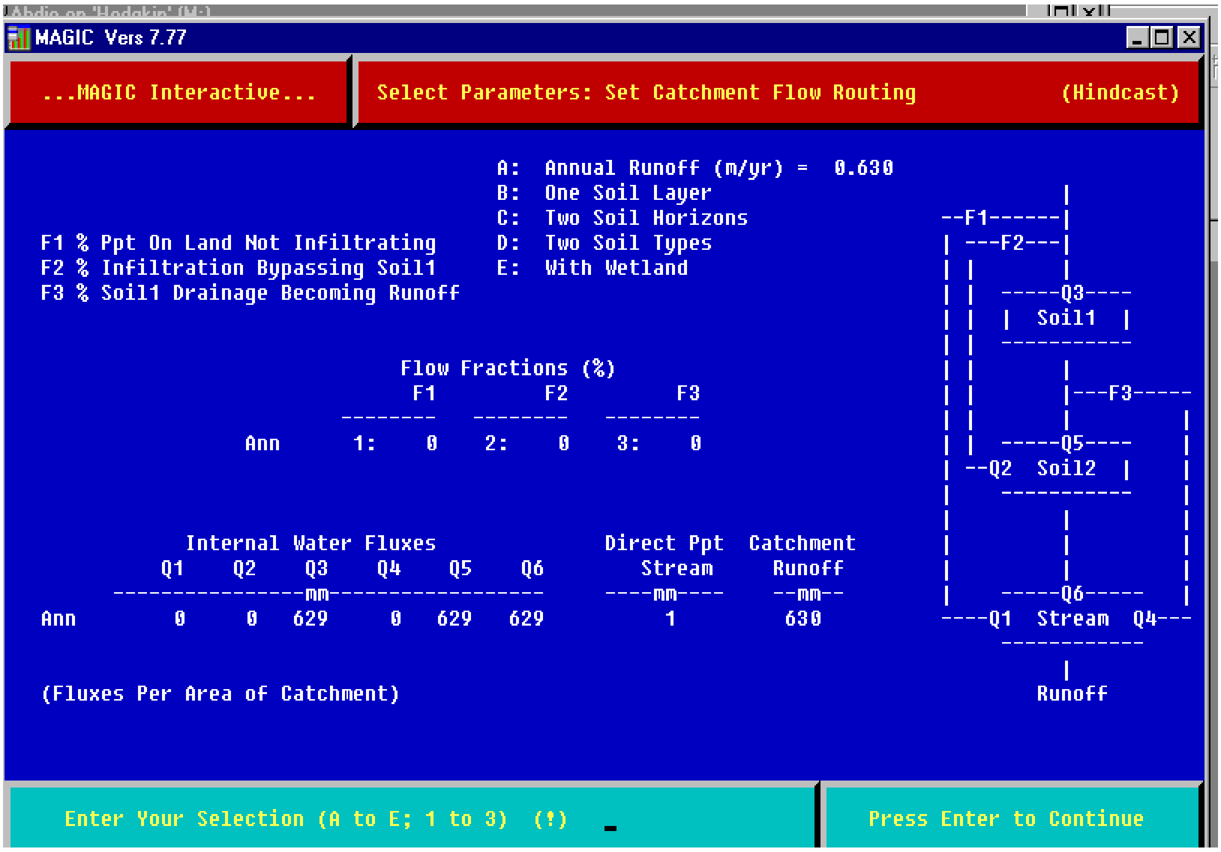
The concentrations of toxic aluminum play essential role in the critical load concept. The molar Ca^{2+}/Al^{3+} ratio in soil water is used as an indicator of vegetation damage. If the molar Ca^{2+}/Al^{3+} ratio is less than 1.0 there may be harmful effects on forests (Cronan and Grigal, 1995). In the Nordic countries, with acid surface waters, the most vulnerable species are fish and the critical load is calculated as the difference between the alkalinity produced by weathering and the critical leached alkalinity. If the steady state mass balance method (SSMB) is used in calculation of the critical load, the following two ways have been applied (Sverdrup and de Vries, 1994):

1. Plant criterion (CL_p): The given molar ratio of base cations to aluminum is directly related to vegetation damage.
2. Soil stability criteria (CL_{Al}): Possible structural changes in the soil due to aluminum depletion from the soil. The assumption here is that the leached aluminum is equal to the weathered aluminum, which is assumed to be the double of the total weathering of base cations.

2.8. The MAGIC model

The MAGIC model is an intermediate complexity process oriented model of catchment soil and stream water chemistry. (Cosby et al., 1985). It is a dynamic acidification model incorporating a number of processes, which are assumed to be important for predicting long term responses to acid deposition in soil and surface water. Major soil processes in MAGIC are base cation exchange in soils, aluminum complexion in solution, sulfate adsorption in soils and mineral weathering. Deposition is given as annual average wet deposition, a dry deposition factor relative to wet deposition and annual precipitation amount.

MAGIC operates with two soil layer components arranged vertically and assumed to be homogeneous (see figure 2.1). Common temporal resolution is annual, but monthly output can also be obtained.



```
  ...MAGIC Interactive...    Select Parameters: Set Catchment Flow Routing          (Hindcast)

                                         A:  Annual Runoff (m/yr) =  0.630
                                         B:  One Soil Layer                             |
                                         C:  Two Soil Horizons                --F1------|
   F1 % Ppt On Land Not Infiltrating     D:  Two Soil Types                   | ---F2---|
   F2 % Infiltration Bypassing Soil1     E:  With Wetland                     | |       |
   F3 % Soil1 Drainage Becoming Runoff                                        | |  -----Q3----
                                                                              | |  |  Soil1  |
                                                                              | |  -----------
                                 Flow Fractions (%)                           | |       |
                                  F1         F2         F3                    | |       |---F3-----
                            --------   --------   --------                    | |       |         |
                    Ann      1:    0    2:    0    3:    0                    | |  -----Q5----    |
                                                                              | --Q2  Soil2  |    |
                                                                              |    -----------    |
                                                                              |         |         |
               Internal Water Fluxes              Direct Ppt  Catchment       |         |         |
             Q1    Q2    Q3    Q4    Q5    Q6        Stream     Runoff        |         |         |
         ----------------mm------------------     ----mm----    --mm--        |    -----Q6-----   |
   Ann        0     0   629     0   629   629          1         630          ----Q1  Stream  Q4---
                                                                                   -------------
                                                                                        |
   (Fluxes Per Area of Catchment)                                                     Runoff

     Enter Your Selection (A to E; 1 to 3)  (!)  _          Press Enter to Continue
```

Figure 2.1. *The figure shows the watershed with two soil-layer components arranged vertically in MAGIC model, version 7.77.*

2.8.1. Parameter selection and model calibration

The source of parameter values depends on how and where the model is to be used. The parameter values may be estimated by fitting equations to the data from the system, or from data available in the literature. When data are not available, an iterative process of matching model output to observed system behavior maybe used for parameter estimation. MAGIC is a time dependent model and the model calibration requires:

i) Background year, a year in which we assume there was no pollution (e.g. 1895 in China)

ii) A reference year, a recent year for which there is data.

In this study the model was calibrated by running hindcast simulations from 1895 to 2000. Moreover, when parameters are estimated from observed data, one should seek the parameters that lead to the best fit between model output and the observed data.

3. Site Description

In this chapter, the Tie Shan Ping and the Lei Gong Shan sites will be described. Air temperature, climate, topography and vegetation of the Tie Shan Ping area will be generally described in section 3.1. A particular description of soil conditions for different plots in Tie Shan Ping will also be presented in the same section. The Leigong area and the Lei Gong Shan catchment will be described in section 3.2.

3.1. Congqing area

Chongqing municipality was previously a part of Sichuan province. It is situated at the upper reaches of the Yangtze River at the confluence of Yangtze River and Jialing River between 105°17' - 110°1' east longitude and 28°0' - 32°3' north latitude (see figure 3.1). The area of the whole Chongqing municipality is 82400 km2 with about 30.40 million people. The urban population of the city is about 6 million (travelchinaguide.com).

3.1.1. Topographical description of the Tie Shan Ping catchment

The Tie Shan Ping forest area (29°38’N, 106°41’E) is located about 25 km northeast from the center of Chongqing city. The forest area is partly protected and the Tie Shan Ping catchment is located within the protected area. The area of the experimental field is about 12—16 ha at an elevation of about 450m. Topographical map for Tie Shan Ping with location of the sampling plots is shown in figure 3.2.

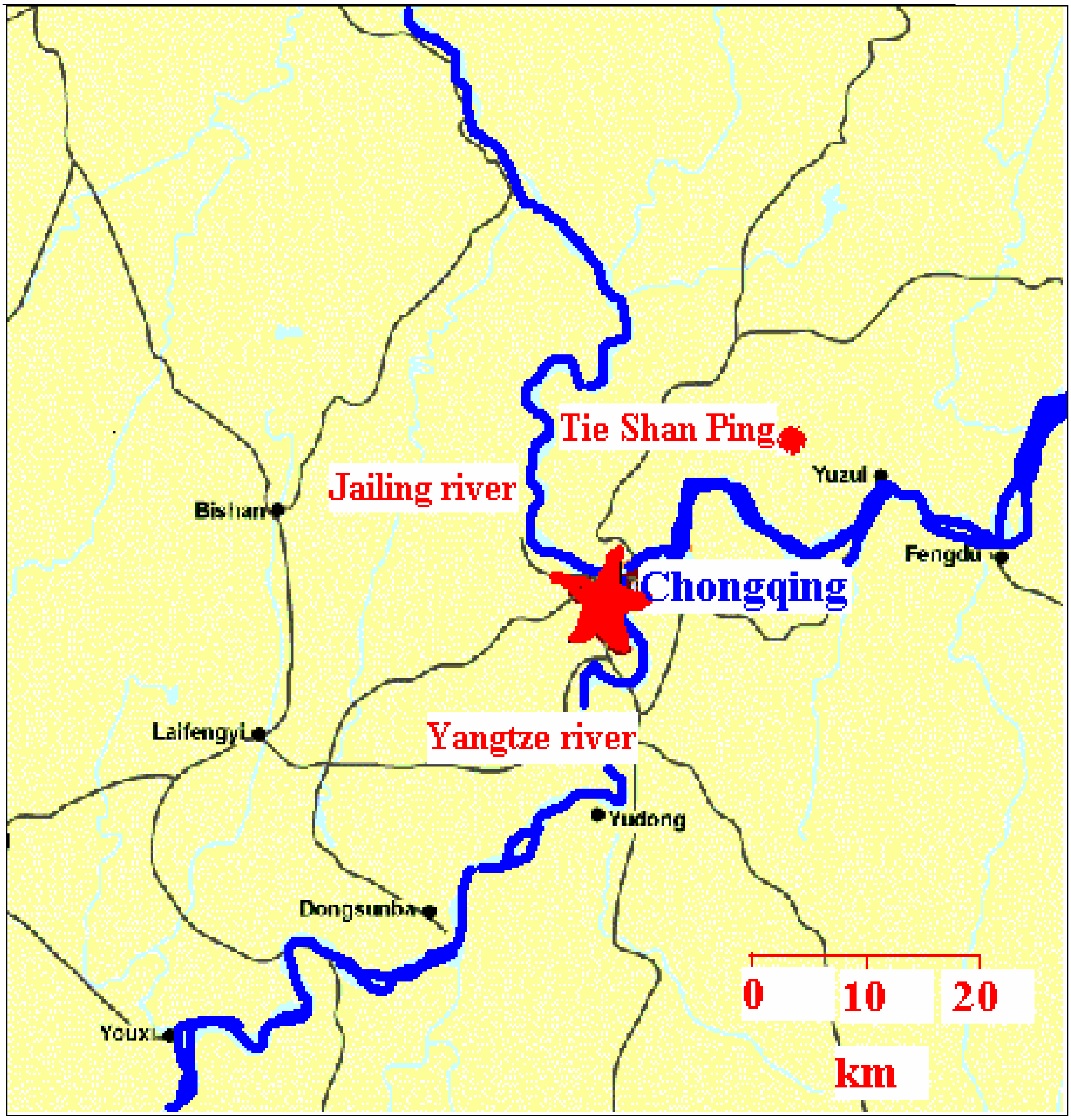


Figure 3.1 *Map of Chonqing area with location of Tie Shan Ping. The map is taken from (maps-of-china, 2002) with an approximated scale.*

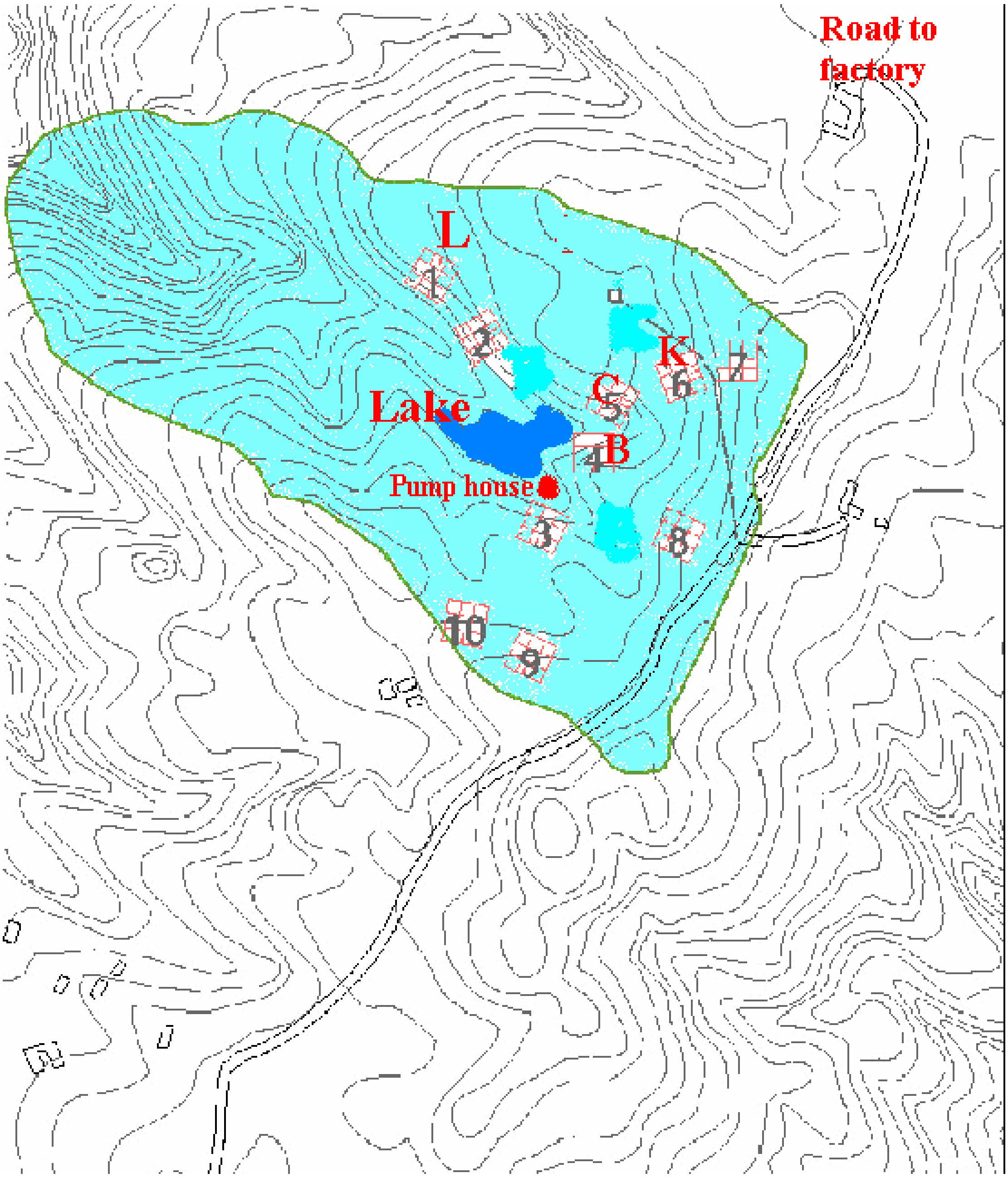
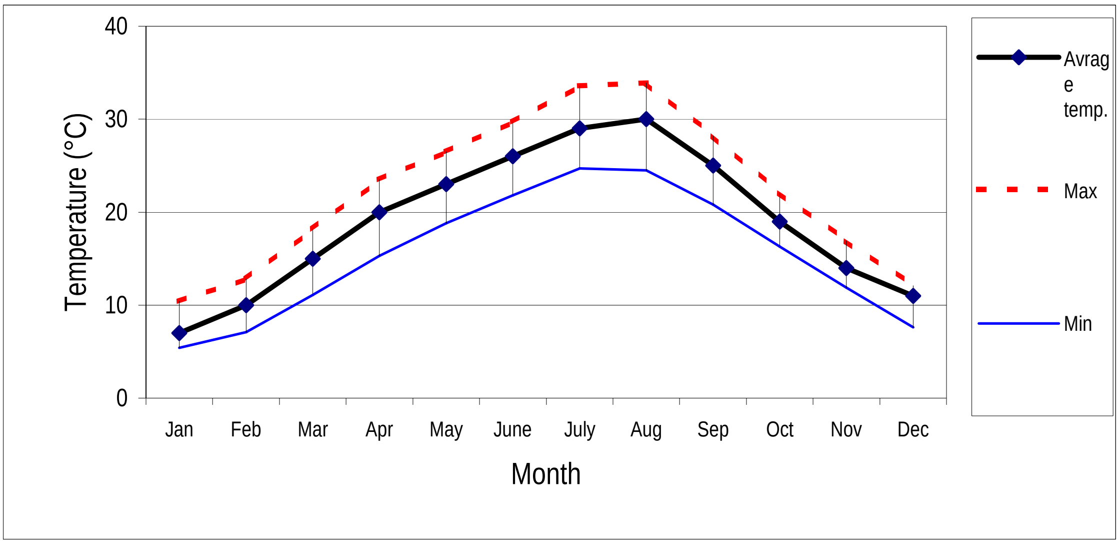
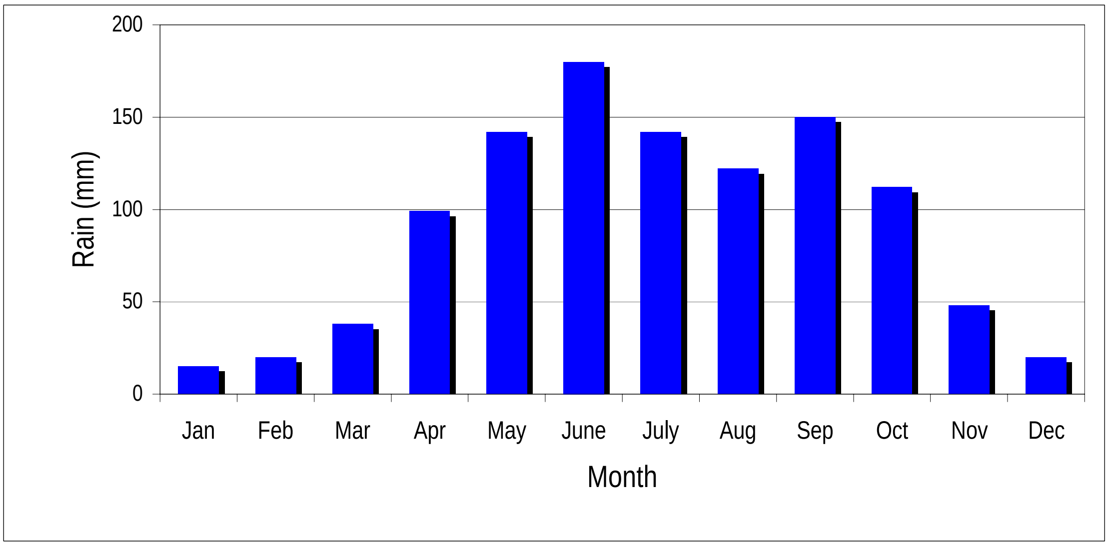


Figure 3.2 ***Map of Tie Shan Ping catchment, showing the different plots where the soil samples were collected. The letters indicates the new established soil water plots, and the numbers are macro plots. Note that only plot B, C, K and L are discussed in this thesis. (Scale 1:6150). The map is taken from http://folk.uio.no/rvogt/Impacts/Manuals/Field-manuals/***

3.1.2. Climate

In general Tie Shan Ping has a subtropical humid monsoon climate; little frost and snow and much fog all the year round. There are 4 distinct seasons with warm winter, hot summer, early spring and a short autumn. The yearly average temperature is 19.1°C, and the variation between highest and lowest monthly temperature is 23°C. August is the warmest month followed by July with (30°C and 29°C) respectively, and January is the coldest with about (7°C). Higher temperature variation is recorded in the summer than in the winter. As shown in the figure 3.3, the variation between different days in August is about 9.4°C, whereas in January it is about 5°C. The yearly precipitation amount is 1088 mm and 85 % of the rain falls during the summer (figure 3.3). A long rainy season extends between April and October with plenty of night rains. These climate data are in good agreement with a humid subtropical climate defined in Strahler (1970).





Figur 3.3 *Temperature and precipitation data for Chongqing. The data is based on values from six different weather stations in Chongqing center for the period 1951-2000 (China-travel-guide 2002)*

3.1.3. Vegetation

Forest covers about 62.5% of the area, which stretch 164m→593m above the sea level (Lydersen et al., 1997). The forest area is dominated by Masson pine (*Pinus massionana*), but there are also some other trees e.g. bamboo, oak and citrus. The trees were planted approximately forty years ago, because the forest was logged between 1958 and 1962 during *The Great Leap Forward.*

3.1.4. Soil type

The main soil type is locally Yellow Mountain soil, and the soils are rich in finer particles and are reported to be homogeneous (Larsen et al 1998). Haplic acrisol is the corresponding name in the FAO classification system (FAO 1998). High density and relatively low porosity were found in Tie Shan Ping soil due to a large fraction of fine secondary silt and clay mineral. The bulk densities are increasing from 1.25 kg dm^{-3} in the A-horizon to 1.34 kg dm^{-3} in the B-horizon. Water retention characteristics are similar for the A and B-horizon and typical for clay rich soils. The soils are mainly composed of quarts and clay minerals, 74 % of the soils composed of quartz and 14 % clay minerals. Water contents in the A-horizon decrease from 36% qt field capacity to 22% at wilting point. (Lydersen et al., 1997).

Lydersen et al (1998) described generally in TSP soil to have relative high quartz content. This is also the case in Liu Chong Guan (LCG) soil. Tangvold, 2002, found far less quartz content in Liu Chong Guan soil than what Lydersen has reported. Tangvold 2002 found for example 12% quartz content in B-horizon in Liu Chong Guan chatchment, where Lydersen's observation in the same horizon is 72%. Survey on mineralogy are performed on the clay fractionation, and in the case of Lydersen et al. (1998) the fraction included silt, which may be contributed to higher contents of quarts in TSP.

3.1.5. The different plots and profile description

Within the catchment there are 10 forest *macro plots* (see Figure 3.2). Each forest macro plot consists of a 30x30m square. In the centre of each macro plot is located a 10x10m *core plot* comprising the ground vegetation micro plots which are marked similarly. Five 1-m^2 *micro plots* are randomly placed in each 10x10m-core plots; i.e. a total of 50 1-m^2 plots in the site. In the Tie Shan Ping catchment 18 soil samples were collected from 4 different plots referred to as plot B, C, K and L. These four plots are located within *intensive macro-plots*. The locations of these four plots are shown in figure 3.2. These plots have an average slope of 10°.

4 lysimeters and equipment for measuring temperature and moisture have been installed in each of these plots (see table 3.1). Detailed profile descriptions for the different plots are presented in tables 7.a—7.d. in Appendix 7

Table 3.1 *The depth of the different lysimeters in the different plots in Tie Shan Ping (note lysimeters are not installed at the same depth)*

			Depth limit	**Lysimeter depth**	**Lys. Numb**
Plot	**Location**	**Horizon**	**cm**	**cm**	
A	In water saturated bottom of valley, below soilwater spring	A	20	15	A1
		B	-	30	A2
B	Intensive MACROPLOT 4	L	+2	0	B0
		AB	3		
		B1	12	6	B1
		B2	27	15	B2
		B3		30	B3
C	Intensive MACROPLOT 5	L	+2	0	C0
		AB	2		
		B1	12		
		B2	22	15	C1
		B3	-	30	C2
		B3	-	60	C3
		BC	-	75	C4
D	(old lys. plot 9 and 4)	A	2		
		B1	12		
		B2	22	15	D1
		B3	-	30	D2
		B3	-	60	D3
		BC	-	75	D4
E		B1	12		
		B2	22	15	E1
		B3	-	30	E2
K	New plot below the road into the catchment (old lys. plot 10) Intensive MACROPLOT 6	L	+2	0	K0
		A	5	2	K1
		B1	20	8	K2
		B1	20	15	K3
		B2	30	30	K4
L	Along the path on the northern ridge over the dam (old lys. plot 11) Intensive MACROPLOT 1	L	+2	0	L0
		A	2	1	L1
		B1	12	7	L2
		B2	32	22	L3
		B3	-	36	L4

Picture 1 ***vegetation***

Picture 2 ***Oak plants***

Picture 3 *Spectacles Lake*

Picture 4 ***soil profile***

Picture 5 ***vegetation***

Picture 6 ***vegetation***

Figure 3.4 *Pictures from Tie Shan Ping catcment, the pictures are taken by Dr Rolf Vogt in the year.2000*

3.2. The Leigong Mountain and Lei Gong Shan catchment

The Leigong Mountain is situated outside of the village Lei Gong Shan, 40 km southeast of the town Kaili and 140 km east of Guiyang in the Guizhou province. The Lei Gong Shan catchment (26°10'N, 108°10'E) is located in the middle of the mountain and at elevations from 1400m to 1800m, above the sea level. The height of the mountain reaches 2178.8 m above the sea level. The area of the mountain is 710 000 Chinese mu, corresponding to about 473,3 km^2. The sampling site is 200 meters from a plant bottling natural water.

The area of the study site is 1.2 km^2 and a small road crosses the catchment (figure 3.5). All soil water-sampling plots are located below the road. Nine soil samples have been collected from three different sample points, below the road near the site and along the road in the site in order to study the difference in soil quality. Three horizons at each sample point (O, A and B) were collected. In figure 3.5, the map of the catchment is shown with the locations where the samples were collected. One sample point is located along the road and the two others are located down below the road.

3.2.1. Climate

10 weather stations exist in these mountains, 5 of which have data from the last three decades (Lydersen et al. 1998). Measurements from these weather stations are mainly air temperature, wind speed and direction, and amount of precipitation. A weather station located downstream of the catchment was in use more than three years from 1985—1988. Based on data from this weather station, annual precipitation in the catchment area varied from 1200 to 1600 mm. Approximately 80% of the rain falls during April to September. Annually the area receives only about 3685.10^6 Jm^{-2} of solar radiation. The annual mean temperature varies with the altitude. It is 14—16 °C at the foot, 11.7 °C midway and 9.2 °C at the top of the hills. Only two mountain areas in China have more fog than Leigong Mountain, and up to 315 foggy days have been recorded at this weather station (in 1987). The relative humidity also varies with altitude. It is 85% at 1100 m above the sea level, 88% at 1600 m above the sea level and 91% at the top of the Mountain (Zhou and Mo, 1989)

3.2.2. The Leigong soils

Soils from Leigong Mountain are mainly of the classes' mountain yellow soil, yellow-brown and shrubby-meadow soil. Mountain yellow soil is the predominant type. Haplic acrisol is the corresponding name in the FAO classification system (FAO 1998). The soil is rather deep, containing abundant humus and appropriate content of moisture. The soil texture is loamy and the reaction is acid (Zhang et al., 1989).

3.2.3. Vegetation

Subtropical evergreens such as *Castanopsis, Lithocarpus, Schima and Maglietia* dominate the Mountain forest at elevations below 1300m. Mountain mixed evergreen-deciduous forest are found at 1300—2100m altitude, and Chinese fir followed by Masson pines are the dominant species in the Lei Gong Shan catchment (Fang 1989). The trees were planted forty years ago, because a large part of the forest was logged between 1958 and 1962 during the *Great Leap Forward.*

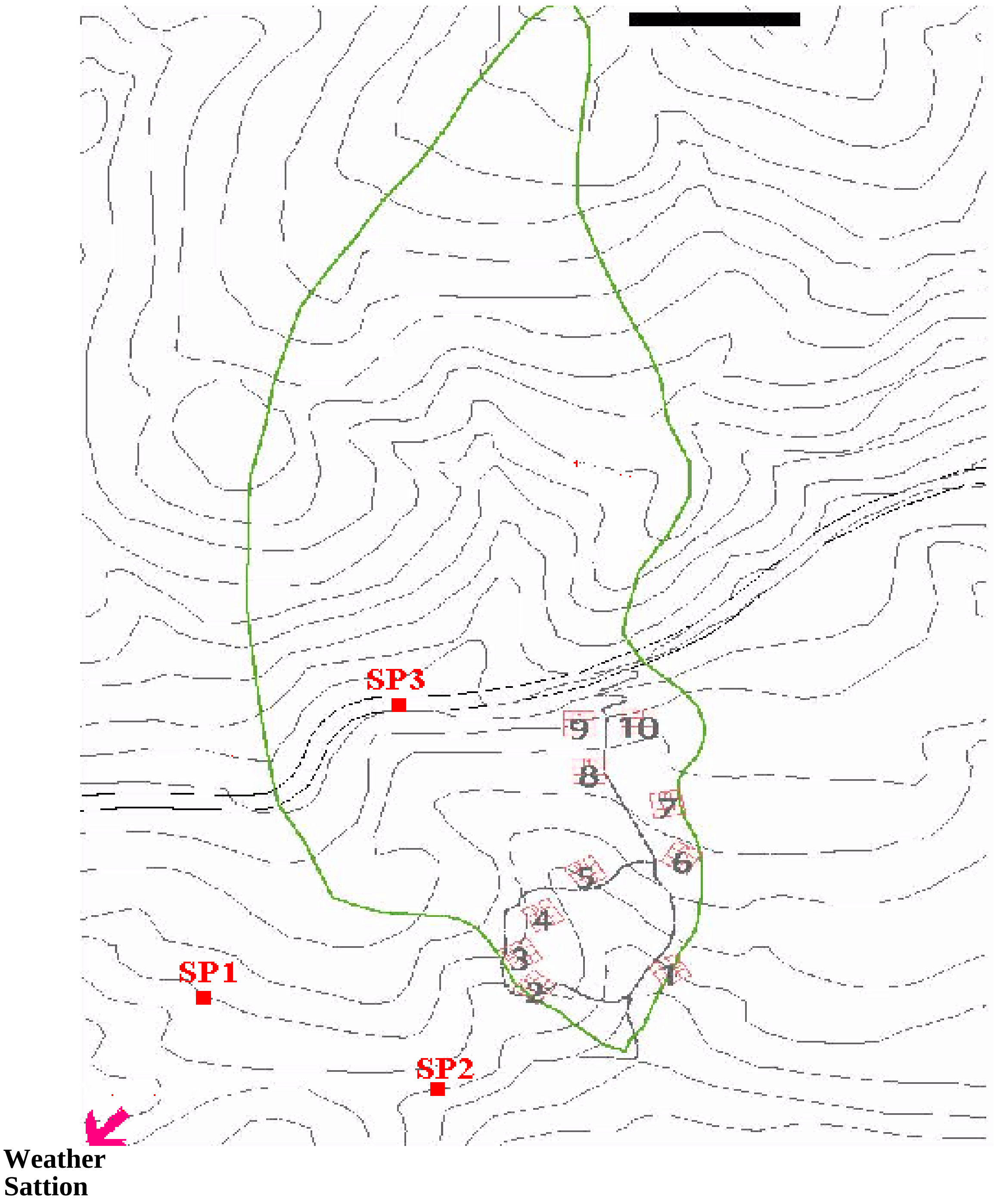


Figure 3.5 Map of Lei Gong Shan catchment, showing the different sample-points where the soil samples have been collected. The map is without scale and is taken from IMPACTS home page *http://folk.uio.no/rvogt/Impacts/Manuals/Field-manuals/*

4. Methods and analysis

4.1. Sampling

Equipment for sampling precipitation, throughfall and soil water has been installed during 1997 to 1998 within the Tie Shan Ping catchment. In present work four new plots were established in Tie Shan Ping (plot B, C, K and L) (see map 3.2). In total 18 soil samples were also collected from these 4 plots.

From the Lei Gong Shan catchment area, 9 soil samples were collected from three different locations (sample points 1, 2 and 3) (see figure 3.5). Soil was sampled from different depths at 0—10 cm O, A, and AB-horizons, at 10—30 cm in the B1and B2-horizons and at 30cm→ cm in the B3-horizon. The soil samples from the both catchments were collected in April 2000 and pre-treatment was performed in Norway a short time after sampling.

C and N analyses of the soil samples were done at Department of Soil and Water Sciences, Agricultural University of Norway. The soils' bulk density, porosity and moisture characteristics were determined at Skogforsk (NISK) (Norwegian Forest Research Institute) and the soil mineralogy was determined at Department of Geology, University of Oslo. Data on soil water chemistry from Tie Shan Ping are provided by Dr Zhao Dawei, Chongqing Institute of Environmental Science and Monitoring (CIESM).

4.2. Cation exchange capacity CEC

The cation exchange capacity (CEC) of soils is the sum of all cations (in equivalents) adsorbed the exchange complex; it may be given in the unit meq/kg (dry soil). The method used to determine the effective cation exchange capacity, CEC_E, is described in Hendersot and Duqette (1986). The method is comparable to the combined ISO11260 and ISO/TC190/SC3 standards. For the extraction we used a standard procedure (Central laboratory manual); 30.0mL 0.10M $BaCl_2$ solution were extracted with 1.50g and 4.50g of an organic and a mineral soil, respectively, for each soil sample two replicates were analyzed.

4.2.1. Calculation of Effective Cation Exchange Capacity (CECE)

To convert the activity measure of H^+ to concentration the activity of H^+ ($\{H^+\}$) has been divided with the activity coefficient.

$$[H^+] = \frac{\{H^+\}}{f_{H^+}} = \frac{10^{-pH}}{0.7828}$$

The exchangeable amount of the different cations in the soil has been calculated from the concentration in the extracts ([X]), the amount of soil (1.5 or 4.5g) and volume (30mL) of extractant solution. All concentrations in the supernatants have been translated into centimol equivalents ($\text{cmol}_\text{e}\ \text{L}^{-1} = \text{n A cmol L}^{-1}$).

$$(\text{X})\ (\text{in cmol}_\text{e}/\text{kg}_\text{soil}) = [\text{X}]\ (\text{in cmol}_\text{e}/\text{L}) \cdot \frac{30\text{mL}}{\text{g}_\text{soil} \cdot \frac{w_{dm}}{100}}$$

(w_{dm})[11] is defined as dry matter content in %.

The sum of all cations of soil gives the CEC_E.

$$CEC_E = \frac{\sum (Ca^{2+}, Mg^{2+}, Na^+, K^+, Al^{3+}, H^+)\text{cmol}_\text{e}}{\text{kg}_\text{soil} \cdot \frac{w_{dm}}{100}}$$

The base saturation of the soil is defined as the percentage of sum base cations (Ca + Mg + Na + K) relative to the CEC.

$$\%\text{BS} = \frac{\sum (\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+)}{\text{CEC}} \cdot 100$$

The percentage of aluminum compared with the CEC_E gives the Aluminum Saturation (AlS).

$$\%AlS = \frac{\sum (Al^{3+})}{CEC_E} \cdot 100$$

---

[11] The dry matter content (w_{dm}) is described in ISO11465, using air-dried soil passed through a 2.00mm aperture sieve.

4.2.2. Cation Exchange reactions in the MAGIG model

The most important cation exchange reactions incorporated in this model are.

$2Al^{3+} + 3CaX_2 = 3Ca^{2+} + 2AlX_3$ (eq. 4.1)

$Ca^{2+} + 2NaX = 2Na^{+} + CaX_2$ (eq. 4.2)

$Mg^{2+} + 2NaX = 2Na^{+} + MgX_2$ (eq. 4.3)

$K^{+} + NaX = Na^{+} + KX$ (eq. 4.4)

Cations adsorbed on the soil are CaX_2, MgX_2, AlX_3, NaX and KX and cations dissolved in the soil water are Al^{3+}, Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}. The total cation exchange capacity (CEC) of the soil based on above assumptions is thus defined as

$CEC = 3[AlX_3] + 2[CaX_2] + 2[MgX_2] + [NaX] + [KX]$

The equivalent fraction of a single exchangeable ion of these adsorbed cations is e.g. $E_{Ca} = 2[CaX_2]/CEC$

4.3. Analytical methods

4.3.1. Atomic absorption spectroscopy

Base cations and aluminum were analyzed by flame atomic absorption spectroscopy (FAAS), according to standard procedures. The concentrations of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}, were determined using a Shimadzu AA-670 spectrophotometer, an acetylene/air flame, with 50:50 gas flow. The amount of Al^{3+} was measured by a Shimadzu AA-670 spectrophotometer, an acetylene/nitrous oxide flame with 40:20 gas flow (Skoog et al., 1992).

10 % of an ion buffer containing La_2O_3 dissolved in HCl is added to all samples, standards and blanks. This solution consists 1% of La_2O_3 (by weight) in 50% HCl. The addition of an excess lanthanum ion minimizes the interference of sulfate in the determination of calcium and magnesium, and that of aluminum in the determination of magnesium (Skoog & Leary, 1992). Lanthanum ions work also as an ion buffer because of its low ionization energy.

4.3.2. Potentiometry

pH in soil extracts was measured by using an Orion pH-meter (models EA-920 and SA-250) with Orion electrodes (model 81-72BN). Two buffers of pH 4.01 and 7.00 were calibrated to correct for drift in the instrument, and all measurements took place at room temperature.

4.4. Quality control

Sample replicates and the use of intercalibration solutions and statistical treatment have been used to identify errors and minimize uncertainties in the data.

4.4.1. Ion balance as data quality control

The ion balances (IB)[12] often gives a good check on data quality. In this thesis only data with ratios of Electro Neutrality (EN)[13] less than ±10% were used. A large number of soil solution samples (219) were analyzed and only 121 samples (55%) had an Electro Neutrality EN < ±10%. However, the quality of Chinese data has recently improved (Vogt, personal communication).

4.4.2. Electro neutrality in the MAGIG model

The principal of the charge balance requires that $\Sigma\, z_i c_i = 0$

Where c_i is the molar concentration of the *i*th charged species in the solution, and z_i is the charge of that species. The different species included in the model and the charge balance for the model is given in eq. 4.5

$$[H^+]-[OH^-]+2[Ca^{2+}]+2[Mg^{2+}]+[Na^+]+[K^+]+3[Al^{3+}]+2[Al(OH)^{2+}]+[Al(OH)_2{}^+]-[Al(OH)_4{}^-]$$
$$+2[AlF^{2+}]+[AlF_2{}^+]-[AlF_4{}^-]-2[[AlF_5{}^{2-}]-3[[AlF_6{}^{3-}]+[Al(SO_4)^+]-[Al(SO_4)_2{}^-]-[Cl^-]-[F^-]-[NO_3{}^-]$$
$$-2[SO_4{}^{2-}]-[HCO_3{}^-]-2[CO_3{}^{2-}] = 0 \qquad \text{(eq.4.5)}$$

4.4.3. Conductivity

Comparison of the measured and calculated conductivity can also be used to check the data quality. For most samples we are dealing with the Debye-Hückel equation[14] may be a satisfactory approximation. The total conductivity of the solution (EK) is calculated by summarizing the products of activities and molar conductivity (λ) for each ion:

---

[12] Ion balance = $Al_{eq} + Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4{}^+ + Fe^{3+} - (SO_4{}^{2-} + NO_3{}^- + Cl^- + F^-$ + organic charge)

[13] Electro Neutrality (EN %) = {(Σ cations - Σ anions) / (Σ cations + Σ anions)}.100 were cations and anions are given in eq/L

[14] Debye-Hückel approximation (when I < 0.01) for activity (a):

$a = C.\, f$, $\log f = 0.51 \cdot Z^2 \cdot \sqrt{I}$ Z is ionic charge, I is ion strength in solution and C concentration in molar.

$EK = \Sigma(a \cdot \lambda)$

Theoretical values for λ are given in the table below.

Table 4.1 *Theoretical values of molar conductivity (λ)for some ions at (25 °C) (S.cm² /mol).*

	H^+	Al^{3+}	Na^+	K^+	Mg^{2+}	Ca^{2+}	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^{2-}
λ	349,6	189	50,1	73,5	106,0	119,0	71,4	76,3	160,0	44,5

4.4.4. Check of the instrument

All solution samples were determined successively. Standards were analysed among the real samples to correct for drift in the instrument. On the AAS instrument standard solutions were run before and after running the real solutions for each element. The blank solution was run on AAS for every 5/6 samples.

4.4.5. Inter calibration solutions

On the Atomic Absorption Spectroscopy we have used house standard calibration samples, which have been analysed together with real samples. The intercalibration solutions used for AAS were analyzed at Norwegian Institute for Water Research NIVA. Total description of the calibration solutions used is given in Appendix 4.

4.5. MAGIC model as a methodical tool

To describe the future effects of acid deposition on terrestrial and aquatic systems, process-oriented models of catchment soil water and stream water are necessary. Thus the MAGIC model is used as a methodic tool in this study. In the present modeling work, we applied the MAGIC model to the Tie Shan Ping catchment in Chongqing to hindcast the past situation of soil acidification and to predict possible soil responses to assumed future deposition scenarios.

4.5.1. Model structure

The MAGIC model is based on equilibrium reactions involving dissolved CO_2, a solid phase of aluminum hydroxide, aluminum and base cations in soil water and aluminum and base cations adsorbed on the soil. The equilibrium model is divided into three parts:

i) Soil and soil-water cation exchange reactions, *ii)* Inorganic aluminum reactions, and

ii) Dissolved inorganic carbon reactions.

4.5.2. Soil cation exchange reactions

Cosby et al. (1985), assume that Al^{3+}, Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} are involved in cation exchange between soil and soil solutions, while Reuss and Johnson emphasized only Ca^{2+}, in their theoretical treatment (Reuss and Johnson 1986). Exchange reactions with aluminum species other than Al^{3+} may be neglected in some instances according to Reuss 1983. Cosby et al. (1985) point out that e.g., if exchange of $Al(OH)^{2+}$ complex does occur in the soils, this simple lumped approach may be unable to simulate that behavior.

4.5.3. Equations, variables, parameters and constants in the model

In table 4.2 is presented some of the equations, parameters and variables in the MAGIC model. 24 equations describe the reactions that determine the chemical composition of soil water in this model. These 24 equations contain 33 variables and 21 parameters; 16 of these parameters are thermodynamic constants.

Table 4.2 *Equations, variables, parameters and constants for soil water cation exchange reactions included in MAGIC model (Cosby et al.,1985)*

Equations for soil water cation exchange reactions in MAGIC

$E_{Al} + E_{Ca} + E_{Mg} + E_{Na} + E_{K} = 1$ **(eq. 4.6)**

$BS = E_{Ca} + E_{Mg} + E_{Na} + E_{K} = 1 - E_{Al}$ **(eq. 4.7)**

$S_{AlCa} = \{Ca^{2+}\}^3 E_{Al}{}^2 / \{Al^{3+}\}^2 E_{Ca}{}^3$ **(eq. 4.8)**

$S_{CaNa} = \{Na^{+}\}^2 E_{Ca} / \{Ca^{2+}\} E_{Na}{}^2$ **(eq. 4.9)**

$S_{MgNa} = \{Na^{+}\}^2 E_{Mg} / \{Mg^{2+}\} E_{Na}{}^2$ **(eq. 4.10)**

$S_{KNa} = \{Na^{+}\} E_{K} / \{K^{+}\} E_{Na}$ **(eq. 4.11)**

Variables for soil water in MAGIC

Cations: $[Al^{3+}]$, $[Ca^{2+}]$, $[Mg^{2+}]$, $[Na^{+}]$ and $[K^{+}]$

Exchange cation fractions: E_{Al}, E_{Ca}, E_{Mg}, E_{Na}, E_{K}

Base saturation: BS

Parameters for soil water in MAGIC

Selectivity coefficients: S_{AlCa}, S_{CaNa}, S_{MgNa}, S_{KNa}

Braces {} indicate activities, and brackets [] indicate molar concentrations.

Equations 4.8 to 4.11 in table 4.2 are the Gaines Thomas equilibrium expressions. Selectivity coefficients denote by S are not true thermodynamic equilibrium constants. They vary from soil to soil and may vary from time to time for a single soil and thus these coefficients must be treated as parameters, and the values must be estimated from field data or selected by an appropriate calibration.

4.5.4. Aluminum reactions in the model

The concentration of Al^{3+} in soil water is assumed to be in equilibrium with some solid phase of $Al(OH)_3$. The following reversible reaction is assumed to occur as the aqueous concentrations of H^+ and Al^{3+} vary.

$$3H^+ + Al(OH)_3(s) = Al^{3+} + 3H_2O \qquad \text{(eq. 4.12)}$$

The equation 4.13 in table 4.3 shows the equilibrium expression for the reaction.

The equilibrium constant K_{Al} is a model parameter to be estimated for each application.

There are also other aqueous phase reactions in the model. These reactions include hydration and complexation of aluminium with SO_4^{2-} and F^-. The equilibrium expressions for the reactions are given (eq.4.14—4.25) in table 4.3.

The thermodynamic equilibrium constants for these reactions should not vary with different applications of the model. They are, however, temperature dependent and appropriate corrections must be made (Cosby et al.,1985).

Table 4.3 *Equations, variables, parameters and constants for inorganic aluminum and carbon reactions included in MAGIC model (Cosby et al.,1985)*

Equations for inorganic aluminum and carbon reactions in MAGIC	
$K_{Al} = [Al^{3+}]/[H^+]^3$	**(eq. 4.13)**
$K_{Al1} = \{Al(OH)^{2+}\}\{H^+\} / \{Al^{3+}\}$	**(eq. 4.14)**
$K_{Al2} = \{Al(OH)_2^{+}\}\{H^+\}^2 / \{Al^{3+}\}$	**(eq. 4.15)**
$K_{Al3} = \{Al(OH)_3^{0}\}\{H^+\}^3 / \{Al^{3+}\}$	**(eq. 4.16)**
$K_{Al4} = \{Al(OH)_4^{-}\}\{H^+\}^4 / \{Al^{3+}\}$	**(eq. 4.17)**
$K_{Al5} = \{AlF^{2+}\} / \{Al^{3+}\}\{F^-\}$	**(eq. 4.18)**
$K_{Al6} = \{AlF_2^{+}\} / \{Al^{3+}\}\{F^-\}^2$	**(eq. 4.19)**
$K_{Al7} = \{AlF_3^{0}\} / \{Al^{3+}\}\{F^-\}^3$	**(eq. 4.20)**
$K_{Al8} = \{AlF_4^{-}\} / \{Al^{3+}\}\{F^-\}^4$	**(eq. 4.21)**
$K_{Al9} = \{AlF_5^{2-}\} / \{Al^{3+}\}\{F^-\}^5$	**(eq. 4.22)**
$K_{Al10} = \{AlF_6^{3-}\} / \{Al^{3+}\}\{F^-\}^6$	**(eq. 4.23)**
$K_{Al11} = \{Al(SO_4)^{+}\} / \{Al^{3+}\}\{SO_4^{2-}\}$	**(eq. 4.24)**
$K_{Al12} = \{Al(SO_4)_2^{-}\} / \{Al^{3+}\}\{SO_4^{2-}\}^2$	**(eq. 4.25)**
$K_{CO2,1} = \{CO_2(aq)\}\{H^+\} / \{PCO_2\}$	**(eq. 4.26)**
$K_{CO2,2} = \{HCO_3^{-}\}\{H^+\} / \{CO_2(aq)\}$	**(eq. 4.27)**
$K_{CO2,3} = \{CO_3^{2-}\}\{H^+\} / \{HCO_3^{-}(aq)\}$	**(eq. 4.28)**
$K_w = \{H^+\}\{OH^-\}$	**(eq. 4.29)**

Variables

Strong acid anions: $[Cl^-]$, $[F^-]$, $[NO_3^-]$ and $[SO_4^{2-}]$

Inorganic aluminum species: $[Al^{3+}]$, $[Al(OH)^{2+}]$, $[Al(OH)_2^+]$, $[Al(OH)_3^0]$, $[Al(OH)_4^-]$ $[AlF^{2+}]$, $[AlF_2^+]$, $[AlF_3^0]$, $[AlF_4^-]$, $[[AlF_5^{2-}]$, $[[AlF_6^{3-}]$, $[Al(SO_4)^+]$, $[Al(SO_4)_2^-]$

Inorganic carbon species: $[HCO_3^-]$, $[CO_2(aq)]$ and $[CO_3^{2-}]$

Dissolution of water: $[H^+]$ and$[OH^-]$

Partial pressureCO_2: PCO_2

Parameters

Thermodynamic equilibrium constants (functions of temperature): K_{Al1}—K_{Al12},

Aluminum solubility constant: K_{Al}

Braces {} indicate activities, and brackets [] indicate molar concentrations.

4.5.5. CO_2 reactions in the Model

We assume that soil water is in equilibrium with CO_2 in the soil air. The equilibrium expressions for the involved reactions are listed (eq.4.26—4.29) in table 4.3. The equilibrium constants for these reactions depend strongly on temperature.

4.5.6. MAGIC model data inputs

Data from both laboratory and field studies has been used as far as possible. Atmospheric deposition of base cations from previous field observations in Tie Shan Ping catchment 1996—1998 and recent laboratory studies, composition of wet deposition in the catchment, ion concentrations of throughfall and soil water at different plots were available (Larsen, et al 1998 and Lund 2001). Deposition is given as annual wet deposition concentrations, dry deposition factors relative to wet deposition and annual precipitation amount. Dry deposition factors for the major ions were assumed partly based on throughfall. Weathering rates of minerals and vegetation uptake rates are given as annual fluxes for each ion and they were calibrated. Initial base saturation in the year of start of hindcast, average temperature, CO_2 and organic acid concentration (DOC) is given as input data. The model calculates soil water ion concentrations and soil base saturation in the two soil layers for the reference year.

The result obtained from the model output for soil water chemistry matched with the field observations (see table 5.5 in chapter 5). However, adjustments were necessary for some cases because of difficulties in transferring experimental values directly to field observations.

5. Result and Discussion

The result chapter is divided into two parts. Part one (5.1), deals with experimental results and part two (5.2) deals with modeling results. The experimental results discussed are based on 18 soil samples and 121 soil-water samples from four plots (plot B, C, K and L) in Tie Shan Ping, as well as 9 soil samples from Lei Gong Shan, taken at three different sample points within and near the catchment. The soil samples were collected in April 2000 and analyzed at Department of Chemistry, the University of Oslo in the year 2000 and early 2001.

In part two (5.2) the modeling results are based on soil-water data from Tie Shan Ping. The soil-water samples were analyzed in Chongqing. Dr Zhao Dawei in Chongqing Institute of Environmental Science and Monitoring (CIESM) in China provided the soil water data. The label explanations are shown in table 5.0

Table 5.0. *The label explanation table*

Code	**Explanation**
SP-1, SP-2 and SP-3	Sample point 1, sample point 2 and sample point 3
B, C, K and L	Plot B, plot C, plot K and plot L
B-O, K-AB, L-B3	Plot B O-horizon, plot K AB-horizon, plot L B3- horizon etc.
B-Topsoil	**Topsoil:** In the most cases is defined as O and A/AB-horizon and in few cases with B1-horizon, B-Topsoil is for example plot B, O, AB and B1-hrizon
B-Subsoil	**Subsoil:** Is defined as B2 and B3. B-Subsoil is for example plot B, B2 and B3-horizon

5.1. Soil results from Tie Shan Ping (TSP) and Lei Gong Shan (LGS)

5.1.1. Soil properties

The pH (in $BaCl_2$) in the Tie Shan Ping soil varies from 2.86 in the top horizon in plot C to 4.85 in the deeper horizon of plot B. In the same horizons the pH in water ranged from 3.55 to 5.48. The pH variation for different horizon within the same plot is larger than pH variation for different plots within the catchment (see figure 5.1). The soil samples from Lei Gong Shan are taken from three different random locations. Sample-points 1 and 2 are located near the catchment, but sample point 3 lies along the road in the catchment (see the map of the catchment in chapter 3, figure 3.5). In the Lei Gong Shan soil the pH (in $BaCl_2$) ranged between 3.88 in the O-horizon in sample-point 3 and 4.91 in B-horizon in sample-point 1. The pH in water varied between 4.41 and 5.59 in the same horizons. The pH difference between the two sample points near the catchment is small, while the pH at the site in the catchment is somewhat lower. Soils from Lei Gong Shan show higher pH than soils from TSP in all horizons. The soil pH for both catchments increases with depth. (The data for all samples are given in an Appendix 3). The average values in pH for upper and deeper soils for the three sample points in Lei Gong Shan and the four plots in Tie Shan Ping are shown in table 5.1. Based on these average values Lie Gong Shan shows higher pH values than TSP in the averages of upper and deeper soils respectively.

Table 5.1 *Average values for pH in the upper and lower soils for four plots in Tie Shan Ping and three sample points in Lei Gong Shan.*

	TSP		LGS	
	Top soil	sub soil	top soil	sub soil
pH (in $BaCl_2$)	3.45	3.87	4.25	4.64
pH (H_2O)	4.06	4.48	4.86	5.23

….

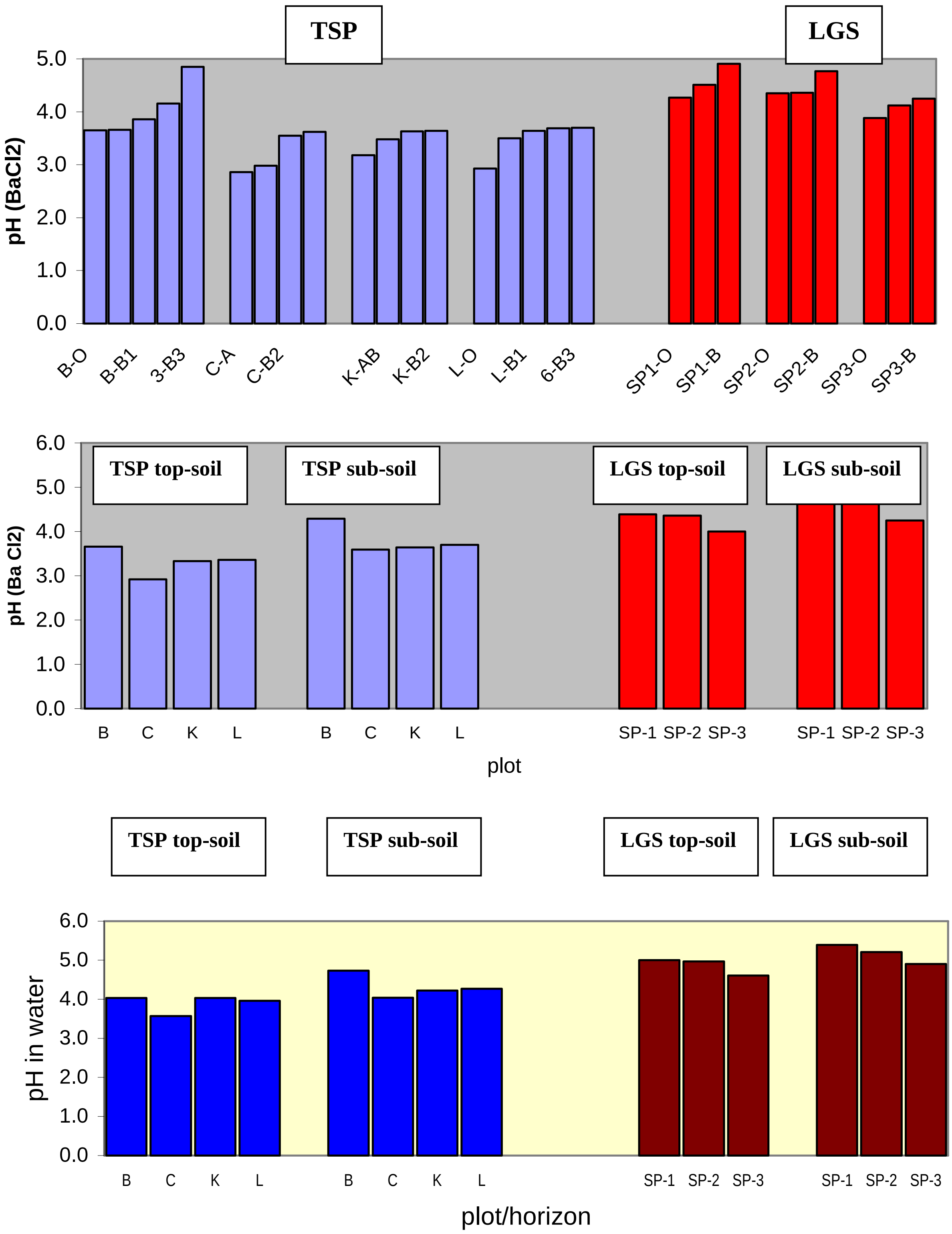


Figure 5.1. *The figures show pH (in $BaCl_2$ and water) of soils from TSP and LGS, upper figure shows the results of pH in $BaCl_2$ for all horizons, the middle figure shows the median pH (in $BaCl_2$) for top and sub soils and the lower figure shows the median pH in water for top and sub soils.*

5.1.2. Cation exchange capacity CEC

The effective cation exchange capacity of the Tie Shan Ping soil varies from more than 101 meq/kg in the topsoil in plot B to about 18 meq/kg in the deeper horizon in plot C. In the soils from Lei Gong Shan CEC_E varies from 19 meq/kg in the mineral horizons up to 236 meq/kg in the organic horizons. Figure 5.2 shows the effective cation exchange capacity for soils from TSP and LGS. Both in TSP and LGS, CEC_E decreases with horizon depth, except for plot K in TSP where CEC_E is higher in the B2-horizon than the B1. Compared to the other plots in Tie Shan Ping, plot K was found to have higher CEC_E. Even the deeper horizons of plot K show higher CEC_E than top horizons for plot C and plot L. Higher CEC_E in the O-horizon is to be expected because organic material is an important cation exchanger.

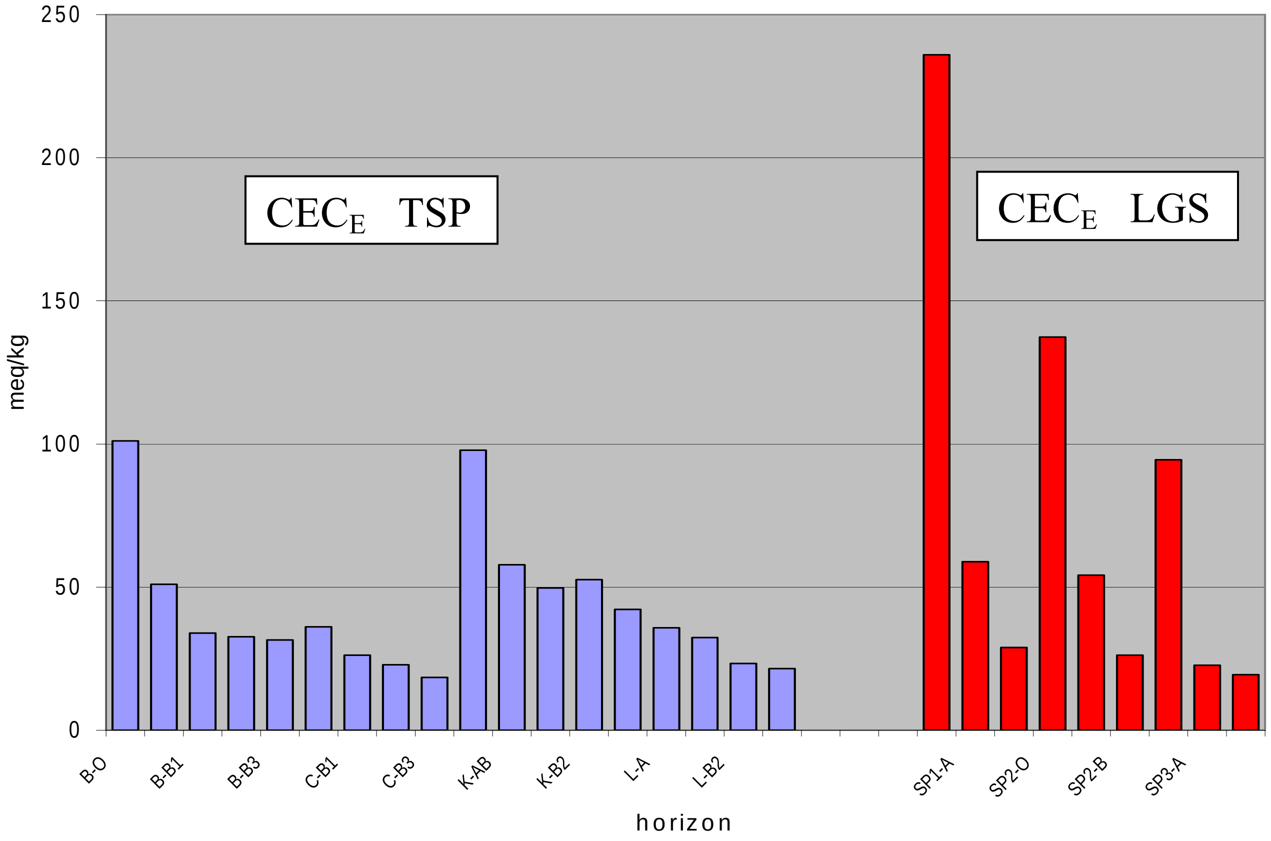


Figure 5.2. *The effective cation exchange capacity, CEC_E, for soil samples from Tie Shan Ping and Lei Gong Shan*

5.1.3. Base saturation BS

Figure 5.3 shows the base saturation (BS) of the soil samples from TSP and LGS. The soils from TSP have low BS; the values vary from about 9 to 20%. Plot K has lower BS than all other plots. Plot C and plot L show generally a decrease in BS with depth except that the A-horizon for plot C and B1-horizon for plot L, both have lower values than the underlying horizons. In plot C and plot K BS varies unsystematically. Soils from Lei Gong Shan have clearly much higher BS than soils from Tie Shan Ping. Sample points 1 and 2 are generally characterized by higher base saturation. In the O-horizon the BS for the sample-points 1 and 2 is 46.2% and 72.7% respectively. In the soils from sample point 3 the BS is low, as low as 3.4% in the B-horizon. BS decreases in LGS with horizon depth except for sample-point 2 where the BS has lower value in the O-horizon than in the A-horizon (all data are given in Appendix 3). The Aluminum Saturation (AlS) in LGS is varying between 26.8% in the upper horizon in sample-point 1 and 94.1% in the deeper horizon of sample point 3. Higher AlS in average and corresponding lower pH was found in Tie Shan Ping; AlS is varying between 66.3% in the top horizon in plot L and 88.1% in the deep soils of plot K. Based on these average values Lie Gong Shan shows lower AlS than TSP in the average of upper and deeper soils respectively (see table 5.2). The great difference when compared to the Tie Shan Ping might suggest that there is different mineralogy between these catchments and probably different weathering history. TSP has a much warmer climate and hence a more developed soil.

Table 5.2 *Average values for Aluminum Saturation in the upper and deeper soils for four plots in Tie Shan Ping and three sample points in Lei Gong Shan.*

	TSP		LGS	
	Upper soil	deeper soil	Upper soil	deeper soil
AlS	77.46	80.52	51.85	57.13

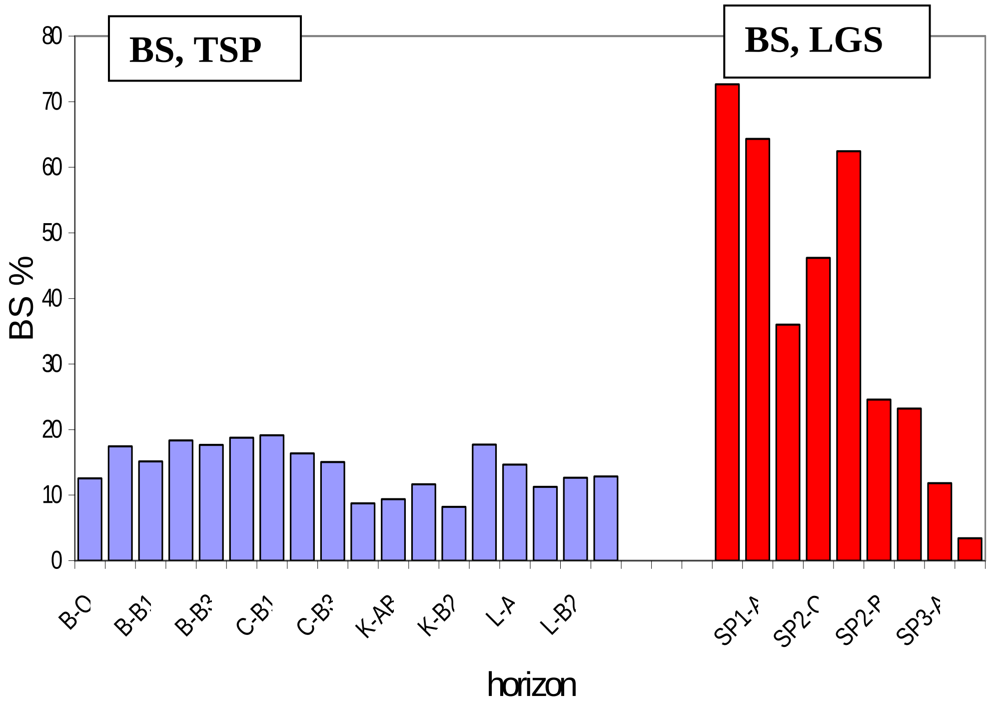
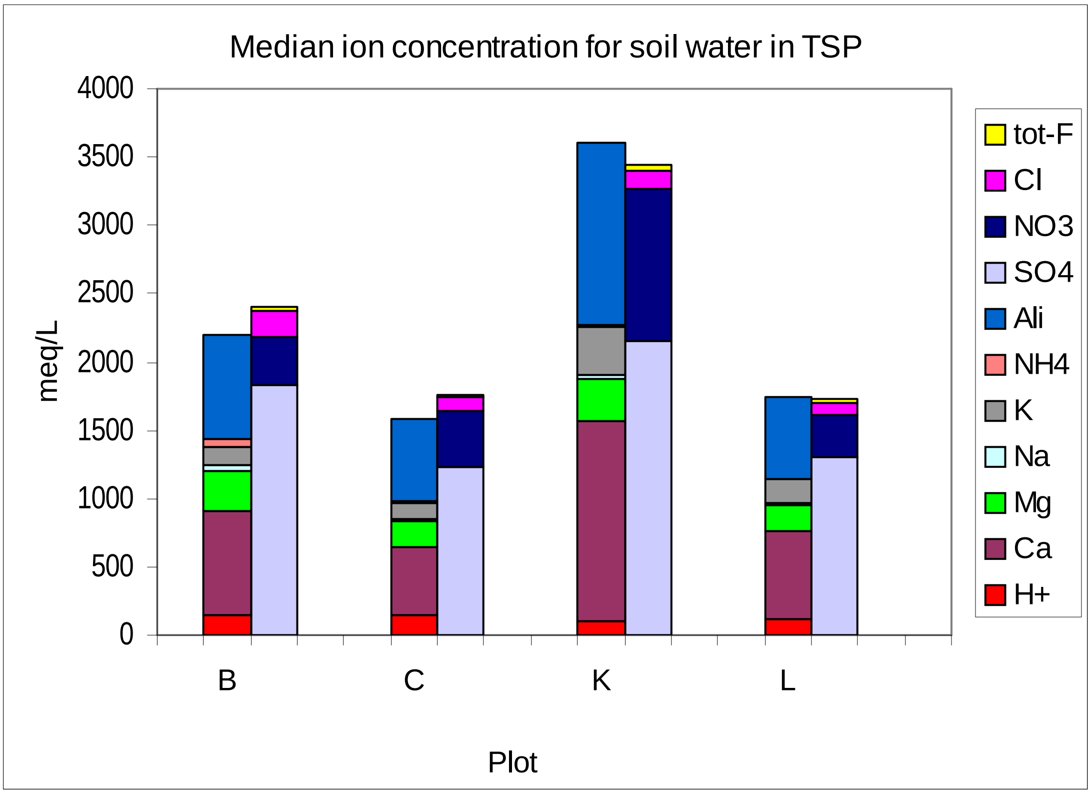


Figure 5.3. *The figure shows base saturation of the soil samples from Tie Shan Ping and Leigong Shan*

5.1.4. Soil water

There are large variations in ion concentrations in soil water within the Tie Shan Ping catchment. The median of the total ion concentration for the cations is an interval between 1408.8 µeq/L and 3750.2 µeq/L while for anions is between 1371.5 µeq/L and 3947.9 µeq/L. Highest ion concentration was found in plot K and the lowest ion concentration in plot C (see figure 5.4). In all plots the total ion concentration decreases from the topsoil to the sub soil except for plot K where the ion concentration in the deeper soils shows higher values than the upper soil. Ca^{2+} is generally the dominant base cation followed by Mg^{2+}, while SO_4^{2-} is the dominant anion followed by NO_3^-. In most cases the concentration of Al^{3+} is higher than Ca^{2+} particularly in plot C where the concentrations of Ca^{2+}+Mg^{2+} are low. Plot K shows very high concentration of NO^-_3. The median concentrations of NO^-_3 in upper and deeper soils are 1124.3 µeq/L and 1351.5µeq/L respectively (soil water data for TSP is given in Appendix 2).



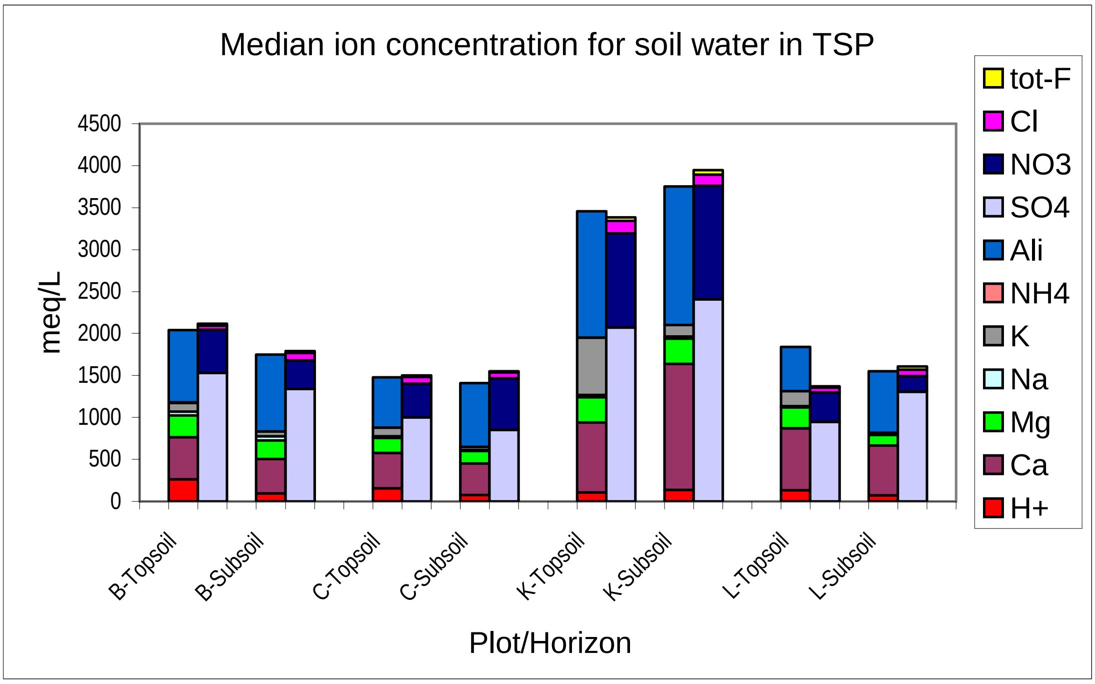


Figure 5.4. *Ion concentrations in soil water in Tie Shan Ping. The upper figure shows median values for concentrations of the ions in plots B, C, K and L. The lower figure shows median values for concentrations of the ions of the topsoil and subsoil in plots B, C, K and L.*

5.2. Modeling result for soils from TSP

5.2.1. Model calibration

The MAGIC model *(Model of Acidification of Groundwater In Catchments)* is calibrated by running hindcast simulations from 1895 to 2000. Median values for composition of wet deposition, based on field study during 1996—1998 are given in table 5.3. Dry deposition factors listed in table 5.3 are based on the observed concentration ratios of throughfall to wet deposition at different plots with some adjustment. Because of very high concentrations for the most elements in plot K, adjustments for many values were necessary. Therefore, higher values for dry deposition factors have been used for plot K. Selected parameter values used in the model are listed in tables 5.4a and 5.4b. Observed values for soil and soil water compositions have been matched with model outputs in tables 5.5a and 5.5b (Data for soil water in TSP is given in Appendix 1)

Table 5.3. *Ion concentrations in precipitation (µeq/L) for three years 1996—1998, and assumed dry deposition factors for year 2000. Values in the first column are average values for three years (Larsen 1998 and Lund 2001)*

Ions	Ion concentration in precipitation	Dry deposition factors used in plot B	Dry deposition factors used in plot C	Dry deposition factors used in plot K	Dry depositi factors for plot L
Ca^{2+}	219	1.0	1.0	1.8	1.5
Mg^{2+}	39	2.0	2.0	2.0	2.0
Na^+	17	1.0	2.0	2.0	2.0
K^+	21	2.0	2.0	3.0	2.0
NH^+_4	64	2.0	2.0	2.0	2.0
SO^{2+}_4	468	2.0	2.0	3.0	1.5
Cl^-	42	1.0	1.5	2.0	1.5
NO^-_3	42	2.0	2.0	3.7	2.0
F^-	1	2.0	2.0	2.0	2.0

Table 5.4a *Parameter values used in the MAGIC simulation in the Tie Shan Ping catchment with regard of 75% sequence.*

	plot B		plot C		plot K		plot L	
Parameters	Upper soil	Deeper soil	Upper soil	Deeper soil	Upper soil	Deeper soil	Upper soil	Deeper soil
Soil depth(m)	0.06	0.25	0.10	0.20	0.15	0.30	0.12	0.35
Density (kg/m^3)	1000	1400	1000	1400	1000.0	1400.0	1000.00	1400.00
CEC (meq/kg)	76.0	32.7	31.2	20.7	77.8	49.7	37.00	22.39
SO^{2-}_{4} halfsat(meq/kg)	10000	10000	10000	12000	12000.0	10000.0	10000	10000
SO^{2-}_{4} maxcap (meq/kg)	10	10.0	10	10	12.0	10.0	10.0	10.0
log10 K{$Al(OH)_3$}	7.25	8.3	7.3	8.4	8.5	8.4	7.60	8.45
H power (Al solub)	3.0	3.0	2.9	3.0	3.0	3.0	3.00	3.00
log10 (SAlCa)	-1.1	-1.5	-1.5	-1.0	0.6	0.8	0.66	-0.20
log10 (SAlMg)	-0.3	-0.7	-1.9	-1.4	-0.3	-0.3	0.12	-0.88
log10 (SAlNa)	-4.1	-4.0	-5.9	-6.7	-4.8	-4.9	-5.69	-5.92
log10 (SAlK)	-2.9	-3.5	-2.7	-4.2	-0.9	-3.0	-2.18	-5.27
Weathering rates (meq/m^2/yr)								
Ca^{2+}	49.0	0.0	23.0	0.0	48.0	408.0	58.0	0.0
Mg^{2+}	69.0	0.0	26.0	0.0	91.0	0.0	57.0	0.0
Na^{+}	8.0	2.0	8.0	0.0	0.0	1.0	0.0	3.0
K^{+}	13.0	0.0	18.0	0.0	353.0	0.0	61.0	0.0
NH^{+}_{4}	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SO^{2+}_{4}	6.0	0.0	0.0	0.0	0.0	300.0	0.0	270.0
Cl^{-}	0.0	21.0	0.0	0.0	0.0	0.0	0.0	15.0
NO^{-}_{3}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F^{-}	11.0	3.0	10.0	0.0	24.0	7.0	8.3	12.0
Uptake (% of external sources)								
Ca^{2+}	0.0	22.0	0.0	12.0	0.0	0.0	0.0	23.0
Mg^{2+}	0.0	17.0	0.0	18.0	0.0	5.0	0.0	53.0
Na^{+}	0.0	0.0	0.0	47.0	62.0	0.0	74.0	0.0
K^{+}	0.0	42.0	0.0	63.0	0.0	80.0	0.0	94.0
NH^{+}_{4}	0.0	0.0	0.0	0.0	0.0	0.0	90.0	0.0
SO^{2+}_{4}	0.0	14.0	30.0	16.0	9.0	0.0	25.0	0.0
Cl^{-}	35.0	0.0	26.0	17.0	8.0	9.0	56.0	0.0
NO^{-}_{3}	0.0	34.0	0.0	0.0	0.0	0.0	14.0	47.0
F^{-}	0.0	0.0	0.0	21.0	0.0	0.0	0.0	0.0
Initial exchangeable base cations (%)								
ECa %	17.6	18.07	26.35	10.85	10.00	10.65	19.25	4.50
EMg %	7.7	9.0	19.35	7.80	13.95	4.85	14.90	2.35
ENa %	1.45	1.5	4.60	3.85	0.85	0.70	1.70	1.70
EK %	1.1	1.05	1.30	1.30	4.00	2.40	3.15	0.80
BS %	**27.85**	**30.25**	**50.60**	**23.80**	**28.80**	**18.60**	**39.00**	**9.55**

Table 5.4b *Parameter values used in the MAGIC simulation in the Tie Shan Ping catchment with regard of 50% sequence.*

	plot B		plot C		plot K		plot L	
Parameters	Upper soil	Deeper soil	Upper soil	Deeper soil	Upper soil	Deeper soil	Upper soil	Deeper soil
Soil depth(m)	0.06	0.25	0.10	0.20	0.15	0.30	0.12	0.35
Density (kg/m^3)	1000	1400	1000	1400	1000	1400.0	1000.00	1400.00
CEC (meq/kg)	76.0	32.7	31.2	20.7	77.8	49.7	37.00	22.39
SO^{2-}_4 halfsat(meq/kg)	10000	10000	10000	12000	12000	10000	10000	10000
SO^{2-}_4 maxcap (meq/kg)	10	10.0	10	10	12	10	10	10
log10 K{Al(OH)$_3$}	7.25	8.3	7.3	8.4	8.5	8.4	7.95	8.45
H power (Al solub)	3.0	3.0	2.9	2.95	3.0	3.0	3.00	3.00
log10 (SalCa)	-1.1	-1.5	-1.7	-1.3	0.6	0.6	0.50	-0.20
log10 (SalMg)	-0.3	-0.7	-2.0	-1.7	-0.3	-0.6	0.10	-0.88
log10 (SalNa)	-4.1	-4.0	-5.9	-6.9	-4.8	-5.0	-5.85	-5.92
log10 (SAlK)	-2.9	-3.5	-2.7	-4.4	-0.9	-3.0	-2.27	-5.27
Weathering rates (meq/m^2/yr)								
Ca^{2+}	39.0	0.00	23.0	0.0	52.0	405	58.0	0.0
Mg^{2+}	68.0	0.00	26.0	0.0	93.0	0.0	57.0	0.0
Na^+	8.0	1.00	8.0	0.0	0.0	0.0	0.0	3.0
K^+	13.0	0.00	18.0	0.0	356.0	0.0	61.0	0.0
NH^+_4	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SO^{2+}_4	0.0	0.00	0.0	0.0	0.0	300	0.0	270.0
Cl^-	0.0	21.00	0.0	0.0	0.0	0.0	0.0	15.0
NO^-_3	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
F^-	11.0	2.00	10.0	0.0	24.0	7.0	8.3	12.0
Uptake (% of external sources)								
Ca^{2+}	0.0	24.00	0.0	12.0	0.0	0.0	0.0	23.0
Mg^{2+}	0.0	17.00	0.0	18.0	0.0	4.0	0.0	53.0
Na^+	0.0	0.00	0.0	47.0	65.0	14.0	74.0	0.0
K^+	0.0	42.00	0.0	63.0	0.0	80.0	0.0	94.0
NH^+_4	0.0	0.00	0.0	0.0	0.0	0.0	90.0	0.0
SO^{2+}_4	0.0	15.00	30.0	16.0	9.0	0.0	25.0	0.0
Cl^-	35.0	0.00	26.0	17.0	8.0	9.0	56.0	0.0
NO^-_3	0.0	35.00	0.0	0.0	0.0	0.0	14.0	47.0
F^-	0.0	0.00	0.0	21.0	0.0	0.0	0.0	0.0
Initial exchangeable base cations (%)								
Eca %	30.5	30.6	28.2	10.8	13.8	12.1	36.0	13.0
EMg %	12.9	12.0	18.1	6.6	13.5	5.9	23.0	5.2
Ena %	2.3	1.9	4.1	3.3	1.4	0.8	3.1	1.9
EK %	1.9	1.5	1.4	1.4	3.9	2.3	3.9	1.2
BS %	**53.6**	**46.0**	**51.8**	**22.1**	**32.6**	**21.1**	**66.0**	**21.3**

5.2.2. Deposition sequences and historical changes in the catchment

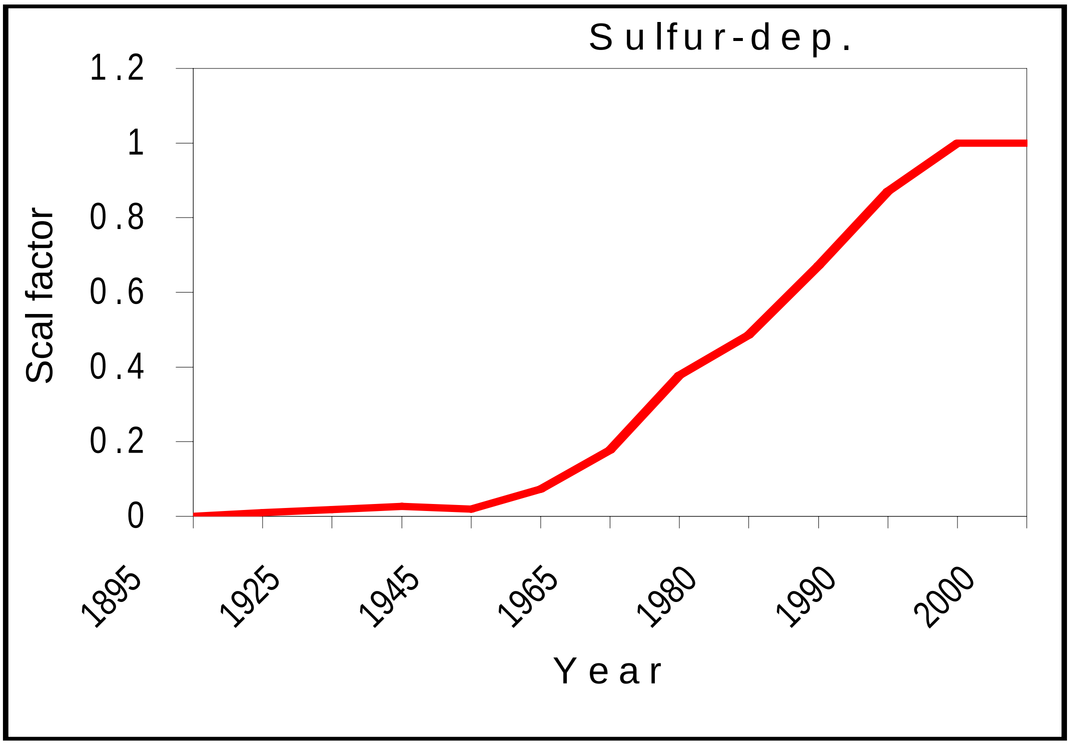
Historical simulations in this catchment were carried out for the period of 1895—2000. The hindcast deposition sequences for calcium in figure 5.5 are based on historical estimates of sulfur emissions for China (A.S.L. and Associate, 1996; *)* The deposition sequence for NO_3^- was assumed to have the same trend as SO_4^{2-}. All other ions were assumed to be of the same trend as Ca^{2+}.

Two different hindcast deposition sequences were assumed for calcium. In sequence one, 75% of calcium is of anthropogenic origin and sequence two, 50% of calcium is anthropogenic. For sequence one, BS and E_{Ca} for soil and ratio of Ca/Al and pH for soil-waters show very minor decrease all the way between the initial year and up to 1960 then start to fall a little faster. For sequence two, the BS and E_{Ca} for soil and the ratio of Ca/Al and the pH for soil-waters decreased very slowly from the background year (1895) up to 1960 then started to fall very fast between 1960—1995, which is much faster than sequence one. Sequence one seems probably more realistic than sequence two (see figure 5.6).

The model outputs for exchangeable base cations in soils and the ion concentrations in soil waters in the year 2000 are compared to the observed values in tables 5.5a and 5.5b. Al^{3+} concentration of the output model values diverges from the observed values, but for all other ions satisfactory agreement between the model outputs and the observed values have been obtained when both sequences are applied. The trends of base saturation (BS) in soils and concentrations of (Ca^{2+} + Mg^{2+}), SO^{2-}_4, Al^{3+}, pH and molar ratio of Al/(Ca+Mg) R_{CL} in soil waters for both layers between the background year 1895 and the reference year 2000 are given in figures 5.7.

Increased deposition of sulfur leads to increased SO_4^{2-} concentrations in soil waters. This increase is mainly accompanied by deposition of base cations particularly Ca^{2+} + Mg^{2+}. The highest SO_4^{2-} concentrations in soil waters were found in plot K and the lowest concentration of Ca^{2+} is found in plot C. Modeled concentrations of Al^{3+} for both soil layers (upper and deeper) increased considerably, especially during the last three decades because of soil acidification and increased ionic strength in soil waters. The lowest Al^{3+} concentration and relatively the highest pH were found in the upper soil in plot L. The model results show decrease of pH and BS for both layers in all plots when both sequences are applied. The BS decreases are 38.9 to 47.9 % and 24.5 to 50.8 % in the upper and deeper soils respectively for all plots. According to the model results this is a clear indication that acid deposition has resulted in soil acidification in the Tie Shan Ping catchment.

The $Al^{3+}/(Ca^{2+}+Mg^{2+})$ ratio (R_{CL}) in the soil waters increases for the both soils. The modeled R_{CL} ratios for plot C are 2.10 and 1.52 in the deeper and upper soils respectively. In plot B the R_{CL} ratio for the deeper soil exceeds by 1.73. If this ratio is exceeding a critical value, which is usually 1 in Europe, a potential danger for vegetation has been suggested. *(Prietzel, J. and Feger, K.H, 1992; Sverdrup, H and de Vries, W., 1994).* According to the model acidification of soil waters has been going on in both soils for the last 100 years. The low concentrations of Ca^{2+} for plot C with high Al^{3+} concentrations result in disturbingly large values of R_{CL}.



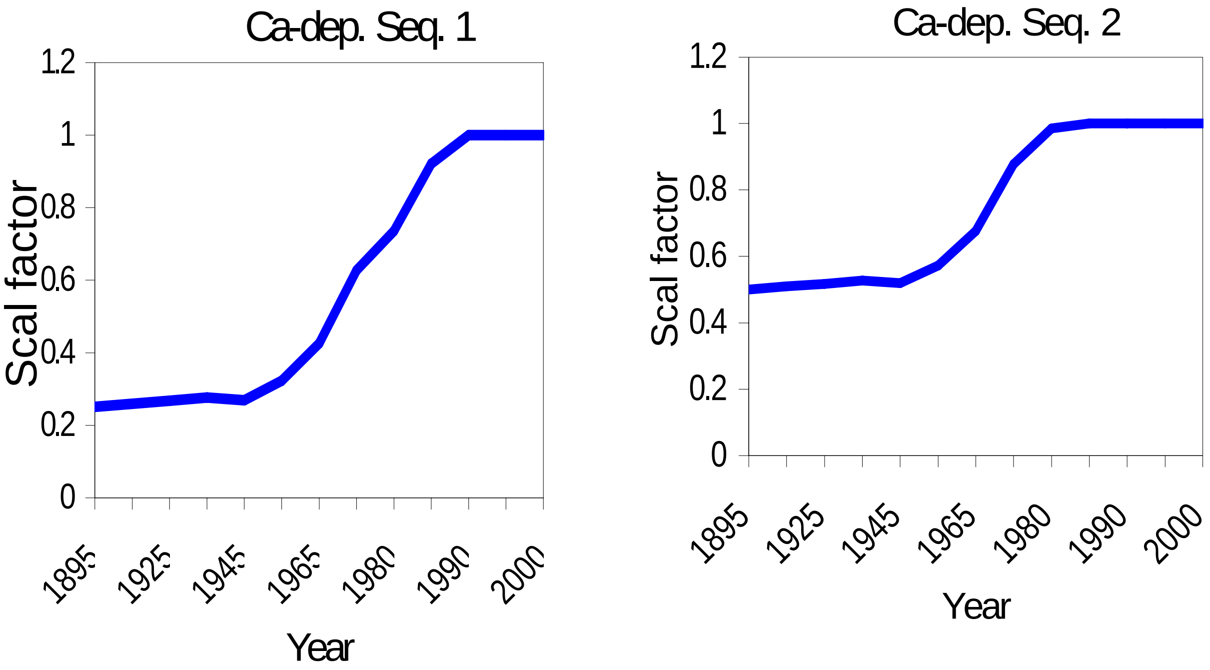


Figure 5.5a *Assumed deposition sequences for calcium for a period between 1895-2000. The sequences are based on sulfur emissions record for China. (A.S.L. and Associate, 1996;)*

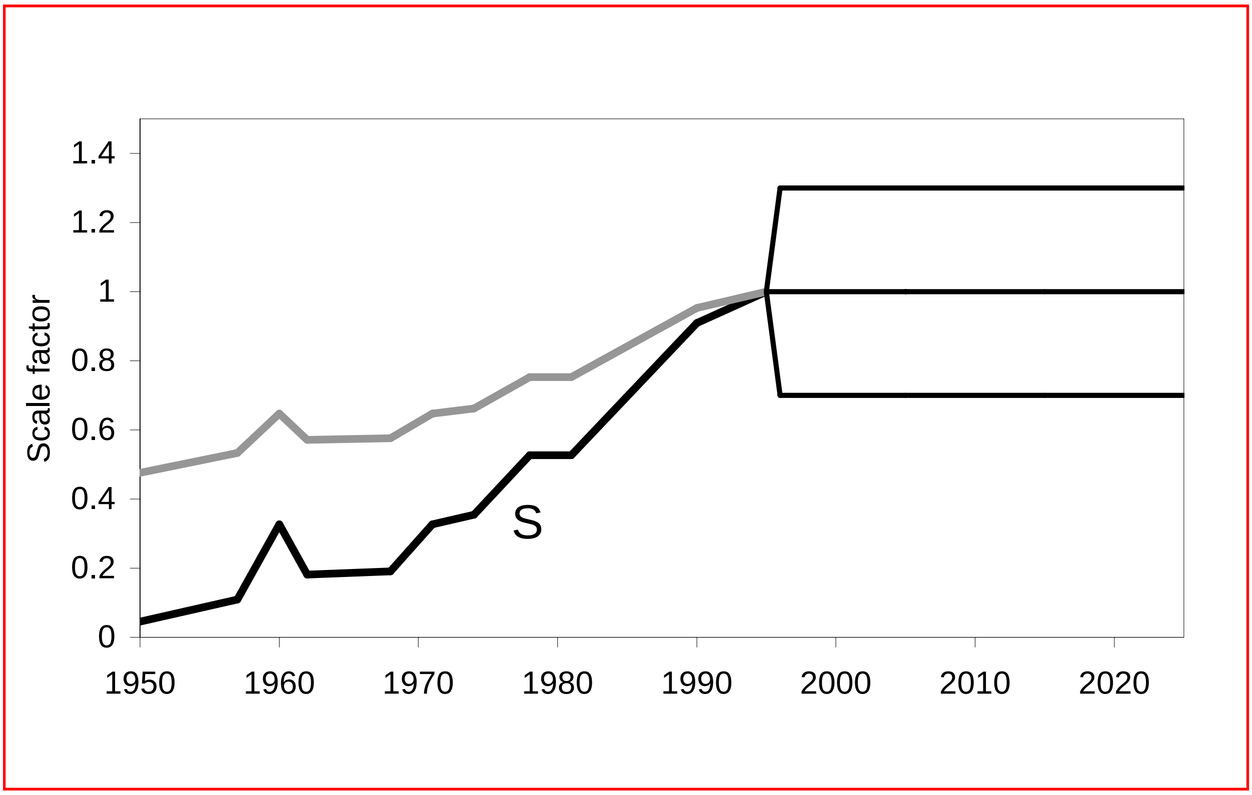


Figure 5.5b *Hind cast and forecast deposition sequences. Nitrate follows the sulfur deposition sequence; the other ions follow the calcium deposition sequence. The figure is taken from Larsen et al 1998.*

5.2.3. Parameter selection

Final parameter values used in the MAGIC model are given in Tables 5.4a and 5.4b. There are many parameters influencing the result of the MAGIC model such as ion concentrations in precipitation, dry deposition factors, the solubility constant for Al(OH)3, weathering rates, soil sulfate adsorption capacity, the selectivity coefficient for exchange of Al3+ with base cations, cation exchange capacity CEC, the depth of the soil, density, porosity, Dissolved Organic Carbon (DOC) and temperature. The interdependency of different parameters and their effects on the output results make choosing of parameters difficult. However, a set of numbers of different values has been tested for each parameter in different simulations. High values for weathering rates have been generally used in many cases.

5.2.4. Soils and soil water characteristics

Tables 5.5a and 5.5b shows the observed values for soil properties and soil-water composition for plots B, C, K and L in Tie Shan Ping. The observed values are compared with the model output. For the exchangeable base cations in soils in the year 2000, the values of the model output are in very good agreement with the observed data. Plot K has higher soil-water concentrations of Ca^{2+}, SO_4^{2-} , Al^{3+} and much higher concentration of NO_3^- than the other plots. It has also lower BS in both layers. Comparing plot C to other plots, concentrations of the most ions are low. High concentrations of SO_4^{2-} were found generally in all plots. Also very low concentration of NH_4^- was found in all plots except in the upper soil of plot B. In Tie Shan Ping there are large variations in soil properties and soil-water conditions between different plots within the catchment. The reason is probably difference in topography and vegetation.

Table 5.5a *Comparison of observed values(median concentration of 18 soil samples from TSP analyzed in Oslo and 121 soil water samples analyzed in Chongqing) and model outputs for soil and soil water in the Tie Shan Ping catchment, reference year 2000. Sequence 75%*

	Plot B				**Plot C**				**Plot K**				**Plot L**			
	Soil 1		**Soil 2**		**Soil 1**		**Soil 2**		**Soil 1**		**Soil 2**		**Soil 1**		**Soil 2**	
	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model
pH	3.58	3.6	4.02	4.0	3.81	3.8	4.11	4.1	3.97	4.0	3.87	3.9	4.17	4.2	4.13	4.2
Ca^{2+}µeq/l	501.02	500.6	407.66	404.5	421.68	420.5	374.52	373.6	834.12	839.2	1503.82	1498.4	737.81	739.9	589.85	585.5
Mg^{2+}µeq/l	259.95	258.8	221.87	219.9	179.34	178.5	147.75	148.9	301.09	300.4	298.62	303.3	247.61	244.7	126.77	125.0
Na^+ µeq/l	45.67	45.5	49.89	48.7	21.31	21.3	12.92	12.3	24.34	24.3	23.38	23.5	14.66	14.5	16.96	17.0
K^+ µeq/l	101.91	101.8	59.59	59.5	101.79	101.9	37.77	38.0	683.34	686.2	138.68	140.1	179.27	178.4	11.05	11.6
NH_4^+µeq/l	10.27	9.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_4^{2+}µeq/l	1531.1	1522.9	1341.48	1337.1	1000.08	1005.6	852.67	850.1	2069.09	2061.5	2407.68	2398.4	946.02	951.5	1306.41	1310.7
Cl^- µeq/l	52.46	52.0	85.15	85.3	81.01	81.4	67.30	67.6	147.31	147.2	134.76	134.0	53.90	53.7	76.19	77.5
NO_3^- µeq/l	511.05	513.2	340.80	339.7	400.13	400.3	614.22	608.7	1124.30	1127.0	1351.53	1338.5	354.51	353.1	188.15	187.1
F^- µeq/l	21.95	21.3	25.42	24.4	19.21	19.4	15.40	15.3	41.98	41.9	53.95	53.3	17.05	17.0	37.37	36.1
Al^{3+} µeq/l	856.66	1117.8	913.40	1069.6	599.55	744.7	758.03	893.5	1505.0	1633.0	1649.0	1888.5	525.30	529.6	733.65	705.5
ECa %	9.61	9.6	11.05	11.3	9.96	10.0	7.43	7.4	3.70	3.7	5.16	5.8	6.89	6.8	7.01	7.0
EMg %	2.74	2.7	3.44	3.3	5.73	5.7	4.07	4.0	2.62	2.6	2.35	3.0	3.51	3.6	2.52	2.5
ENa %	1.45	1.4	1.44	1.4	2.26	2.3	2.86	2.9	1.17	1.1	0.95	1.1	2.40	2.4	2.28	2.3
EK %	1.24	1.2	1.18	1.1	1.01	1.0	1.35	1.3	1.57	1.6	1.47	1.5	1.75	1.7	0.93	0.9
BS %	15.00	14.9	17.06	17.0	18.96	19.0	15.71	15.7	9.06	9.0	11.67	10.3	14.55	14.5	12.74	12.7

Table 5.5b *Comparison of observed values(median concentration of 18 soil samples from TSP analyzed in Oslo and 121 soil water samples analyzed in Chongqing) and model outputs for soil and soil water in the Tie Shan Ping catchment, reference year 2000. Sequence 50%*

	Plot B				*Plot C*				**Plot K**				**Plot L**			
	Soil 1		**Soil 2**		**Soil 1**		**Soil 2**		**Soil 1**		**Soil 2**		**Soil 1**		**Soil 2**	
	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model	Obser.	Model
pH	3.58	3.6	4.02	4.0	3.81	3.8	4.11	4.1	3.97	4.0	3.87	3.9	4.17	4.2	4.13	4.1
Ca^{2+}µeq/l	501.02	500.8	407.66	408.5	421.68	420.5	374.52	373.9	834.12	833.5	1503.82	1495.4	737.81	737.9	589.85	582.9
Mg^{2+}µeq/l	259.95	259.7	221.87	221.2	179.34	178.7	147.75	1489	301.09	297.7	298.62	291.5	247.61	243,7	126.77	124.0
Na^{+} µeq/l	45.67	45.5	49.89	49.0	21.31	20.3	12.92	12.5	24.34	24.2	23.38	22.5	14.66	14.9	16.96	17.9
K^{+} µeq/l	101.91	101.0	59.59	59.1	101.79	101.9	37.77	38.0	683.34	681.7	138.68	139.0	179.27	178.5	11.05	10.8
NH_4^{+}µeq/l	10.27	9.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_4^{2+}µeq/l	1531.1	1531.8	1341.48	1333.5	1000.08	1002.6	852.67	849.5	2069.09	2062.8	2407.68	2411.4	946.02	952.5	1306.41	1306.7
Cl^{-} µeq/l	52.46	52.0	85.15	85.3	81.01	81.4	67.30	67.6	147.31	147.2	134.76	134.0	53.90	53.7	76.19	77.5
NO_3^{-} µeq/l	511.05	511.6	340.80	344.0	400.13	400.3	614.22	608.1	1124.30	1127.0	1351.53	1351.5	354.51	353.3	188.15	187.9
F^{-} µeq/l	21.95	21.3	25.42	26.0	19.21	19.4	15.40	15.3	41.98	41.9	53.95	53.0	17.05	17.0	37.37	36.1
Al^{3+} µeq/l	856.66	969.8	913.40	1055.1	599.55	688.7	758.03	819.6	1505.0	1584.0	1649.0	1786.5	525.30	522.6	733.65	868.5
ECa %	9.61	9.6	11.05	11.0	9.96	10.0	7.43	7.4	3.70	3.7	5.16	5.2	6.89	6.9	7.01	7.0
Emg %	2.74	2.7	3.44	3.4	5.73	5.7	4.07	4.0	2.62	2.6	2.35	2.4	3.51	3.5	2.52	2.4
ENa %	1.45	1.4	1.44	1.4	2.26	2.3	2.86	2.9	1.17	1.1	0.95	1.1	2.40	2.4	2.28	2.4
EK %	1.24	1.2	1.18	1.2	1.01	1.0	1.35	1.3	1.57	1.6	1.47	1.5	1.75	1.7	0.93	0.9
BS %	15.00	15.0	17.06	17.0	18.96	19.0	15.71	15.7	9.06	9.0	11.67	10.3	14.55	14.5	12.74	12.7

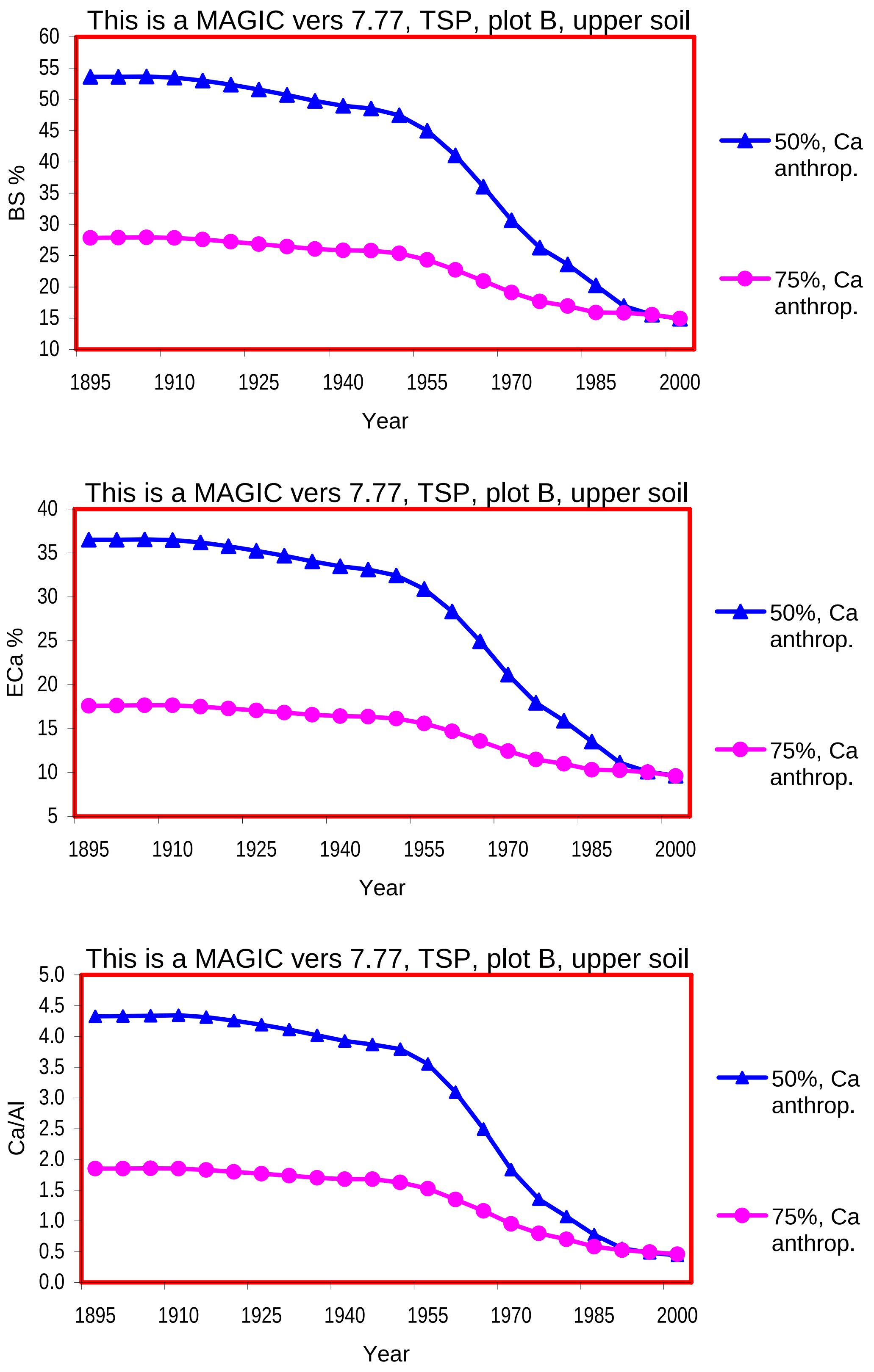


Figure 5.6. *The fugure shows the model results for BS and ECa for soil and Ca/Al ratio for soil water in plot B, corresponding to two different hindcast deposition sequences.*

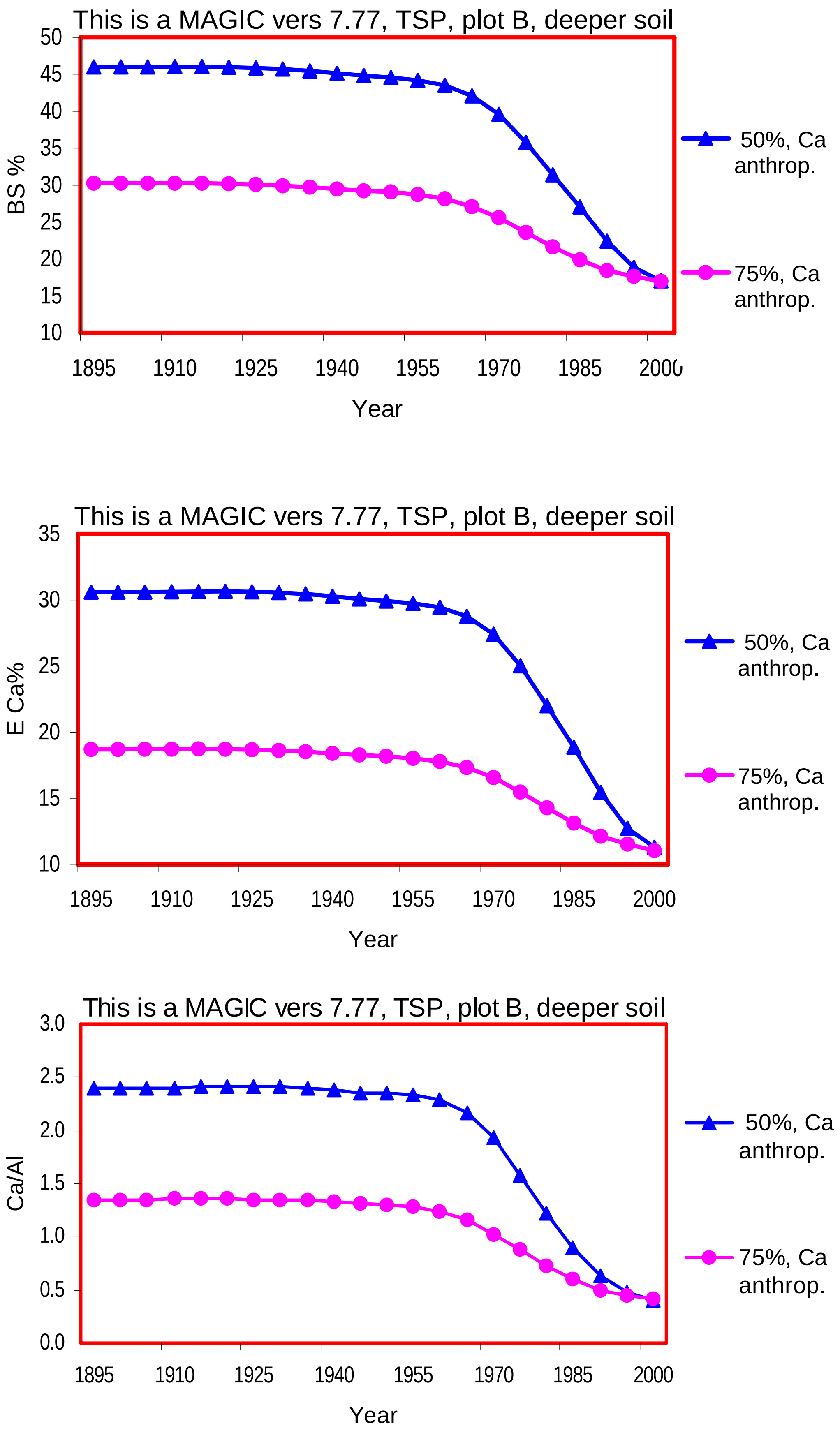
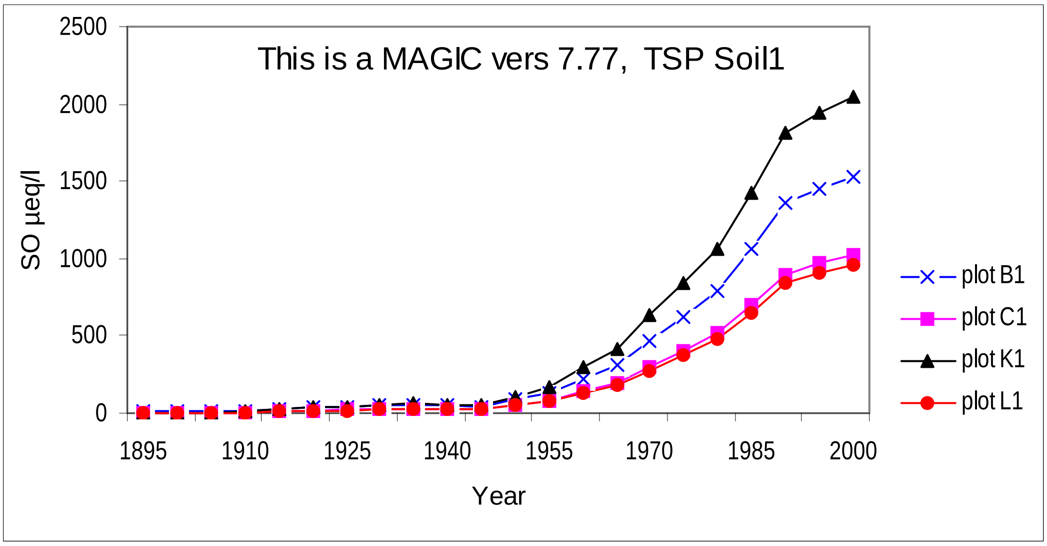
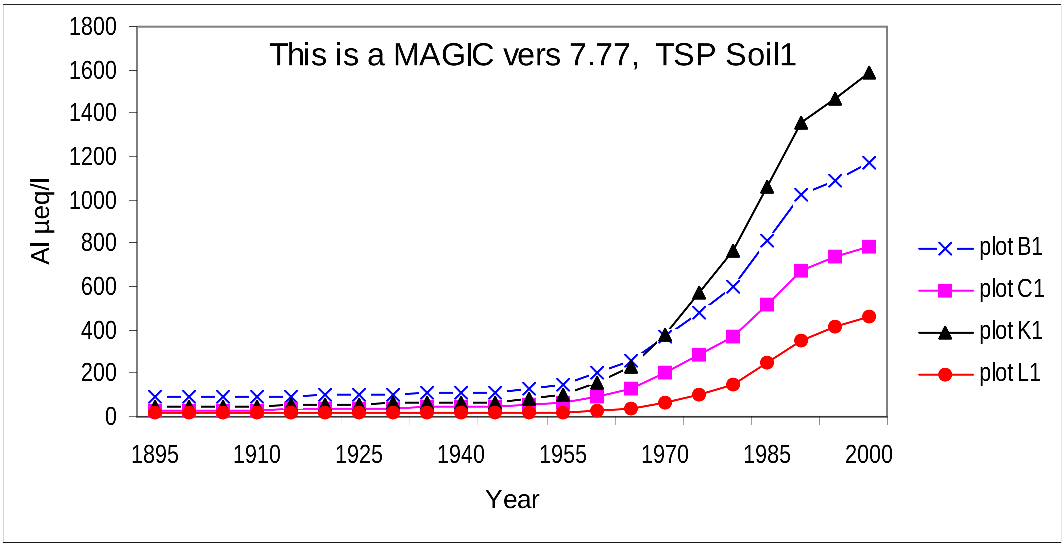


Figure 5.6 *(continued)*





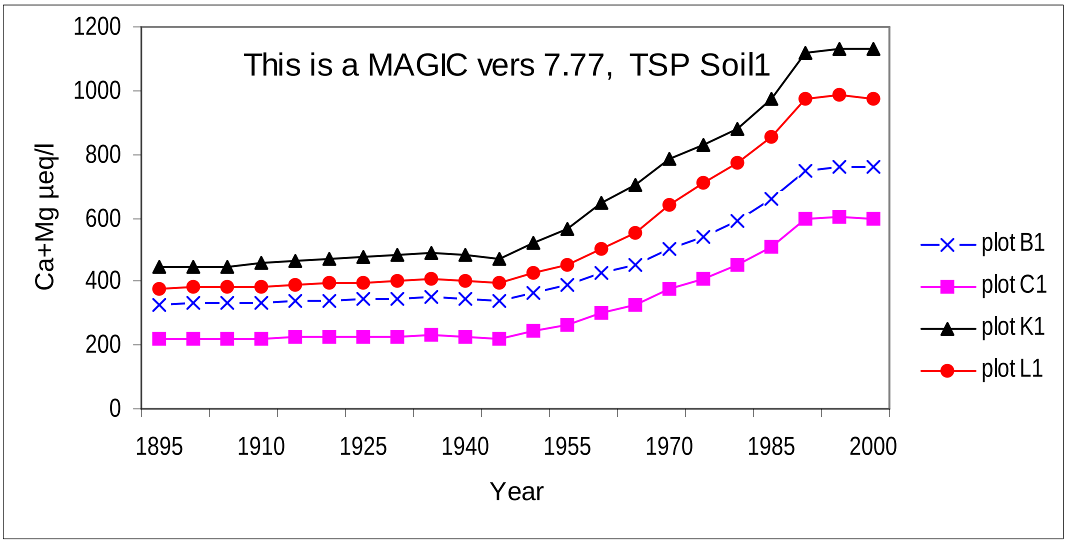
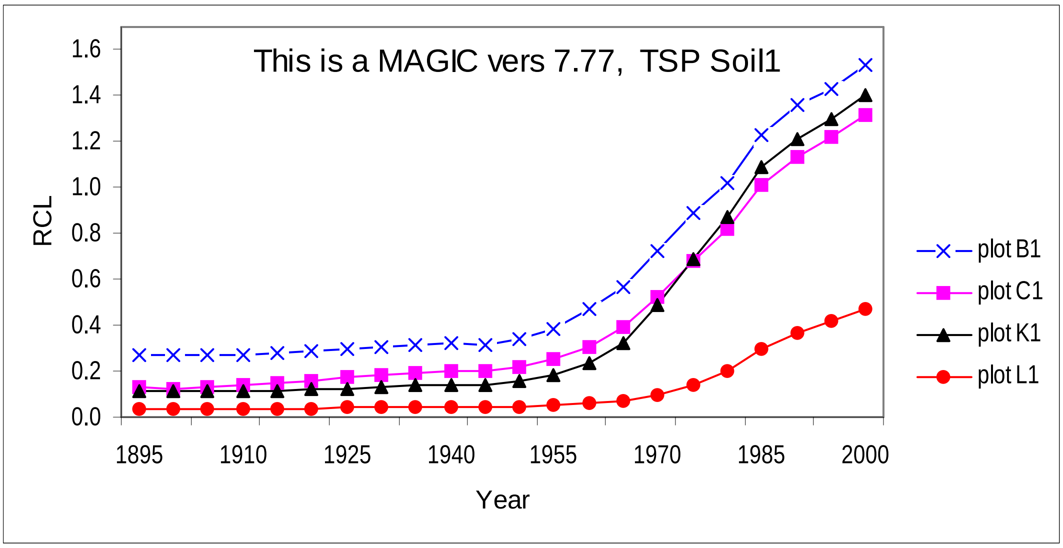
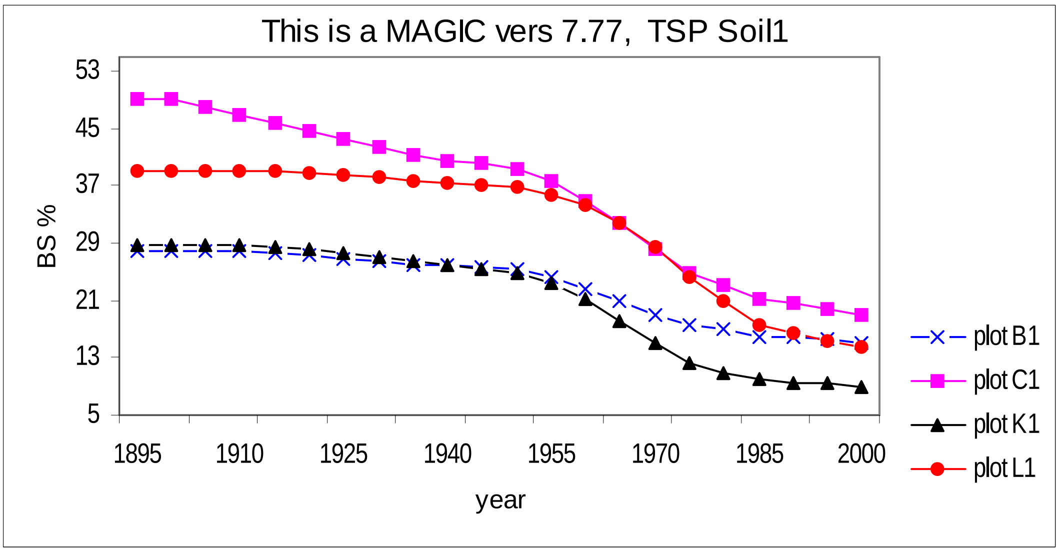
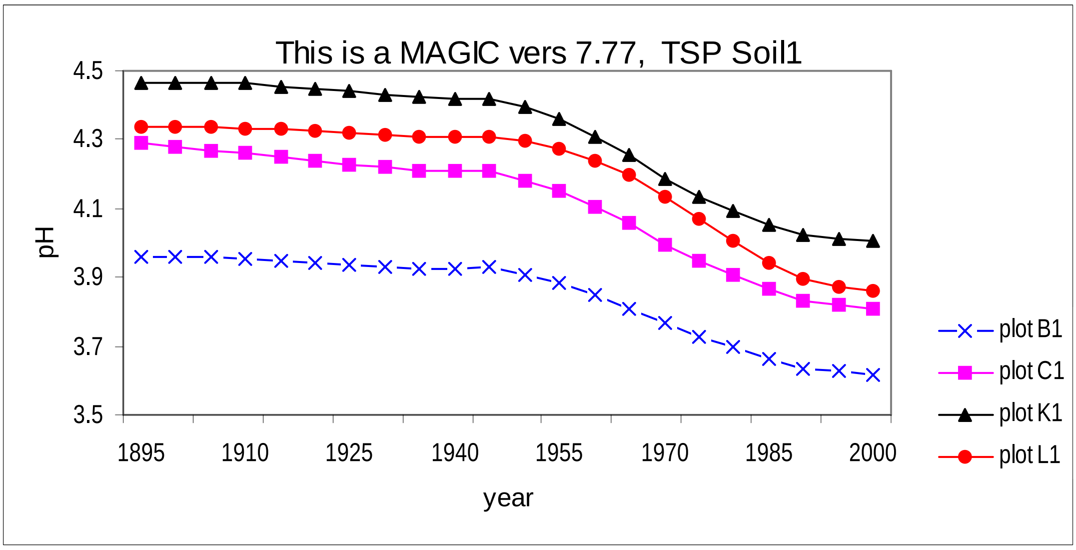


Figure 5.7 *The figure shows the results of the model simulation for soils and soil-waters in the TSP catchment for the period of 1895-2000 (75%, sequence is used)*







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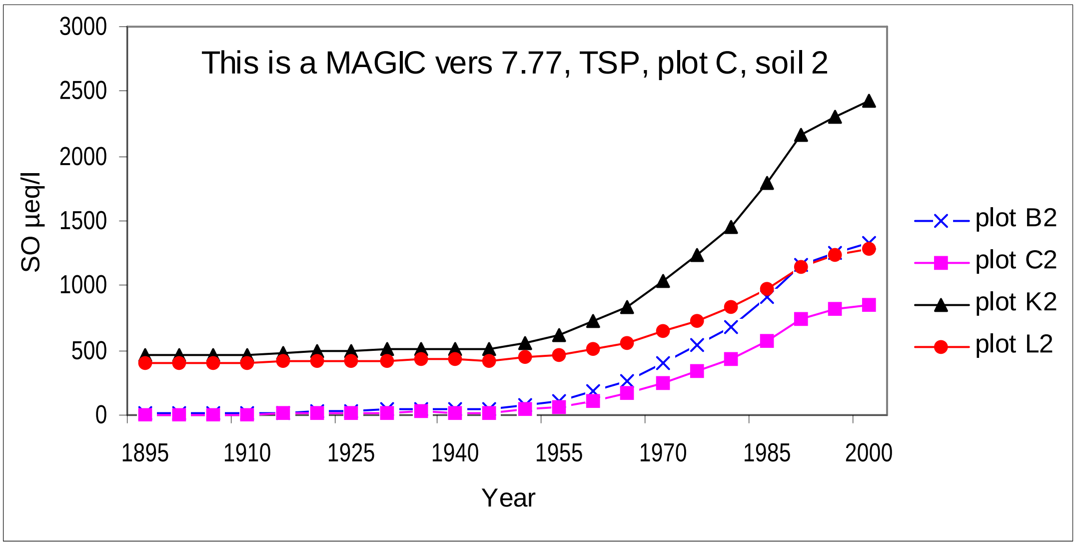

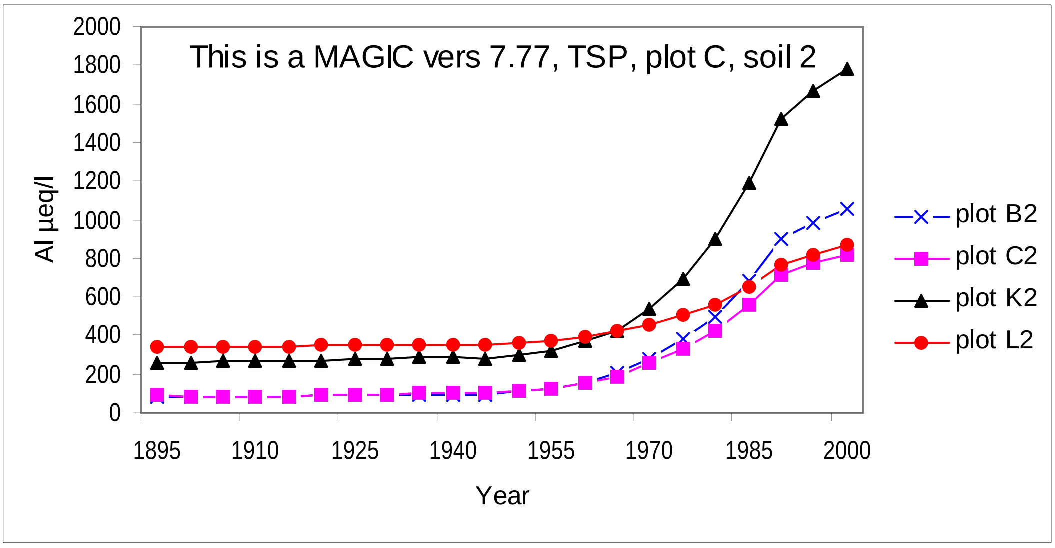

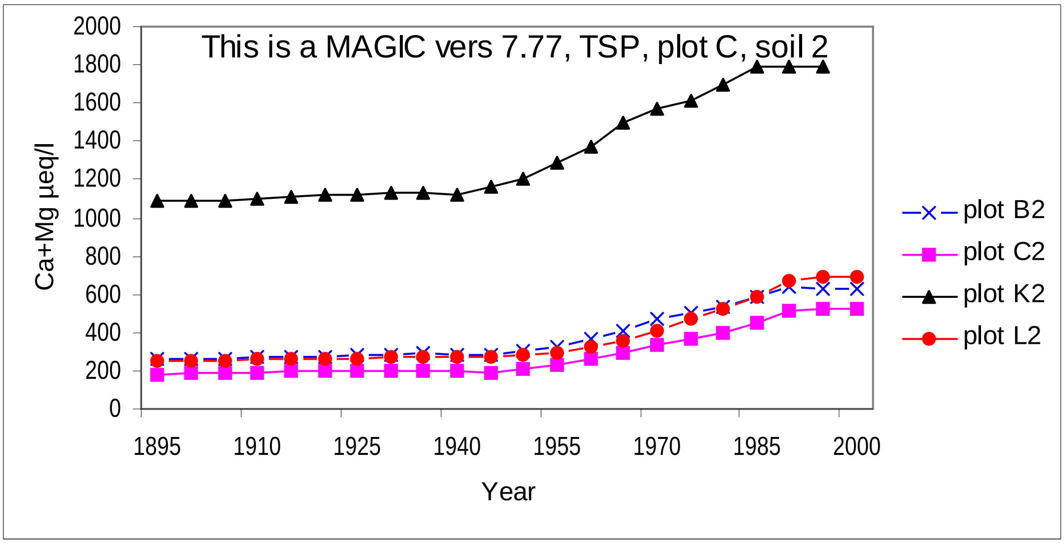

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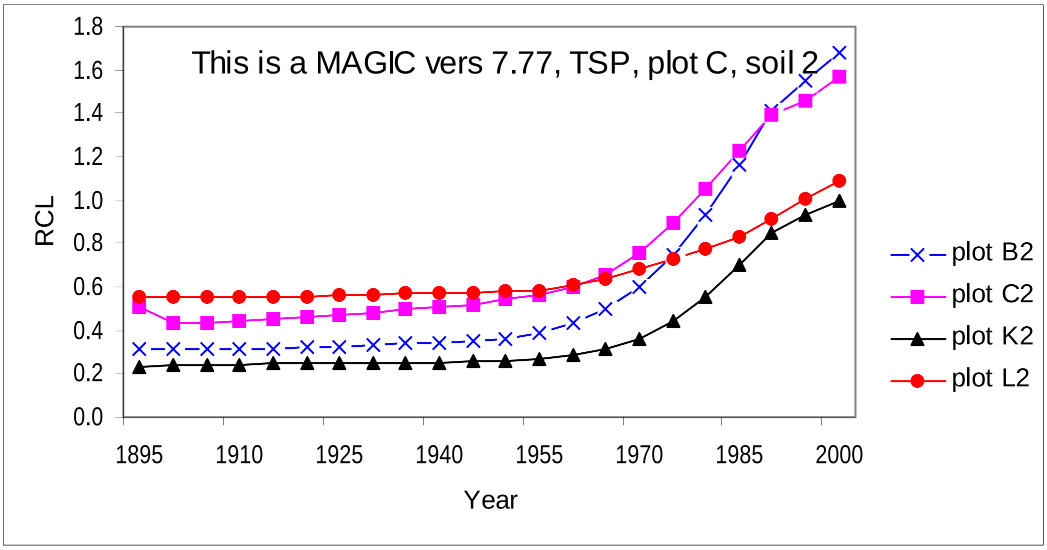

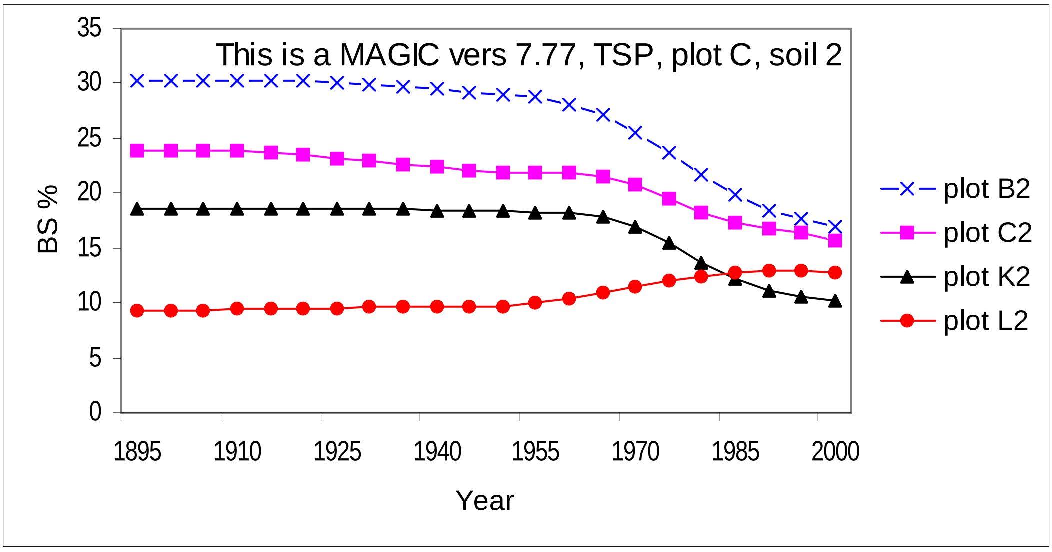

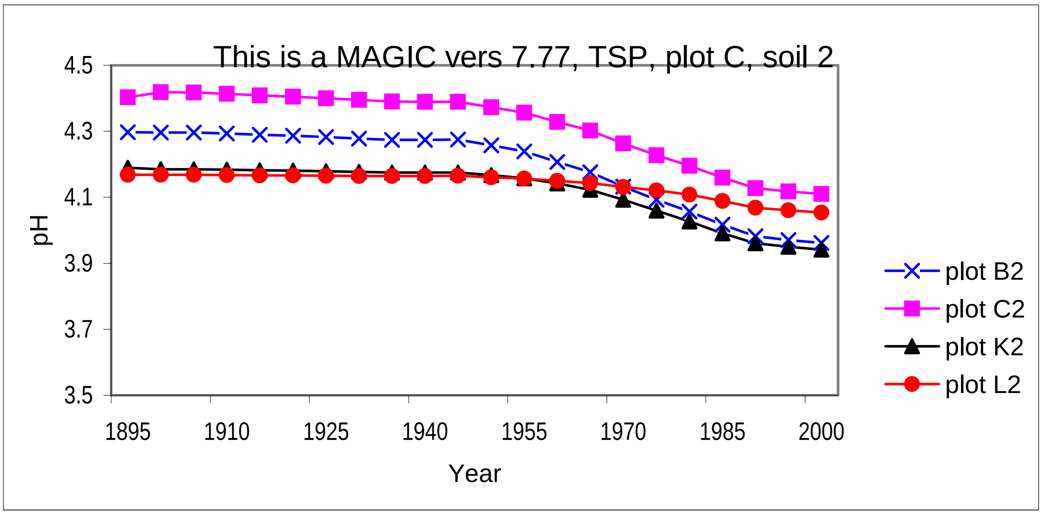

Figure 5.7 *(Continued)*

5.2.5. Model dependence on some key parameters

The solubility constant for Al(OH)3 is an important parameter. This constant, together with power of H+ and DOC influences greatly the model results, particularly pH and BS. When this constant is increased, also the selectivity constant e.g. SAlCa, will change. This results in decrease in the sum of base cation concentrations and the H+ concentration, and, in most cases leads to increase in the concentration of Al3+. Lower values for logK{Al(OH)3} has been used in the upper soils comparing to the deeper soils. For H-power same values have been used in both soils, but higher values for DOC have been suggested in the upper soils comparing to the deeper soils. Table 5.6 shows an interval of parameter values for DOC, H-power and the solubility constant of Al(OH)3 used in model calibration for different simulations. Some simulation results for plot B with use of different parameters within the selected interval are given in figure 5.8.

Table 5.6. *An interval selected for changing in the model parameters for logK{$Al(OH)_3$}, H^+ power and DOC in the MAGIC calibration*

logK{$Al(OH)_3$}		DOC values mmol/m^3		H^+ power
Upper soil	Deeper soil	Upper soil	Deeper soil	Both soils
{6.5, 8.5}	{7.0, 9.0}	{60, 240}	{20, 120}	{2.7, 3.0}

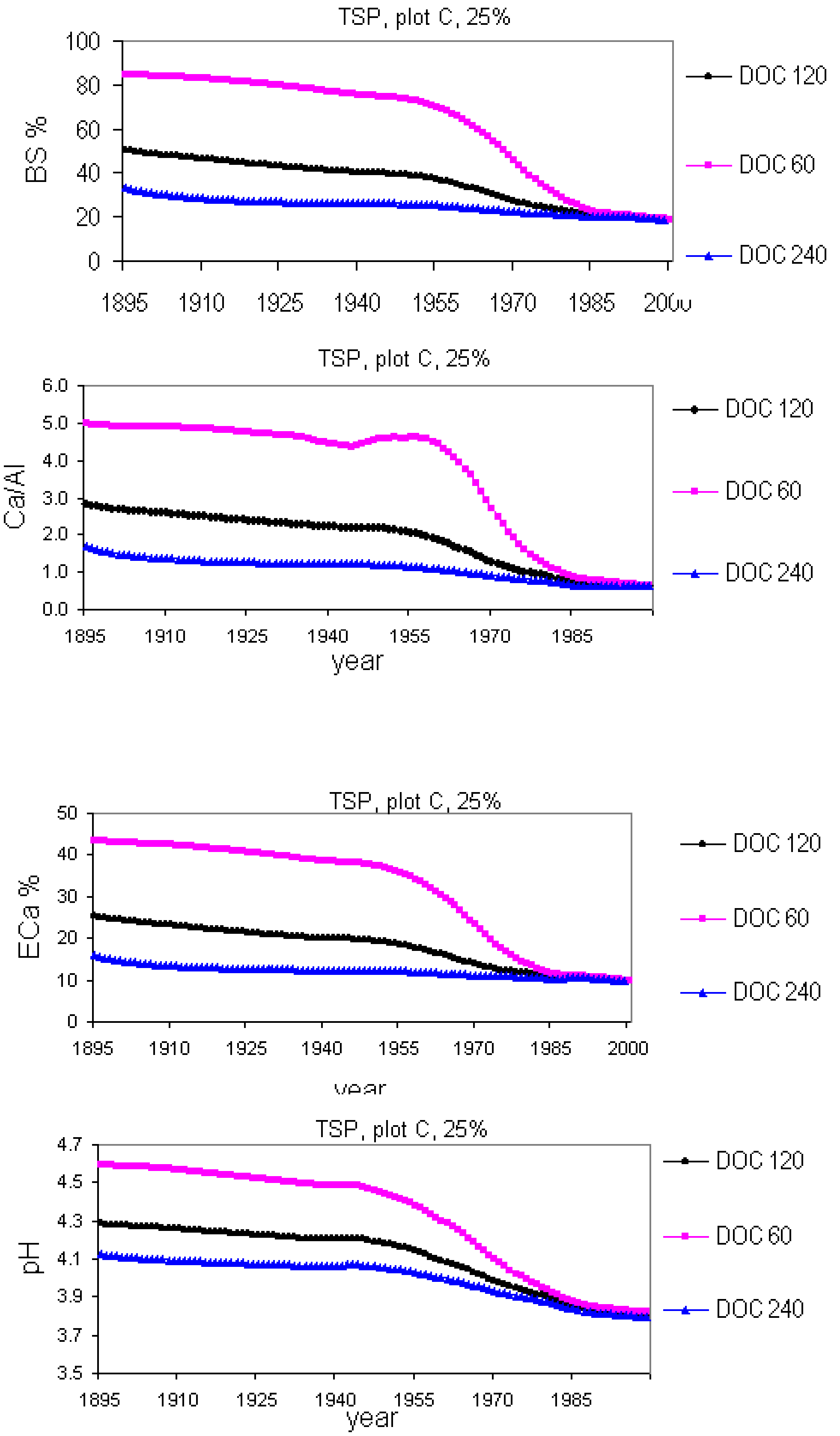

Figure 5.8a *Results of BS for soil and pH, ECa and Ca/Al for soil waters in plot B, corresponding to different values of DOC*

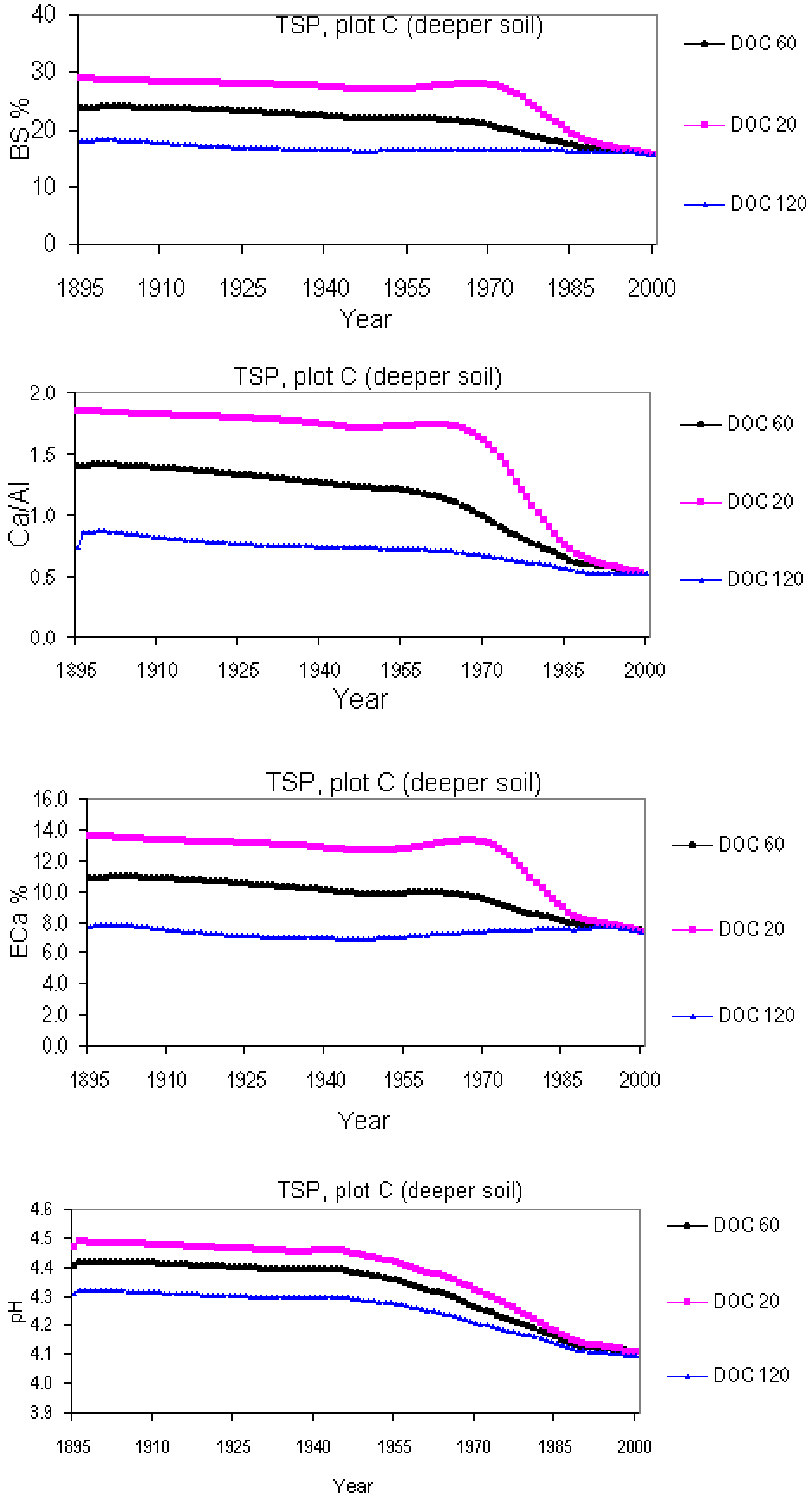

Figure 5.8a *(Continue)*

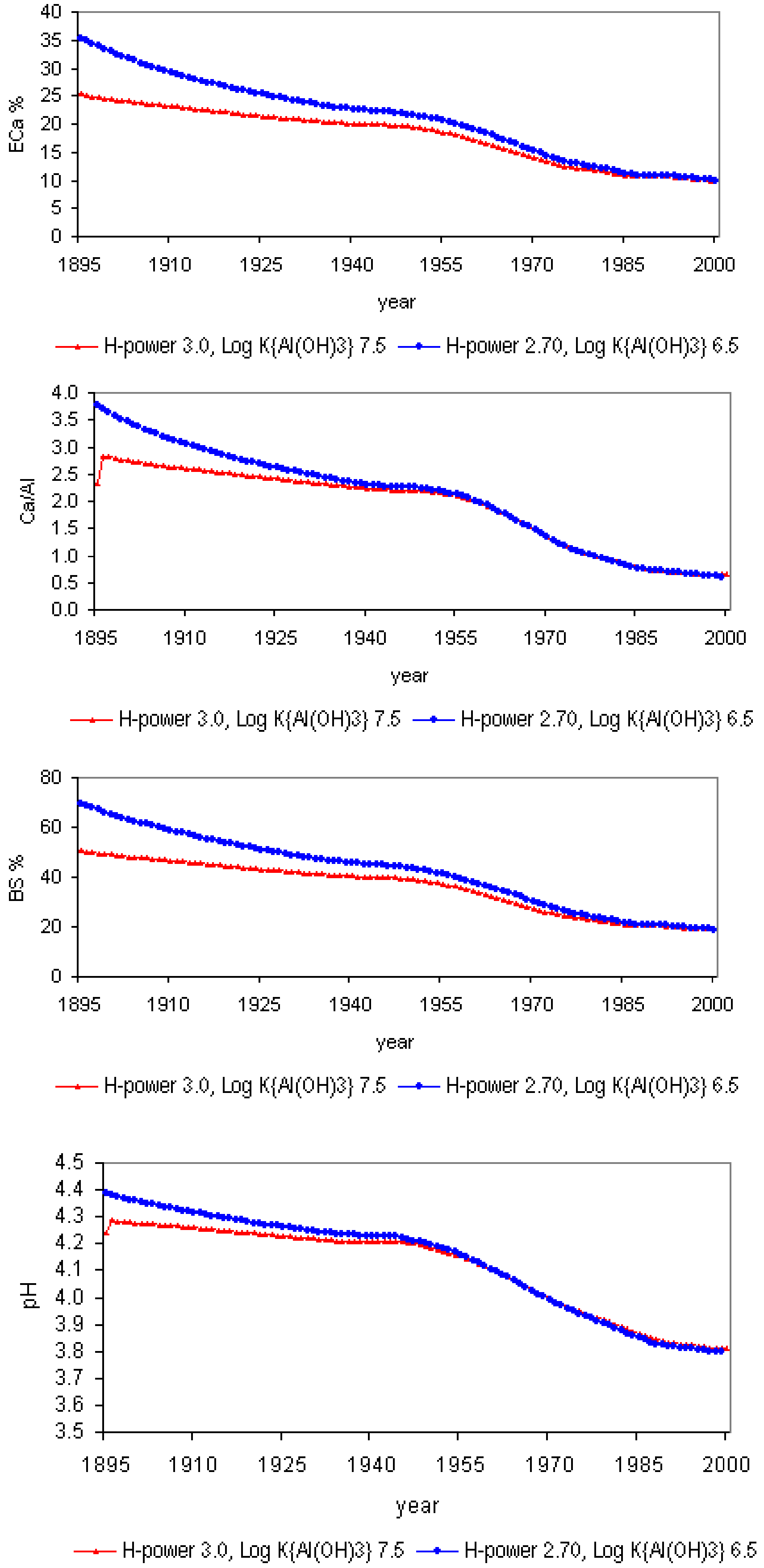

Figure 5.8b. *Results of BS for soil and pH, ECa and Ca/Al for soil waters in plot B, corresponding to different values of Aluminum constant and power of H.*

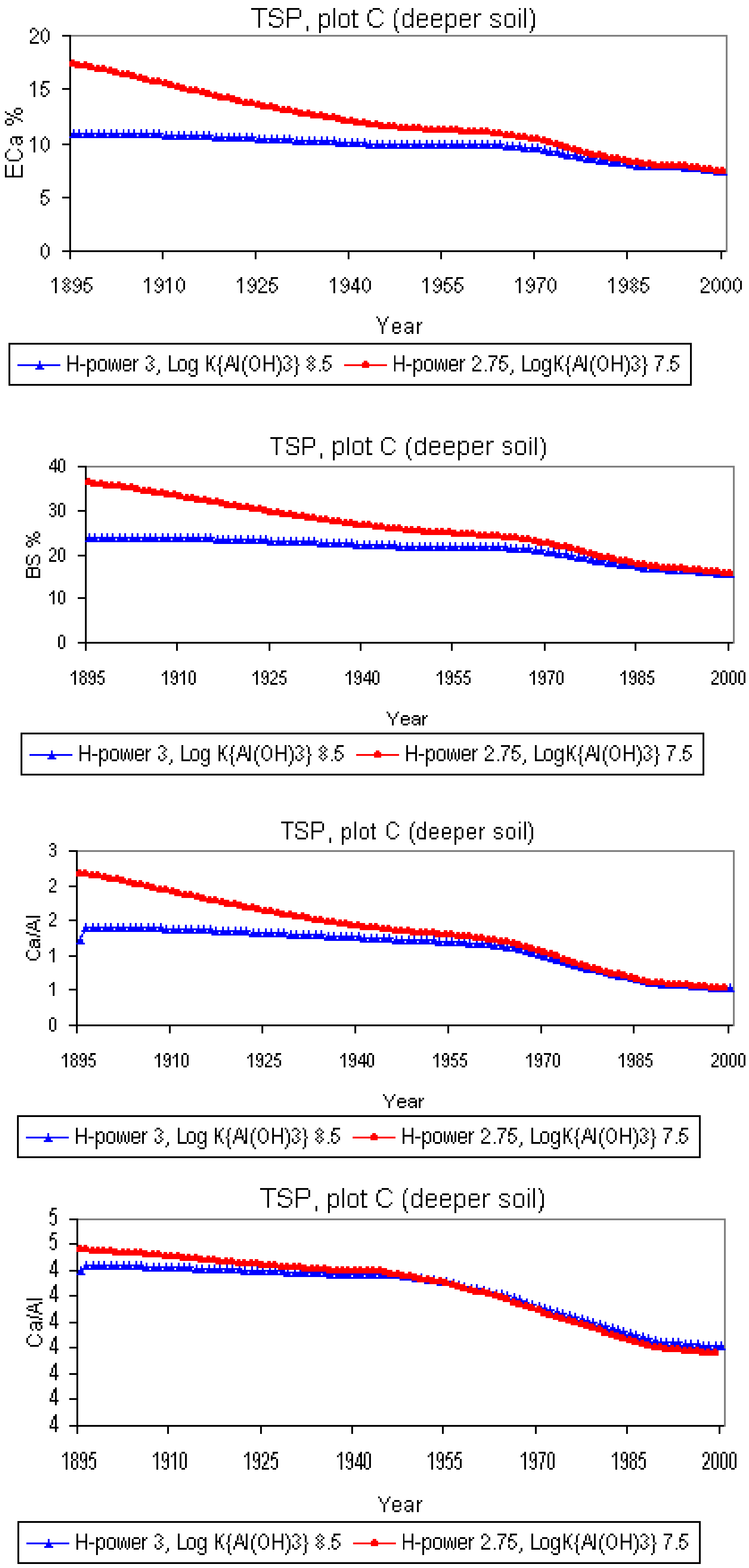

Figure 5.8b *(Continue)*

5.2.6. Prediction for different scenarios

Five possible future deposition scenarios for model predictions during the period 2000—2050 have been assumed. In scenario 1, the deposition for all ions is assumed to be at the present level (2000). In scenarios 2 and 3 deposition of all ions increased by 30% and decreased by 30% respectively. In scenario 4, the deposition of all ions except SO_4^{2-} decreased by 30%, while keeping the deposition of SO_4^{2-} at the present level. And in scenario 5, the deposition of SO_4^{2-} increased by 30%, while the deposition of all other ions is kept at the present level. The response of soils and soil waters for both soils (upper and deeper) in plot B for different forecast scenarios for the period of 2000—2050 are shown in figure 5.9.

The model prediction in scenario 5 (30% increase of SO_4^{2-} and constant of base cations) shows the most serious soil acidification. Serious soil acidification is predicted also in scenario 4, where deposition of base cations decreases by 30% and no change is made by deposition of SO_4^{2-}. These forecast results illustrate the importance of base cations and sulfate. This modeling result support previous model studies. (Larsen 1998 and Liao 1998). The model predicts if deposition of all ions (both base cations and SO_4^{2-}) is increased by 30%, a slow soil acidification will continue over the next fifty years. If deposition does not change over the next 50 years as we assumed in scenario 1, base saturation in the catchment will continue to decrease slowly. Reduction of soil acidification is predicted in scenario 3, where it is assumed the deposition of all ions (both SO_4^{2-} and base cations) is decreased by 30%. The pH increase and concentrations of base cations, SO_4^{2-} and Al^{3+} decrease according to the model predictions for 2050, compared to the values in the year 2000, for the both soils.

5.2.7. Discussion

The soil samples from Lei Gong Shan have been taken from three different random sample-points within and near the catchment. The different physico-chemical soil properties of different sample-points within and outside of this small catchment make it difficult to describe the whole catchment. Similarly, the different physico-chemical soil properties of different plots within the Tie Shan Ping catchment also make it difficult to describe the whole catchment and to determine proper input parameter values. The very high ion concentrations in soil water of plot K and relatively low ion concentrations of plot C led to difficulties in choosing input parameters suitable for the entire catchment.

There are very high concentrations of NO_3^- in plot K and very low concentration of NH_4^+ in all plots except the upper soil of plot B. We assumed 100% nitrification of NH_4^+ for both soil layers.

One problem is that the data used in the model simulation are produced in different time and analyzed by different people. Ion concentration in precipitation in table 5.3 is for example based on field study during 1996 to 1998. Observed values from soil and soil waters in tables 5.5 are for example sampled 2000 and 2001. A further problem is that the MAGIC model (described in sections 2.8 and 4.5) uses only two soil layers. This may often lead to difficulties in lumping soil horizons.

Most of the field observation values are generally close to the calculated results. The largest deviations are for Al^{3+} and this cannot be remedied by simply changing one parameter. The MAGIC model uses the relationship $K_{Al(OH)3} = [Al^{3+}]/[H^+]^n$. Previous model studies such as Liao et al 1998, used n equals 3. Several studies show that the exponent n in field conditions is often lower than this value (Berggren, D. and Mulder J., 1995.; Stone, A. and Seip, H.M., 1990.; Reuss, J.O., Walthall, P.M., Roswall, E.C., and Hopper, R.W.E., 1990). This was also believed to be the case in in Tie Shan Ping catchment, (Larsen, T., Xiong, J., Vogt, R.D., Seip, H.M., Liao, B. and Zhao, D., 1997). Within the chosen interval in the table 5.5 the model gives the best fit for the upper end of the chosen interval for H-power and the medium of log $K\{Al(OH)_3\}$. Thus the final results presented here were obtained with $n = 3$.

The modeled $Al^{3+}/(Ca^{2+}+Mg^{2+})$ ratio (R_{CL}) in all plots except the upper soil for plot L in the year 2000 is exceeding 1 regardless of what deposition sequence was applied. Similarly, the observed R_{CL} in all plots except the upper soil for plot L and the deeper soil for plot K in the year 2000 is exceeding 1. In the upper soil for plot C the modeled and the observed R_{CL} ratio is 1.52 and 1.0 respectively and in the deeper soil the modeled and the observed R_{CL} is 2.10 and 1.45. In plot B the observed R_{CL} ratio for the deeper soil is 1.45. The $Al^{3+}/(Ca^{2+}+Mg^{2+})$, which is often used as an indicator parameter for aluminum toxicity in the soil waters, is high for all plots except the upper soil for plot L. The modeled R_{CL} ratio in the upper soil for plot L is 0.47 and 0.59 with the use of 75% and 50% deposition sequences respectively and the observed value is 0.53. The deeper soil for modeled and observed values in this plot is also exceeding 1 in the year 2000. The outcome of this modeling clearly shows that the sequence where 50% of Ca^{2+} is of anthropogenic origin results in higher values for R_{CL} than the 75%

sequence. A high $Al^{3+}/(Ca^{2+}+Mg^{2+})$ may lead to possible harmful effects on vegetation (Prietzel, J. and Feger, K.H, 1992).

The lack of data for calcium in historical deposition increases the uncertainties of reconstructing a proper deposition sequence for the element. Historical deposition for calcium is derived from the deposition sequences for sulfur, which is also based on assumptions and has large uncertainties. Both deposition sequences in figure 5.5 (sequence 1 which is 75% of calcium and sequence 2 which is 50% of calcium are of an anthropogenic origin) give acceptable agreement with the observed values, particularly the sequence one. The trend of BS is similar to the previous MAGIC study in China. (Larsen et al 1998, Liao et al 1998).

The model predictions of future soil conditions (figure 5.9) depend strongly both on sulfur deposition and calcium deposition. The most serious soil acidification is predicted for the scenario where the present SO_4^{2-} deposition increases with 30% and base cations deposition remains unchanged. The scenario with 30% decrease of both base cations and SO_4^{2-} depositions predicts the opposite trend in this modeling study. If the depositions continue at the same level as today, the base saturation in the catchment will continue to decrease slowly.

The deposition of both base cations and anions has many sources of uncertainties. However, these modeling results clearly illustrate the importance of the base cations, especially calcium. Total or partial removal of the anthropogenic alkaline dust without any reduction in sulfur emissions may lead to harmful effects on vegetation due to the soil acidification (Larsen and Carmichael, 2000). Thus it is very important to consider not only the sulfur emission, but also the deposition of base cations when assessing the impact of emissions on soil properties.

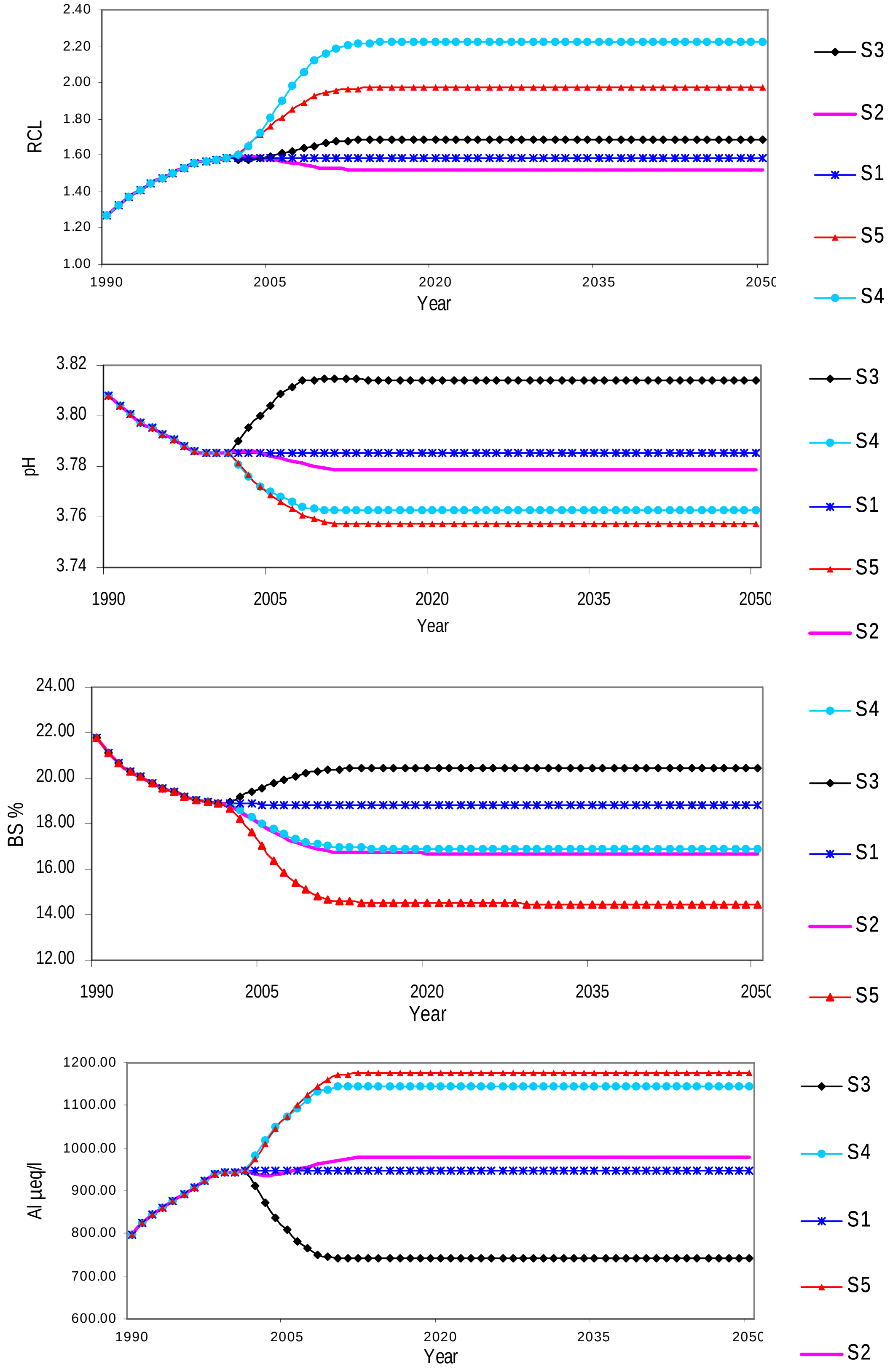

Figure 5.9 *Future trend of soils and soil waters in TSP to five assumed deposition scenarios for the period of 2000-2050. The figure show a predicted results for plot B (top soil)*

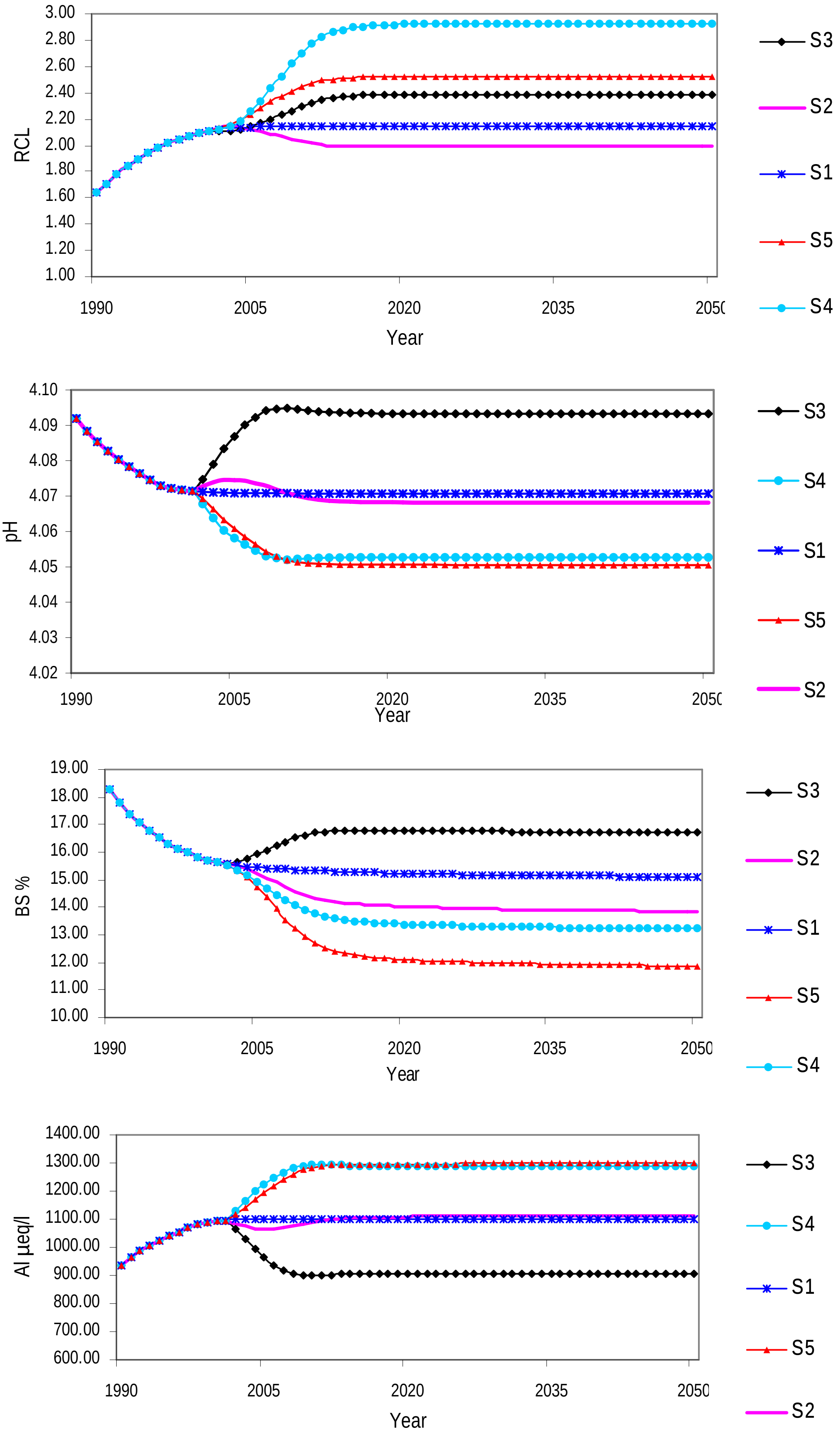

Figure 5.9 *(sub soil)*

6. Conclusions

There is different mineralogy between TSP and LGS, and probably different weathering history. TSP has a much warmer climate and hence a more developed soil. The average pH (in water) for upper and deeper soils in TSP is 3.9 and 4.31 and in LGS is 4.9 and 5.2 respectively. AlS for upper and deeper soil in TSP is 77.5% and 80.5% respectively. For LGS, AlS is 51.9% and 57.2% in the upper and deeper soils respectively. LGS soils have higher BS and CEC than TSP soils especially in the O-horizon.

The high SO_4^{2-} emissions from industries and households cause low pH in precipitation and high deposition of sulfate in Tie Shan Ping. In soil water Al^{3+} is the dominant cations, while Ca^{2+} is the dominating for base cation.

The model studies of Tie Shan Ping catchment indicate that serious soil acidification has been going on in both soils for the last 40 years. The future trend in deposition of base cations is as important as the trend in sulfur deposition. A 30% increase in sulfur deposition without further additional deposition in base cations seems to lead to deterioration of soils in Tie Shan Ping. On the other hand a 30% reduction in sulfur deposition is likely to result in improved soil conditions.

$R_{CL} = Al^{3+}/(Ca^{2+}+Mg^{2+})$, often used as an indicator parameter for aluminum toxicity in the soil waters, is high. The R_{CL} ratio in all plots is far greater than 1, which is often regarded as a critical value in Europe.

The largest deviations between observed and calculated values are for Al^{3+}. For all other ions the calculated concentrations are very close to the field observations.

The outcome of the model results show that the deposition sequence where 50% of Ca^{2+} is of anthropogenic origin results in higher values for R_{CL} than the the deposition sequence where 75% of Ca^{2+} is of anthropogenic origin. Both sequences give an acceptable result and in general no significant differences have been found except the trend of base saturation and base cations in soil. However, the fraction of the present calcium deposition originating from anthropogenic sources is not know; thus it is very difficult to construct a reliable deposition sequence for calcium.

Soils, topography and vegetation vary considerably different plots within this small catchment. Therefore, to choose proper input parameters for the whole catchment is very complicated.

The model results depend strongly on the solubility constant for Al(OH)3, H-power, DOC concentration, dry deposition factors and weathering rates, which are difficult to determine both in the field and in the laboratory. It is recommended to use the results of field and laboratory studies as far as possible in determining input values and to use comparison between modeled and observed values for final adjustments.

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Appendix 1
Chemical data for soil water Tie Shan Ping 1995—1998

Date	Collector #	µeq/l H+	µeq/l Na	µeq/l NH4	µeq/l K	µeq/l Mg	µeq/l Ca	µeq/l Ali	µeq/l F	µeq/l Cl	µeq/l NO3	µeq/l SO4	µeq/l sum+	µeq/l sum-	% cat-an % sum
apr-95	1	11.7	27.3	375.4	42.8	13.0	299.0	8.8	3.5	31.7	90.3	584.0	778.1	709.5	4.6
jun-95	1	35.5	2.9	56.4	7.5	5.8	62.9	12.2	0.0	11.5	18.3	140.3	183.2	170.1	3.7
jul-95	1	74.1	0.5	27.8	11.9	11.8	52.9	8.4	0.5	4.8	17.1	157.5	187.6	179.9	2.1
sep-95	1	35.5	6.9	120.6	23.0	19.5	147.9	37.8	0.1	13.7	35.9	302.4	391.2	352.2	5.3
des-95	1	363.1	34.1	44.6	46.5	57.6	432.9	28.4	4.0	54.2	132.5	885.9	1007.3	1076.5	-3.3
jan-96	1	257.0	32.0	333.7	32.7	42.4	340.3	6.2	24.3	99.0	126.6	742.0	1044.4	991.9	2.6
feb-96	1	251.2	77.4	272.7	51.2	90.5	585.9	26.0	4.7	118.9	108.9	965.9	1354.9	1198.3	6.1
mar-96	1	109.6	21.5	258.1	23.1	40.5	269.9	54.4	0.0	59.5	101.3	486.9	777.1	647.7	9.1
apr-96	1	89.1	27.3	164.3	18.8	51.8	306.1	32.5	0.1	35.6	66.4	461.9	690.0	564.0	10.0
jul-96	1	28.8	7.3	17.8	5.8	6.3	55.9	5.6	0.1	7.8	5.6	111.1	127.6	124.6	1.2
sep-96	1	81.3	8.6	63.9	10.1	16.5	140.6	11.3	0.6	18.8	30.7	241.9	332.4	291.9	6.5
okt-96	1	195.0	16.7	70.3	22.3	54.9	272.4	22.9	1.1	35.0	40.0	463.7	654.4	539.8	9.6
nov-96	1	147.9	6.2	68.8	10.3	11.3	106.6	5.4	9.5	33.7	33.7	320.0	356.5	396.8	-5.3
des-96	1	416.9	53.5	69.9	36.6	77.8	668.7	62.2	0.4	79.0	91.0	1114.3	1385.5	1284.7	3.8
jan-97	1	478.6	174.9	150.2	96.2	321.3	832.9	109.8	0.1	192.1	131.8	1733.7	2163.9	2057.6	2.5
feb-97	1	69.2	84.2	117.8	27.6	58.4	389.0	66.5	1.1	58.2	63.5	870.6	812.7	993.4	-10.0
apr-97	1	407.4	77.4	34.9	35.9	54.7	268.0	82.5	0.0	102.1	29.7	757.4	960.9	889.3	3.9
jul-97	1	40.7	5.7	9.5	17.9	19.9	147.4	11.8	0.6	11.0	6.0	195.1	252.8	212.8	8.6
aug-97	1	5.6	7.0	15.3	147.8	110.3	131.0	0.8	25.0	21.7	1.0	318.0	417.9	365.7	6.7
okt-97	1	85.1	4.8	41.5	16.6	16.0	133.0	9.0	2.3	16.2	12.5	264.0	306.0	295.0	1.8
nov-97	1	223.9	25.8	46.7	15.2	42.1	387.4	26.6	3.5	66.0	30.5	687.9	767.6	787.9	-1.3
des-97	1	269.2	15.0	181.2	34.0	43.2	253.5	46.2	1.0	58.4	107.7	731.1	842.2	898.2	-3.2
jan-98	1	380.2	11.5	13.3	25.1	41.1	294.9	42.3	1.1	59.0	132.1	725.3	808.4	917.4	-6.3
feb-98	1	208.9	11.2	117.0	16.4	24.4	153.2	9.7	7.1	37.0	52.7	398.0	540.7	494.8	4.4
mar-98	1	134.9	10.2	110.4	15.4	44.1	282.9	22.2	0.2	26.6	73.0	478.8	620.3	578.6	3.5
apr-98	1	42.5	12.3	80.3	11.5	26.0	121.6	9.6	2.3	34.1	31.7	244.0	303.7	312.0	-1.3
mai-98	1	26.3	7.3	101.5	7.6	9.1	53.7	5.0	1.0	34.6	29.6	183.2	210.4	248.4	-8.3
jun-98	1	34.7	7.6	77.1	9.6	10.9	67.4	2.4	8.2	16.4	27.4	186.8	209.5	238.8	-6.5
jul-98	1	32.4	9.6	28.5	9.9	27.8	124.3	3.8	3.2	29.3	13.2	218.0	236.3	263.8	-5.5

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aug-98	1	58.9	7.0	18.8	5.0	5.8	30.4	4.4	0.9	16.8	9.3	105.0	130.3	132.0	-0.6
Date	**Collector #**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**% cat-an**
		H+	**Na**	**NH4**	**K**	**Mg**	**Ca**	**Ali**	**F**	**Cl**	**NO3**	**SO4**	**sum+**	**sum-**	**% sum**
sep-98	1	102.3	5.2	18.8	6.1	9.9	40.4	5.1	0.6	15.2	6.3	165.4	187.9	187.5	0.1
okt-98	1	112.2	9.6	36.3	9.7	9.5	40.0	3.3	2.2	15.7	16.6	168.2	220.6	202.6	4.2
nov-98	1	195.0	18.3	113.1	32.5	53.5	341.3	68.3	0.2	37.0	66.1	697.3	822.0	800.6	1.3
des-98	1	204.2	15.2	164.1	34.8	36.2	264.0	35.9	0.5	51.6	103.9	561.0	754.4	717.1	2.5
apr-95	2	41.7	184.0	2062.3	170.1	452.6	2282.5	72.5	10.4	264.3	544.8	4139.7	5265.6	4959.2	3.0
mai-95	2	186.2	35.7	52.1	406.4	127.1	618.3	11.1	43.2	129.3	7.8	1034.0	1436.9	1214.3	8.4
nov-95	2	676.1	36.3	355.6	84.0	122.6	1080.4	162.8	0.6	221.0	101.6	2206.1	2517.8	2529.4	-0.2
jan-96	2	1698.2	139.2	1014.5	186.2	311.0	1654.3	165.1	2.6	331.5	465.3	4953.6	5168.5	5752.9	-5.4
feb-96	2	1698.2	226.6	648.6	201.8	349.7	1946.2	123.1	6.3	328.1	526.6	4258.8	5194.3	5119.8	0.7
apr-96	2	346.7	68.3	827.7	189.3	223.0	1186.7	104.2	18.4	68.5	172.1	2199.9	2945.8	2459.0	9.0
mai-96	2	338.8	65.2	668.6	158.8	136.6	571.9	36.7	6.2	111.7	188.4	1675.8	1976.6	1982.1	-0.1
jun-96	2	245.5	23.9	296.0	149.1	134.1	403.7	75.1	0.1	59.5	60.3	1170.8	1327.5	1290.7	1.4
jul-96	2	58.9	52.6	6.1	204.9	225.5	546.9	82.4	0.1	134.8	1.0	1099.1	1177.3	1235.1	-2.4
aug-96	2	20.0	14.8	138.0	55.8	69.9	552.9	24.6	0.7	47.1	59.4	641.5	876.0	748.6	7.8
okt-96	2	1071.5	37.8	319.3	165.0	210.7	1269.0	157.3	1.1	227.6	126.6	2970.1	3230.6	3325.4	-1.4
nov-96	2	631.0	6.1	199.0	72.1	87.2	693.6	54.0	2.6	97.6	85.6	1557.3	1743.0	1743.1	0.0
des-96	2	1513.6	171.8	1003.4	299.2	418.0	3353.5	308.4	0.7	416.1	713.0	5432.0	7067.9	6561.7	3.7
jan-97	2	2041.7	303.6	1220.7	386.2	616.3	3413.3	742.0	0.1	380.8	493.5	6612.1	8724.0	7486.5	7.6
feb-97	2	1905.5	307.1	737.3	314.6	623.7	3428.3	709.5	0.1	448.5	714.5	6915.6	8026.1	8078.7	-0.3
mar-97	2	602.6	43.1	346.5	101.0	153.9	793.5	189.6	0.1	136.8	232.6	1790.3	2230.1	2159.8	1.6
apr-97	2	1122.0	46.1	66.5	137.6	172.8	853.3	274.8	0.2	145.3	1.0	2370.3	2673.2	2516.7	3.0
mai-97	2	239.9	23.5	319.3	72.1	69.9	307.4	62.6	0.4	48.0	77.1	896.7	1094.8	1022.2	3.4
jun-97	2	114.8	21.7	221.7	95.9	124.3	375.3	63.1	0.2	48.5	48.7	775.6	1016.9	873.0	7.6
aug-97	2	87.1	10.0	313.8	31.7	74.9	373.8	29.2	2.8	51.1	9.7	947.8	920.4	1011.3	-4.7
sep-97	2	263.0	27.3	16.0	75.5	157.2	700.1	108.3	0.1	107.2	39.8	981.0	1347.4	1128.1	8.9
okt-97	2	457.1	15.1	98.3	64.5	149.1	609.3	92.4	0.5	71.1	49.7	1546.7	1485.8	1667.9	-5.8
nov-97	2	1096.5	47.8	589.8	160.4	305.3	1866.4	432.6	0.2	234.7	281.3	4831.9	4498.8	5348.1	-8.6
des-97	2	169.8	16.7	154.2	92.0	76.9	273.5	48.5	0.9	73.3	84.7	774.9	831.8	933.9	-5.8

Appendix 1

Chemical data for soil water Tie Shan Ping 1995—1998

jan-98	2	2398.8	90.5	876.5	494.1	720.8	3252.7	727.6	0.3	397.7	500.0	7919.6	8561.0	8817.6	-1.5
mar-98	2	1096.5	51.3	663.6	228.9	291.3	1375.3	182.9	0.3	223.7	261.3	3620.8	3889.8	4106.1	-2.7
Date	**Collector #**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**% cat-an**
		H+	**Na**	**NH4**	**K**	**Mg**	**Ca**	**Ali**	**F**	**Cl**	**NO3**	**SO4**	**sum+**	**sum-**	**% sum**
apr-98	2	100.3	11.9	184.0	48.3	34.3	180.2	17.4	1.5	59.8	68.3	461.9	576.4	591.4	-1.3
mai-98	2	61.7	7.9	197.4	33.8	19.4	98.3	8.8	0.0	45.4	56.2	355.5	427.2	457.1	-3.4
jun-98	2	30.9	8.9	181.3	97.7	66.5	194.4	15.7	0.4	44.0	41.8	507.5	595.4	593.6	0.1
jul-98	2	138.0	12.2	123.1	82.6	88.2	291.9	31.3	0.2	62.9	35.3	640.2	767.3	738.6	1.9
aug-98	2	134.9	5.2	63.2	81.8	54.5	183.1	24.2	0.2	31.7	34.3	426.8	546.9	492.9	5.2
sep-98	2	195.0	6.1	107.4	92.7	88.0	287.1	18.2	1.1	53.5	56.8	727.7	794.7	839.0	-2.7
okt-98	2	154.9	14.1	114.8	149.9	92.2	295.9	20.3	1.0	66.2	58.6	661.6	842.0	787.4	3.4
nov-98	2	891.3	100.0	1713.0	833.8	1012.1	4606.0	680.5	0.3	510.6	611.2	8693.1	9836.8	9815.2	0.1
des-98	2	933.3	91.3	759.5	1230.2	905.2	2734.7	332.7	0.9	609.3	570.9	6250.3	6986.9	7431.4	-3.1
apr-95	3	1202.3	933.5	579.3	1376.0	2283.5	6230.4	367.8	0.9	658.7	1047.7	12366.2	12972.7	14073.4	-4.1
mai-95	3	102.3	32.1	516.1	378.1	124.3	598.8	5.3	97.4	129.2	1.0	1258.0	1757.1	1485.6	8.4
aug-95	3	75.9	43.1	325.4	121.0	109.0	427.9	12.0	4.9	76.4	103.1	748.0	1114.3	932.4	8.9
nov-95	3	933.3	207.5	947.4	247.3	23.1	1422.2	163.4	0.7	285.2	234.5	3024.7	3944.3	3545.2	5.3
des-95	3	2754.2	64.8	780.6	295.7	442.7	1865.4	363.1	0.3	291.4	332.1	6628.9	6566.4	7252.7	-5.0
jan-96	3	2570.4	187.0	1017.8	289.0	334.9	2697.2	287.9	0.8	376.3	475.3	6872.2	7384.3	7724.6	-2.3
mar-96	3	1122.0	52.2	445.7	113.8	143.2	689.7	270.6	0.2	154.3	264.5	2093.2	2837.1	2512.1	6.1
mai-96	3	616.6	39.6	651.4	141.2	109.4	484.6	21.7	22.7	120.2	157.9	1630.0	2064.4	1930.8	3.3
jun-96	3	691.8	17.0	22.7	285.9	272.4	518.0	88.9	0.1	141.3	11.9	1541.4	1896.7	1694.8	5.6
jul-96	3	144.5	24.4	66.5	112.8	96.3	309.4	49.5	0.2	67.7	13.1	688.6	803.4	769.5	2.2
sep-96	3	346.7	33.5	255.6	94.9	92.2	432.2	67.5	0.4	82.4	84.5	992.3	1322.5	1159.6	6.6
okt-96	3	1096.5	38.7	419.1	164.7	160.5	962.6	72.6	6.0	170.7	151.6	2679.5	2914.7	3007.7	-1.6
nov-96	3	660.7	19.6	238.4	94.6	88.9	628.8	45.0	3.2	104.1	85.2	1537.5	1775.9	1730.0	1.3
des-96	3	2290.9	158.3	964.6	493.6	581.8	3902.4	416.0	0.5	370.7	863.0	7871.7	8807.6	9105.9	-1.7
jan-97	3	3388.4	358.9	1549.5	590.3	802.3	4326.6	969.8	0.1	538.5	733.0	11783.6	11985.8	13055.2	-4.3
feb-97	3	2754.2	263.2	661.4	379.0	1438.4	2809.5	774.4	0.2	444.0	687.0	7391.5	9080.1	8522.7	3.2
mai-97	3	218.8	30.0	553.3	140.9	111.1	553.4	107.9	0.2	70.8	141.6	1776.0	1715.4	1988.6	-7.4
jul-97	3	177.8	21.7	320.4	281.9	222.2	610.8	141.3	0.1	84.3	1.6	1580.1	1776.1	1666.1	3.2

Appendix 1
Chemical data for soil water Tie Shan Ping 1995—1998

aug-97	3	275.4	18.3	469.6	117.4	102.0	509.0	64.4	0.0	91.1	74.7	1411.7	1556.1	1577.5	-0.7
sep-97	3	70.8	28.4	453.5	213.8	186.8	980.6	59.2	0.3	200.8	179.0	1602.1	1993.1	1982.2	0.3
okt-97	3	831.8	21.7	274.3	178.3	247.4	883.3	162.7	0.3	119.6	126.8	2536.4	2599.5	2783.2	-3.4
Date	**Collector #**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**μeq/l**	**% cat-an**
		H+	**Na**	**NH4**	**K**	**Mg**	**Ca**	**Ali**	**F**	**Cl**	**NO3**	**SO4**	**sum+**	**sum-**	**% sum**
nov-97	3	1148.2	83.5	384.2	174.9	390.9	2161.3	315.5	0.5	323.0	319.8	4863.3	4658.5	5506.7	-8.3
des-97	3	208.9	15.3	141.6	193.1	125.1	403.2	94.0	0.4	99.3	111.6	1118.3	1181.2	1329.6	-5.9
feb-98	3	316.2	16.4	274.4	185.2	90.8	400.7	109.2	0.2	86.0	134.0	1146.6	1393.0	1366.9	0.9
mar-98	3	436.5	29.4	375.8	104.0	161.0	765.0	177.6	0.0	99.9	177.6	1513.8	2049.2	1791.3	6.7
apr-98	3	87.1	14.0	135.7	41.1	40.0	157.4	23.8	0.8	43.4	63.7	369.7	499.0	477.7	2.2
mai-98	3	39.8	3.9	118.2	27.2	16.9	70.1	7.0	0.4	30.0	27.7	241.9	283.1	300.0	-2.9
jun-98	3	4.4	4.5	70.6	73.5	37.9	76.2	7.0	0.8	27.5	14.1	212.0	274.1	254.4	3.7
jul-98	3	51.3	6.4	50.8	59.1	57.0	172.7	12.7	0.3	29.1	16.4	353.7	409.9	399.5	1.3
aug-98	3	81.3	4.7	36.9	19.7	17.6	68.5	5.3	0.6	21.8	12.0	179.6	234.1	213.9	4.5
sep-98	3	190.5	4.3	48.8	33.1	35.6	147.8	15.7	0.4	32.0	31.2	403.6	475.8	467.2	0.9
okt-98	3	97.7	10.3	51.6	29.7	23.9	74.1	0.9	6.0	28.6	16.6	224.0	288.0	275.2	2.3
nov-98	3	575.4	50.9	387.0	263.4	292.9	1247.6	168.1	0.5	193.2	187.1	2840.8	2985.4	3221.6	-3.8
des-98	3	676.1	58.7	64.3	247.6	168.7	618.8	143.0	0.2	172.6	141.3	1680.5	1977.2	1994.6	-0.4
mai-95	4	426.6	58.3	176.8	361.9	156.3	964.1	73.1	0.5	131.2	74.8	2013.7	2217.2	2220.2	-0.1
jul-95	4	724.4	21.3	212.3	185.9	213.1	582.9	320.2	0.1	93.9	11.9	2118.8	2260.2	2224.8	0.8
nov-95	4	1479.1	59.2	176.8	118.4	168.7	1496.6	246.3	0.4	137.9	127.4	3341.6	3745.1	3607.3	1.9
des-95	4	2818.4	77.0	388.6	215.9	455.9	1745.6	494.6	0.2	353.7	255.3	6482.6	6195.9	7091.9	-6.7
feb-96	4	5011.9	186.2	1101.0	312.0	436.1	2496.1	183.4	3.7	458.7	598.7	6893.8	9726.7	7954.7	10.0
mar-96	4	2398.8	69.6	571.6	187.2	227.9	1153.8	478.8	0.1	205.9	284.5	4732.2	5087.7	5222.7	-1.3
apr-96	4	1621.8	94.8	393.6	177.0	232.1	1057.9	25.4	225.4	60.9	66.1	2680.0	3602.6	3032.5	8.6
jun-96	4	588.8	37.4	192.4	234.8	183.5	585.4	257.9	0.0	79.5	26.0	1727.5	2080.2	1833.1	6.3
jul-96	4	416.9	44.4	188.5	182.6	129.2	448.1	46.3	1.2	76.2	0.8	1352.7	1456.0	1430.9	0.9
okt-96	4	1047.1	30.0	220.6	96.4	135.8	859.3	95.5	3.1	198.0	162.9	2218.6	2484.8	2582.6	-1.9
nov-96	4	871.0	18.3	144.1	67.0	95.5	696.1	90.6	1.0	88.0	46.0	1624.3	1982.6	1759.3	6.0
des-96	4	2290.9	235.8	363.1	314.6	409.8	2495.1	367.9	0.2	411.8	367.7	6644.8	6477.1	7424.6	-6.8
jan-97	4	4168.7	331.5	770.6	404.1	576.0	3118.9	873.2	0.1	520.5	374.2	10380.9	10242.9	11275.6	-4.8

Appendix 1
Chemical data for soil water Tie Shan Ping 1995—1998

feb-97	4	3311.3	241.8	400.8	270.3	540.6	2754.6	1015.9	0.0	406.8	302.2	7328.8	8535.4	8037.8	3.0
apr-97	4	1905.5	73.1	208.4	135.8	1847.4	138.2	432.7	0.0	173.5	39.7	3667.3	4741.1	3880.5	10.0
mai-97	4	724.4	38.3	360.3	91.1	97.9	451.6	157.6	0.2	71.1	60.0	1905.2	1921.3	2036.6	-2.9
jul-97	4	676.1	18.7	235.6	111.0	126.7	548.9	183.7	0.1	49.4	11.1	1633.2	1900.7	1693.7	5.8
Date	**Collector #**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**% cat-an**
		H+	**Na**	**NH4**	**K**	**Mg**	**Ca**	**Ali**	**F**	**Cl**	**NO3**	**SO4**	**sum+**	**sum-**	**% sum**
aug-97	4	398.1	28.7	225.6	107.4	952.1	60.9	101.9	0.0	107.2	61.1	1431.6	1874.7	1599.9	7.9
sep-97	4	398.1	23.1	283.3	279.3	244.4	701.6	180.8	0.1	169.3	51.3	1718.2	2110.6	1938.8	4.2
okt-97	4	1174.9	25.6	293.8	147.1	225.5	1036.0	193.4	0.0	112.0	81.3	3230.2	3096.2	3423.5	-5.0
nov-97	4	1513.6	50.4	786.1	276.5	451.8	2245.6	314.7	0.1	482.7	442.9	5868.8	5638.6	6794.4	-9.3
mar-98	4	57.5	46.1	594.3	1212.6	827.8	3162.3	616.4	0.2	767.3	314.5	5872.3	6517.1	6954.2	-3.2
apr-98	4	0.5	22.5	91.9	513.0	218.9	578.0	50.4	2.1	252.7	67.3	981.9	1475.2	1304.1	6.2
mai-98	4	0.3	9.0	206.2	110.5	102.9	373.5	2.8	3.0	63.8	40.0	598.0	805.2	704.8	6.7
jun-98	4	0.9	5.8	113.1	56.5	55.1	351.3	1.2	3.1	54.4	23.4	472.0	584.0	553.0	2.7
jul-98	4	14.1	9.1	124.7	74.9	77.0	543.9	29.9	0.2	56.3	23.4	774.3	873.8	854.2	1.1
aug-98	4	37.2	5.3	26.1	20.0	20.5	193.1	44.7	0.1	27.5	14.7	268.1	346.9	310.4	5.6
sep-98	4	38.0	10.9	62.6	107.4	71.6	558.9	100.0	0.1	61.4	39.8	796.5	949.5	897.7	2.8
okt-98	4	16.2	16.1	67.6	80.8	49.9	312.4	50.1	0.1	77.3	21.6	489.6	593.2	588.7	0.4
nov-98	4	33.9	57.4	687.4	324.8	332.4	2589.9	771.4	0.1	235.0	182.2	5042.2	4797.3	5459.6	-6.5
okt-96	5	691.8	35.7	477.3	14.6	390.9	1067.9	76.3	4.3	153.2	145.5	2299.3	2754.4	2602.2	2.8
nov-96	5	871.0	42.2	184.6	110.7	113.1	842.4	87.0	2.9	134.3	82.7	2118.6	2251.0	2338.5	-1.9
jan-97	5	3311.3	308.0	1219.6	529.4	1061.5	6971.4	1403.2	0.3	478.1	462.1	13229.3	14804.4	14169.8	2.2
feb-97	5	2454.7	390.4	909.2	368.3	855.8	5529.2	1203.7	0.2	662.9	574.1	11134.0	11711.3	12371.3	-2.7
mar-97	5	977.2	100.5	299.9	114.3	172.8	924.2	513.2	0.1	235.3	134.3	2276.3	3102.2	2645.9	7.9
apr-97	5	1412.5	363.2	314.3	157.6	228.8	1373.8	359.9	0.2	175.7	82.9	3482.8	4210.1	3741.6	5.9
mai-97	5	346.7	33.1	523.9	90.5	100.4	586.4	127.5	0.4	77.3	91.6	1867.9	1808.5	2037.2	-5.9
jun-97	5	195.0	44.4	185.7	97.7	102.0	442.1	112.0	0.2	85.8	9.0	1051.2	1178.9	1146.1	1.4
jul-97	5	512.9	12.5	286.6	103.8	111.9	560.4	250.7	0.1	65.7	1.0	1704.2	1838.8	1771.0	1.9
aug-97	5	64.6	30.3	321.7	60.6	70.7	354.3	28.1	2.7	47.7	4.5	899.8	930.3	954.7	-1.3
sep-97	5	46.8	49.6	345.9	145.8	217.2	1024.0	103.4	0.1	170.7	171.3	1567.0	1932.8	1909.1	0.6
okt-97	5	794.3	20.1	281.1	114.3	249.3	1328.9	223.7	0.2	103.0	100.5	3310.9	3011.7	3514.6	-7.7
jan-98	5	316.2	40.5	350.4	445.8	446.8	2457.2	0.0	0.0	326.9	228.2	4174.5	4057.0	4729.6	-7.7

Appendix 1
Chemical data for soil water Tie Shan Ping 1995—1998

feb-98	5	151.4	19.1	266.4	312.3	172.5	978.1	231.1	0.2	142.7	140.8	2178.9	2130.8	2462.6	-7.2
mar-98	5	44.7	17.4	192.4	271.1	211.5	978.1	173.8	0.1	135.4	111.9	1656.8	1888.9	1904.2	-0.4
mai-98	5	1.1	6.5	117.5	55.5	48.5	192.1	0.0	0.0	30.7	21.4	335.2	421.3	387.4	4.2
jun-98	5	1.5	8.3	85.9	73.1	46.5	207.1	0.0	0.0	66.0	18.7	330.6	422.4	415.3	0.8
jul-98	5	20.0	24.9	134.2	187.5	97.9	498.0	0.0	0.0	115.7	17.9	782.4	962.4	916.0	2.5
Date	**Collector #**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**µeq/l**	**% cat-an**
		H+	**Na**	**NH4**	**K**	**Mg**	**Ca**	**Ali**	**F**	**Cl**	**NO3**	**SO4**	**sum+**	**sum-**	**% sum**
aug-98	5	38.9	7.4	42.5	62.2	41.1	186.6	0.0	0.0	43.4	18.4	360.4	378.7	422.2	-5.4
sep-98	5	22.9	6.7	70.1	182.8	84.2	346.3	0.0	0.0	63.4	33.7	655.6	713.1	752.7	-2.7
okt-98	5	1.2	7.0	98.1	275.7	108.6	297.4	0.0	0.0	76.4	24.4	590.9	788.1	691.7	6.5
des-98	5	28.2	148.8	517.2	552.5	304.5	1716.7	0.0	0.0	268.5	209.7	3497.8	3267.7	3976.0	-9.8
apr-97	6	6.9	13.1	75.9	11.7	51.2	343.0	8.7	0.1	30.3	47.5	405.7	510.5	483.6	2.7
jun-97	6	1.3	25.1	136.9	25.3	4.4	73.0	3.9	5.8	30.9	17.3	236.0	269.9	290.0	-3.6
okt-97	6	74.1	4.6	90.4	14.7	14.4	92.8	6.4	3.5	14.5	33.0	248.0	297.4	298.9	-0.3
nov-97	6	5.5	19.5	224.0	232.0	92.2	282.9	43.4	1.0	72.5	89.5	811.3	899.5	974.4	-4.0
jan-98	6	2041.7	54.8	451.8	267.8	488.8	2248.6	590.8	0.3	278.1	232.2	6092.8	6144.3	6603.5	-3.6
mar-98	6	691.8	39.1	248.4	206.7	229.6	1182.7	142.7	0.3	172.1	105.3	2419.3	2740.9	2697.0	0.8
apr-98	6	80.7	17.8	148.1	82.4	63.7	237.9	0.0	0.0	50.1	71.2	509.6	630.6	630.9	0.0
mai-98	6	24.5	7.4	161.9	87.7	43.0	127.8	0.0	0.0	39.7	28.7	380.0	452.3	448.4	0.4
jun-98	6	4.2	17.9	205.2	199.9	105.3	228.1	0.0	0.0	86.3	29.5	549.2	760.6	665.1	6.7
jul-98	6	89.1	11.8	118.4	132.4	98.7	275.1	0.0	0.0	59.8	27.4	637.1	725.5	724.3	0.1
aug-98	6	61.7	2.8	47.5	64.8	38.8	107.8	0.0	0.0	28.0	19.7	275.2	323.2	323.0	0.0
sep-98	6	195.0	8.8	117.8	100.3	79.6	279.1	0.0	0.0	60.9	41.1	685.0	780.5	787.0	-0.4
okt-98	6	109.6	11.0	67.6	49.4	32.1	110.3	0.0	0.0	44.6	34.4	381.4	380.0	460.4	-9.6
nov-98	6	812.8	81.8	571.0	271.1	306.1	1545.5	0.0	0.0	169.5	258.5	3853.8	3588.3	4281.9	-8.8
des-98	6	758.6	102.2	344.3	296.7	188.4	938.2	0.0	0.0	160.8	248.4	2300.6	2628.4	2709.8	-1.5
jan-98	7	3467.4	73.1	548.3	602.1	586.7	2843.5	695.4	0.4	485.2	338.7	9281.2	8816.3	10105.4	-6.8
feb-98	7	1548.8	46.1	497.3	367.8	263.6	1851.9	241.2	0.3	386.5	193.5	4485.8	4816.6	5066.1	-2.5
mar-98	7	1096.5	39.3	251.1	245.6	230.7	1290.0	174.9	0.1	231.6	115.0	3132.0	3328.1	3478.7	-2.2
apr-98	7	160.9	16.2	157.1	61.3	47.7	217.7	0.0	0.0	66.1	58.1	541.9	660.8	666.0	-0.4
mai-98	7	75.9	7.6	161.9	45.2	24.8	102.7	0.0	0.0	37.5	30.5	356.2	418.0	424.3	-0.7
jun-98	7	32.4	9.4	120.5	108.3	65.1	193.6	0.0	0.0	52.0	26.9	421.6	529.3	500.5	2.8

Appendix 1
Chemical data for soil water Tie Shan Ping 1995—1998

jul-98	7	112.2	14.9	138.2	121.7	103.7	436.1	0.0	0.0	73.9	28.9	910.5	926.9	1013.2	-4.5
aug-98	7	162.2	4.8	43.1	35.6	29.0	145.7	0.0	0.0	30.3	22.6	374.3	420.4	427.3	-0.8
sep-98	7	323.6	9.9	114.0	68.5	61.6	261.7	0.0	0.0	62.1	48.1	723.9	839.3	834.1	0.3
okt-98	7	213.8	13.9	85.9	73.9	53.5	203.6	0.0	0.0	58.1	41.4	537.8	644.6	637.3	0.6
nov-98	7	1659.6	137.0	1230.7	787.8	913.4	4785.7	0.0	0.0	527.5	535.4	9968.8	9514.1	11031.7	-7.4
des-98	7	1380.4	72.2	759.5	644.5	514.3	2405.3	0.0	0.0	375.5	516.1	5636.1	5776.2	6527.6	-6.1
		µeq/L	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**µeq/L**	**% cat-an**
		H+	**Na**	**NH4**	**K**	**Mg**	**Ca**	**Ali**	**F**	**Cl**	**NO3**	**SO4**	**sum+**	**sum-**	**% sum**
Medians	1	106.0	11.3	70.1	18.3	32.0	203.4	12.0	1.0	34.3	34.8	430.0	580.5	517.3	2.5
	2	338.8	36.3	313.8	149.1	149.1	693.6	82.4	0.5	111.7	84.7	1557.3	1743.0	1743.1	0.1
	3	391.6	29.7	350.6	169.8	124.7	604.8	91.5	0.4	111.8	130.4	1560.7	1836.4	1760.6	1.1
	4	700.3	37.8	223.1	179.8	216.0	698.9	182.1	0.2	121.6	63.6	2066.3	2238.7	2222.5	1.5
	5	173.2	31.7	283.8	130.1	142.8	883.3	95.2	0.1	125.0	87.3	1786.0	1910.8	1973.1	0.1
	6	80.7	17.8	148.1	100.3	79.6	275.1	0.0	0.0	59.8	41.1	549.2	725.5	665.1	-0.3
	7	268.7	15.6	159.5	115.0	84.4	348.9	0.0	0.0	70.0	53.1	817.2	883.1	923.7	-1.5
1996	1	147.9	21.5	70.3	22.3	42.4	272.4	22.9	0.6	35.6	66.4	463.7	690.0	564.0	6.1
1997	1	154.5	20.4	44.1	30.8	49.0	260.7	36.4	1.0	58.3	30.1	709.5	790.2	838.6	2.2
1998	1	107.3	9.9	78.7	10.7	25.2	122.9	7.3	1.1	31.7	30.7	231.0	270.0	287.9	-0.3
1996	2	488.8	58.9	484.0	175.6	216.8	940.2	93.3	1.9	123.3	149.3	1937.9	2461.2	2220.5	0.4
1997	2	457.1	27.3	313.8	95.9	153.9	700.1	108.3	0.2	107.2	77.1	1546.7	1485.8	1667.9	1.6
1998	2	154.9	12.2	184.0	97.7	88.2	291.9	24.2	0.3	62.9	58.6	661.6	794.7	787.4	-1.3
1996	3	691.8	38.7	419.1	141.2	143.2	628.8	72.6	0.5	141.3	151.6	1630.0	2064.4	1930.8	2.2
1997	3	275.4	28.4	453.5	193.1	222.2	883.3	141.3	0.2	119.6	141.6	1776.0	1993.1	1988.6	-3.4
1998	3	97.7	10.3	70.6	59.1	40.0	157.4	15.7	0.4	32.0	31.2	369.7	475.8	467.2	1.3
1996	4	1334.5	57.0	291.9	184.9	205.7	958.6	139.5	1.1	143.0	114.5	2449.3	3043.7	2807.5	3.4
1997	4	1174.9	38.3	293.8	147.1	451.8	701.6	193.4	0.1	169.3	61.1	3230.2	3096.2	3423.5	3.0
1998	4	16.2	10.9	113.1	107.4	77.0	543.9	50.1	0.2	63.8	39.8	774.3	873.8	854.2	2.7
1997	5	653.6	47.0	318.0	114.3	195.0	974.1	237.2	0.2	136.8	96.0	2072.1	2472.3	2341.6	1.0
1998	5	25.5	12.8	125.8	229.3	103.3	422.2	0.0	0.0	96.1	29.0	719.0	875.2	834.4	-1.6
1997	6	6.2	16.3	113.6	20.0	32.8	187.9	7.5	2.2	30.6	40.3	326.8	404.0	391.3	-1.9
1998	6	109.6	17.8	161.9	132.4	98.7	275.1	0.0	0.0	60.9	41.1	637.1	760.6	724.3	0.0

Appendix 1

Chemical data for soil water Tie Shan Ping 1995—1998

1998	7	268.7	15.6	159.5	115.0	84.4	348.9	0.0	0.0	70.0	53.1	817.2		883.1	923.7	-1.5
1996	Bulk	148	21	70	22	42	272	23	1	36	66	464				
1997	Bulk	154	20	44	31	49	261	36	1	58	30	709				
1998	Bulk	107	10	79	11	25	123	7	1	32	31	231				
Average 96-98		**137**	**17**	**64**	**21**	**39**	**219**	**22**	**1**	**42**	**42**	**468**				

Appendix 2
Chemical data for soil water
Tie shan Ping 2001

Log Number	Plot	Lysimeter Number	pH	H+ ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	NH4 ueq/L	Ali ueq/L	SO4 ueq/L	NO3 ueq/L	Cl ueq/L	tot-F ueq/L	Alo uM	IB ueq/l	IB %
30	B	0	3.34	457.09	4762.7	970.71	85.25	449.34	1157.2	1419.6	7837.2	515.88	501.23	131.59	43.37	-11.58	-0.06
625	B	0	5.72	1.91	941.66	312.77	12.83	472.35	569.17	59.18	1624.5	267.45	297.01	32.53	19.27	134.76	2.94
710	B	0	4.20	63.10	2307.0	769.17	49.37	710.96	952.32	281.49	4129.2	457.04	345.53	42.64	35.95	94.00	0.94
115	B	0	3.59	257.04	4134.9	925.47	186.82	774.13	1202.2	1285.5	7714.4	207.84	711.93	131.59	81.17	0.42	0.00
285	B	0	3.67	213.80	1320.9	460.68	124.62	443.20	824.05	209.46	2791.6	162.42	293.63	38.69	25.57	310.38	4.51
200	B	0	3.34	457.09	1795.5	417.08	76.12	475.68	885.13	490.95	3625.2	365.79	299.55	65.27	43.74	241.68	2.70
370	B	0	3.85	141.25	723.59	259.95	23.62	253.95	400.92	137.42	1474.0	123.05	170.08	20.74	10.75	152.80	4.10
455	B	0	5.73	1.86	724.64	181.31	6.26	225.87	260.32	19.95	1028.8	104.19	109.05	11.90	19.27	166.30	6.22
540	B	0	4.37	42.66	1723.1	692.25	61.77	487.19	950.10	223.20	3301.7	280.19	227.20	32.06	27.80	339.12	4.23
541	B	1	3.59	257.04	234.59	208.05	30.88	60.84	5.33	636.68	1136.7	235.53	46.46	17.58	19.27	-2.84	-0.10
456	B	1	3.58	263.03	335.50	183.28	14.75	75.93	0.00	672.69	1175.8	361.36	30.52	16.74	10.75	-39.21	-1.25
371	B	1	3.54	288.40	501.02	259.95	45.67	106.90	12.77	856.66	1531.1	574.40	52.46	21.95	26.69	-108.54	-2.55
201	B	1	3.54	288.40	885.77	430.24	57.42	123.96	23.27	1519.4	2543.2	686.45	275.55	39.95	63.75	-216.75	-3.15
116	B	1	3.76	173.78	863.82	404.33	48.28	101.91	10.27	1446.2	2468.2	511.05	189.12	38.32	62.27	-158.05	-2.53
Med	**Top-B**		**3.58**	**263.03**	**501.02**	**259.95**	**45.67**	**101.91**	**10.27**	**856.66**	**1531.1**	**511.05**	**52.46**	**21.95**	**26.69**	**-108.54**	**-2.53**
117	B	2	4.00	100.00	649.73	266.12	34.93	45.22	0.00	1795.3	2170.5	636.15	187.01	19.74	81.91	-122.02	-2.07
372	B	2	3.78	165.96	781.48	341.40	69.60	128.64	79.96	1861.8	2025.3	1335.1	154.3	35.27	44.48	-121.11	-1.74
542	B	2	3.98	104.71	558.91	269.50	33.67	143.14	4.55	974.58	1367.5	771.41	66.00	23.63	26.32	-139.46	-3.23
Med			**3.98**	**104.71**	**649.73**	**269.50**	**34.93**	**128.64**	**4.55**	**1795.3**	**2025.3**	**771.41**	**154.29**	**23.63**	**44.48**	**-122.02**	**-2.07**
543	B	3	3.98	104.71	373.42	202.20	49.89	59.59	6.94	913.40	1341.5	303.89	69.05	25.42	20.01	-29.68	-0.86
373	B	3	4.06	87.10	534.46	248.44	53.94	61.4	0.00	1073.9	1375.2	570.69	136.66	30.27	12.60	-53.61	-1.28
458	B	3	4.02	95.50	407.66	221.87	28.66	42.30	0.00	679.34	1144.4	340.80	85.15	20.63	17.79	-115.64	-3.77
Med	**Sub-B**		**4.02**	**95.50**	**407.66**	**221.87**	**49.89**	**59.59**	**0.00**	**913.40**	**1341.5**	**340.80**	**85.15**	**25.42**	**17.79**	**-53.61**	**-1.28**

Appendix 2
Chemical data for soil water
Tie shan Ping 2001

Log Number	Plot	Lysimeter Number	pH	H+ ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	NH4 ueq/L	Ali ueq/L	SO4 ueq/L	NO3 ueq/L	Cl ueq/L	tot-F ueq/L	Alo uM	IB ueq/l	IB %
34	C	0	3.54	288.40	2692.7	533.07	44.80	639.10	392.87	2040.2	6599.3	400.78	273.04	96.33	120.09	-1209.0	-8.94
629	C	0	5.60	2.51	1046.0	237.74	8.70	421.97	812.39	134.10	1911.2	333.23	240.52	41.69	39.29	105.82	2.05
714	C	0	4.18	66.07	1864.9	500.99	30.45	534.76	2355.5	530.84	4547.2	1099.5	352.86	32.53	48.93	-271.02	-2.30
119	C	0	3.60	251.19	2939.3	602.58	90.04	857.25	516.25	2193.2	7239.7	602.45	366.68	105.80	77.84	-864.86	-5.49
204	C	0	3.88	131.83	2836.5	736.26	96.56	987.16	1132.8	1120.4	6162.7	489.28	492.48	100.01	75.24	-202.96	-1.42
289	C	0	3.81	154.88	1613.4	406.05	54.70	568.39	710.49	714.81	3549.8	381.11	249.06	45.27	36.32	-2.54	-0.03
374	C	0	3.83	147.91	839.86	215.53	21.97	280.04	372.04	330.25	1609.7	267.29	107.75	27.63	19.27	195.23	4.63
459	C	0	5.10	7.94	1239.6	211.67	11.09	174.08	169.47	100.85	1437.5	214.41	100.41	21.05	33.36	141.26	3.83
544	C	0	3.94	114.82	1393.3	363.03	36.36	280.29	681.90	490.06	2667.6	428.34	146.62	30.85	62.64	86.35	1.30
35	C	1	3.77	169.82	500.52	168.64	15.22	43.73	2.50	1004.1	1221.2	606.89	101.12	20.27	15.57	-276.68	-7.64
630	C	1	3.80	158.49	388.89	187.97	21.31	113.68	20.99	486.51	787.2	476.38	73.76	25.11	10.75	-96.85	-3.69
715	C	1	3.89	128.82	421.68	179.34	22.18	86.18	0.00	447.72	884.7	396.75	51.05	17.63	18.90	-167.51	-6.61
545	C	1	3.81	154.88	346.62	184.85	21.31	117.97	8.27	410.38	830.6	354.19	47.98	13.21	21.50	-1.72	-0.07
460	C	1	3.84	144.54	267.98	136.56	11.05	101.79	0.00	371.26	798.4	275.19	39.32	10.69	11.49	-90.43	-4.19
375	C	1	3.81	154.88	330.85	172.34	19.92	127.36	0.00	599.55	1000.1	320.09	98.61	13.11	11.86	-26.98	-0.95
290	C	1	3.74	181.97	521.98	253.78	24.27	139.89	0.00	873.28	1257.1	618.74	294.47	19.21	24.46	-194.31	-4.64
205	C	1	3.72	190.55	597.34	229.52	29.14	65.47	0.00	1051.7	1215.3	762.17	208.30	23.95	34.10	-46.02	-1.05
120	C	1	3.82	151.36	486.15	170.45	18.18	40.18	0.00	934.24	1244.0	400.13	81.01	20.42	27.43	55.02	1.55
Med	**Top-C**		**3.81**	**154.88**	**421.68**	**179.34**	**21.31**	**101.79**	**0.00**	**599.55**	**1000.1**	**400.13**	**81.01**	**19.21**	**18.90**	**-90.43**	**-3.69**
36	C	2	4.17	67.61	373.27	149.06	8.70	26.80	0.00	909.86	846.6	642.43	79.60	15.90	15.57	-259.24	-8.91
716	C	2	4.14	72.44	375.77	146.43	18.79	68.54	0.00	610.63	712.7	586.01	55.00	14.90	20.39	-216.96	-8.61
206	C	2	4.08	83.18	416.54	175.47	13.83	34.06	0.00	905.42	858.7	741.58	79.68	17.37	10.75	-68.83	-2.07
461	C	2	4.00	100.00	286.34	136.15	12.01	41.48	0.00	580.71	920.0	231.82	44.68	11.69	7.78	-51.54	-2.18
Med	**Sub-C**		**4.11**	**77.81**	**374.52**	**147.75**	**12.92**	**37.77**	**0.00**	**758.03**	**852.7**	**614.22**	**67.30**	**15.40**	**13.16**	**-142.90**	**-5.39**
462	C	3	3.91	123.03	242.28	185.01	17.01	23.55	0.00	869.96	1236.3	159.28	94.77	26.32	11.49	-55.81	-1.87

Appendix 2
Chemical data for soil water
Tie shan Ping 2001

Log Number	Plot	Lysimeter Number	pH	H+ ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	NH4 ueq/L	Ali ueq/L	SO4 ueq/L	NO3 ueq/L	Cl ueq/L	tot-F ueq/L	Alo uM	IB ueq/l	IB %
44	K	0	4.08	83.18	2438.2	506.75	35.89	368.78	31.21	1911.7	4260.2	901.99	298.71	84.85	40.03	-611.20	-5.83
639	K	0	5.49	3.24	1060.4	253.37	8.70	495.37	381.48	68.71	1188.2	588.75	159.65	23.95	7.41	294.85	6.99
724	K	0	4.51	30.90	1418.2	341.40	13.05	429.90	70.52	543.92	1658.3	877.00	141.60	19.74	25.65	25.72	0.47
129	K	0	4.29	51.29	2290.5	894.21	68.07	1813.2	4.44	2536.7	5175.1	572.63	1260.8	104.64	81.91	545.32	3.69
214	K	0	4.57	26.92	1886.3	501.81	56.55	659.81	457.56	561.87	3312.1	592.46	315.07	56.58	31.13	-125.40	-1.49
299	K	0	4.55	28.18	1607.4	501.81	35.80	720.93	104.67	766.89	2642.6	722.07	242.86	39.21	20.39	118.88	1.60
384	K	0	4.37	42.66	740.56	214.71	40.80	348.83	204.90	377.91	1192.8	444.30	107.47	21.69	5.56	204.08	5.46
469	K	0	5.88	1.32	961.62	195.29	4.52	230.78	28.65	35.46	999.3	313.24	86.17	9.90	5.93	49.10	1.71
554	K	0	4.61	24.55	1280.5	411.32	9.22	984.09	144.38	251.57	1684.3	1075.8	156.26	26.95	10.75	162.30	2.68
45	K	1	3.99	102.33	1890.8	386.23	16.75	231.39	0.00	1362.0	2214.3	1811.4	172.62	55.80	46.70	-578.92	-7.30
555	K	1	3.62	239.88	728.08	336.46	19.79	240.40	8.66	1309.2	1958.8	783.01	89.41	55.27	33.99	-306.17	-5.60
725	K	1	3.70	199.53	1140.3	491.12	33.49	299.22	0.00	1745.5	2432.6	1296.2	275.01	75.27	42.62	-572.78	-7.55
555	K	1	3.62	239.88	728.08	336.46	19.79	240.40	8.66	1309.2	1958.8	783.01	89.41	55.27	33.99	-4.06	-0.07
470	K	1	3.72	190.55	708.12	279.70	18.36	190.53	0.00	1139.3	2041.7	500.08	60.93	52.64	11.86	-128.89	-2.49
385	K	1	3.75	177.83	1285.5	338.93	27.62	258.81	0.00	1514.9	2453.4	1038.9	92.23	56.85	34.47	-37.74	-0.52
300	K	1	3.90	125.89	2256.1	533.81	44.48	246.92	4.72	1522.7	2910.8	1952.6	144.42	62.32	35.58	-335.60	-3.42
215	K	1	3.91	123.03	2022.1	413.38	27.32	273.87	21.88	1868.5	2350.3	1980.2	118.81	47.06	34.84	253.66	2.74
130	K	1	4.14	72.44	2072.0	389.52	43.93	250.88	0.00	1527.1	2568.8	1111.9	127.07	40.79	45.22	507.30	6.18
Med			**3.75**	**177.83**	**1285.5**	**386.23**	**27.32**	**246.92**	**0.00**	**1514.9**	**2350.3**	**1111.9**	**118.81**	**55.27**	**34.84**	**-128.89**	**-2.49**
641	K	2	3.94	114.82	795.95	303.55	13.14	719.66	10.05	1610.3	1949.0	1242.5	123.54	37.11	32.99	-156.32	-2.39
726	K	2	4.02	95.50	872.30	298.62	20.66	629.12	0.00	1399.7	2097.9	1084.2	171.07	46.85	28.54	-407.08	-6.37
131	K	2	4.07	85.11	1654.3	420.37	33.28	616.85	0.00	2398.2	1698.9	1966.8	280.31	73.80	65.23	1188.3	12.88
386	K	2	3.91	123.03	1249.1	419.96	36.76	784.87	0.00	1988.2	2915.0	1164.4	270.78	50.79	33.73	200.81	2.23
471	K	2	4.00	100.00	629.27	226.23	22.92	652.14	0.00	1104.9	2334.9	390.62	69.11	31.42	13.71	-90.60	-1.63
556	K	2	3.89	128.82	589.35	251.73	25.75	714.54	9.44	1327.7	2040.3	781.88	71.36	35.21	29.28	118.54	1.98
Med	**Top-K**		**3.97**	**107.41**	**834.12**	**301.09**	**24.34**	**683.34**	**0.00**	**1505.0**	**2069.1**	**1124.3**	**147.31**	**41.98**	**31.13**	**13.97**	**0.18**

Appendix 2
Chemical data for soil water
Tie shan Ping 2001

Log Number	Plot	Lysimeter Number	pH	H+ ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	NH4 ueq/L	Ali ueq/L	SO4 ueq/L	NO3 ueq/L	Cl ueq/L	tot-F ueq/L	Alo uM	IB ueq/l	IB %
47	K	3	4.37	42.66	1809.5	288.75	20.01	416.86	0.00	1031.8	2172.7	1471.9	145.54	38.16	17.05	-456.92	-6.35
642	K	3	4.16	69.18	1479.6	295.33	21.18	408.67	13.33	1052.8	1786.8	1171.4	254.99	61.06	18.53	-177.09	-2.78
727	K	3	4.24	57.54	1673.7	300.26	31.10	387.19	0.00	1106.0	2252.2	1140.7	182.21	25.79	19.27	-300.30	-4.35
557	K	3	4.17	67.61	1202.2	276.41	35.23	399.72	5.78	885.47	1769.6	998.07	139.42	18.90	21.50	-53.60	-0.92
472	K	3	4.22	60.26	1305.0	247.61	37.36	385.66	0.00	888.80	1805.1	980.82	117.90	22.48	7.41	-1.69	-0.03
387	K	3	4.14	72.44	1391.8	264.07	29.80	467.75	30.82	1052.8	1646.5	1477.7	121.85	31.58	22.24	31.87	0.48
302	K	3	4.26	54.95	1552.0	270.48	20.88	361.11	0.00	1111.6	1846.3	1665.3	97.03	24.21	25.20	-261.93	-3.74
217	K	3	4.31	48.98	1604.1	371.01	78.73	384.64	0.00	519.76	1802.9	1402.9	99.29	25.16	19.64	-322.94	-5.10
Med			**4.23**	**58.90**	**1515.8**	**282.58**	**30.45**	**393.46**	**0.00**	**1042.3**	**1804.0**	**1287.1**	**130.64**	**25.48**	**19.46**	**-219.51**	**-3.26**
48	K	4	3.97	107.15	1628.8	291.21	15.22	96.67	0.00	1655.7	2849.1	1029.8	134.69	52.64	29.28	-653.55	-8.74
643	K	4	3.80	158.49	1509.1	307.67	23.92	198.71	7.72	1508.3	2139.5	1609.2	249.63	64.22	34.84	-696.75	-9.38
728	K	4	3.89	128.82	1497.1	283.81	35.89	182.09	0.00	1602.5	2172.7	1407.6	218.32	55.27	28.54	-493.50	-6.84
218	K	4	3.92	120.23	1578.9	306.02	16.18	114.06	0.00	1609.1	2773.6	1155.1	128.90	57.37	34.47	-370.43	-4.71
388	K	4	3.84	144.54	1531.0	321.65	22.84	129.15	0.00	1642.4	2453.4	1357.9	125.24	59.48	36.32	-204.45	-2.63
303	K	4	3.90	125.89	1456.2	309.15	19.23	102.81	0.00	1824.1	2549.1	1098.0	117.90	48.95	12.60	23.41	0.31
473	K	4	3.84	144.54	1498.6	282.58	24.71	148.20	0.00	1744.4	2361.9	1415.5	134.83	50.01	13.34	-119.27	-1.53
558	K	4	3.83	147.91	1309.4	284.63	32.19	178.76	15.55	1697.8	2095.0	1345.2	148.93	48.16	24.09	29.06	0.40
Med	**Sub-K**		**3.87**	**136.68**	**1503.8**	**298.62**	**23.38**	**138.68**	**0.00**	**1649.0**	**2407.7**	**1351.5**	**134.76**	**53.95**	**28.91**	**-287.44**	**-3.67**

Appendix 2
Chemical data for soil water
Tie shan Ping 2001

Log Number	Plot	Lysimeter Number	pH	H+ ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	NH4 ueq/L	Ali ueq/L	SO4 ueq/L	NO3 ueq/L	Cl ueq/L	tot-F ueq/L	Alo uM	IB ueq/l	IB %
49	L	0	3.21	616.60	3855.5	701.96	27.53	417.37	428.96	670.48	5472.4	292.92	362.17	92.11	18.53	344.05	2.69
729	L	0	4.18	66.07	2111.4	525.67	16.31	301.52	444.23	141.85	2559.5	628.57	136.80	23.32	28.54	226.15	3.27
559	L	0	4.23	58.88	922.70	235.27	41.32	250.63	314.85	231.62	1419.9	212.32	83.72	14.90	17.79	324.48	8.57
474	L	0	5.89	1.29	682.42	141.25	6.18	171.01	100.90	44.33	769.5	90.55	92.46	11.37	5.93	183.48	8.69
389	L	0	3.73	186.21	560.41	165.76	14.44	251.14	191.57	80.90	1057.7	91.41	120.44	13.79	11.86	167.12	6.11
304	L	0	3.46	346.74	1275.0	350.20	47.19	483.35	544.74	178.42	2719.6	133.48	207.60	28.58	15.57	136.43	2.16
219	L	0	3.31	489.78	2626.9	646.59	48.28	731.68	1060.6	405.61	5087.7	387.23	355.68	70.53	28.54	108.23	0.91
50	L	1	3.59	257.04	1449.2	533.56	18.18	292.06	0.00	498.70	2206.0	441.08	160.38	30.85	20.76	95.32	1.65
645	L	1	3.49	323.59	1450.9	459.86	20.88	283.62	18.05	602.88	1078.7	1994.2	95.62	26.32	27.43	-174.16	-2.80
730	L	1	3.49	323.59	1712.2	501.81	23.49	260.60	26.65	681.56	1607.2	1847.5	103.80	37.37	34.10	-223.29	-3.20
305	L	1	3.55	281.84	1305.5	477.95	32.06	312.52	0.00	543.03	1850.5	832.34	117.90	24.32	15.20	127.82	2.21
135	L	1	3.63	234.42	1468.1	524.60	24.71	328.12	0.00	591.79	2517.9	323.72	216.26	31.79	32.62	82.13	1.31
390	L	1	3.66	218.78	723.69	248.27	31.23	267.25	0.00	275.95	1133.4	334.76	68.54	17.84	15.94	210.66	6.35
475	L	1	3.70	199.53	547.43	176.04	5.87	197.94	0.00	196.16	838.5	325.65	50.55	11.74	11.12	96.51	3.79
560	L	1	3.49	323.59	1041.0	361.71	23.36	262.39	12.77	165.13	1379.7	747.55	89.67	21.84	23.72	-48.87	-1.10
Med			**3.57**	**269.44**	**1377.3**	**468.90**	**23.42**	**275.43**	**0.00**	**520.87**	**1493.5**	**594.31**	**99.71**	**25.32**	**22.24**	**88.72**	**1.48**
51	L	2	3.90	125.89	774.49	322.06	14.66	151.27	0.00	733.65	1649.4	354.51	148.51	28.53	15.20	-228.23	-5.52
646	L	2	3.80	158.49	737.81	250.74	12.53	192.39	11.77	525.30	893.8	817.67	68.68	18.84	15.57	-31.23	-0.88
731	L	2	3.84	144.54	861.82	247.61	14.44	183.37	0.00	556.33	946.0	1002.7	50.21	17.05	15.57	-136.30	-3.50
561	L	2	3.77	169.82	514.00	190.85	17.40	179.79	6.11	392.31	941.0	329.84	53.90	11.05	14.46	134.45	4.79
476	L	2	3.91	123.03	407.26	146.84	5.44	143.11	0.00	282.60	913.0	132.19	19.66	9.53	9.27	33.92	1.55
391	L	2	3.89	128.82	598.83	241.86	18.92	179.27	0.00	421.13	1164.8	232.15	40.90	16.84	13.71	134.19	4.41
221	L	2	3.87	134.90	881.78	375.95	26.75	171.35	0.00	823.41	1747.8	482.51	138.01	18.79	21.13	27.06	0.56
Med	**Top-L**		**3.87**	**134.90**	**737.81**	**247.61**	**14.66**	**179.27**	**0.00**	**525.30**	**946.0**	**354.51**	**53.90**	**17.05**	**15.20**	**27.06**	**0.56**

Appendix 2
Chemical data for soil water
Tie shan Ping 2001

Log Number	Plot	Lysimeter Number	pH	H+ ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	NH4 ueq/L	Ali ueq/L	SO4 ueq/L	NO3 ueq/L	Cl ueq/L	tot-F ueq/L	Alo uM	IB ueq/l	IB %
647	L	3	4.02	95.50	459.60	150.38	19.36	35.34	11.27	672.69	1058.5	322.75	44.93	18.21	14.46	-155.49	-5.69
732	L	3	4.09	81.28	486.05	139.85	19.14	38.11	0.00	731.43	1067.2	426.89	41.46	22.63	13.71	-231.16	-8.01
222	L	3	4.10	79.43	557.41	133.10	11.83	15.04	0.00	971.92	1472.7	227.79	107.38	26.48	28.91	-65.60	-1.82
307	L	3	4.06	87.10	555.42	141.58	19.75	11.82	0.00	935.34	1424.0	300.98	120.98	25.06	13.71	-120.05	-3.31
392	L	3	4.09	81.28	570.04	144.21	21.44	16.37	0.00	816.76	949.6	258.42	75.79	21.63	13.34	344.70	11.66
477	L	3	4.05	89.13	498.68	148.16	13.35	22.30	0.00	746.95	1336.1	192.00	33.00	23.69	6.30	-66.21	-2.13
562	L	3	3.96	109.65	418.18	154.66	27.40	35.55	6.44	682.56	1175.6	187.49	27.42	19.63	11.49	24.33	0.86
Med			**4.06**	**87.10**	**498.68**	**144.21**	**19.36**	**22.30**	**0.00**	**746.95**	**1175.6**	**258.42**	**44.93**	**22.63**	**13.71**	**-66.21**	**-2.13**
648	L	4	4.11	77.62	546.43	128.33	15.44	29.79	18.71	596.23	1095.5	235.94	65.64	32.48	12.60	-154.59	-5.72
733	L	4	4.45	35.48	630.27	124.22	21.31	17.90	0.00	734.76	1116.7	269.71	56.41	36.74	11.12	-85.21	-2.96
563	L	4	4.10	79.43	585.86	140.01	50.85	34.04	8.94	730.32	1231.7	200.71	58.11	37.37	11.49	101.56	3.22
478	L	4	4.12	75.86	598.18	126.77	13.18	11.05	0.00	729.21	1313.6	183.94	76.19	37.21	7.04	-56.71	-1.79
393	L	4	4.13	74.13	586.46	128.66	18.70	9.33	0.00	733.65	1306.4	188.15	108.45	39.00	11.12	-91.08	-2.85
308	L	4	4.15	70.79	589.85	124.38	14.01	6.75	0.00	746.95	1325.1	170.72	117.11	39.85	13.34	-100.01	-3.12
223	L	4	4.18	66.07	656.07	119.69	16.96	9.28	0.00	797.92	1451.7	159.39	109.10	40.11	14.83	-94.28	-2.75
Med	**Sub-L**		**4.13**	**74.13**	**589.85**	**126.77**	**16.96**	**11.05**	**0.00**	**733.65**	**1306.4**	**188.15**	**76.19**	**37.37**	**11.49**	**-91.08**	**-2.85**

Appendix 3a

Table 3a.1 *The table shows exchangeable ions in TSP based on* ***$BaCl_2$*** *extraction. Aluminum is the dominant ion and calcium is clearly the dominating base cation. Magnesium show generally higher values than the monovalent base cations potassium and sodium.*

Plot	pH in H_2O	pH in $BaCl_2$	H meq/kg	K meq/kg	Na meq/kg	Mg meq/kg	Ca meq/kg	Al meq/kg
B-O	3.97	3.25	14.39	1.12	1.82	2.57	7.22	74.00
B-AB	4.07	3.26	4.69	0.60	0.57	0.77	6.94	37.38
B-B1	4.08	3.46	2.96	0.49	0.48	1.42	2.74	25.81
B-B2	4.64	3.86	1.18	0.40	0.47	1.12	3.99	25.48
B-B3	5.48	4.03	0.80	0.36	0.45	1.08	3.68	25.16
C-A	4.12	3.58	2.24	0.32	0.69	2.68	3.09	27.11
C-B1	4.58	4.05	0.76	0.29	0.68	1.06	2.98	20.43
C-B2	4.71	4.12	0.65	0.27	0.58	0.86	2.04	18.47
C-B3	4.67	4.13	0.63	0.28	0.58	0.81	1.10	15.05
K-O	4.02	3.46	8.87	1.44	1.15	2.63	3.35	80.36
K-AB	4.16	3.48	2.83	0.97	0.67	1.48	2.30	49.61
K-B1	4.18	3.54	2.46	0.84	0.52	1.39	3.05	41.46
K-B2	4.25	3.64	1.95	0.66	0.45	1.00	2.19	46.35
L-O	4.03	3.58	6.73	1.40	1.52	1.69	2.88	28.03
L-A	4.00	3.60	2.14	0.40	0.65	1.23	2.97	28.42
L-B1	4.22	3.64	1.95	0.27	0.58	1.00	1.80	26.79
L-B2	4.28	3.69	1.74	0.22	0.54	0.63	1.57	18.64
L-B3	4.25	3.70	1.70	0.20	0.48	0.50	1.57	17.00

Appendix 3b

Table 3b.1 *The table shows effective cation exchange capacity* CEC_E *in meq/kg, BS, AlS and HS in percent for the TSP catchment.*

Plot	CEC_E meq/kg	BS %	ALS %	HS %
B-O	101.11	12.58	73.19	14.23
B-AB	50.95	17.43	73.37	9.20
B-B1	33.90	15.14	76.13	8.73
B-B2	32.65	18.35	78.04	3.61
B-B3	31.53	17.68	79.79	2.53
C-A	36.15	18.78	75.01	6.21
C-B1	26.21	19.14	77.95	2.90
C-B2	22.86	16.38	80.79	2.83
C-B3	18.46	15.04	81.53	3.43
K-O	97.80	8.76	82.17	9.07
K-AB	57.85	9.37	85.75	4.88
K-B1	49.72	11.67	83.38	4.95
K-B2	52.61	8.19	88.10	3.71
L-O	42.25	17.72	66.34	15.93
L-A	35.80	14.65	79.37	5.99
L-B1	32.40	11.28	82.69	6.03
L-B2	23.33	12.64	79.89	7.47
L-B3	21.46	12.84	79.23	7.93

Appendix 3c

Table 3c.1 *The left side of the table shows exchangeable ions in LGS based on* **$BaCl_2$** *extraction. Aluminum and calcium are generally the dominated ions. Magnesium is dominating the rest of base cations. The right site of the table shows effective cation exchange capacity* CEC_E *in meq/kg, BS, AlS and HS in percent for the LGS catchment*

Sample	**pH in (H_2O)**	**pH in $BaCl_2$**	**Al^{3+} meq/kg**	**Mg^{2+} meq/kg**	**Ca^{2+} meq/kg**	**K^+ meq/kg**	**Na^+ meq/kg**	**CEC_E meq/kg**	**BS %**	**AlS %**	**HS %**
SP1-O	4.84	4.27	63.14	23.46	140.57	4.13	3.34	1944.01	64.11	23.60	0.51
SP1-A	5.15	4.51	20.73	2.41	33.70	0.88	0.87	2265.79	10.75	5.88	0.07
SP1-B	5.39	4.91	18.38	1.30	8.02	0.27	0.81	2291.03	1.63	2.89	0.02
SP2-O	4.96	4.35	72.74	18.71	36.32	5.42	2.99	2447.19	11.98	13.73	0.22
SP2-A	4.98	4.36	19.98	5.84	23.99	3.16	0.83	2302.50	9.17	5.42	0.10
SP2-B	5.21	4.77	19.34	0.98	4.02	0.67	0.77	1854.86	0.87	2.59	0.02
SP3-O	4.41	3.88	71.46	1.62	14.88	3.02	2.39	1673.37	2.97	9.67	0.46
SP3-A	4.81	4.12	19.34	0.66	0.82	0.51	0.68	1008.81	0.31	2.27	0.08
SP3-B	4.90	4.25	18.27	-0.64	0.48	0.11	0.72	322.88	0.07	1.94	0.05

Appendix 4

Preparation of intercalibration solutions

The preparation of intercalibration solutions is an important part of the chemical analysis. More important, determination of these solutions within each run and comparison of results obtained from different analysis in order to identify errors. They are used to check data quality and argument for its reliability. The history of intercalibration used in my analysis is as follows:

Preparation of the AAS intercalibration solutions

Following points must take into regard for preparation of intercalibration:

1. The actual concentration in different field. (Here e.g. China, Poland and Norway)
2. The different instrument used for analysis, their different modes, their detection limits for the different elements.
3. The linear range of the instrument.
4. The ionic balance of the solution prepared.

The intercalibrations were supposed have the following ions:

Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, H^+, F^-, Cl^-, NO_3^-, SO_4^{2-}

Three different solutions were to be prepared:

1. Solution I: Contains water samples from different fields in China, Poland and Norway. Nothing was added to this solution since its content suited the Norwegian field levels.
2. Solution II: Is a synthetic solution, i.e. contains no real samples from the field. The concentrations were chosen to suit the Chinese field levels.
3. Solution III: Contained water samples from different fields in China, Poland and Norway. Several salts were added to much the solution comparable to the Chinese field levels.

Table 4.a *Ion concentrations in the intercalibration solutions, in μeq/L*

Ion	**Solution1** (Analyzed)	**Solution 2** (Theoretical)	**Solution 3** (Analyzed prior to addition)	**Solution 3** (Theoretical added amount)	**Solution 3** (Theoretical expected concentration)
K	2	15	3	30	33
Na	99	50	115	30	145
Mg	20	50	25	80	105
Ca	14	300	18	600	618
H	22	252	22	230	252
Al	15	105	15	300	315
F	2	15	2	30	32
Cl	110	62	138	180	318
NO_3	9	93	6	120	126
SO_4	45	602	63	940	1003

Table 4.b *Salts and acids used in preparing the intercalibration solution*

	Solution II		**Solution III**		
salt	**Theoretical amount needed (g/5L)**	**Weighed amount (g)**	**6.1. Salt**	**Theoretical amount needed (g/5L)**	**Weighed amount (g)**
H_2SO_4	0.0615900	0.06259	H_2SO_4	0.067473	0.07454
$CaSO_4 x 4H_2O$	0.1561515	0.16385	$CaSO_4. 4H_2O$	0.374763	0.37799
$MgSO_4$	0.0150458	0.01582	$MgSO_4$	0.028885	0.02962
$AlCl_3$	0.0026667	0.00270	$AlCl_3$	0.0048002	0.04885
$Al(NO_3)_3 x9H_2O$	0.058144	0.05817	$Al(NO_3)_3 .9H_2O$	0.090030	0.09265
NaCl	0.0146107	0.01700	K_2SO_4	0.015683	0.01563
KF	0.0043572	0.00537	NaF	0.007557	0.00740

Table 4.c *Achieved concentrations and ionic balance in the intercalibration solution after the addition of salts*

		Solution 1		**Solution 2**	
Ion	**Atom weight g/mol**	**Theoretical concentration µeq/L**	**Achieved concentration µeq/L**	**Theoretical concentration µeq/L**	**Achieved concentration µeq/L**
Na	22.99	50	58.18	145	144.37
K	39.10	15	18.49	33	32.90
Ca	40.08	300	314.79	618	622.6
Mg	24.31	50	52.57	105	107.2
Al	26.98	105	105.17	315	321.2
H	1.008	252	255.27	252	268.3
Σ Cations		**772**	**804.47**	**1479**	**1496.6**
F	19.00	15	18.49	32	31.32
Cl	35.45	62	58.18	318	321.2
NO_3	62.01	93	93.02	126 (126)	129
SO_4	96.066	602	622.63	1003	1033.22
Σ Anions		**772**	**804.47**	**1479**	**1515**

Appendix 5
Historical sulfur emission of China

CHINA HISTORIC GLOBAL SULFUR EMISSIONS

Year	H.Coal	B.Coal	Oil	Smelting	Total
kt/a	kt/a	kt/a	kt/a	kt/a	
1851	0	0	0	0.0947	0.0947
1852	0	0	0	0.189	0.189
1853	0	0	0	0.284	0.284
1854	0	0	0	0.379	0.379
1855	0	0	0	0.474	0.474
1856	0	0	0	0.568	0.568
1857	0	0	0	0.663	0.663
1858	0	0	0	0.758	0.758
1859	0	0	0	0.853	0.853
1860	0	0	0	0.947	0.947
1861	0	0	0	1.04	1.04
1862	0	0	0	1.12	1.12
1863	0	0	0	1.21	1.21
1864	0	0	0	1.3	1.3
1865	0	0	0	1.38	1.38
1866	0	0	0	1.46	1.46
1867	0	0	0	1.55	1.55
1868	0	0	0	1.63	1.63
1869	0	0	0	1.71	1.71
1870	0	0	0	1.79	1.79
1871	0	0	0	1.86	1.86
1872	0	0	0	1.94	1.94
1873	0	0	0	2.02	2.02
1874	0	0	0	2.09	2.09
1875	0	0	0	2.17	2.17
1876	0	0	0	2.24	2.24
1877	0	0	0	2.31	2.31
1878	0	0	0	2.38	2.38
1879	0	0	0	2.45	2.45
1880	0	0	0	2.53	2.53
1881	0	0	0	2.55	2.55
1882	0	0	0	2.56	2.56
1883	0	0	0	2.56	2.56
1884	0	0	0	2.57	2.57
1885	0	0	0	2.56	2.56
1886	0	0	0	2.56	2.56
1887	0	0	0	2.54	2.54
1888	0	0	0	2.53	2.53
1889	0	0	0	2.5	2.5
1890	0	0	0	2.48	2.48
1891	0.983	0	0	2.45	3.43
1892	1.97	0	0	2.41	4.38
1893	2.95	0	0	2.37	5.33
1894	3.94	0	0	2.33	6.27
1895	4.92	0	0	2.28	7.2
1896	5.91	0	0	2.23	8.14
1897	6.9	0	0	2.17	9.07
1898	7.88	0	0	2.11	9.99
1899	8.87	0	0	2.04	10.9
1900	9.86	0	0	1.97	11.8
1901	10.9	0	0	1.99	12.8
1902	11.8	0	0	2.01	13.9
1903	12.8	0	0	2.03	14.9
1904	13.7	0	0	2.04	15.7
1905	15	0	0	2.06	17.1
1906	112	0	0	2.08	114
1907	112	0	0	2.09	114
1908	112	0	0	2.1	114
1909	112	0	0	2.12	114
1910	112	0	0	2.13	115
1911	113	0	0	2.14	115
1912	113	0	0	2.15	115
1913	160	0	0	2.16	162
1914	176	0	0	2.17	179
1915	168	0	0	2.17	170
1916	199	0	0	2.18	201
1917	211	0	0	2.19	214
1918	230	0	0	2.19	232
1919	251	0	0	2.2	253
1920	154	0	0	2.2	156
1921	256	0	0	2.22	258
1922	264	0	0	2.25	266
1923	306	0	0	2.27	309
1924	322	0	0	2.3	324
1925	303	0	0	2.32	305
1926	288	0	0.0158	2.35	290
1927	302	0	0.0238	1.5	304
1928	314	0	0.0238	0.897	315
1929	318	0	0.0317	1.79	320
1930	326	0	0.396	1.3	327
1931	341	0	0.483	1.13	343
1932	330	0	0.554	0.894	332

Appendix 5
Historical sulfur emission of China

Year	H.Coal	B.Coal	Oil	Smelting	Total
kt/a	kt/a	kt/a	kt/a	kt/a	
1933	355	0	0.689	0.851	357
1934	410	0	0.729	1.01	412
1935	452	0	1.12	1.16	455
1936	500	0	1.31	1.32	503
1937	467	0	1.54	1.47	470
1938	361	0	2.15	1.63	364
1939	435	0	3.04	1.78	440
1940	557	0	4.63	1.94	563
1941	694	0	5.25	2.09	701
1942	733	0	6.46	2.24	742
1943	634	0	2.45	2.39	639
1944	642	0	1.58	2.53	646
1945	331	0	1.37	2.68	335
1946	206	0	0.536	2.83	209
1947	221	0	0.471	2.97	224
1948	156	0	0.549	3.12	160
1949	408	0	0.874	3.26	413
1950	519	0	1.46	3.4	524
1951	666	0	2.15	3.55	672
1952	835	0	2.93	3.69	842
1953	868	0	4.11	11.2	884
1954	1039	0	5	12	1056
1955	1223	0	11	15	1249
1956	1371	0	12	17	1400
1957	1630	0	12	21	1663
1958	3392	0	19	35	3446
1959	4642	0	25	54	4722
1960	4997	0	30	71	5098
1961	3491	0	24	81	3596
1962	2755	0	25	93	2873
1963	2718	0	28	93	2838
1964	2689	0	35	91	2816
1965	2901	0	44	90	3035
1966	3149	0	55	89	3292
1967	2572	0	54	79	2705
1968	2766	0	61	87	2914
1969	3358	0	81	93	3532
1970	4467	0	117	92	4675
1971	4944	0	137	105	5186
1972	5175	0	151	117	5443
1973	5266	0	174	129	5569
1974	5216	0	217	141	5574
1975	6094	0	244	139	6476
1976	6117	0	265	130	6511
1977	6698	276	318	134	7426
1978	7538	295	335	135	8303
1979	7743	300	332	134	8509
1980	7542	289	364	135	8329
1981	7573	278	326	138	8315
1982	8447	0	298	141	8886
1983	9060	0	281	140	9482
1984	10015	0	294	143	10452
1985	11066	0	298	148	11513
1986	11326	0	314	179	11818
1987	11715	0	343	224	12282
1988	12355	0	328	256	12939
1989	13303	0	331	252	13886
1990	13626	0	325	263	14214

Appendix 6

Chinas energy consumption from 1965—2000

Million tonnes	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982
oil	11.0	14.1	13.9	15.2	20.4	28.2	38.4	44.2	53.8	61.9	68.3	78.0	82.4	91.3	91.1	88.0	84.8	82.4
gass	0.8	0.9	0.9	1.1	1.9	3.3	4.3	4.9	6.4	7.7	8.7	9.8	10.9	11.7	12.4	11.7	10.4	9.5
coal	165.6	180.6	126.0	166.3	177.3	196.5	213.0	216.9	228.0	239.7	250.9	263.1	276.3	296.3	327.5	314.4	310.4	333.1
hydrology	1.9	1.9	1.7	2.0	2.0	2.1	2.5	2.8	3.2	3.6	3.8	3.8	4.0	3.7	4.2	4.9	5.5	6.2
nuclear	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
primary	179.3	197.4	142.4	184.6	201.6	230.1	258.2	268.8	291.4	312.8	331.6	354.8	373.6	402.9	435.1	419.0	411.0	431.2

Million tonnes	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	**2000**
oil	84.7	86.5	90.3	100.0	105.3	110.2	112.3	110.3	117.9	129.0	140.5	149.5	160.7	174.4	185.6	190.3	207.2	**226.9**
gass	10.7	10.8	11.5	12.1	12.8	12.7	12.9	13.2	13.4	13.6	14.6	14.9	15.9	15.9	17.4	17.4	19.3	**22.3**
coal	357.3	394.9	436.5	445.8	460.2	484.9	522.7	533.6	534.9	549.5	570.3	606.4	635.7	676.9	649.3	616.8	512.7	**480.1**
hydrology	7.2	7.2	7.9	8.1	8.6	9.4	10.2	10.9	10.8	11.4	12.4	14.3	16.0	16.1	16.1	17.1	16.8	**19.0**
nuclear	-	-	-	-	-	-	-	-	-	0.1	0.4	3.6	3.3	3.7	3.7	3.9	3.8	**4.3**
primary	459.8	499.4	546.2	566.0	586.9	617.1	658.0	668.0	677.0	703.7	738.2	788.8	831.6	887.0	872.1	845.4	759.7	**752.7**

Appendix 7

Plot B

Table 7.1 *Soil samples from plot B, Tie Shan Ping.*

Horizon	Depth /cm	Munsell soil Color	Profile description
O	0—+2		O – Horizon shows many fine pores, and some stones were observed in the underlying horizons. No change in color between B1 and B2-horizon, but more stones was found in B2-horizon. The horizon border between B2 and B3 was clear by change in color. B3 are sediments and few fine roots were found down to B3-horizon.
AB	0—3	Yellow Brown 10 YR 5/4	
B1	3—12	Strong Brown 7,5 YR 5/8	
B2	12—27	Strong Brown 7,5 YR 5/8	
B3	27→	Browns yellow 10 YR 6/8	

Plot C

Table 7.2 *Soil samples from plot C, Tie Shan Ping.*

Horizon	Depth /cm	Munsell soil Color	Profile description
A	0—2	Yellowish Brown 10 YR 5/4	Non-decomposed tree litter. This plot has very thin organic layer and soil samples were not collected from the O-horizon. The horizon border is marked by a change in color between A and B1 horizons. Some stones were found in B2-horizon and even more stones in B3-horizon.
B1	2—12	Brown 7,5 YR 4/4	
B2	12—22	Brown 7,5 YR 5/6	
B3	22→	Brown 7,5 YR 5/6	

Appendix 7

Plot K

Table 7.3 *Soil samples from plot K, Tie Shan Ping.*

Horizon	Depth /cm	Munsell soil Color	Profile description
O	0—2		The organic layer in O-horizon was thicker in this plot compared to the other plots. Midium large roots were found in A-horizon. Horizon border was clear by change in color between A and B-horizons. Few midium large roots were found in the B1-horizon and there were no roots found in B2-horizon. There were no stones observed in the whole profile
AB	2—5	Very dark grayish brown 10 YR 3/2	
B1	5—20	Strong brown 7,5 YR 4/6	
B2	20→	Strong brown 7,5 YR 4/6	

Appendix 7

Plot L

Table 7.4 *Soil samples from plot L, Tie Shan Ping.*

Horizon	Depth /cm	Munsell Color	Profile description
O	0—1		Some small stones were found in the thin O–horizon. A few fine roots were found both in the A and the B1-horizon. Horizon border was clear by change in color between A and B1-horizons, and by a diffuse change in color between B1 and B2. Very few fine and medium roots were found from B2 down to the B3-horizon, and the horizon border was clear by change in color between these horizons. Stones were observed in all horizons, but more rocks and big stones were found in B3
A	1—2	Very dark brown 10 YR 2,5/2	
B1	2—12	Strong brown 7,5 YR 4/6	
B2	12—32	Strong brown 7,5 YR 5/8	
B3	32→	Reddish yellow 7,5 YR 6/8	

Appendix 7

Lysimeter depth /cm							
Plot B		**Plot C**		**Plot K**		**Plot L**	
AB	2	A	2	O	2	A	2
B1	8	B1	10	AB	6	B1	7
B2	15	B2	18	B1	15	B2	22
B3	30	B3	30	B2	30	B3	36