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Title: Analysis of a system response and effects of acidification on a freshwater ecosystem

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Abstract

Natural processes occurring in the environment have been studied from ancient times. Because of their complexity, their behaviour is complicated to predict. Modelling reality is an integral part of most of the research and analysis of complex systems. There is awareness that there is often a need to accept models whose properties differ significantly from those in the system that is modelled. Acceptance of this state is a direct result of the need to conduct some research, when implementation of a real-time system is too expensive, too difficult or too dangerous and often quite impossible.

Acidification of aquatic ecosystems is considered one of the major international issues connected to environmental threat in Europe. Many lakes in Scandinavia suffer from chronic acidity – a state in which water has a constant low pH level. Freshwater acidification is a common problem in areas of high sulphur and nitrogen deposition as atmospheric pollution is the major cause of acid rain that leads to acidification. These substances reach surface water not only from rain but also via run-off from the entire catchment. However, run-off might be neutralized due to buffering characteristics of the soil, i.e. containing base character compounds. In Sweden, acidic run-off from the catchment relates to the areas where subsoil is developed on acid granite bedrock. Because acid rain is correlated with climate change and atmospheric pollution, it becomes a very complex system where not all of the factors are known.

The primary aim of this study was to develop a computer model that allows one to foresee the long-term effects of the system behaviour to the deposition of acidifying compounds built in Powersim environment. Also the influence and effects of lake liming were modelled.

Keywords: acidification, acid rain, system analysis, modelling, Powersim

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Abbreviations

CLRTAP	Convention on long-range transboundary air pollution
ELS-model	Effect-load-sensitivity model
EPA	Environmental Protection Agency
ICP-Forests	International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests
ICP-Waters	International Co-operative Programme on Assessment and Monitoring of the Effects of Air Pollution on Rivers and Lakes
MAGIC	Model of Acidification of Groundwater in Catchments
WFD	Water Framework Directive

1 Introduction

In systems theory, it is assumed that part of reality can be considered as a set of hierarchical systems which are in relationships to each other. The natural environment as part of the geographical environment is subject to constant change resulting from changing external conditions, both by endogenous energy caused by the Earth's interior and exogenous energy from the cosmos and anthropogenic impact on the environment generated by socio-economic conditions. An increase of the anthropogenic factors that modify the natural cycle occurring in the environment is associated with the development of human civilization. Environment according to the Ludwig von Bertalanffy theory (1962) is presented as a megasystem (collection of systems and subsystems) that combines two basic categories of geographical space in the system. The main subject in the environment system is the physical part of the geographical space, consisting of abiotic and biotic components of nature. It is characterized by a specific structure, shaped by interactive internal relationships between the various components and external connections with the environment (Laszlo et al. 1998).

In recent years, attention has been paid to protection of the environment, mainly due to the progressive degradation occurring in the environment. Water is one of the basic components of the life that enables the proper functioning of living organisms, including humans. Two-thirds of the Earth's surface is covered by water bodies of the seas and oceans. 99% of the water reserves are stored in glaciers, vapour in the atmosphere, salty seas and oceans. Only 1% is liquid fresh waters in rivers and lakes that need to be protected.

Natural acidification of lakes and rivers has been taking place since the dawn of time. However, the recent acidification of freshwater ecosystems cannot be attributed to natural causes (Jenkins et. al. 1990). Responsible for current acidification are factories producing acidic pollutants leading to the creation of acid rain.

Acidification of freshwater ecosystems is a bigger problem in the uplands, mostly because of the poorly weathered rocks and thin soils on poorly buffered geologies (Kiley 1996). Most of the water entering the lake passes through the ground which is naturally acidic as a consequence of the underlying acidic geology such as granite and a peat-based soil – typical for the Scandinavian area (Chen et al. 1982). Acidification is a process of increasing the hydrogen ion concentration in the water formed from the dissociation of acids. Responsible for the freshwater acidification is acid deposition that represents a mix of air pollutants - primarily sulphur dioxide, nitrogen oxides and carbon dioxide. Long term atmospheric deposition of acid has caused the acidification of Swedish lakes (Almer et al. 1974). Present in precipitation, sulphuric and nitrogen acids are leading to the acidification of many water reservoirs, which causes serious damage to local ecosystems, such as habitat loss. Under natural conditions, in an atmosphere devoid of anthropogenic origin contaminants, precipitation pH value should be at the level 5.5-5.6. If the pH in the rainfall is reduced to ~ 5.0, it is assumed that the precipitation is acidic and it is often called "acid rain". It was found (Skjelkvåle et al. 2001) that declining pH is accompanied by a reduction in the biological productivity of the freshwater.

The increasing acidification of the environment creates an imbalance that threatens many species of flora and fauna. Potential mitigation techniques may be possible by policy changes in these areas where high acidification process is likely to occur. Reduction of acidogenic pollutant emissions into the atmosphere aims to inhibit the acidification and to create the conditions that will allow ecosystems to re-establish natural balance. ICP-Waters is one of the programs acting on behalf of the executive body CLRTAP signed in Geneva in 1979. Work of these programs allows control and corrects the acidogenic pollution emissions to the atmosphere in Europe. Since its inception, sulphur emission decreased by 80%, but there was no change in the environment due to another acidifying compound – NO_3 . Nowadays all European countries are obligated to reduce emissions until 2020, which will result in even lower emissions and possibility a faster recovery from acid deposition.

2 Review of the literature

Acid deposition

Most natural lake water has a pH range from 6 to 9 (Hultberg et. al 1994). The pH symbol is a negative decimal logarithm of the concentration of hydrogen ions - H^+ . The pH of aqueous solutions (I) can be expressed numerically by using the hydrogen ion concentration:

$$pH = -\log(H^+) \quad (1)$$

The hydrogen ion concentration in natural waters is primarily dependent on the dissociation and hydrolysis of dissolved compounds in them. For most waters, pH depends on the concentration of carbonic acid and its ions. The value of pH in waters that contain humic substances is dependent on the organic acids. pH below 5,6 means that the lake is acidified. Acidification as a consequence of acid rain is a major environmental problem in the Nordic countries and has resulted in reduced biodiversity (Almer 2014). After years of research it has been estimated that more than 17 000 lakes in Sweden are acidified due to the increase of acidic pollutants emission (Swedish EPA 2006). The enormous amounts of air pollutants are emitted from combustion of fossil fuels. In the Baltic Sea region power plants are the main sources of air pollutants (Pęcherzewski 1991).

Acidification also causes problems when it comes to sustainable development. It affects humans and their economy because of the environmental management performance. Freshwater environments provide important environmental services on both local and global scales. The most important services are biodiversity conservation and water supply, mostly for cities and agriculture. However, environmental services are changing causing reductions in biodiversity and loss of resilience. WFD forced the participating countries to reach good ecological status

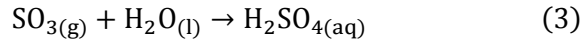
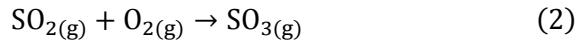
(GES) by 2015. WFD defines good ecological status as: “*the values of the biological quality elements for the surface water body type show low levels of distortion resulting from human activity but deviate only slightly from those normally associated with the surface water body type under undisturbed conditions.*”¹ As a part of the European Union, Sweden has applied lime to accomplish the requirements, both biological and chemical. To reach good ecological status, water bodies need to be close to the undisturbed state, which is usually described as pre-industrial (WFD 2000). Pre-industrial state is usually defined as reference conditions that water bodies had before 1860. To determine the pre-industrial reference state of freshwater ecosystems the hydrogeochemical model called MAGIC is used. However, there are no measurements from these times, so the model has a simplified procedure and the results can be questioned.

In highly polluted air environments the levels of certain gases can be higher than the natural levels occurring in the atmosphere. Pollutants can be divided into two groups: primary pollutants (SO_x , CO, NO_x) that are emitted by identifiable man-made sources and secondary pollutants that are formed in the atmosphere by chemical reactions of the primary pollutant (Kiley 1996). The only difference between regular and acidic precipitation is pH level.

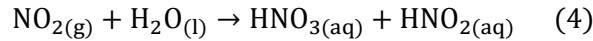
Acid rain is caused by nitrogen dioxide (NO_2) and sulphur dioxide emissions (SO_2) and formed after they combine with humidity in the atmosphere and make sulphuric and nitric acids. Before sulphur dioxide and nitrogen oxide become acids, they need to go through several complex chemical reactions with the moisture in the atmosphere. In heavily industrialized areas or in those under their direct influence, the pH value in 90-95% of cases is determined by the introduction to the atmosphere of various industrial gases resulting from combustion, such as hydroxides and oxides of sulphur, nitrogen and carbon. Emissions of these gases are transformed into sulphate and nitrate particles in the atmosphere. As a result, further chemical transformations taking place in the hydrated layers of the atmosphere transform these particles to the aggressive sulphuric acid (H_2SO_4), nitric acid

¹ EC 2000; Annex V p. 45

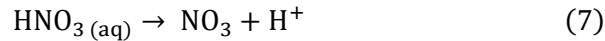
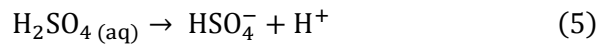
(HNO₃). In the gaseous phase, sulphur dioxide forms sulphate ion (2) and sulphuric acid (3) (Phamornsuwana 2008).



Nitrogen oxide reactions are oxidized in the clouds to form nitric acid.



Under natural conditions the rainfall pH is in 80-90% of cases determined by CO₂ occurring in the air as well as sulphur compounds, nitrogen compounds and methane as natural products of decomposition of organic matter (Tilling et al. 1992). Sulphuric (5, 6) and nitric (7) acids dissolve in moisture and dissociate to release H⁺:

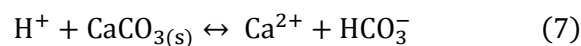


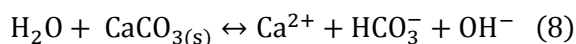
Increased concentrations of hydrogen ions also leads to soil acidification. Soil acidifies not only because of acid rain but also by anisotropic human activity which often substantially modifies the natural processes and leads to the changes in the properties of the selected elements of the natural environment (Fölster et al. 2007). These changes lead to the modification of the ecosystem's internal structure, as well as the course of its borders. Acidified runoff enters the freshwater ecosystems and is determined by regional climate and bedrock geochemistry (Castendyk et al. 2009). Soils bind cations as they release sulphate, which is the main reason for delay in recovery. The risk that soils start to release nitrogen in the form of nitrate is small and only the nitrate form would have an acidifying effect. Runoff and water quality in Scandinavia are usually restored by soil and water liming.

Neutralization

Effects of acidification were discovered in early 1960's. Since then, after several decades of acid deposition the base saturation in soils has changed. To the forest floor, precipitation arrives in the form of rainwater from the crown of the tree. Rainwater running down the trunks creates a path that goes to the soil and then to the surface water. In the literature (Kiley 1996, Moldan et. al 2004) one can find data indicating a decrease in the pH of rainwater after passing through the treetops, although there is also a lot of research that does not confirm that the fallout under the crowns of trees is characterized by a lower pH in relation to precipitation in the direct open-space area (Van Breemen et al. 1989). Lower pH is due to the wash of the acid components, such as SO_4^{2-} and NO_3^- , and associated molecules that are adsorbed on the surface of the plant as a result of dry and wet deposition (Butler et al. 1995). Low base saturation index is the reason why freshwater ecosystem cannot be fully neutralized during rainfall passage through the soils of the catchments. To neutralize the combined introduced acidity by acid rain and the natural one, application of lime can be performed (Olem 1991). In the small scale, liming began in the mid-1970s. After that period in the beginning of the 1980s, liming was used on a larger scale as a part of the restoration process to detain acidification (Swedish EPA 2006). One of the most direct methods is by direct liming of surface waters mostly by using planes or helicopters, which helps to access the difficult to reach areas. Liming means the addition of limestone, primarily calcium carbonate (CaCO_3), to neutralize acid levels in waters and soils (Helfrich et al. 2009). When calcium carbonate dissolves, it provides calcium ions and carbonate ions. The carbonate ion reacts with acid and forms bicarbonate. This reaction neutralizes the acid, by improving the pH value. Calcium carbonate is used as the base because it is a natural high purity mineral that dissolves slowly producing a long lasting treatment.

The dissolution of calcite particles in water occurs along two reactions (7, 8). When water pH is below 4.4, the first reaction (7) will dominate (Sverdrup, Warfvinge 1988).





The amount of lime is dependent on the pH, precipitation and lime quality, which refers to the size of the particle and neutralising value. The higher the neutralising value the less lime can be used (Bolland et al. 2004). Application of lime in the water bodies aims to increase lake water pH and recover ecosystems to a pre-acidification state. However, liming does not fix the acidity and is a costly operation that is only beneficial in the short term. As the limestone breaks down, the water slowly turns back into an acidic level if any action will be taken. To maintain the pH levels, more and more calcium has to be added to the water (Downey 2012).

The liming strategy is included in a guidance for lake liming called "Handbok för kalkning av sjöar och vattendrag" and is recommended by the Swedish EPA.

Table 1. Guideline values for dose to lime lakes

Goal pH	Volume dose (g/m ³) with lowest pH _{oalk}		
	4.4	4.9	5.4
≥ 5.6	8	5	2
≥ 6	12	9	6

Doses included in the handbook (*tab.1*) are only for guidance and the actual needs may vary slightly and change from year to year due to fluctuations in climate. To calculate lime requirement (9), the values of areal dose (10) and catchment area are required

$$\text{LR} = \text{CA} \cdot \text{AD} \quad (9)$$

where:

LR - Lime requirement (kg/year)

CA – catchment area (ha)

AD – areal-dose (kg/ha/year)

$$\text{AD} = \text{VD} \cdot \text{SR} \cdot 0.315 \quad (10)$$

where:

VD – volume dose (g/m^3);

SR – run-off rate ($\text{l}/\text{s}/\text{km}^2$)

0.315 – constant to obtain year unit

Lime application is affected by a lake retention time. In a lake with long turnover, duration of lime is extended compared to one with short turnover. Based on turnover Swedish EPA recommends a lime application according to table 2.

Table 2. Recommended lime spreading time intervals

Retention time	Spread interval
Years	years
0.5 – 1	1
1 – 2	1
2 – 3	2
>3	3

International agreements

The recent decrease in acid deposition is connected to national and international efforts. International negotiations on emission reductions have been conducted under the CLRTAP. As the result of negotiations, the protocol in 1985 was founded. The main goal was to reduce sulphur emissions by 30% by 1993 compared with 1980 levels. A second protocol for sulphur was signed in 1994 and pledged a half cut in emissions by the year 2000 (or for some countries 2010), compared to the 1980 levels. In 1987 an agreement to freeze NO_x emission rates by 1994 emissions arose. The goal was reached ahead of schedule, in 1988. The most important protocol that is still used today was signed in 1999 in Gothenburg and entered into force in 2005. A “multi-effect, multi-pollutant” protocol defines the emission ceilings for four air pollutants: sulphur, NO_x , volatile organic compounds (VOC_x) and ammonia. In 2012 after intense negotiations, new amendments to the Gothenburg Protocol were adapted. The main goal for years to come includes national emission reduction for air pollutants to be achieved in 2020 and not to be exceeded.

The revised protocol specifies emission reduction in terms of percentage reductions from base 2005 to 2020, which means that emission reductions in the whole EU are expected to be 66% for SO₂ and 50% for NO_x.

Only with lower emissions level can a return to natural chemical, biological and ecological conditions be expected. A lowered emission equals reduced depositions to or below the relevant critical loads, which can slow the pace of acidification. It is predicted that the smallest decreases in sulphur and nitrate will occur in the southern counties of Sweden, because this region is the most exposed to the deposition from neighbouring countries, where reductions were not as high as in Sweden.

Environmental sustainability

Sustainable development implies the rational use of natural resources of the Earth. Sustainable development maintains the balance between the needs of different people all over the world and the environment. Environmental sustainability is about making decisions and taking actions that are in the interest of environmental protection and an environmentally sustainable future. A healthy and clean environment is a prerequisite for the fulfilment to support human life. The first definition of sustainable development appeared in the report "Our Common Future", developed in 1987 by the World Commission on Environment and Development. The definition describes the sustainable development as: *"development that meets the needs of the present without compromising the ability of future generations to meet their own needs."* (Report of the World Commission on Environment and Development: Our Common Future 1987). Three main areas affecting the sustainability were identified: environment, economic and social (*fig. 1*). The goal of sustainable development is to maintain these systems.

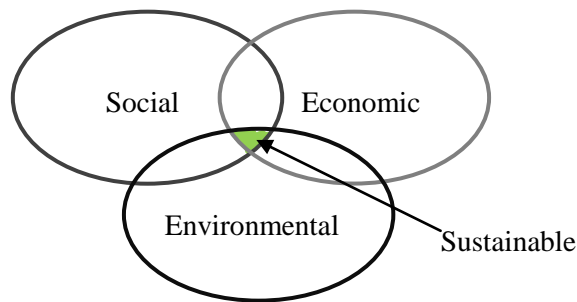


Figure 1. Three main areas affecting the sustainability of the global economy

The European Union has had its own sustainable development strategy since 2001, when a document “A Sustainable Europe for a Better World: A European Union Strategy for Sustainable Development” was adopted in Gothenburg. In 2006, as a result of a two-year evaluation of the actions under the Strategy adopted in Gothenburg, a renewed Sustainable Development Strategy was developed. The goal is to achieve greater consistency and efficiency in their efforts to implement the principles of sustainable development in the European Union.

Introduction of international agreements have resulted in reduced emissions of SO_2 and NO_3 which resulted in reduced acid deposition. However, is it possible to return to pre-acidification state? To achieve the sustainable development of a freshwater ecosystem, it is important to consider ecosystem resilience (Walker & Salt 2006). The amount of resilience a system possesses relates to the ability to return to the steady state following a perturbation. The term ecological resilience was introduced by Holling in 1973. The purpose was to describe the relationship between resilience and stability in ecological systems. As mentioned above the system’s resilience depends on how much disturbance it can take before it changes to a different state. The stable system is described by the speed of reaching equilibrium; that is the faster it is reached, the more stable it is. Sustainable development must be a dynamic process in order to maintain system resilience due to complexity and uncertainty of natural systems (Newman 2005). Freshwater ecosystems are described as complex adaptive systems, where components are independent but with the variations occurring in the system components changing over time. The ongoing system creates cyclic movements that alternate between long

periods and shorter periods, called adaptive cycles. The development of ecosystem occurs in cycles of disturbance and disruption, caused by external and internal factors. Disorders trigger natural processes of adaptation and structures better adapted to changing environmental conditions.

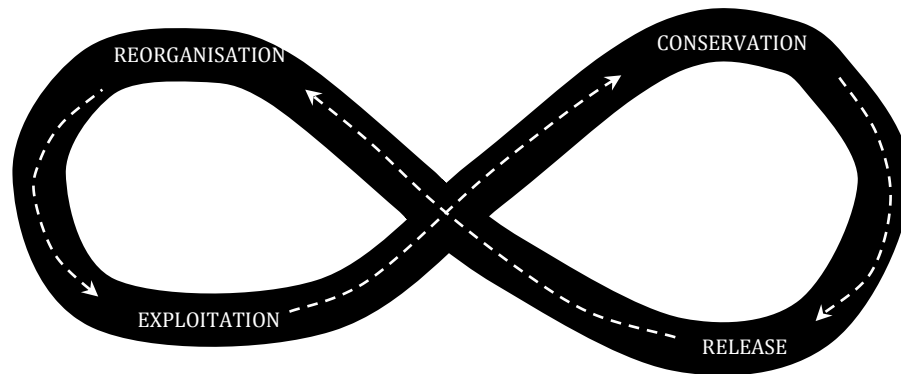


Figure 2. Adaptive cycles

The adaptive cycle has two major transitions called foreloop and backloop. The first phase describes a stable phase with an incremental phase of growth and accumulation, called foreloop. The phase referred to as the backloop begins with entering the phase called release, where energy is released and the systems leads to renewal.

Adaptive cycles help to interpret system behaviour that link together system organization, resilience and dynamics.

Modelling the environment

Modelling the environment allow researchers and managers to predict consequences of action and policies in environmental management. Ecosystems can be modelled at many scales from small to large e.g. from a bottom of a lake to the whole basin. Models represent some aspects of a real system and it is easier to work with them than with the actual system (Folke 2006). According to systems theory, to model complex units created by the multiple interaction of components and to concentrate on the dynamics that define the characteristic properties, relationships and functions between them and that are internal or external to the system, the model must be kept as simple as possible. To represent interrelationships

between the real system, models use mathematical equations. The most known method of modelling and managing a complex system which changes over time is system dynamics. System dynamics is a method of analysing problems which deal with feedback loops and time delays that are affecting the system behaviour. It represents stocks, flows and feedback loops.

There are many different types of models which are designed to meet given requirements determined by the modeller. A model can be deterministic, where a single value is an input for each parameter and there is a single model result and certainty is assumed in all aspects, or it can be stochastic; with a range of possible values that gives variable output.

Computer simulation models need software that can help transform and perform calculations to the computer, such as Powersim, Stella or Vensim, that support dynamic modelling. However, modelling predictions should always be regarded as uncertain, because a model is just simplification.

3 Materials and methods

Study area

Lake Örvattnet (59° 44'N, 12° 44'E), situated in the Värmlands county, 10 km northeast of Arvika municipality in western Sweden has an area of 0.68 km² and estimated catchment area of 2.98 km². The outflow of the lake flows into Lake Mängen, with estimated runoff of 0.01 m³/km²·s. The research area is located in the humid continental climate zone and it is surrounded by forest. The bedrock is made of granite and migmatized gneiss (Ek at al. 1995). The area is not cultivated and most of the natural vegetation is intact. The lake gets its water from rain and melted snow. It is assumed that groundwater is stored in the bedrock and its transport to the lake is minimal.

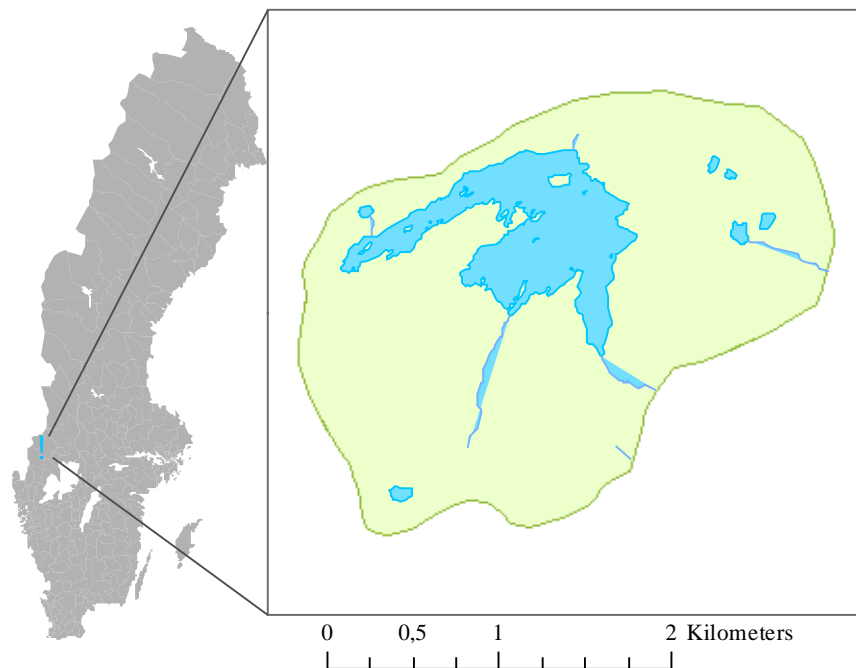


Figure 3. Location of the study area. The lake Örvattnet catchment (scale 1:44 000)

Since 1967 Lake Örvattnet has been monitored and there is slight evidence that lake is recovering by itself from acidification, although pH is not increasing. The beginning of acidification is dated by the end of 1960's where pH decreased below 5 (Ek at al. 1995). Increased acidity reduced plant production and the amount of fish in the water. In 2008 the ecological status of the lake was classified as “moderate”, which means moderate deviations from the reference conditions (WFD 2000).

Lake Örvattnet was selected as a case study because it is well suited to simulate the changes in the lake pH caused by acid deposition. According to Ek at el. (1995) the lake was not limed and the alkalinity in the lake is close to zero (Persson 2009). Studies (Ek at al. 1995, Åkerblom 2003 & Persson 2009) show that deposition of NO_3^- increased until 1985 but it was not yet contributing to acidification. Since 1990 the deposition of NO_3^- has decreased by 30% in Sweden.

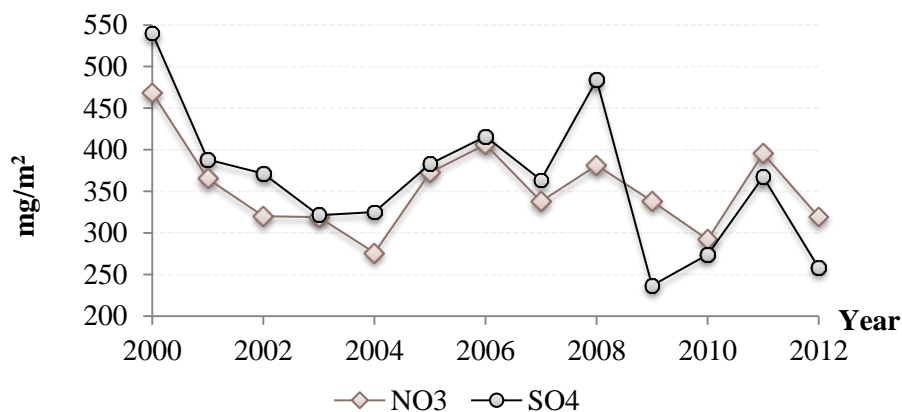


Figure 4. Changes in deposition of SO_4^{2-} and NO_3^- in the whole catchment area during 2000 – 2010

Increase in pH is connected with the decrease in deposition from the atmosphere of SO_4^{2-} and NO_3^- due to the introduction of protocols aimed to reduce emissions. However, the deposition varies from year to year, mostly because of the influence from other neighbouring countries.

Model presentation

The model was built to be applicable to any location in Sweden, providing there is some knowledge of the lake data such as hydrology and water chemistry. The model was built in Powersim software, which belongs to the dynamic systems modelling software group. This software group is used to study long term processes occurring in the real system, where a system is a set of elements connected to each other and both the objects and the relationships between them are their characteristics. Each system has a defined purpose for which it is created and the environment in which they work. To build a model in Powersim, it is required to construct a diagram, where parameters influencing each other are connected. Graphic representation of the model is a simplified and intuitive description, while being sufficiently developed to take into account several elements and aspects of modelled system. A Powersim model is easily modifiable and allows modelling at different levels of abstraction. Acidification model is an expanded version of the classical ELS-model (*fig. 5*) developed to predict the pollutant concentration.

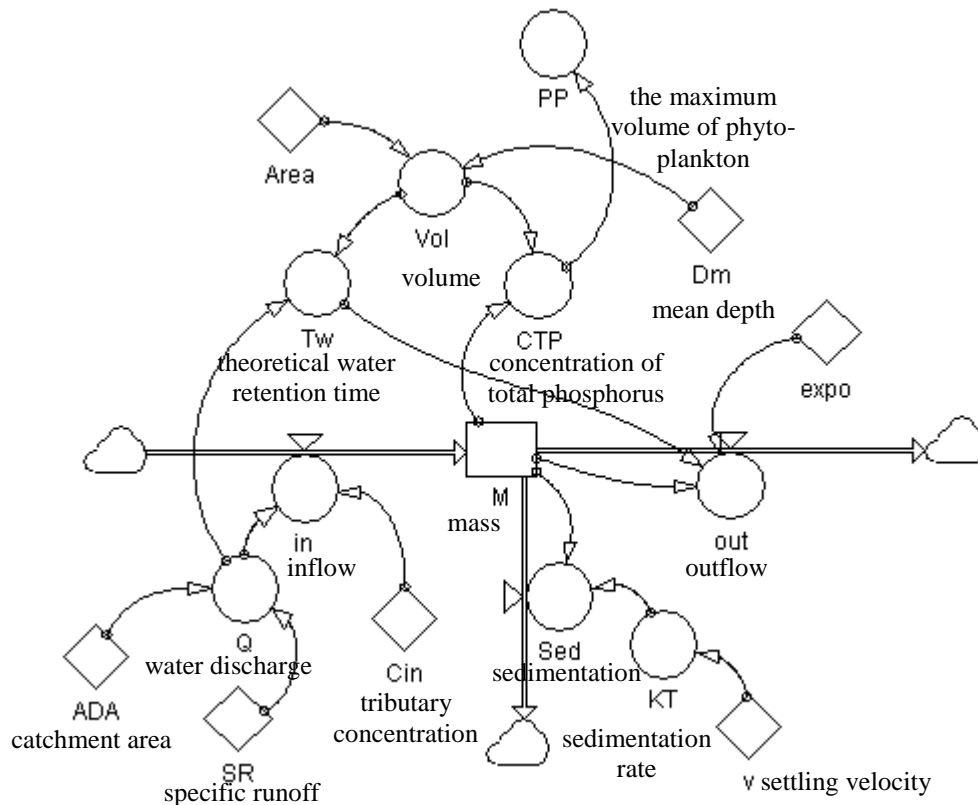


Figure 5. The 'classical' ELS-model (adapted from Håkanson 1999)

The simulation proceeds from 2000 until 2020. The time step is set to 0.001 year. All estimated values are in the power of current emission protocol assumptions.

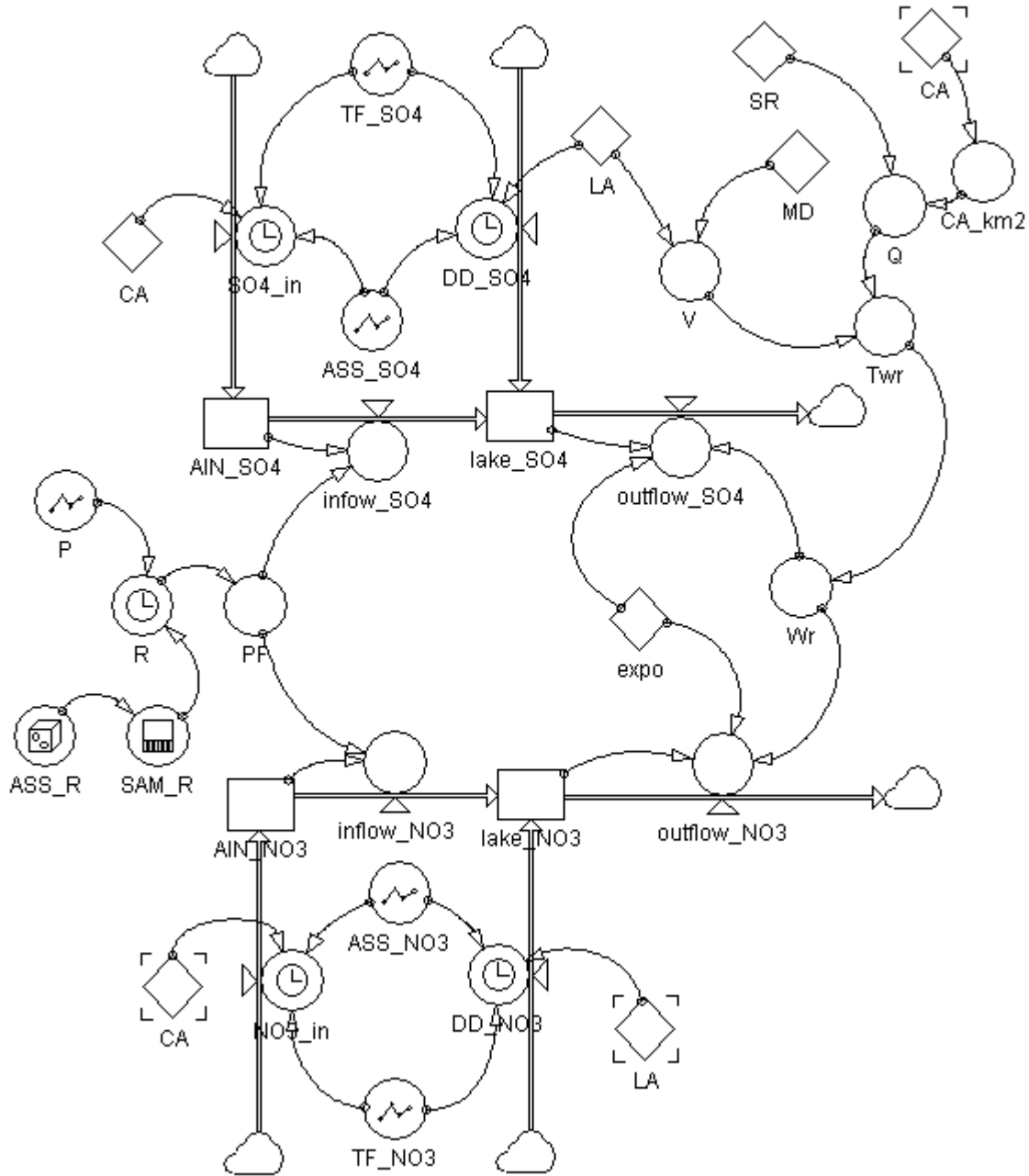


Figure 6. The lake acidification model

Table 3. Panel for acidification model constants

Shortcut	Full name	Dimension	Value
CA	catchment area	km ²	2.98
expo	exponent for the retention rate	-	1
LA	lake area	km ²	0.68
SR	specific runoff	m ³ /km/s	0.001
MD	mean depth	m	5
AIN	amount in inflows	mg	SO ₄ : 1873450755 NO ₃ : 1504319645
TF	total fallout on catchment and lake area	mg/m ²	
P	precipitation 2000-2012	mm/year	
ASS	assumption of deposition	mg/m ²	*
DD	direct deposition to the lake	mg	
in	inflow from the catchment area	-	

* all equations and values are located in appendix I – table 9

Table 4. Panel for acidification driving variables

Shortcut	Full name	Dimension	Equation
PF	precipitation factor	-	R/650*
Wr	water retention	year	$1.386 / (Twr^{((10/(Twr+10-1)+0.5)/1.5)})^{**}$
Twr	theoretical lake water retention	year	V/Q
Q	water discharge	m ³ /year	(SR·60·60·24·365) · CA
outflow	outflow from the lake	mg/year	lake/(Wr ^{expo})
V	volume of the lake	m ³	MD·LA
inflow	total inflow	mg/year	AIN·PF
R	precipitation	mm/year	IF(TIME>2012, SAM_R, P)
SAM_R	estimated rain every time step	mm/year	SAMPLE(ASS_R, 0, 1)
ASS_R	estimated rain for 2013-2020	mm/year	NORMAL(785,128)***

* 650 is the reference value for the annual precipitation for European catchments/lakes (Håkanson 1999)

*** retention function (from Håkanson, 1999), where 10 is the retention rate constant and 1.386 emanates from the definition of the half-life*

**** 785 is the average precipitation value estimated from rainfall in period 2000-2012, 128 is standard deviation for these values*

The fundamental assumption made in the problem is that the entire lake volume is treated as one compartment, which means that there is no distinction between surface water and deep water. The effect of this assumption is that the pollutants are distributed and mixed evenly within the whole lake.

Lime application

To increase the pH of the lake, liming to the whole catchment was introduced. There are circumstances under which direct lake liming is unlikely to work as well as catchment application. Swedish guideline for liming does not recommend direct liming in lakes with short retention times (less than 6 months) or large precipitation, such as study area, Lake Örvattnet. Direct lake liming must be repeated at frequent intervals, which might increase the cost of liming. But, liming of water bodies and soils is interference in the environment and in no way an acceptable ecologically sound solution to the acidification problem (Brocksen et al. 1992). However, restoration of ecosystems, especially the water bodies, has benefits to all users of these water resources.

Sub-model for liming (*fig. 7*) was adapted from Lars Håkanson (1999), which is a mass-balance model for calcium. Liming model can be used to plan an optimal liming program (Håkanson 1999). Lakes with low pH values after reintroduction of species have been shown to have increased heavy metals concentrations in fish tissue (Rubin et al., 1992) and liming can be a solution to this problem.

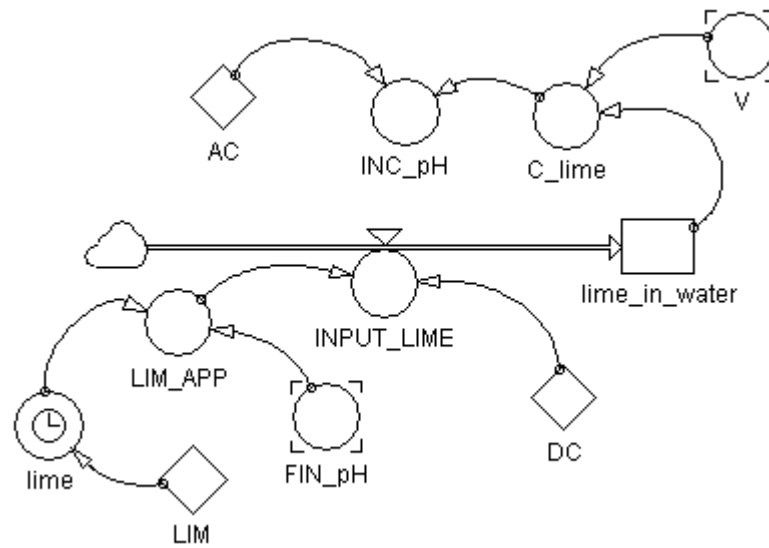


Figure 7. Sub-model for lake liming (adapted from Håkanson 1995)

Table 5. Panel for liming sub-model constants

Shortcut	Full name	Dimension	Value
DC	distribution coefficient	-	0.5
AC	additive constant	-	0.01
LIM	amount of lime added	t/year	0.05
lime_in_water	amount of lime in the water	t	0

Table 6. Panel for liming sub-model driving variables

Shortcut	Full name	Dimension	Equation
INC_pH	increase in pH due to liming	-	$\text{IF}(\text{LOG}(\text{C_lime}+0.001)>0, \text{LOG}(\text{C_lime}+0.001)-\text{AC}, 0)$
lime	amount of lime added	t/year	$\text{IF}(\text{TIME}>2013, \text{LIM}, 0)$
LIM_APP	amount of lime added	t/year	$\text{IF}(\text{FIN_pH}>6.15, 0, \text{lime})$
INPUT_LIME	amount of lime added	t/year	$\text{LIM_APP} \cdot \text{DC} \cdot 0.442 \cdot 0.715$
C_lime	concentration of lime in water after application	mg/m^3	$\text{lime_in_water}/(\text{V} \cdot 10^{-9})$
FIN_pH	final pH of the lake	-	*

* sub-model for calculating pH is included in appendix II

Calibration of the model variables

The acidification model with lime application is defined as a mixed model, which includes several variables. 10 lakes (*tab., 12 appendix I*) were chosen for the model calibrations to define parameters boundaries (*tab. 7*). This means that the model will not be valid for the lakes with parameters outside the range.

Model variables should be calibrated to find that parameter values, that makes the model behaviour realistic as possible to the system behaviour.

Table 7. Boundaries set by 10 different lakes

	Catchment area	Lake area	Average mean depth	Initial pH
	km ²	km ²	M	-
MIN	0.014	0.0325	0.75	5.9
MAX	20.500	5.1800	12.1	7.1

To calibrate the model parameters for Lake Örvattnet, sensitivity analyses on variable parameters were performed using an iterative trial and error method to calculate the response curve and reach the minimum error.

The distribution coefficient shows the amount lime directly transported to the sediments compared with the amount added to the lake. Distribution coefficient has an impact on the response curve because of the small amount of lime added to the lake. However, parameter was calibrated to 0.5, which agrees with researches (Warfvinge1988, Håkanson 1999) about lime dissolution in the freshwater ecosystems.

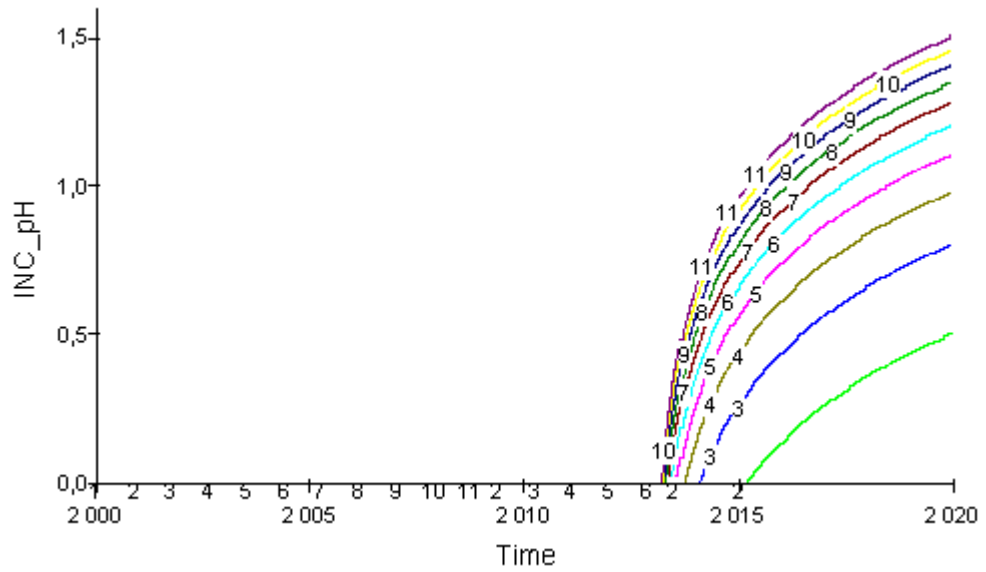


Figure 8. Sensitivity test for distribution coefficient variable (where the lines represent the values: 2-0.1, 3-0.2, 4-0.3, 5-0.4, 6-0.5, 7-0.6, 8-0.7, 9-0.8, 10-0.9, 11-1)

However, the most sensitive variable is the additive constant which describes the influence of pH by the lime concentration. The performed test showed that the additive constant is connected to the amount of lime added to the lake. With an increase in the additive constant value, the pH value first drops down below 0.

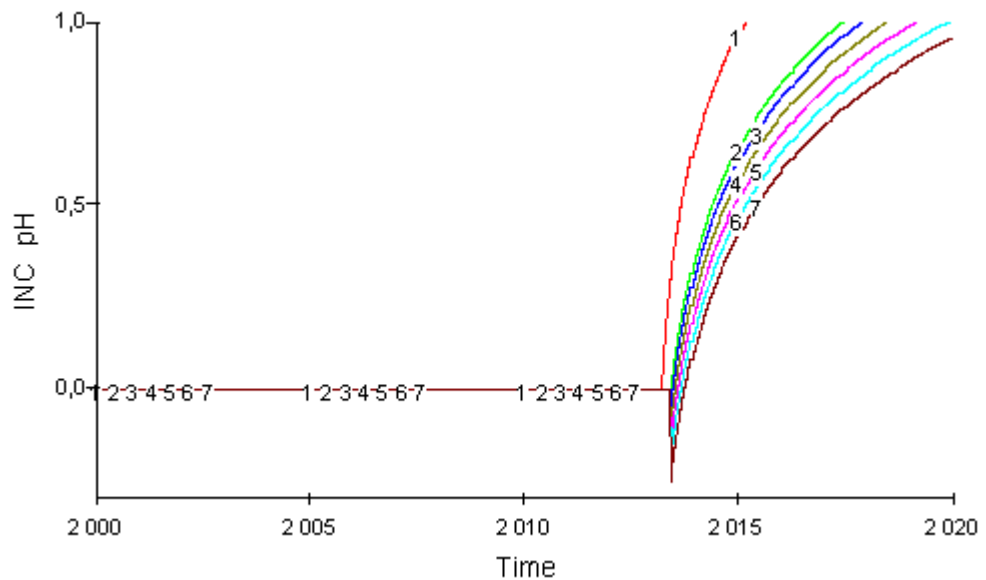


Figure 9. Sensitivity test for additive constant variable (where the lines represent the values 1-0.01, 2-0.05, 3-0.1, 4-0.15, 5-0.2, 6-0.25, 7-0.3)

Validation of the lake acidification model

A validation test is conducted by determination of model variables by testing the model output against measured data.

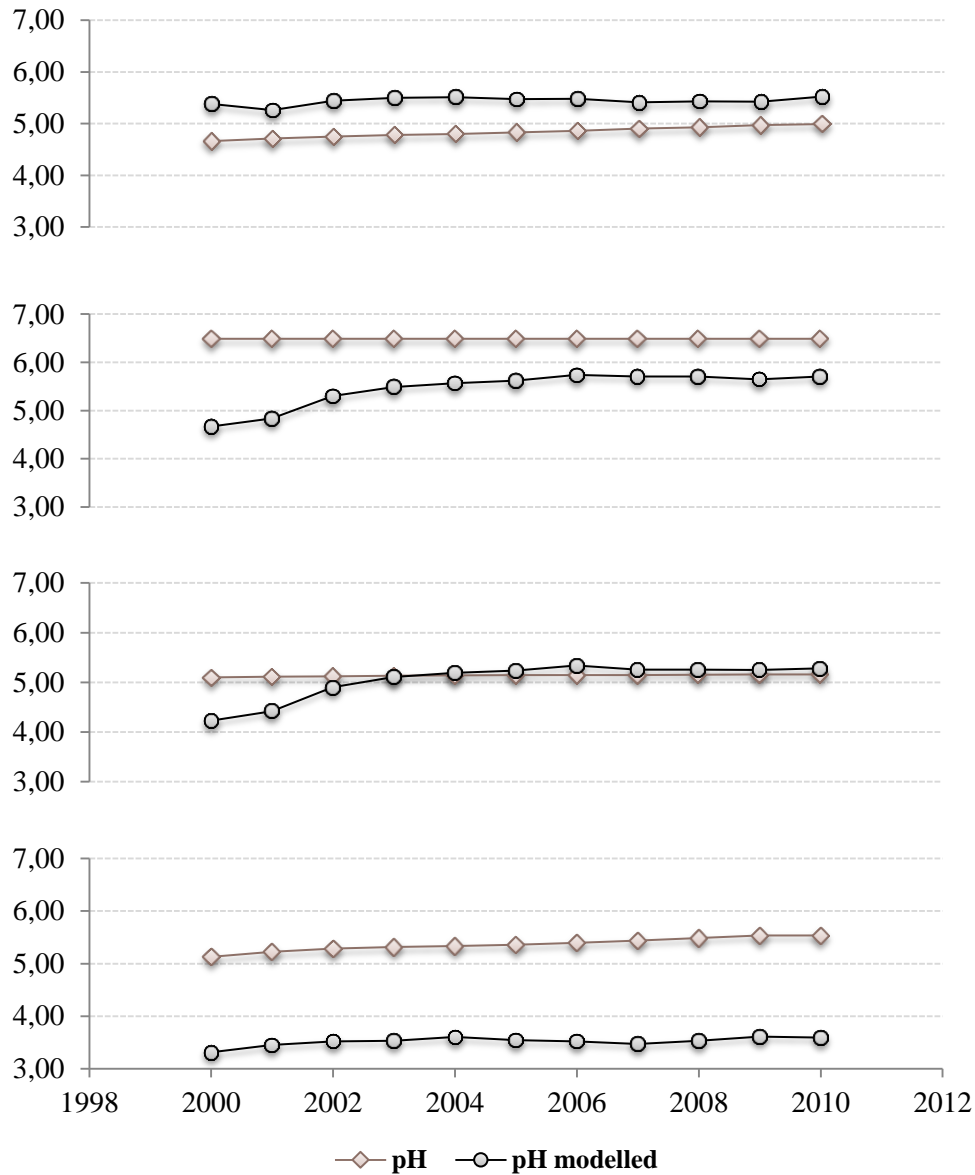


Figure 10. pH calculated for lakes (from the top): 1- Örvattnet, 2- Klutsjön, 3- Svartgölen, 4- Månserudstjärnet

Because lakes are situated all over the Sweden on different soils, the modelled pH differs from the one measured in the reality. The reason for lower modelled pH in lakes Klutsjön (2) and Månserudstjärnet (4) might be the different bedrock than

the one assumed in the model. Lakes are located on more alkaline soils which mean that there are more base cations to neutralize the acid.

4 Results

The main aim of this study was to develop a predictive model to be used in practical water management. 20 years simulation of acid deposition gives the following conclusions.

Amount of acidic compounds in the lake water remains high during the whole simulation period (*fig. 11*). The amount of deposition and precipitation after 2012 is estimated, which means that the result from this period can vary. However, simulation reinforces the picture of very slow recovery of the system with lower deposition which will result in increase in pH.

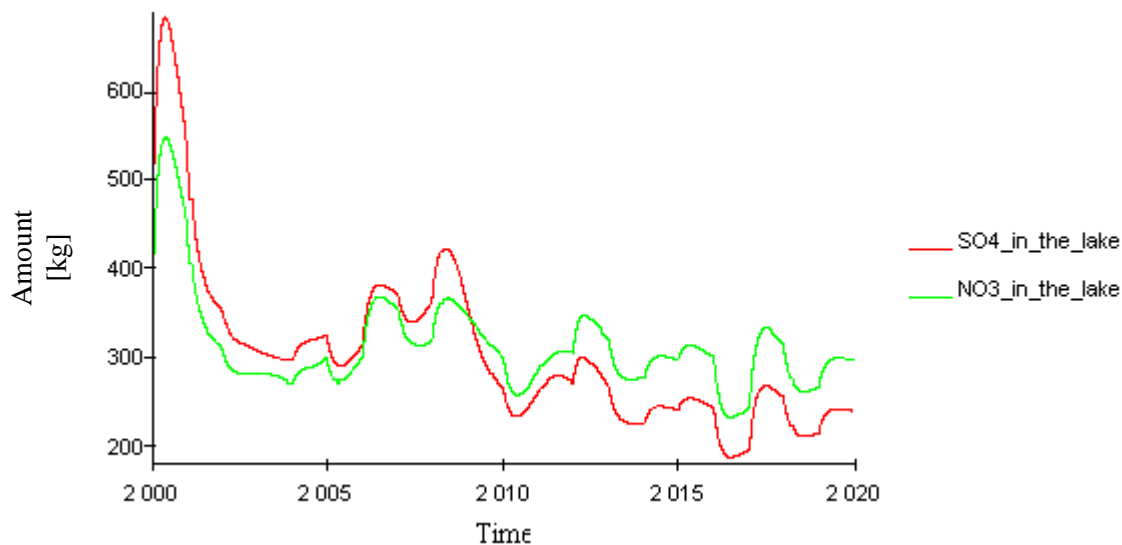


Figure 11. Decrease in the amount of sulphur and nitrogen compound in the lake

Variations occurring after year 2012 are caused, by assumed values in precipitation and deposition. Deposition should decrease by 66% for sulphur and 50% for nitrogen from the amount obtained in 2005. It is assumed that every year decreases by the same percentages (*tab. 10-11, appendix I*), despite the fact that the deposi-

tion starts to decrease since 2010. The system corresponds to the reduced deposition with a slow increase in the pH (fig. 12).

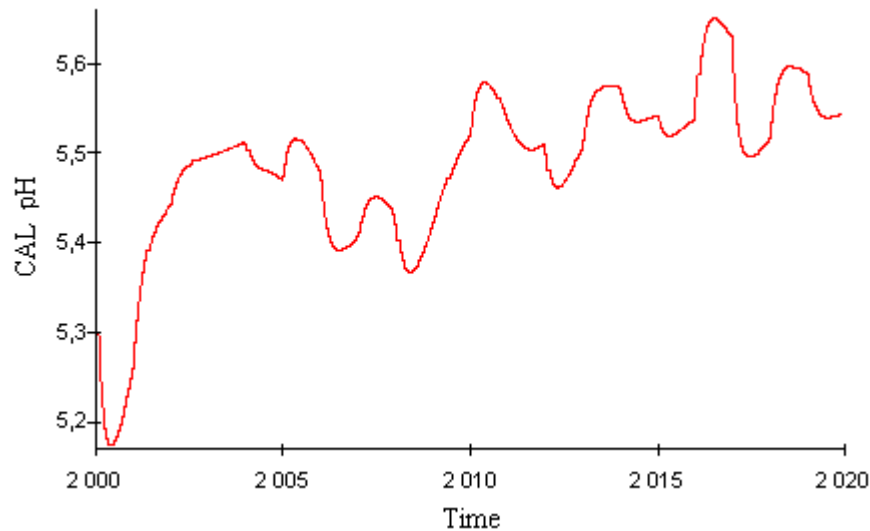


Figure 12. Simulated pH of the lake

As the model was simplified, the modelled pH is higher than the one occurring in the MAGIC database (IVL Svenska Miljöinstitutet). However MAGIC database also contains modelled pH value. Fluctuations are given by the assumptions in the deposition and precipitation after the year 2012.

The acidification model assumes that the water composition contains only clean water with addition of SO_4^{2-} and NO_3^- before liming. Consequently, other ion inputs have not been considered in this study. In the freshwater ecosystem the compounds responsible for neutralizing, such as Ca^{2+} , Na^+ , K^+ , are already located in the water and soil or occur in precipitation. Without reliable data on them, a number of assumptions have to be made, which create uncertainty and difficulties in validating the model.

Other reason why modelled pH is higher might be the fact that biological processes occurring not only in the water but also in the soil are not taken into account. Lake Örvattnet shorelines are surrounded by a forest dominated by spruce, pine and birch (Ek et al. 1995). Forest soils usually have few layers depending on the depth and presence of minerals. Each layer has a different chemistry and thus the

compounds entering the water depend on which layers they have moved through. Water that moves over the surface is more acidic than the precipitation, because it is collecting acids from the forest floor. Also, the influence of ammonia (NH₃) deposition is not modelled.

Liming in the simulation was applied in 2014 with the dose calculated from the Swedish EPA. The aim of liming sub-model was to predict how big will be the change in pH with liming applied and if liming is a necessary interference with the ecosystem.

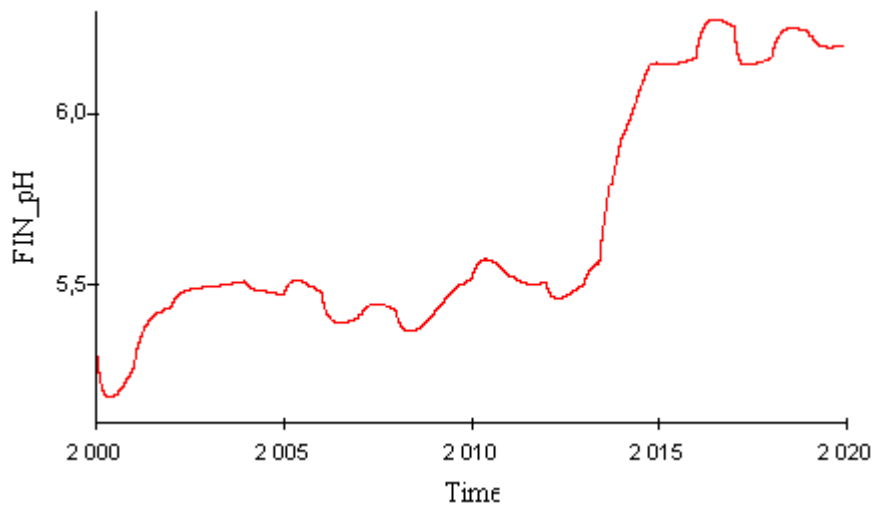


Figure 13. pH of the lake after lime added in 2014

Assuming that limestone dose is sufficient and there are no other influences to the catchment area, it would appear that application of limestone to the land can be a satisfactory way of making acid waters chemically acceptable for flora and fauna to reintroduce. Also, during the simulation pH increases slowly by less than 1 unit of pH during 6 years (*fig. 14*).

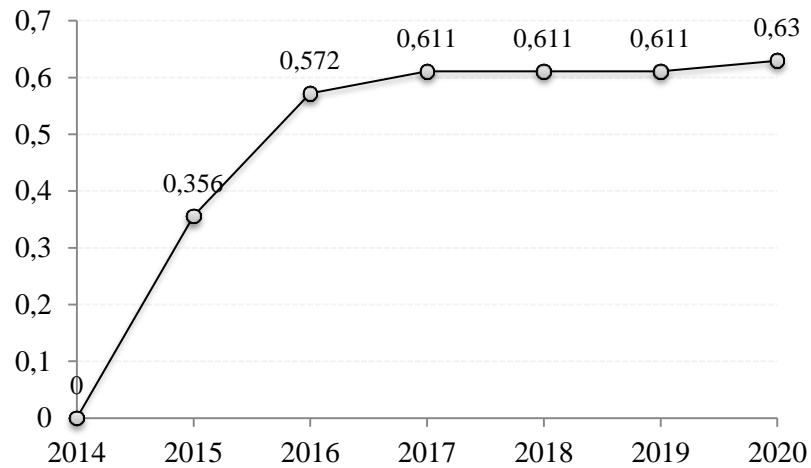


Figure 14. Increase in pH unit with lime applied

During the 2014-2020 simulation, the pH increased from 5.51 (year 2013) to 6.2 pH unit. However, pH increases slowly by itself (*tab. 8*), which is a result of lower deposition.

Table 8. Increase in pH without lime and with lime application after 2013

	pH	
	without lime	with lime
2014	5,58	5,93
2015	5,55	6,15
2016	5,54	6,17
2017	5,63	6,26
2018	5,52	6,17
2019	5,59	6,24
2020	5,55	6,20

Variation in pH is due to different high values of precipitation assumed. Also, the model assumes that lime is added to the water only when pH is lower than 6.15, which is according to the MAGIC library pH of the lake before industrial times (1860). However, there are years when pH is higher than 6.15 due to less deposition from the atmosphere.

5 Conclusions

A model as a simplification of the real processes occurring in a natural environment is difficult to validate. Especially, for predictions for periods prior to the existence of direct measurement records. The acidification model takes into account the deposition of sulphuric and nitric acids directly into the lake and on the catchment area. To simplify the model many processes, such as activity of the oxidizing bacteria (*Acidithiobacillus* sp., *Desulfovibrio* sp.) and their influences on pH, sulphate reduction and partial acid neutralization caused by the bedrock are not included. Moreover, the level of uncertainty with all of these processes can result in increased inaccuracy of the prediction. Even the existing databases used in the modelling are too uncertain to make reliable predictions. But these data are used to test the usefulness of models used to predict action results in the environment. If model outcomes fit the field measurements and correctly predict the ecosystem behaviour, modelling can be made with some degree of confidence. However, the most important action is to better understand the biological, chemical and physical processes occurring in the ecosystems, such as acidification and recovery of aquatic ecosystems, which might help to develop more accurate environmental databases. But, acidification is not a local environmental problem. The load of sulphur is still high, because emissions reductions in other European countries have been much smaller than in Sweden (Håkanson 1999).

Liming the lakes in Sweden has given good results as a method of mitigation. However, limestone application to the catchment area in sufficient quantities might have some adverse effects on the flora and fauna occurring in the area, especially if they are acidophilic. Lakes with low water retention time can re-acidify because of increasing concentrations of acid in the water. Re-acidification can be

predicted by the knowledge of hydrologic processes occurring in the lake. Meanwhile, the variations in hydrology are introducing the uncertainty in predictions. The acidification process can only be stopped by international co-operation and introduction of new, environmental friendly methods to developing countries that will eliminate the amount of used fossil fuels. According to Swedish Environmental Protection Agency the environmental quality objectives related to deposition from human activities will not be achieved before 2020 despite the fact that sulphur atmospheric deposition has fallen. But, even with lowered emissions and deposition, the risk of acidification will still be high because of acidified soils. Also, recovery from acidification in Swedish ecosystems can be influenced by climate change. These changes include increased leaching of N and base cation weathering (Wright et al. 2006). As Moldan (et al. 2013) noticed, increased leaching of NO_3 and chronic deposition of acidic compounds can lead to increase in acidification.

All of these uncertainties make it harder to convince decision makers that further action is necessary. In consequence, most of the EU member states have lowered the emissions only to the required level. That means the reductions will be lower than expected by CLRTAP in Geneva. As a result, all the uncertainties involved in the use of the models should be studied along with the effects of different emission scenarios on the results (EPA, 2000).

An acidification model should account for more factors, but the aim in this context is to develop a model of the system response to the actions introduced within the system. The acidification model needs to be improved, by introducing:

- soil sub-model and forest sub-model that will include chemical reactions occurring in the soil layers (such as denitrification, mineralization and decay) and sulphur, nitrogen, ammonium cycles
- aluminium leaching sub-model and concentration in animals sub-model
- biological reductions and oxidations
- microbial activity

By introducing base cations to the model, it will be possible to achieve more realistic results in pH changes. However, the predictions will still be dependent on the assumptions made for precipitation and deposition. pH might vary a lot depending on the location of the studied area.

Lake Örvattnet was used as an example in modelling because of its history. Lake is in a fact an un-limed lake, which allows predicting the change in pH without previous influences from calcium. However, this lake is used as a reference lake to control biota, and chemistry, which means that it should not be limed in reality. With lower deposition the lake started to recover and pH is slowly increasing and species are re-establishing.

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Appendix I

Appendix I contain all statistical results that are not presented in the report.

Table 9. Expanded equations from table 1

Shortcut	Equation
TF*	<u>SO₄²⁻</u> GRAPH(TIME,2000,1,[593.93,388,371.07,321.29,324.86,382.86,415.71,363.41,484.17,236.61,274.02,367.43,258.23"Min:100;Max:600"])
	<u>NO₃⁻</u> GRAPH(TIME,2000,1,[468.51,365.13,320.08,318.94,276.06,372.49,406.31,337.57,381.13,338.13,292.41,395.41,319.34"Min:100;Max:600"])
P**	GRAPH(TIME,2000,1,[1100,800,700,700,800,600,800,700,900,900,700,700,800"Min:600;Max:1200"])
ASS***	<u>SO₄²⁻</u> GRAPH(TIME,2013,1,[366.6,350.3,334,317.8,301.5,285.2,269,252.7"Min:250;Max:400"])
	<u>NO₃⁻</u> GRAPH(TIME,2013,1,[349.2,325.9,302.6,279.4,256.1,232.8,209.5,186.2"Min:180;Max:350"])
in	<u>SO₄²⁻</u> IF(TIMEIS(2000,2012), (TF_SO4*CA), ASS_SO4) OTHERWISE
	<u>NO₃⁻</u> IF(TIMEIS(2000,2012), (TF_NO3*CA), ASS_NO3) OTHERWISE

SO₄²⁻:

IF(TIMEIS(2000,2012), (LA*TF_SO4), ASS_SO4) OTHER-

WISE

DD

NO₃⁻:

IF(TIMEIS(2000,2012), (LA*TF_NO3), ASS_NO3) OTHER-

WISE

SO₄²⁻:

Lake***** 427498830

NO₃⁻:

343267570

* Yearly deposition data were acquired from SHMI website (2000-2012).

** Yearly climate data were acquired from SHMI website. The precipitation dataset consist of yearly-averaged rainfall measurements.

*** Assumption in deposition after year 2012, were calculated according to the protocol aiming the reduction by 66% compared to the level in 2005. It is assumed that every year since 2012 deposition is decreasing by 16.3 mg/m² for SO₄ and 23.3 mg/m² for NO₃

**** Amounts of the compounds in the lake from the deposition in 1999(in mg)

Because the lake is situated on the border of 4 grids in SMHI database, average values for total fallout were calculated (*fig. 4*) and introduced to the model.

Table 10. Calculation of total fallout for SO₄²⁻ (in mg/m²)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Dep	548.85	388.90	395.58	330.98	340.95	370.00	402.62	334.02	454.12	218.70	273.84	365.47	256.89
	553.39	400.41	377.22	314.59	321.63	388.65	421.96	334.30	458.28	226.42	273.47	363.53	253.97
	515.56	366.31	340.79	305.40	311.00	379.01	413.82	393.89	512.87	246.31	274.01	374.08	262.12
	541.94	396.39	370.70	334.18	325.85	393.78	424.44	391.43	511.43	255.00	274.75	366.66	259.95
Adep	539.93	388.00	371.07	321.29	324.86	382.86	415.71	363.41	484.17	236.61	274.02	367.43	258.23

Table 11. Calculation of total fallout for NO₃⁻ (in mg/m²)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Dep	480.83	369.63	339.06	328.71	287.39	372.45	403.80	324.50	369.35	327.67	287.47	384.24	328.86
	472.12	369.88	325.06	312.70	270.58	378.61	420.38	315.37	367.00	316.67	290.28	375.24	308.64
	456.38	353.15	296.76	306.04	268.86	366.20	397.03	358.87	396.10	362.47	292.90	418.21	326.17
	464.70	367.85	319.43	328.28	277.42	372.70	404.05	351.53	392.06	345.69	297.59	403.96	313.70
Adep	468.51	365.13	320.08	318.94	276.06	372.49	406.31	337.57	381.13	338.13	292.06	395.41	319.34

Dep - Deposition on the surrounding areas; Adep – Average deposition

Table 12. Lakes used to set boundaries

Lake	Coordinations		Catchment area km ²	Lake area km ²	Average mean depth m	Initial pH
	X	Y				
Örvattnet	6626820	1328600	2.980	0.6800	5	6.5
Kuppersjön	6225630	1434230	3.010	0.3400	3	6.1
Salbosjön	6635410	1449550	20.500	5.1800	9.4	5.9
Byxsjön	7074800	1594410	7.560	1.1174	4	6.5
Klutsjön	6892760	1346020	3.610	0.6880	1.14	6.6
Tivsjön	6950560	1524250	13.500	5.1050	12.1	7.1
Sänkesjön	6377340	1370450	0.812	0.0495	1.09	6.2
Abborregöl	6416230	1492870	0.014	0.0325	3.4	6.3
Svartgölen	6430270	154320	0.270	0.0710	3	5.9
Månsrudstjärnet	6591570	1303720	1.200	0.0773	0.75	6.5
MIN			0.014	0.0325	0.75	5.9
MAX			20.500	5.1800	12.1	7.1

Appendix II

Appendix II contains all sub-models and equation not presented in the thesis.

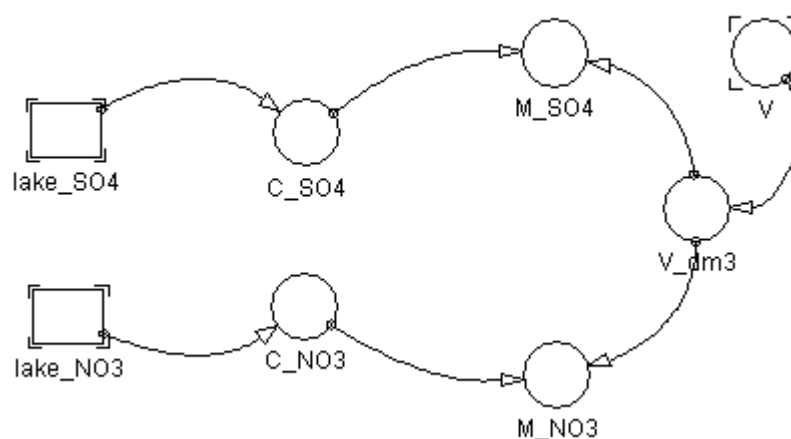


Figure 15. Sub-model for concentration calculations

Table 13. Panel for concentration sub-model driving variables of concentration calculation

Shortcut	Full name	Dimension	Equation
			<u>SO_4^{2-}</u> :
C	concentration in the water	mole	$(\text{lake_SO4} \cdot 0.001) / 98.0785^*$
			<u>NO_3^-</u> :
			$(\text{lake_NO3} \cdot 0.001) / 63.0128^{**}$
			<u>SO_4^{2-}</u> :
M	molarity of compounds	M	$\text{C_SO4} / \text{V_2}$
			<u>NO_3^-</u> :
			$\text{C_NO3} / \text{V_2}$
V_2	volume of the lake	dm^3	$\text{V} \cdot 1000$

*98.0785 is a molar mass of SO_4

**63.0128 is a molar mass of NO_3

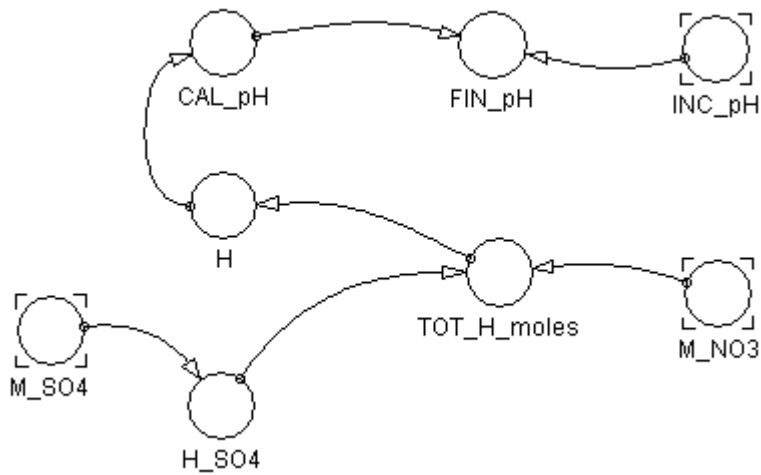


Figure 16. Sub-model for pH calculations

Table 14. Panel for sub-model driving variables of pH calculation

Shortcut	Full name	Dimension	Equation
FIN_pH	final pH of the lake	-	$CAL_pH + INC_pH$
CAL_pH	calculated pH from the deposition data	-	$-\text{LOG}(H)$
H	amount of H ⁺ ions	moles	TOT_H_moles
TOT_H_moles	total moles of H ⁺ in the water	moles	$H_SO4 + M_NO3$
H_SO4	total moles from SO ₄	moles	$M_SO4 \cdot 2$

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