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Results of national lake surveys 1995 in Finland, Norway, Sweden, Denmark, Russian Kola, Russian Karelia, Scotland and Wales

**Acid
Rain
Research**

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Abstract:

In the autumn of 1995, national lake surveys were conducted in six Northern European countries on the initiative of the environmental authorities in Sweden, Finland and Norway. The project was subsequently expanded to include Denmark, Russian Kola, Russian Karelia, Scotland and Wales. This report therefore provides the first united evaluation of lake water chemistry in the whole of northern Europe. The results show that the lake water chemistry in this area (except Denmark) are characterized by low ionic strength (dilute) waters, with low content of nitrogen and phosphorus. In Finland, Norway, Sweden, Russian Kola and Karelia more than 50% of the lakes have low critical load (CL) values for sulphur acidity (S) ($CL < 60 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) while Scotland, Wales and Denmark have very few lakes with low CL for S. The highest percentage (27%) of lakes with exceedance of CL for S is found in Norway. In Russian Kola, Sweden and Finland 17, 9 and 9% of the lakes respectively have exceedance of CL for S. In Scotland, critical loads for sulphur acidity are exceeded in only 1% of the total lake population, while 24% of Welsh lakes are exceeded. For Denmark and Russian Karelia the number of sampled lakes is too low to give reliable estimates. In total, this adds up to approximately 22,000 lakes in Northern Europe where CL for S is exceeded. However, this number of lakes is a minimum value as exceedance of CL for N is not included in the calculation due to lack of catchment data.

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Preface

The three Nordic countries Finland, Norway and Sweden initiated a joint Nordic Lake Survey in the fall of 1995. A working group, supported financially by the Nordic Council of Ministers (NMR), prepared standard protocols for this purpose, which used similar lake selection criteria and harmonised analytical procedures. Subsequently the project was expanded to include Denmark, Russian Kola, Russian Karelia, Scotland and Wales.

This report presents the first international evaluation of lake water chemistry in Northern Europe based on a statistical selection of lakes. The survey includes about 5700 lakes, covering about 3% of the total lake population in the area.

Each country was responsible for the survey in their respective countries.

Many people have contributed to the planning, sampling, analytical programme and evaluation and we are grateful for their input. In particular we wish to thank Juha Kämäri, Irma Mäkinen, Riitta Niinioja from Finland, Anders Berntell, Bert Karlsson and Torgny Wiederholm from Sweden, Pjotr Lozovik and Nikolai Filatov from Russia and Max Posch from the Netherlands for their contribution to this work.

We finally wish to thank NMR for supporting this project.

Oslo, 1. August 1997

Arne Henriksen
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Preface 2. edition

According to new information on S-deposition for Scotland and Wales, the CL-exceedance values are recalculated for for these two regions. The new exceedance values differed so much from the numbers presented in the first edition of this report, that we found it necessary to include these corrections in the 2 edition of the report.

The correction are found in chapter 5.3 and in abstract and summary.

Oslo, 1. December 1997

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Summary

Background

In the autumn of 1995, national lake surveys were conducted in six Northern European countries on the initiative of the environmental authorities in Sweden, Finland and Norway. These countries have previously carried out nation-wide lake surveys, mainly on a regional basis. The 1995 surveys were, however, co-ordinated with respect to lake selection strategy, analytical methods, sampling techniques and sampling period. The project was subsequently expanded to include Denmark, Russian Kola, Russian Karelia, Scotland and Wales. This report therefore provides the first united evaluation of lake water chemistry in the whole of Northern Europe.

The countries included in this survey, cover a geographic area of ca. 1,400,000 km². This is about 13% of Europe's total area including the European part of Russia, and 28% of Europe excluding Russia. The total number of lakes (>4 ha) in the study area is ca. 155,000 and of these 5,690 lakes are sampled in this survey. This correspond to 3.7 % of the total lake population giving a sampling density of one lake per 252 km².

Key objectives

The key objectives of this integrated survey were to assess the status of the lakes with respect to:

- general water quality,
- occurrence and large scale regional variation of acidification,
- establishing a new reference dataset to quantify the future effects of the second sulphur protocol (UN/ECE, 1994),
- establishing the effects of nitrogen deposition on lake water chemistry in connection with the development of critical loads for nitrogen under Working Group on Effects established by the Executive Body of the United Nations Economic Commission for Europe's (UN/ECE) Convention on Long Range Transboundary Air Pollution (LRTAP),
- establishing the eutrophication status and
- the concentrations of heavy metals.

Water chemistry

The results from the survey show that the lake water chemistry in the Northern European countries, with the exception of Denmark, is dominated by low ionic strength (dilute) water, with low concentrations of nutrients (nitrogen and phosphorus compounds). This is mainly due to low weathering rates, low intensity of agriculture and low population density.

There are, however, general differences in the lake water chemistry between the countries, due to differences in hydrology, precipitation chemistry and amount, soil cover, and vegetation. From Western Norway, Scotland and Wales to Eastern Finland and Karelia, there is a gradient from high to low precipitation (3500 to 600 mm·yr⁻¹) and from mountain areas with thin and patchy soils to forested areas with thick soils. This is reflected in lake water chemistry with low concentrations of base cations (Ca, Mg, Na, K), alkalinity (HCO₃⁻) and total organic carbon (TOC) in the western areas to higher concentrations in the eastern areas. An exception from this is high TOC levels in lakes in

Scotland and Wales. Median values for base cation concentrations are three times higher in Sweden, Finland, Scotland and Wales than in Norway and TOC concentrations vary even more.

The lakes in Denmark are influenced by a different bedrock mineralogy than the other countries in the survey, and there is also much more intensive agricultural activities in their catchments. The Danish lakes generally have much higher ion concentrations and high concentrations of nitrogen (N) and phosphorus (P).

The acidification situation - critical load and exceedances

The acidification situation can be quantified by calculating critical loads and their exceedances. The highest percentage of lakes (27%, total. 10,000 lakes) with exceedances of critical load for S was found in Norway, where lakes with highest exceedances also are located. This is due to a combination of high S-deposition and very low critical loads, especially in the southernmost parts of Norway. Also Russian Kola has a high percentage of lakes with exceedance of critical load for S (17%, approximately 3,500 lakes). This is due to the high emission of S from the smelter industries in this area, and consequently high S-deposition in the areas near the factories. The critical load of S is exceeded in 9% of the lakes in both Finland and Sweden (approximately 6,000 Swedish lakes and 3,000 Finnish lakes). In Scotland, critical loads for sulphur acidity are exceeded in only 1% of the total lake population, while 24% of Welsh lakes are exceeded. For Denmark and Karelia the number of sampled lakes was too low to give reliable estimates. In total, this adds up to approximately 22,000 lakes in Northern Europe where CL for sulphur acidity is exceeded.

The SSWC-method to calculate critical loads and exceedances usually includes both S and N acidity, in such a way that present N-leaching is considered in the calculation of critical load exceedance. To do this, we must ensure that no anthropogenic sources of NO_3 other than long range transported nitrogen compounds are included in the N_{leach} term. At present such a separation is not possible for the lake survey data. Therefore we have restricted the calculations to deal with critical loads of acidity and exceedance of sulphur acidity only. If the acidifying potential of N-deposition is taken into account the critical load exceedance will increase, and thus also the percentage of exceeded lakes in this report. This is especially the case for Scotland and Wales, which had much higher concentrations of nitrate in the lakes than the other countries.

1. Introduction

During the past decade extensive lake surveys have been conducted in a number of north-European countries to establish the extent of surface water acidification and to quantify long term chemical changes. Recent surveys in Finland in 1987 and Sweden in 1990 were based on a statistical selection of lakes, while the Norwegian survey in 1986 was based on subjectively selected lakes weighted towards acid sensitive regions. In the United Kingdom lakes were selected (1990-1992) by sampling the most sensitive lake or stream (where no lake was present) in each 10 km grid square. In Denmark, few lakes are sensitive to acidification and the majority are affected by nutrient enrichment. Thus, lake surveys similar to those above, have not previously been carried out in Denmark.

The data from these surveys provided a common database for calculating critical loads for surface waters which were used to support the negotiations for the second sulphur protocol signed in Oslo in June 1994.

The next phase of the critical loads programme includes both nitrogen and sulphur deposition and consequently the data requirements for the steady state and dynamic freshwater models are much more extensive. Based upon the co-operative experience gained from previous surveys, as well as subsequent evaluation of the data, the Nordic countries (Finland, Norway, Sweden) decided to carry out a joint Nordic Lake Survey in the fall of 1995. The Nordic Council of Ministers (NMR), which has supported projects dealing with critical loads of air pollutants since 1985, subsequently established a working group which concluded that any integrated programme of sampling would be greatly enhanced if adjacent countries with similar lake properties were included. By 1995, with some financial support, Denmark, Russian Kola and Karelia, Scotland and Wales joined Finland, Norway and Sweden in the common

lake survey. Sampling took place between September 1995 and January 1996 using the same statistical lake selection criteria's and harmonised sampling procedures.

The key objectives of this integrated survey were to assess the status of the lakes with respect to:

- general water quality,
- occurrence and large scale regional variation of acidification,
- establishing a new reference dataset to quantify the future effects of the second sulphur protocol (UN/ECE, 1994)
- establishing the effects of nitrogen deposition on lake water chemistry in connection with the development of critical loads for nitrogen under Working Group on Effects established by the Executive Body of the United Nations Economic Commission for Europe's (UN/ECE) Convention on Long Range Transboundary Air Pollution (LRTAP),
- establishing the eutrophication status and
- the concentrations of heavy metals.

Information on the lake populations and overview of previous lake surveys in Finland, Norway, Sweden, Denmark, Russian Kola, Russian Karelia and Scotland and Wales was presented in a previous report (Henriksen *et al.*, 1996). This report also includes the manual for selection criteria and sampling methods, quality assurance and control aspects, and results from intercalibration exercises for chemical and physical methods.

Although each country will report their own survey data in the appropriate style and language to their respective national authorities, this second report gives an evaluation of the total data set in a common format and mapping style.

2. Lake selection and extent of the survey

2.1 Selection

Finland, Norway and Sweden

For Finland, Norway and Sweden the lakes were selected at random from the national registers with the common requirements that:

- a minimum of 1% of the lakes within any county/region shall be included
- the proportion of lakes in size classes 0.04-0.1, 0.1-1, 1-10 and 10-100 km² shall be 1:1:4:8 and all lakes >100 km² shall be included.

The final selection of lakes in the different counties/regions was made in slightly different ways, but with a common goal of achieving a larger proportion of lakes in areas with a high degree of acidification or critical load exceedance. Also in areas with more variable lake chemistry (as estimated from previous surveys) (Sweden) or few lakes (Finland), a larger proportion of lakes were sampled.

Thus the proportion of lakes in the two smallest size classes was selected as follows:

Finland: 1.5% in North-eastern Lapland, 2% in inland and remaining parts of Northern Finland, 4% in coastal counties/regions.

Norway: 1.2% in Northern Norway, 2.1% in middle Norway and 3.0% in southern and Eastern Norway.

Sweden: 2% in Northern and 8% in southern Sweden; percentage in areas in between depending on the variability in alkalinity as measured in the previous survey and modified so that a similar number of lakes per NILU-grid (50×50 km²) would be achieved.

The number of lakes to be sampled in the larger size classes was achieved by multiplying the basic percentages by the factors 4 or 8 for these size classes on a county or region basis. The number of lakes selected in each country is shown in Table 2.1.

Denmark

In Denmark a selection of 19 lakes from the Danish Nationwide Monitoring Programme (administrated by the National Environmental Research Institute (NERI)) were included. These lakes are not based on a statistical selection, but the lakes are distributed all over the country.

Russian Kola and Russian Karelia

The lake selection in the Russian Kola was made by the Institute of North Industrial Ecology Problems (INEP). The lakes were selected randomly from geographical maps (1:100,000) according to the selected size classes used in the Northern European Survey. More dense sampling was carried out in areas affected by acid deposition and in areas sensitive to acidification.

The lake selection in Russian Karelia was made by the Northern Water Problems Institute (NWPI) in Petrozavodsk. Due to the lack of a complete data register for lakes, the random selection used in the Nordic countries could not be applied. The selection was restricted to lakes situated near the Finnish border and accessible by car.

United Kingdom (Scotland and Wales)

There is no inventory of UK lakes. Therefore, for reasons of data availability and logistics, the 1995 survey was limited to Scotland and Wales. All lakes down to 2 ha are available from the Ordnance Survey in digitised form in Scotland. For Wales, a cut off at 4 ha was made. The statistical selection was made on the basis of 100 km² blocks in Scotland, with no weighting for acidification status, but using the agreed size range weighting of 1:1:4:8 for the four size classes. For Wales, the country was taken as a single unit with no acidification weighting applied. Because of the small number of lakes involved a weighting of 1:1:2 was used (no lakes > 10 km²).

Table 2.1 Lake size distribution and number of lakes selected.

Size class area (km ²)	1 0.04-0.1	2 0.1-1	3 1-10	4 10-100	5 >100	Total > 0.04
Finland						
Total	14717	12311	2164	276	47	29515
Selected	305	272	200	50	46	873
Percentage	2.1	2.2	9.2	18.1	98	3.0
Norway						
Total	21218	16417	2139	164	7	38845
Selected	429	362	178	30	7	1006
Percentage	2.1	2.2	8.7	18.3	100	2.6
Sweden						
Total	35802 ¹	20484	3599	379	24	60264 ¹
Selected	1373	900	640	139	23	3075
Percentage	3.8	4	17.7	36	96	3.2
Denmark						
Total	365	269	69	6	0	709
Selected	1	10	6	2	0	19
Percentage	0.3	3.7	8.7	33	-	2.6
Russian Kola						
Total	7519	7283	830	73	7	15712
Selected	189	195	62	11	3	460
Percentage	2.5	2.6	7.4	15	42.8	2.9
Russian Karelia²						
Selected	0	5	14	8	2	29
Scotland						
Total	3517 ³	1369	147	21	0	5054 ¹
Selected	76	35	20	5	0	136
Percentage	2.2	2.6	13.6	23.8	0	2.7
Wales						
Total	160	79	16	0	0	255
Selected	30	15	7	0	0	52
Percentage	18.8	19.0	43.8	0	0	20.4

¹ Estimated² No complete lake register exists for this region³ Lakes larger than 0.02km²

2.2 Exclusion

For lakes in Finland, Norway and Sweden, the following types of lakes were excluded:

1. Hydro-electric power reservoirs with > 5m regulation
2. Catchment area/lake area > 100/1 (Norway and Sweden only)
3. Maximum lake depth < 1 m
4. Extension of rivers
5. Treatment ponds and similar water bodies
6. Limed lakes (Finland and Norway)

If such lakes were selected they were substituted as follows:

Finland: The selection procedure included ca. 40 percent oversampling. If a lake was excluded the lake was replaced with the first lake from the spare list of the same size category and watershed number. If these types are absent on the list, then the nearest one on the list (within the size category) was selected. The criterion lake/watershed ratio 1:100 was not used because chain-type lakes are common in Finland, but short retention time river extensions were excluded.

Norway: The random selection programme selected twice the required number of lakes for

each class and region. If a lake was excluded, the first on the spare list was selected. If a lake was excluded because of liming a similar lake nearby in the same size class was selected. The latter was done to ensure that areas with many limed lakes (these are the most acidified areas) also were represented in the lake populations.

Sweden: An excluded lake was replaced by the next, randomly chosen lake within the same size class and county.

In the other countries, the lake exclusion criteria's were used as guidelines.

2.3 Extent of the survey

The countries included in the Nordic Lake survey, covers a geographic area of ca. 1,400,000 km². This is about 13% of Europe's total area including the European part of Russia, and 28% of Europe excluding Russia.

The total number of lakes in the study area is ca. 155,000 and of these 5,690 lakes are sampled in this survey. This is 3.7 % of the total lake population (> 4 ha). The lake density is about 1 lake per 9 km², and the sampling density is 1 lake per 252 km².

Table 2.2 Numbers of lakes in the study area

	Number of lakes > 4ha	No of lakes sampled	% of total lake population	Area km ²	Lake density km ² /lake	Sampling density km ² /lake
Finland	29,515	873	3.0	337,032	11.4	386
Norway	38,845	1,006	2.6	323,895	8.3	322
Sweden	60,264	3,075	7.9	486,661	8.1	158
Denmark	709	19	2.7	43,069	60.7	2267
Russian Kola	15,712	460	2.9	144,900	9.2	315
Russian Karelia	-	29	-	-	-	-
Scotland	5,054	136	2.7	78,775	15.6	579
Wales	255	52	20.4	20,768	81.4	399
Total	150,354	5650	3.7	1,435,100	9.2	252

3. Methods

3.1 Sampling

The samples were collected during or shortly after the autumn overturn in all countries (Table 3.1). They were visited either by foot or by helicopter depending of the accessibility of

the lakes, following the procedures given in the previous report (Henriksen *et al.*, 1996).

Table 3.1 Sampling periods in the different countries

Country/Region	Sampling period - 1995
Finland	mid September - end November
Norway	mid September - end November
Sweden	end August - mid December
Denmark	October 1996
Russian Kola	August - October
Russian Karelia	October
Scotland and Wales	December - January

3.2 Analytical work

All analytical work was carried out by national laboratories with extensive Quality Assurance/Quality Control routines. In addition several intercalibrations have been conducted (Henriksen *et al.*, 1996). The recommended analytical methods and detection limits are

described in the first report (Henriksen *et al.*, 1996).

The laboratories responsible for the analyses were:

- Finland and Karelia Regional Environment Centres (3-13 depending on the variable) and Finnish Environment Institute (FEI), Helsinki, Finland
- Norway and Denmark Norwegian Institute for Water Research (NIVA), Oslo, Norway
- Sweden Department of Environmental Assessment at the Swedish University of Agricultural Sciences (SLU), Uppsala, Sweden
- Russian Kola Russian Kola Institute of North Industrial Ecology Problems (INEP), Apatity, Murmansk Region, Russia
- Scotland and Wales Freshwater Fisheries Laboratory (FFL), Faskally, Pitlochry, Perthshire, Scotland

The variables measured are shown in Table 3.2.

Table 3.2 Variables analysed for the national lake surveys

Variable	Finland			Norway	Sweden	Russian Kola	Scotland
	Russian Karelia			Denmark			Wales
	A	B	C				
pH	x			x	x	x	x
Conductivity	x			x	x	x	x
Temperature	x			x	x	x	x
Alkalinity	x			x	x	x	x
SO ₄		x		x	x	x	x
Cl		x		x	x	x	x
F		x		x	x	x	
Ca, Mg, Na, K		x		x	x	x	x
NO ₃ -N	x			x	x	x	x
NH ₄ -N	x			x ²	x	x	x
Tot-N	x			x	x	x	x
Tot-P	x			x	x	x	x
TOC		x	x	x	x	COD _{Mn}	x
Tot. monom. Al			x ¹	x	1/3	x	x
Non-labile Al			x ¹	x	1/3	1/3	x
"Trace" metals			1/2	x	1/3	x	x
SiO ₂		x		x	x	x	x
Absorbance					x		x
TIC		x	x				
Colour	x				x	x	
Turbidity	x						
Phosphate-P	x					x	x

¹For every second lake in size classes 1+2

²For eutrophic lakes only

A = Laboratories of Regional Environmental Centres (13)

B = Regional Laboratories (3)

C = Finnish Environment Institute

3.3 Statistics

The lakes from Norway, Sweden and Finland were selected by stratified sampling in order to give a complete coverage of different regions and lake sizes. Because this sampling strategy favoured acidified regions and large lakes, we had to deweight samples from over-represented strata in order to provide unbiased descriptive statistics for each nation; therefore each lake in a sparsely sampled stratum (region, size class) "weights" more in a statistical calculation than a lake in a densely sampled stratum. The deweighting scheme adjusted the influence of lakes from different strata by giving them weights which were inversely proportional to their sampling

frequency. The weights for the different strata were calculated as:

$$w_j = \frac{p_{\min}}{p_i}$$

where p_{\min} is the sampling frequency for the stratum with lowest sampling frequency and p_i is the sampling frequency for the other strata, respectively.

Data from lakes in Denmark and Karelia are not deweighted due to the non-statistical selection methods, and lack of information on total number lakes in the different populations.

4. Water chemistry in Northern Europe 1995

4.1 Factors influencing water chemistry

The chemical composition of surface waters in an undisturbed system is mainly determined by the contribution of ions from atmospheric deposition and weathering and ion exchange in the catchment. Atmospheric deposition is influenced by sea salts and long-range transported air pollutants. In Northern Europe contributions from soil dust and volcanic emissions are very small. The chemical composition of precipitation depends on distance from sea and anthropogenic pollution sources which is modified by a number of processes when passing through a catchment. Such processes are biological (microbial activity, uptake by growing plants, release of ions through decomposition etc.) and chemical (weathering, ion exchange, adsorption and desorption, redox processes, precipitation and dissolution). Biological processes usually result in modification of ion composition or removal of ions, while weathering gives a net contribution. The total sum of ions from deposition and weathering together with all the various processes occurring in a catchment determines the chemistry of the runoff water. Additional, but often similar, in-lake processes can further modify the ion composition.

The different processes in the soil are related to catchment characteristics such as:

- geology
- meteorology/hydrology
- precipitation chemistry and amount
- soil thickness and type of soil
- vegetation - forested / non forested areas

4.1.1 Geology

The area of investigation in this survey consists of two major geological provinces; the Precambrian and the Caledonian. Within the framework of European geology, the Norwegian, Swedish, Finnish and Russian Kola Precambrian is a part of the Fennoscandian or Baltic shield.

At various times since Precambrian the Baltic shield has been below sea level and consequently acquired a covering of sediments. When the continental crust rose above the sea again, most of these deposits were eroded by ice and flowing water. Small remnants of younger, sedimentary rocks can however still be found over the Baltic shield in certain parts of southern and Central Sweden.

The Caledonian mountain chain, formed 300-400 million years ago, also consist largely of sedimentary rocks. The Caledonian chain goes from the British Isles, beneath the North Sea through Norway and the northern part of Sweden and up to Spitsbergen.

Even younger bedrock from Cretaceous and Tertiary (< 100 million years) is found in Denmark, which, like the areas of the continent of Europe further south, is covered by very thick sedimentary deposits.

The Precambrian rocks are dominated by gneisses and granitic gneisses with low weathering rates, and low content of base cations (Ca, Mg, Na and K) and high content of SiO₂ ("acidic rocks"). The Caledonian province also include rocks of more basic characters, such as gabbro, greenschists etc. with less SiO₂, ("basic rocks"). Bedrock with low weathering rates release much less base cations and hydrogen carbonate than bedrock with high weathering rates. In general, younger rocks, especially sedimentary ones, weather far more readily than Precambrian rocks.

4.1.2 Meteorology/hydrology

There is a wide range of precipitation amounts in the study area, and the precipitation patterns depend on distance from the sea and topography.

In Norway there is a sharp gradient in precipitation from 5000 mm·yr⁻¹ close to the coast in Western Norway to 300 mm·yr⁻¹ in the driest areas in Central Norway, east of the mountain chains. This orographic precipitation pattern is caused by the steep topography of the western coast of Norway. When the wet airmasses move westward over the North Sea, meeting the steep mountains at the coast, they are forced up to higher altitudes where the air cools down and the moisture in the air condenses. Precipitation increases up to a maximal zone 30-40 km from the coast, while the regions behind the mountains in the eastern parts of Norway receive dry air with little precipitation. This precipitation pattern continues into Sweden, thereafter increasing in precipitation towards the east and the Gulf of Bothnia.

In Scotland and Wales only a few mountain regions hinder the air masses from west to east. Nevertheless precipitation amounts range from 3500 mm·yr⁻¹ in the west to 600 mm·yr⁻¹ on the eastern fringes.

Within Sweden, there is a large gradient from the mountainous areas close to Norway (1500 mm·yr⁻¹), through western part of Sweden (800-1000 mm·yr⁻¹) to rather dry areas in the eastern parts (<600 mm·yr⁻¹). The evapotranspiration magnifies these variations so that the runoff in northern, rainy parts of Sweden is close to the precipitation amounts, while in the

dry eastern parts of the country, the runoff is about 200 mm·yr⁻¹ and in some places down to 100 mm·yr⁻¹. In these areas the evapotranspiration leads to a concentration of deposited ions by about three to six times.

Within Finland the precipitation exhibits a less variable pattern compared to Norway and Sweden. The precipitation in Southern and Central Finland is on average 600-800 mm·yr⁻¹ and in Northern Finland, 500-600 mm·yr⁻¹.

Russian Kola, which is also close to the sea, has relatively low precipitation amounts. This is due to the prevailing weather systems, with very little wind from north.

In Denmark there is some variation in the precipitation, especially from west to east. In Jutland, precipitation is highest in the central part (around 900 mm·yr⁻¹), and in general this region receives higher precipitation amount than in the eastern part of Denmark. The lowest precipitation levels in Denmark are found along the west coast of Zealand (around 500 mm·yr⁻¹).

Precipitation amount is very important in determining the fluxes of the ions; i.e. how much ions are transported through the catchment. With high precipitation, the dilution effect is significant, while very low precipitation amounts result in very little dilution and even concentration if the evapotranspiration is high.

Table 4.1 Percentiles for runoff (mm) for the sampled lakes.

Runoff, mm							
percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	239	242	280	315	356	387	403
Norway	315	444	705	1159	1701	2457	3150
Sweden	101	198	299	300	347	599	945
Denmark	113	185	247	284	378	785	3760
Russian Kola	315	315	350	381	412	507	633
Scotland and Wales	658	828	1124	1414	1726	2173	2570

References:

Finland: Hyvärinen *et al.*, 1995,

Sweden: SMHI, Vattenföring i Sverige, Svenskt vattenarkiv.

Norway: Norwegian Water and Energy Administration (NVE) (mean values for 1961-1990),

Denmark: unpubl. results (J.P.Jensen),

Kola: Murmansk Regional Department of Hydrometeorology,

Scotland and Wales: Institute of Hydrology, official data.

4.1.3 Precipitation chemistry

The chemistry of the precipitation is mainly a function of sea salt inputs and long-range transported air pollutants and/or local air pollutants.

Long-range transported air pollutants mainly have their sources from industrial emissions in Central Europe. In Northern Europe, the gradient in concentrations of S and N decreases from south to north. Sulphur concentrations in precipitation range from about 1.5 mg S·l⁻¹ in Scotland, Wales, Denmark and Southern Sweden to less than 0.2 mg S·l⁻¹ in the northern parts of Finland, Sweden and Norway (EMEP, 1993). The deposition pattern of S is somewhat different to this due to the large range in precipitation over the countries. Annual total deposition of sulphur varies from >1.0 g S·m⁻²·yr⁻¹ in Scotland, Wales and Denmark and in South-Western Norway and Sweden to <0.2 g S·m⁻²·yr⁻¹ in the northernmost part of the countries (EMEP, 1993). Due to local S-emissions from Cu-Ni smelters, one third of Russian Kola exceeds S-deposition values of 1.0 g S·m⁻²·yr⁻¹, and only remote areas in eastern parts of Kola receives <0.4 g S·m⁻²·yr⁻¹.

N-concentrations (NH₄-N+NO₃-N) range from 2 mg N·l⁻¹ in Scotland, Wales, Denmark and Southern Sweden to <0.1 mg N·l⁻¹ in the north (EMEP, 1993). Annual total deposition of nitrogen (NO₃-N + NH₄-N) range from 1.7 g N·m⁻²·yr⁻¹ in Denmark and Southern Sweden, 1.1 g N·m⁻²·yr⁻¹ in Scotland and Wales, 0.8 g N·m⁻²·yr⁻¹ in Southwestern Norway to <0.1 g N·m⁻²·yr⁻¹ in the northern-most parts of the Scandinavian countries and Russian Kola (EMEP, 1993).

Seasalt concentrations in precipitation are a function of distance from sea and precipitation amounts. In Norway, most of the seasalt aerosols are "washed out" of the air close to the coast in the areas with high precipitation. In Scotland and Wales the seasalt aerosols are transported further inland than in Norway and occasionally, sea-salt increases occur in all

Scottish lakes. In Denmark there is also high concentrations of sea-salts in the precipitation.

In areas located long distance from the sea, and with low precipitation, the seasalt content in precipitation is much lower.

In general the patterns in wet deposition of long-range transboundary air pollution (N and S) is roughly spatially correlated with the regional acidification situation in the lakes.

4.1.4 Soils

The source of the soil base cations in a catchment is weathering of minerals in the bedrock and the surficial deposits. Most of the weathering takes place in the surficial deposits. Characteristics of the deposits, such as thickness and grain size, largely determine the contact time between the water and the mineral material. Ion concentrations in runoff water generally increase with increasing retention time in the catchment.

Most of the surficial deposits in the study area were deposited during the deglaciation period from 13.000 to 8.500 years ago. As the ice disappeared, huge quantities of sediments were deposited. After deglaciation, the Precambrian shield was bare or with only a thin or discontinuous cover of surficial deposits (mostly till). This is the dominant soil type in large parts of Norway, Scotland and Wales. Thick deposits of till occur in Sweden, Finland, Russian Kola and northern parts of Denmark. The glacial deposits are derived from the underlying bedrock, and consequently consists of the same - mostly weathering resistant mineral material - as in the underlying bedrock.

Soils in forested areas contain more organic material than in non-forested areas. High content of organic materials are also found in the tundra areas in Russian Kola and in peatland areas in the other countries. These soil types generate high runoff of organic matter to the lakes resulting in high TOC-

levels and organic acidity, which again influence the pH of the lake.

Due to the isostatic uplift of Scandinavia after the last deglaciation, old marine deposits are found in many places in lowland areas, and this is an important soil type in most low level areas of Sweden and on the western coast of Finland and in South-eastern Norway.

4.1.5 Vegetation

The vegetation types in the Nordic region range from nemoral, to boreo-nemoral, boreal and alpine zone (Nordic Councils of Ministers, 1993). The nemoral vegetation zones are found in Denmark, the far south and west of Sweden and the southern coast of Norway. The nemoral zone consists mainly of deciduous forest.

About half of the total sampled area is forested. The non-forested parts are found in both uplands (mainly western areas of each country) and lowland areas in the north and along the coasts.

Trees utilize large amounts of deposited nitrogen, and forested areas have a much higher capacity to retain the incoming nitrogen than other vegetation or non-forested areas.

A distribution of the main landscape types in the countries are found in Table 4.2. This table clearly illustrates the difference in vegetation types between the countries, and these patterns also explain some of the differences seen in lake water chemistry between the countries.

Table 4.2 Distribution of the main landscape types in the countries

References: Finland: Aarne, 1994, Norway: Låg, 1981. Sweden: National Atlas for Sweden. Denmark: Danmarks Statistik, 1994 and unpubl. results (J.P.Jensen),

	Mountains	Forest	Mires	Heathers	Tundra	Water	Cultivated land	Built up areas
	%	%	%	%		%	%	%
Finland	<1	75	5			10	7	3
Norway	48	36	7			5	3	1
Sweden	8	65	8			9	8	2
Denmark		10	3			2	79	6
Russian Kola	21	39	26		33	8.1	0.1	0.1
Scotland	4	15	38 ¹	2		2	37 ²	2
Wales	3	16	31 ¹	2.5		0.4	44 ²	3

¹ Mainly heather/peat moorland

² Includes managed grasslands

4.2 Results

The presentation of the lake water chemistry results focus on the large scale differences in lake water chemistry between each country and sets this in context of regional patterns in geology, meteorology, precipitation chemistry, soils and vegetation which is outlined in the previous chapters.

The lake water chemistry is presented as point maps, percentile tables and cumulative frequency diagrams. Point maps for chloride (Cl) non-marine sulphate (SO₄*), non-marine base cations (BC*), alkalinity (Alk), pH, nitrate (NO₃⁻), organic carbon (TOC) and total phosphorous (total P) for all the sampled lakes are presented in Figures 4.1 to 4.8. Cumulative distribution curves for the same variables are shown in Figure 4.9 and 4.10. Percentiles (2.5, 10, 25, 50, 75, 90 and 97.5) for the same variables are presented in Table 4.6.

The effect of stratification on the selection of the lakes has been investigated by plotting cumulative frequencies for deweighted and non-deweighted values. The effect of the stratification is, for most constituents, very small. However, there are differences for "acidification" variables, i.e. ions that are long-range transported, such as sulphate and nitrate, and related variables such as pH and alkalinity. This is because Norway, Sweden and Finland selected a higher percentage of lakes in acidified areas in the southern parts of the countries, than in the less polluted areas further north. For variables such as TOC, total P, Cl and BC* there are very small differences in cumulative frequency diagrams and percentile calculations between the deweighted and non-deweighted data.

However, all data (except Denmark and Russian Karelia) are deweighted in order to provide unbiased descriptive statistics for each nation (sec. 3.3).

4.2.1 Sea salts

It is generally accepted that sea salts are transported with precipitation in proportions

similar to those in sea water, and that chloride in lake water is usually derived from sea salts in precipitation. Lakes in denser populated areas are affected by human impacts, including waste waters, fertilizers, farming and road de-icing, thus elevating the chloride content as well.

In most of the countries the highest values of chloride were found along the coastal zone (Figure 4.1).

Scotland, Wales and Denmark show significantly higher values of chloride than the other countries. The 50 percentile range for Scotland and Wales at 324 µeq/l was approximately tenfold greater than the 50 percentile values for the other countries (except for Denmark). All lakes in Scotland and Wales, are relatively close to the sea, and these areas are therefore continually affected by sea salts in precipitation.

The high chloride values in the Danish lakes are most probably due to sources in the catchments (human activities and seawater influenced deposits) and human activity, and not generally due to input from seasalts.

The chloride concentrations in Norwegian lakes show a steep gradient from very high levels close to the sea, to extremely low values within 100-200 km from the coast. This is due to the high precipitation amounts along the coast, as described in the previous chapter, which efficiently "washes" the sea salts out of the air, so that very little is transported inland.

From Southern Sweden through Finland and Russian Karelia there is a small decreasing gradient in chloride with high levels in most of Southern Sweden and a decrease in Finland from the coastal area in west and south to low values in east and north.

Chloride levels in the lakes in Russian Karelia continue this downwards trend to very low levels. In these areas the precipitation is low, and sea salts have been transported over long

distances. However, in Russian Kola there were high levels of chloride along the coast and decreasing values towards central and southwestern regions.

Areas in Southern Sweden which lie below the highest coast line after the last deglaciation are influenced by sea water. Lakes in contact with marine deposits from this time can contain water with high concentrations of chloride and sulphate. This is also the case for lowland areas along the coast in Southern Norway and Western Finland. The altitude of the highest coast line after the last deglaciation varies from about 100 to 250 m above the present sea level.

4.2.2 Base cations and alkalinity

Non-marine base cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and hydrogencarbonate (HCO_3^-) are derived principally from weathering reactions and ion-exchange processes in the catchments. Bedrock and soils are thus the main source of these ions in runoff water. Soil thickness and hydrological flow path are important factors in determining base cation fluxes. Weathering processes release equal amounts of base cations and hydrogen carbonate (alkalinity).

The lowest concentrations of non-marine base cations (Figure 4.2) are found in Southern and Western Norway, in the mountainous areas of Sweden bordering Norway and in the northern part of Russian Kola. Higher concentrations of non-marine base cations are found in Southern Sweden, and in scattered areas in Finland and the northern parts of Norway and Sweden (Figure 4.2). Lakes in Scotland, Wales and Denmark have the highest concentrations of base cations (Table 4.6).

The Danish lake chemistry differs in most cases from lakes in the other countries. The concentrations of all solutes was very high. This reflects high contribution from weathering but also a greater thickness of surficial material.

The precipitation amount is also an important factor for determining non-marine base cation concentrations and alkalinity. In areas with the same type of bedrock geology, i.e. which have the same weathering rates, there are lower concentrations in the high precipitation areas due to dilution. This is evident at sites in Russian Kola and northernmost Norway, where there is an increasing gradient in non-marine base cation and alkalinity from the coast and towards south, with decreasing precipitation.

The influence of acidic deposition on lake runoff water is mainly a function of the acidifying potential of sulphur and nitrogen deposition and the geologic and hydrologic characteristics of the catchment. When this potential exceeds the ability of the catchment to produce alkalinity, the lake water will lose all its alkalinity and become "acidic". Catchments with thin soils and bedrock with low weathering capacity such as gneisses and granitic gneisses normally have low acid neutralizing capacity. The southern parts of Norway and Sweden have the greatest proportion of lakes which have lost their alkalinity (Figure 4.3). The same areas also have very low concentrations of non-marine base cations.

The sensitivity of a lake, with respect to acidification, can roughly be evaluated from the non-marine base cation and alkalinity levels. An alkalinity value (or more exactly acid neutralizing capacity - ANC) of $20 \mu\text{eq}\cdot\text{l}^{-1}$ can be chosen as a reference value for very sensitive lakes (Henriksen *et al.*, 1990). 40 percent of lakes in Wales and 37 percent of the lakes in Norway had an alkalinity less than $20 \mu\text{eq}\cdot\text{l}^{-1}$. In Sweden and Russian Kola, the percentages were 14 and 16, respectively. The lowest percentage of such lakes was found in Finland (9 percent) and in Scotland (10 percent). In Denmark, there were three sampled lakes with alkalinity $< 20 \mu\text{eq}\cdot\text{l}^{-1}$ (Table 4.3).

Table 4.3 Percent and numbers of lakes with alkalinity < 20 $\mu\text{eq}\cdot\text{l}^{-1}$

	% lakes with alkalinity < 20 $\mu\text{eq}\cdot\text{l}^{-1}$	total number of lakes with alkalinity < 20 $\mu\text{eq}\cdot\text{l}^{-1}$
Finland	9.3	2,744
Norway	39.3	15,266
Sweden	13.5	8,135
Denmark ¹	15.0	106
Russian Kola	19.2	3,016
Scotland and Wales	33.0	1,751

¹These values are based on very few non-statistical selected lakes, and is therefore not reliable.

4.2.3 Non-marine sulphate

Sulphuric acid in the deposition is considered to be the major driving force leading to acidification of surface waters. Sulphate (SO_4^{2-}) is in general a "mobile anion", which means that nearly all of the sulphate in deposition is transported through the catchment. There is little or no net storage of sulphate in the catchment (with the exception of peatlands). Therefore, as sulphate moves through the catchment, equivalent concentrations of cations are also transported. These cations are mainly calcium (Ca^{2+}), magnesium (Mg^{2+}), H^+ and aluminium (Al^{3+}).

High non-marine sulphate (SO_4^*) lakes (Figure 4.4) are found in Wales and southern Scotland, Southern and Eastern Norway, Southern Sweden and Finland, and some areas in Russian Kola. The pattern of frequency distribution of non-marine sulphate concentrations is relatively similar for all countries with Norway showing the lowest 50 percentile value of 26 $\mu\text{eq}\cdot\text{l}^{-1}$ and Finland showing the highest value of 57 $\mu\text{eq}\cdot\text{l}^{-1}$. In Sweden and Finland, concentrations increase in a north-south direction. However, in Russian Kola, lakes with high values are centered around large point sources of SO_2 emissions. In Norway and Scotland the gradient appears to be a more west to east direction which reflects the deposition and precipitation patterns. Exceptionally low

values of non-marine sulphate were recorded in Scotland with occasional "negative" values (2 lakes). This appears to be due to the ability of the sea-salt impacted soils to adsorb both marine and anthropogenic derived sulphate, thus underestimating non-marine concentrations (Anderson *et al.*, 1996).

Some lakes in Denmark also have "negative" non-marine sulphate concentrations, largely due to geological inputs of chloride from "fossile" sodium chloride. The chloride correction method, which is used to calculate the non-marine components of the ions, assume however, that all chloride is derived from sea salts.

The geographical distribution of sulphate concentrations do therefore not directly reflect the acidification status in each country due to large differences in runoff and base cation levels.

4.2.4 pH

Most oligotrophic lakes not influenced by human activities will have a pH above 6. Such lakes are dominated by hydrogencarbonate ions. pH values below 6 in unpolluted lakes can be caused by organic anions (humic acids), or an exceptionally dilute water quality. Acid rain can acidify lake water to $\text{pH} < 6$ and in such lakes strong acid anions (sulphate + nitrate) will make up an increasing contribution to the total anion concentration. When pH falls below 5, the water is either dominated by acid anions, or organic anions or a mixture of both.

The lowest pH values (fig 4.5) caused by acidic deposition were found in Southern and Western Norway and in South-western Sweden. There were also some low pH lakes scattered throughout Sweden, Finland, Scotland and the eastern parts of Russian Kola, which were influenced by both acidic deposition and organic acids, while low pH sites in the northern areas of each country were usually associated solely with organic acidity. Very high pH lakes were found scattered in regions in Southern, Eastern and

Central Sweden and in the mountains along the border of Norway, and in Denmark. These lakes are associated with high input of base cations and bicarbonate through weathering in the catchment.

In general, lakes dominated by organic acidity have been "acidic" for many centuries while lakes with high concentration of non-marine sulphate and nitrate have recently been acidified by antropogenic pollution, but at some times in the past (< 100 years ago) have probably been non-acidic with hydrocarbonate as the major anion.

The number and percentage of lakes with pH <5 and <5.5 in each country/region are shown in Table 4.4.

4.2.5 Nitrate

Acid precipitation contains high concentrations of nitrate and ammonium as well as sulphate. Most deposited N is taken up by vegetation and in soils. Nitrate concentrations in runoff waters are therefore low in areas not impacted by human activities, such as agriculture. If the deposition of nitrogen exceeds the ability of the catchment to assimilate it, then excess N will usually leach

as nitrate and acidify the lake water similar to sulphate.

The highest nitrate concentrations (Figure 4.6) were found in the areas with highest N-deposition such as Scotland and Wales, Denmark, Southern and Western Norway, Southern Sweden and Southern Finland. Low concentrations were found in the northern parts of the Scandinavia, including Russian Kola. The distribution of nitrate varies between countries ranging from a median value of $0.1 \mu\text{eq}\cdot\text{l}^{-1}$ ($1 \mu\text{g N}\cdot\text{l}^{-1}$) in Russian Kola to $6.3 \mu\text{eq}\cdot\text{l}^{-1}$ ($88 \mu\text{g N}\cdot\text{l}^{-1}$) for Scotland and Wales and $36.8 \mu\text{eq}\cdot\text{l}^{-1}$ ($515 \mu\text{g N}\cdot\text{l}^{-1}$) in Denmark.

In the remote upland sites of Scotland and Wales, the higher values appear to reflect significant atmospheric inputs of N; however, in lowland areas agricultural activities dominate. Apart from Scotland and Wales, nitrate concentrations decrease from south to north and reflects both decreasing N-deposition and land management practices.

In Russian Kola, unlike the sulphate pattern, point sources of N-emissions are few, resulting in extremely low nitrate values.

Table 4.4 Number of low-pH lakes in the countries.

	% lakes with pH < 5	total number of lakes with pH < 5	% lakes with pH < 5.5	total number of lakes with pH < 5.5
Finland	0.9	265	7.0	2,066
Norway	8.3	3,224	20.1	7,808
Sweden	3.6	2,169	7.1	4,278
Denmark ¹	5.0	35	5.0	35
Russian Kola	12.6	1,980	18.2	2,859
Scotland and Wales	7.4	393	20.7	1099

¹These values are based on very few non-statistical selected lakes, and is therefore not reliable.

4.2.6 Organic carbon (TOC)

In areas with organic, peaty soils and bogs, runoff waters usually contain humic compounds giving the water a characteristic brown colour. Anionic contributions of these humic compounds can be inferred from concentrations of organic carbon (TOC). When TOC concentrations exceed 2-3 mg/l, the water will have a yellow colour. As the TOC increases in concentration, the colour changes from yellow to dark brown and the potential contribution of organic anions to acidity also increases.

The pattern of TOC (fig 4.7) show a clear increasing gradient from west to east reflecting changes from mountainous non-forested areas with thin soils and high runoff in Norway to lowland areas with forest, thicker soils, lower runoff and more peatlands in Finland. In the same way there is also a slight increasing gradient from north towards south.

The TOC levels in lakes in Scotland and Wales show the same distributions and patterns as lakes in Sweden and Finland, thus increasing from west to east. Lakes in Norway have the lowest values of TOC.

The tundra area in Russian Kola shows somewhat higher TOC levels than lakes located at the same latitude in Finland and Norway, and may be explained by the large areas of wetlands in Russian Kola.

Lakes in Denmark also have high TOC concentrations due to the high biological productivity in the Danish lakes.

4.2.7 Phosphorus

Natural sources of phosphorus are weathering and breakdown of organic matter and from precipitation. In areas not influenced by human activities, total P concentrations are usually low ($< 10 \mu\text{g P}\cdot\text{l}^{-1}$). Different types of human activities, such as agriculture, will increase total P concentrations in lakes.

The pattern of total P in the lakes exhibits a similar picture to that of TOC with some main exceptions. Scotland, Wales and eastern part of Russian Kola which had generally high TOC levels in the lakes had low total P.

Scotland and Wales also shows a gradient of increasing total P from west to east reflecting the higher proportion of agricultural activity in the east. A similar pattern was found in Finnish lakes where the highest total P concentrations were found mostly in lowland (agricultural) areas of Southern and Western Finland. The high total P levels in scattered areas of Finland may be explained by the extensive ditching and fertilizing of Finnish peatlands.

There are two main types of lakes with high concentrations of total P. Firstly natural humic lakes with high TOC and organic N and P, and secondly lakes with high inorganic P in areas with agricultural activity. The first type can be classified as dystrophic lakes, while the second type can be classified as eutrophic lakes. Lakes are classified as oligotrophic ($< 10 \mu\text{g P}\cdot\text{l}^{-1}$), mesotrophic, ($10\text{-}35 \mu\text{g P}\cdot\text{l}^{-1}$) and eutrophic ($> 35 \mu\text{g P}\cdot\text{l}^{-1}$) measured as total P (Table 4.5) (OECD, 1982). The largest percentage of eutrophic lakes, with the exception of Denmark, was found for Finland and Wales. As can be expected, the lowest relative number of such lakes was observed in Norway and Russian Kola.

The relationship between nitrogen and phosphorus (N:P) in lakes give an indication of which of these two nutrients is growth limiting for phytoplankton. The normal ratio between these two elements in algae is about 7. N:P ratios < 12 indicate N-limitation, while ratios > 12 indicate P-limitation. The N:P values (Table 4.5) suggest that most lakes in Northern Europe (except for Denmark) are P-limited ($> 95\%$). However, this describes the situation during autumn circulation when the phytoplankton production is low. Analysis of data from Danish lakes have shown that also Danish lakes in general is P-limited (Kristensen *et al.*, 1990).

Table 4.5 Number and percentage of lakes with different concentrations of total P.

	Oligotrophic <10 µg P.l ⁻¹		Mesotrophic 10-35 µg P.l ⁻¹		Eutrophic >35 µg P.l ⁻¹		N:P	
	numbers of lakes	%	numbers of lakes	%	numbers of lakes	%	median value for N:P	% lakes with N:P < 12
Finland	11,363	38.5	15,495	52.5	2,656	9.0	31	2.7
Norway	36,242	92.2	2,253	6.9	349	0.9	44	2.2
Sweden	35,815	55.8	15,845	40.8	1,320	3.4	39	2.1
Denmark [†]	38	5.3	111	15.7	560	79.0	17	21.0
Russian Kola	11,768	74.9	3,079	19.6	864	5.5	30	5.5
Scotland and Wales	3,907	73.6	945	17.8	457	8.6	86	5.5

[†]These values are based on very few non-statistical selected lakes, and is therefore not reliable.

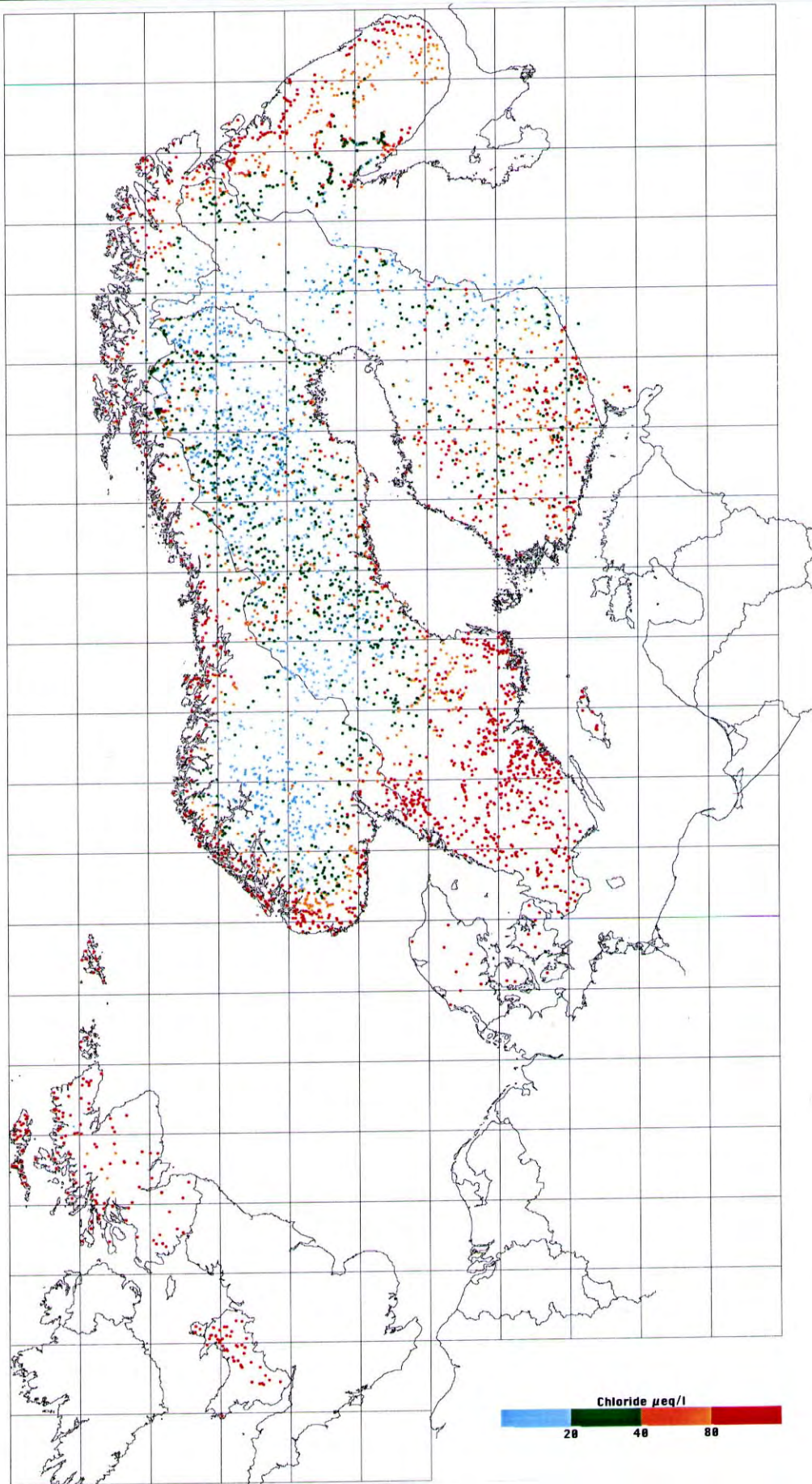


Figure 4.1 Chloride ($\mu\text{eq}\cdot\text{l}^{-1}$) in the investigated lakes.

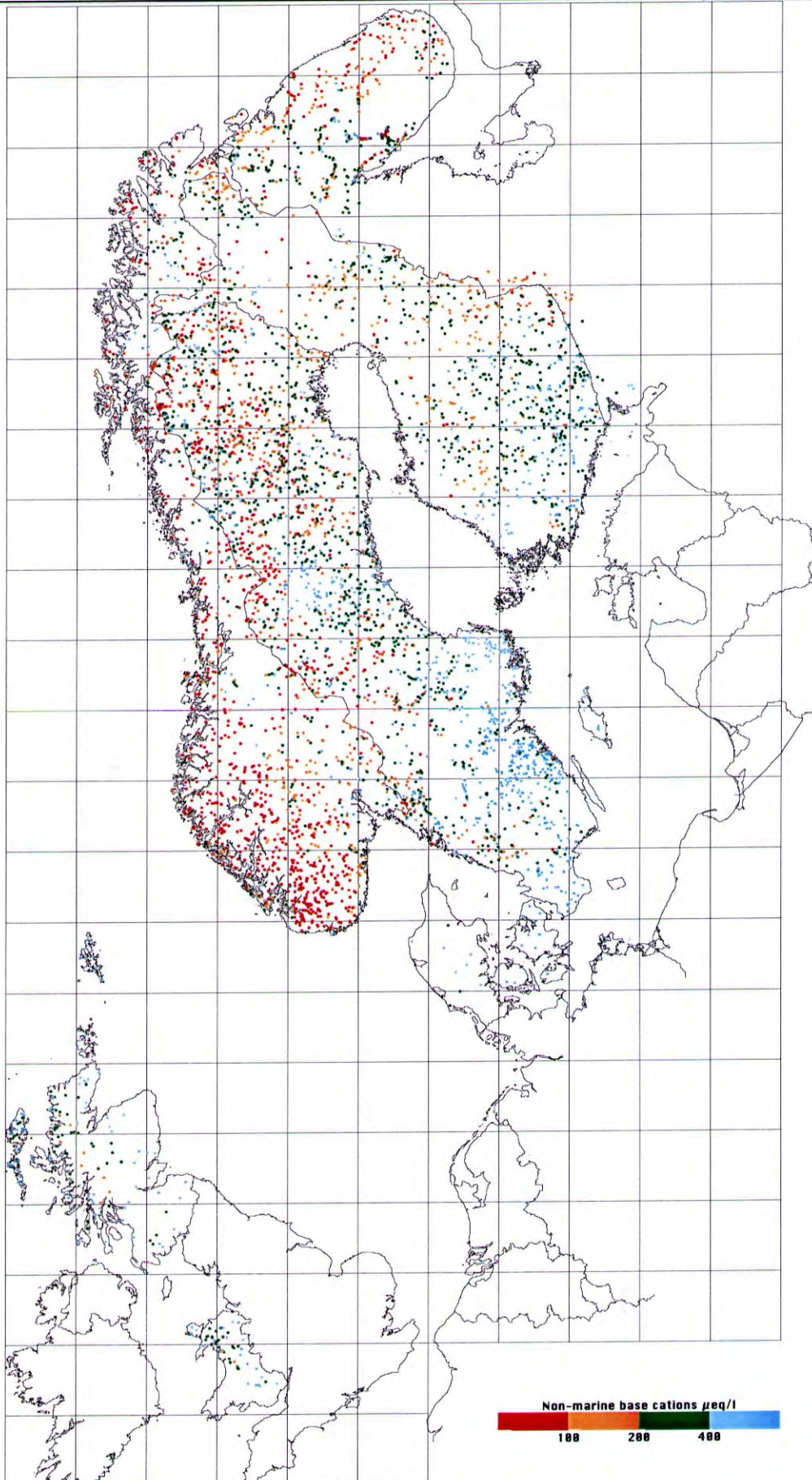


Figure 4.2 Non-marine base cations ($\mu\text{eq}\cdot\text{l}^{-1}$) in the investigated lakes.

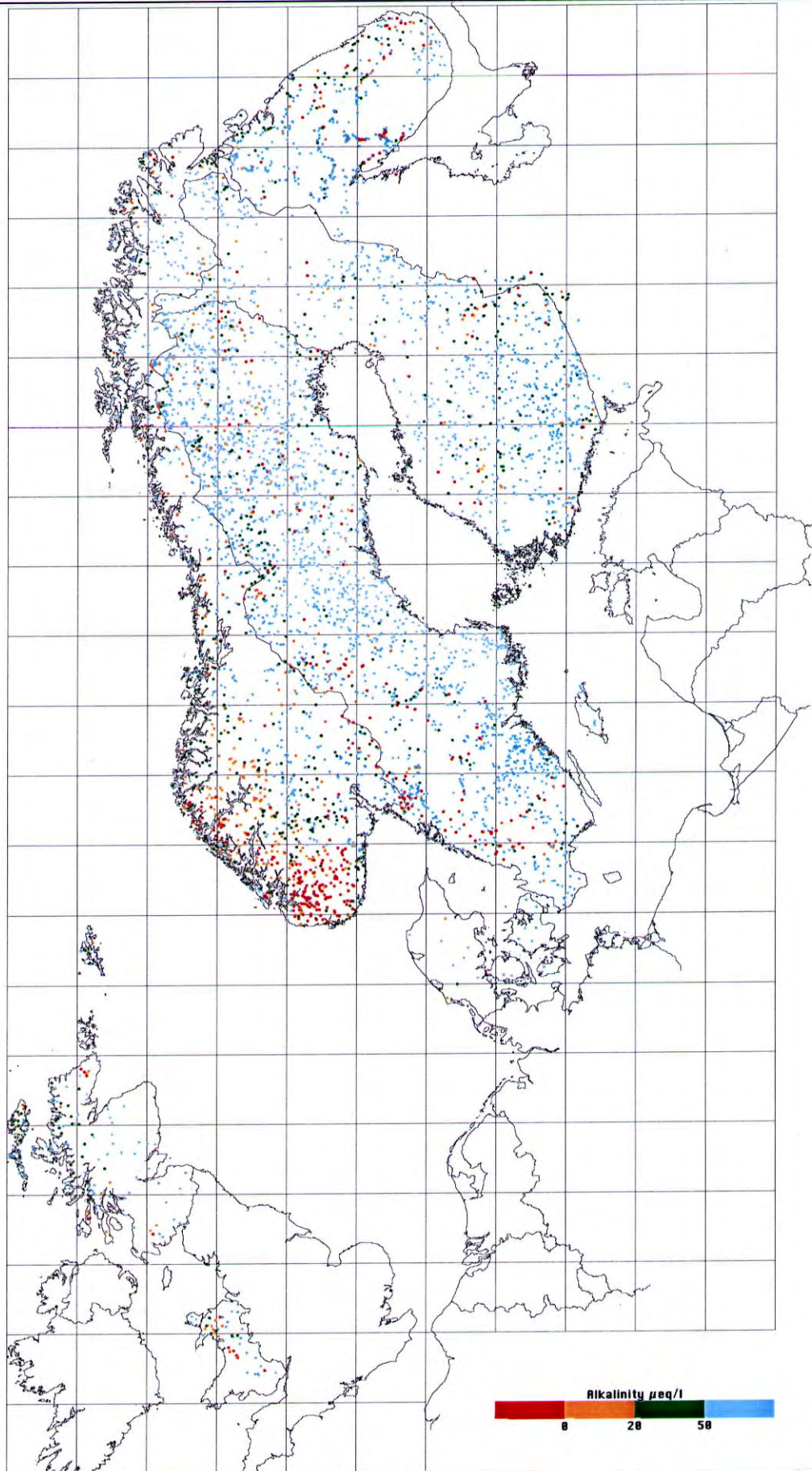


Figure 4.3 Alkalinity ($\mu\text{eq}\cdot\text{l}^{-1}$) in the investigated lakes.

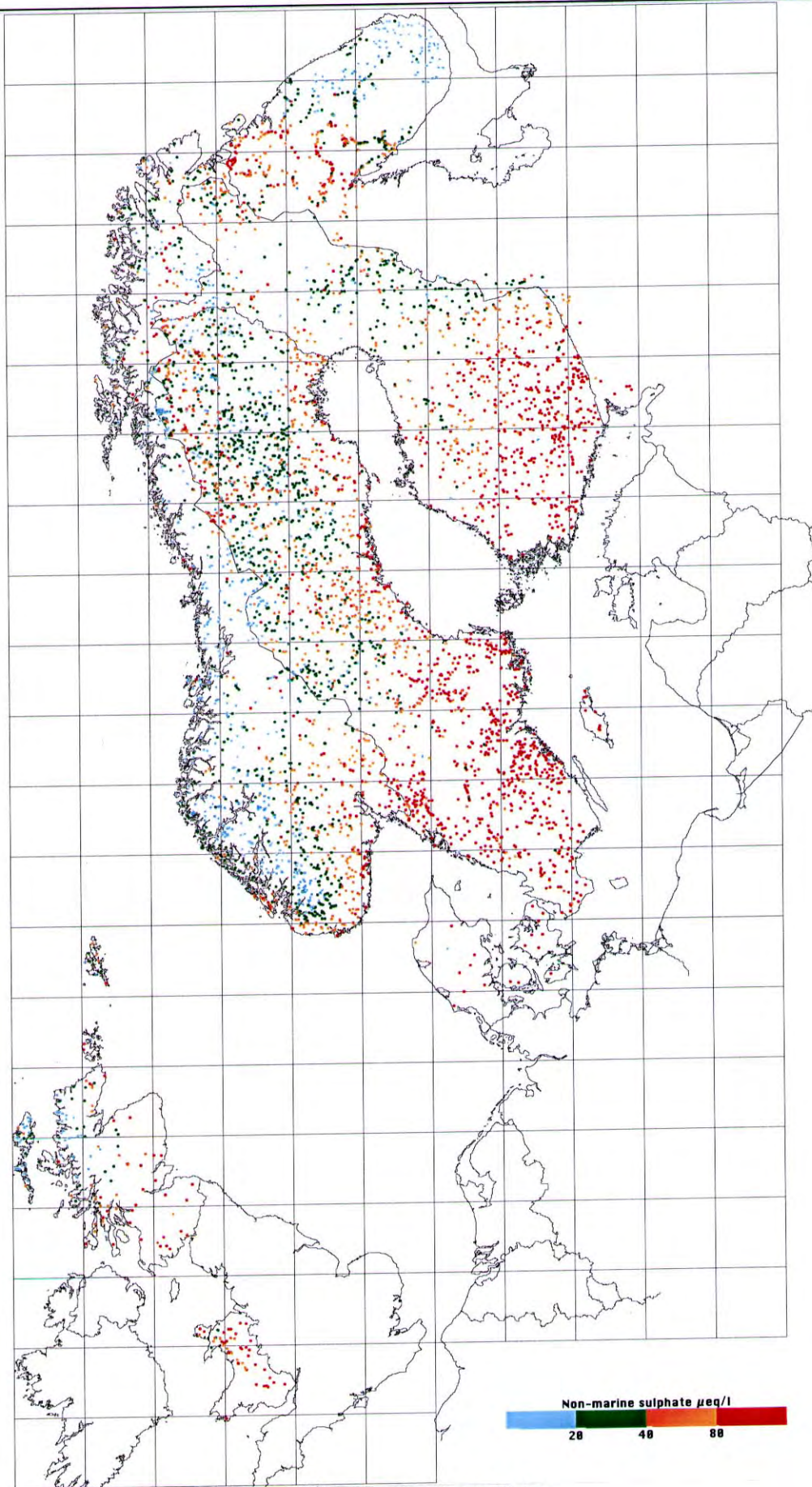


Figure 4.4 Non-marine sulphate ($\mu\text{eq}\cdot\text{l}^{-1}$) in the investigated lakes.

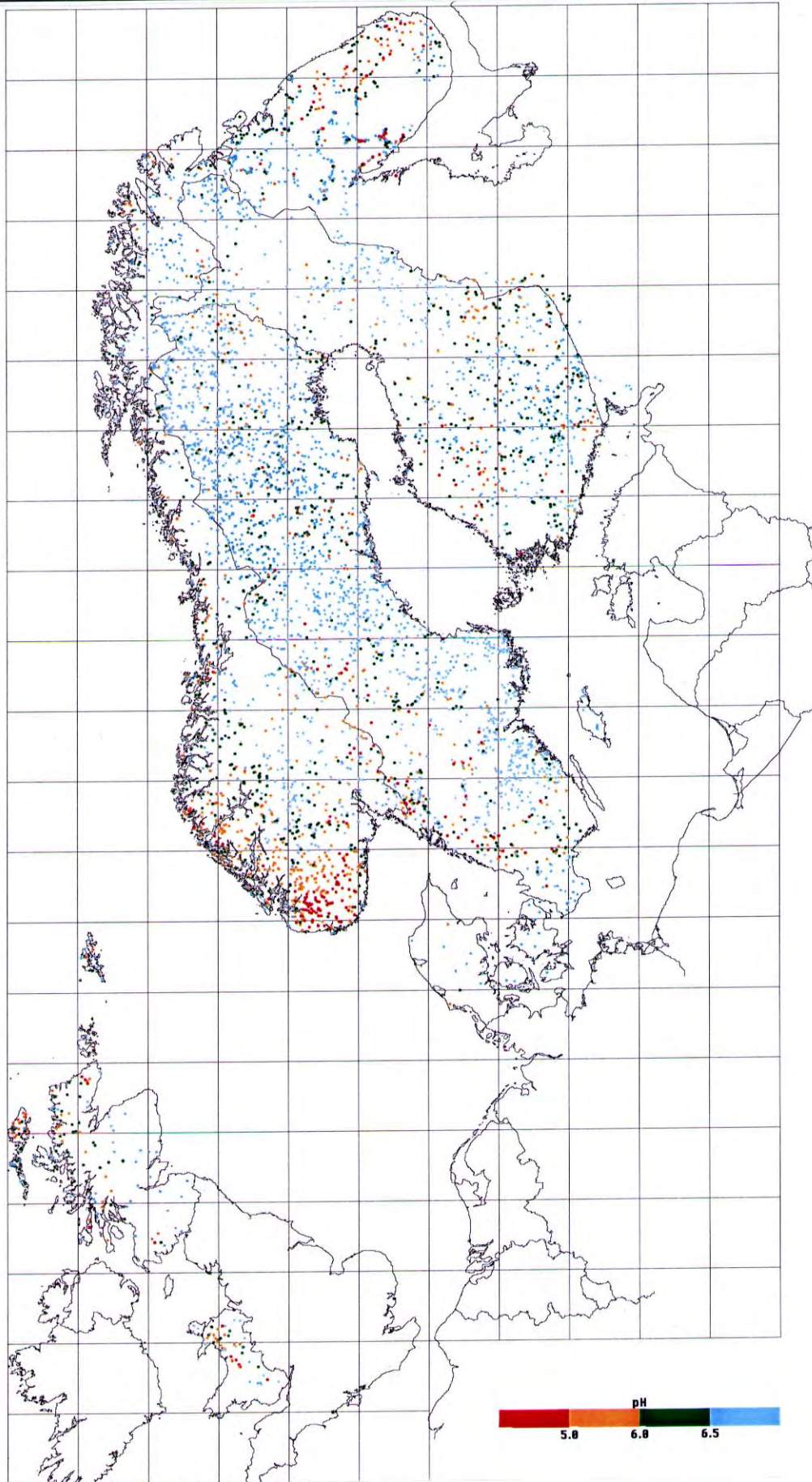


Figure 4.5 pH in the investigated lakes.

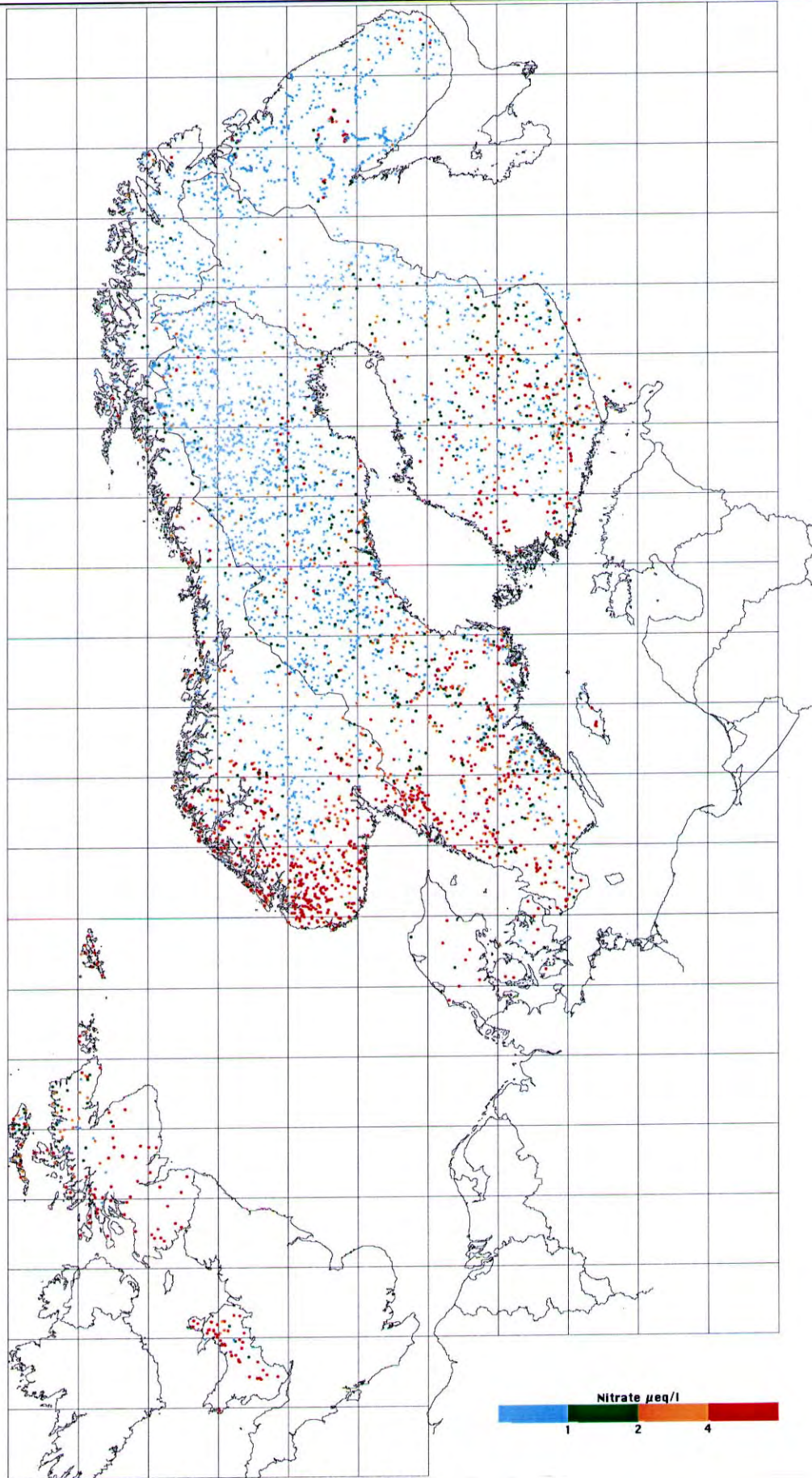


Figure 4.6 Nitrate ($\mu\text{eq}\cdot\text{l}^{-1}$) in the investigated lakes.

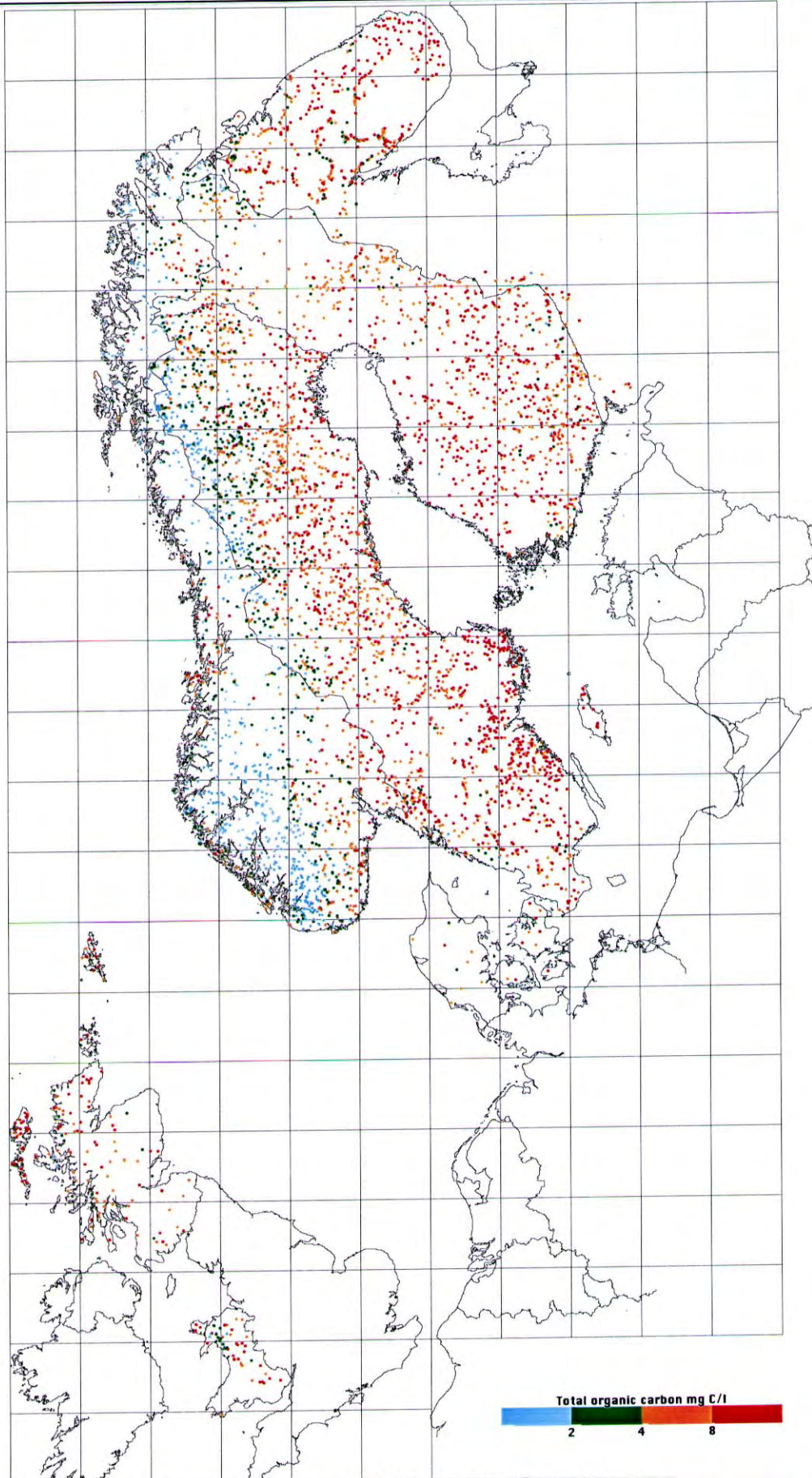


Figure 4.7 Total organic carbon (TOC) (mg C l^{-1}) in the investigated lakes.

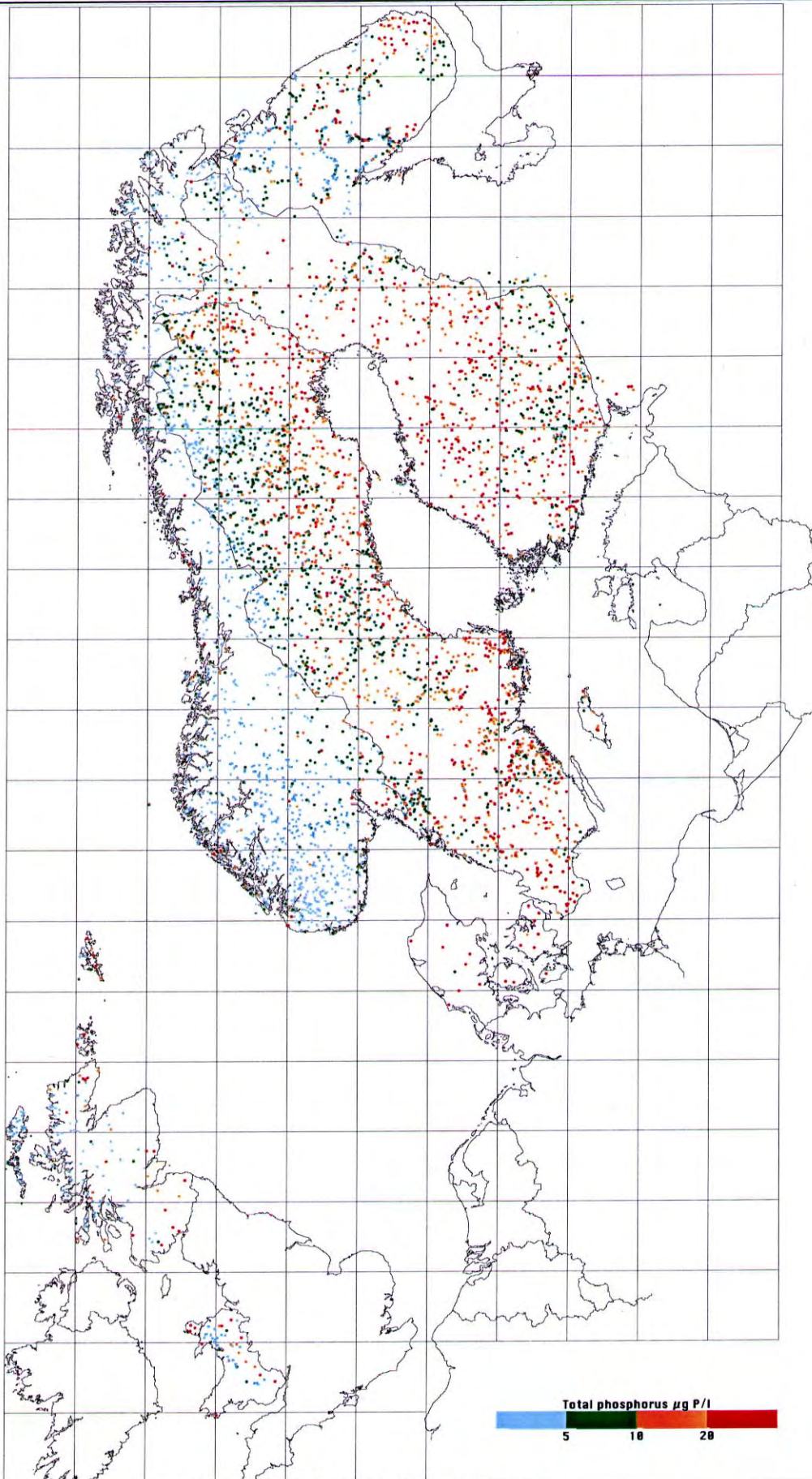


Figure 4.8 Phosphorus (total P) ($\mu\text{g P}\cdot\text{l}^{-1}$) in the investigated lakes.

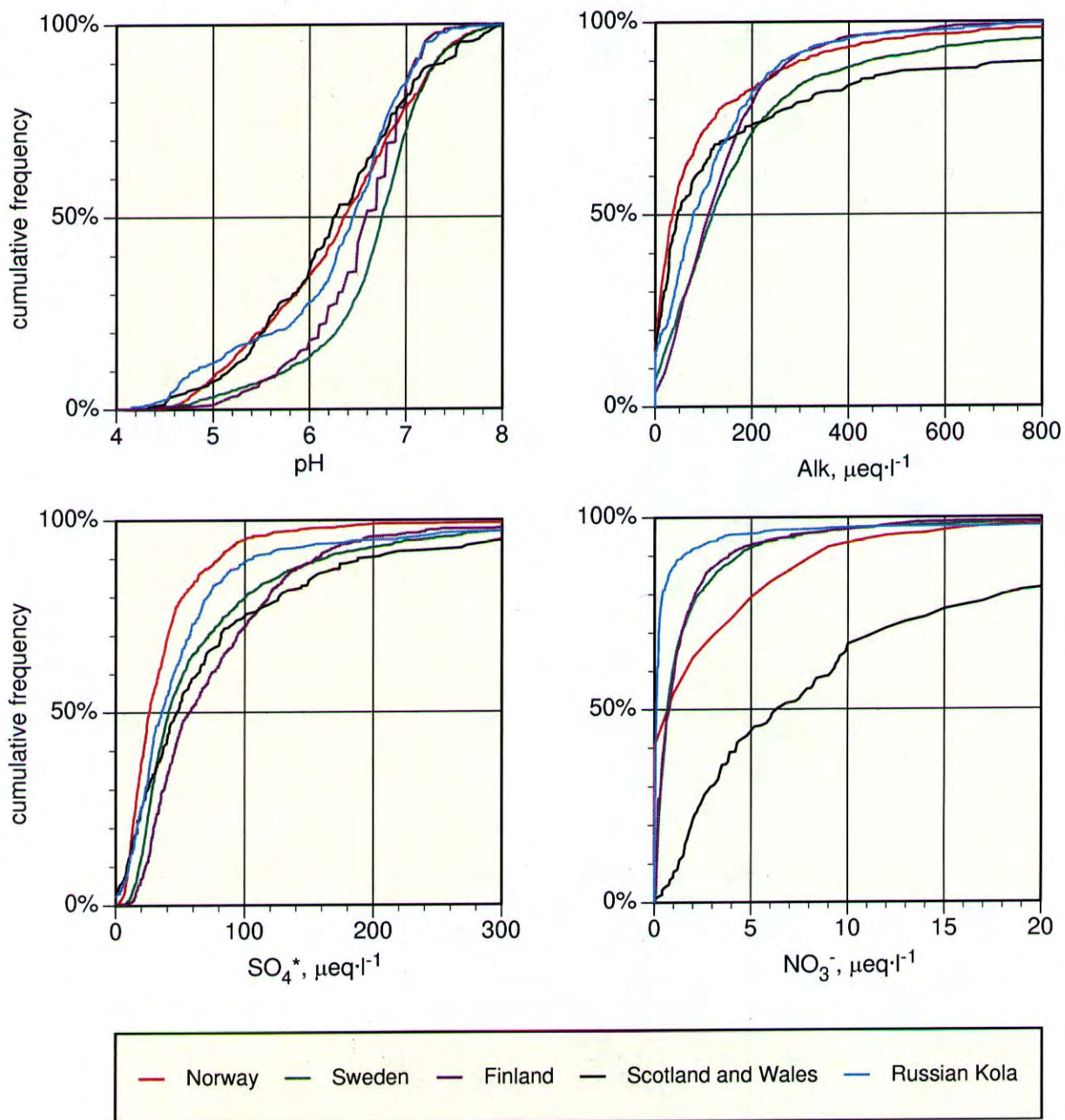


Figure 4.9 Cumulative frequency diagrams for pH, alkalinity, non-marine sulphate (SO_4^*) and nitrate (NO_3^-).

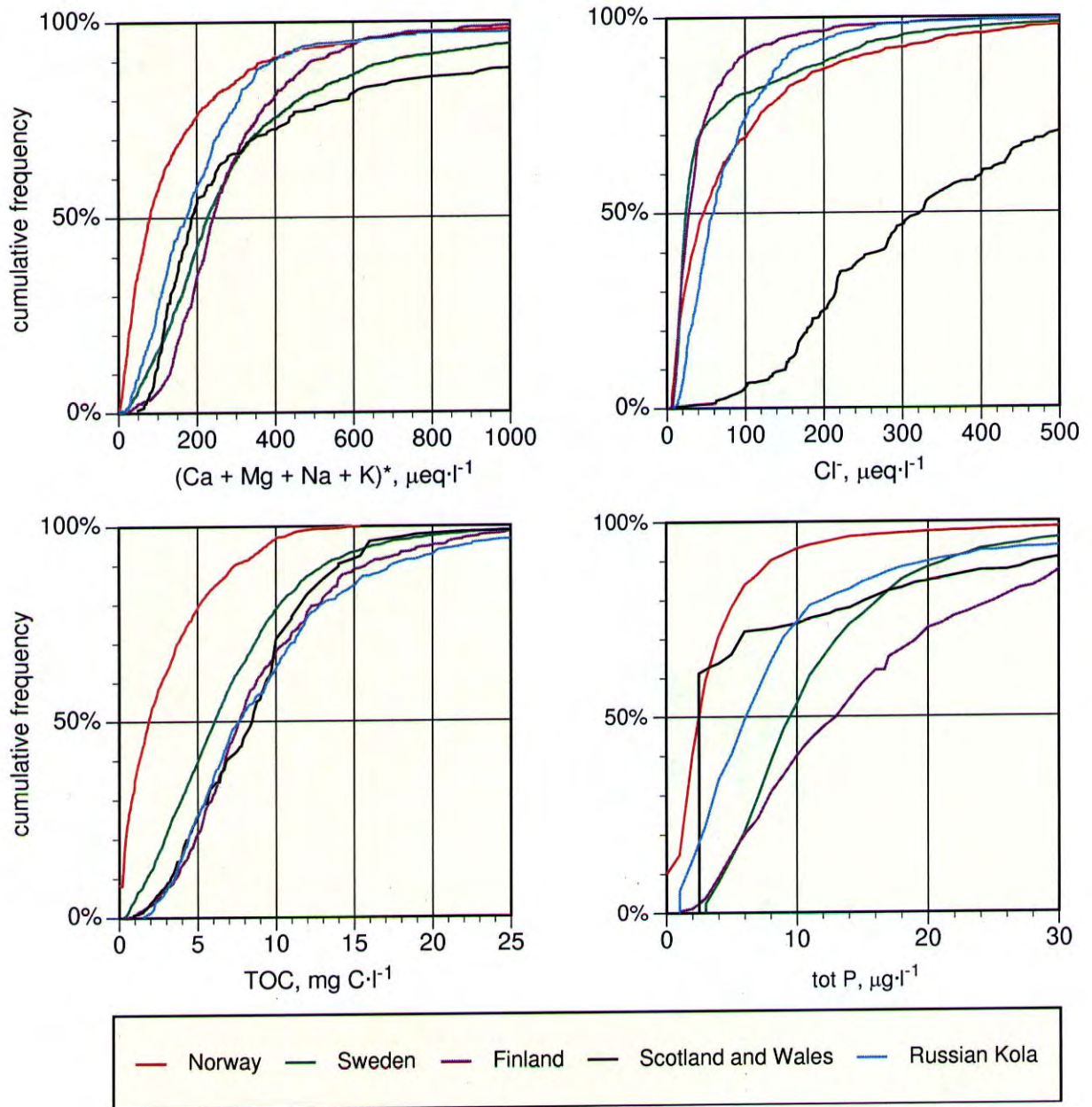


Figure 4.10 Cumulative frequency diagrams for non-marine base cations (Ca+Mg+Na+K)*, chloride (Cl⁻), total organic carbon (TOC) and phosphorous (total P).

Table 4.6 Percentiles for a selection of the variables analysed.

Cl, $\mu\text{eq}\cdot\text{l}^{-1}$							
percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	8	11	16	28	50	93	213
Norway	6	10	18	47	118	243	459
Sweden	8	12	17	24	62	217	401
Denmark	549	607	764	1086	1732	2273	5861
Russian Kola	15	22	36	60	102	154	265
Russian Karelia	6	8	11	11	34	116	133
Scotland and Wales	73	151	200	324	566	982	2484

Non-marine base cations (Ca + Mg + Na + K)*, $\mu\text{eq}\cdot\text{l}^{-1}$							
percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	49	130	173	240	352	490	753
Norway	5	14	33	79	193	367	846
Sweden	30	71	138	226	392	701	1504
Denmark	230	271	1722	3096	4537	5448	6741
Russian Kola	28	51	95	172	277	391	1019
Russian Karelia	46	123	135	157	294	522	721
Scotland and Wales	70	92	122	187	437	1553	3001

Alkalinity $\mu\text{eq}\cdot\text{l}^{-1}$							
percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	-6	22	53	111	181	278	521
Norway	<0	<0	8	36	123	298	667
Sweden	-23	10	49	119	223	446	1081
Denmark	5	25	1508	2222	2897	3716	3833
Russian Kola	<0	<0	32	79	170	266	558
Russian Karelia	-10	20	40	60	105	300	570
Scotland and Wales	--33	-4	13	46	236	978	2313

SO₄²⁻, $\mu\text{eq}\cdot\text{l}^{-1}$							
percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	15	23	34	57	106	155	250
Norway	6	10	15	26	45	80	142
Sweden	12	18	26	41	85	162	317
Denmark	-133	192	407	614	956	1604	2564
Russian Kola	1	10	20	36	65	106	352
Russian Karelia	26	32	34	48	103	138	180
Scotland and Wales	1	9	20	47	100	188	354

pH							
percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	5.12	5.68	6.19	6.58	6.90	7.08	7.29
Norway	4.72	5.07	5.67	6.36	6.92	7.30	7.66
Sweden	4.86	5.76	6.40	6.75	7.03	7.30	7.68
Denmark	5.42	5.98	7.64	7.87	8.05	8.11	8.24
Russian Kola	4.49	4.80	5.92	6.45	6.79	7.11	7.34
Russian Karelia	5.30	5.90	6.10	6.40	6.60	7.00	7.20
Scotland and Wales	4.52	5.16	5.62	6.25	6.76	7.39	7.81

Table 4.6 cont.

NO₃, µeq·l⁻¹

percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	0	0.1	0.2	0.8	1.7	3.8	11.2
Norway	<1	<1	<1	0.7	4.2	8.2	16.4
Sweden	0.1	0.1	0.3	0.7	1.8	4.4	11.5
Denmark	0.7	1.5	7.8	36.8	126.3	153.7	351.6
Russian Kola	0	0	0	0.1	0.3	1.5	10.8
Russian Karelia	0.6	0.7	0.7	1.1	4.4	12.9	15.1
Scotland and Wales	0.4	1.3	2.3	6.3	14.5	30.3	180.9

tot-N, µg N·l⁻¹

percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	119	191	281	401	556	746	1000
Norway	36	51	80	138	240	368	568
Sweden	118	179	270	402	644	953	1423
Denmark	429	639	709	1310	2549	3076	3622
Russian Kola	66	94	135	201	299	478	848
Russian Karelia	91	244	251	303	477	782	1300
Scotland and Wales	148	181	245	322	566	895	2777

TOC, mg C·l⁻¹

percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	1.72	3.57	5.36	7.64	11.56	15.74	22.90
Norway	< 0.2	0.22	0.58	1.87	4.38	7.33	10.54
Sweden	0.69	1.76	3.35	6.07	9.33	13.03	19.73
Denmark	3.02	4.04	4.80	7.40	10.95	17.16	19.04
Russian Kola	2.22	3.51	4.86	7.62	11.82	17.36	26.92
Russian Karelia	1.20	1.20	6.10	7.50	9.90	12.20	15.60
Scotland and Wales	1.78	3.28	4.68	8.47	10.75	14.00	18.24

tot P, µg·l⁻¹

percentiles	2.5 %	10 %	25 %	50 %	75 %	90 %	97.5 %
Finland	2	4	7	13	22	33	59
Norway	< 1	< 1	1	2	5	8	19
Sweden	3	4	6	9	14	21	37
Denmark	10	27	41	75	170	251	471
Russian Kola	1	2	3	6	10	20	49
Russian Karelia	4	5	9	10	18	35	60
Scotland and Wales	3	3	3	3	10.8	29	86

5. Critical loads and critical load exceedances

5.1 Background

Critical loads have been widely accepted as a basis for control strategies for regional air pollution. In order to gain more insight in the magnitude and spatial variation of critical loads, the UN/ECE Executive Body of the Convention on Long-Range Transboundary Air Pollution (LRTAP) has set up a Task Force on Mapping Critical Levels/Loads under the Working Group on Effects. The data from individual countries are collected, mapped and reported by the Coordination Center for Effects (CCE), located at the National Institute of Public Health and the Environment (RIVM) in Bilthoven, the Netherlands (Downing *et al.*, 1993, Posch *et al.*, 1995).

In the Lökeberg meeting document (Grennfelt and Törnelf, 1992) two models, one empirical and one process oriented, for calculating critical loads of acidifying deposition (both S and N) to surface waters, were presented. The first model, the Steady-State Water Chemistry (SSWC) model (UN/ECE, 1996), enables the calculation of critical loads of acidity and present exceedances of incoming total acidity (S+N) over the critical loads. The process-oriented First-Order Acidity Balance (FAB) model allows the simultaneous calculation of critical loads of acidifying N- and S-deposition and their exceedances (Posch *et al.*, 1997). The FAB model is based on the steady-state mass balance principle widely used in many models for computing critical loads for forest soils.

The SSWC-method (see Appendix A) includes both S and N acidity, in such a way that present N-leaching (N_{leach}) is considered in the calculation of critical load exceedance (present $\text{Ex}(\text{Ac})$). To do this, we must ensure that no anthropogenic sources of NO_3 other than long range transported nitrogen compounds are

included in the N_{leach} term. At present such a separation is not possible for the lake survey data. Therefore we have restricted the calculations to deal with critical loads of acidity and exceedance of sulphur acidity only.

The FAB-model can also be applied to the lake survey data, but this requires additional model input data for N, data that is not available at present. It will, however, be possible to work out acceptable estimates for the N input data when all background data for the lakes are available.

5.2 Critical loads for sulphur acidity in the lakes

We have applied the SSWC-method to the lake survey data and calculated the critical loads (CL) for sulphur acidity using the variable ANC limit ($\text{ANC}_{\text{limit}}$) for all lakes (Henriksen *et al.*, 1995). Percentiles and cumulative frequency distributions for the calculated CL are shown in Table 5.1 and figure 5.1.

Scotland, Wales and Denmark had very few lakes with low critical load values. Of the 19 analysed Danish lakes, there are only 2 that have $\text{CL} < 50 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, while in Scotland and Wales there are no lakes with such low values.

Lakes in Finland, Norway, Sweden, Russian Kola and Karelia all had a 50 percentile for critical load around $50 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. However, the frequency distributions were slightly different. Norway had both the highest proportion of low CL lakes ($< 50 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and high CL lakes ($> 100 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). Lakes in Finland showed low variability, with nearly 50% of the lakes with CL at $50 \pm 15 \text{ meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$.

Table 5.1 Percentiles for critical loads using the variable ANC_{limit} ($meq\cdot m^{-2}\cdot yr^{-1}$) and Norwegian background sulphate for all countries, except for Sweden where Swedish values are used (see Appendix A).

Percentile	2.5	10	25	50	75	90	97.5	n
Finland	15	32	46	63	86	117	192	873
Norway	7	15	28	56	115	271	736	1010
Sweden	9	21	39	61	107	215	552	3075
Denmark	1	30	352	780	1167	1409	1625	19
Russian Karelia	15	30	44	48	53	69	110	500
Russian Kola	7	17	36	57	86	126	273	29
Scotland/Wales	81	104	159	207	512	1540	2678	188

The similarity in CL values can look strange in comparison with the differences in BC^* between the countries. The median values for BC^* were twice as high in Russian Kola (191 meq/l) and Karelia (151 meq/l) than in Norway (79 meq/l), while values for Finland (240 meq/l), Sweden (226 meq/l) and Scotland and Wales (262 meq/l) were nearly three times higher than in Norway. However, the critical

load of acidity to freshwaters does not reflect the base cation concentrations, but rather their fluxes. As described in section 4.1.2, the runoff is much higher in Norway, Scotland and Wales than in the other countries, and therefore the CL-values become more similar than could be expected from the base cation concentrations.

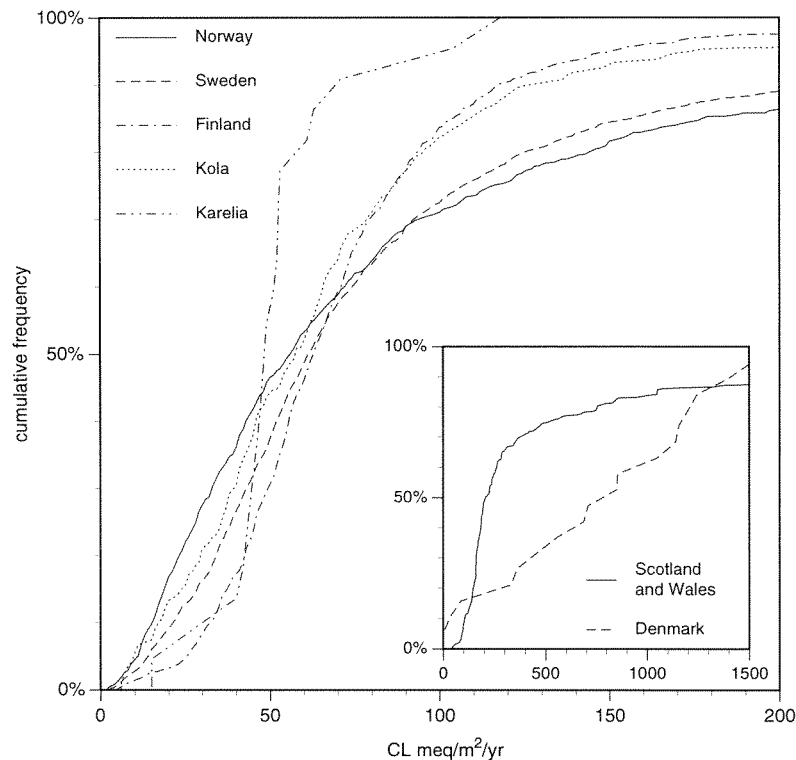


Figure 5.1 Frequency distributions of critical loads for lakes in the different countries.

5.3 Exceedance of critical loads

Critical load exceedances of sulphur acidity have been calculated for all the sampled lakes. Deposition values for each lake were either measured or modeled values provided by each country (Table 5.2).

The results show (Figure 5.2.) that the highest percentage (27%) of lakes (approximately 10,000 lakes) with exceedance of critical loads for S is found in Norway. Also, the lakes with highest exceedance values are found there. The reason is that the highest sulphur deposition in Scandinavia are found in Southern Norway ($>60 \text{ meq}\cdot\text{m}^2\cdot\text{yr}^{-1}$), where lakes with the lowest critical loads are located as well. Wales has a high proportion of exceeded lakes (24%) reflecting the high S deposition loads there. Russian Kola also has a high percentage of lakes with exceedance of critical load for S (17%) (approximately 3,500 lakes), largely because of the high S-emissions from industry in this area, while Finland, Sweden and Denmark all show that 9% of the lakes are exceeded (approximately 6000 Swedish lakes and 3000 Finnish lakes). The number for Denmark is not reliable, due to the low number of investigated lakes (19) and the non-statistical selection. Karelia show few lakes with exceedance, because in this area the

S-deposition is relatively low (ca. $30 \text{ meq}\cdot\text{m}^2\cdot\text{yr}^{-1}$). Since the Karelia survey included few (29) not statistically selected lakes, the number is uncertain. Scotland shows the lowest percentage of exceedance, about 1% of the total lake population, although this only represents two lakes in the survey. The percentage number of exceeded sites in this survey was much lower than that obtained from the survey used to produce the national critical load and exceedance maps for Scotland (Kreiser *et al.* 1995). However the latter study was based on a geographical selection, whereby the most sensitive lake in each 10km square was used. Also, the current statistical survey reflected the skewed distribution of lakes in Scotland where the majority of lakes are located in low deposition areas of the north west. In addition the statistical survey represented only 1.6% of the total lake population in Scotland compared to nearly 9% for the national geographical survey. The overall effect of these two different sampling strategies was that critical load values for this statistical survey were 60% higher than the geographical survey, thus helping to explain the differences between the calculated exceedances for each survey.

Table 5.2 Sources of sulphur deposition measurements used in the exceedance calculations.

Finland	S-deposition for 1990 are calculated with the DAIQURI-model, employing long-range and meso-scale transfer matrices from EMEP(MSC-W and the Finnish Meteorological Institute (Syri <i>et al.</i> , 1997)
Norway	Average yearly values for sulphur deposition for the 5-year period 1988-1992 (Tørseth and Pedersen 1994).
Sweden	Estimated deposition for 1994. (Data from Swedish Meteorological and Hydrological Institute).
Denmark	Deposition estimated by EMEP for 1992 in new EMEP-grids (50x50km) (The Norwegian Meteorological Institute).
Russian Karelia	Deposition estimated by EMEP for 1992 in new EMEP-grids (50x50km) (The Norwegian Meteorological Institute).
Russian Kola	Deposition estimated by EMEP for 1992 in new EMEP-grids (50x50km) (The Norwegian Meteorological Institute).
Scotland/Wales	Deposition data is based on 1989-1992 averages of wet and dry deposition from the UK rain network on a 20 km^2 basis. This is then enhanced to incorporate extent of forest cover, cloud deposition and elevation. (Critical Loads Advisory Group, 1997)

In total, this adds up to approximately 22.000 lakes in Northern Europe where critical loads for sulphur acidity is exceeded. Extensive liming in Sweden, however, lowers the number.

We have not considered the acidifying effects of N-deposition. If present N-leaching is taken

into account the number of exceeded lakes will increase, particularly for lakes in Scotland and Wales, which have much higher concentrations of nitrate than the other countries. Applying the FAB-model to the data, the number of exceeded lakes will increase further, as this model estimates the future potential N-leaching.

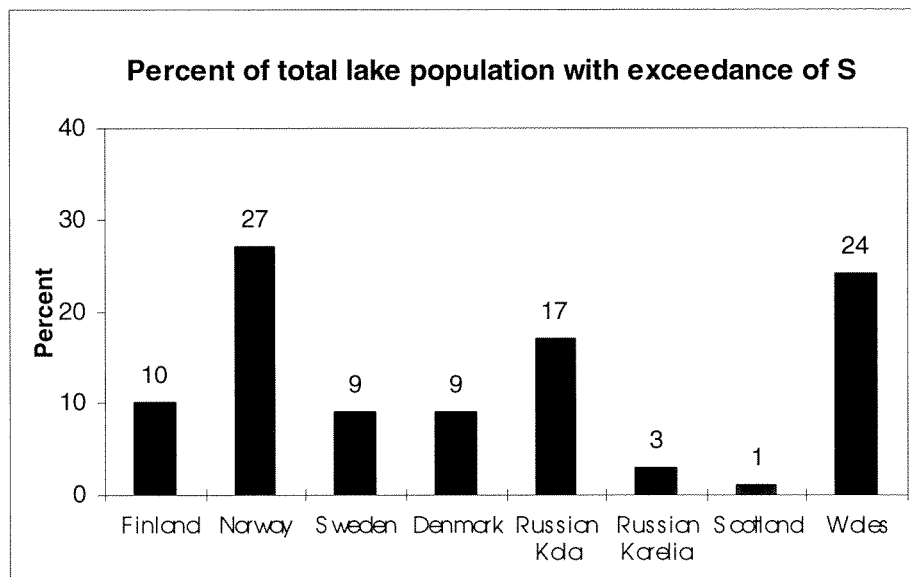


Figure 5.2 Percent of lakes in the different countries with exceedance of sulphur. The deposition data used in the calculations are shown in Table 5.2. The values for Denmark and Karelia are uncertain due to low number of investigated lakes.

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Appendix A.

The Steady-State Water Chemistry method

The Steady-State Water Chemistry (SSWC) method is particularly applicable to surface waters in areas where surface water is the most sensitive ecosystem. It assumes that almost all sulphate in runoff originates from sea salt spray and anthropogenic deposition. The critical load of a lake can be derived from present day water chemistry if weighted yearly mean values, or estimates thereof, are available. This method uses Acid Neutralization Capacity (ANC) (Reuss and Johnsson 1986) as the chemical criterion for sensitive indicator organisms in surface waters. ANC is defined as the difference between base cations (BC) and strong acid anions (AN):

$$[\text{ANC}] = [\text{BC}] - [\text{AN}] = [\text{HCO}_3^-] + [\text{A}^-] - [\text{H}^+] - [\text{Al}^{n+}] \quad (1)$$

where $[\text{HCO}_3^-]$ is the hydrogencarbonate concentration, $[\text{A}^-]$ is the concentration of organic anions, $[\text{H}^+]$ is the hydrogen ion concentration and $[\text{Al}^{n+}]$ is the sum of all positively-charged aluminium.

In order to estimate changes in surface water chemistry due to atmospheric deposition other than sea water it is necessary to subtract the ions that originate from sea salt spray. It is assumed that all chloride in the water comes from sea salt spray, and that all sea salt components are transported and deposited in the same ratio as is found in sea water. Sea-salt corrected values are marked with an asterisk (*) and calculated as:

$$\text{Expressed in } \mu\text{eq/l} \quad [\text{Ca}^*] = [\text{Ca}] - 0.037 \cdot [\text{Cl}] \quad (2)$$

$$[\text{Mg}^*] = [\text{Mg}] - 0.198 \cdot [\text{Cl}] \quad (3)$$

$$[\text{Na}^*] = [\text{Na}] - 0.858 \cdot [\text{Cl}] \quad (4)$$

$$[\text{K}^*] = [\text{K}] - 0.018 \cdot [\text{Cl}] \quad (5)$$

$$[\text{SO}_4^*] = [\text{SO}_4] - 0.103 \cdot [\text{Cl}] \quad (6)$$

Approach

The critical load for a lake is defined based on the pre-industrial leaching of base cations from the catchment area. The total flux 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), non-marine atmospheric deposition (BC_{dep}^*), and net long-term uptake in the biomass (BC_u):

$$\text{BC}_t^* = \text{BC}_w + \text{BC}_i - \text{BC}_u + \text{BC}_{\text{dep}}^* \quad (7)$$

where all parameters are expressed as annual fluxes (i.e. in $\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$). Of these parameters BC_t^* and BC_{dep}^* are calculated directly from runoff, precipitation volume and concentration measurements.

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

$$F = \text{BC}_i / \Delta\text{AN}^* \quad \text{or} \quad \text{BC}_i = F \cdot \Delta\text{AN}^* \quad (8)$$

We now assume:

1. BC_w does not change with changes in acid inputs
2. BC_0 (pre-industrial base cation runoff) = $BC_w + BC_d$
3. Sulphate in runoff is in steady state with sulphur deposition

For the pre-acidification situation we thus have:

$$[BC^*]_0 = [BC^*]_t - F \cdot \Delta[SO_4^*] = [BC^*]_t - F \cdot ([SO_4^*]_t - [SO_4^*]_0) \quad (9)$$

where t refer to the present concentrations and 0 to the pre-acidification concentrations.

The value of F is a function of the base cation concentration, and lies between 0 and 1 (Henriksen 1984). F ranges from near zero for dilute lakes to 1 for lakes with high concentrations of base cations. A reasonable algorithm is (Brakke *et al.*, 1990):

$$F = \sin((\pi/2) \cdot [BC^*]_t / S) \quad (10)$$

If $[BC]_t > S$, F is set to 1. Thus, S is the base cation concentration at which $F = 1$. For Norway S has been estimated to be 400 $\mu\text{eq/l}$.

Background sulphate ($[SO_4^*]_0$) is estimated by a relationship from lakes in Norway which are little affected by acid deposition:

$$[SO_4^*]_0 = 15 + 0.16 [BC^*]_t \quad (\text{where concentrations are in } \mu\text{eq/l}) \quad (11)$$

This equation suggests that there is an atmospheric background contribution of $[SO_4^*]$ which gives an average of 15 $\mu\text{eq/l}$ and a geological contribution which is proportional to the concentration of base cations. For other areas other relationships may exist. For lakes in Sweden we use a slightly different equation (Wilander, 1994).

$$[SO_4^*]_0 = 5 + 0.05 [BC^*]_t \quad (\text{where concentrations are in } \mu\text{eq/l}) \quad (12)$$

Calculating critical load for acidity

The critical load for acidity in freshwaters can now be calculated:

$$CL(Ac) = ([BC^*]_0 - [ANC]_{\text{limit}}) \cdot Q - BC^*_{\text{dep}} \quad (13)$$

where:

$CL(Ac)$ = critical load of acidity in freshwater

$[BC^*]_0$ = preacidification sea-salt corrected base cation concentration

$[ANC]_{\text{limit}}$ = critical ANC concentration

Q = runoff

To avoid damage to biological indicators such as fish a value for ANC_{limit} of 20 $\mu\text{eq/l}$ has been used to date for calculating critical loads. The SSWC-method is sensitive to the choice of the ANC_{limit} . In areas with little acid deposition the probability of acid episodes leading to fish kills is small even if the ANC_{limit} is set to zero, while in areas with high acidic deposition fish kills may occur at this value.

Thus, the ANC_{limit} can be a function of the acidifying deposition to the lake, nearing zero at low deposition and increasing at higher deposition. A formulation for such an ANC_{limit} has been presented (see Henriksen *et al.*, 1995 for details). It should be noted that, although ANC_{limit} is not a common value for all lakes, each lake will have its own value for all depositions, determined by the characteristics of the lake ($[BC^*]_0$ and Q).

The present exceedance of critical load for sulphur acidity can be expressed as:

$$Ex(Ac) = S^*_{dep} - BC^*_{dep} - CL(Ac) \quad (14)$$

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