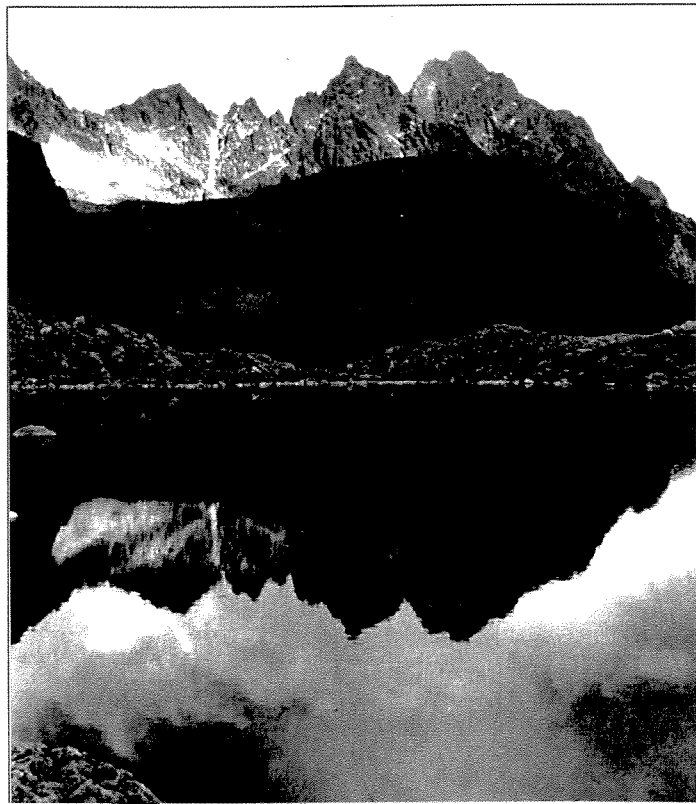# Acid Rain Research

Mapping critical
levels/loads for
the Slovak Republic

NIVA

NIVA - REPORT

Norwegian Institute for Water Research   NIVA

Report Title:	Date:	Printed:
Mapping critical levels/loads for the Slovak Republic	Jan./1995	NIVA 1995

Topic group:

Acid Precipitation

Author(s):

Dušan Závodský	SHMÚ	Boris Cambel	VÚZH
Gabriela Babiaková	SHMÚ	Štefan Rehák	VÚZH
Marta Mitošinková	SHMÚ	Bente M. Wathne	NIVA
Katarína Pukanèíková	SHMÚ	Arne Henriksen	NIVA
Peter Ronèák	SHMÚ	Harald Sverdrup	Lund University
Dušan Bodiš	GÚDŠ	Kjetil Tørseth	NILU
Stanislav Rapant	GÚDŠ	Arne Semb	NILU
Jozef Mind'áš	LVÚ	Dan Aamlid	NISK
Jaroslav Škvarenina	LU		

Geographical area:

Slovakia

Pages:	Edition:
74	

Client(s):	Client ref.:
Norwegian Ministry of Environment	

Abstract:

As a part of the Agreement on Environmental Cooperation between Norway and Slovakia, a project "Mapping Critical Levels/Loads for Slovakia" has started. The results from the first pilot phase are presented. A pilot area (90 grid squares 10 x 10 km) in the mountainous Central Slovakia was chosen. Critical loads for forest soils, surface and groundwaters as well as their exceedance were calculated, using steady-state mass balance model PROFILE for forest soils and steady-state water chemistry method for surface and ground waters. Critical load of acidity exceedances (5 percentile) for forest soils were estimated in 80% of the pilot area. The most frequent exceedance values were found in interval 0.5-2.0 keq.ha^{-1}yr^{-1}. The critical sulphur deposition (calculated on the basis of sulphur fraction) was exceeded in 52% of cases. No acidity exceedance for neither surface nor groundwaters was found in any grid square. The project is planned to continue in 1995.

4 keywords, Norwegian

1. Tålegrenser
2. Slovakia
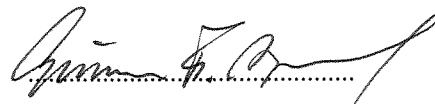3. Jord
4. Vann

4 keywords, English

1. Critical loads of acidity
2. Slovak Republic
3. Soil
4. Water

Project manager

Bente M. Wathne

Bente M. Wathne

For the Administration

Gunnar Aasgaard

Gunnar Aasgaard

MAPPING CRITICAL LEVELS/LOADS FOR

THE SLOVAK REPUBLIC

O-94142

Dušan Závodský [1]
Gabriela Babiaková [1]
Marta Mitošinková [1]
Katarina Pukaneiková [1]
Peter Roncák [1]
Dušan Bodiš [2]
Stanislav Rapant [2]
Jozef Mind'áš [3]
Jaroslav Škvarenina [4]
Boris Cambel [5]
Štefan Rehák [5]
Bente M. Wathne [6]
Arne Henriksen [6]
Harald Sverdrup [7]
Kjetil Tørseth [8]
Arne Semb [8]
Dan Aamlid [9]

[1] SHMÚ,   Slovak Hydrometeorological Institute, Jeséniova 17, 833 15 Bratislava, Slovakia
[2] GÚDŠ,   Dionýz Štúr Institue of Geology, Mlynská dolina 1, 817 04 Bratislava, Slovakia
[3] LVÚ   Forest Research Institute, T.G. Masaryka 22, 960 92 Zvolen, Slovakia
[4] LU   Forest University, Zvolen, Slovakia
[5] VÚZH   Research Institute for Irrigation, Ľubovnianska 3, 851 07 Bratislava, Slovakia
[6] NIVA   Norwegian Institute for Water Research, Brekkevn. 19, P.O.B. 173 Kjelsås, N-0411 Oslo, Norway
[7]   Lund University, Dept. of Chemical Engineering II, P.O.B. 124, S-22100 Lund, Sweden
[8] NILU   Norwegian Institute for Air Research, Instituttvn. 18, P.O.B. 100, N-2007 Kjeller, Norway
[9] NISK   Norwegian Institute for Forest Research, Høgskolevn. 12, N-1432 Ås, Norway

TABLE OF CONTENTS Page

PREFACE

As a part of the Agreement on Environmental Cooperation between Norway and Slovakia a project "Mapping Critical Levels/Loads for Slovak Republic" was established in 1994, with participants from the Norwegian Institute for Water Research (NIVA), and the Slovak Hydrometeorological Institute, with contributions from the University of Lund, Sweden, the Norwegian Institute for Air Research (NILU), Norwegian Forest Research Insitute (NISK), the Dionýz Štúr Institute of Geology in Bratislava, the Forest Research Institute in Zvolen, the Forest University in Zvolen and the Research Institute for Irrigation in Bratislava.

The main objective of this project is Norwegian assistance to the start of the Slovak project for critical loads/levels calculation

- to provide consultation as well as calculation methods
- personal training of Slovak scientists
- harmonisation of Norwegian and Slovak approaches.

The first visit of Norwegian specialists to Bratislava was in June 1994 followed by a Norwegian/Slovak Workshop in Oslo 5 - 7 October 1994. The Workshop started out with scientific lectures which were given by the prominent Scandinavian experts, followed by practical calculations of Critical loads for forest soils, surface and ground waters on the basis of the Slovak input data.

This report presents the results from mapping the pilot area (approximately 20 % of the Slovak territory). In annex 4 and 5 a summary of the prorgramme for the Workshop in Oslo 5 - 7 October 1994 is presented. Annexes 5 - 9 summaries the most central presentations for the practicle work during the Workshop. The project is planned to continue in 1995.

SUMMARY

There is a considerable interest in determining the effects of acidic deposition on various environments, e.g. forest soils and surface waters. One of the important issues is to evaluate and set limits to the deposition of acidic compounds according to their effects on the ecosystem. The limit, or critical loads of acidity to an environment, is defined as "the highest deposition of acidifying compounds that will not cause changes leading to long-term harmful effects on ecosystem structure and function".

As a part of the Agreement on Environmental Cooperation between Norway and Slovakia a project "Mapping Critical Levels/Loads for Slovakia" was started. The results from the first pilot phase of the project are presented in this report. A pilot area (90 grid squares 10 x 10 km) in the mountainous Central Slovakia was chosen. The geological structure of this area composes practically all of the most important geological units, in the structure of Western Carpathians. All the grids are fully or partially covered by forest. Spruce, beech and oak are the prevailing forest species.

Critical loads for forest soils, surface and groundwaters as well as their exceedances were calculated, using steady-state mass balance model PROFILE for forest soils and steady-state water chemistry method for surface and groundwaters.

The most frequent values of critical loads of acidity (5 percentile) for forest soils were in the interval 0.5-2.0 $keq.ha^{-1}.yr^{-1}$. Exceedance of critical loads of acidity was calculated for 80 % of the grids. Because of high sulphur fraction the critical load maps for sulphur as well as for sulphur deposition were nearly identical to those for acidity. However, the exceedance of critical sulphur deposition was found only for 52 % of the grids.

Critical loads of acidity for surface waters were found to be systematically higher than for ground waters. Correlation (r =0.69) between these critical loads was estimated. No acidity exceedance for surface nor ground waters was found.

Critical loads of acidity for waters in the whole pilot area are significantly higher compared to those for forest soils. The forest soil is clearly the most sensitive ecosystem in the area considered. The critical loads reflect to a large extent the geological composition of the study area.

1. INTRODUCTION

There has been considerable scientific and political interest in determining the effects of acid deposition on various environments. Beyond the linkage of atmospheric deposition of strong acids to the effects on forests, lakes, crops, human health and materials, one of the important issues has been in evaluating and setting limits for the deposition of acidic compounds. These limits, or the critical loads of acids in the environment, is defined as "the highest deposition of acidifying compounds which will not cause changes leading to long-term harmful effects on ecosystem structure and function" (Nilsson and Grennfelt, 1988).

Criteria for "unacceptable change" are set relative to effects on terrestrial and aquatic organisms. Both sulphur and nitrogen contribute to the total input of acidifying compounds to an ecosystem. The ratio of sulphur to nitrogen can, therefore, vary without changing the critical load for acidifying compounds. The purpose of determining critical loads is to set goals for future deposition rates of acidifying compounds such that the environment is protected. Critical loads are determined separately for different receptors. Forest soils, ground and surface waters are considered as the most sensitive.

Under the auspices of the Convention on Long - Range Transboundary Air Pollution (the "Geneva Convention"), a "Task Force for Mapping the Critical Loads and the Areas where the Critical Loads are Exceeded" has been formed. A manual for calculating critical loads and their exceedances both for forest soils and for surface waters has been worked out (Sverdrup et al. 1990). Norway has mapped the critical loads of acidity and the exceedance for sulphur to surface water, and a project under the Nordic Council of Ministers has mapped critical loads and their exceedance for surface waters for the three Nordic countries Finland, Norway and Sweden (Henriksen et al. 1990).

The Slovak Republic was established at the beginning of 1993 after the disintegration of the Czechoslovak Federal Republic. Projects of critical load mapping was stagnant. For this reason, as a part of the Agreement on Environmental Cooperation between Norway and Slovakia, a project "Mapping Critical Levels/Loads for Slovakia" was launched in 1994, with participants from the Norwegian Institute for Water Research (NIVA) and the Slovak Hydrometeorological Institute with contributions from the Norwegian Institute for Air Research (NILU), the Norwegian Forest Research Institute (NISK), the Lund University, the Dionýz Štúr Institute of Geology in Bratislava, the Forest Research Institute in Zvolen, the Forest University in Zvolen and Research Institute for Irrigation in Bratislava. The Norwegian partners were asked:

-        to provide assistance to start the Slovak mapping project
-        to provide calculation methods
-        to provide consultation and personal training for Slovak scientists
-        to harmonize the Norwegian and Slovak approaches.

The project is planned as a two years activity. The first visit of Norwegian specialists in Bratislava was realized in June 1994. The Norwegian/Slovak Workshop in Oslo took place 5 - 7 October 1994. Background scientific lectures, appropriate softwares of model PROFILE and SSWC method, including personal training were provided to Slovak partners. In this report the results of mapping critical loads for forest soils, surface and groundwaters from the pilot area (approximately 20 % of the Slovak territory) are presented.

2. DEFINITIONS

Critical loads for "unacceptable change" are set in relation to effects on terrestrial and aquatic organisms. Some useful definitions are given in the box.

DEFINITIONS

Critical load: The highest load that will not lead to long-term harmful effects on biological systems, such as forest decline or decline and disappearance of fish populations.

Receptor: An ecosystem which may potentially be affected by atmospheric inputs of sulphur and nitrogen (soil, ground water, surface water).

Biological indicator: Selected organism(s) or populations which are sensitive to chemical changes as a result of atmospheric inputs of sulphur and nitrogen (forest, fish, invertebrates).

Critical chemical value: The value of a critical chemical component or combinations of components above or below no rise to a harmful response in a biological indicator is given (pH, ANC, Al/Ca ratio).

The critical load definition provides a framework for making numerical estimates of the loads at which adverse effects occur. Such estimates may be based upon a number of different methods and the selection of method depends to a large extent upon the receptor chosen and the availability of relevant data for the calculations. The effects on sensitive biological indicators are used to identify harm to forest and freshwater systems. Organisms are often efficient "integrators" of the chemical conditions in their environment and may thus provide convenient means of measuring effects. All the methods for calculating the critical loads for acidity of freshwaters use chemical data, often making assumptions regarding the water chemistry to acidification. The critical chemical value is based on present knowledge of the ecological tolerance of sensitive biological species to water chemistry.

3. CALCULATION METHOD

3.1. Receptors mapped: Forest soils

Critical loads of acidity, CL(A), for forest soils in the pilot area of Slovakia were calculated using the steady state mass balance model (SSMB), implemented as the PC version of the PROFILE model (Sverdrup et al. 1990, Sverdrup and Warfwinge 1992, 1993, 1994).

The input data needed for calculation:

- precipitation
- runoff   - nitrogen uptake
- sulphur deposition   - temperature
- NO_3^- deposition   - weathering rate
- NH_4^+ deposition   - fraction of weathering being Na
- base cation deposition   - thickness of organic layer
- base cation uptake   - thickness of E/A or second layer

CL(A) and exceedance of critical loads of acidity Ex(A) are direct outputs from the PROFILE model. The critical load values in this report are calculated as 5 percentile values from ecosystem cover on a 10 x 10 km grid.

Critical load of sulphur, CL(S), has been defined from the critical load of acidity by allocating a part of the allowable acidity deposition to the sulphur deposition:

$$CL(S) = S_f \cdot CL(A)$$

where S_f is sulphur fraction, defined as:

$$S_f = \begin{cases} \dfrac{S_{dep}}{S_{dep} + N_{dep} - N_u - N_i} & \text{if } N_{dep} > N_u + N_i \\ 1 & \text{otherwise} \end{cases}$$

where S_{dep} = present sulphur deposition
     N_{dep} = present nitrogen deposition
     N_u = net uptake of nitrogen in the tree biomass
     N_j = net immobilization of nitrogen in the root zone

Base cation deposition and uptake, BC_{dep} resp. BC_u , have been included in the calculation of the sulphur exceedance to allow a direct comparison with modelled deposition patterns. To distinguish this new value from CL(S) the term critical deposition of sulphur CD(S), has been defined as:

$$CD(S) = Sf \cdot (CL(A) + BC_{dep} - BC_u)$$

The exceedance of critical deposition of sulphur is given by:

$$Ex(S) = S_{dep} - CD(S)$$

3.2 Receptors mapped: Surface and groundwater

The basic steady state surface water chemistry method (SSWC) is based on the fact that sulphate found in surface water originates largely from sea salt spray and polluted deposition. The method gives ways of correcting for sea salt and a minor contribution from geological sources and enables calculations of the atmospheric contribution of sulphate in the water (Henriksen *et al.* 1988,1990). This sulphate concentration is then used to obtain the weathering rate of the catchment. The chemical data from the Slovak pilot area indicate that the geology supplies a significant amount of sulphate to the water. This sulphate is assumed to be balanced largely by base cations BC (Ca +Mg). Thus to calculate the critical load, the method must be modified. The atmospheric contributed sulphate in the surface and ground water is estimated by multiplying the sulphur deposition by the ratio of precipitation to runoff. The difference between this value and the sulphate concentration is then assumed to be geologically supplied sulphate. Since this component is balanced by Ca + Mg, this amount must be deducted from the concentration of base cations to obtain those due to weathering and ion exchange processes. To estimate the ion exchanged base cations a modified F - factor has been used because of the very high weathering rate in the surface and ground water. Ignoring nitrate concentration the following calculation method results:

$$SO_{4dep} = S_{dep}.P/Q$$

where S_{dep} = present sulphur deposition in $keq.km^{-2}.yr^{-1}$
P = yearly precipitation in m
Q = yearly runoff in m

$$BC_{geol} = SO_{4r} - SO_{4dep}$$

where BC_{geol} = base cations of geological origin
SO_{4r} = sulphate concentration in runoff water

$$BC_{wt} = BC_t - BC_{geol}$$

where BC_{wt} = present weathering rate
BC_t = present Ca + Mg concentration in runoff water

The F - factor is defined as the change in base cation concentration due to a change in the concentration of sulphate

$$F = BC_{wt} / S$$

where S = base cation concentration at which F=1. A value of 4 $meq.l^{-1}$ for S has been used in this report.

Then : $BC_W = BC_{wt} - F.SO_{4dep}$

The critical loads of acidity (CL) and critical loads exceedance (CL-Ex) are then given:

$$CL = BC_W . Q . 10 \qquad [keq.ha^{-1}.yr^{-1}]$$

$$CL\text{-}Ex = S_{dep} - CL \qquad [keq.ha^{-1}.yr^{-1}]$$

The input data needed for calculation:

- precipitation
- runoff   - sulphate concentration in surface - and/or groundwaters
- sulphur deposition   - basic cation concentration in surface-and/or groundwaters

4. LOCALIZATION OF THE SLOVAK PILOT AREA

Grid size for the construction of critical load maps for Slovakia corresponds to EMEP grid. The EMEP grid cell 50 x 50 km was subdivided into 25 cells, it means that a grid distance of approximately 10 km was chosen. Grids are numbered using a Slovak system of numbering (see ANNEX 1). The pilot area is situated in the Central Slovakia (the map sheet No 36 in scale 1:200 000, 90 grid cells). The pilot area represents about 20 % of the whole county. The pilot area includes the following geographical units: In the northern part from West to East -Malá Fatra (highest summit 1574 m a.s.l.) and the Low Tatras (highest summit Ïumbier 2043 m a.s.l - the highest point of the whole area). In the southern part from West to East - Štiavnické vrchy (highest summit 1009 m a.s.l.), Kremnické vrchy (highest summit 1265 m a.s.l.), Javorie (highest summit 1044 m a.s.l.), Pahorkatina (highest summit 1458 m a.s.l.), Veporské vrchy (highest summit 1439 m a.s.l.) and in the south-eastern part Revúcka Pahorkatina (highest summit 602 m a.s.l.). The lowest location in the south-eastern part of the pilot area is only 200 m a.s.l.

The largest part of this territory belongs to the catchment of River Hron. Northern slopes of the Low Tatras are drained by River Váh and south-eastern part of the area belongs to the catchment of River Ipel.

Geological structure of the area under the study is composed practically of all the most important geological units, participating in the structure of Western Carpathians. From the geological point of view, the mountainous areas of the region may be divided into the following basic parts:

     I. region of ore mountains
     II. region of Central Slovakian neovolcanics

Lowlands region can be divided into the regions of:

     III. intramountaneous depressions
     IV. alluvial deposits of larger rivers

1. Region of ore mountains - the Low Tatras, Malá Fatra, Velká Fatra, Slovak Ore Mountains are in their central parts underlain by various granites, granodiorites and gneisses and to a lesser

extent by amphibolites. Marginal parts of the mentioned mountains are floored by Mesozoic, mainly carbonic rocks, lying in the cover or nappe position

- limestones
- dolomites
- marls and marly limestones

II. Region of Central Slovakian neovolcanics - Štiavnické vrchy and Kremnické vrchy are composed of different varieties of neovolcanic rocks, mainly of andesites, rhyolites and their tuffs.

III. Intramountaneous depressions - are floored predominantly by Tatriary sediments - gravels, sands, clays, sandstones and claystones.

IV. Alluvial deposit of larger rivers - Váh and Hron and their tributaries are underlain predominantly by gravels and sands.

All the grids are fully or partially covered by forest. Three main forest areas (spruce, beech and oak) can be found on the pilot territory.

5. DATA SOURCES

The following data sources have been used for the mapping purpose:

- Geological map of Slovakia
- Geochemical Atlas of Slovakia
- Data base of Dionýz Štúr Institute of Geology, Bratislava
- Soil map of Slovakia (Hraško et al., 1993)
- Slovak forestry inventory (Forest Research Institute, Zvolen)
- Data base of Slovak Hydrometeorological Institute
(precipitation, temperature, runoff, atmospheric deposition and water quality data)

For the assessment of different input parameters to the mass balance equations the following approaches were used:

Base cation release by weathering

Due to lack of soil mineralogy data, the base cation weathering rates have been calculated on the basis of bedrock geology (14 bedrock minerals were taken into account), soil texture, wetness and temperature, using PROFILE model version "Multimashine". SW was provided by prof. Sverdrup. The model estimated weathering rates, w_0 , were corrected according to recommendation for high precipitation area of Vienna seminar in 1993 (UBA Report 93 - 083):

$$w = w_0 \cdot 10^{\left(\frac{A}{281} - \frac{A}{273+T}\right)}$$

where   A = 3500 was used
         T = temperature in Centigrades

Precipitation	-	Long-term isohyetal lines map of Slovakia was taken.
Runoff	-	Long-term average specific runoff lines map of Slovakia was used.
Temperature	-	The last decade average temperature isolonies map was constructed for the area under the study

Deposition data

Net deposition of sulphate, nitrate, ammonium and base cations have been estimated from Slovak EMEP concentrations and grid precipitation amount. Dry and occult deposition, including leaching effect of base cations from assimilation apparatus have been estimated from wet deposition using enrichment factor:

H^+, sulphate, basic cations   factor = 2
nitrate and ammonium   factor = 1.5

The factor values respect the empirical results from some Slovak forest research stands and correspond to the results from Austria, Germany and the Scandinavian countries. (Škvarenina,1993,1994; Paèes, 1995; Moldan, 1987)

Nitrogen and base cation uptake in biomass

The forest harvest data as well as the data on element contents in trees have been used. Percentage of species in each grid have been respected.

Nitrogen immobilization in soils

Nitrogen immobilization has been estimated upon the basis of C:N ratio of soil types according to the German approach.

Thickness of organic layer, xH, thickness of E/A or second layer, xE, and granularity of soils, Z (% of particles < 0,001 mm)

According to percentage of soil sub-types in each grid. The data from following table have been used:

	Soil units	xH m	xE m	Z %
H_1	Eutric Cambisols to Dystric Cambisols,associated with Rankers and with Stagno-gleyic Cambisols	0.15	0.20	30
H_3	Eutric Cambisols, ass. with Calcaric Regosols	0.15	0.20	30
H_6	Stagno-gleyic Cambisols, ass. with Planosols, local Gleysols	0.15	0.20	30
H_7	Dystric Cambisols, ass. with Rankers	0.15	0.20	30
H_8	Dystric Cambisols, ass. with leached Rendzinas	0.15	0.20	30
H_{10}	Dystric Cambisols, ass. with Spodo-dystric Cambisols and with Rankers	0.15	0.20	30
H_{11}	Stagno-gleyic Cambisols, local Dystric Planosols and Dystric Gleysols	0.15	0.20	30
I_1	Albic Luvisols to Albo-gleyic Luvisols, ass. with Plano-gleyic Luvisols	0.15	0.10	20
I_2	Albic Luvisols to Albo-gleyic Luvisols, ass. with Rendzinas	0.15	0.10	20
I_3	Albic Luvisols, ass. with Eutric Cambisols, local Pararendzinas	0.30	0.10	20
I_4	Albo-gleyic Luvisols, ass. with Plano-gleyic Luvisols, local Cambisols	0.15	0.10	20
R_1	Rendzinas and Calcic Cambisols ass. with Calcaric Lithosols	0.20	0.25	0
R_2	(Ortic and Lithic) Rendzinas and Chromic Rendzinas	0.20	0.15	0
R_3	Leached Rendzinas and Calcic Cambisols,ass. with Calcaric Lithosols and Rock-debris Rendzinas	0.20	0.25	0
R_4	Leached Humic and Tangel Rendzinas, ass. with Calcaric Lithosols	0.20	0.25	0
R_5	Pararendzinas and Regosols, ass. with eroded Orthic Luvisols	0.20	0.25	0
R_6	Pararendzinas, Regosols and Calcic Cambisols	0.20	0.25	0
P_1	Ferro-Orthic Podzols, ass. with Lithosols and with Rankers	0.10	0.10	10
P_2	Spodo dystric Cambisols, ass. with Rankers and with Lithosols	0.10	0.10	10
P_3	Ferro-humic Podzols ass. with Histo-humic Podzols and with Rankers	0.10	0.10	10
N_1	Eutric Fluvisols, ass. with Fluvi-eutric Gleysols	0.25	0.25	0
N_3	Calcaric Fluvisols ass. with Fluvi-calcaric Gleysols	0.25	0.25	0
N_4	Fluvi-eutric Gleysols and Verti-eutric Gleysols, ass. with other Gleys.	0.55	0.25	0
N_5	Fluvi-eutric Gleysols, ass. with other Gleysols	0.55	0.05	0
L_3	Fluvi-calcaric Phaeozems, ass. with calcaric Fluvi-haplic and Fluvi-vertic Phaeozems and with calcaric Fluvi-mollic Gleysols, local Eutric and Lepto-eutric Histosols	0.35	0.50	25
L_4	Fluvi-mollic Gleysols, ass. with Fluvi-gleyic Phaeozems and with Eutric Gleysols	0.40	0.50	40
9_1	Eutric to Dystric Planosols and Plano-gleyic Luvisols	0.45	0.20	15
9_3	Dystric Planosols and Stagno-gleyic Planosols, ass. with Histo-humic Planosols	0.45	0.20	15
r	Dystric Lithosols and Rankers	0.05	0.05	0
M_2	Orthic Luvisols and eroded Orthic Luvisols, ass. with Calcaric Regosols and Pararendzinas	0.10	0.20	15

Sulphate and basic cation concentrations in surface and ground waters

Hydrochemical data base of Slovak Hydrometeorological Institute and Dionýz Štúr Institute of Geology in Bratislava have been used.

The input data for mapping for forest soils (5 percentile) are summarized in ANNEX 2.

6. RESULTS

The results of critical loads and their exceedances calculation from the Slovak pilot area can be found in ANNEX 3, which contains the following map:

Receptor - forest soils
- Critical loads of acidity (5 percentile)
- Exceedance of critical loads of acidity (5 percentile)
- Critical loads of sulphur (5 percentile)
- Critical deposition of sulphur (5 percentile)
- Exceedance of critical sulphur deposition (5 percentile)

Receptor - surface water
- Critical loads of acidity
- Exceedance of critical loads of acidity

Receptor - ground water
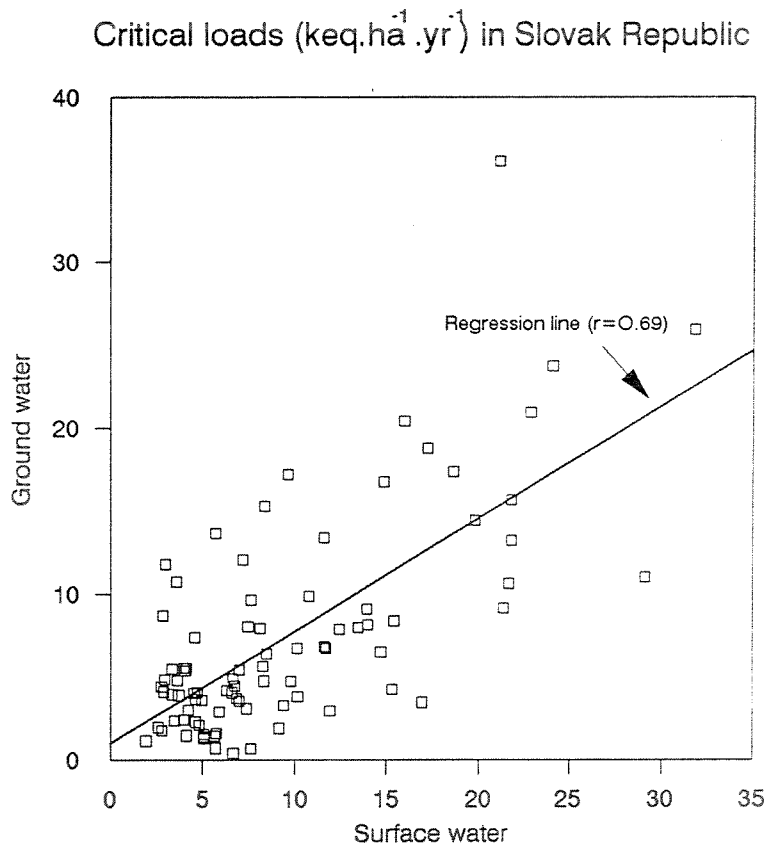- Critical loads of acidity
- Exceedance of critical loads of acidity

Critical load values are expressed in $keq.ha^{-1}.yr^{-1}$. The colour and scale were chosen to allow expression of the differences within the study area. The scale has been shifted to higher values compared to international presentation of critical loads.

The most frequent values of critical loads of acidity for forest soils were in the interval 0.5 -2.0 $keq. ha^{-1}.yr^{-1}$ (52 % of grids). The southern part of the pilot area was the most sensitive (geology e.g. neovolcanies). Marginal part of the grids (8 %) situated in the north-western part of the study area (geology limestones and dolomites) exhibited critical loads values higher than 4 $keq.ha^{-1}.yr^{-1}$. Exceedance of critical loads of acidity was calculated for 80 % of the grids. Because of high sulphur fraction the critical load maps for sulphur as well as for sulphur deposition were nearly identical to those for acidity. However, the exceedance of critical sulphur deposition was not so frequent (only 52 % of the grids). Nitrogen thus plays an important role in these areas.

The critical loads of acidity for surface waters are systematically higher than for ground waters (Figure 1). Correlation (r = 0.69) between these critical loads was found. The calculated values of exceedance show high negative figures for most of the pilot area, indicating that there exists a reserve for additional acid deposition. One grid indicated critical loads exceedance. This grid was not taken into account and will be revaluated. The critical loads reflect the chemical composition of natural waters given by geology. The relative higher sensitivity of the southern part of the pilot area could be partially caused by slow water velocity in the aquifer.

Critical loads of acidity for waters in the whole pilot area are significantly higher compared to those for forest soils. The forest soil is clearly the most sensitive ecosystem in the area considered.

The presented critical loads for forest soils were calculated on the basis of parent rocks geology. This approach involves much uncertainty (mountainous character of territory - effect of erosion). All weathering rates will be recalculated in the near future when soil mineralogical and chemical data from a new pedological and pedochemical map of Slovakia will be available.

Figure 1. Comparison of critical loads for surface and ground water for the pilot area of Slovakia

REFERENCES

Critical Loads of Acidity for High Precipitation Areas. 1993. UBA-Reports 93-083, Vienna, 16 s.

Downing, R.J. & Hettelingh, J.P. & de Smet P.A.M. 1993. Calculation and mapping of critical loads in Europe. Status Report 1993. RIVM Bilthoven, 163 s.

Henriksen, A., Lien, L., Traaen, T.S., Sevaldrud, I.S., and Brakke, D.F. 1988. Lake acidification in Norway - Present and predicted chemical status. Ambio, 17, 17, 259-266.

Henriksen, A., Kämäri, J., Posch, M., L"vblad, G., Forsius, M., and Wilander, A. 1990. Critical loads to surface waters in Fennoscandia. Nordic Council of Ministers, Miljørapport 1990:17. Copenhagen, 44 p.

Hettelingh, J.P. & Downing, R.J. & de Smet, P.A.M. 1991. Mapping critical loads for Europe. CCE Technical Report No.1. Coordination Center for Effects, National Institute of Public Health and Environmental Protection, Bilthoven, 163 s.

Hraško, J. et al. 1993. Soil map of Slovakia, Bratislava.

Moldan, B.& Dvoráková, M. 1987. Atmospheric deposition into small drainage basis studied by geological survey. In: B. Moldan a T. Paces (eds.), GEOMON-International Workshop on Geochemistry and Monitoring in Representative Basins, Geological Survey, Prague 127-129.

Nilsson, J. & Grennfelt, P. 1988. Critical loads for sulphur and nitrogen. Miljørapport 1988, No.15. Nordic Council of Ministers, Copenhagen.

Pačes, T. 1985. Sources of acidification in Central Europe estimated from elemental budgets in small bassins. Nature 315, 6014, 31-36.

Posch, M. et al.: Guidelines for the computation and mapping of critical loads and exceedances of sulphur and nitrogen in Europe. TF on Mapping UN ECE, May 1993.

Sverdrup, H. & de Vries, W. & Henriksen, A. 1990. Mapping critical loads. Nordic Council of Ministers, Miljørapport 1990:14. Copenhagen, 125 p.

Sverdrup, H. & de Vries, W. 1994. Calculation critical loads for acidity with the simple mass balance method. Water, Air and Soil pollution 72, 143-162.

Sverdrup, H. & Warfvinge, P.: Past and future changes in soil acidity and implications for forest growth under different deposition scenarios. Ecological Bulletin. Task Force on Mapping. 7th Meeting, 1-2 June 1992, Berlin (in press.)

Sverdrup, H., & Warfvinge, P. 1995. Critical loads of acidity for Swedish forest ecosystems. Ecological Bulletin 44: XX-22.

Škvarenina, J. 1993. Horizontal precipitation in fir - beech ecosystem as a source of deposition of some chemical elements (in slovak). PhD thesis, Zvolen, 170 p.

Škvarenina, J. 1994. Determination of atmospheric inputs in Abieto - Fagetum ecosystem by balance method (in slovak). In: Zborník prác z Bioklimatologických pracovných dní, 3-5.11.1993, Nitra, SBkS pri SAV Bratislava, p. 99-104.

Warfvinge, P. & Sverdrup, H. 1992. Calculation critical loads of acid deposition with PROFILE - A steady state soil chemistry model. Water, Air and Soil Pollution, 63, 119-143

Wathne, B.M., Mill, W.A., Kot, M.,Rzychon, D.,Henriksen, A., and Tørseth, K. 1993. Critical loads of acidity to lakes in the Polish Tatra. NIVA Report 33, 37 s.

Slovak Pilot Area: Numbering of grids
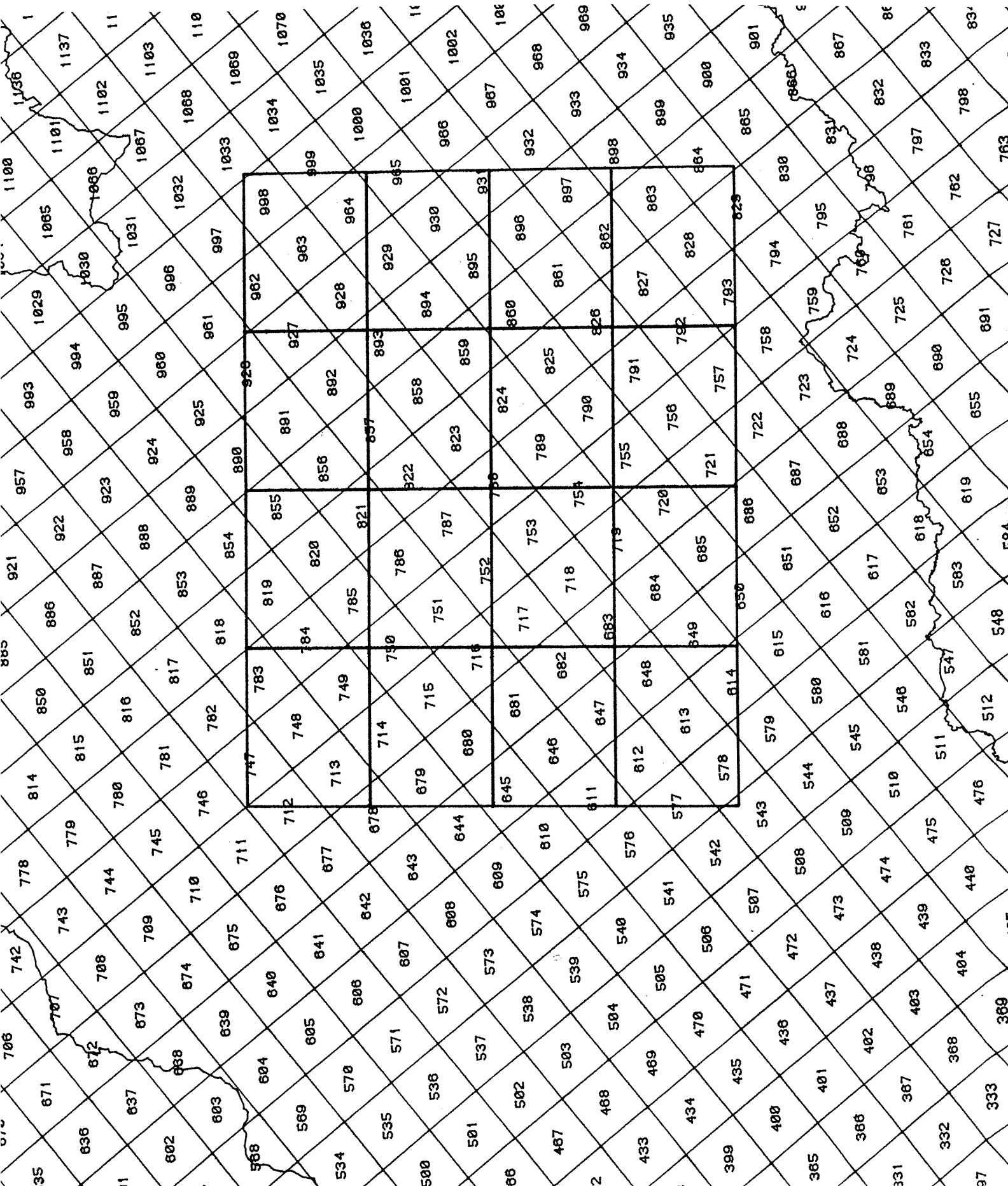
Critical loads of acidity for forest soils - input data for calculation

No.   - number of grid
Prec. - precipitation (m.yr^{-1})
Runoff - (m.yr^{-1})
S   - sulphur deposition (keq.ha^{-1}.yr^{-1})
NO$_3^-$ - deposition of nitrate (keq.ha^{-1}.yr^{-1})
NH$_4^+$ - deposition of ammonium (keq.ha^{-1}.yr^{-1})
BC$_{dep}$ - base cation deposition (keq.ha^{-1}.yr^{-1})

BC$_u$ - base cation uptake (keq.ha^{-1}.yr^{-1})
N$_u$ - nitrogen uptake (keq.ha^{-1}.yr^{-1})
T   - temperature (° C)
w   - weathering rate (keq.ha^{-1}.yr^{-1})
xH - thickness of organic layer (m)
xE - thickness of E/A or second layer (m)
N$_i$ - nitrogen imobilization in the root zone(keq.ha^{-1}.yr^{-1})

No.	Prec.	Runoff	S	NO$_3$	NH$_4$	BC$_{dep}$	BC$_u$	N$_u$	T	w	xE	xH	N$_i$
578	0.75	0.19	1.81	0.54	0.69	0.92	0.96	0.74	8.5	1.37	0.19	0.29	0.5
611	0.80	0.37	1.94	0.58	0.74	0.98	0.73	0.66	7.5	1.24	0.20	0.30	0.5
612	0.80	0.40	1.94	0.58	0.74	0.98	0.61	0.55	8.5	2.74	0.20	0.25	0.5
613	0.80	0.42	1.94	0.58	0.74	0.98	0.73	0.64	8.0	1.30	0.20	0.30	0.5
614	0.65	0.26	1.57	0.48	0.60	0.78	0.99	0.76	8.5	1.37	0.20	0.30	0.5
645	1.00	0.50	2.43	0.73	0.92	1.22	1.00	0.69	6.5	1.11	0.20	0.30	0.5
646	0.70	0.32	1.70	0.51	0.65	0.98	0.75	0.67	9.0	1.44	0.16	0.20	0.5
647	0.75	0.37	1.81	0.54	0.69	0.92	0.86	0.64	8.5	1.37	0.18	0.19	0.5
648	0.75	0.40	1.81	0.54	0.69	0.92	0.66	0.67	8.5	0.03	0.20	0.30	0.5
649	0.75	0.29	1.81	0.54	0.69	0.92	1.01	0.78	8.0	1.30	0.20	0.30	0.5
650	0.55	0.22	1.33	0.41	0.51	0.68	0.99	0.79	9.0	1.44	0.20	0.30	0.5
679	0.70	0.30	1.70	0.51	0.65	0.88	0.71	0.56	8.0	1.30	0.21	0.25	0.7
680	0.85	0.45	2.06	0.63	0.78	1.04	0.67	0.57	7.0	1.17	0.21	0.24	0.5
681	0.80	0.34	1.94	0.58	0.74	0.98	0.75	0.64	7.5	2.38	0.20	0.30	0.5
682	0.70	0.34	1.70	0.51	0.65	0.88	1.02	0.66	9.0	1.44	0.21	0.26	0.5
683	0.75	0.28	1.81	0.54	0.69	0.92	1.01	0.69	8.0	1.30	0.20	0.26	0.5
684	0.70	0.25	1.70	0.51	0.65	0.88	1.07	0.81	8.0	1.30	0.20	0.25	0.5
685	0.70	0.28	1.70	0.51	0.65	0.88	1.07	0.81	8.0	1.30	0.20	0.28	0.5
713	0.85	0.40	2.06	0.63	0.78	1.04	0.66	0.55	7.5	3.61	0.24	0.05	0.5
714	0.75	0.41	1.81	0.54	0.69	0.92	0.42	0.42	7.5	1.24	0.24	0.19	0.5
715	0.90	0.47	2.17	0.66	0.83	1.12	0.38	0.37	6.5	1.11	0.20	0.27	0.5
716	0.90	0.65	2.17	0.66	0.83	1.12	0.62	0.53	5.5	1.00	0.20	0.30	0.5
717	1.00	0.43	2.43	0.73	0.92	1.22	0.74	0.63	7.5	1.24	0.20	0.30	0.5
718	0.70	0.17	1.70	0.51	0.65	0.88	1.12	0.65	9.5	2.79	0.20	0.16	0.5
719	0.85	0.20	2.06	0.63	0.78	1.04	1.05	0.69	7.0	1.17	0.20	0.27	0.5
720	0.80	0.42	1.94	0.58	0.74	0.98	0.94	0.64	7.0	1.17	0.20	0.30	0.5
721	0.75	0.27	1.81	0.54	0.69	0.92	1.05	0.74	8.5	1.37	0.20	0.30	0.5
747	1.30	0.52	3.14	0.95	1.20	1.62	0.82	0.60	5.0	2.79	0.23	0.12	0.8
748	0.75	0.36	1.81	0.54	0.69	0.92	0.54	0.48	8.0	3.80	0.25	0.12	0.5
749	0.90	0.42	2.17	0.66	0.83	1.12	0.36	0.37	7.0	3.43	0.23	0.06	0.5
750	1.45	0.70	3.50	1.05	1.34	1.78	0.55	0.45	4.0	0.86	0.23	0.11	0.5
751	1.00	0.59	2.43	0.73	0.92	1.22	0.68	0.53	7.5	1.24	0.22	0.11	0.7
752	0.75	0.32	1.81	0.54	0.69	0.92	0.89	0.63	9.0	4.21	0.22	0.13	0.5
753	0.80	0.27	1.94	0.58	0.74	0.98	0.77	0.46	8.0	1.30	0.18	0.19	0.5
754	0.70	0.16	1.70	0.51	0.65	0.88	1.09	0.66	8.5	1.37	0.21	0.18	0.5
755	0.75	0.30	1.81	0.54	0.69	0.92	0.58	0.46	7.5	0.38	0.21	0.26	0.5
756	0.70	0.31	1.70	0.51	0.91	0.88	1.07	0.76	8.0	1.30	0.20	0.29	0.5
757	0.65	0.20	1.57	0.48	0.60	0.78	1.07	0.80	9.0	1.44	0.19	0.23	0.6
783	0.75	0.36	1.81	0.54	0.69	0.92	0.37	0.43	8.5	4.00	0.28	0.16	0.5
784	1.30	0.59	3.14	0.95	1.20	1.62	0.36	0.33	5.5	2.94	0.25	0.01	0.5

| No.	Prec.	Runoff	S	NO$_3$	NH$_4$	BC$_{dep}$	BC$_u$	N$_u$	T	w	xE	xH	N$_i$
785	1.50	0.85	3.63	1.11	1.39	1.86	0.50	0.38	3.5	3.76	0.23	0.15	0.5
786	1.25	0.69	3.03	0.92	1.16	1.52	0.68	0.60	5.5	2.94	0.19	0.15	0.9
787	0.75	0.34	1.81	0.54	0.69	0.92	0.89	0.66	8.0	3.80	0.24	0.09	0.7
788	0.75	0.51	1.81	0.54	0.69	0.92	0.69	0.54	7.0	1.17	0.18	0.26	0.7
789	1.00	0.41	2,43	0.73	0.92	1.22	0.78	0.55	6.0	1.06	0.20	0.29	0.5
790	0.75	0.31	1.81	0.54	0.69	0.92	0.52	0.44	8.0	0.40	0.21	0.27	0.5
791	0.70	0.27	1.70	0.51	0.65	0.88	0.99	0.67	8.0	1.30	0.19	0.27	0.6
792	0.65	0.15	1.57	0.48	0.60	0.78	1.09	0.83	9.0	1.44	0.18	0.25	0.6
793	0.55	0.03	1.33	0.41	0.51	0.68	1.05	0.83	10.0	3.67	0.20	0.10	0.5
819	1.30	0.64	3.14	0.95	1.20	1.62	0.39	0.35	4.5	2.65	0.19	0.09	0.9
820	1.20	0.80	2.90	0.88	1.11	1.46	0.32	0.32	4.0	3.97	0.23	0.14	0.6
821	1.50	0.74	3.63	1.11	1.39	1.86	0.36	0.34	3.0	0.24	0.16	0.13	0.9
822	0.80	0.35	1.94	0.58	0.74	0.98	0.71	0.55	7.5	3.61	0.24	0.09	0.7
823	1.15	0.52	2.78	0.83	1.07	1.42	0.47	0.46	5.5	1.00	0.21	0.26	0.8
824	1.20	0.55	2.90	0.88	1.11	1.36	0.35	0.33	5.0	0.44	0.20	0.30	1.0
825	0.95	0.44	1.15	0.70	0.87	1.16	0.50	0.43	6.5	0.34	0.20	0.30	1.2
826	0.80	0.32	1.94	0.58	0.74	0.98	0.87	0.60	7.5	1.24	0.20	0.29	0.7
827	0.65	0.15	1.57	0.48	0.60	0.78	1.09	0.79	9.0	1.44	0.21	0.23	0.5
828	0.60	0.10	1.46	0.44	0.56	0.74	1.18	0.85	9.5	2.56	0.21	0.20	0.5
829	0.60	0.12	1.46	0.44	0.56	0.74	1.05	0.74	10.0	2.69	0.23	0.16	0.5
855	1.00	0.56	2.43	0.73	0.92	1.22	0.29	0.30	7.0	0.36	0.20	0.10	0.8
856	1.50	0.90	3.63	1.11	1.39	1.86	0.26	0.28	2.0	0.21	0.13	0.16	1.4
857	1.00	0.53	2.43	0.73	0.92	1.22	0.48	0.44	6.5	0.51	0.17	0.19	1.0
858	0.90	0.42	2.17	0.66	0.83	1.12	0.40	0.44	6.0	0.49	0.21	0.22	1.1
859	0.95	0.41	2.30	0.70	0.87	1.16	0.28	0.31	6.0	0.33	0.20	0.29	1.4
860	1.10	0.50	2.67	0.80	1.01	1.36	0.37	0.36	5.5	0.31	0.20	0.30	1.5
861	0.90	0.39	2.17	0.66	0.83	1.12	0.84	0.59	7.0	0.36	0.20	0.30	1.2
862	0.75	0.23	1.81	0.54	0.69	0.92	1.13	0.76	8.0	0.60	0.20	0.30	0.6
863	0.65	0.12	1.57	0.48	0.60	0.78	1.09	0.79	9.5	1.51	0.20	0.19	0.5
864	0.65	0.11	1.57	0.48	0.60	0.78	0.99	0.79	9.5	2.56	0.25	0.15	0.5
891	1.45	0.88	3.50	1.05	1.34	1.78	0.27	0.29	4.0	0.26	0.15	0.08	1.2
892	1.40	0.99	3.40	1.02	1.29	1.72	0.28	0.28	4.0	0.40	0.12	0.12	1.4
893	0.85	0.39	2.06	0.63	0.78	1.04	0.42	0.43	6.0	0.49	0.20	0.21	0.8
894	0.80	0.31	1.94	0.58	0.74	1.00	0.36	0.40	7.0	0.54	0.20	0.25	0.5
895	1.25	0.47	3.03	0.92	1.16	1.52	0.38	0.34	5.5	0.31	0.21	0.27	1.4
896	0.90	0.25	2.17	0.66	0.83	1.12	1.01	0.68	6.5	0.51	0.20	0.28	0.9
897	0.75	0.20	1.81	0.54	0.69	0.92	0.95	0.62	8.5	3.26	0.20	0.28	0.6
927	1.50	0.96	3.63	1.11	1.39	1.86	0.25	0.28	3.5	0.25	0.15	0.08	1.2
928	1.50	0.72	3.63	1.11	1.39	1.86	0.27	0.28	3.0	0.36	0.11	0.11	1.5
929	0.80	0.40	1.94	0.58	0.74	0.94	0.28	0.29	6.0	0.49	0.19	0.28	1.4
930	1.25	0.50	3.03	0.92	1.16	1.52	0.32	0.31	5.5	0.31	0.16	0.14	1.3
931	0.90	0.37	2.17	0.66	0.83	1.12	0.93	0.61	7.0	1.44	0.23	0.15	0.9
962	0.90	0.44	2.17	0.66	0.83	1.12	0.29	0.30	6.0	0.33	0.23	0.10	0.5
963	1.45	0.60	3.50	1.05	1.34	1.78	0.29	0.31	5.0	0.37	0.16	0.22	1.0
964	1.00	0.46	2.43	0.73	0.92	1.22	0.29	0.30	5.5	0.46	0.16	0.17	1.3
965	1.10	0.50	2.67	0.80	1.03	1.36	0.30	0.31	5.0	0.29	0.19	0.18	1.2
998	0.90	0.47	2.17	0.66	0.83	1.12	0.27	0.29	6.0	0.41	0.21	0.23	0.6
999	1.40	0.61	3.40	1.02	1.29	1.72	0.27	0.29	3.5	0.38	0.18	0.13	1.1

Critical Loads Maps

Critical Loads and their Exceedance

for Pilot Area of Slovakia

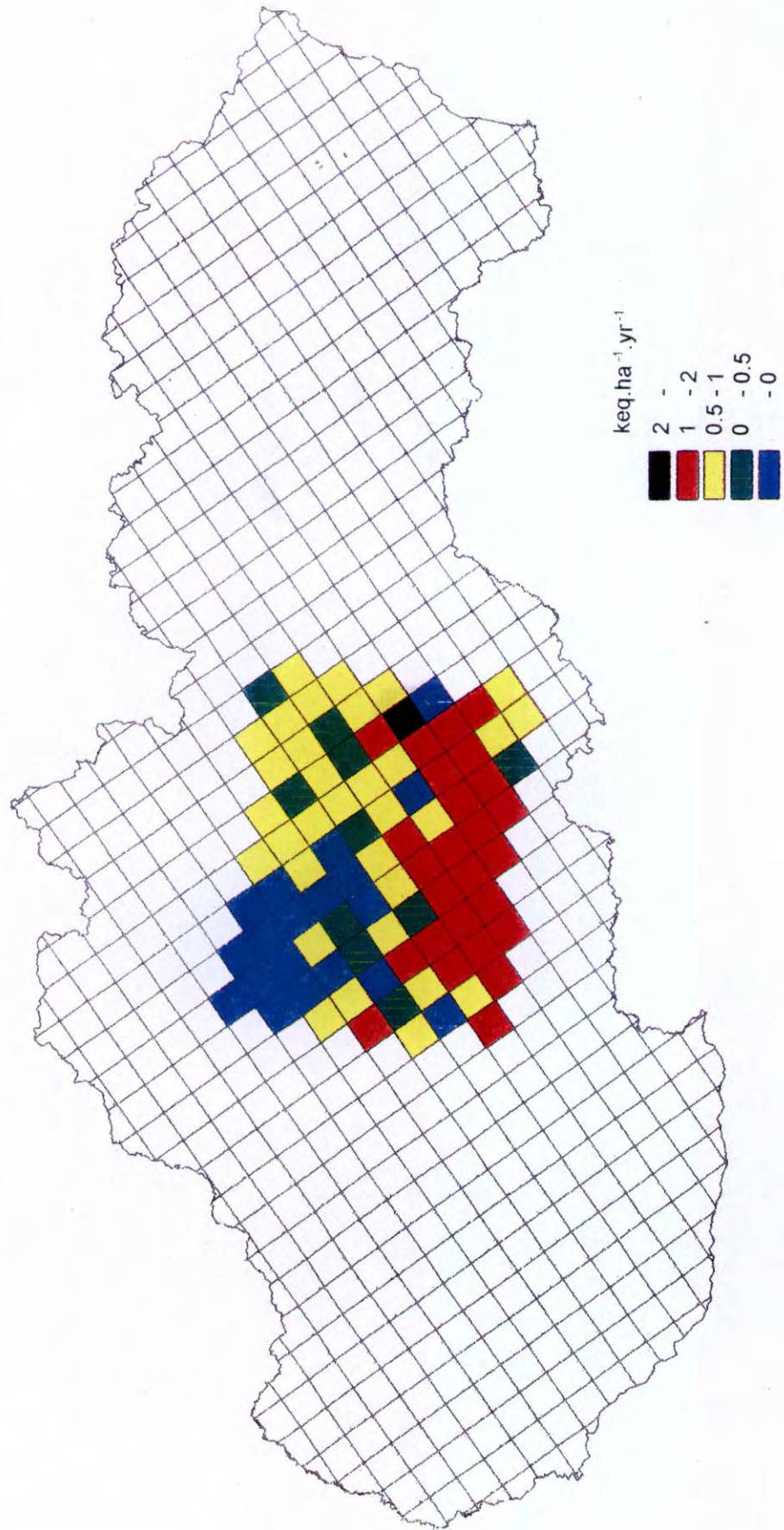# SLOVAK REPUBLIC

Critical Loads of Acidity (5 percentile)
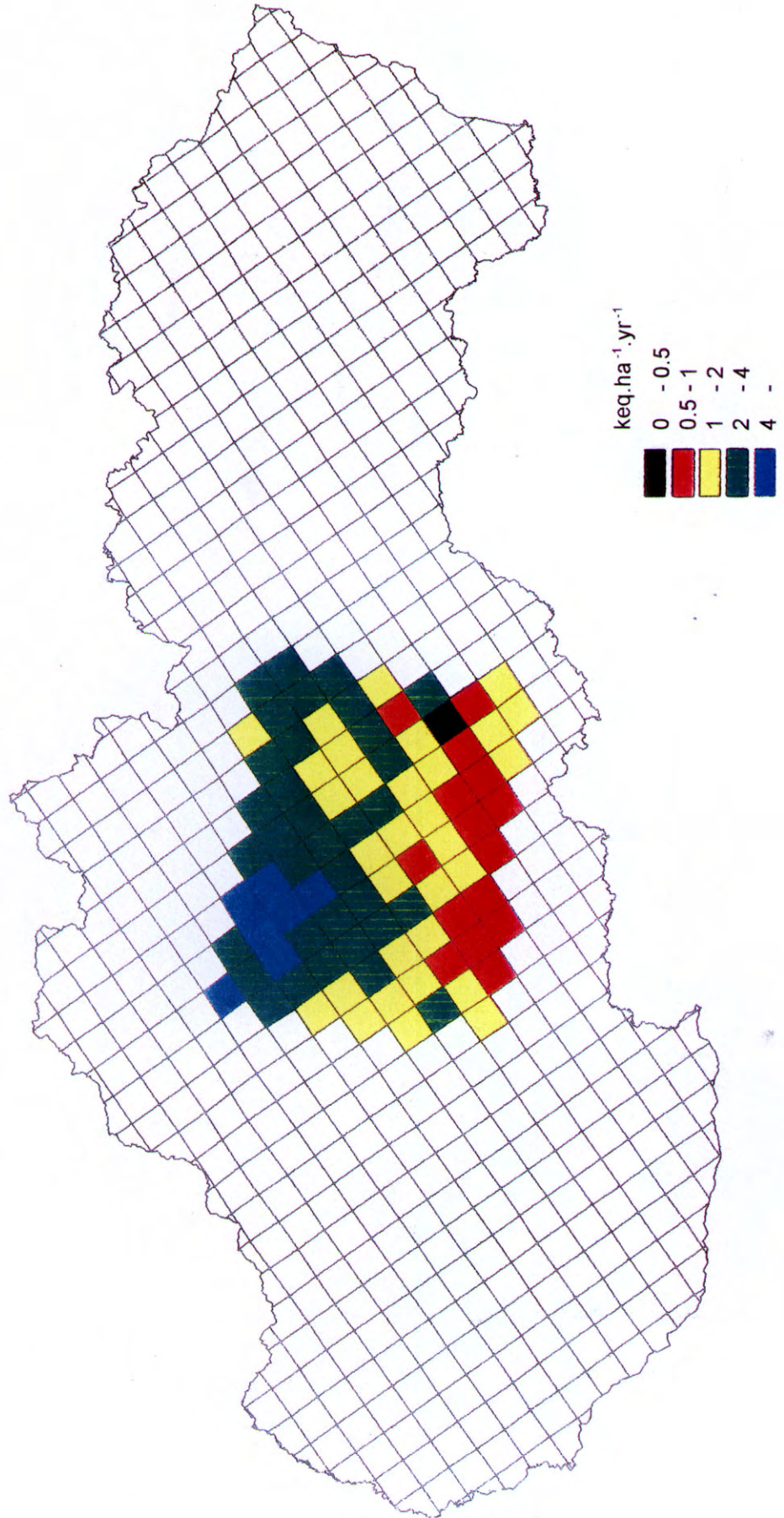
Receptor : Forest Soils

keq.ha^{-1}.yr^{-1}

■	0 - 0.5
■	0.5 - 1
■	1 - 2
■	2 - 4
■	4 -

SLOVAK REPUBLIC

Exceedance of Critical Loads of Acidity (5 percentile)

Receptor : Forest Soils

keq.ha^{-1}.yr^{-1}

2 -
1 - 2
0.5 - 1
0 - 0.5
- 0

SLOVAK REPUBLIC

Critical Loads of Sulphur (5 percentile)

Receptor: Forest Soils

keq.ha^{-1}.yr^{-1}

0 - 0.5
0.5 - 1
1 - 2
2 - 4
4 -
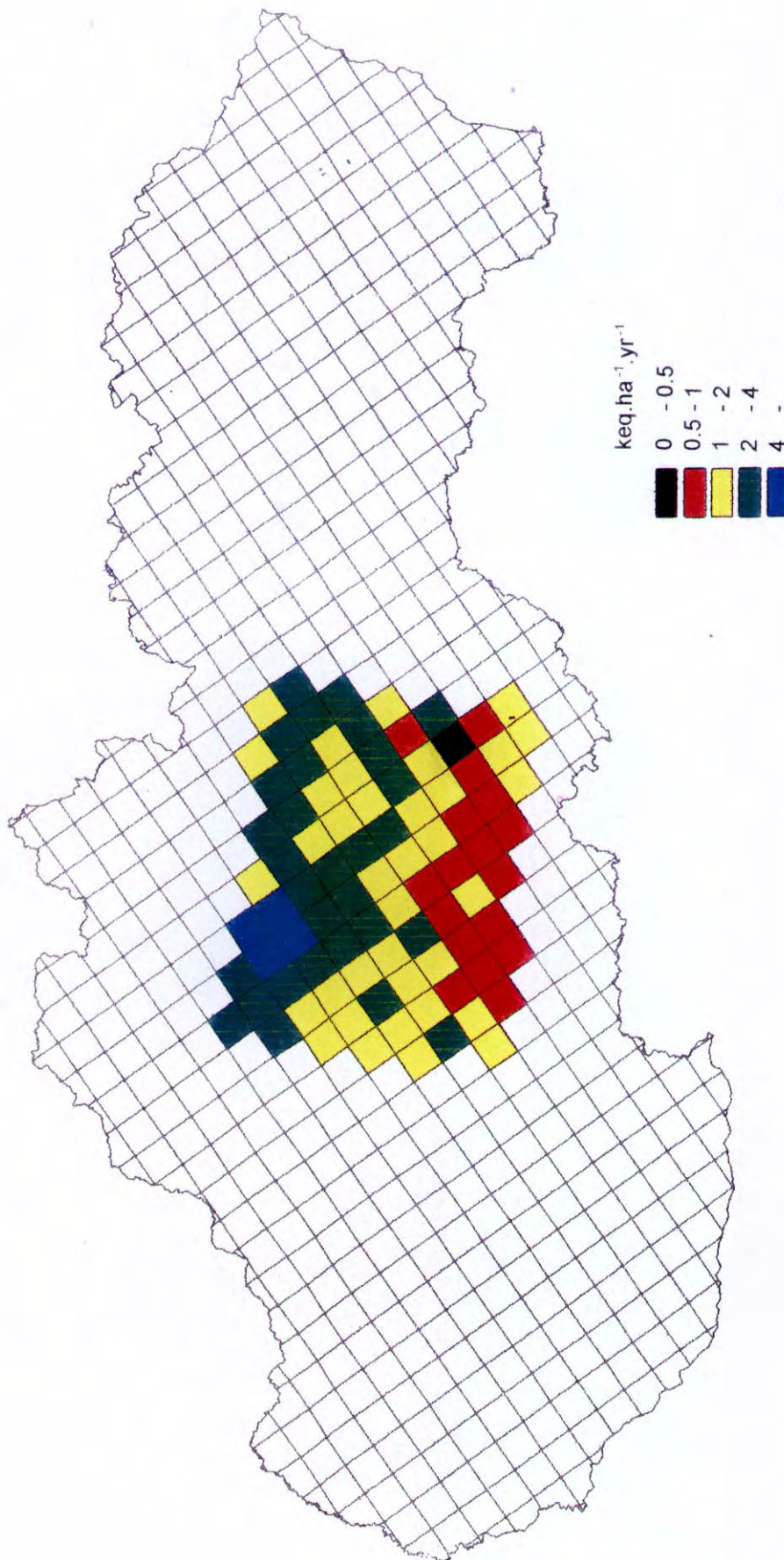
SLOVAK REPUBLIC

Critical Sulphur Deposition (5 percentile)
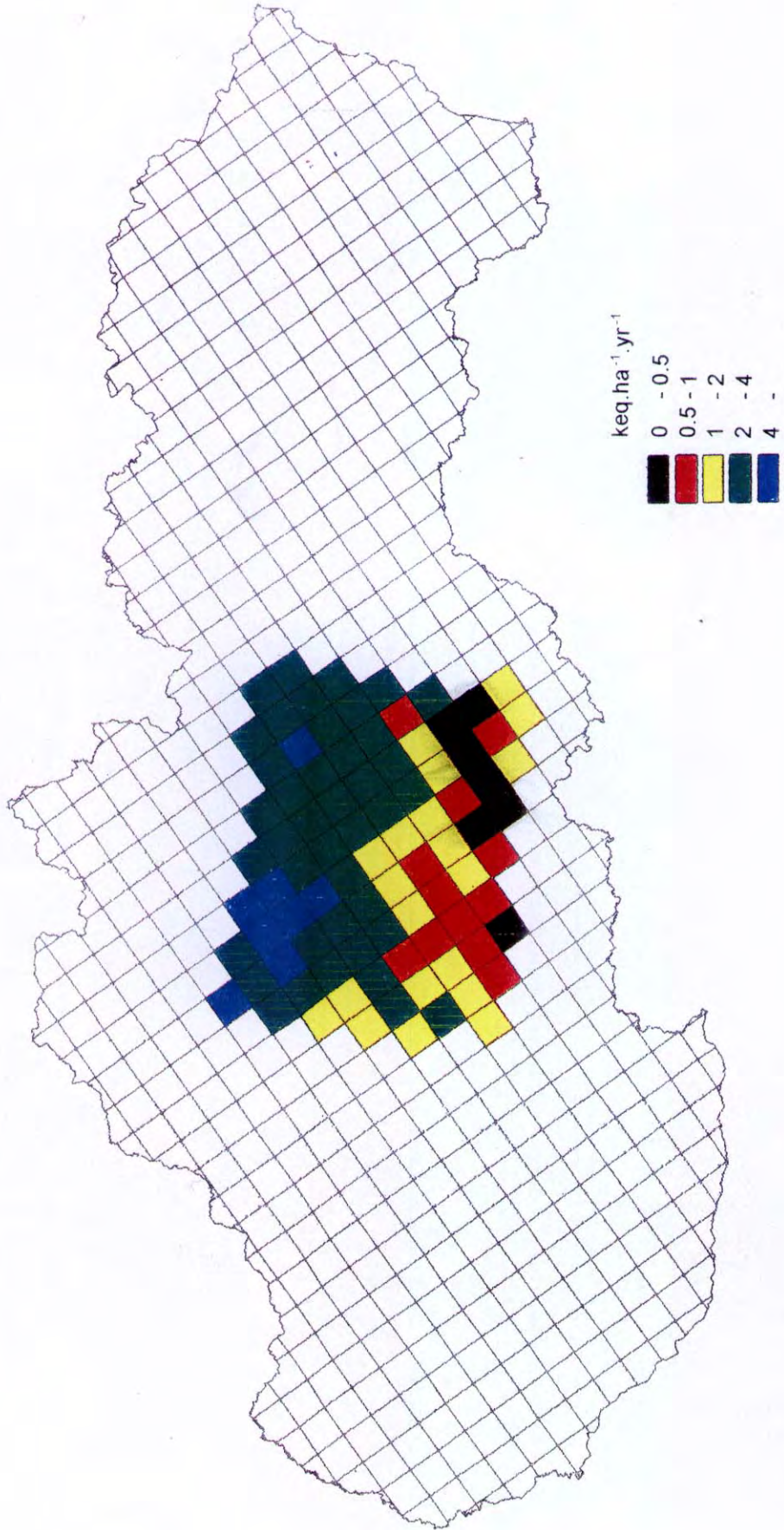
Receptor : Forest Soils

keq.ha^{-1}.yr^{-1}

0   - 0.5
0.5 - 1
1   - 2
2   - 4
4   -

SLOVAK REPUBLIC

Exceedance of Critical Sulphur Deposition (5 percentile)

Receptor : Forest Soils

keq.ha^{-1}.yr^{-1}

2   -
1   - 2
0.5 - 1
0   - 0.5
    - 0

SLOVAK REPUBLIC

Critical Loads of Acidity

Receptor : Surface Water

keq.ha^{-1}.yr^{-1}

0 - 3
3 - 6
6 - 9
9 - 12
>12

SLOVAK REPUBLIC

Exceedance of Critical Loads of Acidity

Receptor : Surface Water

keq.ha^{-1}.yr^{-1}

■	> -3
■	-6 - -3
■	-9 - -6
■	-12 - -9
■	< -12

SLOVAK REPUBLIC

Critical Loads of Acidity

Receptor : Ground Water

keq.ha^{-1}.yr^{-1}

0 - 3
3 - 6
6 - 9
9 - 12
>12

SLOVAK REPUBLIC

Exceedance of Critical Loads of Acidity

Receptor: Ground Water

keq.ha⁻¹.yr⁻¹

> -3
-6 - -3
-9 - -6
-12 - -9
< -12
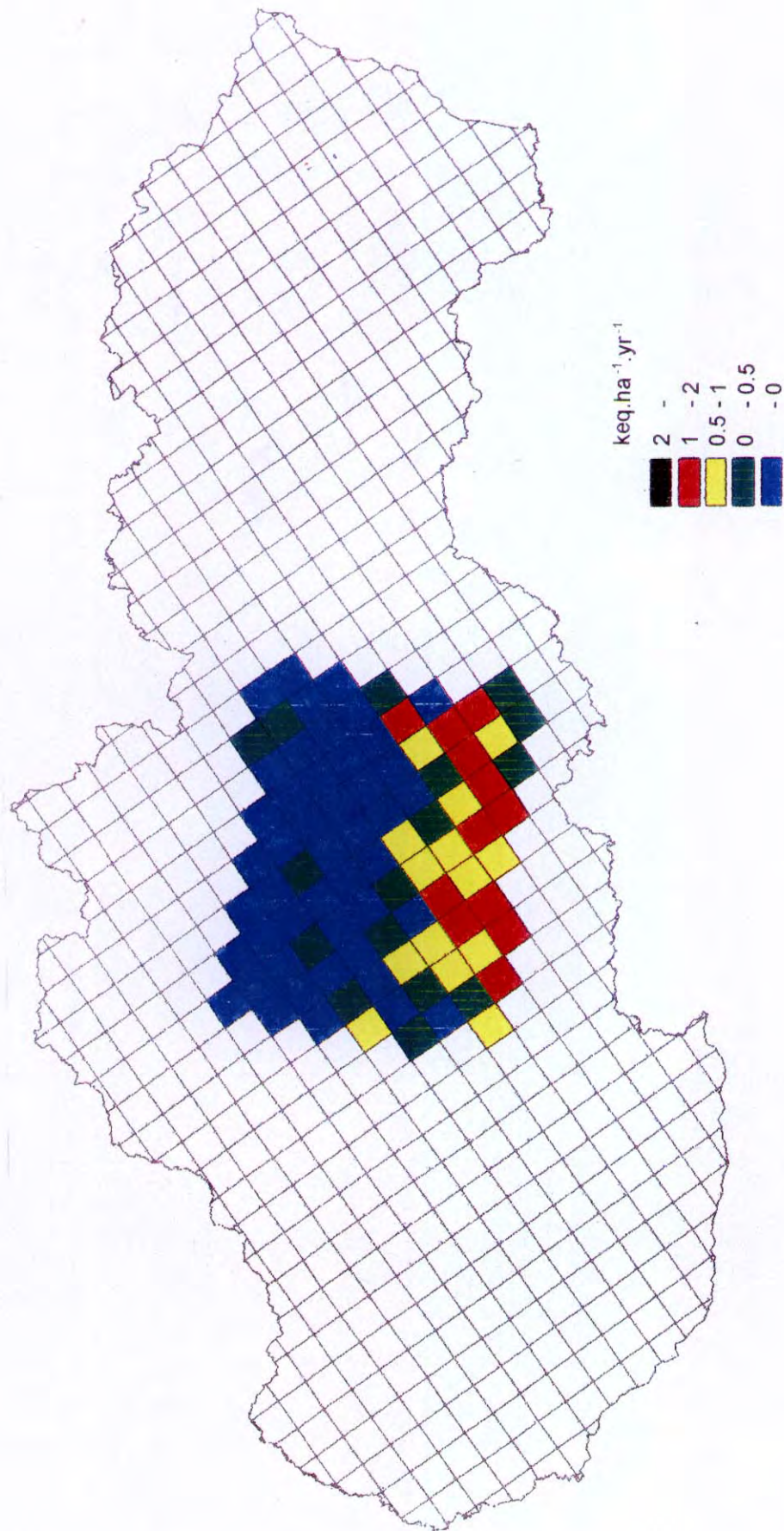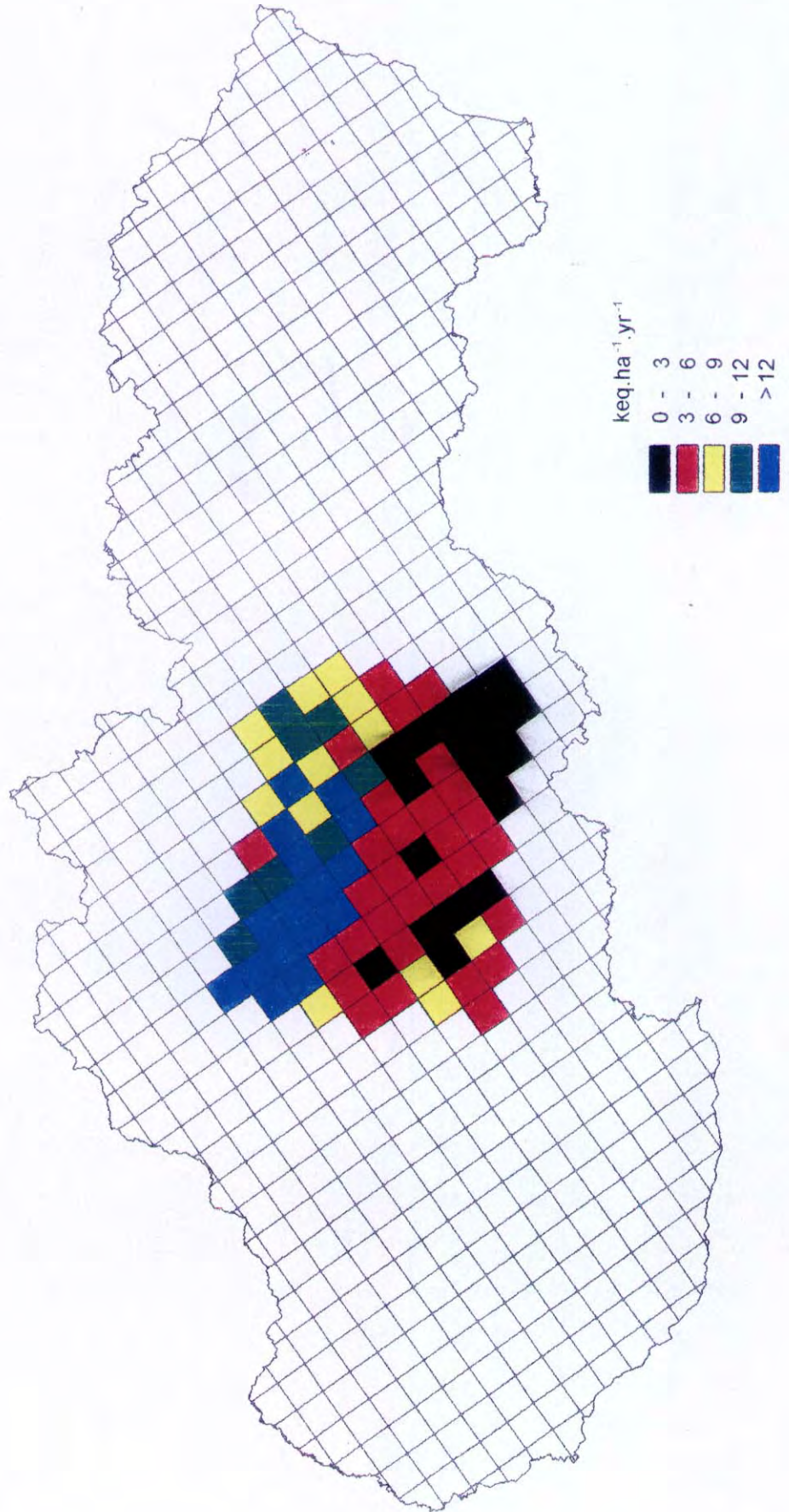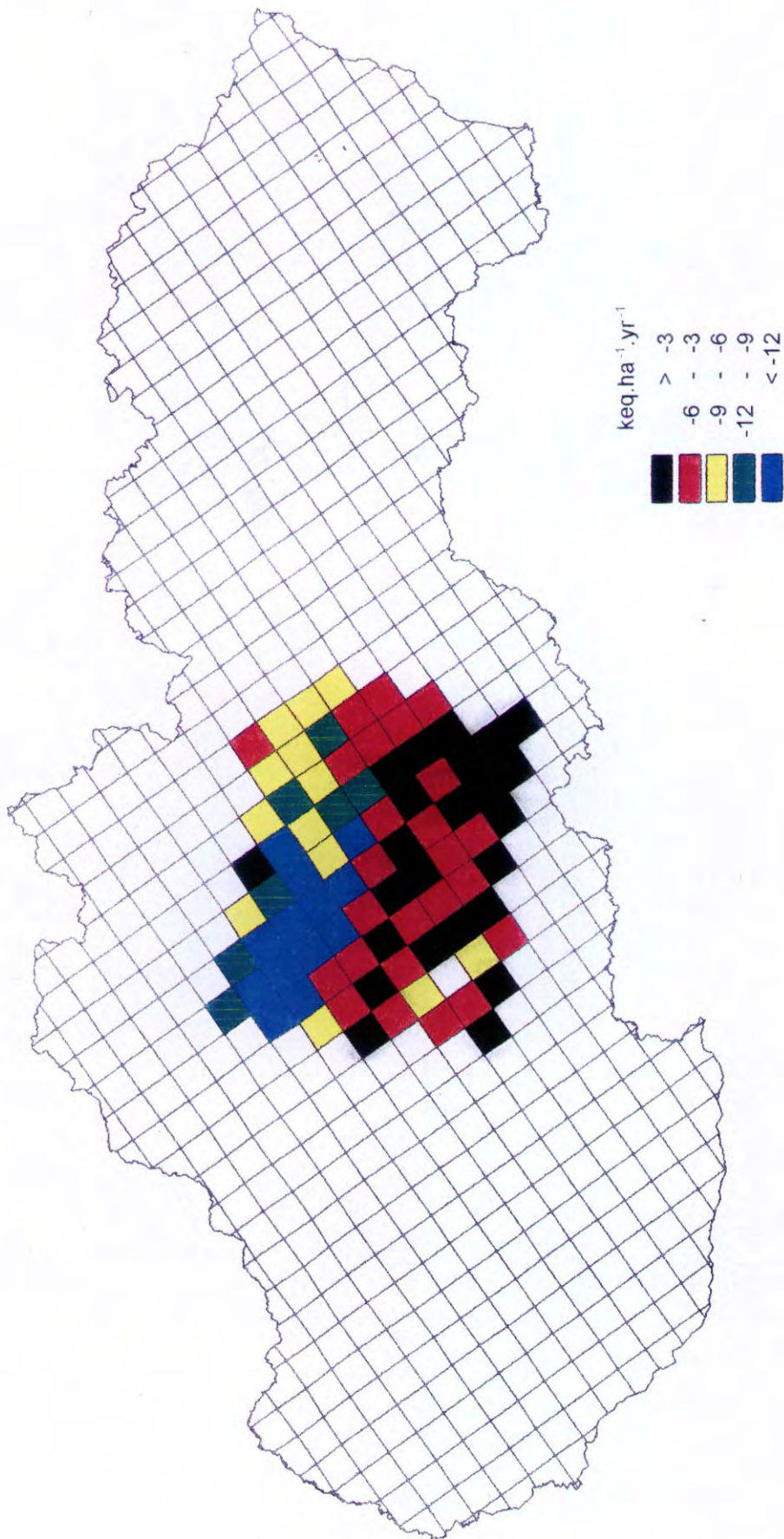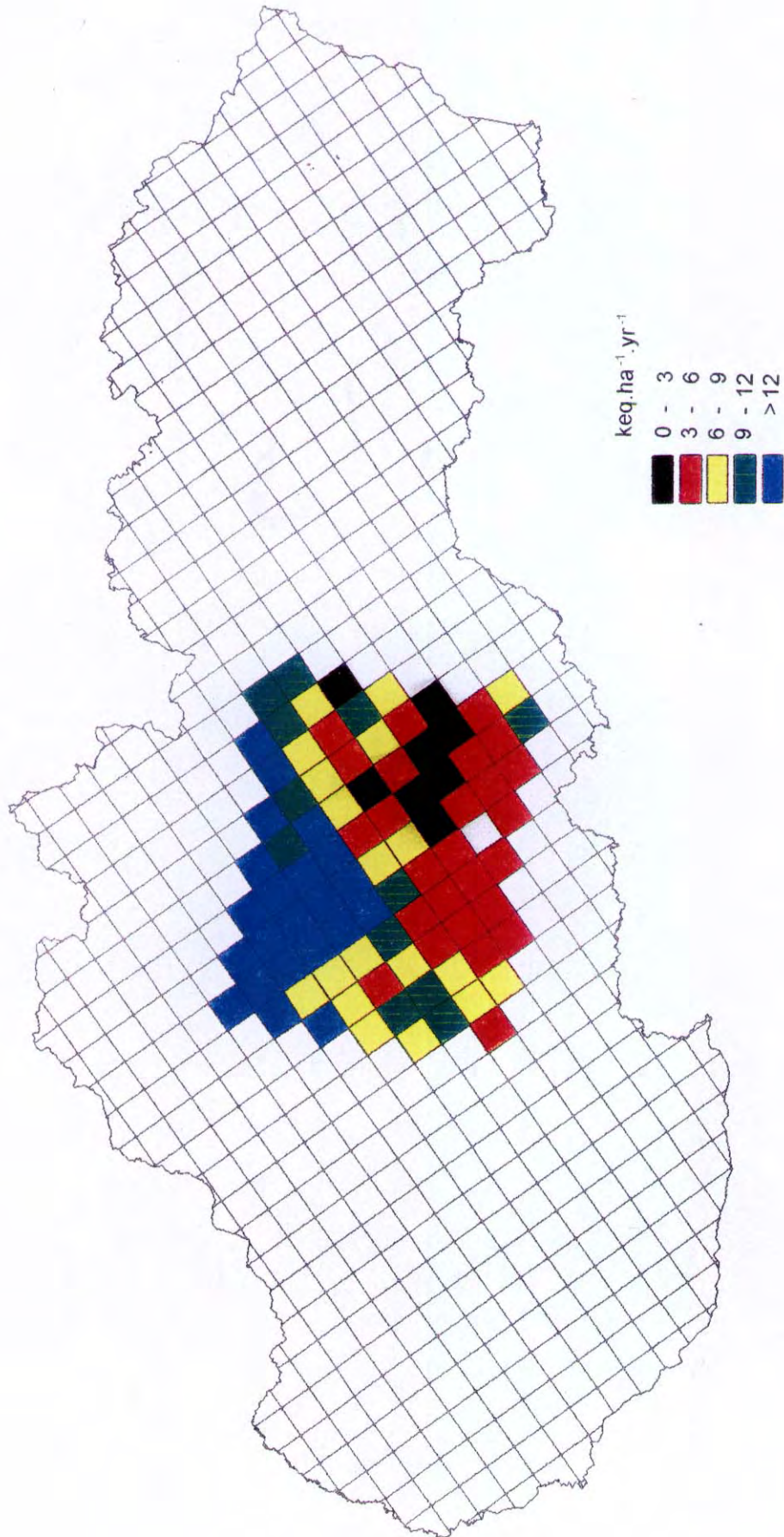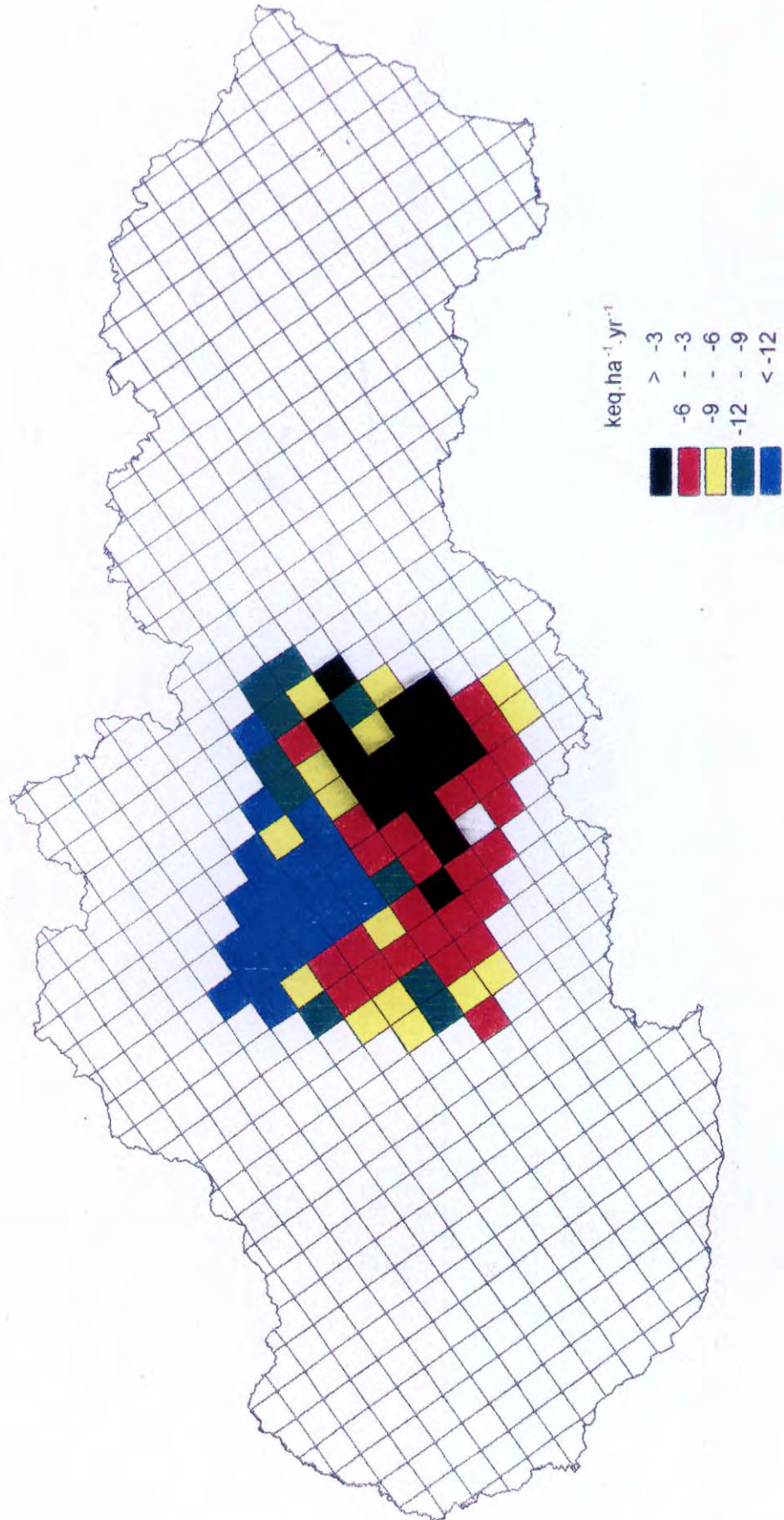
ANNEX 4

Programme for Workshop on

MAPPING CRITICAL LEVELS/LOADS FOR

THE SLOVAK REPUBLIC

Workshop on
MAPPING CRITICAL LEVELS/LOADS FOR THE SLOVAK REPUBLIC

Wednesday October 5.

11.25 Arrival at Fornebu
12.45 Arrival at NILU
13.00 Lunch at NILU with presentation of the institute
14.30 Departure to NIVA
15.00 Arrival at NIVA. Presentation of the institute
17.00 Arrival at hotel
18.00 Dinner

Thursday October 6.
Chair: Bente M. Wathne

9.00 Welcome and practical details
9.15 Tor Johannessen. The Norwegian National Programme on Nature Tolerance Level/Critical
      loads
10.00 Coffee break
10.30 Anton Eliassen. International Cooperation and agreements.
11.15 Kjetil Tørseth. Determining deposition loads and concentration levels from measurements
      at Norwegian monitoring sites.
12.00 Lunch
13.00 Harald Sverdrup. Critical loads for soil
13.45 Dan Aamlid. Critical loads/levels and damage to Norwegian forests
14.30 Coffee break
15.00 - 17.00 Discussions
18.00 Dinner

Friday October 7.
Chair: Bente M. Wathne

9.00 Arne Henriksen. Critical loads for surface water
9.45 Bjørn O. Rosseland. Why fish dies in acid waters
10.30 Coffee
11.00 Working in groups with Slovak data
      Group A, Soil and forest. Responsible: Harald Sverdrup and Mette G. Thomsen
      Group B, Deposition and air. Responsible: Kjetil Tørseth and Arne Semb
      Group C, Surface water. Responsible: Arne Henriksen
12.00 Lunch
13.00 - 17.00 Working groups continue
(14.30 Coffee break)
18.00 Dinner

Saturday October 8.

9.00 - 17.00 Sightseeing in Oslo.

Sunday October 9.

Departure from Fornebu

Norwegian lectureres and resource persons

Tor Johannessen.	State Pollution Control Authority
Anton Eliassen.	The Norwegian Meteorological Institute
Kjetil Tørseth.	Norwegian Institute for Air Research
Arne Semb.	Norwegian Institute for Air Research
Harald Sverdrup.	University of Lund
Dan Aamlid.	The Norwegian Forest Research Institute
Mette G. Thomsen.	The Norwegian Forest Research Institute
Arne Henriksen.	Norwegian Insitute for Water Research
Bjørn O. Rosseland.	Norwegian Insitute for Water Research
Bente M. Wathne.	Norwegian Insitute for Water Research

ANNEX 5

Dušan Závodský

Mapping Critical Levels/Loads for the Slovak Republic

Summary and conlcusions from Norway/Slovak Workshop, Oslo, October 1994

Mapping Critical Levels/Loads for Slovak Republic

(Summary and Conclusions from Norway/Slovak Workshop, Oslo, 5-8 October 1994)

Background

Mapping critical levels/loads (ecological sensitivity of environment) is the international obligation of European countries within the framework of fulfilment of the Convention on Long Range Transport of Air Pollution. The arrangement of this task in Slovak Republic has been stagnant up to the present. For this reason the Project has been proposed within the framework of Norway/Slovakia bilateral co-operation having an objective to develop a manual under the assistance of Norwegian partners and evaluate critical loads in the whole territory of Slovakia for the most sensitive elements of the environment (forest soils and ecosystems, surface waters and groundwaters). The Project has been accepted by the Norwegian government. Grant for its arrangements has been provided by the Norwegian Ministry of Environment. The Project has been planned to last for two years. The major co-operative partners are represented by the Norwegian Institute for Water Research in Oslo (Project manager Mrs. Bente M. Wathne) and the Slovak Hydrometeorological Institute in Bratislava (Project manager Mr. Dušan Závodský). The first stay of Norwegian scientists (Mrs. Bente M. Wathne and Mr. Arne Henriksen) was carried out in June, 7-9, 1994 in Bratislava. The objective of this stay has been mutual exchange of information, specification of input data necessary for critical loads and preparation of Norway/Slovak workshop in Oslo.

Summary of Oslo Workshop

Workshop was held in October, 5-8, 1994 in Oslo, in Scandic Crown hotel. The whole Slovakian Project team took part in this seminar, namely:

Dušan Závodský	- co-ordinator,	Slovak Hydrometeorological Institute, Bratislava
Gabriela Babjaková	- run off data,	Slovak Hydrometeorological Institute, Bratislava
Marta Mitošinková	- deposition data,	Slovak Hydrometeorological Institute, Bratislava
Katarína Pukančíková	- data processing,	Slovak Hydrometeorological Institute, Bratislava
Peter Rončák	- water quality data,	Slovak Hydrometeorological Institute, Bratislava
Dušan Bodiš	- geological data,	Dionýz Štúr Institute of Geology, Bratislava
Stanislav Rapant	- geological data,	Dionýz Štúr Institute of Geology, Bratislava
Jozef Minďáš	- biomass uptake data,	Forest Research Institute, Zvolen
Jaroslav Škvarenina	- forest pedology data,	Forest University, Zvolen
Boris Cambel	- pedology data,	Research Institute for Irrigation, Bratislava

The seminar run in the form of scientific lectures given by the prominent Norwegian experts and practical calculations of critical loads. Mr. Tor Johannessen informed in his introductory lecture about the Norwegian National Programme on Nature Tolerance Level/Critical Loads. Mr. Anton Eliassen presented the results of tasks MSC-W EMEP, referring to mapping critical loads in Europe in EMEP grid. Mr. Kjetil Torseth evaluated the methods of deposition determining upon the basis of Norwegian monitoring sites measurements. Mr. Harald Sverdrup demonstrated model PROFILE for the calculation of critical loads for forest soils. Mr. Dan Aamlid described connections between exceedance of critical loads and forest damage in Norway. Mr. Arne Henriksen demonstrated water chemistry method for critical loads calculation of surface and underground waters. Mr. Bjorn O. Rosseland informed about acidification of Norwegian surface waters and reasons of fish extinction.

Practical part of the workshop was carried out in tree working groups:
- soil and forest, led by Mr. H. Sverdrup
- atmospheric deposition, led by Mr. A. Semb
- surface waters and groundwaters, led by Mr. A. Henriksen

Slovakian participants of the workshop have prepared the input data for calculation of critical loads in the pilot territory (90 squares 10x10 km in the mountainous middle Slovakia, bordered from the North by the mountains the Low Tatras, height differences above 1 500 m).

Steady state mass balance method - model PROFILE - has been used for the calculation of critical levels for forest soils and ecosystems. Because of lack of soil mineralogy the weathering rates were approximated from a combination of soil type, parent geological origin, soil texture, wetness and temperature. Workshop has indicated significant differences between Scandinavian and Slovakian conditions. Slovakian pilot territory comprises five soil types altogether - Cambisols, Remzines, Planosols, Podzols and Fluvisols. The thickness of organic layer is more massive than that usually recommended 0.1 m (default value). Similarly, the thickness of subsurface diagnostic soil horizon is more massive than 0.05 m (default value). Slovakian biomass uptake data have been calculated upon the base of annual increments of stands and not upon the base of the harvest data. Some recalculations had to be done. Broad discussion has been developed about the determination of atmospheric deposition (dry, wet, occult, throughfall and stem-flow data). Deposition velocities depend upon the physiological activity of vegetation, forest stand density, vegetation species, leaf area index, light intensity, temperature, humidity, etc. To complete high resolution data set of this parameters is very difficult. Dry deposition of base cations from airborne soil dust particles has still remained an open problem. As a first approximation it may be assumed that dry deposition of base cations is equal to wet deposition of base cations. Measurements of airborne base cations, NH_3, HNO_3 are desirable. The deposition velocities should be estimated on monthly basis. Throughfall measurements represent a valuable method for the determination of total deposition to forest stands. Calculated data should be compatible with throughfall data. Systematic negative errors of precipitation amount measurements in mountainous locations should be taken into account.

After the revision and recalculation of input data preliminary critical loads for forest soils and ecosystems and their exceedance for 35 squares of Slovakian pilot territory have been calculated by the PROFILE model. The exceedance of critical load (5-percentile) was found in 27 squares.

Some preliminary calculations of critical loads and their exceedance for surface waters and groundwaters have been carried out. The Steady State Water Chemistry Method (SSWC) has been used. Sulphate found in surface water originates mostly from the sea salt spray, polluted deposition and in a minority from geological sources. The method gives the ways of correction the sea salts and geological sulphates to obtain the atmospheric contribution of sulphate in the water. This sulphate concentration is then used to estimate the weathering rate of the catchment. The chemical data for surface water and groundwater brought to the workshop indicate that the geology in the Slovak Republic supplies by the significant amounts of sulphates into the waters. These sulphates are supposed to be balanced mostly by the base cations (Ca + Mg). Thus to calculate critical load, the method had to be modified, taking into account the precipitation and runoff data. Using this modified method the preliminary estimation of critical load values for surface water and groundwater for 25 grid-squares of Slovak pilot territory was conducted. Critical loads are very high and as compared them to the critical loads for soils, there are no critical load exceedance in any grid-square. The critical loads for surface waters are systematically bigger than those ones for ground water. The forest soil is clearly the most sensitive ecosystem in the Slovak pilot territory.

In course of the workshop two visits were carried out, the first one in the Norwegian Institute for Air Research and the second one in the Norwegian Institute for Water Research. On the last day of the workshop in a very beautiful fall weather the guided sightseeing tour of Oslo was organized and participants were deeply affected by many unforgetable impressions.

Conclusions

1. Oslo Workshop on Mapping Critical Levels/Loads for the Slovak Republic was excellently organized. Slovakian participants highly appreciated the lectures of the prominent Scandinavian experts. It is necessary to appreciate and express thanks separately to the leaders of working groups, namely to Mr. A. Henriksen, Mr. A. Sverdrup and Mr. A. Semb as well as to the Norwegian project manager Mrs. Bente M. Wathne. Slovakian representatives highly respect and appreciate giving an assistance from the Norwegian Ministry of Environment and Norwegian Institute for Water Research for this project to be realized. It is necessary to thank extra to Mr. Henriksen and Mr. Sverdrup who provided Slovakian team with SW PROFILE and SSWC method.

2. All participants of seminar stated a significant progress in project arrangements and recommended:
   - to carry out the input data revision upon the basis of results in the workshop
   - to finish the calculations of critical loads of forest soils and ecosystems, surface waters and groundwaters for 90 squares of the pilot Slovakian territory
   - to elaborate the report about the arrangement status of the project in English language and to send the draft of the report in course of December 1994 to NIVA
   - to inform about the arrangement status of the project the Ministry of Environment of the Slovak Republic and to put forward the proceedings into the plan of bilateral co-operation Norway/Slovakia for the year 1995.

Bratislava, 2 November 1994

ANNEX 6

Kjetil Tørseth

Determining deposition loads and concentration levels from

measurements at Norwegian monitoring sites.

Norsk institutt for luftforskning
Norwegian Institute for Air Research

NILU

Workshop on Mapping Critical Levels/Loads for Slovak Republic

Presentation by Kjetil Tørseth, NILU

In order to evaluate critical load exceedances for ecosystems, it is necessary to know the atmospheric inputs of pollutants with sufficient geographical resolution. This presentation gives a description on how the deposition of sulphur and nitrogen components in Norway was estimated on basis of monitioring data for of air quality, precipitation chemistry and precipitation amounts. The presentation was based on the report;

Tørseth, K. and Pedersen, U. (1994) Deposition of sulphur and nitrogen components in Norway, 1988 - 1992. Kjeller (NILU OR 16/94).

Summary:

The total deposition of sulphur and nitrogen components in Norway during the period 1988-1992 has been estimated on the basis of available measurement data, as indicated below.

Precipitation chemistry: Annual weighted mean concentrations of non-seasalt sulphate, nitrate and ammonium for the period 1988-1992 at 39 Norwegian, 37 Swedish and 1 Finish rural monitoring stations.

Precipitation amounts: Yearly values from 786 stations operated by the Norwegian Meteorological Institute (DNMI).

Air chemistry: Mean concentrations of sulphur dioxide, sulphate, nitrogen dioxide, sum of nitrate+nitric acid and sum of ammonium+ammonia for 1988-1992 at 15 Norwegian sites.

Wet deposition: Yearly weighted mean concentrations of SO_4^{2-}, NO_3- and NH_4+ in precipitation were interpolated using the Kriging technique and mean values calculated for each 50x50 km^2 EMEP subgrid. Yearly precipitation amounts at the DNMI sites were multiplied with the grid concentration values to obtain the wet deposition.

Dry deposition: Mean airborne concentrations of SO_2, SO_4^{2-}, NO_2, NH_4++NH_3, NO_3-+HNO_3 were also interpolated using the Kriging technique to obtain values for individual grids. The dry deposition of these components has been estimated considering land use data, duration of snow cover and available dry deposition velocities.

Total deposition: Maps produced using Uniras interpolation routines show the yearly average total deposition of sulphur, oxidised nitrogen and reduced nitrogen for the period 1988-1992.

Working group on atmospheric deposition.

The group discussed available measurement data for air and precipitation chemistry in Slovakia, and how these may be used to map total deposition of sulphur and nitrogen.

Precipitation chemistry(e.g. mean weighted concentrations of major ions in precipitation on an annual basis) does not vary much even between high altitude sites(Chopok, 2004 masl) and sites at lower altitude. Data from the excisting precipitation sampling sites may therefore be used together with precipitation amounts to determine wet deposition in grid squares. This has already been carried out by the Hydrometeorological institute.

The assessment of the dry deposition component is more difficult. Ambient concentrations of sulphur dioxide and nitrogen dioxide are available from several measurement sites, both in urban and rural locations. It is recommended to use monthly averaged deposition velocities, as discussed by Voldner and Sirois(1986,Water, Air, Soil Pollut., 30, 179-186). However, derivation of these deposition velocities also require knowledge of the land use and vegetation cover in the individual grid squares, and assumptions on how the vegetation uptake rates vary with the season.

For sulphur, observations of the chemical composition of canopy throughfall, when compared to precipitation in the open, may give valuable information on the total dry deposition of sulphur dioxide and sulphate particles. Measurements of throughfall are available for one site near Nitra.

There is considerable uncertainty with respect to dry deposition rates for particles. Both sulphate and nitrate in particles are expected to be mainly in the submicron size range and it is recommended to use a low deposition velocity of the order of 0.1-0.2 cm/s. This may also take care of occult deposition in the form of fog droplets. The effects of such deposition (e.g. cloudwater) in the mountains should be investigated.

As a general information source for different aspects of dry deposition is recommended a recent workshop proceedings edited by Lövblad, G., Erisman, J.W., og Fowler, D.(1993): Models and methods for the quantification of atmospheric input to ecossystems. Nordic Ministerial Council, Copenhagen.

ANNEX 7

Harald Sverdrup

CALCULATING CRITICAL LOADS OF ACID DEPOSITION
WITH PROFILE –
A STEADY-STATE SOIL CHEMISTRY MODEL

PER WARFVINGE and HARALD SVERDRUP

*Department of Chemical Engineering II, Lund Institute of Technology, P.O. Box 124,
S-221 00 Lund, Sweden*

Abstract. A steady state soil chemistry model was used to calculate the critical load of acidity for forest soils and surface waters at Lake Gårdsjön in S.W. Sweden. The critical load of all acid precursors (potential acidity) for the forest soil is 1.64 kmol$_c$ ha^{-1} yr^{-1}, and 1.225 kmol$_c$ ha^{-1} yr^{-1} for surface waters. For the most sensitive receptor, the critical load is exceeded by 1.0 kmol$_c$ ha^{-1} yr^{-1}, and a 80% reduction in S deposition is required, if N deposition remains unchanged. The critical load is largely affected by the present immobilization of N in the terrestrial ecosystem which is higher than the base cation uptake. The model, PROFILE, is based on mass balance calculations for the different soil layers. From measurable soil properties, PROFILE reproduces the present stream water composition as well as present soil solution chemistry. The model calculates the weathering rate from independent geophysical properties such as soil texture and mineral composition.

1. Introduction

With the objective to assess the environmental impact of S and N emission, the various bodies within the United Nations Economic Commission for Europe (UN/ECE) is carrying out the task of assessing the 'Critical Load' of acidifying compounds. The Critical Load is defined as:

The maximum deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem structure and function

The Critical Load is thus a property of the ecosystem, indendent of present acid status.

Within the Critical Load exercise, in which all European countries as well as the United States and Canada participate, the levels of tolerance should be assessed for three receptors, forest soils, surface waters and groundwater. For each receptor, a chemical criteria is applied, which, if violated, corresponds to the exceedence of the Critical Load (Sverdrup *et al.*, 1990). As a part of the political process, the levels of exceedence will be calculated to provide foundations for political decisions on abatement measures.

There are basically two different ways to assess the impact of acid deposition on the development of soil chemistry parameters by means of model estimates. First, one may try to reproduce the entire process of acidification by calculating how key soil chemistry quantities have changes from the point in time when the soil was in a pre-industrial steady-state situation with the prevailing ambient

conditions such as precipitation, climatological factors, land use as well as chemical constitution of the precipitation. During the last decade, a number of models directed to assess the long-term impact of acid rain on catchments have been developed. Examples include ILWAS (Chen et al., 1983), MAGIC (Cosby et al., 1985) and Trickle-Down (Schnoor et al., 1984) and SMART (de Vries et al., 1989). These models rely on estimates of prestine conditions. Among these are intensity factors such as deposition composition, soil pH and base saturation, and also capacity factors such as mineral abundance and the cation exchange capacity. One features of dynamic models are that they serve to indicate time scale of the recovery if emission control efforts are implemented.

All dynamic models used for calculating changes in soil chemistry must be triggered from an equilibrium situation. They should also be expected to converge towards a steady-state solution if that the acid deposition is brought to a constant value. The terminal soil chemistry reached in for a constant deposition demonstrates the inherent ability to withstand ultimate acidification of soils and runoff, and reflects the Critical Load of different soil systems.

The modeling strategy adopted in this paper is to make a short-cut past the acidification process itself and directly evaluate the soil's final chemical chemical status for a given set of conditions. With this method the Critical Load of a soil system can be calculated directly, as elated to the soil solution composition, groundwater quality, and the acidification and increase in Al content of surface waters. This modeling method does not, however, give any answer to questions regarding the rates of acidification and recovery of soil profiles. By comparing model output for present deposition with soil data, it is possible to evaluate whether the system has reached a steady-state with the present acid deposition or is still undergoing acidification. From the steady-state approach follows some assumptions that must be stressed:

- The magnitude of capacity factors such as mineral abundance and cation exchange capacity is constant.
- Long term average values for precipitation, uptake etc. must be used as input.
- The effect of seasonal variations in input variables such as soil CO_2 pressure, nitrification rate and soil moisture content can not be addressed.
- The rate of change in soil chemistry over time can not be assessed.

The soil chemistry model PROFILE has been developed as a tool for calculating Critical Loads for the three receptors mentioned above. The objective with this paper is to provide a comprehensive description of the model, the underlying principles and to demonstrate the use of the model. A previous publication (Sverdrup and Warfvinge, 1988a) does not describe the present state of the model.

Despite that a number of chemical model already have developed to assess the environmental impact of acid deposition, the existence of PROFILE is justified for the following reasons:

- The model translates to the Critical Loads concepts due to the steady-state approach

- The weathering rates are calculated from independent geophysical soil data
- The data acquisiton is supported by the state-of-the-art review in the document 'Mapping Critical Loads' (Sverdrup *et al.*, 1990), available through the Environmental Protection Board of all UN/ECE countries.

The chemistry of the PROFILE model has also been implemented as a dynamic model. That model has been given the acronym SAFE, Soil Acidification in Forested Ecosystems (Warfvinge and Sverdrup, 1990a). In a comparative study (Warfvinge and Sverdrup, 1990b) three model, SAFE, SMART and MAGIC have been applied to historical soil data from sites in Southern Sweden.

2. Materials and Methods

Since PROFILE is designed to calculate the steady-state chemistry of soils, groundwater recharge as well as surface waters, the model operates with different system boundaries. The smallest subsystem is a soil horizon as shown in Figure 1. The soil profile itself is divided into compartments corresponding to the natural soil stratification. Within each of these the mixing of the liquid phase is assumed to correspond to a mixed bucket model. It is a formal requirement that each compartment in the model is chemically isotropic, and the division of the soil profile according to the horizons represents an attempt to meet this.

In each of the soil compartments, a number of chemical reactions are included, represented either by equilibrium relationships or kinetic equations. The reaction systems considered are soil solution equilibrium reactions, silicate weathering, uptake of nutrient cations, NO_3^- and NH_4^+, nitrification and cation exchange reactions (Figure 1). All processes interact via the soil solution. For instance, there is no mechanism for roots to strip nutrients directly from weathering materials.

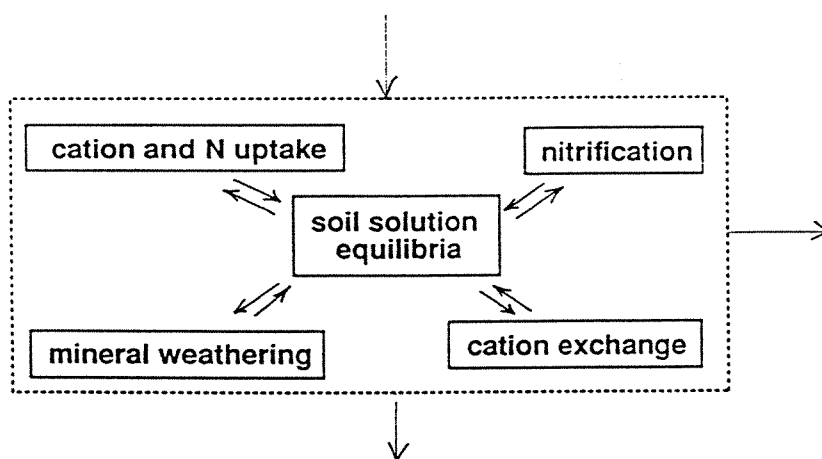These reactions only represent a selection of chemical processes in the soil

Fig. 1. The conceptual structure of one compartment in the PROFILE model.

environment. Consequently a number of general assumptions have been made. The most important of these are:

- Each soil compartment is chemically isotropic and the soil solution perfectly mixed.
- Sulfur reactions do not serve as a net sink or source of acid neutralizing capacity.
- N immobilization can be lumped with N uptake reactions.
- Internal element cycling of elements such as K in the upper soil layers is not modeled.
- Organic complexing of metals such as Al is not modeled.

The first condition is justified by the mere existance of soil horizons, while assuming complete mixing in a soil layer is less obvious. Recent isotope studies in undisturbed soil columns cite 544 show that a mixed bucket series model can be used to describe the water flow through the unsaturated part of a Swedish forest soil. Sulfuric acid adsorption may buffer soil acidification and recovery for a period of a few decades, and in lakes sulfate reduction is a long term source of alkalinity. In acidified soils close to a steady-state, the role of S mineralization affecting the acidity balance of the terrestrial ecosystem is quite unclear (Nilsson, 1985). The last three simplifications are due to the present lack of suitable models for these reaction systems.

The soil column may also be viewed as one unit, as the system boundary in Figure 2 shows. Thereby, the run-off chemistry can be assessed as the integrated result of chemical reactions in the entire soil column. The water leaving a layer may either percolate vertically or flow horizontally. Changing the proportions between these flow paths will alter the relative importance of different soil layers for the chemistry of the dainage water. The effect of acid precipitation on groundwater formation could also be assessed. The PROFILE model can be used for this purpose by calculating the soil water composition down to the groundwater table.

2.1. SOIL SOLUTION MASS BALANCES

For a chemically isotropic soil horizon, one may derive a mass balance for acid neutralizing capacity. It states that the change in ANC must equal the net difference between what enters a soil layer, what leaves it and the rate by which ANC is produced from different sources. In the model, the processes concidered include cation exchange reactions involving H, Al base cations (BC), silicate weathering as well as biological processes that may serve as sinks and sources of ANC. The key mass balance constituing the basis for the soil chemistry model is:

$$\frac{d[ANC]}{dt} = \frac{1}{z\Theta}\left(Q_0[ANC]_0 - \left(Q + z\,\frac{d\Theta}{dt}\right)[ANC]\right) +$$

$$+ R_w + R_{exc} + R_{BC} + R_N \tag{1}$$

where

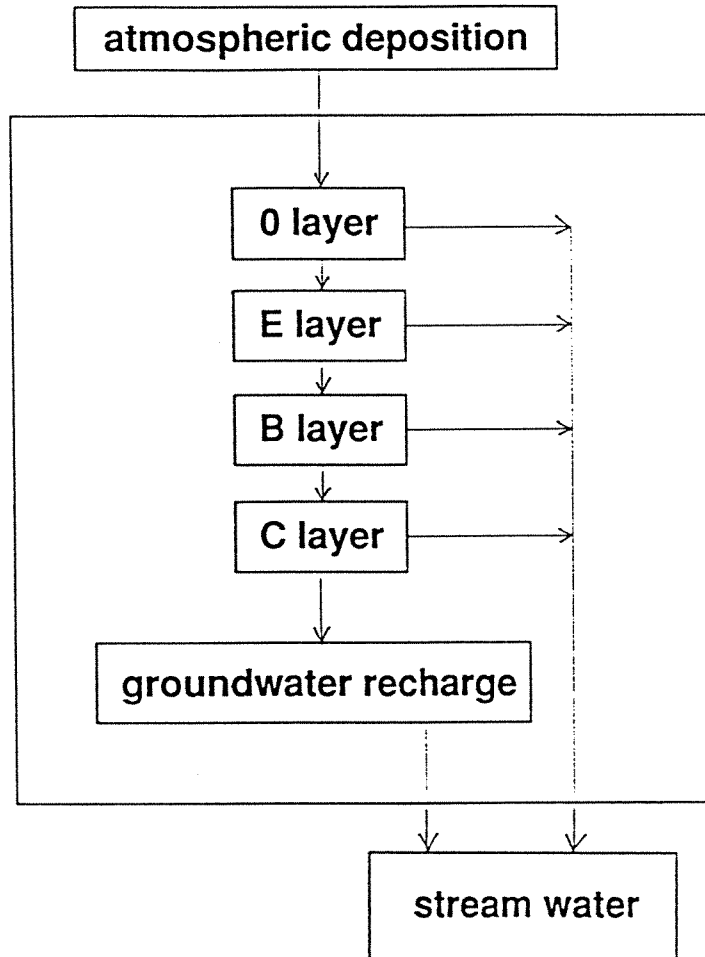z = soil layer height (m)

Θ = soil water content ($m^3\ m_s^{-3}$)

Fig. 2. Water routes possible in the PROFILE model.

Q = Flow rate (m^3 m$_s^{-2}$ yr^{-1})

R_{W} = rate of ANC production from weathering (kmol$_c$ m^{-3} yr^{-1})

R_{exc} = rate of ANC production from cation exchange (kmol$_c$ m^{-3} yr^{-1})

R_{BC} = rate of base cation uptake (kmol$_c$ m^{-3} yr^{-1})

R_{N} = rate of ANC production by N reactions and uptake (kmol$_c$ m^{-3} yr^{-1}).

No subscript refers to condition in the soil layer, and consequently also the leachate from a soil layer. Subscript 0 denotes concentrations in the inflow to the layer, while subscript s refers to bulk volume of soil rather than volume of soil water.

If the path of acidification was to be simulated, this differential equation would be solved together with corresponding equations for other soil components. However, when the 'Critical Load' of a soil system is assessed it may not be necessary to reproduce the entire acidification process, but sufficient to regard only the steady-

state solution to Equation (1), accordingly solving Equation (1) for:

$$\frac{d[ANC]}{dt} = 0 . \tag{2}$$

As obvious from the mass balance for ANC, this solution may be obtained even if the cation exchange phase has not reached a steady state in terms of base saturation. For a soil system to be in true equilibrium however, it is necessary constraint that the distribution of cations on the solid phase should not vary with time. Mathematically, this corresponds to a situation where:

$$R_{exc} \alpha \frac{d}{dt}(CEC\ (\overline{X}_{BC} - \overline{X}_H - \overline{X}_{Al})) = 0 \tag{3}$$

where

CEC = cation exchange capacity in the horizon, arbitrary units

$\overline{X}_i$ = exchangeable fraction of element i.

In all systems, the upper limit of removal of any component in solution is the supply. In order to calculate the ANC production from uptake of base cations and N uptake and other reactions, additional mass balances are required. The general form of all these equations are identical to Equation (1). This leads to the following set of equations to be solved simultaneously:

$$0 = \frac{1}{z\,\Theta}\ (Q_0[ANC]_0 - Q\ [ANC]) + R_w - R_{BC} - R_N \tag{4}$$

$$0 = \frac{1}{z\,\Theta}\ (Q_0[BC^{2+}]_0 - Q\ [BC^{2+}]) + \frac{R_w - R_{BO}}{2} \tag{5}$$

$$0 = \frac{1}{z\,\Theta}\ (Q_0[NO_3^-]_0 - Q[NO_3^-]) - R_{NO_3} + R_{nit} \tag{6}$$

$$0 = \frac{1}{z\,\Theta}\ (Q_0[NH_4^+]_0 - Q[NH_4^+]) - R_{NH_4} - R_{nit} \tag{7}$$

where

R_{NO_3} = Rate of NO_3^- uptake ($kmol_c\ m^{-3}\ yr^{-1}$)

R_{nit} = Rate of nitrification, NH_4^+ uptake ($kmol_c\ m^{-3}\ yr^{-1}$).

R_{NH_4} = Rate of NH_4^+ uptake ($kmol_c\ m^{-3}\ yr^{-1}$).

These first two of these equations must be solved iteratively since the rate of ANC production from weathering, R_w, is a function of pH, which in turn is a non-linear function of the ANC. The solution of Equations (4) to 7 will therefore also include the evaluation of all species that appear in the definition of ANC. With this set of equations, and the functional relationships discussed below, only reacting components in the soil system have to be considered to characterize the soil solution completely. Therefore, the solution of the charge balance becomes redundant, and the fluxes of SO_4^{2-} as well as Cl^- do not have to be included in soil chemistry calculations.

For the uppermost soil layer, the input is the atmospheric deposition.

2.2. SOIL SOLUTION EQUILIBRIUM SUB-MODEL

ANC may be interpreted in terms of dissolved species participating in acid/base transformations in the aqueous phase. In the model it is assumed that the chemical reaction systems of the soil solutions include the auto protolysis of water, the carbonate equilibrium reactions, acid-base reactions of a monovalent organic acid, as well as the precipitation and sub-sequent dissolution reactions of a solid gibbsite phase, producing different charged alumini-hydroxyl species. The solution ANC is defined as:

$$[ANC] = [OH^-]+[HCO_3^-]+2[CO_3^{2-}]+[R^-]-[H^+]-3[Al^{3+}]-$$
$$-2[Al(OH)^{2+}]-[Al(OH)_2^+]. \tag{8}$$

With this definition, it is clear that ANC is a quantity derived from a reduced charge balance from which all solution components that are not believed to participate in acid-base reactions in the liquid phase have been omitted. Such components include SO_4^{2-}, NH_4^+ and BC^{2+}. In an equilibrium situation, each species on the right hand side of Equations (8) can be explicitly calculated from the solution H^+-concentration, and ANC will therefore be a unique function of the solution pH and, most important, *vice versa*. Numerically, ANC may be calculated explicitly from a given pH, while the H^+-concentration corresponding to a given ANC must be calculated iteratively. This is performed by finding the root to the equation:

$$0 = [OH^-]+[HCO_3^-]+2[CO_3^{2-}]+[R^-]-[H^+]-3[Al^{3+}]-$$
$$-2[Al(OH)^{2+}]-[Al(OH)_2^+]-[ANC]. \tag{9}$$

The concentrations of the components evolving from the carbonate buffering system can be calculated after introducing the equilibrium equations of the protolysis reactions of CO_2 and Henry's law for gaseous and liquid phase CO_2-equilibrium.

In the organic soil layers, the buffering reaction of organic components may be important. In PROFILE, dissolved organic carbon (DOC) is modeled as a monovalent organic acid. The dissociation of the acid functional groups of the DOC is quantified using an expression as proposed by Oliver (Oliver et al., 1983).

The equilibrium expressions controlling the concentration of the Al species considered, have such a form that it may be interpreted as an apparent equilibrium with gibbsite. It must be remembered that this model is a simplification, and that the equilibrium expression probably lumps together several different mechanisms for Al concentration control. Both equilibrium and disequilibrium mechanisms are involved, and gibbsite may not necessarily be a part of any of these processes which are most likely to proceed as long non-ideal reaction paths. Many sensitive soils in Europe do not contain gibbsite in detectable amounts (Melkerud, 1983), but operationally the Al concentration is estimated from an assumed equilibrium with a solid phase in most models. The justification for selecting the gibbsite

dissolution/precipitation reaction as the foundation for modeling the Al equilibrium system is primarily that reasonable titration curves can be derived with this aquatic chemistry model. Future versions of PROFILE will include an Al chemistry model based on the kinetics of dissolution and precipitation of primary and secondary minerals (Olausson et al., 1990).

The complete set of equilibrium equations necessary to solve Equation (9) is:

$$[OH^-] = \frac{K_w}{[H^+]} \tag{10}$$

$$[HCO_3^-] = \frac{K_{H_2CO_3} K_{Henry} P_{CO_2}}{[H^+]} \tag{11}$$

$$[CO_3^{2-}] = [HCO_3^-]\frac{K_{HCO_3}}{[H^+]} \tag{12}$$

$$[R^-] = 1\times10^{-6}\,[DOC]\,\frac{K_{org}}{K_{org}+[H^+]} \tag{13}$$

$$[Al^{3+}] = K_G\,[H^+]^* \tag{14}$$

$$[Al(OH)^{2+}] = K_{Al(OH)^{2-}}\,K_G\,[H^+]^2 \tag{15}$$

$$[Al(OH)_2^+] = K_{Al(OH)_2}\,K_G\,[H^+] \tag{16}$$

where

P_{CO_2} = CO$_2$ partial pressure (atm)

DOC = dissolved organic carbon in solution (mg L^{-1})

K_W etc = Aqueous equilibrium coefficients as specified in Table I.

The constant 1×10^{-6} that appears in the expression for $[R^-]$ is an empirical factor

TABLE I

Equilibrium equations and corresponding coefficients included in PROFILE. Units applied are kmol, m³ and atmospheres. References are made to: 1: (Stumm and Morgan, 1983). 2: (Oliver et al., 1983). 3: (Schecher and Driscoll, 1987).

Equilibrium reaction	Equ. coeff.	Value/function	Ref.
$H_2O \rightleftharpoons H^- - OH^-$	K_W	exp-(-6.09 + 4471/T - 0.0171 $* T$)	1
$CO_2(g) \rightleftharpoons H_2CO_3(aq)$	K_{Henry}	exp-(12.59-2198/T - 0.0126 $* T$)	1
$H_2CO_3 - H_2O \rightleftharpoons HCO_3^- - H_3O^-$	$K_{H_2CO_3}$	exp-(-14.82 + 3401/T - 0.0327 $* T$)	1
$HCO_3^- - H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$	$K_{HCO_3^-}$	exp-(-6.53 + 2906/T - 0.0238 $* T$)	1
$RH + H_2O \rightleftharpoons R^- + H_3O^+$	K_{org}	exp-(0.96 + pH - 0.001 $\cdot$ pH^2)	2
$Al(OH)_3 - 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$	K_G	User specified	
$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^-$	$K_{Al(OH)_2}$	5×10^{-10}	3
$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$	$K_{Al(OH)^{2-}}$	1×10^{-5}	3

that converts DOC expressed in mg L^{-1} to carboxyl groups expressed in $kmol_c$ L^{-1} (Ågren and Jacks, 1990).

In general, the pH corresponding to a certain ANC is governed by the carbonate and the organic matter buffer systems at positive values for ANC. i.e. at pH-levels above 5, while the Al buffering system has its effect below this level.

2.3. NITROGEN REACTIONS

In PROFILE, we have not attempted to model the processes that govern the flow of nutrient cations, N compounds and ANC between the soil solution and the roots of the growing plants. PROFILE relies on input data to specify the maximum rates of uptake of different compounds to the vegetation.

Nitrogen reactions are included is that they act as sources or sinks of acidity in the soil (Galloway and Dillon, 1983). The connection to the acidity-alkalinity balance is clear from Equation (9), where the net production is quanitified by the term R_N. Considering only uptake of NH_4^+ and NO_3^- as well as nitrification, the net production of ANC from these reactions is:

$$R_N = R_{NO_3} - R_{NH_4} - 2 R_{nitr}.$$ (17)

The only biological process that is modeled in terms of a kinetic rate expression is nitrification. Regarding N-uptake, PROFILE relies on input data that specifies the maximum yearly uptake, distributed vertically in the horizon. For each soil layer, the constraint for N-uptake can be defined as:

$$R_{NO_3} + R_{NH_4} \leq R_{Nmax}$$ (18)

where

$R_{Nmax} =$ maximum N uptake from the solution in a layer (kmol m^{-3} yr^{-1}).

In PROFILE, the assumption is that ammonia and nitrate are taken up in fixed proportions, provided that both components are in supply. This fixed ratio is refered to as x_{NH_4}. The rate of nitrification is governed by a kinetic expression:

$$R_{nitr} = \frac{k_{nitr} [NH_4^+]}{K_{nitr} + [NH_4^+]}.$$ (19)

The values of the kinetic rate coefficient k_{nitr} and the Michaelis–Menten saturation constant K_{nitr} are discussed in 'Mapping Critical Loads' (Sverdrup et al., 1990).

It is possible to solve for $[NH_4^+]$ by combining Equation (7) with Equation (19) and the condition that $R_{NH_4} = x_{NH_4} R_{Nmax}$. The ammonia concentration is then given as the solution to an ordinary second-order equation:

$$[NH_4^+] = \frac{K_{nit} - \alpha}{2} + \sqrt{(\frac{K_{nit} - \alpha}{2})^2 + K_{nit} (\alpha + \frac{k_{nit}\Theta z}{Q})}$$ (20)

where

$$\alpha = \frac{[NH_4^+]_0 \, Q_0}{Q} - (k_{nit} + x_{NH_4^+} R_{Nmax}) \frac{\Theta z}{Q}.$$

If the ammonia entering a soil layer is sufficient to meet the demand for N we therefore get the following result to enter into the mass balances:

$$[NH_4^+]>0 \quad \begin{cases} R_{NH_4} = \dfrac{Q_0[NH_4^+]_0 - Q[NH_4^+]}{z\Theta} - R_{nit} \\[2mm] R_{NO_3} = \min\left(\dfrac{Q_0[NO_3^-]}{z\Theta} + R_{nit}, \, (1 - x_{NH_4^+}) R_{Nmax} \right) \\[2mm] R_{nit} = \dfrac{k_{nitr}[NH_4^+]}{k_{nitr} + [NH_4^+]} \end{cases} \quad (21)$$

If the supply of NH_4 does not meet the total N uptake demand, however, the solution to Equation (20) becomes 0.

We then get:

$$[NH_4^+]=0 \quad \begin{cases} R_{NH_4} = \dfrac{Q_0[NH_4^+]_0}{z\Theta} \\[2mm] R_{NO_3} = \min\left(\dfrac{Q_0[NO_3^-]}{z\Theta}, \, R_{Nmax} - R_{NH_4} \right) \\[2mm] R_{nit} = 0 \end{cases} \quad (22)$$

The 'min' operator means that the lowest value of thetwo argument in the paranthesis is choosen. This condition prevents uptake of nitrate to exceed the input to the soil layer, which would result in negative concentrations in the calculations.

2.4. BASE CATION UPTAKE

As the N uptake, base cation uptake is represented by a forcing function rather than a process. Furthermore, there is no constraint in the model that base cation uptake should occur in a certain proportion to the N uptake. The only condition is that the uptake cannot be larger than the supply from internal or external sources within a soil layer.

Based on the steady-state mass balance (Equation 5), the uptake expressed per unit soil solution is given as:

$$R_{BC} = \min\left(\frac{Q_0[BC]_0}{z\Theta} + R_w, R_{BCmax} \right). \quad (23)$$

In this case, the 'min' operator puts a constraint on the uptake the sum of what enters the soil layer by convective flow and what is produced not to exceed by chemical weathering.

Due to internal element cycling the actual uptake activity may be larger than

52

CALCULATING CRITICAL LOADS OF ACID DEPOSITION WITH PROFILE

the net removal from the soil solution. A key process to include into the calculations is mineralization of organic matter, primary in the uppermost horizon. Mineralization can be accounted for by assigning a negative value to the uptake rates. The effect is then that base cations, and ammonia is produced. This should be balanced by increased uptake in lower horizons.

2.5. THE WEATHERING RATE SUB-MODEL

In many types of soil systems, weathering of primary minerals provides the long-term neutralization capacity (Reuss *et al.*, 1986). PROFILE has many elements in common with other contemporary soil acidification models (Sverdrup *et al.*, 1990; de Vries *et al.*, 1989). Regarding weathering reactions, however, PROFILE allows the weathering rate to be calculated explicitly from independent soil properties (Sverdrup and Warfvinge, 1988b), rather than being an input to the model. In this context, weathering refers to the release of alkalinity and base cations, rather than the actual dissociation of the silicate structure. The weathering rate constants used in the model are therefore not comparable with rate coefficients determined from Si and Al production experiments.

Several chemical reactions between the mineral and constituents in the liquid solution contribute to the base cation release rate from chemical weathering of silicate minerals, and the total will be the sum of the rates of the individual elementary reactions. For most minerals several dissolution reactions have been experimentally identified (Sverdrup, 1990). These involve many components in the liquid phase; H^+, H_2O, OH^- and dissolved CO_2, as well as Al, cations of the parent mineral and strongly complexing organic ligands.

The total base cation release rate is taken to be the sum of the rates of all the chemical reactions taking place to dissolve the mineral minus the rate of precipitation of secondary solid phases. The rate is proportional to the exposed surface area of the mineral, and by inserting the expression for the concentration of activated complex in the rate equation based on the transition state theory, a general equation for the weathering rate at constant temperature may be derived. Under the conditions prevailing in the natural soil environment, the base cation release rate for a single mineral, r, may be approximated by:

$$r = k_H \cdot \frac{[H^+]^{n_H}}{f_H} + \frac{k_{H_2O}}{f_{H_2O}} + k_{CO_2} P_{CO_2}{}^{n_{CO_2}}$$ (24)

where

k_H	=	rate coefficient for the reaction with H^+ (m s^{-1})
k_{H_2O}	=	rate coefficient for the reaction with H_2O (kmol$_c$ m^{-2} s^{-1})
k_{CO_2}	=	rate coefficient for the reaction with CO_2 (kmol$_c$ atm^{-1} m^{-2} s^{-1})
n_H etc.	=	reaction order of individual reactions
f_H, f_{H_2O}	=	rate reduction factors for product inhibition.

Numerical values for the all coefficients of the minerals at present considered in

TABLE II

Rate coefficients for the base cation release from weathering reactions at a temperature of 8 °C.

Mineral	pk_H	n_H	pk_{H_2O}	pk_{CO}	n_{CO}	k_{Al}	x_{Al}	z_{Al}	k_{Ca}	x_{Ca}	z_{Ca}
K-Feldspar	16.0	0.5	17.2	17.2	0.6	$1\cdot10^{-5}$	0.4	0.14	5×10^{-4}	0.15	0.15
Olligoclase	15.9	0.5	17.0	15.8	0.6	$2\cdot10^{-5}$	0.4	0.14	1×10^{-3}	0.2	0.15
Albite	15.4	0.5	17.0	15.9	0.6	$1\cdot10^{-5}$	0.4	0.14	5×10^{-4}	0.2	0.15
Hornblende	15.4	0.7	17.0	15.9	0.6	$5\cdot10^{-5}$	0.3	0.3	2.5×10^{-3}	0.3	0.3
Pyroxene	13.8	0.7	17.5	15.8	0.6	$5\cdot10^{-4}$	0.2	0.1	2.5×10^{-2}	0.3	0.3
Epidote	12.6	0.8	16.8	15.8	0.6	$5\cdot10^{-4}$	0.3	0.2	2.5×10^{-2}	0.2	0.2
Garnet	12.4	1.0	16.9	15.8	0.6	$1\cdot10^{-3}$	0.4	0.2	5×10^{-2}	0.2	0.2
Biotite	15.3	0.6	17.6	15.8	0.5	$1\cdot10^{-5}$	0.3	0.2	5×10^{-4}	0.2	0.2
Muscovite	15.2	0.5	17.5	16.5	0.5	$1\cdot10^{-6}$	0.4	0.2	5×10^{-5}	0.1	0.1
Chlorite	15.3	0.7	16.7	15.8	0.5	$5\cdot10^{-5}$	0.2	0.1	2.5×10^{-3}	0.2	0.11
Vermiculite	14.8	0.6	17.6	16.5	0.5	$1\cdot10^{-6}$	0.4	0.1	5×10^{-5}	0.2	0.1
Apatite	12.8	0.7	15.8	–	–	–	–	–	3×10^{-4}	0.4	0.2

PROFILE are given in Table II. Reactions with organic ligands have been lumped with the rate of the reaction with water. The two factors reducing the rate of base cation production due to increased concentrations of weathering products, $f_H \cdot f_{H_2O}$ are defined as:

$$f_H = (1 + \frac{[Al^{3+}]}{k_{Al}})^{x_{Al}} + (1 + \frac{[BC^{2+}]}{k_{BC}})^{x_{BC}} \tag{25}$$

$$f_{H_2O} = (1 + \frac{[Al^{3+}]}{k_{Al}})^{z_{Al}} + (1 + \frac{[BC^{2+}]}{k_{BC}})^{z_{BC}} \tag{26}$$

where

k_{Al}, k_{BC} = saturation coefficients for dissolution reduction (kmol$_c$ m^{-3})

$x_{Al}, x_{BC}, z_{Al}, z_{BC}$ = reaction orders.

The rate of weathering reactions in soils are kinetically limited, and hence temperature dependent. The temperature effect is quantified through the Arrhenius equation, stating that the reaction rate coefficient is function of a thermodynamic property the activation energy. In PROFILE, the rate coefficient for a given temperature is calculated as.

$$k_T = k_s \exp -\left(\frac{E_A}{R} (\frac{1}{T} - \frac{1}{273.+8}) \right) \tag{27}$$

where

k_T = rate coefficient at Temperature T
k_s = rate coefficient at 8 °C (Table I)
E_A = activation energy (kJ kmol^{-1})
R = universal gas constant (kJ kmol^{-1} K^{-1}).

TABLE III

Lumped activation energies used to calculate the weathering rate coefficient from 8 C to the temperature T, by means of Equation(27), and stoichometric coefficients representing the relative release of base cations. Source: (Sverdrup, 1990)

Mineral	$E_A R^{-1}$			Base cation content			
	pk_H	pk_{H_2O}	pk_{CO_2}	y_{Na}	y_K	y_{Mg}	y_{Ca}
K-Feldspar	3500	2000	1700	0.0	0.90	–	–
Oligoclase	4200	2500	1700	0.45	–	–	0.55
Albite	3800	2500	1700	0.9	–	–	0.1
Hornblende	4300	3800	1700	–	–	0.67	0.33
Pyroxene	2700	3800	1700	–	–	0.50	0.50
Epidote	2500	3800	1700	–	–	–	1.0
Garnet	2500	3500	1700	–	–	0.25	0.75
Biotite	4500	3800	1700	–	0.20	0.80	–
Muscovite	4500	3800	1700	–	0.80	0.20	–
Chlorite	4500	3800	1700	–	–	1.0	–
Vermiculite	4300	3800	1700	–	0.50	0.50	–
Apatite	3500	4000	1700	–	–	–	1.0

Values used for E_A/R are given in Table III. The effect of the temperature on model is output is often quite large. Typically, a change by 4° results in a change in weathering rate by 30%.

In soils the availability of moisture may be limited causing the activity of the exposed mineral surface to be less than unity. The reactions will only take place on wetted surfaces, and the degree of surface wetting is taken to be proportional to the soil moisture saturation. All surfaces to participate in reaction must be wetted, but there must also be sufficient soil solution present for the weathering process to communicate with other soil processes. In PROFILE the activity of the reacting surface is assumed to be proportional to the soil moisture saturation. For dissolution in the natural soil environment, the rate equation for each soil horizon is:

$$R_w = \sum_{i}^{minerals} (1 - y_{Na}) \, r_i \, A_{exp} \, x_i \, \theta \qquad (28)$$

where

r_i	=	rate of base cation production from mineral i (Equation (24)) $(kmol_c \, m^{-2} \, s^{-1})$
y_{Na}	=	fraction of Na released during weathering of mineral i
A_{exp}	=	exposed surface of the mineral matrix $(m^2 \, m_s^{-3})$
θ	=	the soil moisture saturation
x_i	=	fraction of mineral i in the mineral matrix of the soil horizon.

The exposed surface in the soil horizon can be approximated from a BET analysis of a particle size distribution and the mineralogy (Sverdrup et al., 1990). The soil moisture saturation is calculated by combining the densities of a solid, an

aqueous, and a gaseous phase with the bulk density ρ_{soil} and the volumetric water content Θ:

$$\theta = \frac{2700\ \Theta}{2700 + 1000\ \Theta - \rho_{soil}}. \tag{29}$$

2.6. The ion exchanged sub-model

With the concentrations of all liquid phase components computed, the composition of the exchanger phase may be determined. Three equations are necessary to calculate the charge fractions; two selectivity quations and one total conditions. With the Gapon exchange equations, the condition given by the definition of charge fraction we get:

$$K_{H/Al} = \frac{[H^+]^3\ \bar{X}_{Al}^3}{[Al^{3+}]\ \bar{X}_H^3} \tag{30}$$

$$K_{H/BC} = \frac{[H^+]^2\ \bar{X}_{BC}^2}{[BC^{2+}]\ \bar{X}_H^2} \tag{31}$$

$$1 = \bar{X}_H + \bar{X}_{Al} + \bar{X}_{BC} \tag{32}$$

where

$\bar{X}_H, \bar{X}_{BC}, \bar{X}_{Al}$ = charge fraction of H, BC and Al on cation exchange matrix

$K_{H/Al}$ = Gapon selectivity coefficient for H-Al exchange

$K_{H/BC}$ = Gapon selectivity coefficient for H-Ca exchange.

Solving for $\bar{X}_{Al}$ and $\bar{X}_{BC}$ in Equation (30) and Equation (31) respectively, and substituting these quantities into Equation (32) makes it possible to solve for $\bar{X}_H$ explicitly as:

$$\bar{X}_H = (1 + \frac{K_{H/Al}^{1/3}\ [Al^{3+}]^{1/3}}{[H^+]} + \frac{K_{H/BC}^{1/2}\ [BC^{2+}]^{1/2}}{[H^-]})^{-1}. \tag{33}$$

The calculated value of $\bar{X}_H$ can now be used with the selectivity equation in order to characterize the exchanger phase completely.

2.7. Stream water composition

The composition of the stream water is calculated from a steady-state mass balance, where the system boundary is taken around all soil compartments. This is shown in Figure 3. With this concept it is not necessary to keep track on how water is routed within the soil column. For each component in the solution an equation analogous to Equations (4) to (7) is used. For ANC, the mass balance becomes:
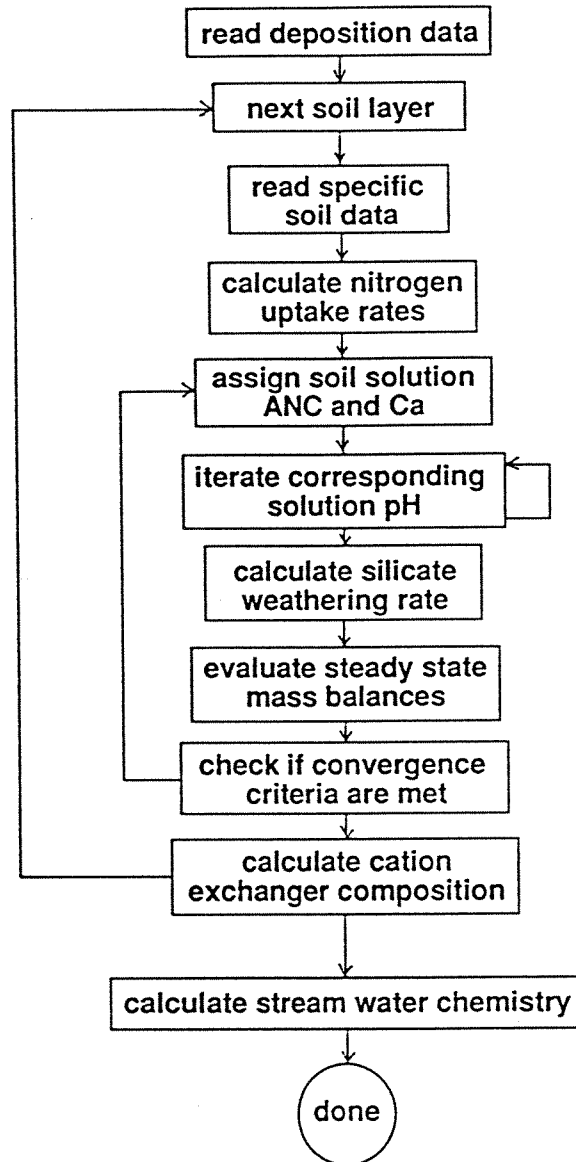
56

read deposition data

↓

next soil layer

↓

read specific
soil data

↓

calculate nitrogen
uptake rates

↓

assign soil solution
ANC and Ca

↓

iterate corresponding
solution pH

↓

calculate silicate
weathering rate

↓

evaluate steady state
mass balances

↓

check if convergence
criteria are met

↓

calculate cation
exchanger composition

↓

calculate stream water chemistry

↓

done

Fig. 3. Calculation order for solving equations in the PROFILE model.

$$Q_{run}\,[ANC]_L = Q_{prec}\,[ANC]_{prec} + \sum^{layers} z\,\theta\,(R_w - R_{BC} + R_N) \qquad (34)$$

where

Q_{run}, Q_{prec} = run-off and precipitation rate (m yr^{-1})

ANC_{run}, ANC_{prec} = ANC of run-off and precipitation (kmol m^{-3})

Corresponding balances are evaluated for BC, NO_3^- and NH_4^+. The pH and the Al

134   PER WARFVINGE AND HARALD SVERDRUP

concentration of the run-off is calculated from the ANC by means of Equation (9).

2.8. COMPUTER IMPLEMENTATION

The equations in the PROFILE model are solved according to the flow sheet in Figure 5.1.8. The iterations are carried out with a Regula–Falsi iteration procedure in order to avoid the hazards involved in applying Newton–Raphsons method on these systems of equations.

PROFILE is available as a computer application for Apple Macintosh computers, and requires fractions of a second of computer time. Input data for soil chemistry

Fig. 4. Data input screens as displayed by the PROFILE computer application.

calculations are entered interactively on two types of screens. On one screen, general data is entered, as shown in the upper part of Figure 4. The nitrification rate is selected according to different classes (Sverdrup *et al.*, 1990). On additional screens, data specific for a each soil horizon is given. Mineralogy is choosen from a selection of twelve common groups of minerals.

A user's manual with cross-references to the 'Mapping Critical Loads' document further facilitates model use. The computer implementation of the model is available through the authors, easy to use and available free of charge for non-commercial use.

Besides calculating soil and stream water chemistry, the model calculates the BC to Al ratio in the soil solution. This quantity is known to serve as an indicator of the potential for forest growth (Huetterman and Ulrich, 1984; and G. van Loenen, 1989). Also, the model summarizes general results such as total weathering rate in the profile, total uptake of N and base cations, acidity produced by N cycling and deposition rates expressed according to different conventions.

3. Results and Discussion

PFOFILE was applied to the research site at Gårdsjön in SW Sweden (Olsson *et al.*, 1985). The model was used to calculated the critical loads of two very similar subcatchment by Lake Gårdsjön, F1 and F3. Calculation were performed with respect to the forest soil and the surface water, applying specific criteria for each system. Input data used for soil chemistry calculations are showed in Table IV. The nitrification rate coefficient was $k_{nitr}=0.005$, and preference of ammonia to nitrate uptake was set to 2:1, expressed as $x_{NH_4^+} = 0.67$.

At present, the total deposition of all acid precursors, the potential acidity, amounts to 2.24 $kmol_c$ ha^{-1} yr^{-1} (Lövblad *et al.*, 1991). The contribution of total acidity deposited with SO_4^{2-} is 1.27, NO_3^- is 0.72 while NH_4^+ contribute 0.62 $kmol_c$ ha^{-1} yr^{-1}. The total atmospheric base cation input is 0.74 $kmol_c$ ha^{-1} yr^{-1}, of which the non-marine part contributes with a net alkalinity input of 0.37 $kmol_c$ ha^{-1} yr^{-1}.

Figures 5, 6 and 7 show PROFILE calculations performed for the subcatchments. Soil solution data was taken from Gieser and Lundström (1991). For comparison, pH measured in water suspension (Melkerud, 1983) was included in Figure 5. While the model calculates a long term value for the soil solution, the measurements represent temporal point data. Therefore the model can be said to describe the annual averageconditions in the profile. It is clear, however, that the model exhibit the same spatial pattern as the data with lower pH values in the upper soil layers. The internal acidity input in the O horizon is nitrification and NH_4^+ immobilization, while weathering and NO_3^- are sources of alkalinity in the lower layers. While H and Al are strongly coupled via the pH-ANC relationship and the Al equilibrium system, and the value of K_G is therefore an immediate link between pH and calculated

TABLE IV

1: (Melkerud, 1983),2: (Lundin, 1982),3: (Castelle and Galloway, 1990),4: (Jacks and Norrström, 1986),5: (Raben, 1988),6: (Persson and Broberg, 1985),7: (Gieser and Lundström, 1991)

Parameter	Unit	Soil layer					Ref.
		1	2	3	4	5	
Soil layer height	m	0.05	0.10	0.10	0.30	0.15	1
Moisture content	$m^3\ m^{-3}$	0.2	0.2	0.2	0.2	0.2	2
Soil bulk density	$kg\ m^{-3}$	800	1200	1400	1600	1600	1
Specific surface area	$m^2\ m^{-3}$	5×10^5	1×10^7	1.5×10^6	1.7×10^6	1.7×10^6	1
CO_2 pressure	times ambient	3	5	10	15	20	3, 4
Inflow	% of precipitation	100	90	80	70	61	a
Percolation	% of precipitation	90	80	70	61	61	a
Mg–Ca+K uptake	% of total max	20	20	30	30	0	5
N uptake /	% of total max	20	20	30	30	0	5
Dissolved organic carbon	$mg\ L^{-1}$	34	76	8	5.9	5.9	5
log Gibbsite eq. constant	$kmol^2\ m^{-3}$	6.5	8.12	9.05	9.27	9.27	6
Mineral		% of total					
K-feldspar		15	15	18	13	19	
Oligoclase		14	14	12	16	14	
Hornblende		0.1	0.5	0.5	1.5	0.5	
Epidote		0.1	0.5	0.5	1.5	0.5	
Garnet		0	0.1	0.1	0.1	0.1	
Biotite		0	0.1	0.5	0.5	0.5	
Chlorite		0	0.4	0.4	0.4	0.4	
Vermiculite		0	3.0	5.0	0	0	
Quartz		70.9	69.0	65.0	63.0	65.0	

a Pure guess.

Al concentration. To obtain the best values for K_G these were actually calculated from the data. The capability of the model to reproduce pH and Al data is therefore dependent on how well it calculates the ANC. At present PROFILE cannot present the calculations of different base cations separately because the vertical distribution of the uptake and regeneration of different base cations are not known. The comparison between measured Ca and calculated BC should therefore not be brought too far.

Critical loads can be evaluated in different ways, depending on what processes in the ecosystem that are regarded as natural processes. The term 'potential acidity' implies that ammonia deposition results in release of acidity, either by direct uptake or nitrification. It is thus defined as:

$$\text{Potential acidity} = SO^*_{4,D} + NO_{3,D} + NH_{4,D} - BC^*_D \tag{35}$$

where $SO^*_{4,D}$, $NO_{3,D}$, $NH_{4,D}$, BC^*_D = Atmospheric deposition ($kmol_c\ ha^{-1}\ yr^{-1}$). Superscript * refers to deposition from non-marine sources, subscript D denotes deposition.

60

Gårdsjön, F1

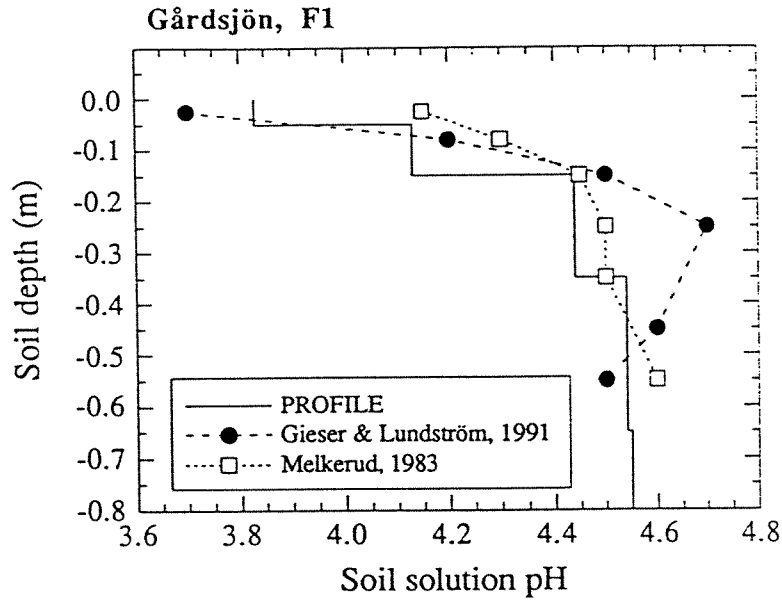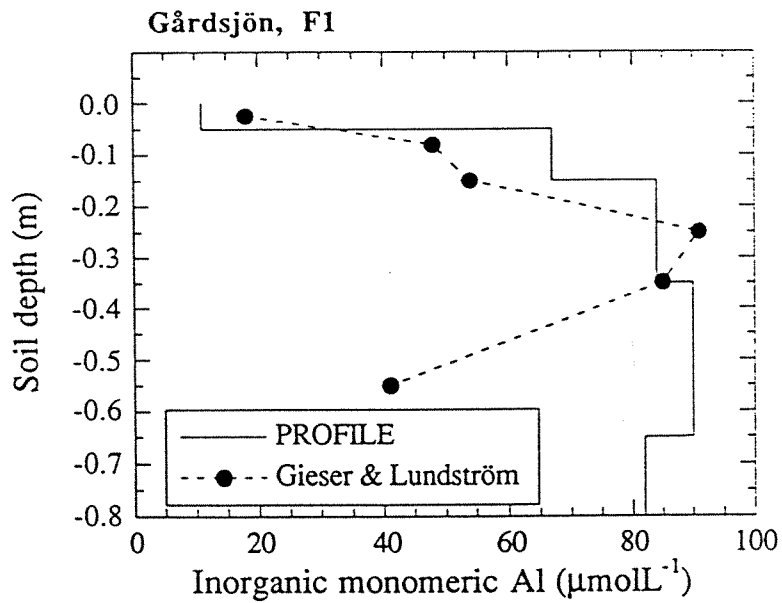Fig. 5. Calculated soil solution pH and data.

Gårdsjön, F1

Fig. 6. Calculated soil solution Al and data.

Gårdsjön, F1

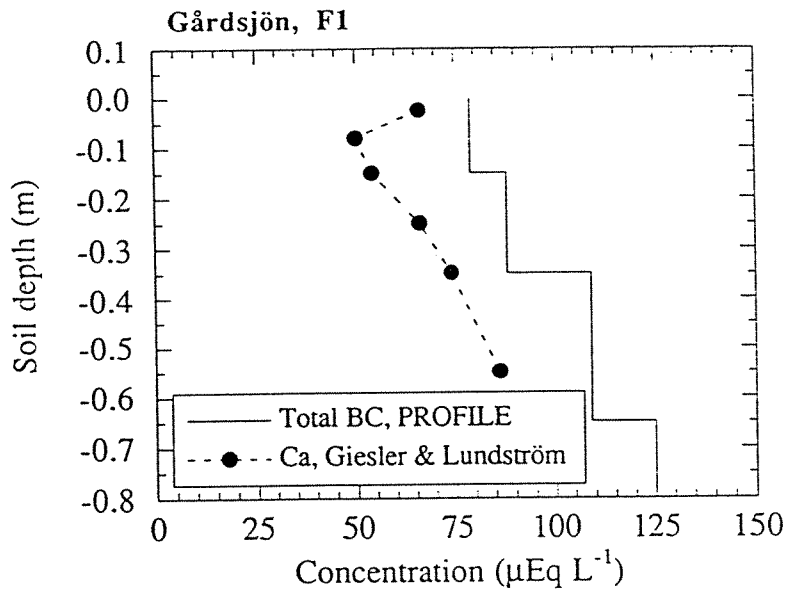Fig. 7. Calculated soil solution base cation concentration and data.

With this definition, the critical load becomes (Sverdrup et al., 1990):

Critical load of Potential acidity =

$$= \sum_{z}^{layers} z \, \Theta \, (R_w - R_{BC} + R_N) - Q_{run} \, [ANC]_L \tag{36}$$

With this definition, the critical load is assessed under the condition that the influence of land use, quantified in the uptake of base cations and N will remain at present level.

Although the definition of the critical load is independent of which receptor that is considered, the actual value depends on if the soil system or the surface water is considered since different critical criteria are applied. This is because that the biological indicators in the two systems are different. The forest stand is the biological indicator for the soil system, while fish populations should protected in surface waters.

For forest soil, the Manual on Mapping of Critical Loads' suggests that the molar ratio of Ca to Al in the soil solution is used as criterion. This quantity is known to serve as an indicator of the potential for forest growth. A low ratio of Ca to Al indicates that the uptake of nutrient cations is subject to competition from Al which specifically inhibits the development of active root tips. The model does not distinguish between the nutrients Ca, Mg and K, and PROFILE therefore calculates the molar ratio between 'base' cations, BC to Al^{3+}.

Figure 7 shows the calculated minimum soil solution BC:Al ratio as the bold

line as a function of deposition of potential acidity. Given that the criteria for forest soils is a BC:Al ratio of 1.0, the critical load of the system is 1.64 $kmol_c$ ha^{-1} yr^{-1}. The S deposition must consequetly be reduced by 50% to reach a target deposition corresponding to the critical load for the forest soil, if N deposition remains unchanged. According to concept of potential acidity, however, the relativ proportions of change in deposition has no influence, as long as the total reduction in deposition of acid precursors is sufficient.

The critical load can also be calculated directly from PROFILE output according to Equation (36). With a calculated weathering rate of 0.584 $kmol_c$ ha^{-1} yr^{-1}, and an ANC in the runoff of -46 μmol m^{-3} (0.252 $kmol_c$ ha^{-1} yr^{-1}) and additional data from Table V, it is evaluated as:

$$\text{Critical load of Potential acidity} = 0.584 - 0.5 + 1.3 - (-0.252) = 1.64. \quad (37)$$

The data that are foundation for setting the critical BC:Al ratio to 1.0 anywhere in the root zone do leave room for different interpretations (Sverdrup et al., 1990; Sverdrup and Warfvinge, 1990). Applying the more strict criteria of [BC]:[Al] = 1.25 leads to a decrease in critical load by 0.20 $kmol_c$ ha^{-1} yr^{-1}, a rather small change as compared to other uncertainties involved. With a criteria of 0.75, however, the critical load will increase by 0.35 $kmol_c$ ha^{-1} yr^{-1}. According to PROFILE calculations the lowest value of the BC:Al ratio in the root zone consistently appears in the B horizon.

The critical load for surface water of the two minicatchments F1 and F3 in the Lake Gårdsjön area was calculated with the same data as for the forest soil. As described above this is performed with Equation (34) and corresponding equations for base cations, NH_4^+ and NO_3^-. Additional input parameters are limited to the K_G, DOC and P_{CO_2} of the stream water. At the pH levels corresponding to the

TABLE V

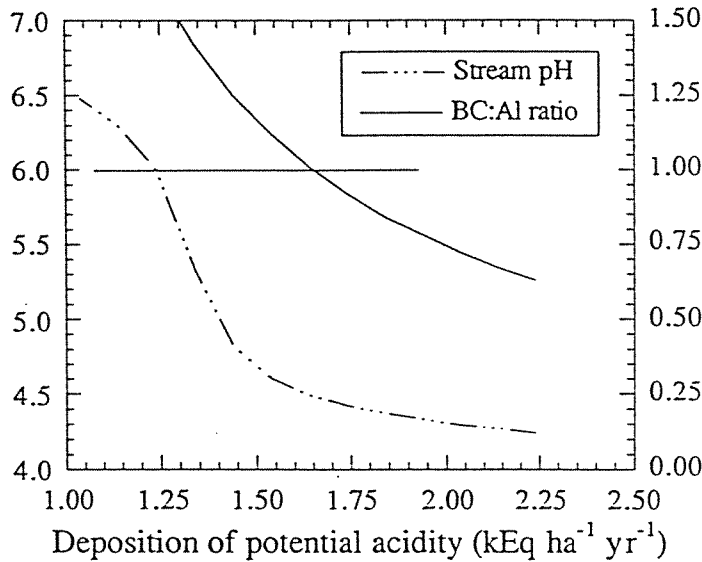| Parameter	Unit	Value
Precipitation	m yr^{-1}	0.9
Runoff	m yr^{-1}	0.56
Temperature	°C	8
Present deposition:		
H_2SO_4	kEq ha-1 yr^{-1}	1.27
HNO_3	kEq ha-1 yr^{-1}	0.72
NH_4^+	kEq ha-1 yr^{-1}	0.62
Ca-Mg+K	kEq ha-1 yr^{-1}	0.74
Non-marine fraction	%	50
Maxiumum uptake		
Ca-Mg+K	kEq ha-1 yr^{-1}	0.50
$NO_3^- + NH_4^+$	kEq ha-1 yr^{-1}	1.30

Fig. 8. Soil solution BC:Al ratio and stream pH as a function of deposition rate, as calculated by PROFILE.

Swedish criteria for surface waters, an ANC of 20 mmol m^{-3}, Al buffering is negligable. The DOC in the streams draining F1 and F3 is 7.7 mg L^{-1} (Persson and Broberg, 1985), while the CO_2 pressure in equilibrium with the stream water was estimated to 2 times atmospheric partial pressure.

The results from these calculations are shown in Figure 8. At present, the runoff from these subcatchments are in the range 4.1 to 4.3 (Hultberg, 1985). This corresponds to the model's predictions of the stream water pH at present deposition. This indicates that the catchments are terminally acidified, i.e. the soil have reached a steady-state with the acid deposition. This conclusion is further supported by a proton budget of the catchment (Nilsson, 1985).

The calculations show that the acid deposition at Lake Gårdsjön would have to be decreased even further in order reach a critical loads, as compared to the critical loads of the soil. The difference can be interpreted by means of Equation (36). While leaching of acidity could be tolerated from the forest soil, a positive ANC is necessary to meet the criterion of pH 6.0 in the runoff. Also, the weathering rate is marginally lower at the lower rate of deposition corresponding to the critical load for the stream waer. The calculation becomes:

$$\text{Critical load of Potential acidity} = 0.567 - 0.5 + 1.3 - 0.132 = 1.235. \qquad (38)$$

The result that the critical loads for the forest soil and the stream water at Gårdsjön are similar should not be made into a general conclusion. In many regions, such as S. Norway, tills may be even more shallow than at Lake Gårdjön, and the weathering capability is very small. In such areas, the most sensitive receptor

is therefore most likely to be the surface waters, while the opposite may be case for Central Sweden and S.E. Norway.

It must be pointed out however, that the observed N uptake largely exceeds the rate of base cation uptake. This indicates an imbalance in the ecosystem that may not correspond to a steady-state situation, unless denitrification is the actual cause of the apparently almost complete N uptake in the terrestrial ecosystem. To avoid this effect, the critical load may therefore be 'cleaned' from factors caused by forestry and pseudy-steady state by deleting the uptake from the critical loads definition. One can therefore calculate a critical load based on the inherent capability of the system to neutralize acid deposition as:

$$\text{Critical load of acidity} = \sum^{\text{layers}} z \,\Theta\, R_w - Q_{run} [\text{ANC}]_L . \tag{39}$$

With this convention, the critical load of acidity for the forest soil becomes 0.84 and 0.435 for surface waters. With this definition, it becomes more obvious that the present imbalance between base cation and N uptake is a very important source of alkalinity in the system. In a longer perspective, the required reductions in S depositions calculated from the critical load of potential acidity will not suffice to meet the critical load. but N deposition must also be reduced. Mathematically, however, the present exceedance of the critical load is identical with the exceedance of the critical load of potential acidity. This is because the uptake terms then are considered as external loads of acidity or alkalinity, comparable with the atmospheric deposition.

4. Conclusions

PROFILE allows the sensitivity of different ecosystems to be quantified in terms of critical loads. The critical load can thus be calculated from geophysical data, and is not based on information of the present state of acidification of a system. The model requires input data, such as minerology, that are not routine measurements in most field projects, and we wish that other researchers in terrestrial sciences are encouraged to consider to put emphasis on gathering such data. The Al chemistry in PROFILE is based on the presence of phase that is still yet to be discovered. PROFILE may provide a framework to explore new hypothesis regarding Al mobility in soils since it makes it possible to separate the primary production of Al from silicate minerals from the influende of secondary phases.

By definition, the critical load should be calculated from long-term conditions. Regarding the N issue, the problem is basically that there is a lack of knowledge how terrestrial ecosystems will respond to high N loads. Here, PROFILE is simple tool for assessing the effects of different N uptake/deposition scenarios.

Acknowledgment

References

Castelle, A. J. and Galloway, J. N.: 1990, 'Carbon Dioxide Dynamics in Acid Forest Soils in Shenandoah National Park, Virginia', *Journal of Soil Science Society of America* 4, 252.

Chen, C. J., Gherini, S., Hudson, R. M., and Dean, S.: 1983, *The Integrated Lake-Watershed Acidification Study*, Final Report EPRI EA-3221, Electrical Power Research Institute, Palo alto, California.

Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N.: 1985, 'Modeling the Effects of Acid Deposition: Assessment of a Lumped Parameter Model for Soil Water and Stream Water Chemistry', *Water Resources Research* 21, 51.

Galloway, J. N. and Dillon, P. J.: 1983, 'Effects of Acid Deposition: The Importance of Nitrogen', in *Ecological Effects of Acid Deposition*, National Swedish Environmental Protection Board, pp. 145–160.

Giesler, R. and Lundström, U.: 1991, 'The Chemistry of Several Podsol Profile Soil Solutes Extracted with Centrifuge Drainage Technique', in Rosén, K. (eds.), *Chemical Weathering under Field Conditions*, Swedish University of Agricultural Sciences, Department of Forest Soils, Uppsala, Sweden, pp. 157–165.

Huetterman, A. and Ulrich, B.: 1984, 'Solid Phase-Solution-Root Interaction in Soils Subjected to Acid Deposition', *Phil. Trans. R. Lond.*, B305,352.

Hultberg, H.: 1985, *Budgets of Base Cations, Chloride, Nitrogen and Sulphur in the Acid Lake Gårdsjön*, Vol. 37 of *Ecological bulletin*, Swedish Natural Science Research Council (NFR), Stockholm, Sweden, pp. 133–157.

Jacks, G. and Norrström, A-C.: 1986, Markkalkning för att åtgärda surt grundvatten (Soil liming for mitigating acid groundwater). Progress report, Department of Land IMprovement and Drainage, Royal Institute of Technology, Stockholm, Sweden.

Keltjens, W. G. and Loenen, E. van: 1989, 'Effects of Aluminium and Mineral Nutrition on Growth and Chemical Composition of Hydroponically Grown Seedlings of Live Different Forest Tree Species', *Plant and Soil* 119, 39.

Lundin, L.: 1982, *Soil Moisture and Ground Water in Till Soil and Significance of Soil type for Runoff*, UGNI Report No. 56, Dept. of Physical Geography, Upsale University, Upsala, Sweden.

Lövblad, G., Andersen. B., Hovman, M., Joffre, S., Pedersen, U., and Reisell, a.: 1991, *Mapping Deposition of Sulphur, Nitrogen and Base Cations to the Nordic Countries*, Nordic Council of Ministers, Copenhagen (in prep.).

Melkerud, P. A.: 1983, *Quaterny Deposits and Bedrock Outcrops in an Area Around Gårdsjön, South-West Sweden, with Physical, Mineralogical Geochemical Investigation*, Reports on Forest Ecology and Forest Soils No.: 40. Swedish University of Agricultural Sciences, Upsala, Sweden.

Nilsson, I. S.: 1985, *Why is Lake Gårdsjön acid? - An Evaluation of Processes Contributing to Soil and Water Acidification*, Vol. 37 of *Ecological Bulletin*. Swedish Natural Science Research Council (NFR), Stockholm, Sweden, pp. 311–318.

Olausson, S., Warfvinge, P., and Sverdrup, H.: 1990, *An Aluminium Model Based on the Kinetics of Dissolution and Precipitation in Relation to the Gibbsite Model*, Presented at Internation Conference on Acidic Deposition, Glasgow 16–21 September 1990.

Oliver, G. G., Thurman, E. M., and Malcolm, R. L.: 1983, 'The Contribution of Humic Substances to the Acidity of Colored Natural Waters', *Geochimica et Cosmochimica Acta* 47, 2031.

Olsson, B., Hallbäcken, L., Johansson, S., Melkerud, P-A, Nilsson, I., and Nilsson, T.: 1985, *The Lake Gårdsjön Area – Physigeographical and Biological Features*, Vol. 37 of *Ecological Bulletin*. Swedish Science Research Council (NFR), Stockholm, Sweden, pp. 10–28.

Persson, G. and Broberg, O.: 1985, *Nutrient Concentrations in the Acidified Lake Gårdsjön: The Role of Transport and Retention of Phosforus, Nitrogen and DOC in Watershed and Lake*, Vol. 37 of *Ecological Bulletin*, Swedish Natural Science Research Council (NFR), Stockholm, Sweden, pp. 158–175.

Raben, G. H.: 1988, *Untersuchungen zur raumeitlichen Entwicklung boden- und wurtzel-chemischer Stressparameter und deren Einfluss auf die Feindwurzelentwicklung in bodensauren Waldgesellschaften des Hils*, Vol. Reihe A, Bd. 38 of *Berichte des Forschungszentrums Waldökosysteme/Waldsterben*, Göttingen, Germany.

Reuss, J., Christophersen, N., and Seip, H. M.: 1986, 'A Critique of Models for Freshwsater and Soil Acidification', *Water, Air, and Soil Pollution* 30, 909.

Schecher, W. D. and Driscoll, C. T.: 1987, 'An Evaluation of Uncertainty Associated with Aluminium Equilibrium Calculations', *Water Resources Research* 23, 525.

Schnoor, G., Palmer Jr., W. D., and Glass, G. E.: 1984, 'Modeling Impacts of Acid Precipitation for Northeastern Minnesota', in Schnoor, G. (ed.), *Modeling of Total Acid Precipitation Impacts*. Butterworth Publishing, London.

Stumm, W. and Morgan, J. J.: 1983, *Aquatic Chemistry*, Wiley Interscience. New York.

Sverdrup, H. and Warfvinge, P.: 1988a, 'Assesment of Critical Loads of Acid Deposition on Forest Soils', in Nilsson, J. (ed.), *Critical Loads for Sulphur and Nitrogen*. Nordic Council of Ministers and The United Nations Economic Commission for Europe (ECE). pp. 81–130.

Sverdrup, H. and Warfvinge, P.: 1988b, 'Weathering of Primary Silicate Minerals in the Natural Soil Environment in Relation to a Chemical Weathering Model', *Water, Air, and Soil Pollution*, 38, 387.

Sverdrup, H. and Warfvinge, P.: 1992, 'A Model for the Impact of Soil Solution Ca:Al Ratio on Tree Base Cation Uptake', *Water, Air, and Soil Pollution*, 61, 365.

Sverdrup, H. U., Vries, W. de, and Henriksen, A.: 1990, *Mapping Critical Loads*. Nord 1990:98. Nordic Council of Ministers.

Sverdrup, H.: 1990, *The Kinetics of Base Cation Release Due to Chemical Weathering*. Lund University, February 1990.

Vries, W. de, Posch, M., and K m ri, J.: 1989, 'Simulation of the Long Term Soil Response to Acid Deposition in Various Buffer Ranges', *Water, Air, and Soil Pollution* 48, 349.

Warfvinge, P. and Sverdrup, H.: 1990a, *Dynamic Modeling of Acidification of Forest Soils*, Presented at International Conference on Acidic Deposition. Glasgow 16–21 September 1990.

Warfvinge, P. and Sverdrup, H.: 1990b, 'The SAFE (Soil Acidification of Forested Ecosystems) Model', in Andersen, B. (ed.), *Soil Acidification Models Applied on Swedish Historic Soils Data*. Nordic Council of Ministers, Copenhagen (in prep.).

Ågren, S. and Jacks, G.: 1990, *Aluminium Mobility and Humic Substances*, Technical Report 1058, Royal Institute of Technology, Stockholm, Sweden.

ANNEX 8

Dan Aamlid

Monitoring of forest damage in Norway - a brief overwiew

68

MONITORING OF FOREST DAMAGE IN NORWAY
- A BRIEF OVERVIEW

Dan Aamlid
Norwegian Institute for Forest Research,
Høgskoleveien 12, N-1432 Ås, Norway

The system for monitoring forest damage i Norway is described. More than 50 000 trees are annually assessed as described by UN ECE/ICP-Forest. A set of 20 plots for intensive forest ecosystem analyses has been run since 1986/88 where a number of variables are measured, including those now being a part of the ICP-Forest Level 2 plots. The forest condition in Norway has slightly deteriorated during the monitoring period. A part of the deterioration may be caused by the contribution of air pollutants, acid rain and ozone.

INTRODUCTION

Alarming reports of "New forest damage" in central Europe in the early 1980s led Norwegian authorities to initiate a programme for monitoring various types of forest damage. Monitoring data has been collected since 1984. According to extensive international co-operation on methodology and exchange of results in this field, Norway carries out measurements of air pollutants in forests, nation-wide surveys of forest growth and vigour, and observations on permanent plots. This paper briefly summarises the forest monitoring system in Norway [1, 2], and some results up to 1993, as they are published elsewhere.

MATERIALS AND METHODS

Permanent research plots

Permanent research plots have been established in mature spruce forest of the bilberry type, at 20 locations distributed throughout the country (Fig. 1). Comprehensive studies of the forest ecosystem are performed. These plots correspond to Level 2 in the ECE-ICP Forests system. Studies that are undertaken at these plots include: Trees and vegetation, air and precipitation measurements, throughfall, litterfall, tree vigour criteria (incl. chemistry of needles), observations of needle fungi, soil profile description and classification, chemical analyses of soil and soil water.

Fig. 1. Location of the permanent research plots (Level 2 plots).

Nation-wide representative surveys
Two nation-wide, representative surveys, are running in Norway:

1) A forest survey is established, named "Monitoring of forest health condition", and corresponds to Level 1 in the ECE-ICP Forests system [3]. It includes monitoring of forests and soils. The survey is based on a 9 x 9 km network of permanent plots in coniferous forests. A 18 x 18 km network is established in the sub-alpine zone, where birch forests are common. Monitoring of about 8000 trees considers variables like crown density and crown colour, which are assessed annually. Monitoring of soils is made every fifth year, on the same sample plot network. The soil profile is described and classified. Soil chemical analysis includes a wide range of parameters for all layers, like pH (H_2O), exchangeable cations, organic C, Kjeldahl N, and soluble P.

2) A system of permanent plots (regionally based) has been run by the civil forest administration on county and district levels [4]. In each district four plots are subjectively laid out, one in each of the cutting classes III (younger production forest), IV (older production forest), V (mature forest), and one in the over-mature (declining) forest. About 800 plots have been established, comprising more than 40 000 trees. Main observations are crown density and crown colour. The plots are revised annually in September by the forest district officers.

RESULTS
The network of different forest monitoring sites has given information about the air pollution load in Norway [5], and a lot of information on the forest condition. The common variable of forest health is crown density. Information on crown density has been given annually for more than 50 000 trees every year since 1988. The average crown density for the whole country seems to have decreased since then. Results from the regionally based plot network has shown a tendency of clustering of yellowish forests along the south-eastern coastline [4]. Monitoring of throughfall chemistry has shown that nitrogen loads to forests are highest in the southern and south-eastern part of Norway [6]. At most plots there are less nitrogen found beneath the crown than above. Soil water studies have shown that the highest levels of total aluminium (tot-Al) occur at the southern plots [7].

CONCLUSIONS
Investigations so far have shown that the deposition of air pollutants is high in south-eastern Norway. However, airborne concentrations of potentially harmful compounds are not high enough, except from ozone, to cause direct injury to trees in Norway. Indirect injury, caused by nutrient leaching, is more likely. So far the results have shown that there has not been any extensive dieback of forests in Norway; the annual death rate of trees has been low and appears normal.

Based on the criteria crown density the vitality of the forest appears to be lower than normal in some areas in southern Norway [8]. This may partly be due to air pollution. However, this result has to be further verified. Most cases of crown discoloration are found in that region, and the number of discoloured (yellow) trees have increased noticeably during the last few years [4]. This may indicate a situation of unbalanced nutrition due to high levels of acid rain or other stresses of natural origin, e.g. drought.

As the forest health monitoring has been running, more clearly we see that forests in southern, south-eastern, and north-eastern parts of Norway, next to Russia, are negatively affected. The causal factors may be several, and they may interact in complex processes. The symptoms are not specific, but their regional co-occurrence may indicate a causal relationship with air pollutants.

REFERENCES

1. Venn, K., Aamlid, D., Sletnes, A.I. & Joranger, E. (1993) Skogskadesituasjonen i Norge. Status 1992. Rapp. Skogforsk. 18/93:1-46.

2. Horntvedt, R., Aamlid, D., Rørå, A. & Joranger, E. (1992) Monitoring programme for forest damage. An overview of the Norwegian programme. Norwegian Journal of Agricultural Sciences 6:1-17.

3. Kvamme, H. & Sletnes, A.I. (1994) Program "Overvåking av skogens sunnhetstilstand". Rapport 1993. Norsk instiutt for jord og skogkartlegging Rapport 1/94:1-28.

4. Solberg, S. (1993) Fylkesvise lokale overvåkingsflater. Vitalitetsregistreringer og kontroll 1993. Rapp. Skogforsk. 23/93:1-27.

5. SFT (Statens forurensningstilsyn) (1993) Overvåking av langtransportert forurenset luft og nedbør. Årsrapport 1992. Rapport 533/93. SFT TA 981/93:1-296.

6. Aamlid, D. (1993) Forurensninger i skog. Analyser av nedbør på intensivt overvåkete forskningsflater i 1992. Rapp. Skogforsk. 23/93:1-27.

7. Frogner, T. (1993) Jordvann i skog. Kjemisk sammensetning av jordvann på intensivt overvåkete forskningsflater. Status og tidsutvikling. Rapp.Skogforsk. 3/93:1-18.

8. Nellemann, C. & Frogner, T. (1994) Spatial patterns of spruce defoliation: Relation to acid deposition, critical loads, and natural growth conditions in Norway. Ambio 23:255-259.

ANNEX 9

Arne Henriksen

Critical loads for surface- and groundwater in the Slovak Republic

Calculation method and preliminary results

Critical loads for surface- and groundwater in the Slovak Republic

Calculation method and preliminary results

During the workshop on 6-7 October 1994 some preliminary calculations for critical loads and exceedances for surface and groundwater were carried out. This short note presents the method used and the results obtained.

The basic Steady State Surface Water Chemistry Method (SSWC) is based on that the sulphate, found in surface water, originates largely from sea salt spray and polluted deposition. The method gives ways of correcting for the sea salts and a minor contribution from geologic sources to obtain the atmospheric contribution of sulphate in the water. This sulphate concentration is then used to estimate the weathering rate of the catchment. The chemical data for surface and groundwater, brought to the workshop, indicate that in the Slovak Republic the geology supplies significant amounts of sulphate to the water. This sulphate is assumed largely to be balanced by base cations BC (Ca + Mg). Thus, to calculate the critical load, the method must be modified. The atmospheric contributed sulphate in the surface and ground water is estimated by multiplying the sulphur deposition by the ratio of precipitation to runoff (Sdep*P/Q). The difference between this value and the sulphate concentration is then the geologically supplied sulphate. Since this component is balanced by Ca+Mg (see above), we deduct this amount from the concentration of base cations to obtain those due to weathering and ion exchange processes. To estimate the ion exchanged base actions we use a modified F-factor because of the very high weathering rate in the surface and groundwater. We thus arrive at the following calculation method:

$SO4_{-dep} = S_{dep}* P/Q$
    where S_{dep} = sulphur deposition in keq/km^2/yr, P = yearly precipitation in m and Q = yearly runoff in m.

$BCgeol. = SO_{4r} - SO4_{-dep}$
    Where $SO_{4r} = SO_4$-concentration in runoff water.

Then: $BC_{wt} = BC_t - BC_{geol}$
    where BC_t = present Ca+Mg-concn. in runoff water.

$F = BC_{wt}/S$
    where S is the BC-concn. giving F = 1. We have set S to 4 meq/l.

$BC_w = BC_{wt} - F*SO_{4-dep}$

Critical load = **CL = BC$_w$*Q*10** (keq/ha/yr)

Critical load exceedance = **CL-EX = S$_{dep}$ - CL** (keq/ha/yr)

Using these equations on some of the data available we arrived at critical load values for surface and groundwater for a selection of the grids (Table 1).

Table 1. Calculated critical loads and critical load exceedances for a selction of grids in the Slovak Republic for surface and ground water in the same grids.
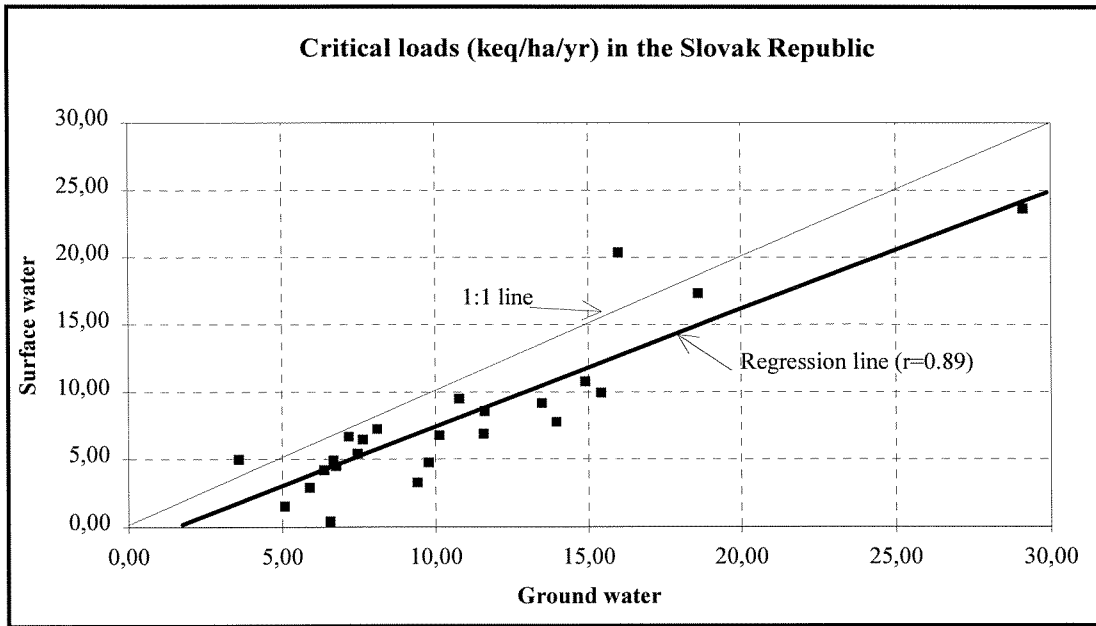
| Grid no | Surface water | | Ground water | |
	Critical load	CL-exceedance	Critical load	CL-exceedance
	keq/ha/yr	*keq/ha/yr*	*keq/ha/yr*	*keq/ha/yr*
612	10,12	-9,22	6,76	-5,86
646	9,78	-8,99	4,75	-3,96
647	11,58	-10,74	6,87	-6,03
648	6,56	-5,72	0,41	0,43
680	6,66	-5,70	4,90	-3,94
681	5,90	-5,00	2,90	-2,00
682	6,76	-5,97	4,49	-3,70
683	5,09	-4,25	1,52	-0,68
713	16,00	-15,04	20,38	-19,42
715	6,37	-5,27	4,19	-3,09
717	9,41	-8,28	3,27	-2,14
748	18,61	-17,77	17,33	-16,49
820	29,11	-27,76	23,64	-22,29
821	14,90	-13,21	10,78	-9,09
822	13,96	-13,06	7,75	-6,85
857	15,42	-14,29	9,95	-8,82
858	7,18	-6,17	6,66	-5,65
892	11,61	-10,03	8,56	-6,98
893	7,46	-6,50	5,41	-4,45
927	13,49	-11,80	9,18	-7,49
928	7,63	-5,94	6,45	-4,76
929	3,59	-2,69	4,97	-4,07
963	10,79	-9,16	9,49	-7,86
964	8,10	-6,97	7,23	-6,10

The critical loads are very high compared to the critical loads for soils, and there are no critical load exceedance in any grid. The critical loads for surface water is systematically higher than for the surface water in all but a few grids (Figure 1). The forest soil is clearly the most sensitive ecosystem in the area considered.

The values used for this exercise are average values for each grid. Whether there are any locations that have low critical loads can be checked in the original database. A short look at it did not indicate low critical load localities, but this should be considered by the Slovak group.

We recommend that the Slovak group proceed with the calculations of the critical loads and exceedances for each remaining grid for the pilot project according to the procedure given above. The values for groundwater, surface water and soil should be compared, and a final conclusion about the most sensitive ecosystem should be drawn.

We may assist in the further calculations and evaluation next year, based on the completed pilot project.

Figure 1. Comparison of critical loads for surface and ground water for a selection of grids in the Slovak Republic. The regression line indicate significantly higher values for groundwater than for surface water.

NIVA Acid Rain Research Reports

1/1982 Henriksen, A. 1982. Changes in base cation concentrations due to freshwater acidification. 50 pp. Out of print.

2/1982 Henriksen, A. and Andersen, S. 1982. Forsuringssituasjonen i Oslomarkas vann. 45 pp. Out of print.

3/1982 Henriksen, A. 1982. Preacidifcation pH-values in Norwegian rivers and lakes. 24 pp. Out of print.

4/1983 Wright, R.F. 1983. Predicting acidification of North American lakes. 165 pp.

5/1983 Schoen, R., Wright, R.F. and Krieter, M. 1983. Regional survey of freshwater acidification in West Germany (FRG). 15 pp.

6/1984 Wright, R.F. 1984. Changes in the chemistry of Lake Hovvatn, Norway, following liming and reacidification. 68 pp.

7/1985 Wright, R.F. 1985. RAIN project. Annual report for 1984. 39 pp.

8/1985 Lotse, E. and Otabbong, E. 1985. Physiochemical properties of soils at Risdalsheia and Sogndal: RAIN project. 48 pp.

9/1986 Wright, R.F. and Gjessing, E. 1986. RAIN project. Annual reportfor 1985. 33 pp.

10/1986 Wright, R.F., Gjessing, E., Semb, A. and Sletaune, B. 1986. RAIN project. Data report 1983-85. 62 pp.

11/1986 Henriksen, A., Røgeberg, E.J.S., Andersen, S. and Veidel, A. 1986. MOBILLAB-NIVA, a complete station for monitoring water quality. 44 pp.

12/1987 Røgeberg, E.J.S. 1987. A coulometric Gran titration method for the determination of strong and weak acids in freshwater. 28 pp.

14/1988 Hauhs, M. 1988. Water and ion movement through a minicatchment at Risdalsheia, Norway. RAIN project. 74 pp.

15/1988 Gjessing, E., Grande. M. and Røgeberg, E.J.S. 1988. Natural Organic Acids. Their Role in Freshwater Acidification and Aluminium Speciation. 28 pp.

16/1988 Wright, R.F. 1988. RAIN project. Annual report for 1987. 77 pp.

17/1988 Wathne, B.M and Røgeberg, E.J.S. 1988. Buffering effects of river substrates under acidic conditions. 19 pp.

18/1989 Lotse, E.G. 1989. Soil Chemistry 1983-86 at the RAIN Project Catchments. 66 pp.

19/1989 Reuss, J.O. 1989. Interpretation of Soil Data from the RAIN Project. 81 pp.

20/1990 Skjelkvåle, B.L. and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. 20 pp.

21/1990 Hindar, A. 1990. Chemistry and fish status of 67 acidified lakes at the coast of Aust-Agder, Southern Norway, in relation to postglacial marine deposits. 47 pp.

22/1990 Henriksen, A. Lien, L. and T. Traaen, T.S. 1990. Critical Loads for Surface Waters. Chemical Criteria for Inputs of Strong Acids. 45 pp.

23/1990 Wright, R.F. 1990. Reversibility of acidification: soils and surface waters. 39 pp.

24/1991 Wright, R.F. RAIN project. Report for the years 1988, 1989 and 1990. 156 pp.

25/1991 Wright, R.F., Holmberg, M., Posch, M. and Warfvinge, P. 1991. Dynamic models for predicting soil and water acidification: Application to three catchments in Fenno-Scandia. 40 pp.

26/1992 Wohlfeil, I.C. and Müller, D.I. 1992. RAIN-project: Vegetation mapping at Risdalsheia 1991. 42 pp.

27/1992 Rosseland, B.O. and Kroglund, F. 1992. Reversibility of acidification; Fish responses in experiments at Risdalsheia. 50 pp.

28/1992 Wathne, B.M., Norton, S.A. and Henriksen, A. 1992. Buffering capacities and effects of river substrates during acidic episodes. 24 pp.

29/1992 Henriksen, A., Mill, W.A., Kot, M., Rzychon, D. and Wathne, B.M. 1992. Critical loads of acidity to surface waters: A case study from Polish Tatra Mountains. 34 pp.

30/1992 Kroglund, F., Dalziel, T., Rosseland, B.O., Lien, L., Lydersen, E. and Bulger, A. 1992. Restoring Endangered Fish In Stressed Habitats. ReFISH project 1988-1991. 43 pp.

31/1992 Rosseland, B.O., Brandrud, T.E., Raddum, G.G. 1992. Effects of Aluminium in Acidified Aquatic Ecosystems. 34 pp.

32/1993 Henriksen, A., Forsius, M., Kämäri, J., Posch, M. and Wilander, A. 1993. Exeedance of Critical Loads for Lakes in Finland, Norway and Sweden: Reduction Requirements for Nitrogen and Sulfur Deposition. 46 pp.

33/1993 Wathne, B.M., Mill, W.A., Kot, M.,Rzychon, D., Henriksen, A., and Tørseth, K. 1993. Critical loads of acidity to lakes in the Polish Tatra Mountains. A study of the yearly variations in the precipitation and water chemistry. 37 pp.

34-A/1994 Lydersen, E. 1994. Long term monitored catchments in Norway - a hydrologic and chemical evaluation -, 306 pp. + Appendix.

34-B/1994 Lydersen, E. 1994. Long term monitored catchments in Norway - a hydrologic and chemical evaluation -, Summary Report, 66 pp.

35/1994 Wright, R.F. 1994. Modelling long-term hydrochemical response at ENCORE catchments in the UK and Norway. 42 pp.

36/1994 Wright, R.F. 1994. RAIN PROJECT. Risdalsheia data report for June 1990 - May 1994. 165 pp.

37/1995 Závodský, D., Wathne, B.M., Henriksen, A., Sverdrup, H. et al. 1995. Mapping critical levels/loads for the Slovak Republic. 74 pp.