Acid Rain Research

REPORT 22/1990

Critical Loads for Surface Waters

Chemical Criteria for Inputs of Strong Acids

Norwegian Institute for Water Research 💧 NIVA

NIVA – REPORT

Norwegian Institute for Water Research NIVA

Report No.: 0-89210	
Sub-No.:	
Serial No.: 2466	
Limited distribution:	

Report Title:	Date:
CRITICAL LOADS FOR SURFACE WATERS – CHEMICAL CRITERIA FOR INPUTS OF STRONG ACIDS	3 September 1990

Author (s):	
Arne Henriksen, NIVA Leif Lien, " Tor S. Traaen, "	**Topic group:** Acid precipitation **Geographical area:** Norway **Number of pages (incl. app.):** 45

Contractor:	Contractors ref. (or NTNF-No)
Working group for the Programme "Naturens Tålegrenser"	

Abstract: Chemical criteria have been established for the critical loads of strong acids to surface waters in Norway. A complete set of data is available for all counties with the exception of North Trøndelag, Nordland, Troms and Finnmark excluding the municipality of South Varanger. Coloured maps for southern Norway have been prepared showing quantitative critical loads for acidic components, areas where the critical load is exceeded, and the regional runoff (export) of sulphur. At present, the critical load has been exceeded in approximately 30% of southern Norway. The most affected counties are East Agder, West Agder, and Rogaland.

4 keywords, Norwegian
1. Tålegrenser
2. Sur nedbør
3. Vannkjemi
4. Innsjøer

4 keywords, English
1. Critical load
2. Acid deposition
3. Water chemistry
4. Lakes

Project leader

Arne Henriksen
Arne Henriksen

For the Administration

Bjørn O. Rosseland
Bjørn O. Rosseland

NORWEGIAN INSTITUTE FOR WATER RESEARCH
Oslo

O - 89210

CRITICAL LOADS FOR SURFACE WATERS

CHEMICAL CRITERIA FOR INPUTS OF STRONG ACIDS

Oslo, 20 March, 1990.

Authors:
Arne Henriksen
Leif Lien
Tor S. Traaen

CONTENTS

PREFACE

The national programme "Naturens Tålegrenser" (Environmental Tolerance Levels) was initiated by the Norwegian Ministry of Environment in Autumn 1988. The programme will give inputs to the Nordic Action Plan against Air Pollution and to the ongoing activities under the Convention on Long-Range Transboundary Air Pollution (The Geneva Convention). It has been decided that for the work under the Geneva Convention critical loads will be used for establishing new agreements on reduced emissions of sulphur, nitrogen and hydrocarbons.

A steering group with members from the Ministry of Environment has the overall responsibility of the programme, while the scientific responsibility is left to a working group with representatives from the Directorate of Nature Management (DN), The Norwegian Polar Institute (NP) and the State Pollution Control Authority (SFT).

The present report is a modified English translation of the programme's second report: "Tålegrenser for overflatevann - Kjemiske kriterier for tilførsler av sterke syrer". Jennifer Follestad did the translation. Thanks are due to Richard F. Wright and Stephen A. Norton for critically reviewing this report.

SUMMARY

In connection with the Convention on Long-Range Transboundary Air Pollution (the Geneva Convention), a working group was set up to compile a manual on the preparation of maps showing critical loads for airborne sulphur and nitrogen. Critical loads are a function of the amount of strong acid loading that result in chemical conditions causing damage to biological indicators (fish, invertebrates) at different ANC (Acid Neutralizing Capacity) values. The critical biological value is defined as $[ANC_l]$, where l=limit. The Norwegian Institute for Water Research (NIVA) has participated actively in this working group. The manual was discussed at a workshop in Bad Harzburg from 6-9 November, 1989. The manual presents three specific methods of calculating critical loads for surface water, groundwater and soil: 1. The Steady State Water Chemistry Method, 2. The Biogeochemical Mass Balance Method, and 3. The Dynamic Modelling Method.

Method 1 is particularly applicable in the case of surface water, while methods 2 and 3 can be used for soil, groundwater and surface water. The first two methods are static, i.e. they calculate the situation at equilibrium, while method 3 also takes into account the time factor in the acidification process.

The water chemistry method, which has been worked out at NIVA, is based on the acid neutralizing capacity of water (ANC - Acid Neutralizing Capacity). ANC is defined here as the difference in the sum of concentrations of base cations (calcium, magnesium, sodium and potassium) and the sum of anions of strong acids (chloride, sulphate and nitrate). ANC is a function of the content of bicarbonate, hydrogen, inorganic aluminium and organic ions in water. If inputs of sulphur and nitrogen via precipitation and dry deposition give concentrations of strong acid anions that are higher than the concentrations of base cations in runoff, the ANC is negative. This means that the critical load has been exceeded.

The concentration of base cations in a lake is the result of inputs due to weathering reactions in the catchment area, atmospheric inputs of base cations, and uptake by vegetation. The critical load for a lake is thus directly related to the weathering rate in the soil of the catchment. The integrated weathering rate for the catchment of a lake is reflected in the chemical composition of the lake and can therefore be calculated in a simple manner. The critical loads for inputs of acids are set relative to the weathering rate. The critical load and the deviation from this value may be quantified by computing fluxes. Assuming that the concentrations measured for a lake are the same as or

approximate the annual weighted mean concentrations, these concen-
trations can be multiplied by the value for the yearly runoff, giving
the annual flux.

The water chemistry method is particularly applicable in areas where
surface water dominates runoff, such as in glaciated areas with
relatively thin soil cover. The chemistry of runoff water from a
catchment area provides the integrated result of most of the processes
taking place in the soil. Therefore, the composition of surface water
will reflect the properties of the soil and consequently be related to
the critical loads of the soil. In areas with thin soils the critical
load for water will normally be lower than for areas with thicker soils
where runoff water is dominated by groundwater.

Coloured maps have been prepared for southern Norway showing the
quantitative area distribution of: (1) critical loads for strong acids
(weathering rate), (2) the present deviation from the critical load,
and (3) sulphur runoff. Each grid of 0.5° in longtitude x 1.0° in
latitude was divided into 16 smaller grids, and a representative lake
water chemistry for each subgrid was established from available data.
Frequency distribution diagrams show that the critical load ($[ANC_1]=0$)
is exceeded presently in about 30% of the land area of southern Norway.
This is in good agreement with the findings from the 1000 Lake Survey
in 1986 which established that fish had disappeared or were damaged in
approximately 22% of the land area of southern Norway. Approximately
70% of the land area in southern Norway maintains positive ANC with
less than 80 keq $SO_4 \cdot km^{-2} \cdot year^{-1}$ (1.28 $gS \cdot m^{-2} \cdot year^{-1}$) in inputs of
strong acids. If inputs were approximately 40 keq $SO_4 \cdot km^{-2} \cdot year^{-1}$ (0.64
$gS \cdot m^{-2} \cdot year^{-1}$) we would find lakes barren of fish or damaged in
approximately 40% of the land area. Today, the inputs of acid to the
most severely affected areas of southeast Norway amount to about 80 keq
$SO_4 \cdot km^{-2} \cdot year^{-1}$ (1.28 $gS \cdot m^{-2} \cdot year^{-1}$). Lakes and rivers in widespread
areas of southern Norway are extremely sensitive to acidification. A
comparison of sulphur deposition and sulphur runoff shows that the
sulphate content of surface water is dominated by atmospheric inputs.

The counties of Agder, Telemark, Akershus/Oslo, and Buskerud have the
lower critical loads, whereas southern Trøndelag, Hordaland, and
Oppland tolerate more acidic precipitation. West Agder receives the
most acidic precipitation followed by East Agder and Telemark. The
combination of a low critical load with highly acidic precipitation
means that critical loads are exceeded in more than 95% of the land
area of the two Agder counties.

1. BACKGROUND

Critical loads for atmospheric input of sulphur and nitrogen to an ecosystem were defined as follows at the Critical Load Workshop at Skokloster in Sweden (Nilsson and Grennfelt, 1988):

> **"The highest deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem, structure and function term."**

This definition can be applied to different receptors: soil, groundwater and surface water. Both sulphur and nitrogen compounds contribute to the total input of acidic compounds to an ecosystem. The ratio of sulphur to nitrogen can, therefore, vary without changing the critical load for acidic compounds.

The time it takes for parts of an ecosystem to be altered by acid inputs can range from minutes and days, as in the case of acid events in watercourses, to decades or centuries, as in the case of soil acidification.

Critical loads for the acidification of surface water have been most thoroughly studied with respect to sulphur inputs. Critical loads for sulphur were exceeded long ago in extensive regions of Norway and in many other countries, and the effects are manifested in the form of acidic, fish-less lakes. In the case of sulphur the cause/effect relationship is well known, and the dose/response relation can be expressed using simple models. The documentation is considerably sparser in the case of nitrogen.

In connection with the Convention on Long-Range Transboundary Air Pollution (The Geneva Convention), a working group has been formed to compile a manual on the preparation of maps showing critical loads for airborne sulphur and nitrogen. NIVA has participated actively in this working group. The manual was discussed at a workshop in Bad Harzburg from 6-9 November, 1989 and further evaluated at a second workshop at the same place from 22-23 May, 1990. (ECE, 1990). The manual describes three distinct methods for calculating critical loads for surface water, ground water and soil:

1. The Steady-State Water Chemistry Method
2. The Steady-State Mass Balance Method
3. The Dynamic Modelling Method

Method 1 is particularly applicable to surface water, while methods 2 and 3 can be used for soil, groundwater and surface water. The first two methods are static, i.e., they compute the situation assuming equilibrium, while method 3 also takes into account the time factor in acidification processes.

The working group for the national programme, "Naturens tålegrenser" (Critical Loads of Nature), has contracted NIVA to prepare maps for critical loads of sulphur and nitrogen in Norway and to make prognoses for different scenarios for reductions in sulphur and nitrogen emissions. The Steady State Water Chemistry Method has been used for this purpose. This report gives a short description of this method and its application in the determination of critical loads for sulphur inputs to surface water in Norway.

2. DEFINITIONS

Definitions of some terms used in the report are as follows:

a) Acid Neutralizing Capacity (ANC):
   The ability of a solution to neutralize inputs of strong acids to a given level.

b) Receptor: An ecosystem which may potentially be affected by atmospheric input of sulphur and nitrogen (e.g. soil, groundwater, surface water).

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

d) Critical chemical value: The value for a critical chemical component or combination of components above or below which does not give rise to a harmful response in a biological indicator (e.g. ANC, pH, Al/Ca ratio).

3. CRITICAL LOADS OF SULPHUR AND NITROGEN TO SURFACE WATERS

3.1 Water chemistry basis

Acidification of surface waters is generally due to inputs of anions of strong acids, primarily sulphate and nitrate, which are deposited in the catchment area via precipitation and dry deposition. The sulphate

ion is normally a mobile anion, i.e., it moves with precipitation through the catchment area and may have an acidifying effect on surface water. Nitrate and ammonium fertilize vegetation. Therefore, most of the nitrogen compounds that are deposited via precipitation and dry deposition are most often taken up by trees and plants. If more nitrogen is deposited than required by vegetation, the excess, mainly in the form of nitrate, will drain into watercourses and have the same acidifying impact as sulphate. It is, therefore, the sum of sulphate and nitrate that must be evaluated. Incorporation of N from NH_4 may also cause acidification; this process is not included in method 1.

Chemical weathering and ion exchange processes supply the majority of cations in lakes and rivers. In pristine clear-water lakes calcium and magnesium are the major cations; bicarbonate is the main anion. In areas near the coast, sodium and chloride (and other marine aerosol salts) will also contribute significantly to the ionic composition of the runoff water. Bicarbonate comes from CO_2 dissolved in the soil water.

In areas with inputs of atmospheric pollutants, the catchment areas receive appreciable amounts of hydrogen, sulphate, nitrate, and ammonium ions via precipitation and dry deposition. In order to estimate changes in surface water due to atmospheric sources other than sea water it is necessary to subtract the ions that are from to sea salt spray. For this purpose it is assumed that all chloride in the water originates from sea salt spray, and that all sea salt components are deposited in the same ratio as is found in sea water. Sea salt corrected values are marked with an asterisk (*).

Expressed in µeq/l

$$[Ca^*] = [Ca] - 0.037 \cdot [Cl] \qquad (1)$$
$$[Mg^*] = [Mg] - 0.198 \cdot [Cl] \qquad (2)$$
$$[Na^*] = [Na] - 0.858 \cdot [Cl] \qquad (3)$$
$$[K^*] = [K] - 0.018 \cdot [Cl] \qquad (4)$$
$$[SO_4^*] = [SO_4] - 0.103 \cdot [Cl] \qquad (5)$$

The ion balance in surface water is expressed by the following equation:

$$[Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+]+([H^+]+[\Sigma Al^{n+}]) =$$
$$[HCO_3^-]+[SO_4^{2-}]+[NO_3^-]+[Cl^-]+[A^-] \qquad (6)$$

where all values in brackets are in equivalents. Here, $[A^-]$ is the concentration (in equivalents) of organic anions. $[A^-]$ can be estimated either by multiplying the TOC concentration by an empirically determined factor, or from the ion balance by assuming that no ions

other than those are given in Equation (6) contribute to the ion balance.

$[\Sigma Al^{n+}]$ is the equivalent sum of all positively charged aluminium species. The average charge of dissolved Al is a function of pH and varies from 3^+ at a pH of 4 to 0 at a pH of around 5.

Assuming that the chloride originates only from sea water, we can correct the concentrations in Equation (11) using Equations (1)- (5):

$[BC^*]$ (non- marine base cations) $= [Ca^{*2+}]+[Mg^{*2+}]+[Na^{*+}]+[K^{*+}]$ (7)

$[AN^*]$ (non-marine acidic anions) $= [SO_4^{*2+}]+[NO_3^-]$ (8)

By rearranging and inserting in Equation (11) we get:

$[BC^*]-[AN^*]=[HCO_3^-]+[A^-]-([H^+]+[\Sigma Al^{n+}])$ (9)

The right side of the equation corresponds to a general definition of alkalinity (ANC = Acid Neutralizing Capacity). Note that organic anions ($[A^-]$) are included in this definition. The general definition is as follows (Reuss and Johnson, 1986):

$[ANC] = ([CO_3^{2-}]+[HCO_3^-]+[OH^-]+[A^-])-([H^+]+[Al^{3+}]+[AlOH^{2+}]+$
$[Al(OH)_2^+])$ (10)

For Norwegian water quality, CO_3^{2-}, OH^- and NH_4^+ are normally negligible and thus deleted from equation (10). If we sum up all the inorganic Al-ions, ANC is thus defined by the right side of equation (9).

This gives us:

$$[BC^*] - [AN^*] = [ANC] \qquad (16)$$

[ANC], therefore, provides a measurement of the chemical deviation from a "critical situation" (critical chemical concentration) for a lake or river. This difference does not provide a quantitative measurement of the extent to which the critical load is exceeded, only whether a critical concentration is exceeded or not. Quantative calculations must be computed in transport loads or fluxes (see below).

When simply calculating ANC in accordance with Equation (16) it is not necessary to correct for sea salts, because all contributions of sea salt are found on the left side of the equation and marine cations are

balanced by marine anions.. However, when calculating the weathering rate and related quantities, one must correct for sea salts.

In Equation (14) organic anions ($[A^-]$) and inorganic aluminium are found on the right side. This implies that these act more as a buffer than as an acid when strong acids are contributed. These ions together with bicarbonate determine the pH of water. Therefore, at a given [ANC] pH will be determined by the ratio of concentrations of bicarbonate to organic anions, because inorganic Al is normally of minor significance when [ANC] is positive. This may seem paradoxical because biological damage thresholds are often linked to the pH value. It has, however, been observed that when the content of humic compounds increases (increasing $[A^-]$), fish and other organisms tolerate lower pH values. Thus it seems more appropriate to relate the critical load to an [ANC] value rather than to a pH value.

In a lake, therefore, the critical load for inputs of acidic components is directly linked to the concentration of base cations. If inputs of sulphur and nitrogen give concentrations of the anions of strong acids (sulphate and nitrate) higher than the concentrations of base cations, the lake is become acidic.

Critical loads must be related to organisms, although it is the chemical conditions that determine the critical loads. The values for critical loads for surface waters must, therefore, be expressed as an amount or concentration of one or more chemical parameters that may range from negative to positive values. The critical load for a particular organism will then lie along a scale, and the different organisms may have different values on the scale. The chemical value for the critical load for a given organism can be determined by a combination of empirical data and experiments. The parameter ANC appears to be suited for use as the chemical criterion for biological indicators in surface water. An evaluation of the relationship between ANC in surface water and the bioindicators, fish and invertebrates, is given in a separate report (Lien et al. 1990).

The critical biological value may be termed $[ANC_l]$ (l=limit), such that:

$$\Delta CC = [ANC] - [ANC_l] \tag{12}$$

where ΔCC is the deviation from a critical concentration. Negative

values for ΔCC mean that a critical concentration has been exceeded. By combining Equations (11) and (12) we get:

$$\Delta CC = [BC^*] - [AN^*] - [ANC_1]$$ (13)

Equation (13) provides an indication of the deviation from the critical load. The quantative calculation of this deviation is shown below.

3.2. The critical load concept

Some fractions of the base cations in runoff are contributed via precipitation and dry deposition. These are partly attributable to sea salts and partly to terrestrial sources of anthropogenic and natural origin. The runoff of base cations from a catchment area (BC_t^*) is a result of the balance between inputs from weathering reactions (BC_w), ion exchange processes (BC_i), atmospheric deposition (BC_d^*), and removal via uptake in the biomass (BC_u).

The sensitivity of a lake to acidic inputs is directly related to the weathering rate in the catchment area, and may be expressed as:

$$BC_w = BC_t^* - BC_i + BC_u - BC_d^*$$ (19)

All parameters in Equation (19) are expressed in annual area transport values (e.g. $keq.km^{-2} \cdot year^{-1}$).

It is assumed that BC_w does not change with changes in acid inputs. For ecosystems at steady state throughout, BC_i would be zero; such is not the case for systems undergoing acidification.

Assuming that BC_u can be ignored (as in areas with no land disturbance) we get:

$$BC_w = BC_t^* - BC_d^* - BC_i$$ (20)

All parameters in equation (20) are expressed as an annual flux (i.e. $keq \cdot km^{-2} \cdot year^{-1}$).

Here BC_t^* can be determined from the present concentrations of base cations ($BC_t^* = Q \cdot [BC^*]$) where Q is the mean annual runoff, and $[BC^*]$ is the mean concentration of non-marine base cations. BC_d^* can be derived from deposition data, and BC_i is attributable to changes in inputs of acidic anions (ΔAN^*). If we put $BC_i = \Delta BC^*$, we have a factor, F (Henriksen, 1984, Brakke et al., 1990).

$$F = \Delta BC^* / \Delta AN^* \quad \text{or,} \quad \Delta BC^* = F \cdot \Delta AN^* \tag{21}$$

This definition is based on the assumption that a change in atmospheric inputs of sulphate and nitrate will result in a change in the concentrations of base cations in runoff water. The "original" base cation runoff (BC_0^*) is the sum of BC_w and BC_d^*, assuming that BC_d^* has not changed. Thus we get (in concentrations):

$$[BC_t^*] = [BC_0^*] + [\Delta BC^*] \tag{22}$$

i.e. $\quad [BC_t^*] = [BC_0^*] + F \cdot [\Delta AN^*] \tag{23}$

Assuming the significance of NO_3 in the period prior to acidification to be minor ($NO_3 \approx 0$) we obtain the following equation for the "original" base cation concentration.

$$[BC_0^*] = [BC_t^*] - F \cdot [\Delta SO_4^*] \tag{24}$$

Hence:

$$[\Delta SO_4^*] = [SO_{4t}^*] - [SO_4^*{}_0] \tag{25}$$

where $[SO_{4t}^*]$ is the current concentration of non-marine sulphate and $[SO_4^*{}_0]$ is the "original" concentration of sulphate or the background concentration. In order to estimate $[BC_0^*]$, therefore, the values of F and $[SO_4^*{}_0]$ must be known.

The value of F, which is a function of the base cation concentration, normally lies between 0 and 1 (Henriksen, 1984). F may vary in a given lake over a period of time. F approaches zero in dilute lakes and is closer to 1 where there are high concentrations of base cations. There are no absolute figures for F, and F must be estimated using available data. A reasonable estimate would be (Brakke et al., 1990):

$$F = \sin([BC^*] \cdot 90/S) \tag{26}$$

S is the base cation concentration at which F=1.0. For Norway S is estimated to be 400 μeq/l.

This means that F = 0 at $[BC^*] = 0$ and F = 1 when $[BC^*]$ 400 ueq/l. For values of $[BC^*]$ higher than 400, F is set at 1.

It remains to estimate $[SO_4^*{}_0]$, the background concentration of sulphate. It is assumed that this consists of an atmospheric background

input and a geologically derived input. An analysis of chemical data from lakes in parts of western and northern Norway where there is little acidic precipitation gives the following relation:

$$[SO_4{}^*_0] = 15 + 0.16 \cdot [BC^*] \ (\mu eq/l) \qquad r = 0.38, \ n = 143 \qquad (27)$$

At $[BC^*] = 100$, for example, $[SO_4{}^*_0] = 31$ ueq/l. This empirical relationship is used to estimate background concentrations of sulphate for surface waters in Norway, and the results below indicate that the method is valid. The following equation can be used to estimate the original base cation concentration. These empirically-based relations may differ in other countries.

$$[BC_0{}^*] = [BC_t{}^*] - \sin([BC^*_t] \cdot 90/400) \cdot ([SO_{4t}{}^*] - 15 - 0.16 \cdot [BC_t{}^*]) \quad (28)$$

This equation assumes that concentrations of nitrate $[NO_3]$ and organic anions $[A^-]$ are not altered with changes in sulphate concentrations.

4. CALCULATION OF CRITICAL LOADS

Calculations of critical loads can be quantified by computing fluxes or amounts transported. Assuming that concentrations given for a lake are the same or similar to the weighted annual mean concentrations, these may be multiplied by the mean value of the annual runoff (Q). Figure 1 indicate that this is a reasonable assumption. We then get the annual loss of base cations (BC^*_l) (Eq.(29)):

$$[BC_0{}^*] \cdot Q = BC_l = BC_w + BC_d{}^* - BC_u \qquad (29)$$

If we rearrange this equation we get an estimate of the integrated weathering rate of the catchment area of the lake:

$$BC_w = [BC_0{}^*] \cdot Q - BC_d{}^* + BC_u \qquad (30)$$

This is a simple way of calculating the weathering rate of catchment areas.
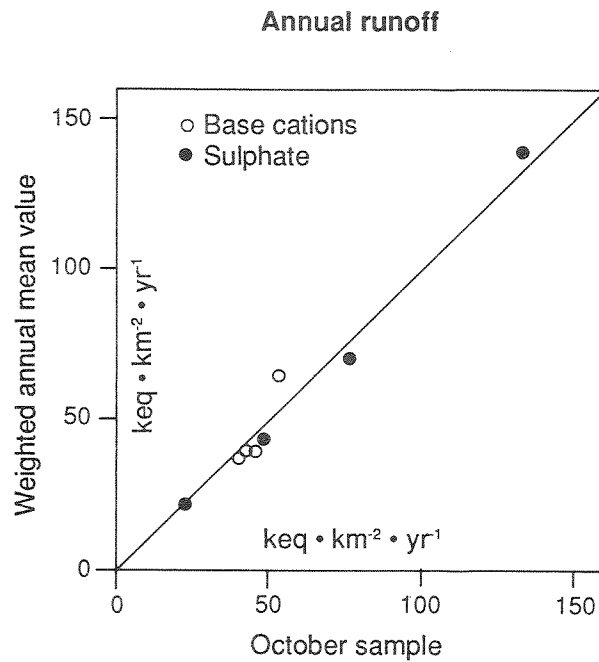
Annual runoff

Figure 1. Comparison of weighted annual mean concentrations (52 samples) and the concentrations in a single sample taken in October for base cations and sulphate. The data are from the calibrated catchments Birkenes, Storgama, Langtjern and Kårvatn in Norway.

The critical load for a lake can be calculated quantatively by equation (16), which is based on the definition that inputs of acidic components to a catchment shall not exceed the runoff of base cations (BC^*_1) from the catchment area and the lake shall remain at a biologically safe ANC level. The critical load (CL) in the case of acidic anions for a given organism is thus given by the equation:

$$CL = BC_w - [ANC_1] \cdot Q \tag{31}$$

By substituting BC_w from equation (30) and assuming that BC_u is almost zero at a "steady state", we get the critical load of acidity:

$$CL = ([BC_0^*] - [ANC_1]) \cdot Q - BC_d^* \tag{32}$$

In other countries the ratio H^+/SO_4 in precipitation may be lower than one. If this is caused because a part of the SO_4 is balanced by base cations (i.e. as in Finland), and if the amounts of nitrate and ammonium are equal, then: $H^+ = SO_4^* - BC_d^*$. Then, equation (32) is reduced to:

$$CL = ([BC_0^*] - [ANC_1]) \cdot Q \tag{32a}$$

This equation actually gives the critical load for the sum of acid anions, but if we assume that background concentrations of nitrate can be ignored, the equation gives us the critical load for sulphate. Note that the critical load for sulphur can be calculated from Equation (32) (using Equation 28, a given value for ANC_l, and empirical values for Q and BC^*_d), but not the critical load for nitrogen.

We are also able to and to calculate the extent to which critical loads for acidic components are exceeded or below the limit. The essential equations are Equation (31) and the following equation deduced from Equations (31) and (32):

$$CL_{ex} = BC_w - ([AN_t^*] - [ANC_l]) \cdot Q \qquad (33)$$

$$\text{that is: } CL_{ex} = ([BC_0^*] - [AN_t^*] - [ANC_l]) \cdot Q - BC_d^* \qquad (34)$$

5. PREPARATION OF CRITICAL LOAD MAPS

The following maps have been recommended (ECE, 1990).

- Receptor maps for vegetation, soil, groundwater, lakes and rivers.
- Deposition maps for pollutant components (H^+, SO_4^{2-}, NO_3^-, and NH_4^+)
- Critical load maps.
- Maps showing where critical loads are exceeded.

Map resolution should be flexible, so that each country can work on the scale that is appropriate to its own data. The main maps should not have a resolution coarser than 0.5^0 in longitude by 1.0^0 in latitude (approximately 50 x 60 km in central Europe and 50 x 50 in the southern part of Norway). These grids can be divided into smaller units as desired, dependent on the data density for each individual country. In the case of the deposition maps, the EMEP grid based on 150 x 150 km squares is acceptable.

The critical load for the given receptor can be determined in different ways within each single grid: weighted area values, most sensitive receptor, a subjective estimate of the representative value, etc.

For Norway we divided each 0.5^0 x 1.0^0 grid into 16 subgrids (figure 2). The EMEP grids for southern Norway are also shown in figure 2. Each subgrid covers an area of approximately 12x12 km in southern Norway. This basic unit is used for all maps. For maps and calculations where deposition data are used, the deposition values are estimated for each single sub-grid in accordance with the isoline map for the pollutant components in question (see figures 3-6).
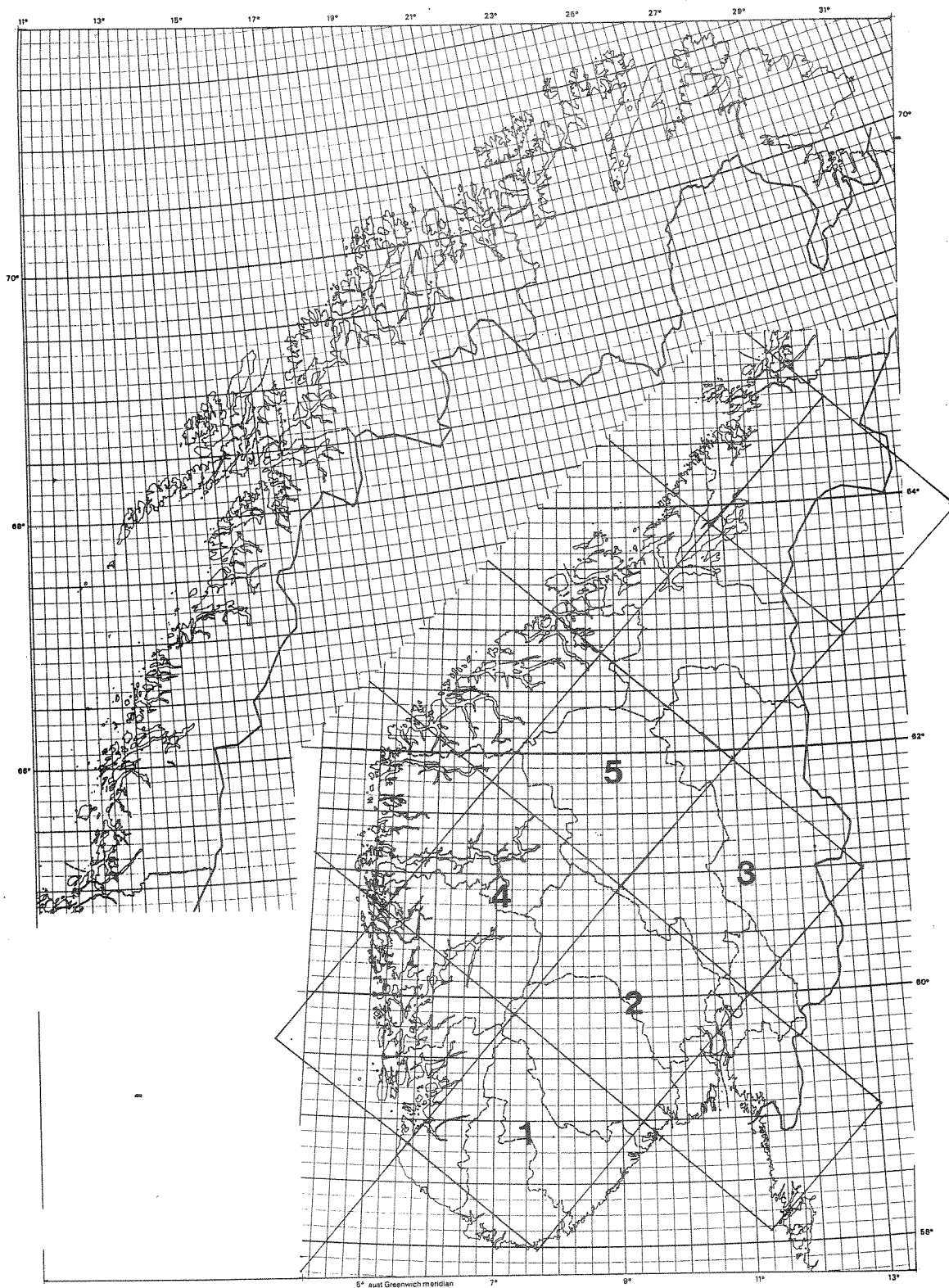
Figure 2. Map of Norway with grid systems for the preparation of
critical loads for surface water. Each grid of 0.5⁰ in
longitude x 1.0⁰ in latitude is divided into 16 sub-grids.
The EMEP grids (150x150 km) that cover southern Norway are
also drawn on the map. The figures refer to their use in
figure 14.

Figure 3. Mean concentrations of sulphate (non-marine) in precipitation at Norwegian background stations in the period from 1985-1988 (SFT, 1989).

NO$_3$-N, mg/l

0.10

0.13

64°

0.08

0.10

0.20

0.18

62°

0.30

0.12

0.20

0.31

0.13

0.31

0.20

0.40

0.43

0.40

0.50

60°

0.48

0.27

0.21

0.46

0.48

0.30

0.29

0.60 0.50

0.54

0.60

0.55

0.40

58°

0.46

0.50

5° aust Greenwich meridian   7°   9°   11°   13°

Figure 4. Mean concentrations of nitrate in precipitation at Norwegian
          background stations in the period from 1985-1988 (SFT, 1989).

NH$_4$-N, mg/l

0.10

0.27

64°

0.20

0.11

0.26

62°

0.09

0.26

0.10

0.16

0.20

0.26

0.47

0.30

0.30

0.40

0.52

0.47

60°

0.50

0.31

0.18

0.40

0.46

0.50

0.30

0.60

0.50

0.40

0.54

0.40

0.58

0.50

0.54

58°

0.60

5° aust Greenwich meridian   7°   9°   11°   13°

Figure 5. Mean concentrations of ammonium in precipitation at Norwegian
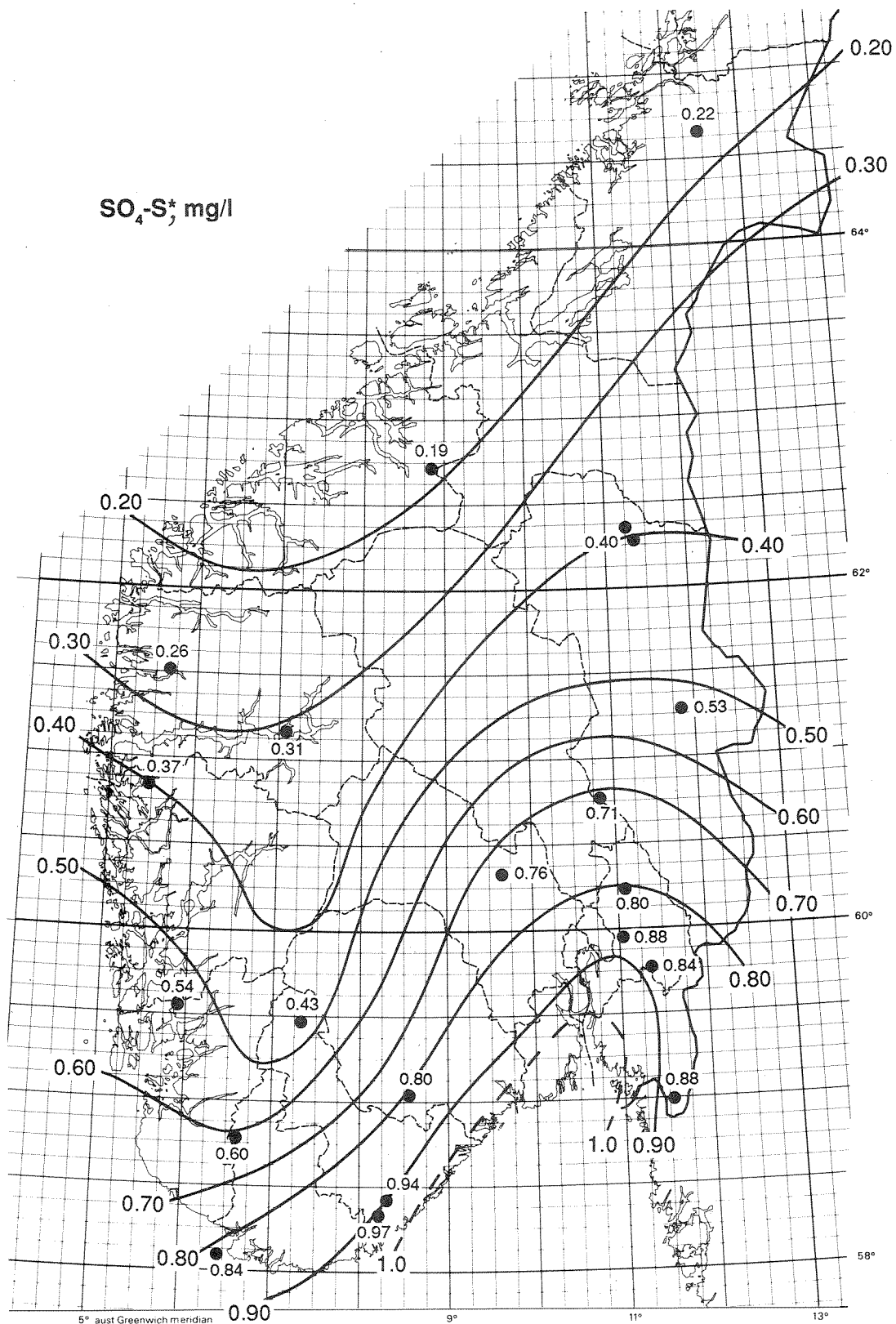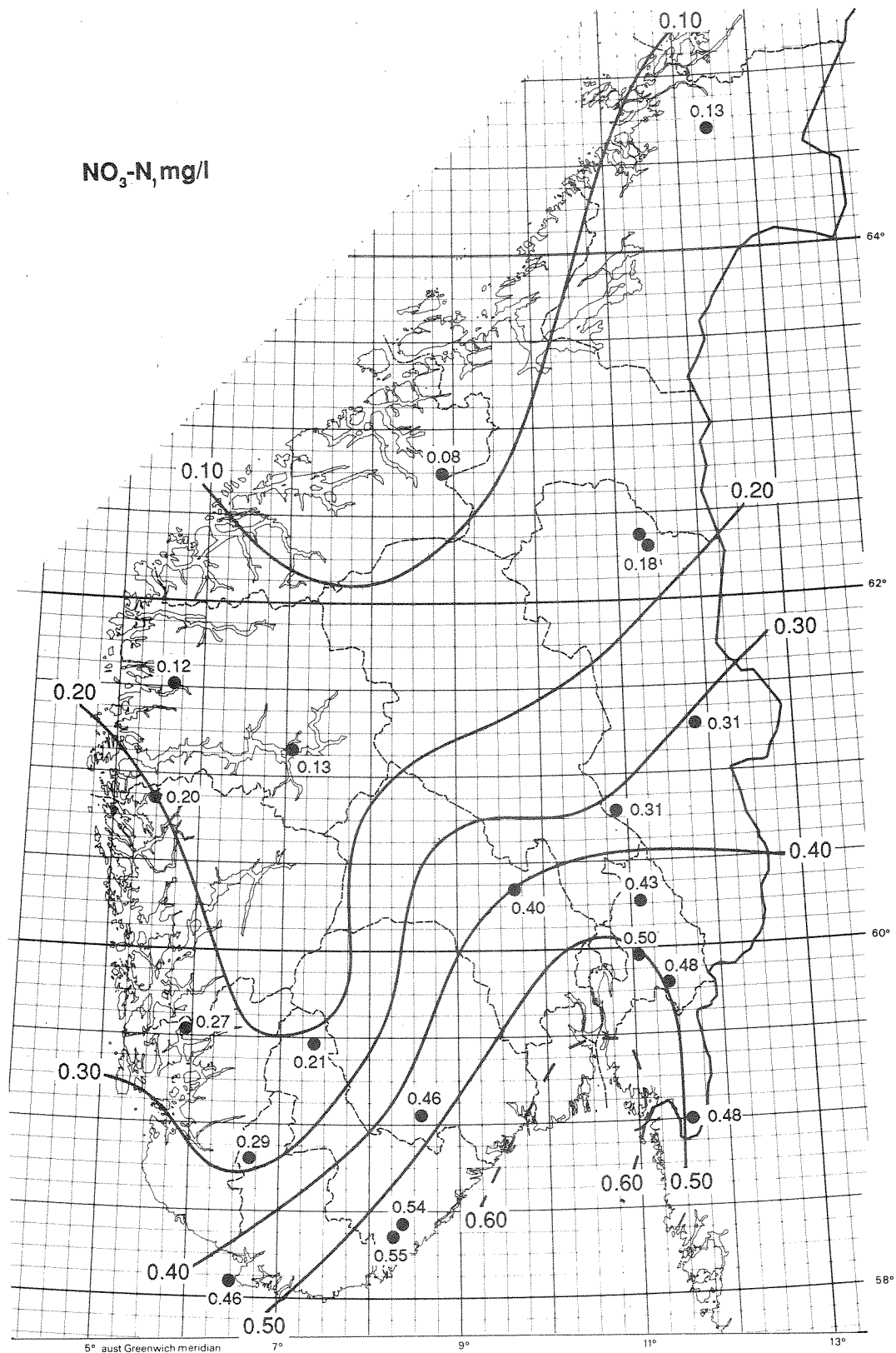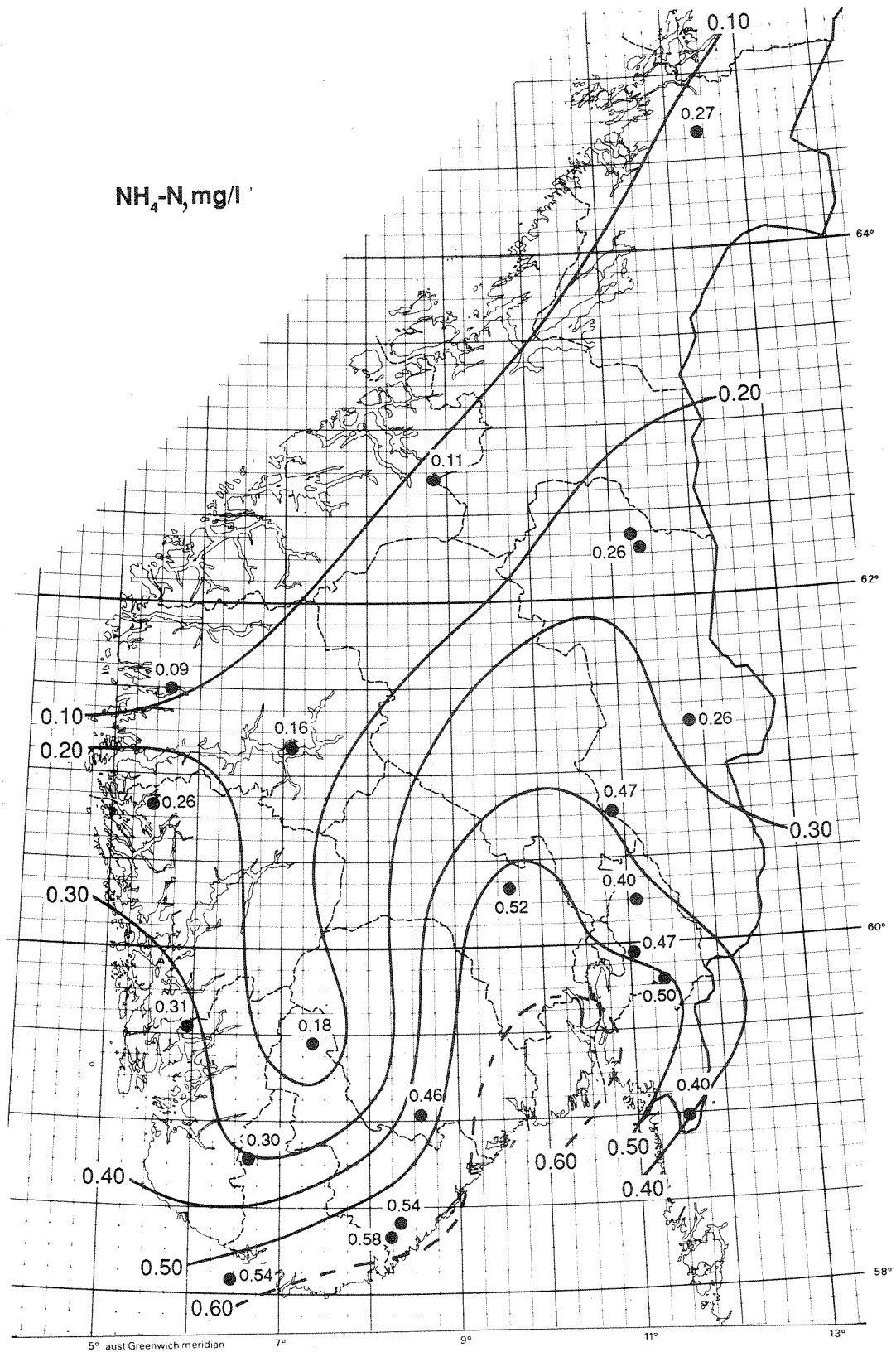background stations in the period from 1985-1988 (SFT, 1989).

Figure 6. Mean concentrations of calcium (non-marine) in precipitation
at Norwegian background stations in the period from 1985-1988
(SFT, 1989).

6. DATA REQUIREMENTS

An estimate of the average water chemistry for each square can be carried out using appropriate statistical methods if the water chemistry for all surface water in the actual grid is known. However this is seldom the case, so that approximate methods must be employed.

For grids where data are not available or not reliable, data may be collected for lakes or rivers which are considered to be sufficiently representative of the grid in question. Locations may be selected on the basis of personal assessment or statistical methods.

Data for the following chemical components should be available: pH, conductivity, Ca, Mg, Na, K, Cl, SO_4, NO_3, alkalinity, labile Al and TOC.

7. DETERMINATION OF CRITICAL LOADS FOR SULPHUR IN SURFACE WATER IN NORWAY

7.1 General

The method described above (Method 1) is especially applicable to areas where surface water dominates runoff, such as in glaciated areas with relatively thin soil cover. because the runoff water from a catchment area provides an integrated result for most of the processes that take place in the soil, the composition of surface water will reflect the soil's properties and will therefore reflect the soil's critical loads.

It may prove more difficult to apply this method in areas with thick soils where the runoff water is dominated by groundwater. Here, the soil may be more sensitive than the runoff water. This situation is uncommon in most of Norway, parts of Sweden, England, USA, Finland and Canada, but it is probable in most regions of central Europe. However, in cases where surface water shows little sensitivity on account of geologically favourable conditions it is unclear to what extent the soil is more sensitive than the runoff water. Such areas exist in Norway and a closer examination is called for.

The water chemistry method assumes that sulphate is a mobile anion and that the acidity of precipitation is equivalent to the concentration of sulphate in precipitation, i.e. that there are equal amounts of H^+-ions and SO_4 ions in precipitation, as is the case in Norway (fig.7a). Thus, the acidity of precipitation can be traced directly via the sulphate concentrations in runoff water. The ratio of these ions in precipitation differs in other countries (fig. 8a), and this must be taken into account when applying the water chemistry method in these areas.
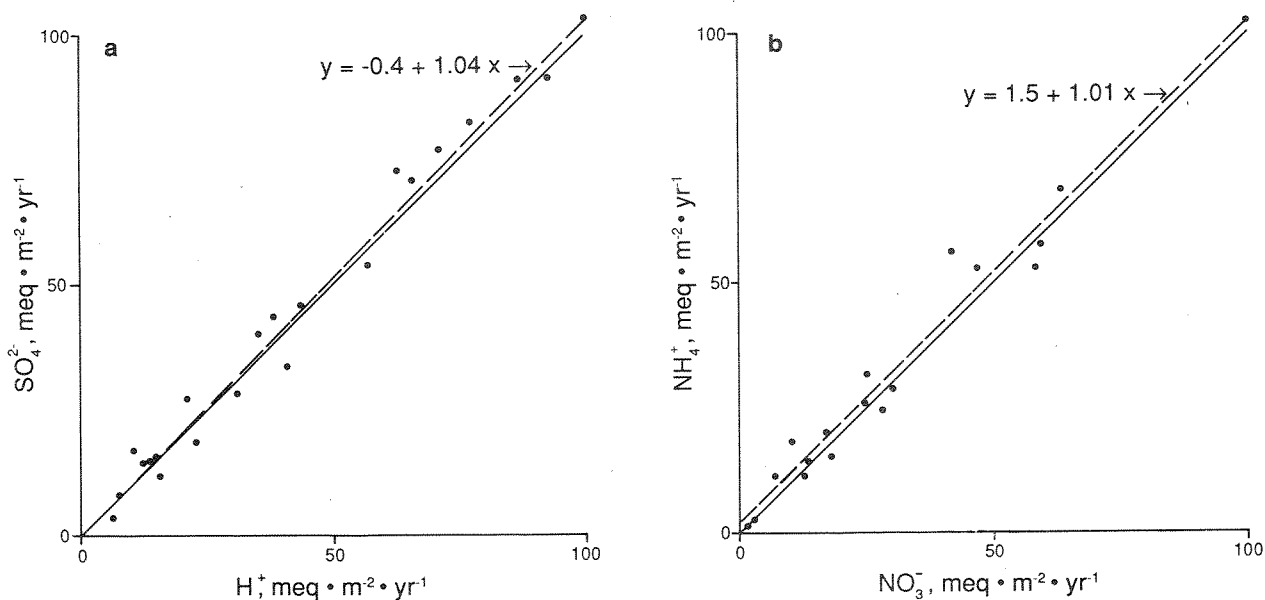
Precipitation in Norway

Figure 7. a) The ratio of hydrogen (H^+) to sulphate (SO_4^-) in precipitation in Norway.

         b) The ratio of ammonium (NH_4^+) to nitrate (NO_3^-) in precipitation in Norway.

The points are based on mean values for the period from 1985-1988 (SFT, 1989).
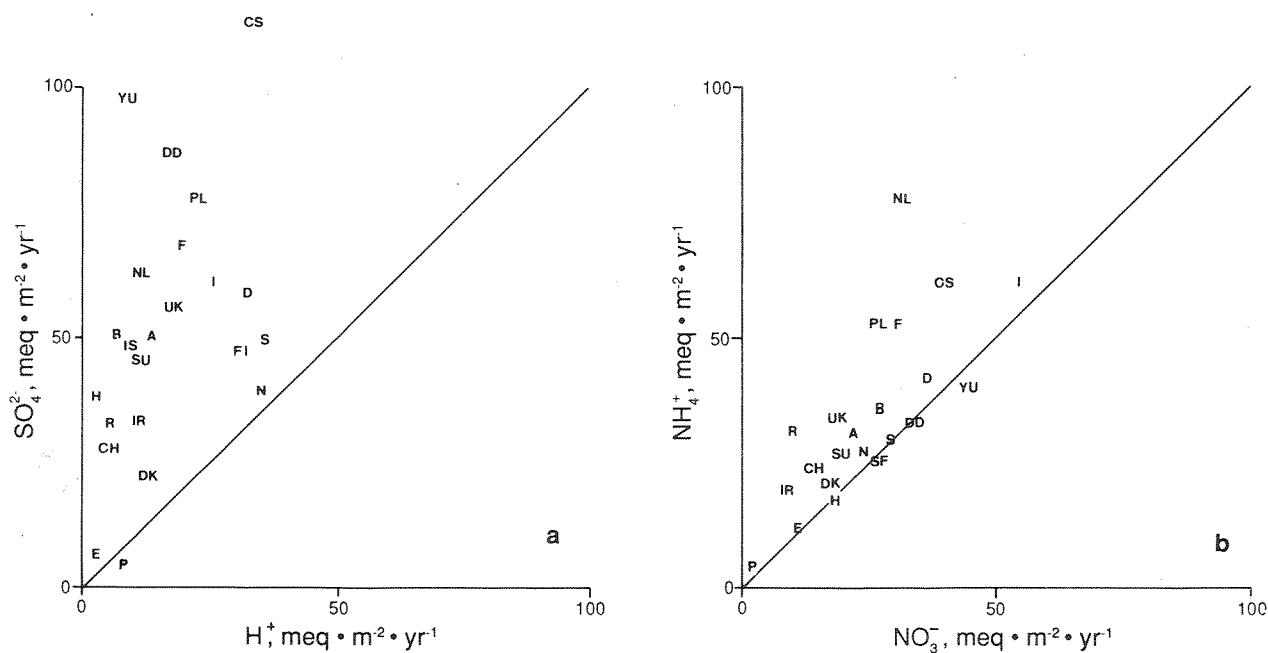
Precipitation in Europe

Figure 8. a) The ratio of hydrogen (H^+) to sulphate (SO_4^-) in precipitation in Europe.

         b) The ratio of ammonium (NH_4^+) to nitrate (NO_3^-) in precipitation in Europe.

The points are based on mean values for 1986 (Schaug et al. 1988).

7.2 Method

Every square of 0.5⁰ in latitude and 1.0⁰ in longtitude was divided into 16 subgrids (figure 1). The map series M 711 (1:50,000) was used as the basis for the selection of lakes and rivers. Each main grid covers four M 711 maps so that the subgrids are easy to identify on these maps.

In order to compute the chemistry of surface water in a subgrid, the water chemistry of lakes and rivers located within the grid and with acceptable data was compared. The chemistry of the lake that was judged to be most typical was chosen to represent the grid. If there were wide variations within a subgrid, the most sensitive area was selected to represent the subgrid if it amounted to more than 25% of the grid's area. Sensitivity was evaluated on the basis of water chemistry, topography, and bedrock geology. Table 1 shows that the variation in chemistry within one typical square may be small. The table shows the mean values and standard deviation for the eight lakes compared with values for the lake selected.

Table 1. A comparison of the mean values for eight lakes in a subgrid (58.30-7-2) with values for the lake selected. RAL (Reactive Al), ILAL (Non-labile Al), in µg/l, ANC in µeq/l, the others in mg/l.

	pH	Ca	Mg	Cl	SO$_4$	NO$_3$	TOC
Mean	4.85±.10	.27±.06	.11±.11	1.1±.2	2.1±.1	159±41	.6±.1
Lake	4.81	.32	.11	1.1	2.1	175	.5

	Na	RAL	ILAL	ANC
Mean	.68±.05	134±25	11±1	-36±7
Lake	.65	123	10	-36

7.3 Data

7.3.1. Precipitation

Precipitation data are derived from the annual reports of the monitoring programme (SFT 1989). The weighted mean values for the years 1985-1988 were averaged for each precipitation station, and isopleth maps for each relevant component were prepared in cooperation with the Norwegian Institute for Air Research (NILU) (figures 3-6). Concentration values for precipitation components were interpolated between the isopleths for each individual square and stored in the data base.

7.3.2. Water

Data from the 1000 Lake Survey and the monitoring programme were used together with data from reports from NIVA and other institutions (see chapter 12. Data Sources). Data from samples collected in the autumn after water circulation were preferred, but in some cases data from samples collected at other times of the year were also used. This was necessary for grids with low sensitivity to acidic precipitation located in areas where inputs of acidic precipitation are small. Data for each subgrid are stored in a ND-5100 PC in the RESA (RESearchers Archive) system which was originally developed by NIVA. Additional stored data included precipitation chemistry, runoff amounts, and dominant geology of each grid. The mean annual runoff was read off from the runoff map prepared by the Norwegian Water and Energy Works (NVE). The geology was determined from the geological map of Norway (1:1,000,000) prepared by the Norwegian Geological Survey.

8. PRESENTATION OF DATA

8.1 Calculation of runoff

In order to quantify critical loads and margins for critical loads and for deposition data, it is essential to have data on areal deposition and runoff for the various components for each grid square.

The amount of precipitation can be estimated from the following equation:

$$\text{Runoff (Q) = Precipitation (N) - Evapotranspiration (F)} \qquad (34)$$

The runoff figures are known. Data on evapotranspiration over the entire country is needed to estimate the amount of precipitation in each grid. Evaporation values for southern Norway (Søgnen, 1967) (figure 9) have been used to assess evapotranspiration in each subgrid. These values were entered into the database. The amount of precipitation was then calculated from Equation (34). If the amount of precipitation is multiplied by the weighted annual mean concentration in precipitation, an estimate of the mean wet deposition of the component of interest is given for each subgrid.

Runoff in Norway ranges from 150 $1 \cdot sec^{-1} \cdot km^{-2}$ in parts of western Norway to approximately 10 $1 \cdot sec^{-1} \cdot km^{-2}$ in parts of Finnmark and eastern Norway. Total export per year are obtained by multiplying the concentrations in lakes (C $\mu eq/1$) by the annual runoff. The annual export then becomes:

$$R_{keq} = C \cdot Q \cdot 0.0315 \; keq \cdot km^{-2} \cdot år^{-1} \tag{35}$$

Inputs of sulphur via precipitation and dry deposition are most frequently expressed as $gS \cdot m^{-2} \cdot year^{-1}$. In this case we get:

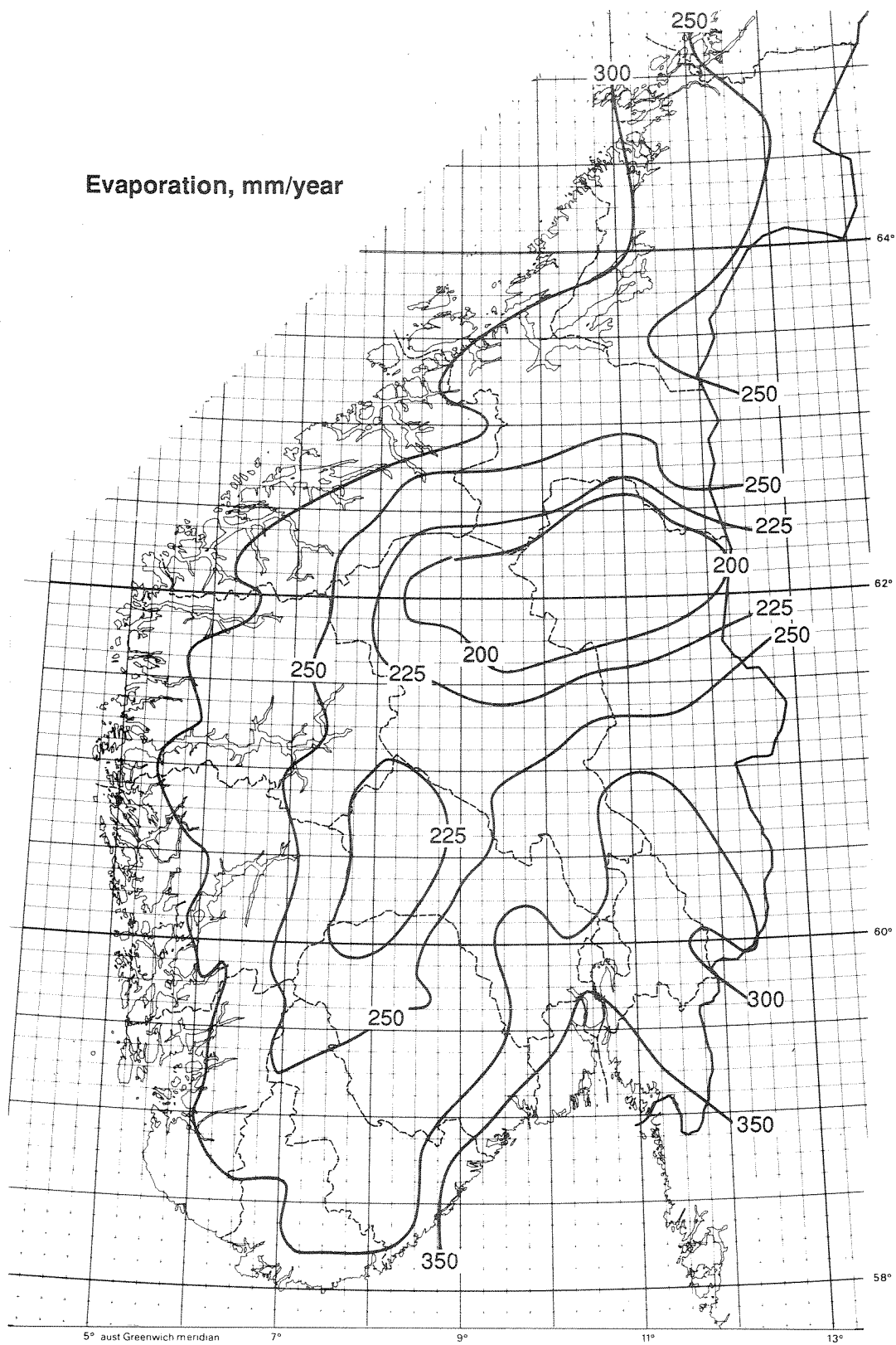$$R_S = 0.016 \cdot R_{keq} \tag{36}$$

Evaporation, mm/year

Figure 9. Annual values for evapotranspiration in southern Norway (Søgnen, 1967).

8.2 Annual wet deposition

To calculate the annual wet deposition of a precipitation component (C) we must multiply the weighted annual mean concentration (ueq/l) by the amount of precipitation (litres per year). This can be done in the following manner:

$$C \cdot N = C \cdot (Q + E)$$

where E is the evapotranspiration and Q is the discharge.

E is normally given in mm/year. The precipitation amount expressed in $l \cdot km^{-2} \cdot sec^{-1}$ is;

$$N = Q + 0.0317 \cdot E \tag{37}$$

and we obtain:

$$C_{dep} (keq \cdot km^{-2} \cdot year^{-1}) = 0.015 \cdot C(\mu eq/l) \cdot N(l \cdot km^{-2} \cdot sec^{-1}) \tag{38}$$

8.3. Sulphur runoff due to precipitation

In order to compare sulphur inputs via precipitation plus dry deposition with export of SO_4 from catchment areas, the export figures must be corrected for any geologically derived sulphate. This correction is given by Equation (27). Thus, we have the concentration of sulphate in the runoff water which is due to precipitation:

$$[SO_{4n}] = [SO_{4t}{}^*] - 0.16 \cdot [BC_t{}^*] \tag{39}$$

Expressed as an annual runoff we get:

$$S\text{-}flux_1 (gS \cdot m^{-2} \cdot year^{-1}) = 5.04 \cdot 10^{-4} \cdot [SO_{4n}] \cdot Q \tag{40}$$

$$S\text{-}flux_2 (keq \cdot km^{-2} \cdot year^{-1}) = 3.15 \cdot 10^{-2} \cdot [SO_{4n}] \cdot Q \tag{41}$$

8.4 Critical load

This factor (CL) is calculated from Equation (32):

$$CL = ([BC_0{}^*] - [ANC_1]) \cdot Q - BC_d{}^* = [TL] \cdot Q - BC_d{}^* \tag{42}$$

where $[TL] = ([BC_0{}^*] - [ANC_1])$, and $[BC_0{}^*]$ is calculated from equation (28).

Expressed as an annual runoff we get:

$$CL\text{-}flux_1 (gS \cdot m^{-2} \cdot year^{-1}) = 5.04 \cdot 10^{-4} \cdot [TL] \cdot Q - BC_d^* \tag{43}$$

$$CL\text{-}flux_2 (keq \cdot km^{-2} \cdot year^{-1}) = 3.15 \cdot 10^{-2} \cdot [TL] \cdot Q - BC_d^* \tag{44}$$

8.5 Deviation from the critical load

This factor is calculated as follows:

$$CL_{ex} = ([BC_0^*] - [AN_t] - [ANC_1]) \cdot Q = [DL] \cdot Q \tag{45}$$

where $[DL] = ([BC_0^*] - [AN_t] - [ANC_1])$. If the critical load is exceeded, the value will be negative; if it is not exceeded the value will be positive.

Expressed as an annual runoff we get:

$$CL_{ex}\text{-}flux_1 (gS \cdot m^{-2} \cdot year^{-1}) = 5.04 \cdot 10^{-4} \cdot [DL] \cdot Q \tag{46}$$

$$CL_{ex}\text{-}flux_2 (keq \cdot km^{-2} \cdot year^{-1}) = 3.15 \cdot 10^{-2} [DL] \cdot Q \tag{47}$$

9. RESULTS

9.1 Preparation of maps

The value of each parameter is expressed as a colour ranging from red to blue (fig.10 to 12). Green is not used in order not to confuse colour-blind persons. $[ANC_1]$ has been set equal to zero. The reason for this is that many Norwegian lakes have ANC-concentrations of zero or less in their natural state due to very low base cation concentrations and small amounts of organic anions. If a higher ANC_1 is used (say 20 µeq/l), the critical load would be negative in large areas of Norway.

Red indicates the lowest critical level or the highest excess of SO_4, whereas blue indicates the best conditions. All values are expressed both in $keq \cdot km^{-2} \cdot year^{-1}$ and in $gS \cdot km^{-2} \cdot year^{-1}$, using the same colour codes.

SOUTHERN NORWAY – INPUTS OF STRONG ACIDS

COLOUR MAPS FOR CRITICAL LOADS, SULPHUR RUNOFF AND CRITICAL LOAD EXCEEDANCE.

The coloured maps are shown on the next three pages, the figure captions are given below.

Figure 10. Critical loads for inputs of strong acids in southern Norway. Critical loads are calculated from $[ANC_1] = 0$, i.e. the biological indicators tolerate concentrations of $[ANC_1]$ down to 0 µeq/l. If $[ANC_1]$ is set higher, the critical loads will be lower than indicated in the figure. If, for example, $[ANC_1] = 10$µeq/l the critical load will be 10 $\mu eq \cdot km^{-2} \cdot year^{-1}$ lower in areas with approximately 1,000 mm annual precipitation. At lower/higher amounts of precipitation the deducted concentration will be lower/higher than 10 $keq \cdot km^{-2} \cdot year^{-1}$.

Figure 11. Sulphur runoff from lakes in southern Norway.

Figure 12. Areas in southern Norway where the critical load is exceeded (yellow-red) / is not exceeded (light blue-dark blue). This map arises from the difference between figures 11 and 10.

SOUTHERN NORWAY
Critical load - surface waters

NATURENS
TÅLEGRENSER

keq · km⁻² · yr⁻¹	gS · m⁻² · yr⁻¹
0 - 12.5	0 - 0.19
12.5 - 25	0.20 - 0.39
25 - 37.5	0.40 - 0.59
37.5 - 50	0.60 - 0.79
50 - 62.5	0.80 - 0.99
62.5 - 75	1.00 - 1.19
75 - 87.5	1.20 - 1.39
87.5 - 100	1.40 - 1.59
100 - 112.5	1.60 - 1.79
> 112.5	> 1.80

NIVA

0   100   200 km

This map is produced and printed by Statens kartverk 04-90

SOUTHERN NORWAY
Sulphur runoff - surface waters

NATURENS
TÅLEGRENSER

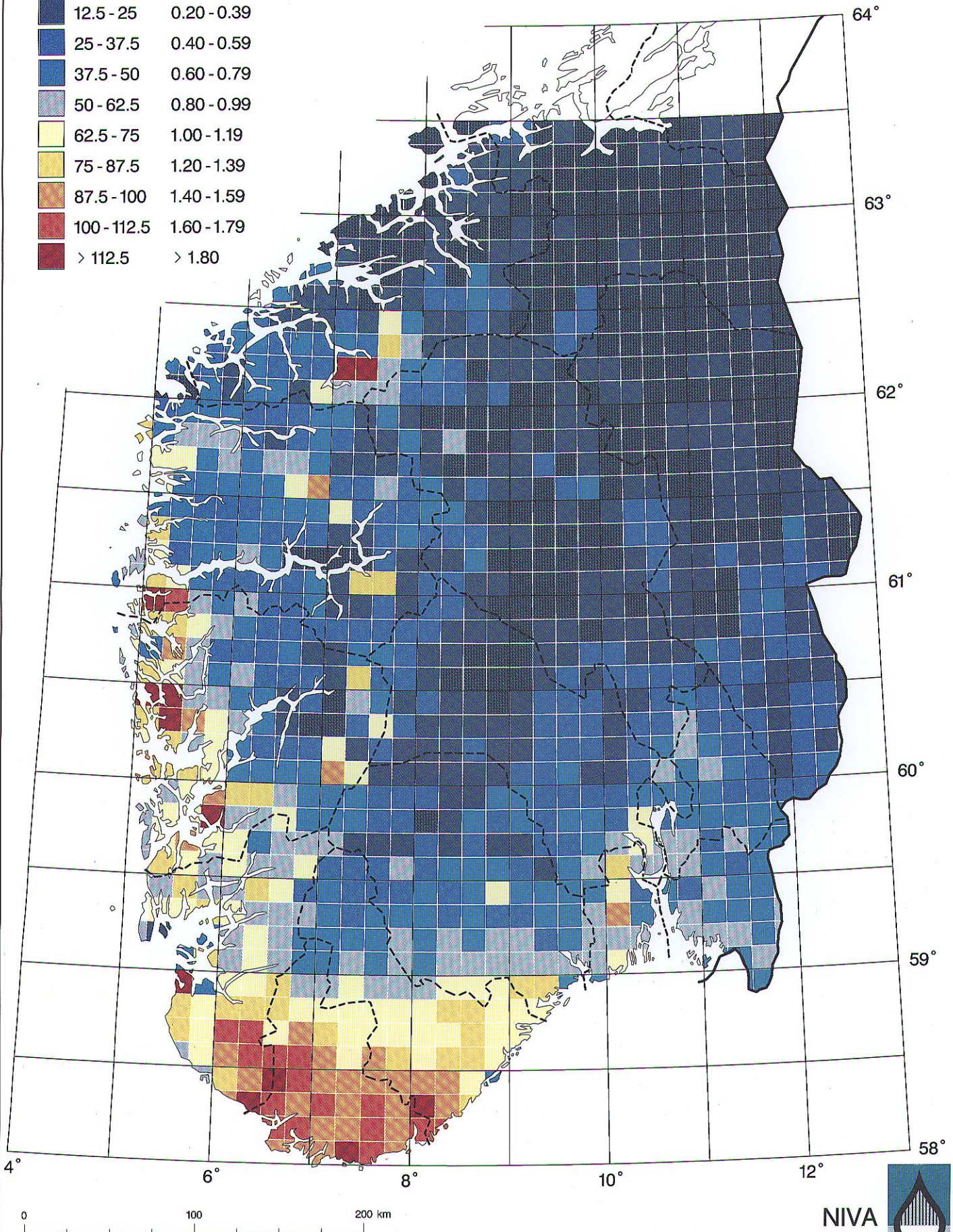| keq · km^{-2} · yr^{-1}	gS · m^{-2} · yr^{-1}
0 - 12.5	0 - 0.19
12.5 - 25	0.20 - 0.39
25 - 37.5	0.40 - 0.59
37.5 - 50	0.60 - 0.79
50 - 62.5	0.80 - 0.99
62.5 - 75	1.00 - 1.19
75 - 87.5	1.20 - 1.39
87.5 - 100	1.40 - 1.59
100 - 112.5	1.60 - 1.79
> 112.5	> 1.80

64°
63°
62°
61°
60°
59°
58°

4°   6°   8°   10°   12°

0   100   200 km

NIVA

This map is produced and printed by Statens kartverk 04-90

SOUTHERN NORWAY
Critical load exceeded
– surface waters

NATURENS
TÅLEGRENSER

keq · km⁻² · yr⁻¹	gS · m⁻² · yr⁻¹
> 50	> 0.80
50 - 37.5	0.79 - 0.60
37.5 - 25	0.59 - 0.40
25 - 12.5	0.39 - 0.20
12.5 - 0	0.19 - 0.00
0 - -12.5	-0.01 - -0.19
-12.5 - -25	-0.20 - -0.39
-25 - -37.5	-0.40 - -0.59
-37.5 - -50	-0.60 - -0.79
< -50	< -0.80

0   100   200 km

NIVA

This map is produced and printed by Statens kartverk 04-90
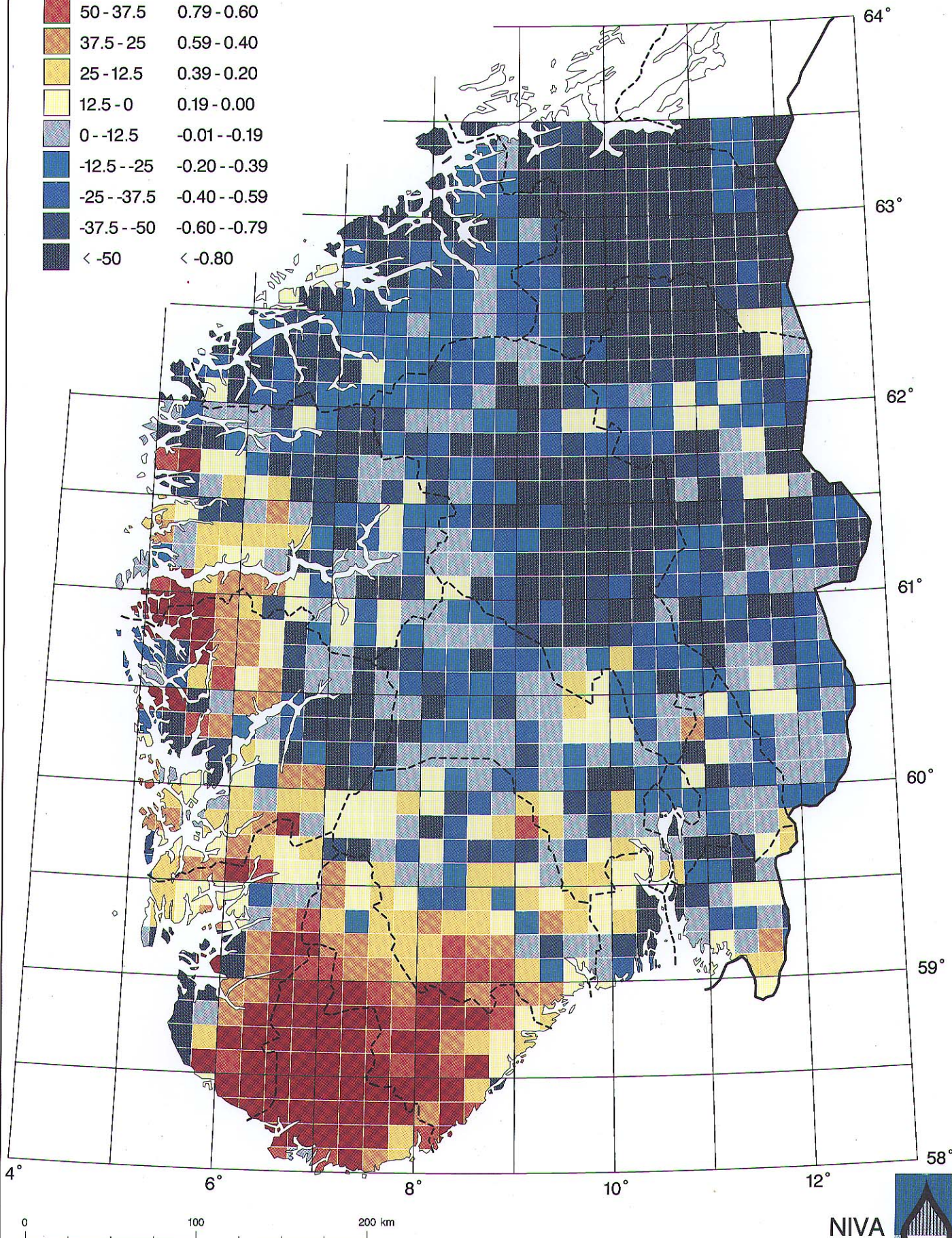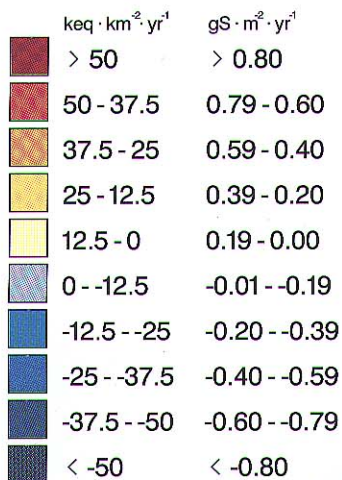
Critical loads for inputs of acid compounds are low in extensive areas
of southern Norway (figure 10). Southeast Norway and large parts of
eastern and western Norway in particular are extremely sensitive to
inputs of acidic deposition. The central areas of eastern Norway and
southern Trøndelag are less sensitive.

Sulphur runoff (export) in southern Norway is clearly related to
sulphur deposition (figure 11). The highest runoff is found in
southern and western Norway. Sulphur runoff is less in eastern Norway,
largely because of the lower amounts of precipitation. However,
concentrations in precipitation (figure 3) are just as high in eastern
Norway as in parts of southern and western Norway. A number of grids
have highly elevated sulphur runoff (e.g. the square at 59.30^0 N. in
latitude, 8^0 E.in longitude). This is attributable to the fact that the
"geological" correlation (Equation 27) does not function satisfactorily
for some locations, particularly where the runoff water is affected by
glaciers. The high values for sulphur runoff are also due to higher
amounts of precipitation on glaciers. However, only a very few grids
are affected, and overall this is of little significance. If we combine
the critical load map and the sulphur runoff map we get a map which
illustrates where and to what extent critical loads are exceeded or not
(figure 12). The largest margins are to be found in southeastern Norway
and parts of western Norway whereas in the central areas of eastern
Norway and southern Trøndelag levels are well below the limit. This map
correlates extremely well with a map which depicts damage to fish
populations in southern Norway (Henriksen et al., 1989).

9.2 Frequency Distribution Diagrams

In order to make prognoses for the response to changes in inputs of
atmospheric pollutants, the EMEP-grid system is most often used. These
are approximately 150x150 km and cover about 115 subgrids (see figure
2). Only four of the EMEP squares are located entirely within Norway's
borders; the remainder also include the ocean or parts of Sweden. We
can employ different graphic methods to depict the properties of the
EMEP squares because the water chemistry for each individual sub-grid
is representative of its area. Frequency distribution diagrams, for
instance, will provide the areal distribution of the chemical
properties within each EMEP grid by summing up all the subgrids. The
same procedure can be applied to the whole of southern Norway, to
regions and to counties.

We illustrate the use of this method for the whole of southern Norway
as well as five of the EMEP grids in Norway and five counties (East and
West Agder, Telemark, Buskerud and Oppland (see figure 2). We have
calculated the critical load, and the deviation from the critical load
(critical load exceedance), and the two have been cumulated for each

individual EMEP grid and each county. We have also calculated the sulphur runoff for the same EMEP grids and counties and compared this with the amounts of sulphur deposited via precipitation.

9.2.1. Southern Norway

Figure 13a shows the areal distribution of the critical load for acid inputs. Approximately 70% of the area of southern Norway tolerates less than 80 $keq \cdot km^{-2} \cdot year^{-1}$ in inputs of acidic components (e.g. sulphur) and in about 40% of the area we would find fishless lakes if inputs of acid were 40 $keq \cdot km^{-2} \cdot year^{-1}$. Today acid inputs to the most seriously affected areas of southeastern Norway are approximately 80 $keq \cdot km^{-2} \cdot year^{-1}$, so that with this acid loading fish populations in lakes and rivers would disappear or be severely damaged in about 70% of southern Norway. This shows that the surface water in large areas of southern Norway is very sensitive to acidification.

Figure 13b indicates the distribution of CL_{ex} (Equation 45) in runoff water in southern Norway. The critical load is <u>not</u> exceeded in about 70% of the area, i.e. the critical load for acid inputs <u>is</u> exceeded in about 30% of the area of southern Norway. This correlates well with the findings of the 1000 Lake Survey which showed that in roughly 22% of the area of southern Norway fish had either disappeared or were damaged (Henriksen et al., 1989). A comparison with the map illustrating critical load exceedances (figure 13) and the map that shows damage to fish populations (Henriksen et al., 1989) also indicates a very good correlation between the location of areas where the critical load is exceeded and areas where fish have disappeared or are damaged. Two different surveys provide the same result, thus strengthening the validity of the water chemistry method.

Figure 14 shows sulphur runoff in southern Norway compared to inputs of sulphur via precipitation. The regression equation suggests that there is an clear connection in each single square between inputs of sulphur via precipitation and sulphur in runoff. The frequency distribution curves are very similar (figure 13). Below the 50% point the deposition curve is below the runoff curve; i.e. sulphur runoff is greater than input. Conversely, in the case of high sulphur inputs sulphur runoff is less than the input. However, the deviations are relatively minor. Taking into account the uncertainties in the calculations, especially the input values where the evaporation value is not certain, the curves are surprisingly similar. This curve indicates clearly, therefore, that the sulphate content of runoff water in southern Norway is mainly attributable to sulphur input via precipitation.

Southern Norway

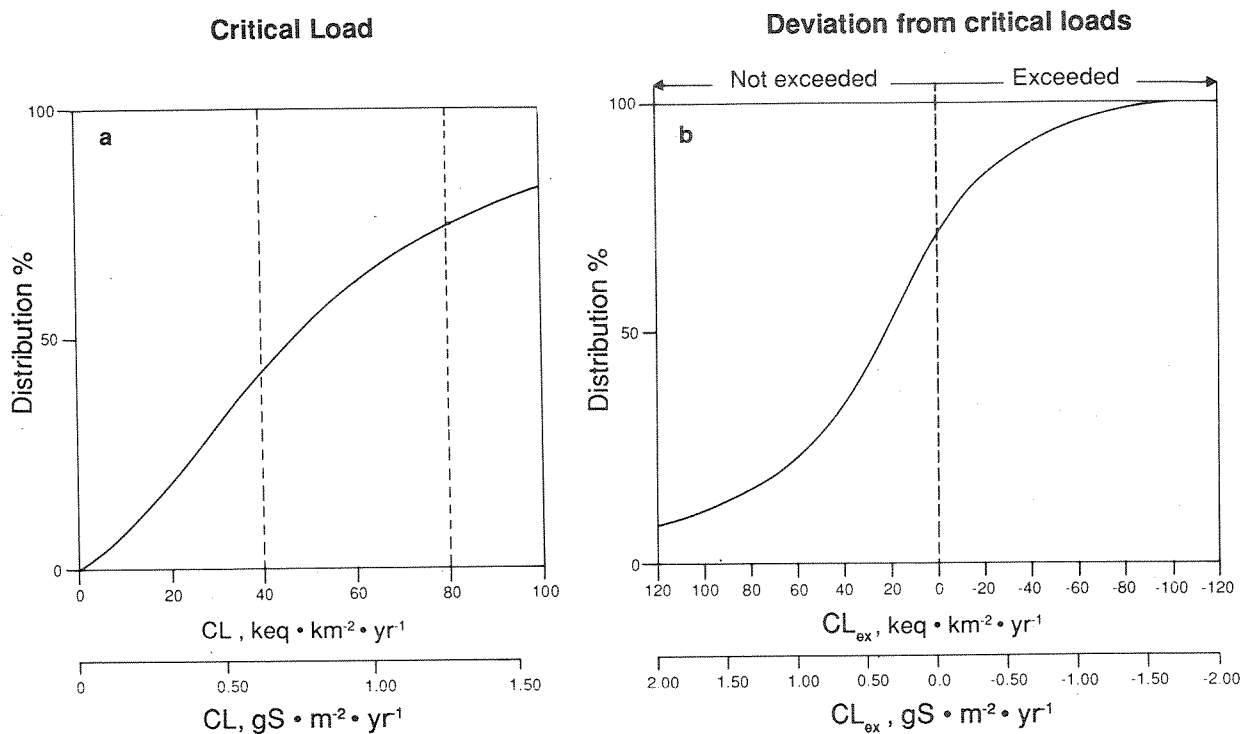**Critical Load**

Deviation from critical loads

Figure 13. Frequency distribution diagrams for critical loads in southern Norway. a) gives the area distribution of critical loads, b) gives the area distribution where these are exceeded/not exceeded (see figures 10 and 12).

Southern Norway

--- Sulphur deposition (wet) (S_d)
— Sulphur runoff (S_r)
(non-marine)

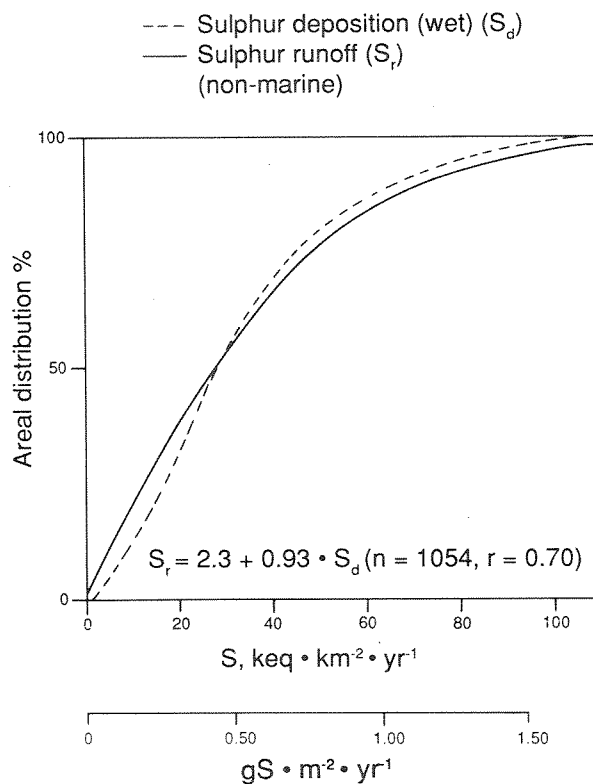$$S_r = 2.3 + 0.93 \cdot S_d \,(n = 1054, r = 0.70)$$

Figure 14. Frequency distribution diagrams for sulphur deposition and sulphur runoff in southern Norway (see figure 11).

At present, coverage for the remainder of Norway is inadequate, apart from the municipality of South Varanger in Finnmark. This area is subject to severe pollution from point sources within the Soviet Union. The one at Nikel emits approximately 280,000 tonnes of sulphur per year. The area was extensively surveyed during the 1000 Lake Survey in 1986, and several lakes have been monitored since then in connection with the monitoring programme.

9.2.2. EMEP squares

We have calculated critical loads and the extent to which they are exceeded or not for five EMEP squares in Norway. These are marked with their respective numbers in figure 15 (see also figure 1). The critical loads vary from square to square. Square 1 (the "Birkenes square") and square 2 (the "Oslo square") are clearly more sensitive to acid precipitation (figure 14a). More that 90% of the area in these squares does not tolerate acid inputs in excess of 80 $keq \cdot km^{-2} \cdot year^{-1}$. The critical load at $ANC_1 = 0$ is exceeded in about 90% of the area of square 1. In the remaining squares the area where the critical load is exceeded is considerably less. The Birkenes square has been selected by the authorities as a "model square" in order to evaluate the impact of reduced inputs of acidic precipitation. The square is well suited to this purpose; it has the lowest critical load for acidic precipitation and it has the highest inputs of acidic precipitation. Scenarios for reduced inputs which give politically acceptable conditions in this square will most probably lead to acceptable conditions in the rest of the country.

9.2.3. Counties

Frequency distribution diagrams for the five counties, East Agder, West Agder, Oppland, Buskerud and Telemark (figure 15) show that the Agder counties have the lowest critical loads (figure 15a), and that Oppland tolerates the most acidic precipitation. Figure 16b shows that West Agder receives the most acidic precipitation, followed by East Agder, Telemark, Buskerud and finally Oppland. The combination of low critical load and high input of sulphur means that critical loads are exceeded in most of the area of the Agder counties. In comparison, Oppland with its high critical loads and low sulphur input is safe from serious damage.

Critical loads

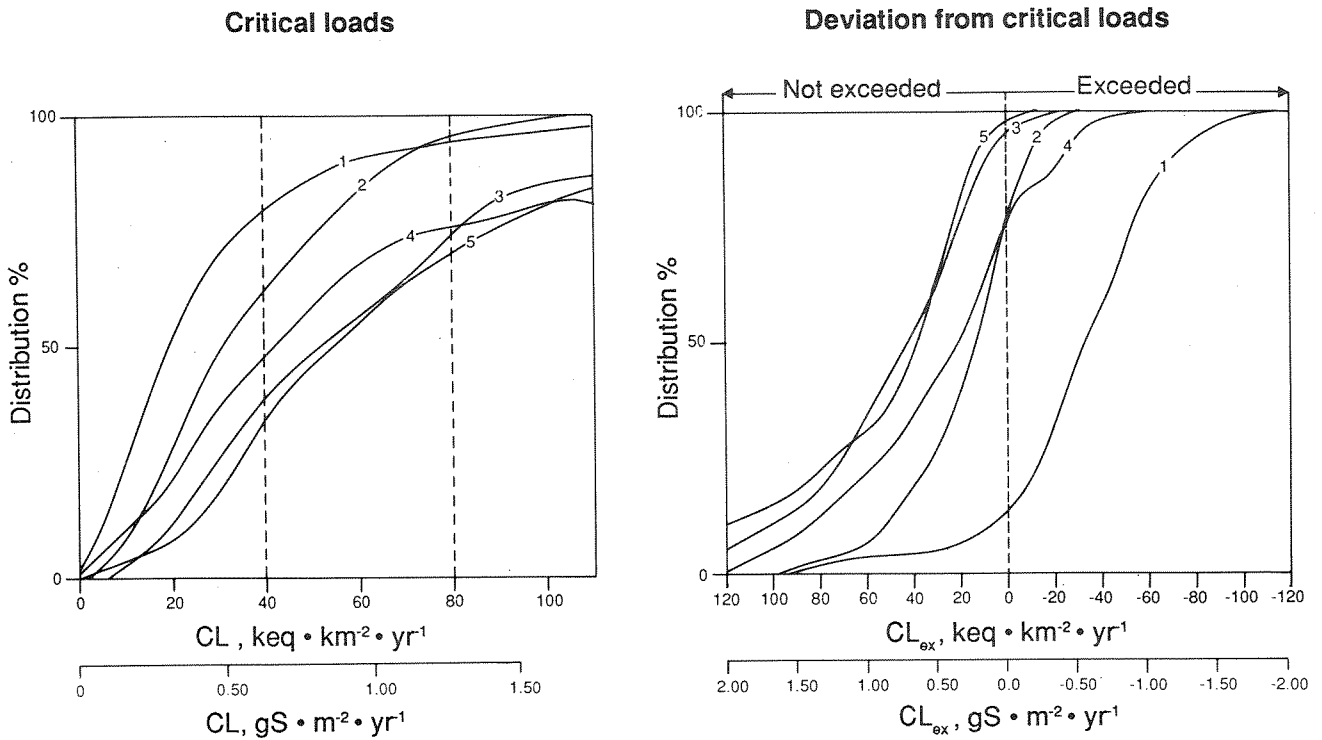**Deviation from critical loads**

Figure 15. Frequency distribution diagrams for critical loads in five EMEP squares in southern Norway (see figure 2). a) gives the area distribution of the critical loads, b) gives the distribution of areas where the critical load is exceeded.

Counties in Southern Norway

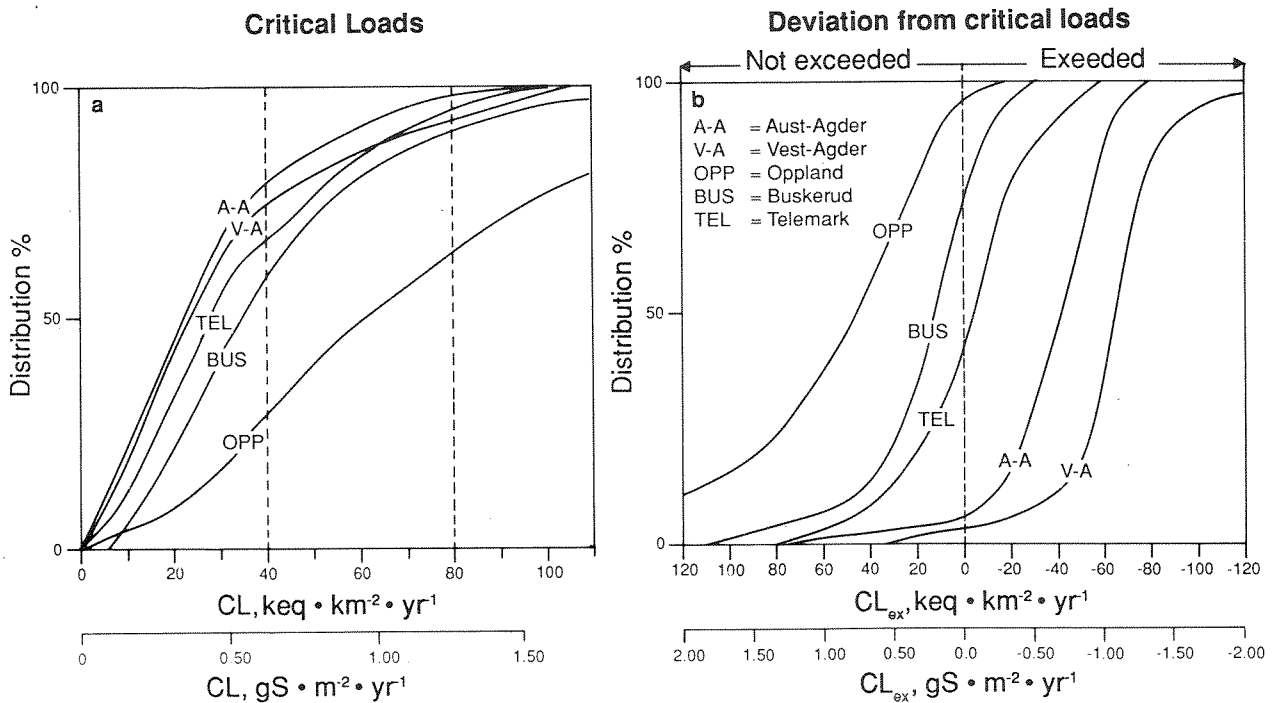**Critical Loads**

Deviation from critical loads

Figure 16. Frequency distribution diagrams for critical loads in five counties in southern Norway (see figure 2). a) gives the area distribution of the critical loads, b) gives the distribution of areas where they are exceeded.
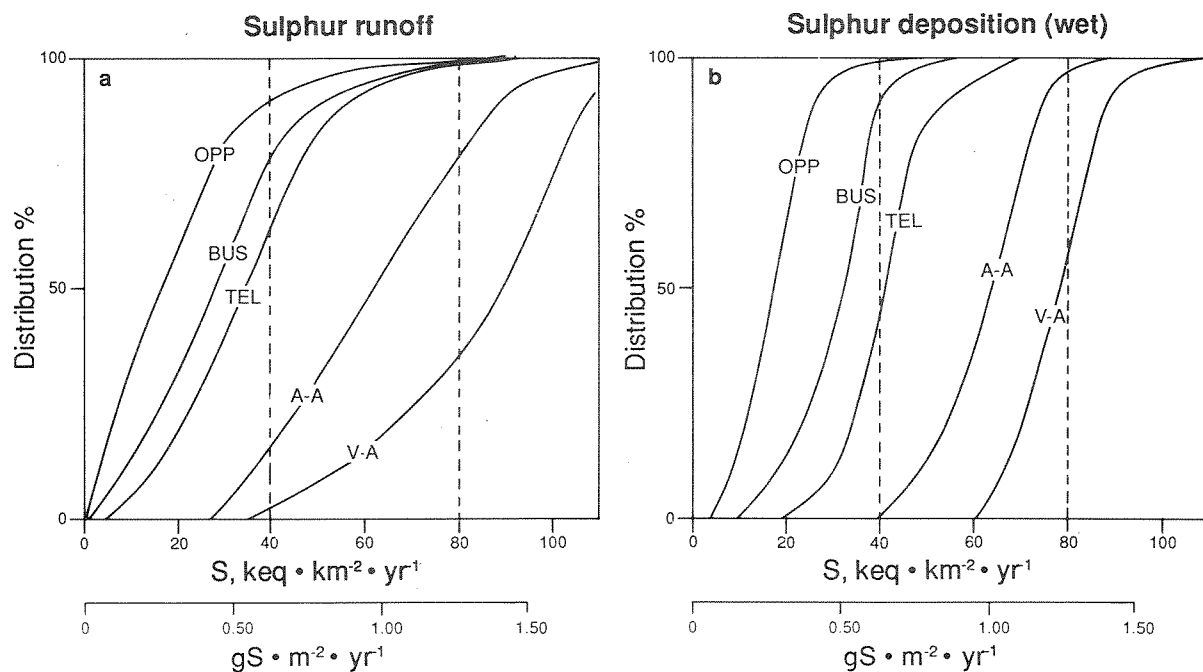
Counties in Southern Norway

Figure 17. Frequency distribution diagrams for sulphur runoff (a) and sulphur deposition via precipitation (b) in five counties in southern Norway.

Table 2 gives a relative comparison of conditions in all counties of southern Norway and the municipality of South Varanger. The first two columns give the area percentage where the critical load is given by two chemical criteria, with ANC_1 values at 0 and 10 $keq \cdot km^{-2} \cdot year^{-1}$ respectively. For some counties (e. g. East and West Agder and Vestfold) the variations in areal values between the two criteria are small, whereas for others (e.g. South Varanger, Buskerud, Sogn and Fjordane) the variation is appreciably greater. In the case of the latter group there are extensive areas which are on the borderline; in Buskerud, for instance, the ANC is between 0 and 10 in approximately 20% of the area. There is an even greater spread in the municipality of South Varanger where the area is about 35%. Consequently, the area estimates in Table 2 for this group are rather more uncertain than estimates for the first group.

Table 2. Critical load data for counties in southern Norway and the
municipality of South Varanger in Finnmark.
Unit keq.km^{-2}·year^{-1}.

	Critical loads			
County	% area where exceeded		% area below threshold	
	ANC$_1$ ≤0	ANC$_1$ ≤10	40	80
West-Agder	97	97	75	92
East-Agder	95	96	80	98
Rogaland	72	78	42	74
Vestfold	54	69	25	74
Østfold	42	67	45	86
Telemark	61	70	70	96
Hordaland	46	59	35	61
Akershus/Oslo	22	47	40	92
Sogn and Fjordane	33	56	40	77
Buskerud	20	47	60	90
Hedmark	8	24	50	75
Oppland	5	17	29	65
Møre and Romsdal	3	7	20	71
Sør-Trøndelag	2	4	22	46
Suthern Norway	33	40	43	74
South Varanger	15	50	68	99

The last two columns in Table 2 give the area percentage within each
county where critical loads are below 40 and 80 keq.km^{-2}·year^{-1}
respectively. In West Agder the mean deposition (wet) of sulphur is 80
keq.km^{-2}·year^{-1} (Figure 2). The last column in Table 2 shows   the
extent of the area of each county where the critical load would be
exceeded if the whole of southern Norway were subject to such levels of
atmospheric inputs of sulphur. The Agder counties, Telemark,
Akershus/Oslo and Buskerud are the most "sensitive" counties, while
South Trøndelag, Hordaland and Oppland are the least sensitive. The
municipality of South Varanger is particularly sensitive; the critical
load would have been exceeded in over 99% of the area if sulphur
deposition was equal to that in West Agder. According to NILU, sulphur

deposition in West Agder in 1985 averaged approximately 95 keq·km^{-2}·year^{-1} (1.5 g S·m^{-2}·year^{-1}), whereas in South Varanger it was about 55 keq·km^{-2}·year^{-1} (0.9 g S·m^{-2}·year^{-1}) in the eastern parts. Any increase in sulphur deposition in this area will have severe consequences for fish populations in rivers and lakes.

10. DISCUSSION

The acid which is contributed to catchment areas is from anthropogenic production of SO_2 and NO_x. This means that sulphate and nitrate in precipitation are closely correlated to the acid contributed to the watershed. Consequently the estimated reduction in acids in precipitation will yield a corresponding reduction in inputs of sulphur and nitrogen. The ratio of H$^+$ to SO_4 in precipitation in Norway is approximately 1:1 (figure 7a). . The sulphate ions can be treated as a tracer for the input of acids. For this reason we can use the Water Chemistry Method to estimate the critical load for sulphur. The problem is more complicated in the case of critical loads for the input of nitrogen. Figure 7b shows that the ratio of NO_3 to NH_4 in precipitation in Norway is about 1:1. When all the nitrogen is not taken up, the excess will normally be found in runoff water in the form of nitrate. Nitrate has the same acidifying impact as sulphate because it is also a strong acid anion. The concentration of this ion cannot be used as a tracer for the input of nitric acid because only part of the nitrogen input remains in the runoff water in the form of nitrate. Therefore, it is not possible to employ the same procedure as used for sulphur to determine the critical load for nitrogen. The problem must be approached differently.

One water locality has been selected as representative of each single square in the colour maps. In the case of East and West Agder and some other areas in southern Norway, the number of lakes for which chemical data are available is so high that it is possible to compare the chemistry of the lake selected with the other lakes in the square (Table 1). A preliminary assessment of a limited number of squares shows that the lakes selected are representative. Nevertheless, in extensive areas of southern Norway the data available for each square are not extensive. It is important to carry out local surveys of lake in these areas to check the representativeness of the values which form the basis for the preparation of the coloured maps.

An important application of the existing data base is to make prognoses of the impact of changes in inputs of sulphur and nitrogen via precipitation and dry deposition. Both simple empirical models and more

complicated mathematical models can be used for this purpose. The results of such calculations can be presented in several ways. The colour map may be most appropriate when wishing to show where critical loads are exceeded due to changes in the pattern of input, while the frequency distribution map may be more suitable when changes in area are of interest.

11. LITERATURE

Brakke, D.F., Henriksen, A. and Norton, S.A.. 1990. A variable F-factor to explain changes in base cation concentrations as a function of strong acid deposition. Verh. Internat. Verein. Limnol. 24 (In press).

ECE, 1990. DRAFT MANUAL on Methodologies and Criteria for Mapping Critical Levels/Loads and Geographical Areas where they are exceeded. Prepared by the Workshop and Task Force on Mapping with the assistance of the Secretariat of the United Nations Economic Commission for Europe (UN-ECE).

Henriksen, A. 1984. Changes in base cation concentrations due to freshwater acidification. Verh. Internat. Verein. Limnol. 22, 692-98.

Henriksen, A., Lien, L., Rosseland, B. O., Traaen, T. S. and Sevaldrud, I. S. 1989. Lake Acidification in Norway. Present and predicted fish status. AMBIO 18. no. 6: 314-321.

Lien, L., Henriksen, A., Raddum, G.G. and Fjellheim, A.. 1990. Tålegrenser for overflatevann - fisk og evertebrater. (Critical loads for surface waters - fish and invertebrates) (in Norwegian). Naturens Tålegrenser, NIVA O-89185. Fagrapport nr. 3.

Nilsson, J. and Grennfelt, P. (eds.). 1988. Critical Loads for Sulphur and Nitrogen - Report from a Workshop held at Skokloster, Sweden, March 19-24, 1988. UN-ECE and Nordic Council of Ministers, Nord 1988:15.

Reuss, J.O. and Johnson, D.W.. 1986. Acid Deposition and the Acidification of Soils and Waters. (Springer, New York, 1986).

Schaug, J., Skjelmoen, J.E., Walker, S.E., Harstad, A., Nodop, K. and Pacyna, J.M.. 1988. Co-operative Programme on Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP). Data Report 1986, Part 2: Monthly and seasonal summaries. Norsk institutt for luftforskning (NILU), Lillestrøm.

Sverdrup, H.U., de Vries, W. and Henriksen, A. 1990. Mapping Critical Loads. Criteria, calculation methods, input data, and calculation examples for mapping critical loads and areas where they have been exceeded. Background document prepared for the Workshop and Task Force on mapping critical loads and levels, at Bad Harzburg November 6-9, 1989.

Søgnen, R., 1967. Nedbør, tilløp og fordunstning. (Precipitation, runoff and evapotranspiration) (in Norwegian). Vassdragsdirektoratet, Hydrologisk avdeling. Rapport nr. 14/67.

(lyn-n) hen-89210

APPENDIX

This appendix is a concentrated description of the Steady-State-Water Chemistry Method presented as part of a poster at the" International Conference on Acidic Deposition, Its Nature and Impacts", Glasgow, 16-21 September 1990.

THE STEADY-STATE WATER CHEMISTRY METHOD

The total flux of non-marine base cations from a catchment area (BC^*_t) is a result of the balance between inputs from weathering reactions (BC_w), ion-exchange processes (BC_i), non-marine atmospheric deposition (BC^*_d), and net long-term uptake in the biomass (BC_u):

$$BC_w = BC^*_t - BC_i + BC_u - BC^*_d, \qquad (1)$$

where all parameters are expressed as an annual flux (i.e. $keq.km^{-2} \cdot year^{-1}$) and the asterisk denotes the non-marine fraction. Of these parameters BC^*_t and BC^*_d are calculated directly from runoff and precipitation volume and concentration measurements.

BC_i is related to long-term changes in inputs of acidic anions (ΔAN^*) by the F- factor (Henriksen 1984, Brakke et al., 1990):

$$F = BC_i / \Delta AN^* \quad or, \quad BC_i = F \cdot \Delta AN^* \qquad (2)$$

For Norway, we assume:

1. $BC_u \approx 0$ in areas with no change in biomass,
2. BC_w does not change with changes in acid inputs,
3. BC^*_d has not changed,
4. $NO_3 \approx 0$ prior to acidification,
5. BC^*_0 ("original" base cation runoff) $= BC_w + BC^*_d$,

For the pre-acidification situation, we have:

$$BC^*_0 = BC^*_t - F \cdot \Delta SO_4^* = BC^*_t - F \cdot (SO_4^*_t - SO_4^*_0), \qquad (3)$$

where $\Delta SO_4^* = SO_4^*_t - SO_4^*_0$; $SO_4^*_t$ is the current flux of non-marine sulphate, and $SO_4^*_0$ is the "original" flux of sulphate or background.

To estimate BC^*_0, values of F and $SO_4^*_0$ must be estimated.

The value of F is a function of the base cation concentration, and normally lies between 0 and 1 (Henriksen, 1984). F may vary for a given lake over a period of time. F ranges from near zero in dilute lakes to 1 for lakes with high concentrations of base cations. F is estimated using available data. A reasonable algorithm is (Brakke et al., 1990):

$$F = \sin([BC^*_t] \cdot 90/S) \tag{4}$$

(Brackets indicate concentrations). S is the base cation concentration at which F=1.0. For Norway S is estimated to be 400 μeq/l. This means that F = 0 at $[BC^*]$ = 0 and F = 1 when $[BC^*]$ = 400 ueq/l. If $[BC^*]$ > 400, F is 1.

Background sulphate $[SO_4{}^*_0]$ is estimated from the relationship between $[SO_4{}^*_t]$ and $[BC^*_t]$ from lakes in parts of western and northern Norway where there is little acidic precipitation:

$$[SO_4{}^*_0] = 15 + 0.16 \cdot [BC^*_t] \ (\mu eq/l) \qquad r = 0.38, \ n = 143 \tag{5}$$

This equation suggests that there is an atmospheric background contribution of $[SO_4{}^*]$ which gives an average of 15 ueq/l and a geological contribution which is proportional to the concentration of base cations.

Combining equations (3), (4) and (5), we get:

$$BC^*_0 = ([BC^*_t] - \sin([BC^*_t] \cdot 90/400) \cdot ([SO_4{}^*_t] - 15 - 0.16 \cdot [BC^*_t])) \cdot Q \tag{6}$$

This relationship may differ in other countries where assumptions 1-5 do not hold.

CALCULATION OF THE CRITICAL LOAD

The critical load for a particular organism is expressed as a flux or concentration of one or more chemical parameters ranging from negative to positive values. The concentration value for the critical load for a given organism can be determined by a combination of empirical and experimental data. Acid Neutralization Capacity (ANC) appears to be well-suited as the chemical criterion for sensitive indicator organisms in surface waters. ANC is defined as the difference between non-marine base cations ($Ca^*+Mg^*+Na^*+K^*$) and strong acid anions ($NO_3+SO_4{}^*$):

$$[ANC] = ([BC^*] - [AN^*]) = ([HCO_3{}^-] + [A^-] - ([H^+] + [\Sigma Al^{n+}]) \tag{7}$$

where $[A^-]$ is the concentration of organic anions, and $[\Sigma Al^{n+}]$ is the sum of all positively-charged aluminium species. The critical biological value of ANC is termed $[ANC_l]$ (l=limit).

The critical load (CL) for a lake can now be calculated quantitatively and is the load of acidic inputs equal to the original flux of base cations in runoff (BC^*_0) from the catchment area. CL for acidic anions for a given organism is thus given by the equation:

$$CL = ([BC^*_0] - [ANC_l]) \cdot Q - BC^*_d \tag{8}$$

In the general case, this equation gives the critical load for the sum of acid anions. If we assume that background concentrations of nitrate are zero, the equation yields the critical load for sulphate.

To calculate the extent to which critical loads for acidic components are exceeded (Critical load exceedance), we have:

$$CL_{ex} = CL - [AN^*_t] \cdot Q, \tag{9}$$

where $[AN^*_t]$ is presentday concentrations of strong acid anions ($SO_4^* + NO_3$). Substituting equation (8) into equation (9) we get:

$$CL_{ex} = ([BC^*_0] - [ANC_1]) \cdot Q - BC^*_d) - ([AN^*_t] \cdot Q) \tag{10}$$

which simplifies to:

$$CL_{ex} = ([BC^*_0] - [AN^*_t] - [ANC_1]) \cdot Q - BC^*_d \tag{11}$$

$[BC^*_0]$ is calculated with equation (7) with empirical values of $[BC^*_t]$, $[SO_4{}^*_t]$, and Q. $[ANC_1]$ is defined. BC^*_d and $[AN^*_t]$ are also empirical.

Norwegian Institute for Water Research ⬤ 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 report for 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.

13/1987   Wright, R.F. 1987. RAIN project. Annual report for 1986. 90 pp.

14/1988   Hauhs, M. 1988. Water and ion movment 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.