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Abstract

In the autumn of 1995, national lake surveys were conducted in the Nordic countries. The surveys were co-ordinated with respect to lake selection strategy, analytical methods, sampling techniques and sampling period. The 11 heavy metals investigated in nearly 3000 lakes show in general low values and distinct geographical patterns. Direct and indirect influence of long-range transported air pollution is the major important factor for distribution of Pb, Cd, Zn and also to a certain degree Co. TOC-levels in lakes are important for Fe and Mn but also to a certain degree As, Cr and V. Bedrock geology is the major controlling factor for Cu and Ni, with exception of areas around the smelters at Kola, where the Cu and Ni concentrations in lakes are very high. Bedrock and overburden geology is also an important factor for controlling the concentration levels of As, Co, Cr and V. The results indicate that heavy metal pollution in lakes is a minor ecological problem on a regional scale in the Nordic countries. Certain areas in particular in southern Norway and Sweden however, are affected by influence of long-range transport leading to increase in Pb, Cd and Zn in lakes above limits set by environmental authorities. Since aquatic biota in these areas already is under stress due to effects of acid rain, this may be an important environmental problem. Hg is not included in the Nordic Lake Survey, but from other work indicates that Hg is a significant environmental problem in many lakes, in southern Finland and Sweden.

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Heavy metal surveys in Nordic lakes; harmonised data for regional assessment of critical limits

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Preface

The results presented here represents the first regional evaluation of heavy metals in lakes in the Nordic countries including Russian Kola.

This project is a continuation of the NMR-project "Nordic Lake Survey 1995" (Henriksen *et al.* 1996, 1997, 1998). The Nordic Lake Survey was used to assess the status of the Nordic lakes with respect to general water quality, and to establish a new comparable database for calculating critical loads for sulphur and nitrogen in lakes in the Nordic countries for the ongoing work under the UN/ECE LRTAP Convention.

As a part of the Nordic Lake Survey, samples from lakes in Finland, Norway, Sweden and Denmark were analysed for heavy metals and other trace metals by the ICP-MS method. These analyses were conducted with extra financial support in Norway from the Ministry of Environment, Norwegian Institute for Air Research (NILU) and Norwegian Institute for Water Research (NIVA), and we would like to acknowledge their support. We also acknowledge the financial support from the Swedish Environmental Protection Agency and the work by Mr. Anders Berntell in the early stages of planning for the whole project.

Oslo, 1 May 1999

Brit Lisa Skjelkvåle

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Summary

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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. The surveys were coordinated with respect to lake selection strategy, analytical methods, sampling techniques and sampling period.

In addition to major element chemistry, about 3000 lake samples in Finland, Norway, Sweden, Denmark and Russian Kola were also analysed trace metals. The lakes were statistically selected. This is the first assessment of levels and distribution of heavy metals in Nordic lakes. The elements discussed here are; Cd, Pb, As, Zn, Cu, Ni, Co, Fe, Mn, Cr and V.

The purpose of the project was to:

- present baseline data for heavy metals in lakes in the Nordic countries
- estimate the relative importance of different sources for heavy-metal concentrations in these lakes; atmospheric contribution (long-range, local), point sources, geological conditions, marine contribution, mobilisation due to acidification etc.
- utilise the results of the surveys in the current development work of critical loads and levels for heavy metals under the UN/ECE - LRTRAP Convention.

The ecological relevance of the concentrations is evaluated in the light of existing information on critical concentrations in aquatic environments from the national water quality criteria.

Results

The 11 heavy metals measured in nearly 3000 lakes in the Nordic countries in the autumn of 1995, show in general low values and distinct geographical patterns.

The levels and distribution of heavy metals in Nordic lakes are controlled by several factors of which the following are the most important:

- anthropogenic sources
 - direct deposition from long-range air pollution
 - indirect effects of long-range air pollution by increased leaching due to acidification
 - local point sources
- water chemical conditions – particularly levels of TOC
- bedrock geology

Of the anthropogenic sources, long-range transported air pollutants acting both directly through deposition or indirectly through increased mobilisation due to acidification contribute to the large scale patterns of heavy metals in the Nordic lakes. Local emission sources must be of extreme strength, such as the smelter industry on the Kola peninsula and Rönnskär in Sweden, to have an evident influence the regional levels of heavy metals in lake waters. With these exceptions there is no clear sign of regional increase in heavy metal concentration in lakes around any of the known local point sources in Norway, Sweden and Finland. However, these industries sources may contribute to wastewater in specific rivers or lakes.

Soil- and surface-water pH and the concentration of total organic carbon (TOC) are important for the mobilisation of metals from the catchment to the runoff water. In particular TOC is an important factor and explains the large-scale variation in heavy metal concentration in lakes. The statistical analysis showed that about 40% of the total variance in the data material could be explained by variance in TOC and pH (where TOC is the most important of the two).

Bedrock and overburden mineralogy is an important source for heavy metals in lake water. Metals are released during weathering, and both the content of the metals in the minerals and the weathering rate are important factors. In some areas a small group of lakes show higher concentrations of a certain element relative to other lakes in the vicinity. This is interpreted as a geochemical influence from bedrock and overburden.

With some exceptions, the content of TOC in the waters is more important for controlling heavy metal concentration in lakes than the mineralogy of the bedrock and overburden. Also influence of long-range transport is more important for the regional patterns for some of the heavy metals than the mineralogy of the bedrock and overburden on the Nordic scale.

Although all the elements show different regional patterns and concentration levels, the 11 elements fall into 3 groups, based on geographical distribution patterns and results from the statistical analysis:

1. Pb, Cd, Zn, (Co)
2. Fe, Mn, (As, Cr, V)
3. Cu, Ni, (As, Co, Cr, V)

Direct and indirect influence of long-range transported air pollution is the most important factor for distribution of Pb, Cd, Zn and also to a certain degree Co. TOC-levels in lakes are important for Fe and Mn and also to a certain degree As, Cr and V. Bedrock geology is the major controlling factor for Cu and Ni with exception of areas around the smelters at Kola. As, Co Cr and V are also classified together with Cu and Ni; their geographical concentration gradient is not as strong as for the other elements in group 1 and 2, and bedrock geology is also an important factor for controlling the concentration levels of these elements. With exception of the smelters at Kola and Rönnskär in Sweden it is not possible to detect any clear influence from other point sources in the Nordic countries on lake water content of heavy metals on a regional scale.

The results indicate that heavy metal pollution in lakes is a minor ecological problem on a regional scale in the Nordic countries. Certain areas however, in particular in southern Norway and Sweden, are affected by long-range transport leading to increase in Pb, Cd and Zn in lakes above limits set by environmental authorities in Norway and Sweden. Since aquatic biota in these areas already is stressed due to effects of acid rain, this may be an important environmental problem in such areas.

Hg is not included in the Nordic Lake Survey, but from other work it is demonstrated that Hg in fish has increased substantially, and that this is a large environmental problem.

The present work gives status of heavy metals for *lakes* in the Nordic countries. There are indications that especially in small streams there may be generally higher levels of heavy metals than in lakes, and thus, the ecological problem of heavy metals may be larger for running waters than for lakes.

There is no room for increases in concentrations of heavy metals in lakes. Ongoing and future reductions in acidification should decrease deposition and leaching of heavy metals.

These data for 11 heavy metals in Nordic lakes provide baseline information for following up the Heavy Metals protocol, with regard to reductions or stabilisation of emission of heavy metals in the future.

1. Introduction

1.1 Background and aims

Heavy metals are a natural part of the environment, but human activities including metals smelting and processing, fuel combustion and road transport, contribute significantly to total environmental exposure to these substances.

The levels of heavy metals in surface waters is dependant on several factors; airborne contribution from anthropogenic activity and local point sources, natural in bedrock and soils and natural contribution from soil dust. In addition, conditions in the catchment are important for the mobility and availability of heavy metals in the water.

The atmospheric deposition of heavy metals exhibits large-scale gradients that can be related to long-range transport from anthropogenic source areas (Pacyna *et al.* 1995, AMAP 1998). The results of transport models on the sources of heavy metals in the North Sea and Baltic sea has lead to the conclusion that as much as 50% of Pb and Hg and between 30 and 50% of As, Cd, Cr, Cu, Ni and Zn enter these areas through atmospheric deposition. Hg and Pb are transported on hemispheric-wide scale. A number of heavy metals concentrated on fine particles including Cd, As, V, Zn and Ni can be transported on a regional scale, e.g. a few thousand kilometres. Some elements like Cr and Mn are emitted on coarse particles and their transport within air masses is limited to shorter distances.

Heavy metals are emitted from high temperature processes, such as coal and oil combustion in electric power generating

stations and heat producing and industrial plants, internal combustion engines, roasting and smelting of ores in non-ferrous metal smelters, melting operations in ferrous foundries, refuse incineration and cement and glass industry. Recently, regional emission inventories of European countries have been compiled (Table 1.1) (Berdowski *et al.* 1997).

Emissions from natural sources, such as wind-blown dust, volcanic eruptions, biomass burning, as well as evaporation from soils with geological deposits, can form an important contribution to the total emissions of Hg, As, Cu and Zn, at least in certain areas (Nriagu and Pacyna, 1988).

Geochemical sources control regional patterns of As, Cu and Ni in lakes and streams especially in areas with relatively low atmospheric deposition (Tarvainen *et al.* 1997). Land use such as cultivation, fertilization and ditching in the catchment area has an effect on the metal concentrations in the lakes. In most cases this is difficult to distinguish from the natural geochemical signal. Locally, point source effluents directly to lakes can have significant effect, but the scope in this report is mainly on large-scale variation and regional phenomena.

Environmental conditions, such as hydrology and soil texture in the catchment and chemical characteristics of water entering the lake (pH, organic carbon and suspended material) control finally the metal concentrations in the lake.

Table 1.1 Annual 1990 emissions in tonnes per year for the Nordic countries (from Berdowski *et al.* 1997)

	As	Cd	Cr	Cu	Ni	Pb	Zn
Finland	4.60	3.66	10.4	36.7	71.3	215	143
Norway	0.98	2.42	3.64	46.4	37.0	226	78.0
Sweden	5.50	2.04	23.0	26.5	26.0	537	228
Denmark	3.81	2.12	5.69	23.4	43.9	179	66.0

The present project is an expanded evaluation of the NMR-project "Nordic Lake Survey 1995" (Henriksen *et al.* 1996, 1997, 1998). The Nordic Lake Survey was used to assess the status of the Nordic lakes with respect to general water quality, and to establish a new comparable database for calculating critical loads for sulphur and nitrogen in lakes in the Nordic countries. This critical loads work is used for the ongoing work under the UN/ECE Convention on long-range transboundary air pollution (LRTAP).

In addition to major element chemistry, trace metals were also analysed for about 3000 lakes in Finland, Norway, Sweden, Denmark and Russian Kola. This is the first common presentation of levels and distribution of trace metals/heavy metals in Nordic lakes. The elements discussed here are; Cd, Pb, As, Zn, Cu, Ni, Co, Fe, Mn, Cr, V.

The purpose of the present project is to:

- present baseline data for heavy metals in lakes in the Nordic countries
- estimate the relative importance of different sources on the concentrations found in lakes: atmospheric contribution (long-range, local), point sources, geological conditions, marine contribution, mobilisation due to acidification etc.
- utilise the results of the surveys in the current development work of critical load and level for heavy metals under the Heavy Metals Protocol under UN/ECE - LRTRAP Convention.

The ecological relevance of the concentrations is evaluated in the light of existing information of critical concentrations in aquatic environments from the national water quality criteria.

1.2 Major results from the "Nordic lake Survey 1995"

Autumn 1995, national lake surveys were conducted in six Northern European countries on the initiative of the environmental authorities in Sweden, Finland and Norway

(Henriksen *et al.* 1996). The surveys were coordinated 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.

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,
- establishment of a new reference dataset to quantify the future effects of the second sulphur protocol (UN/ECE, 1994),
- establishment of 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),
- establishment of the eutrophication status
- concentrations of heavy metals.

The results from the survey (Henriksen *et al.* 1997, 1998) 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 slow 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 and higher concentrations in the eastern areas (Figure 1.1). 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. TOC concentrations differ even more. The lakes in Denmark are influenced by different overburden mineralogy than the other countries in the survey, and their catchments are also influenced to a greater

extent by intensive agricultural activities. The Danish lakes generally thus have much higher of major ions and nitrogen (N) and phosphorus (P).

The acidification situation is quantified by calculating critical loads and exceedances. In approximately 22,000 lakes in Northern Europe, critical loads for sulphur acidity are exceeded (Henriksen *et al.* 1997, 1998).

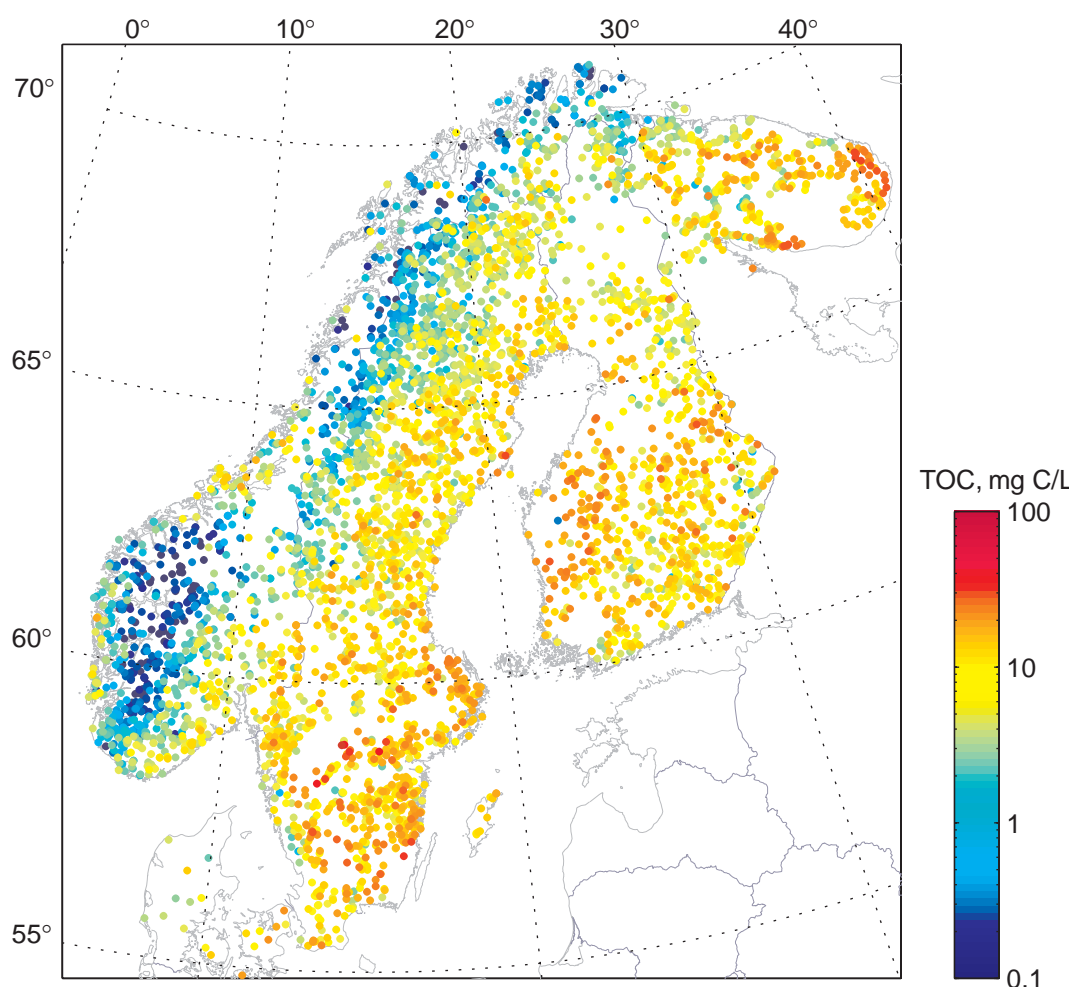


Figure 1.1. Total organic content (TOC mg C/L) in ca. 5.500 lakes in the Nordic countries as of autumn 1995 (from Henriksen *et al.* 1997,1998)

1.3 Previous lake surveys on heavy metals in the Nordic countries

Finland

Concentrations of metals (Cd, Pb, Ni, Cu, Zn, Mn, Al and Fe) were measured 1987 in 256 lakes as part of a nationwide acidification survey (Verta *et al.* 1990, Mannio *et al.* 1993). Concentrations generally followed the pattern of atmospheric deposition observed in snowpack and moss chemistry. The lakes were separated into groups according to the same level of metal deposition using maps of metal concentration in forest moss. Metal concentrations in lakes were most significantly correlated to lakewater acidity and to the concentration of organic carbon. In a stepwise regression analysis, these two variables, together with a few catchment characteristics, accounted for ~ 70 % of the variation of Fe and Al, and from 20 to 50 % of the variation of the other metals. Copper concentration in lakes was significantly explained by the regional Cu concentration in the fine fraction of till.

Distributions of Mn, Zn, Cu, Ni, Cr, Pb, As and Cd in Finnish surface waters were studied by comparing two survey data sets; samples from 154 headwater lakes in 1992 and samples from 1165 headwater streams collected during the environmental geochemical mapping program in 1990 (Mannio *et al.* 1995, Tarvainen *et al.* 1997).

The concentrations of Cr occur in brown waters, rich in humic matter, while Mn and Zn concentrations are controlled by acidity, with a tendency to be elevated in low-pH waters. The high Ni concentrations in lakes in southwestern Finland probably are due to anthropogenic input, while Ni anomalies in stream and lake water in eastern Finland are correlated with high Ni contents of glacial till. The Pb concentrations in lakes are mainly due to inputs of airborne anthropogenic pollutants.

Tarvainen *et al.* (1997) compared heavy metal concentrations in surface waters with land-use of the catchment and showed that the percentage of arable land correlated positively

with As, Ni, Cu, Mn, and Zn in small streams. Clay soils normally contain more heavy metals than till, and fertilizers are a likely additional source. Peatlands correlated positively with Cr and Pb, both in streams and headwater lakes. The lakes with highest As (and Cu) concentrations were found in an area with greenstones and As-rich black schists.

Norway

The only previous survey of heavy metals in Norwegian lakes was conducted in 1974-75 in 165 small, pristine lakes. As part of the project "Acid precipitation – effects on forest and fish"(SNSF) (Overrein *et al.* 1981) the samples were analysed for Mn, Fe, Cu, Zn, Cd and Pb. A spatial relation between concentration and polluted precipitation was evident for some metals. For Zn and to a lesser extent for Pb, the data suggested that a substantial part was derived from atmospheric supply in lake waters of southern Norway (Wright and Henriksen, 1978; Henriksen and Wright, 1978). Later evaluation of these data (Steinnes and Henriksen, 1993) suggested that Pb and Cd values from this survey was too high to be reliable, and that Mn and to some extent Fe are affected by acidic precipitation enhancing the leaching of these metals from mineral in soils and lake sediments. For Zn, it was concluded that airborne supply to the lakes and their catchments appears to strongly affect the lake water concentration.

Sweden

Several studies of trace metal concentrations in Swedish lakes have been made in the past. Most studies covered only a limited number of lakes. The study by Borg (1987) covered 59 lakes in forested areas. A comparison between the mean values for these lakes and median concentrations for the Swedish lake survey indicate that those two samples of Swedish lakes are quite similar (Wilander *et al.* 1998). Borg and Johansson (1989) evaluated mass balances for heavy metals for several forested lakes based on estimates of metal deposition and transport from drainage areas. Areal losses of metals were generally higher in areas with a low soil pH. For Cu, Zn, and Cd the direct inputs by deposition were lower than the fluxes from the drainage area. In the case of Pb, however, the contributions from both sources

were about equal. The great importance of the soil as a store for metals was emphasised. In a SEPA report (1993) the state of the Swedish environment with respect to heavy metals is reviewed and assessed.

Denmark

No survey of heavy metals has been previously conducted in Denmark on a regional basis.

Russian Kola

Ni and Cu concentrations were measured in 270 lakes on Russian Kola in 1990-1992. The research was concentrated on impacted areas

around the Ni-Cu smelters. (Moiseenko, 1992, Moiseenko *et al.* 1995). Surface waters with high levels of Ni (>20 mg/l) and Cu (>10 mg/l) were located within 30 km distance from the smelters. In lakes near the industrial centers the heavy metal content correlates with Ca and Mg concentrations indicating that both come from dust emission from the smelters. Elevated concentrations of Ni and Cu (Ni up to 3 mg/l, Cu - 1 mg/l) were also found at distances more than 30 km from the smelters. Background concentrations of Ni and Cu were low in remote east and south-west provinces.

2. Methods

Methods for lake selection and sampling methods are described in detail in Henriksen *et al.* (1996, 1997). A brief summary is given here.

2.1 Lake 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 should be included
- the proportion of lakes in size classes 0.04-0.1, 0.1-1, 1-10 and 10-100 km² should be 1:1:4:8 and all lakes >100 km² should 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 Northeastern Lapland, 2% in inland and remaining parts of Northern Finland, 4% in coastal counties/regions.

Norway: 1.2% in Northern Norway, 2.1% in Central 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.

In Finland and Norway, the trace elements were analysed for the same number of lakes (with only small differences) as the original lake survey. For Sweden and Finland, the trace elements were analysed for a subset of the original selection. The original criterias for number of selection of lakes in each region is still met. However, due to contamination during sampling, Cd, Pb, Zn and Cu had to be excluded from the observations in Northern Sweden (see 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

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.

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)

In Sweden, 216 lakes in the county Norrbotten in northern Sweden were excluded for Cd, Pb, Zn, Cu, due to contamination during sampling.

Table 2.1 Lake size distribution and number of lakes selected.

Size class area (km²)	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	175	152	103	31	3	464
Percentage	1.2	1.2	4.8	8.9	6.4	1.6
Norway						
Total	21218	16417	2139	164	7	38845
Selected¹	419	353	177	29	7	985
Percentage	2.0	2.2	8.3	17.7	100	2.5
Sweden						
Total	35802 ²	20484	3599	379	24	60264 ²
Selected³	418	347	207	58	6	1036
Percentage	1.2	1.7	5.8	15.3	25.0	1.7
Selected⁴	301	286	179	50	4	820
Percentage	0.84	1.4	5.0	13.2	16.6	1.4
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

¹ As is analysed for only 520 of the Norwegian samples² Estimated number, due to lack of detailed information about lakes < 0.1 km²³ Numbers of Swedish lakes analysed for As, Ni, Co, Fe, Mn, Cr, V⁴ Numbers of Swedish lakes analysed for Cd, Pb, Zn, Cu. Lakes from Northern Sweden (Norrbotten county) is excluded for these elements due to contamination during sampling.

2.2 Sampling

The samples were collected during or shortly after the autumn overturn in all countries (Table 2.2). They were visited either by foot or by helicopter depending of the accessibility of the lakes, following the procedures given by Henriksen *et al.* 1996.

Table 2.2 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

2.3 Analytical methods

Elements analysed in the national lake surveys and the detection limits are shown in table 2.3.

Finland

The Finnish samples were analysed at the Finnish Environmental Institute by ICP-MS (Perkin-Elmer Sciex Elan 5000). Samples were preserved with 0.5 ml conc. HNO₃ (suprapur) and kept cool (+4°C). Riverine Water Reference Material for Trace Metals (SLRS-2, National Research Council, Canada) was used as a reference sample. The ICP-MS -method used in the Research Laboratory of FEI is nationally accredited by the Centre for Metrology and Accreditation.

Norway

The Norwegian samples were analysed at Norwegian Institute for Air Research (NILU) by ICP-MS (Fisons Elemental PQ2+). The instrument was run with standard conditions. All calibration standards, blanks and samples contained 1% HNO₃ and 50 ng ml⁻¹ Sc, In and Re (internal standards). The analysis was performed with a procedure based on scan, which means that the whole mass-spectra from mass 5 to 240 was recorded. Quality control was performed by daily analysing a reference

solution at 1.0 ng/ml for all elements of interest prepared by certified standards from Spex Industries, USA.

Denmark

The Danish samples were analysed at Norwegian Institute for Water Research (NIVA) by ICP-MS. The analysis was performed with a peak jump procedure under standard instrumental conditions as recommended by the manufacturer. Each element was determined individually against calibration graphs prepared from multi-element standard solutions. Standards and samples were prepared with 10% HNO₃ and added rhodium (Rh) at a concentration of 10 ng/ml as internal standard. Quality Control was performed by daily analysing a certified reference standard (SLRS-2 Nat.Res.Council Canada).

Sweden

The Swedish samples were analysed at the Swedish University for Agricultural Sciences, Department of Environmental Assessment by ICP-MS Elan 6000 (Perkin-Elmer). All elements were determined individually, and the calculations of concentrations were based on calibration curves for each element. SRLS-2 water used as an independent control. The control was injected after every 20 samples. If the results obtained deviated more than 5-20%, depending on the metal, then a new calibration was made.

Russian Kola

The Russian samples were analysed at the Institute of North Industry Ecological Problems, Apatity. Only Zn, Cu, Ni, Fe and Mn were determined. The Russian samples were determined by atomic absorption spectroscopy (GAAS, model Perkin-Elmer - 5000, Corp., Norwalk, USA), equipped with graphite furnace HGA-400 and hydride system MHS-10. Standard solutions with appropriate concentration for each element were made from 1000 ppm AAS stock standards (Merk, Darmstadt, Germany). Quality of analytical results was repeatedly tested in the intercalibration.

Table 2.3 Elements and detection limit (µg/L) analysed in the national lake surveys

	Finland	Norway	Sweden	Denmark	Russian Kola
	µg/L				
Cd	0.03	0.02	0.003	0.03	
Pb	0.03	0.03	0.02	0.03	
As	0.06	0.1	0.03	0.06	
Zn	0.3	0.3	0.2	0.3	0.02
Cu	0.07	0.2	0.04	0.07	0.1
Ni	0.04	0.1	0.05	0.04	0.1
Co	0.03	0.02	0.005	0.15	
Fe	2	15	2	5	0.1
Mn	0.6	0.2	0.4	0.05	0.05
Cr	0.1	0.1	0.05	0.1	
V	0.03	0.3	0.03	0.03	

2.4 Statistical methods

2.4.1 Stratification

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

2.4.2 Imputation of left censored observations

The chemical analyses include observations reported as less than the detection limit. These “left-censored” data preclude statistical estimation, and it thus necessary to manipulate the censored observations. Censored data are sometimes substituted by a constant set to half the value of the detection limit.

Here we have a new method to model the distribution of observation under the detection limit. This method is named “imputation of left censored-values”. The method is described in detail in Appendix A. The results of the imputation procedure simulate the values under the detection limit, and give a dataset of 2485 observation for 10 elements.

The imputation procedure was performed for Pb, Cd, As, Zn, Cu, Ni, Co, Fe, Mn, Cr and V for data from Finland, Norway and Sweden (excluding the 216 samples in Northern Sweden). The Danish data were not used because they are not statistical selected, and the Russian Kola data were not used because they included only 5 elements (Cu, Zn, Ni, Fe and Mn). As was analysed for only 50% of the Norwegian lakes, and was therefore not used.

2.4.3 Multivariate statistics

Principal component analysis (PCA)

Principal component analysis (PCA) is a special factor analysis which transforms the original set of intercorrelated variables into a set of uncorrelated variables, that are linear combinations of the original variables. The first principal component is the linear combination of the variables that accounts for a maximum of the total variability in the dataset. The second principal component explains a maximum of the variability not accounted for by the first component, and so on. The objective is to find a minimum number of principal components that explains most of the variance in the data set. The principal

components are statistically independent and, typically, the first few components explain almost all the variability in the whole dataset. A wide range in concentration makes normalisation necessary if all the elements are to be given equal weight in the analysis.

Redundancy analysis (RDA)

The multivariate relations between concentrations of the heavy metals and explanatory variables are analysed by redundancy analysis (RDA). RDA is a constrained form of multivariate regression. It is intermediate between principal component analysis and separate multiple regression analysis for each dependant variable. Whereas PCA is an eigenvector extraction technique using only a matrix of input variables (Y-matrix), RDA is a constrained form in the sense that the underlying dimension in the Y-matrix (the latent variables) are forced to be multiple regressions of the independent variables (the Z-matrix). For a detailed treatment on RDA see ter Braak and Prentice (1988).

RDA leads to an ordination diagram that simultaneously displays the main pattern of the dependant variables (the Y-matrix) as far as this variation can be explained by the independent variables (the Z-matrix) and the main pattern in correlation coefficients between dependant and independent variables. In the ordination diagram, points indicate dependent variables, whereas arrows indicate the independent variables. Vectors (indicated by arrows) pointing roughly in the same direction indicate that the variables are positively correlated, vectors crossing at right angles indicate near-zero correlation, and vectors pointing in opposite directions indicate high negative correlation. The length of the vectors indicates the importance of the variables in the analysis; longer vectors indicate more confidence in the inferred correlation.

3. Levels and geographical distribution of heavy metals in the Nordic countries, including Russian Kola

This chapter presents major sources, geographical distribution patterns, and general levels of each of the elements. For each element there is a Nordic map with concentrations in lakes and a percentile table based on weighted and imputed values (Figures 3.1 – 3.11 and Tables 3.1 – 3.11)

3.1 Pb – Lead

Leaded gasoline is the major source of increased environmental levels of lead on a global scale. Other anthropogenic sources include mining and metallurgic industries, ammunition and in some places incineration. The regulation or banning of Pb containing products (e.g. gasoline additives, paint) has reduced emissions to the environment considerably in the last decade. 1990, atmospheric Pb emissions had declined to ca. one third of the level in 1975 (Olendzynski *et al.* 1995) and the trend is further declining in Europe. The European moss survey (Rühling and Steinnes, 1998) shows that the concentration of Pb in moss in southern Norway has decreased by about 30% from 1990 to 1995.

A northwards decrease in concentration in lakes, parallel to the pattern from the moss survey, is very clearly seen in the case of Pb.

This pattern is evident in Norway, Sweden as well as in Finland. Elevated concentrations are virtually absent in northern areas in all these countries. Lower concentrations are detected also in lakes at higher altitudes. The largest number of value over 0.7 µg/L, is recorded in southernmost Norway. Typical values range from 0.06 to 0.4 µg/L. Concentration distributions are very similar in Norway and Sweden. The level is somewhat lower in Finland, especially the highest values are missing. This could be due to the longer distance from major sources in Central Europe.

Anthropogenic deposition explains most of the Pb distribution in surface waters. Mobility of lead in soil is relatively low leading to accumulation in forest floor, but catchment mass-balance studies suggest some outflow (Borg and Johansson, 1989). Sediment studies indicate that a minor part of the Pb burden of the lakes is derived from overburden or bedrock in comparison to anthropogenic (atmospheric) sources (Johansson 1989, Verta *et al.* 1989). High Pb values in central western Finland are connected with TOC content probably due to leaching of organic-complexed Pb from the catchment. This was also the result from earlier surveys of headwater lakes (Mannio *et al.* 1995).

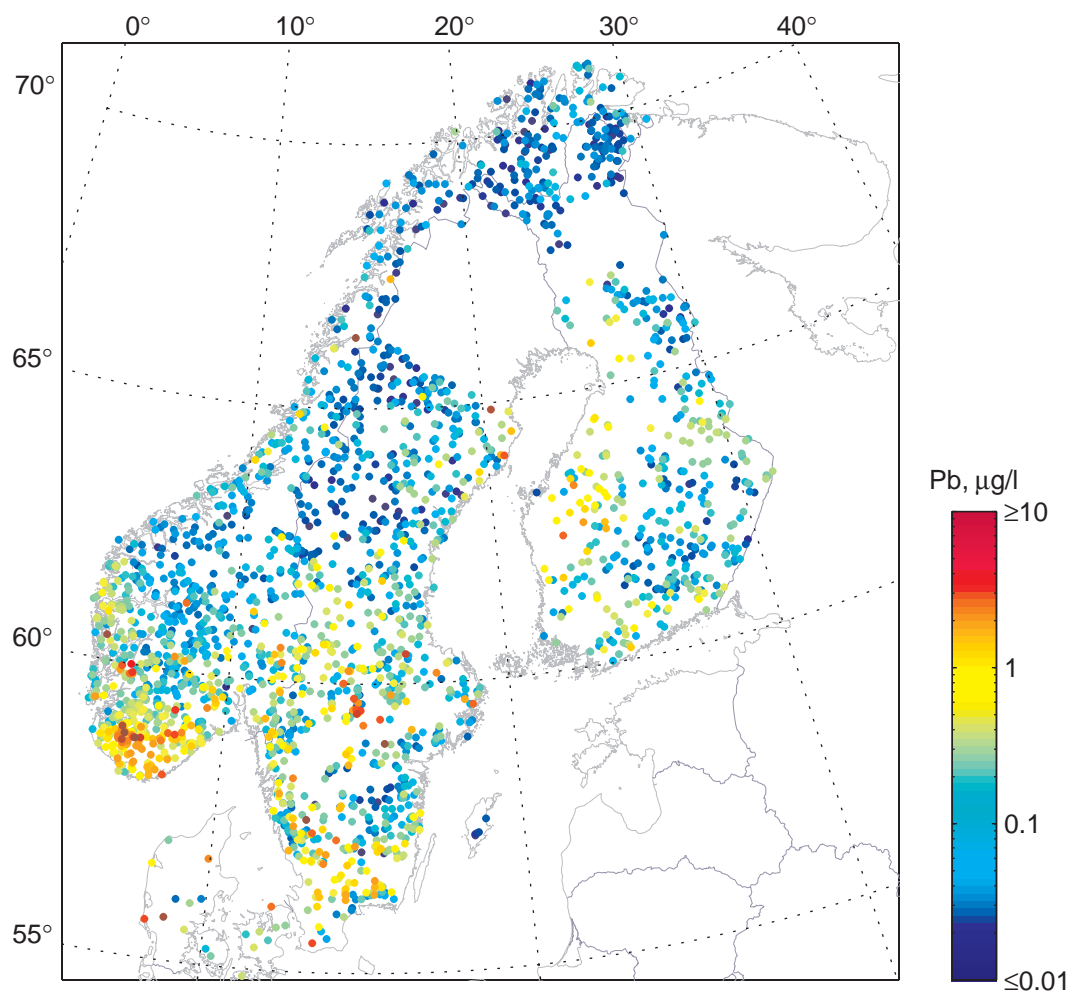


Figure 3.1 Pb concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.1 Weighted and imputed percentiles for Pb in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Pb in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Pb-82		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.00 %	2.78	15.0	12.9	8.12	
	99.50 %	2.07	7.69	6.26		
	97.50 %	0.93	1.76	1.77		
	90.00 %	0.60	0.74	0.75		
quartile	75.00 %	0.37	0.32	0.36	0.61	
	50.00 %	0.17	0.14	0.16	0.38	
quartile	25.00 %	0.078	0.071	0.066	0.26	
	10.00 %	0.032	0.036	0.036		
	2.50 %	<i>0.024</i>	<i>0.019</i>	<i>0.020</i>		
	0.50 %	<i>0.017</i>	<i>0.010</i>	<i>0.008</i>		
minimum	0.00 %	<i>0.014</i>	<i>0.004</i>	<i>0.003</i>	0.05	

3.2 Cd – Cadmium

Cd is a by-product in the production of Zn and Pb, and the pyrometallurgical production of Zn is the most important anthropogenic source of Cd to the environment. Other major sources are iron and steel industry, fossil fuel combustion and waste incineration. Cd is used in many applications, including alloys, pigments, metal coatings, batteries and in the electronics industry. It is also a contaminant in chemical fertilizer, manure and sewage sludge.

In addition to deposition of long-range transported Cd, acidification of soils increases leaching of Cd from the catchments. It is therefore both a direct and indirect effect on Cd-levels in lakes from long-range anthropogenic air pollutants (Borg and Johansson, 1989)

Although Cd is known to be long-range transported in the atmosphere, the pattern of Cd concentration in Nordic lakes decreases less distinctly northwards than in the case for Pb. Values greater than 0.05 µg/L are typical in southern Norway as well as central Sweden. Extensive liming activities in southern Sweden

may have diminished the number of lakes with high concentrations (Lyderesen og Løfgren, 1999).

Elevated values are also found in northernmost Norway and Finland and scattered throughout central Norway and Western Finland as well as in Central Sweden, especially in the ore-rich belt in Dalecarlia. Areas with possible local atmospheric influence include the Odda zinc smelter in SW Norway, Rönnskärsverket in Sweden and Harjavalta in SW Finland. Emissions from Kola could contribute to the levels in northern areas of both Norway and Finland. These point sources do not influence the regional pattern of Cd in lakes.

Typical Cd values in lakes are below 0.03 µg/L, which was the detection limit of the analysis in Norway and Finland. Therefore concentration distributions are to some extent difficult to compare between Nordic countries. However, it seems that the highest 10 percent of the values are comparable in Norway and Sweden, but clearly lower in Finland.

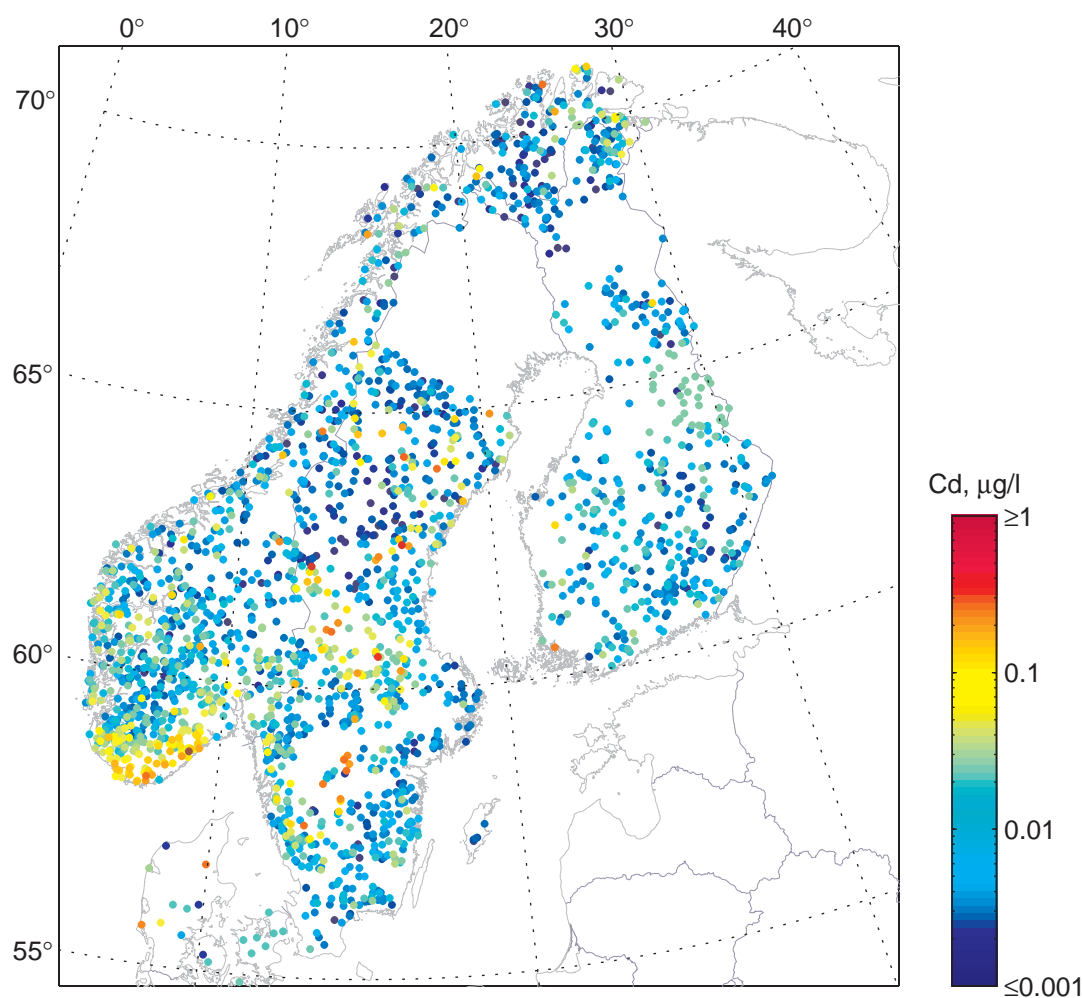


Figure 3.2 Cd concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.2 Weighted percentiles for Cd in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Cd in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Cd-48		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.00 %	0.230	1.07	0.540	0.266	
	99.50 %	0.054	0.209	0.279		
	97.50 %	0.030	0.114	0.124		
	90.00 %	0.030	0.055	0.052		
quartile	75.00 %	0.021	0.028	0.023	0.050	
median	50.00 %	0.011	0.012	0.010	0.050	
quartile	25.00 %	0.006	0.006	0.006	0.020	
	10.00 %	0.003	0.003	0.003		
	2.50 %	0.002	0.001	0.001		
	0.50 %	0.001	0.001	0.001		
minimum	0.00 %	0.001	0.000	0.001	<0.005	

3.3 As – Arsenic

The main atmospheric sources of As are combustion processes of coal and fuel oils as well as Cu, steel and glass industry.

The deposition pattern of As in the Nordic countries is dominated by the influence of long-range transport (Rühling and Steinnes, 1998). However, the geographical distribution of As in lakes is not effected the deposition pattern.

The geographical distribution pattern of As, show a very strong gradient from low values in west, to higher values in east. In addition, there is an area with higher As values in northeastern Sweden, central west Finland and in a limited area in western Norway. These areas are most probably influenced by As-containing minerals in the bedrock and overburden, as there is no indication of elevated As in deposition due to industry in the area. The emission from Kola smelters, clearly seen in the moss survey data (Rühling and Steinnes 1998), is not reflected in the lakes in northern Finland and Norway.

The areas with high As concentrations in lakes in central west Finland, central northern Sweden, and western Norway, indicate that the most important source of As is geochemical. The elevated concentrations of As in lakes around the Rönnskär smelter in northern Sweden, however, is mainly due to emissions from the smelter.

In Finland, the distribution pattern of As in stream waters is similar to the distribution in the fine fraction of glacial till and arable soils (Tarvainen *et al.* 1997). Lowest values were recorded in areas of Archean gneiss in eastern and northern Finland, and highest in areas of volcanic-sedimentary rock and clay soils in southern and western Finland.

Typical As values in this survey are in the range from 0.1 to 0.4 µg/L. With one exception, all lakes in Denmark have relatively high concentrations > 1 µg/L. Other regions with elevated levels are southern and central-northern Sweden and western Finland. Overall, concentration levels of As are much lower in Norway than in other Nordic countries.

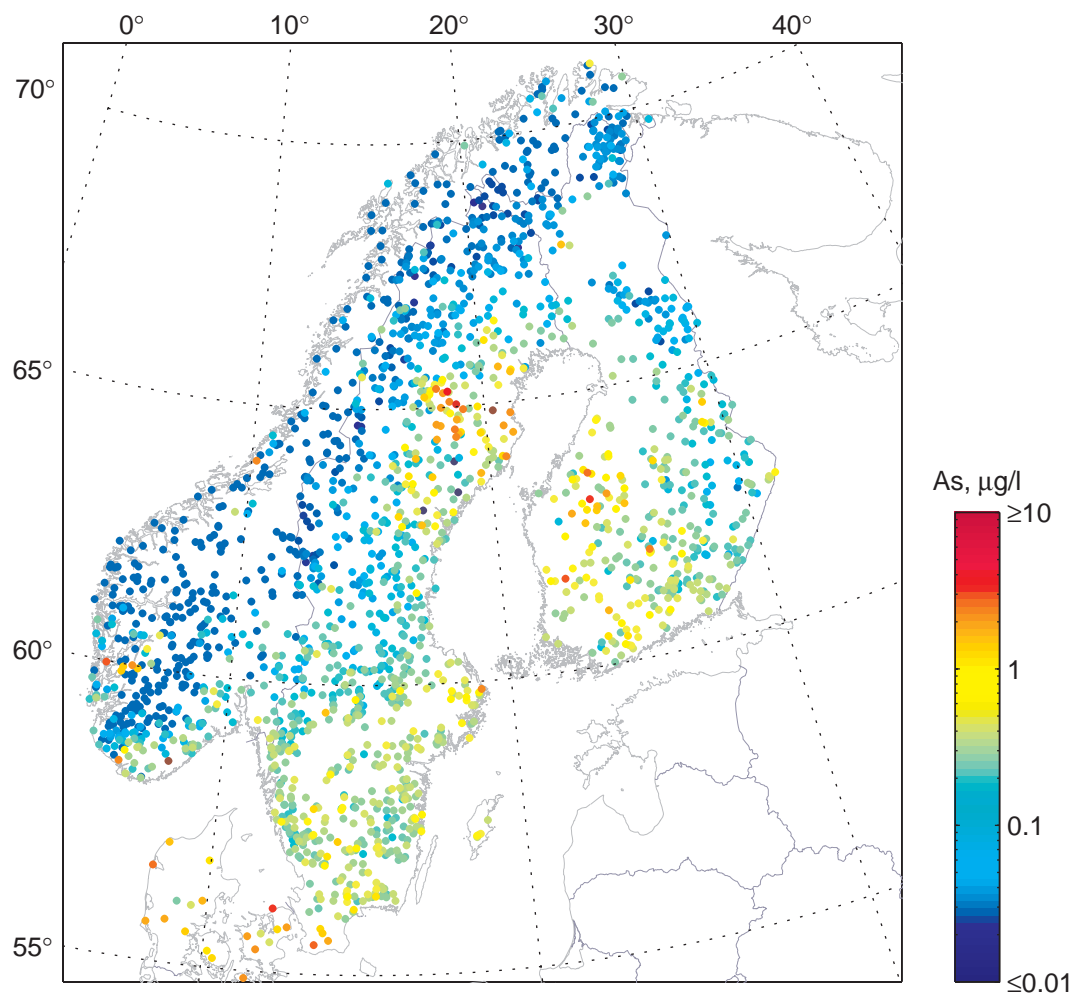


Figure 3.3 As concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.3 Weighted percentiles for As in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of As in Danish lakes. The As-values are not imputed

As-33		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	4.06	12.7	126	4.0	
	99.5 %	2.40	2.02	4.59		
	97.5 %	1.19	0.56	1.77		
	90.0 %	0.70	0.27	0.70		
quartile	75.0 %	0.47	0.14	0.43	1.65	
median	50.0 %	0.29	<0.05	0.28	1.20	
quartile	25.0 %	0.17	<0.05	0.15	1.00	
	10.0 %	0.08	<0.05	0.07		
	2.5 %	<0.03	<0.05	<0.03		
	0.5 %	<0.03	<0.05	<0.03		
minimum	0.0 %	<0.03	<0.05	<0.03	<0.3	

3.4 Zn – Zinc

Most Zn emissions to the atmosphere come from the non-ferrous metal industry, iron and steel production and coal combustion. Atmospheric Zn emissions have declined to ca. one third of the level in 1970 (Olendrzynski *et al.* 1995). Besides atmospheric deposition, catchments with arable land receive Zn load from fertilizers.

In general, the highest Zn-values are found in lakes in southern parts of the Nordic countries and at lower altitudes. Concentration distributions are very similar in Norway and Sweden. Finland and Kola lack both very high and low values. Typical values range from 0.7 to 3 µg/L. High values, over 10 µg/L, are found in southern Norway and southwestern Sweden. In Norway, the highest Zn values coincide with the highest Cd and Pb values,

indicating the same atmospheric sources and leaching processes from the catchments for these elements. High Zn concentrations in headwater lakes and streams seldom are correlated with bedrock or till geochemistry (Tarvainen *et al.* 1997). High Zn concentrations in the fine fraction of till are found in metamorphic volcanogenic-sedimentary areas in southern Finland, along the Lake Ladoga - Bothnian Bay zone and in central Lapland (Koljonen 1992). High Zn values are more likely to occur in acid surface waters.

The Danish lakes show in general much higher Zn concentrations than the other lakes in the other Nordic countries. This may be due to influence from fertilizing.

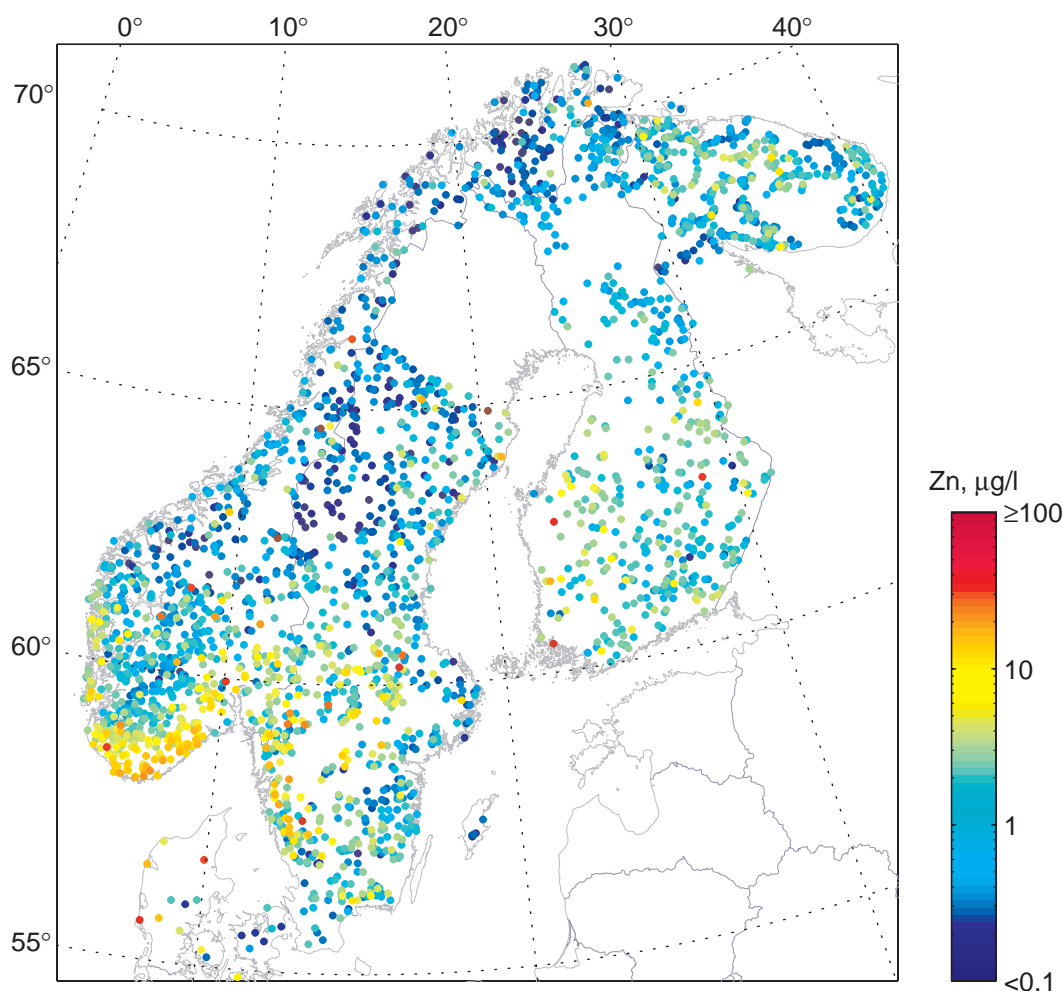


Figure 3.4 Zn concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996).

Table 3.4 Weighted percentiles for Zn in the total lake population in Finland, Norway, Sweden and Kola. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Zn in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Zn-30		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	55.0	139	426	47	9.3
	99.5 %	12.7	29.0	25.1		7.6
	97.5 %	7.3	11.6	12.4		5.0
	90.0 %	4.4	5.9	5.3		3.5
quartile	75.0 %	3.2	2.6	2.8	12.6	2.3
median	50.0 %	2.2	1.1	1.5	7.4	1.4
quartile	25.0 %	1.4	<i>0.54</i>	0.60	<0.5	0.81
	10.0 %	0.91	<i>0.25</i>	0.20		0.46
	2.5 %	0.57	<i>0.13</i>	<i>0.15</i>		0.22
	0.5 %	<i>0.17</i>	<i>0.09</i>	<i>0.08</i>		0.12
minimum	0.0 %	<i>0.07</i>	<i>0.08</i>	<i>0.07</i>	<0.5	0.1

3.5 Cu - Copper

Copper industry is the major source of atmospheric Cu. Other important contributors are industrial combustion processes and road transport (Berdowski *et al.* 1997). In Kola Peninsula, large smelters are important atmospheric sources of Cu which clearly affect the lakes in their vicinity. Small local point sources of emissions exist in all Nordic countries.

There is a decreasing level of Cu in lakes from southern parts of Norway, Finland and Sweden up to the Arctic Circle. Regions with high concentrations are distinguished through out Kola Peninsula, south from Hardangerfjorden on the western coast of Norway, southern coast of Norway, southeastern coast of Sweden and western coast of Finland. Till geochemistry is reflected in the Cu distribution patterns in southern Finland (Tarvainen *et al.* 1997). Also the sulphide ore belt which crosses Finland from Lake Ladoga to Bothnian Bay can be assumed to contribute to the Cu concentrations in surface waters in that area. The Cu anomaly in western Norway is also most probably due to a geochemical anomaly. Elevated Cu levels in lakes in coastal lowland areas can be partly explained by the area of arable land in the catchment. Clay deposits have higher Cu content than coarser grained soils, and Cu-enriched fertilizers are applied to fields (Kauranne and Sillanpää, 1992). In a Finnish stream survey, the highest Cu concentration

were found in rivers with arable land in their catchments (Tarvainen *et al.* 1997).

Concentration distributions of Cu are very similar in Norway, Sweden and Finland. Typical values lie between 0.2 and 0.7 µg/l. Extreme values (> 3 µg/L) are found in the whole western Kola Peninsula near the smelters in Nikel and Monchegorsk.

More than 50 years of mining and smelters «Severonickel» and «Pechenga-nickel» at the Kola Peninsula have caused surface water pollution in the vicinity of these factories. The annual emission (1990) of Cu is 1600 tonnes/yr. Along with the metal pollution the S-emission is about 516 000 tonnes/year. Acid deposition can favour the release of trace metals from soil and rock, as well as mining waste rocks and tailing. Areas with high concentrations of Cu are located in a 30-40 km zone around the smelters. The Cu deposition within 10 km distance from the smelters is about 280 mg/m²year, while at 60 km distance it is 6 mg/m² year. Up to 95% of the deposited Cu are bound and retained in the upper organic layer of the soils. Background concentrations of Cu as well as other elements in remote lakes (> 100 km from industrial centres) exceed those for other Arctic regions (AMAP, 1997). This may be due to remote distribution of aerosols, geochemical features of the region and release of metals by acid rain or global airborne transport.

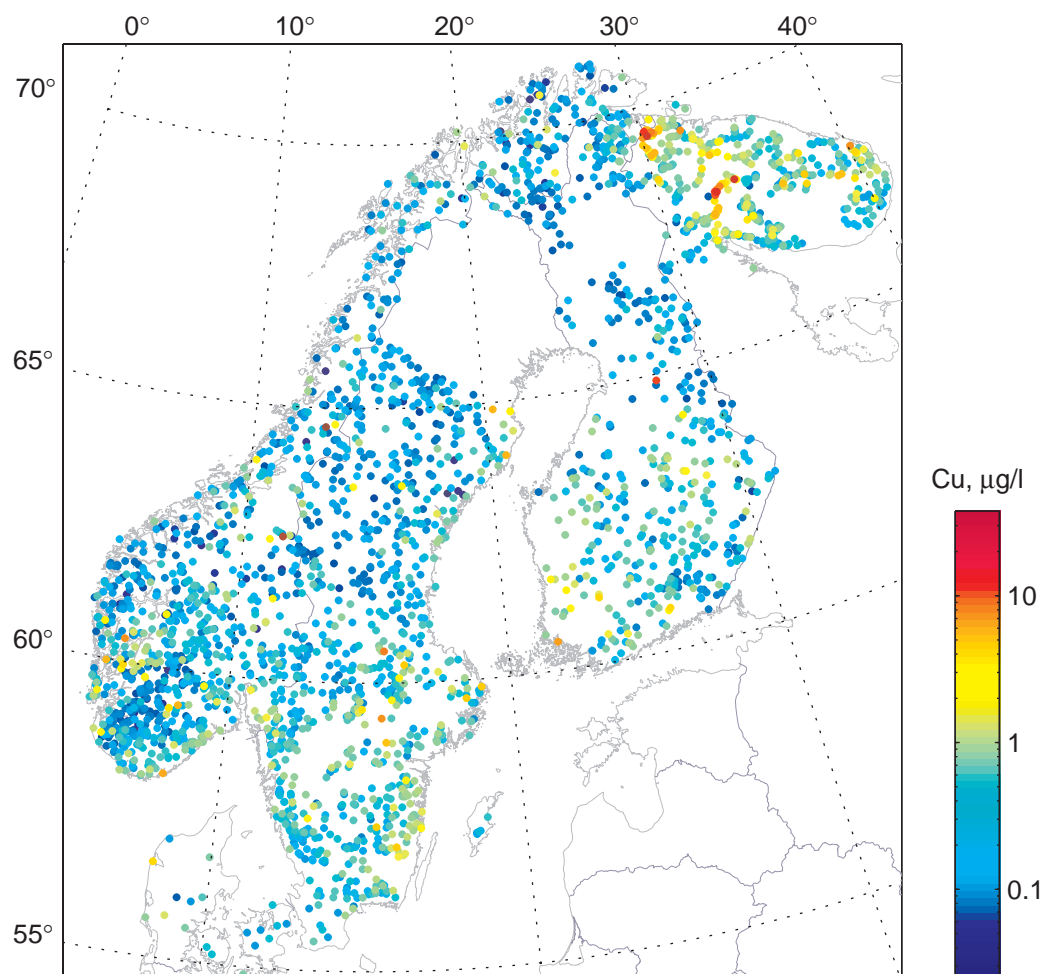


Figure 3.5 Cu concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.5 Weighted percentiles for Cu in the total lake population in Finland, Norway, Sweden and Kola. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Cu in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Cu-29		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	13.0	37.7	8.2	3.2	20.0
	99.5 %	2.73	3.0	4.6		18.4
	97.5 %	1.7	1.7	1.72		5.9
	90.0 %	1.0	0.90	0.99		2.9
quartile	75.0 %	0.67	0.52	0.62	0.9	1.3
median	50.0 %	0.42	0.33	0.36	0.6	0.73
quartile	25.0 %	0.25	<i>0.19</i>	0.23	0.5	0.45
	10.0 %	0.15	<i>0.12</i>	0.15		0.28
	2.5 %	0.10	<i>0.06</i>	0.09		0.14
	0.5 %	0.07	<i>0.04</i>	0.04		0.1
minimum	0.0 %	<i>0.07</i>	<i>0.03</i>	<i>0.02</i>	<0.1	0.1

3.6 Ni - Nickel

Major atmospheric sources of Ni are thermal power plants, especially oil burning, and more locally steel industry and smelters.

Large smelters on the Kola Peninsula are the most important Ni source in the study area with over 2460 tonnes/yr emissions (1990) to the atmosphere. In this area there is high concentrations of Ni in lakes close (30-40 km) to the smelters. The deposition of Ni is 50 mg/m²/year within 10 km from the smelters, decreasing to 5 mg/m²/year at 60 km. Up to 90 % of the Ni-deposition is bound and retained in the upper organic layer of the soils. In spite of high level of Cu deposition compared to Ni, the migration capacity of the latter in water is higher (Lukina and Nikonov, 1995).

The regional distribution and the concentration range for Ni are remarkably similar to those of Cu. These elements derive from similar geochemical sources and the anthropogenic emissions are often co-located. Regions with high concentrations are distinguished throughout the Kola Peninsula stretching to the

Finnish territory, in lowlands and coastal zone throughout southern Sweden and Finland and Denmark.

Nickel concentrations are distributed similarly in Sweden, Finland and slightly lower in Norway. Kola shows the same distribution as Sweden and Finland up to the 75-percentile, while from 75-100 percent, the Kola values are higher. Typical values range from 0.1 to 0.7 µg/L. Extreme values in Kola are not so frequent for Ni as for Cu.

Lakes with high values are scattered throughout the countries reflect geological sources, e.g. high Ni concentrations in eastern and southwestern Finland are correlated with Ni anomalies in the fine fraction of till (Salminen, 1995). Probably both the influence of atmospheric deposition from the Kola and Ni in parent till (further west) is seen as elevated Ni concentrations in northeastern Norwegian and Finnish lakes.

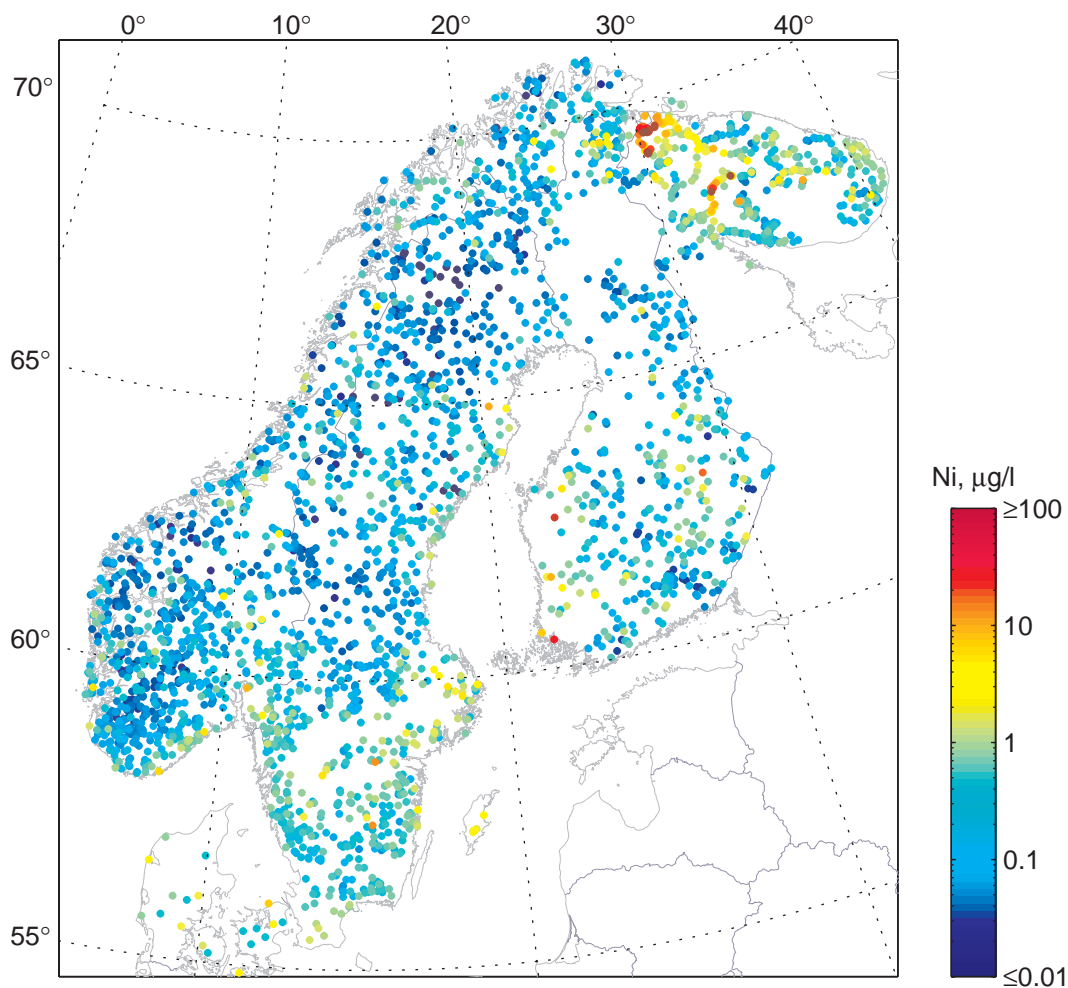


Figure 3.6 Ni concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.6 Weighted percentiles for Ni in the total lake population in Finland, Norway, Sweden and Kola. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Ni in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Ni-28		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	47.6	7.05	11.1	5.3	450
	99.5 %	7.01	3.17	5.74		50.4
	97.5 %	2.56	1.42	1.84		4.3
	90.0 %	1.18	0.69	0.90		1.7
quartile	75.0 %	0.64	0.44	0.59	2.56	0.72
	50.0 %	0.37	0.24	0.35	1.0	0.33
quartile	25.0 %	0.22	0.13	0.18	1.0	0.1
	10.0 %	0.14	<i>0.07</i>	0.09		0.1
	2.5 %	0.04	<i>0.03</i>	<i>0.04</i>		0.1
	0.5 %	<i>0.03</i>	<i>0.01</i>	<i>0.03</i>		0.1
minimum	0.0 %	<i>0.02</i>	<i>0.01</i>	<i>0.01</i>	<0.5	0.1

3.7 Co – Cobalt

Co in deposition is usually linked to soil dust and local pollution sources (Berg *et al.* 1994). The similarities in patterns between Co and the elements related to long-range air pollutants (Pb, Cd and Zn) are most probably due to increased leaching of Co due to acidification.

The geographical pattern of Co is very much resembles those of Pb, Cd and Zn with the highest values along the coast of southern Norway and southwestern Sweden.

Typical values of Co range from 0.02 – 0.1 µg/L. The distribution is very similar in all countries (including Denmark).

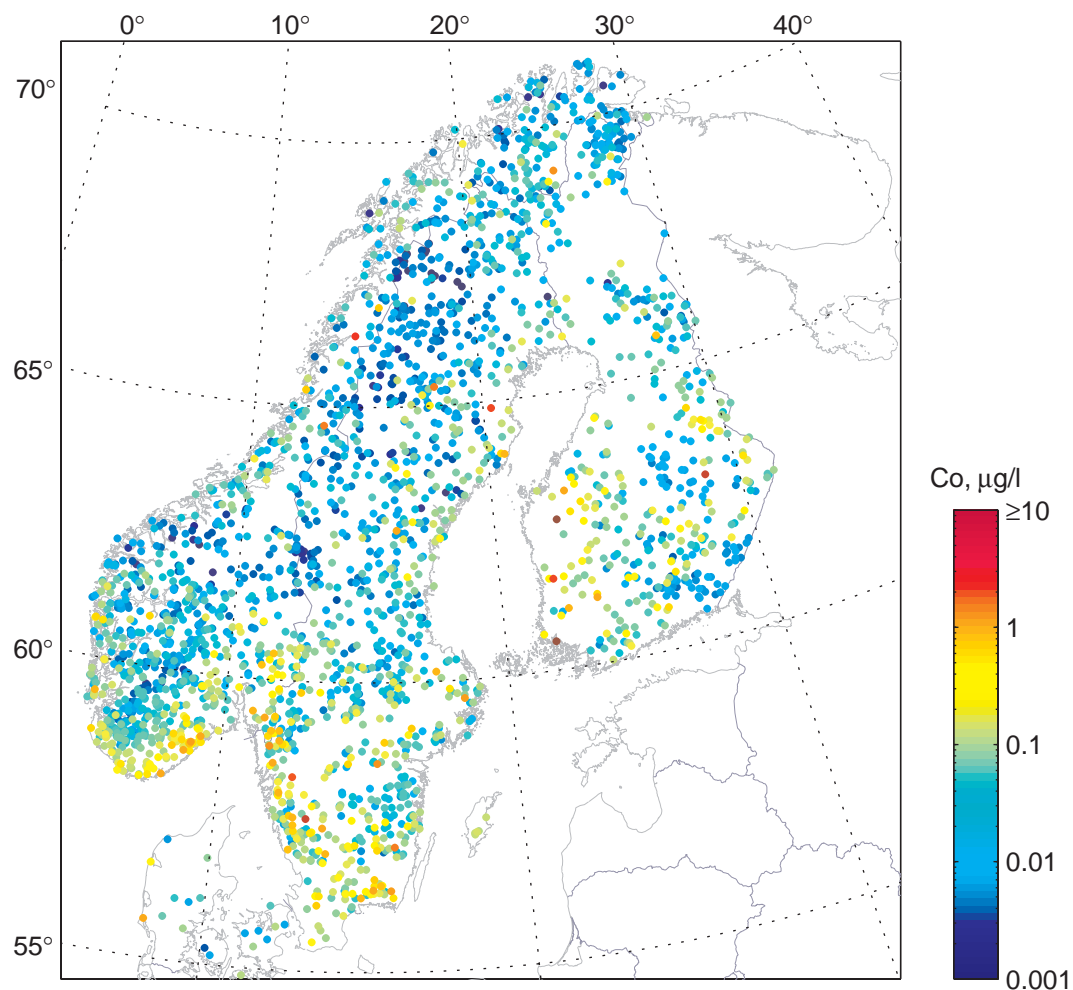


Figure 3.7 Co concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.7 Weighted percentiles for Co in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Co in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Co-27		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	20.3	3.2	5.5	0.79	
	99.5 %	2.4	0.96	1.4		
	97.5 %	0.43	0.41	0.65		
	90.0 %	0.25	0.17	0.26		
quartile	75.0 %	0.13	0.078	0.12	0.12	
	50.0 %	0.058	0.045	0.055	0.07	
quartile	25.0 %	0.030	0.021	0.025	0.05	
	10.0 %	<i>0.022</i>	<i>0.009</i>	0.009		
	2.5 %	<i>0.012</i>	<i>0.004</i>	<i>0.004</i>		
	0.5 %	<i>0.006</i>	<i>0.002</i>	<i>0.002</i>		
minimum	0.0 %	<i>0.001</i>	<i>0.001</i>	<i>0.001</i>	<0.05	

3.8 Fe – Iron

Fe is a major element and essential to all organisms. It is the most abundant heavy metal in the earth crust, and also in surface waters. Fe is distributed in the environment by windblown soil dust and emitted to the atmosphere mainly from iron and steel industry and iron mining. However, the regional pattern of Fe in lakes does not reflect the emissions or windblown dust, or the concentration in till (Lahermo *et al.* 1995a). The most important factor regulating the concentration of iron in surface waters is the amount of humic matter as a complexing and transporting agent (e.g. Perdue *et al.* 1976, Borg, 1987, Verta *et al.* 1990).

Fe occurs as Fe^{2+} (reduced) or Fe^{3+} (oxidised) in natural waters depending on the redox potential. Since the oxidation potential of the transition from Fe^{2+} to Fe^{3+} falls within the range found in natural waters, the concentration of Fe primarily depends on the redox-potential, water temperature and the concentration of organic ligands present. High

concentrations of Fe in surface water are common in areas draining catchments with high proportion of bogs due to low redox potential (anaerobic conditions). The regional pattern of Fe concentrations in the lakes therefore resembles the TOC pattern (Figure 1.1)

Typical values of Fe in lakes range from ca. 100 to 1000 $\mu\text{g/L}$ in Finland, from 50 to 600 $\mu\text{g/L}$ in Sweden, and from 15 to 150 $\mu\text{g/L}$ in Norway. The differences in Fe reflect the differences in TOC levels in lakes in the different countries. More than 10% of the lakes in Finland and Sweden have Fe-concentrations $> 1000 \mu\text{g/L}$. Maximum values in each country are probably in lakes influenced by ores and mining activities.

The highest concentrations of Fe are found in lowland areas in Finland, Sweden and eastern Kola, where organic rich peatland surround the lakes. The lowest values are found in alpine areas with thin soils and sparse vegetation.

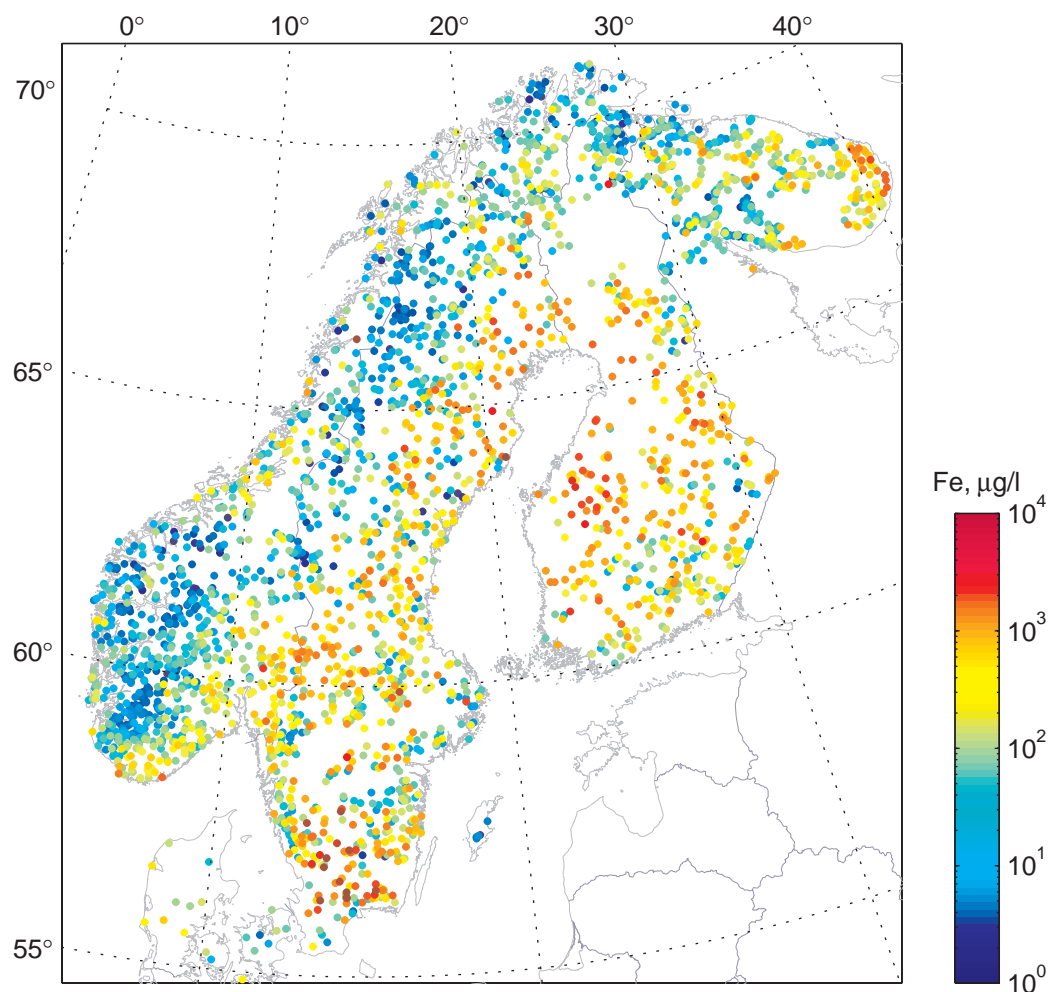


Figure 3.8 Fe concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.8 Weighted percentiles for Fe in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Fe in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Fe-26		Finland	Norway	Sweden	Denmark	Russian Kola
Quantiles						
maximum	100.0 %	3900	7680	10150	490	2500
	99.5 %	3635	1542	7663		1807
	97.5 %	2431	588	2385		1193
	90.0 %	1397	282	1162		529
quartile	75.0 %	839	136	586	231	236
median	50.0 %	412	53	213	129	92
quartile	25.0 %	150	17	53	76	36
	10.0 %	45	7.3	21		15
	2.5 %	15	2.9	4.1		6
	0.5 %	1.7	0.6	1.4		3
minimum	0.0 %	1.5	0.1	1.0	8	3

3.9 Mn – manganese

Mn is a common heavy metal in the earth crust, third abundant after Fe and Ti (titanium). On a global scale, roughly half of the Mn emissions to the atmosphere originate from wind blown soil particles (Nriagu and Pacyna, 1988). Anthropogenic Mn is emitted from non-ferrous metal industry and combustion processes.

The regional pattern of Mn in lakes shows a gradient from low values in western Norway and the alpine regions in Norway and Sweden to higher concentrations in lakes in Denmark, southern Sweden, southeastern Norway and eastern end of Kola. Scattered high values occur throughout the southern half of Finland. Typical values in Finland and Sweden range from 5 to 40 µg/L and from 1 to 10 µg/L in Norway and Kola.

The Mn pattern resembles the Fe pattern although the values are lower. Both Fe and Mn

are strongly related to organic matter, but in two different ways. Fe and Mn are released from Fe/Mn-oxides in bog areas where the redox potentials are so low that Mn and Fe are reduced to Fe^{2+} and Mn^{2+} . In the water Fe is strongly bound to humic substances, while Mn is free.

Headwaters in Scandinavia with high Mn concentrations are often characterised by low pH (e.g. Borg 1983, Mannio *et al.* 1993). In western Finland lake water acidity is often controlled by humic substances, and thus Mn concentration is elevated in the humus-rich, acid lakes of peatland areas.

The geochemical composition of bedrock and till seems to have a stronger impact on Mn than on Fe concentration in streams (Lahermo *et al.* 1995b).

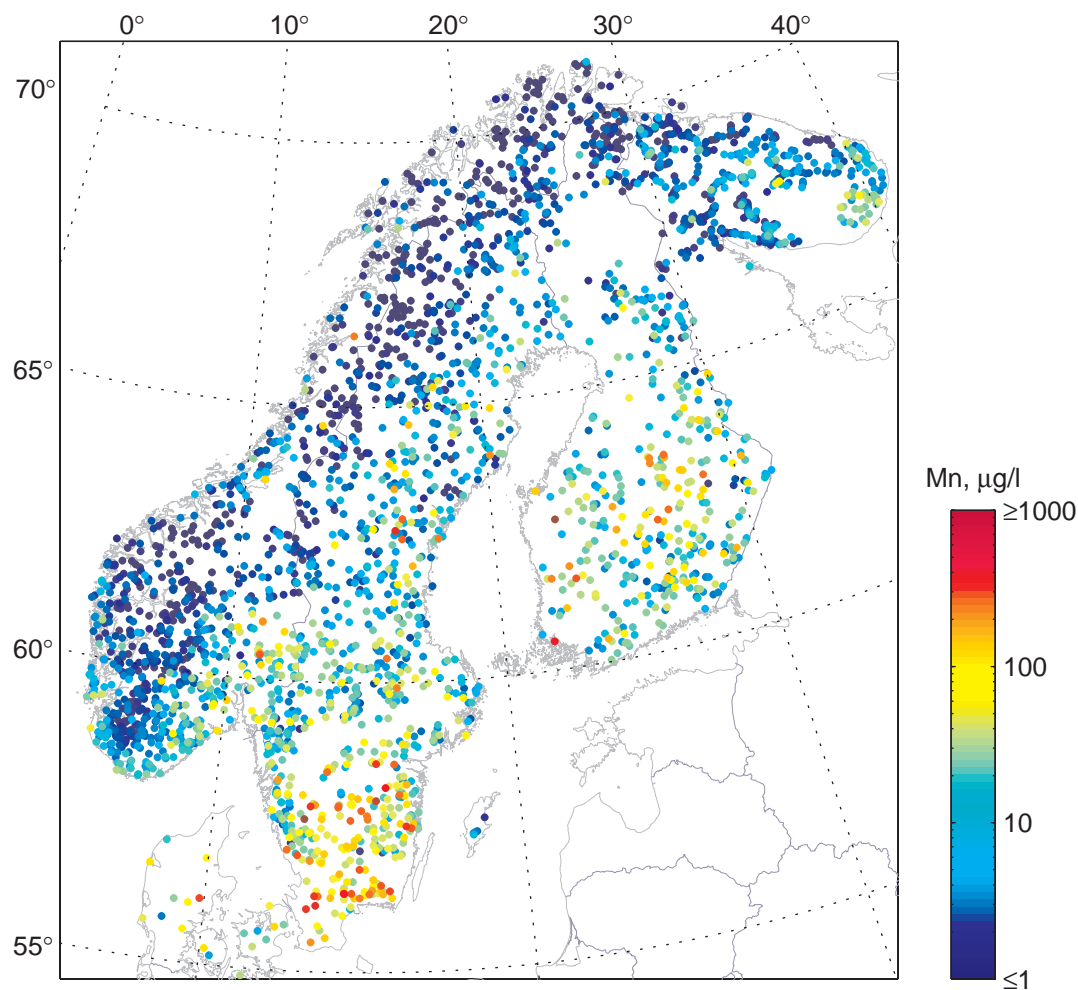


Figure 3.9 Mn concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.9 Weighted percentiles for Mn in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Mn in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Mn-25		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	2600	327	3530	364	77
	99.5 %	316	101	474		64
	97.5 %	117	52	276		38
	90.0 %	84	20	78		21
quartile	75.0 %	41	6.8	37	80	12
median	50.0 %	21	2.3	14	48	5
quartile	25.0 %	8.2	0.9	4.7	27	2
	10.0 %	2.9	0.4	1.5		1
	2.5 %	0.7	0.1	0.4		0.5
	0.5 %	0.2	0.0	0.1		0.2
minimum	0.0 %	0.0	0.0	0.0	6	0.2

3.10 Cr – Chromium

The prominent anthropogenic emission sources of Cr include combustion of coal and fuel oils and the production of iron and steel. On a global scale, more than half of the Cr emissions to the atmosphere comes from wind blown soil particles (Nriagu and Pacyna 1988). Ferrochrome and stainless steel plants e.g. in Finland are, even after major emission reductions, the most important point sources of Cr to the atmosphere (Mukherjee 1998). A major point source in Norway is the ferrochrome smelter in Mo i Rana, northern Norway.

The geographic distribution of Cr in Nordic lakes is more similar to the distribution of the soil derived elements Mn and Fe, and less similar to the geographic distribution of the heavier and more anthropogenic influenced elements.

The Cr concentrations are generally higher in Finland than in Sweden and much higher than

in Norway. Typical values are from 0.2 to 0.5 µg/L in Finland and 0.03 to 0.15 in Norway. This is most probably due to the fact that elevated Cr concentrations are found in brown coloured, humic lakes. Lowland humic lakes are abundant in western and central eastern Finland. Most of the Cr in these areas is derived from geological sources.

Near the southern coast of Finland, atmospheric sources are also likely. Cr anomalies around the fine steel industries in Tornio are hardly detectable in lakes, in comparison to the moss surveys (Rühling *et al.* 1992, Rühling and Steinnes, 1998). The high values > 1 µg/L in lakes on the western coast of Norway in the Hardangerfjorden area, are most probably due to the mineralogy of the bedrock. One lake with high Cr-concentration is found close to the ferrochrome smelter in Mo i Rana.

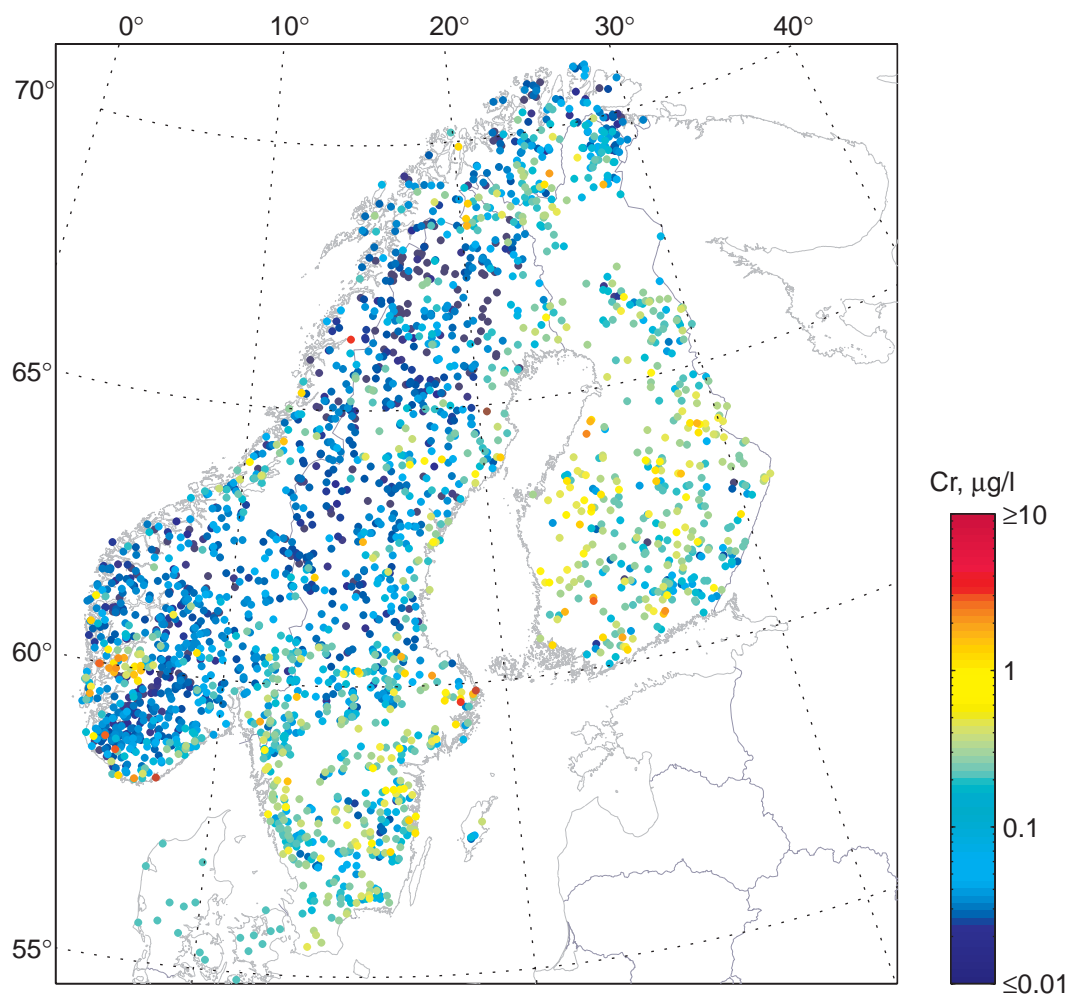


Figure 3.10 Cr concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.10 Weighted percentiles for Cr in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of Cr in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

Cr-24		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	2.83	6.14	27.7	0.5	
	99.5 %	2.11	2.05	1.35		
	97.5 %	1.23	0.93	0.78		
	90.0 %	0.68	0.31	0.46		
quartile	75.0 %	0.46	0.14	0.28	<0.5	
	50.0 %	0.29	<i>0.070</i>	0.13	<0.5	
quartile	25.0 %	0.19	<i>0.035</i>	<i>0.044</i>	<0.5	
	10.0 %	0.10	<i>0.016</i>	<i>0.025</i>		
	2.5 %	<i>0.030</i>	<i>0.008</i>	<i>0.010</i>		
	0.5 %	<i>0.007</i>	<i>0.003</i>	<i>0.005</i>		
minimum	0.0 %	<i>0.007</i>	<i>0.001</i>	<i>0.003</i>	<0.5	

3.11 V - Vanadium

V is relatively common metal in the earth's crust. Combustion processes, especially oil, in industry and power plants are the most important atmospheric emission sources of V.

The deposition pattern of V is dominated by long-range transport (Rühling and Steinnes, 1998).

The regional patterns of V in lakes in the Nordic countries is very similar to that of Cr. Typical values range from 0.1-0.7 µg/L in Finland, 0.06-0.3 µg/L in Sweden and 0.05-0.2 µg/L in Norway. Humic-rich lakes generally have higher V concentrations.

Cr, As and V all show a very clear anomalies south of Hardangerfjorden at the western coast of Norway, probably due to the mineralogy of bedrock and overburden.

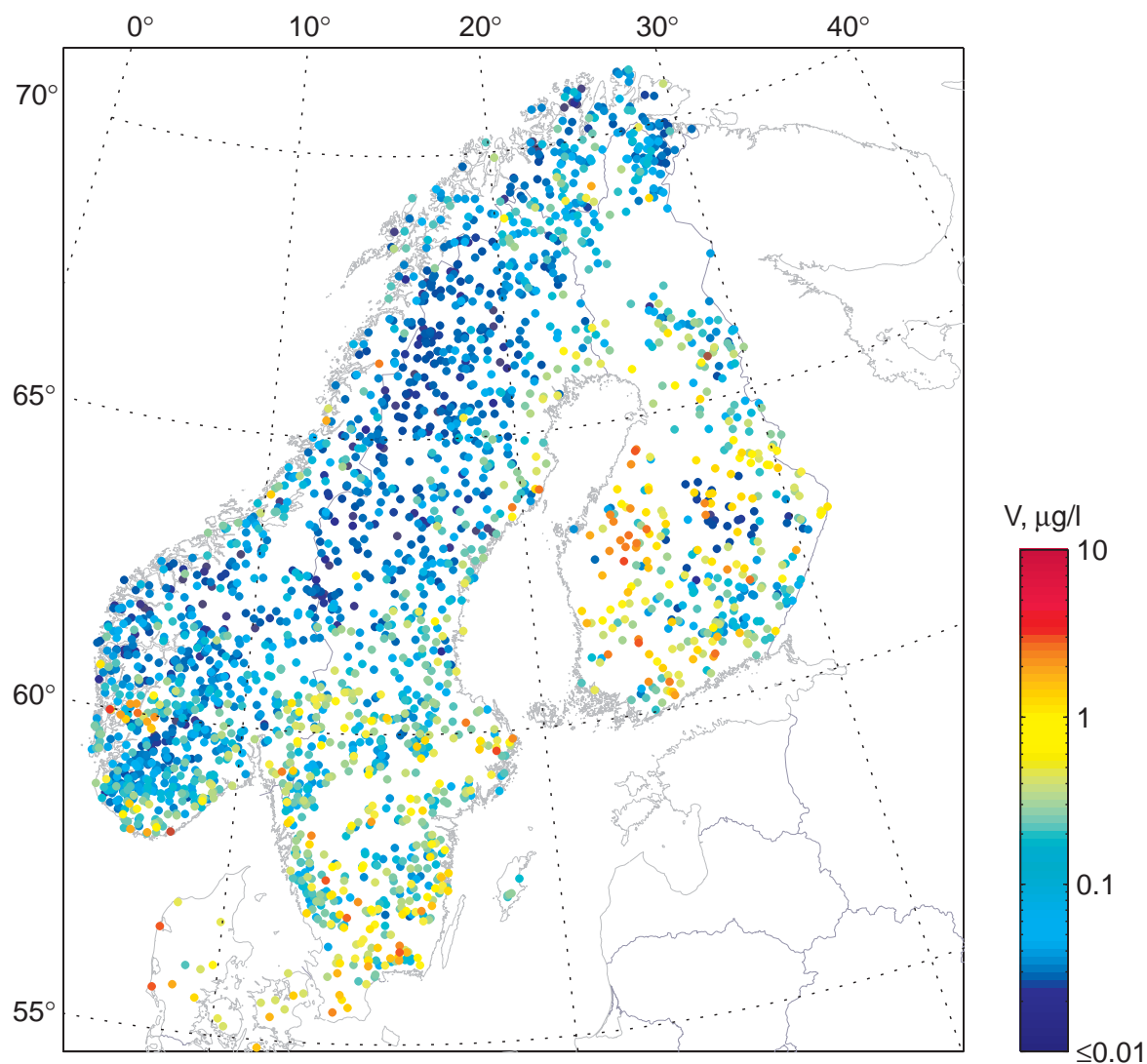


Figure 3.11 V concentration ($\mu\text{g/l}$) in lakes in the Nordic countries autumn 1995 (Denmark autumn/winter 1996)

Table 3.11. Weighted percentiles for V in the total lake population in Finland, Norway and Sweden. For Denmark, the numbers are based on only 19 not-statistically selected lakes, and are therefore only indicative of the general levels of V in Danish lakes. The imputed numbers under the analytical detection limit are showed in italic.

V-23		Finland	Norway	Sweden	Denmark	Russian Kola
maximum	100.0 %	8.34	5.92	3.68	3.3	
	99.5 %	3.13	2.23	2.50		
	97.5 %	2.25	0.72	1.09		
	90.0 %	1.08	0.33	0.61		
quartile	75.0 %	0.68	<i>0.20</i>	0.31	1.2	
median	50.0 %	0.29	<i>0.10</i>	0.15	1.0	
quartile	25.0 %	0.13	<i>0.05</i>	0.06	<1	
	10.0 %	0.04	<i>0.03</i>	0.03		
	2.5 %	0.03	<i>0.01</i>	0.02		
minimum	0.5 %	0.02	<i>0.006</i>	0.009		
	0.0 %	0.01	<i>0.003</i>	0.007	<1	

3.12 Summary of concentration distribution

Log-normal distribution of all elements from Finland, Norway, Sweden and Kola are given in figure 3.12-3.14.

show the 0.5, 2.5 and 10percentiles while the vertical liners on the high (right) end show the 90, 97.5, and 99.5 percentile. The dots show all the observed values.

The “box” show the 25, 50 and 75 percentiles, while the vertical lines on the low (left) end

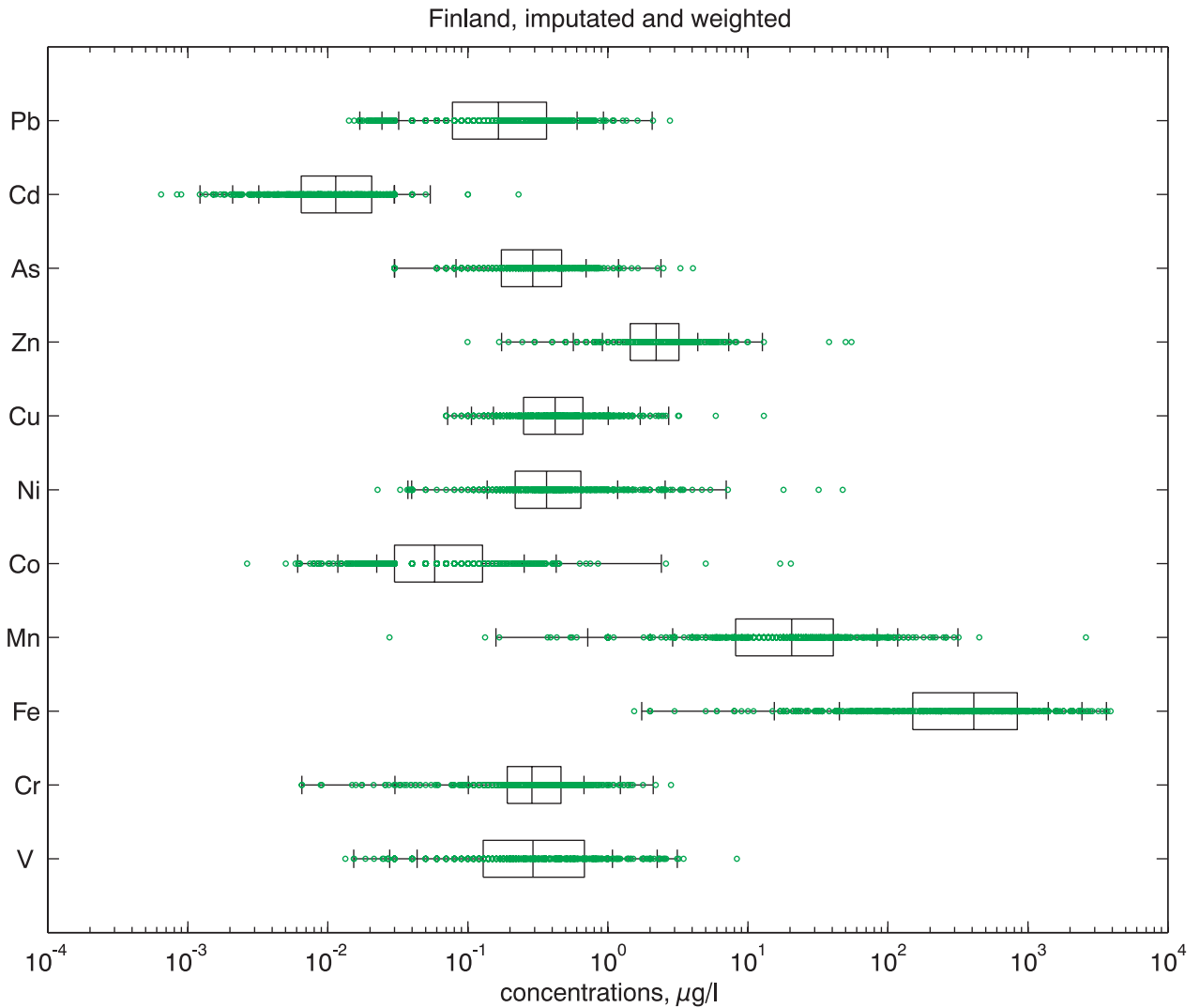


Figure 3.12 Box- and whisker plot of imputed and weighted data for Finland. As is not imputed (but weighted)

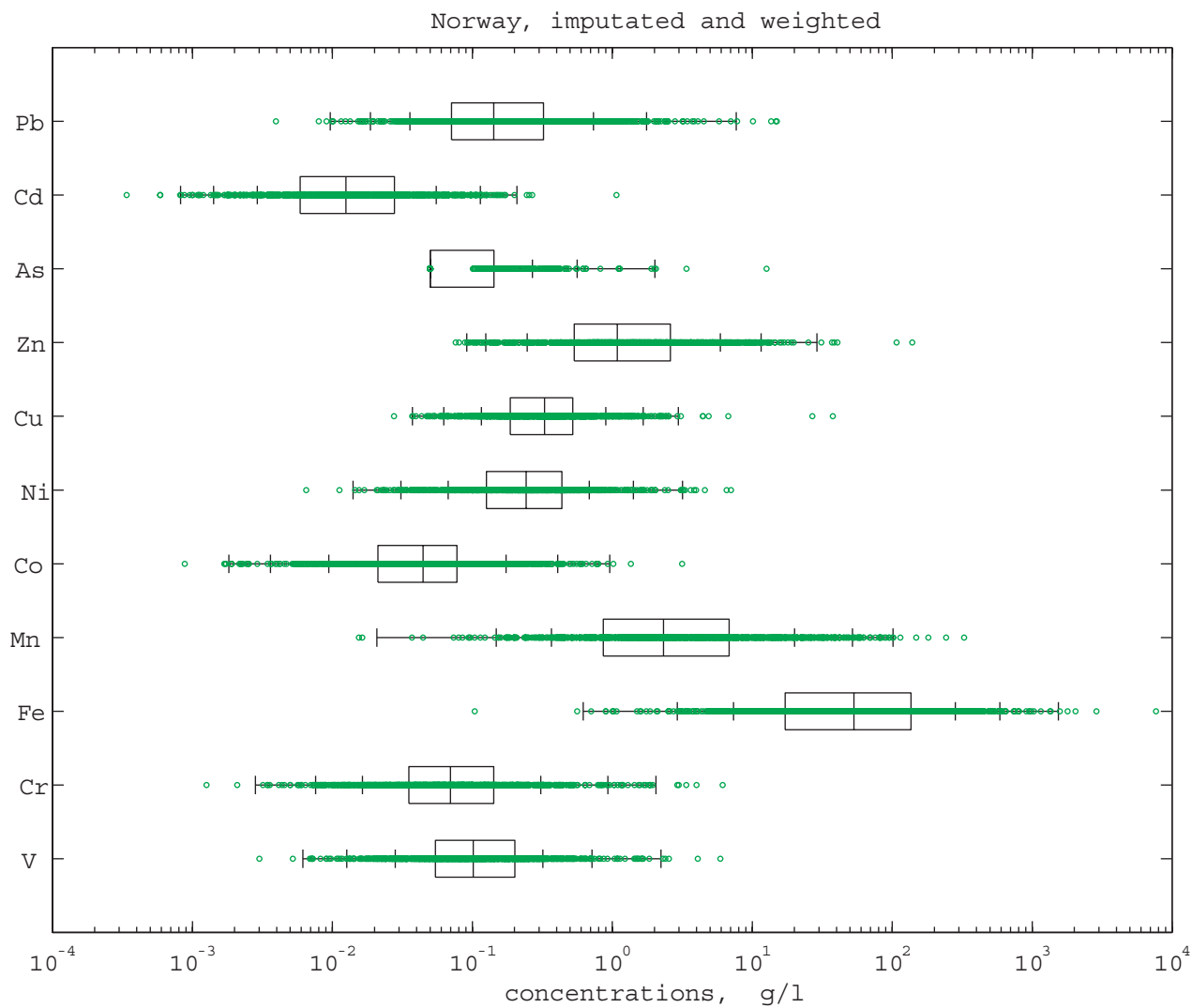


Figure 3.13 Box- and whisker plot of imputed and weighted data for Norway. As is not imputed and not weighted.

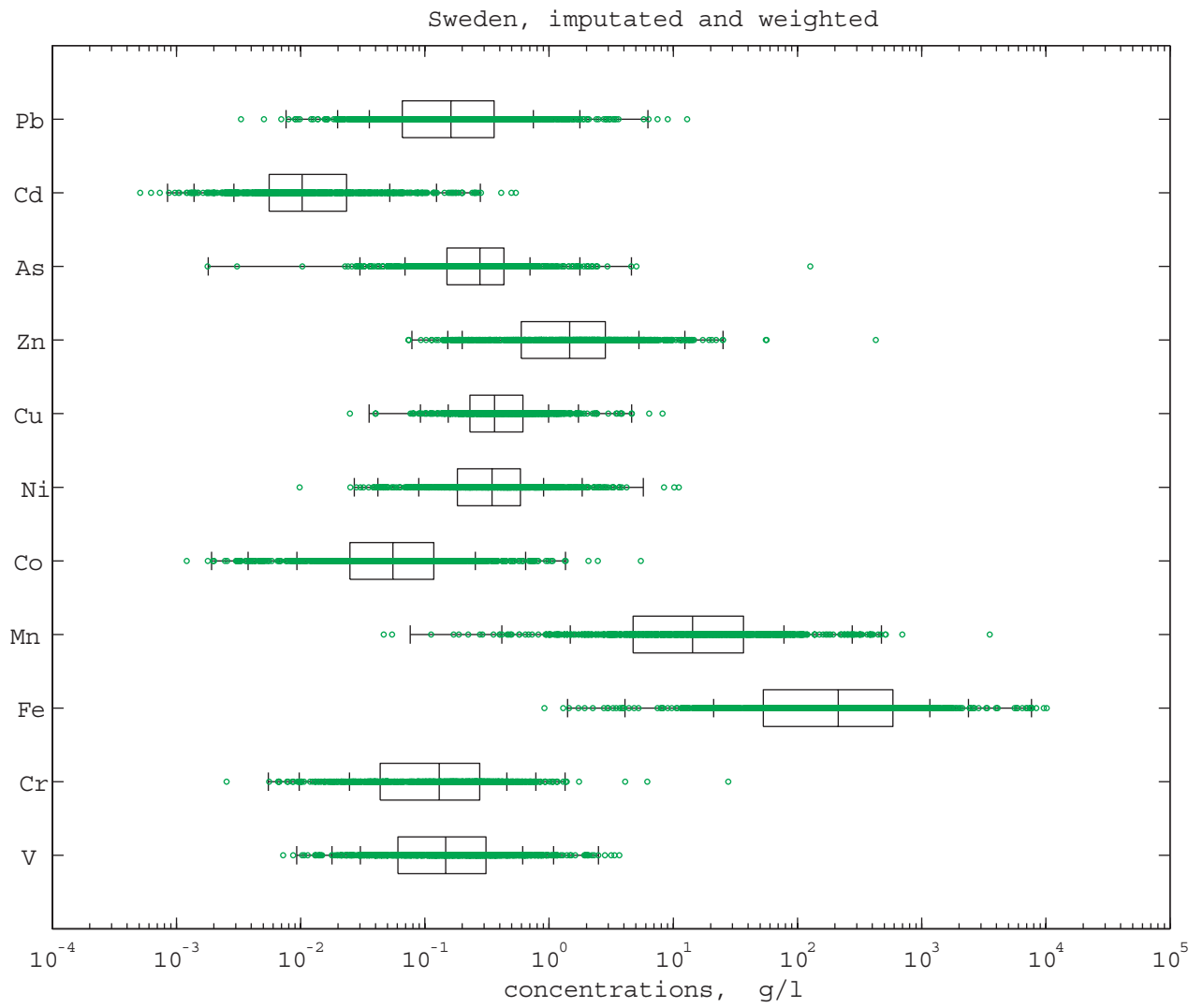


Figure 3.14 Box- and whisker plot of imputed and weighted data for Sweden. As is not imputed (but weighted).

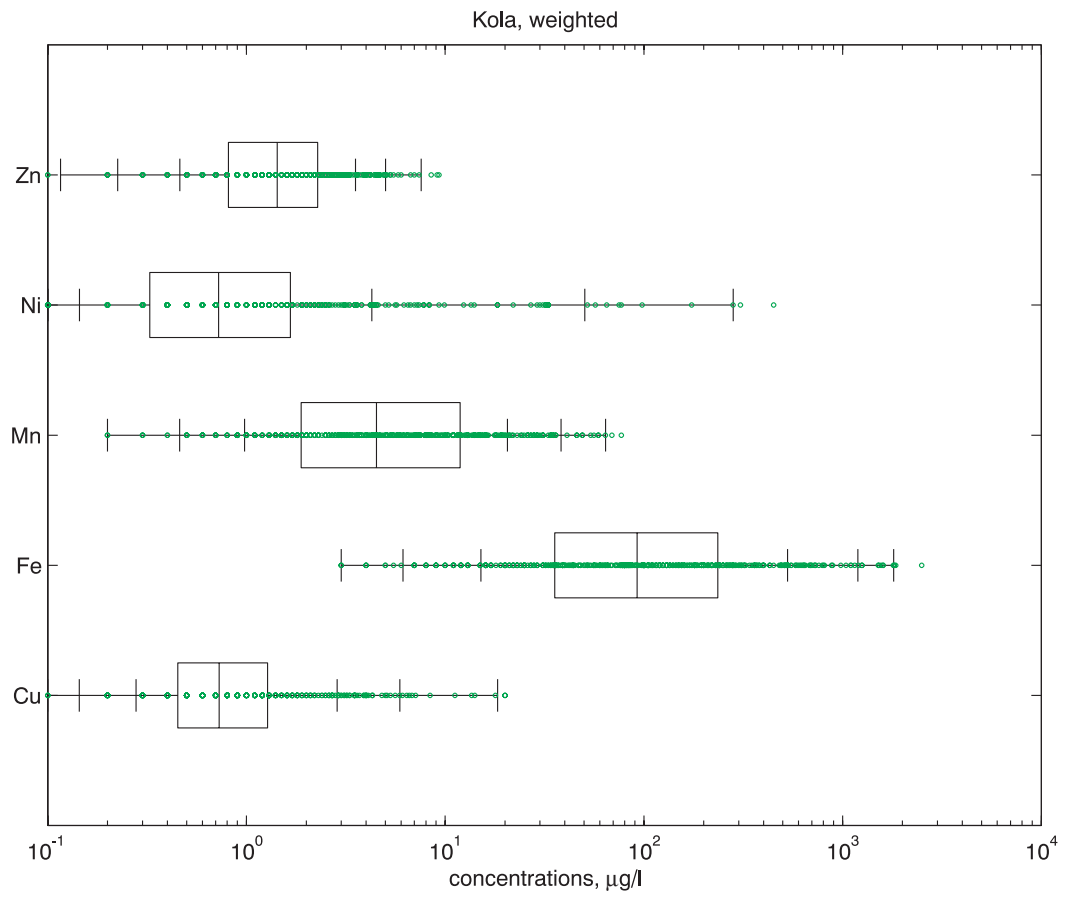


Figure 3.15 Box- and whisker plot of weighted data for Kola. These data are not imputed.

4. Statistical analysis of the element distribution

In this section we have used statistical techniques to investigate the data with regard to:

- relations between the elements
- relations to explanatory variables
- relations between ecoregions

The statistical analysis is performed on the imputed dataset for Finland, Sweden and Norway (see 2.4.2 and Appendix A) and only for the 10 elements Pb, Cd, Zn, Cu, Ni, Co, Mn, Fe, Cr and V.

4.1 Relation between the elements

Correlation analysis

Correlation analysis between log-transformation of the 10 elements (Table 4.1, Figure 4.1) show that all correlations are positive and that all the correlations are statistically significant ($p < 0.01$). This observation itself is very interesting, in that there seems to be one or some few common factors that are very important for the concentration levels of all the 10 elements investigated.

Table 4.1 Correlation coefficients between the elements involved in the statistical analysis. The calculation is performed on the log-transformed values in the imputed dataset based on 2678 observations from Finland, Norway and Sweden. All correlations are significant on $p < 0.01$

	ln(V)	ln(Cr)	ln(Fe)	ln(Mn)	ln(Co)	ln(Ni)	ln(Cu)	ln(Zn)	ln(Cd)	ln(Pb)
ln(V)	1.0000	0.7387	0.7053	0.5555	0.6744	0.4853	0.4928	0.4550	0.2235	0.5182
ln(Cr)		1.0000	0.5828	0.5040	0.5188	0.5764	0.5183	0.3920	0.1816	0.2732
ln(Fe)			1.0000	0.7160	0.6257	0.4255	0.3682	0.4213	0.2022	0.4203
ln(Mn)				1.0000	0.6340	0.4876	0.3981	0.4445	0.1703	0.3468
ln(Co)					1.0000	0.6083	0.4635	0.6029	0.3584	0.5398
ln(Ni)						1.0000	0.6459	0.3135	0.1641	0.1200
ln(Cu)							1.0000	0.4074	0.3112	0.2786
ln(Zn)								1.0000	0.6147	0.6874
ln(Cd)									1.0000	0.5314
ln(Pb)										1.0000

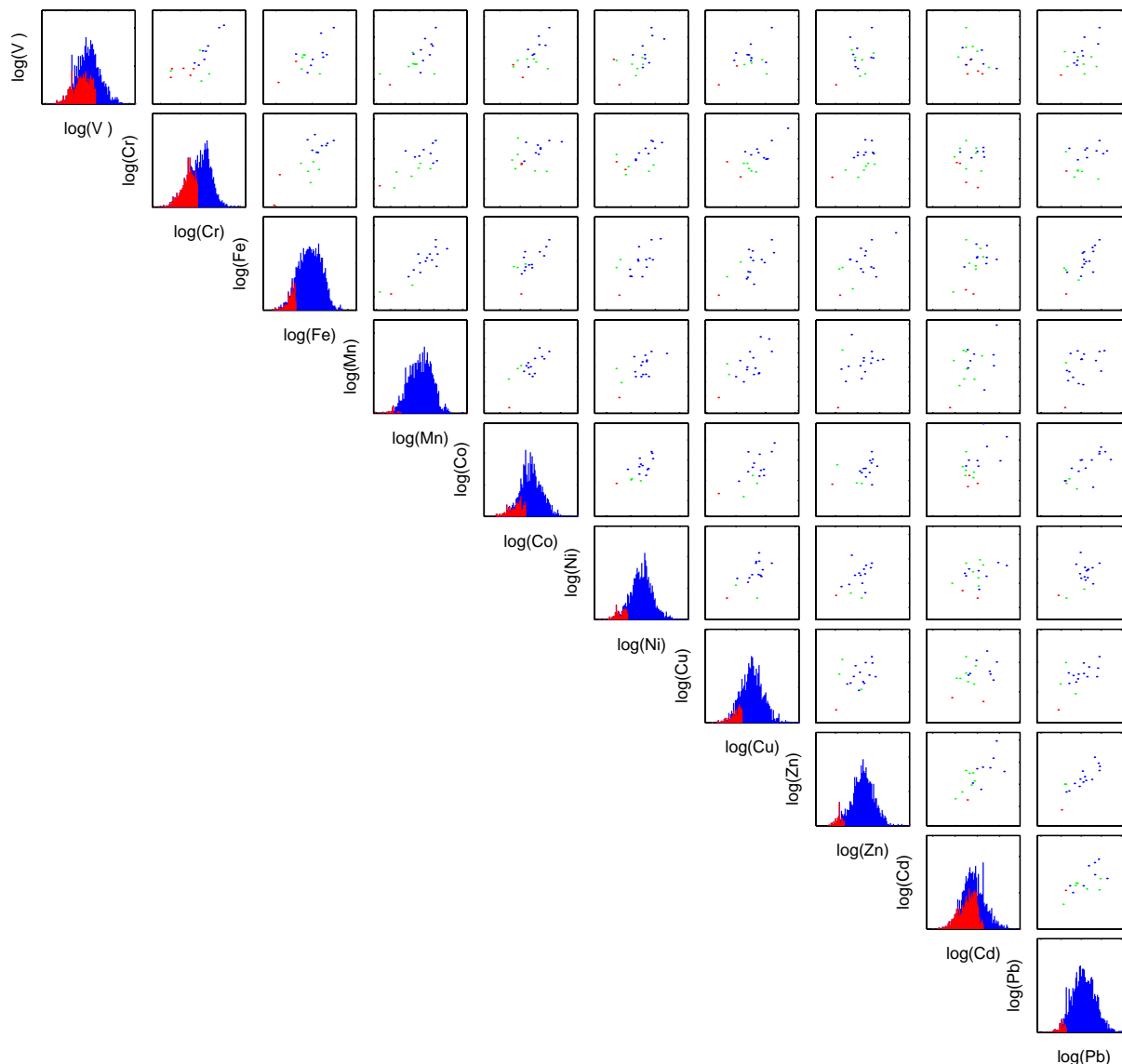


Figure 4.1 Scatter plot matrix of the data in the imputed dataset. Blue dots: uncensored observations, green dots: singly imputed observations, red dots: doubly imputed observations. Univariate distributions of uncensored (blue) and imputed (red) observations on the diagonal.

Principal component analysis (PCA)

The results of the PCA are shown in Table 4.2 and the results are projected into a biplot in Figure 4.2. The table shows that the cumulative fraction of total variance increases gradually from axis F1 to F7 with no distinct cutoff. This means that it is not possible to identify some few axis that describe most of the variance in the dataset. The first axis describes about 50% of the total variance in the

dataset, while the second axis describes about 15% and the next axes < 10% each.

In the first factor (F1) (Table 4.2) all the elements have about the same (low) loading. This is a consequence of what is shown in table 4.1, that there is a positive relationship between all the elements. The interpretation of this is that there is some common factor that is

important for the concentration levels of all heavy metals in lakes.

The second factor (F2) contains strong loading on Pb, Cd and Zn. The next factors are loaded on Ni and Cu (F3), Mn and Co (F4) and Cr, Fe and Mn (F5). Each of these axes explains very little of the variation in the total dataset, and interpretation of these axes may not be very meaningful.

The projection of the PCA to a biplot (Figure 4.3) shows that three main groups of elements can be identified;

- Fe and Mn
- Cd, Pb and Zn,
- Cu, Ni, Cr, Co and V

Fe and Mn show a very strong loading on PCA-axis 1. As concentrations of Fe and Mn in lakes are dependent on TOC, this first axis

can be interpreted to be controlled by the influence of TOC. Cd, Pb and Zn have a strong loading on PCA-axis 2. These elements are known to be very influenced by deposition of long-range transported air pollutants, either directly or indirectly, and therefore this axis are interpreted to be controlled by the influence of long-range transported air pollutants. Cd, Pb and Zn also have a low but positive loading on PCA-axis 1. The third group of elements Cu, Ni, Cr, Co and V shows a loading close to zero on PCA-axis 2, Ni and Cr on the negative side while Co is most positive, indicating an influence of long-range transport for this element, either directly or indirectly. All elements show positive loading on PCA-axis 1, Cu and Ni very low, while Co, V and Cr is more positive, indicating an influence of TOC for all the elements investigated here.

Table 4.2 Principal component analysis (PCA) of the 10 elements of the imputed dataset from Finland, Norway and Sweden. The first 7 axis are shown. The values in bold are those elements that explains most of the variance on axis.

	F1	F2	F3	F4	F5	F6	F7
ln(V)	0.36	-0.13	-0.21	-0.47	-0.14	-0.02	0.21
ln(Cr)	0.33	-0.27	0.04	-0.53	0.29	-0.30	-0.37
ln(Fe)	0.34	-0.45	-0.42	0.07	0.33	0.15	0.34
ln(Mn)	0.33	-0.17	-0.30	0.54	0.28	0.23	-0.27
ln(Co)	0.37	0.01	-0.07	0.28	-0.44	-0.36	0.22
ln(Ni)	0.30	-0.34	0.45	0.26	-0.20	-0.32	0.10
ln(Cu)	0.29	-0.14	0.58	-0.08	-0.02	0.68	0.05
ln(Zn)	0.32	0.42	0.07	0.10	-0.05	-0.07	-0.65
ln(Cd)	0.21	0.56	0.31	0.04	0.56	-0.24	0.38
ln(Pb)	0.28	0.48	-0.21	-0.19	-0.41	0.27	0.07
eigen value	5.2	1.5	0.9	0.6	0.4	0.4	0.3
% var	52.3	15.0	9.4	5.9	4.4	4.0	3.3
% cum	52.3	67.3	76.7	82.7	87.0	91.0	94.3

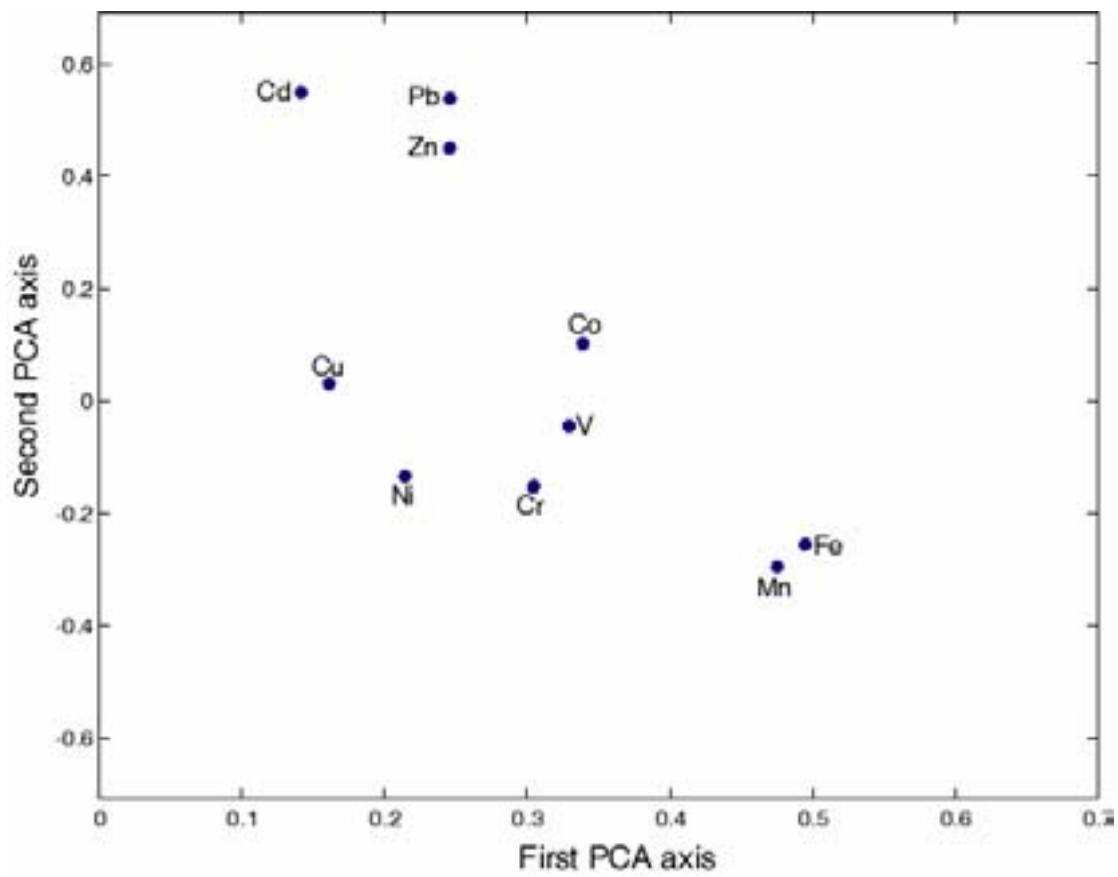


Figure 4.2 Biplot of the Principal component analysis of the 10 elements in the log-normal imputed dataset from Finland, Norway and Sweden. (Note that this is not a biplot of the to first axis F1 and F2, but a projection of all the 10 F-axis into a 2-dimensional plot).

4.2 Relation to explanatory variables

In the redundancy analysis (RDA) we try to relate the variance in the dataset to some explanatory variables. The RDA was first performed with many explanatory variables to ensure that we did not overlook any possible relationship. These were pH, TOC, Ca+Mg, Cl, NO₃, SO₄, S-deposition, N-deposition and runoff. This analysis showed that Cl explain very little and runoff was inversely related to Ca+Mg and therefore the influence of runoff could be “included” with Ca+Mg. NO₃ was very closely related to N-deposition and also N-deposition and S-deposition were also very closely related. We therefore chose S-deposition to represent the influence of long-range transport. SO₄ was very closely related to TOC, but explained very little (short vector).

S- and N-deposition and runoff are from national databases as described in Henriksen *et al.* (1997, 1998) as well as water chemistry data.

Based on the findings from the study of the geographical maps and the PCA and the introductory RDA we chose four main explanatory variables to be tested in a RDA:

1. influence of long-range transported air pollutants expressed by deposition of S
2. influence of weathering expressed by concentration of non-marine Ca+Mg
3. influence of organic matter expressed by TOC
4. influence of acidification expressed by H⁺

The RDA-analysis could also have used other explanatory variables such as catchment

characteristics and heavy metal deposition. Unfortunately, these data were not available for the full dataset, and could therefore not be used. Point sources and geological anomalies will not be described in a statistical model, as the large-scale patterns will dominate. Due to lack of data on bedrock geology in the catchments, it is not possible to analyse regional differences in lake water chemistry due to bedrock geology. However, we think we have chosen the four variables that will explain most of the regional variance in the total dataset.

The input variables do not have a normal distribution, and there is also a certain degree of correlation amongst them. Output of the RDA (Figure 4.3, bottom panel) shows orientation of all the four explanatory variables. The scatterplot (Figure 4.3 upper panel) show how much each of the explanatory variables contributes to each of the axis. The first RDA axis is dominated by the influence of TOC ($r = 0.84$). This reflects a strong positive relationship between TOC and all the metals included in the analysis, in particularly Fe and Mn. This axis explains nearly 80% of the variance in the log-transformed dataset. The second RDA axis is dominated by the influence of H^+ ($r = 0.92$) and to a certain degree S-deposition ($r = 0.62$). This is logic as there is relation between S-deposition and pH in lake waters. Low pH is also due to high

content of TOC, but acidification due to acid deposition is pressing pH even lower than pH in high TOC lakes (Lydersen, 1998). The second RDA axis indicates a strong positive relationship between H^+ (S-deposition) and Cd, Zn, and Pb. Non-marine Ca+Mg have a strong negative correlation to this axis ($r = -0.78$). Concentration of non-marine Ca+Mg is positive related to weathering rates and negative to runoff. High weathering rates gives high concentrations, while high runoff dilutes the concentrations. The negative correlation between Ca+Mg and H^+ can be explained with that acidification is most common in areas with low buffer capacity (low weathering rates of Ca and Mg). RDA-axis 2 explains about 15% of the variance in the log-transformed dataset.

In the end, the results of the RDA were tested with a Monte Carlo permutation test, showing that the RDA relationship was significant on <1% level.

The two first axes describe 95% of the variance that can be described with RDA. But since the RDA-analysis is based on output from the PCA which again do not describe the total variance in the dataset, it is estimated that the RDA-analysis performed here describe only about 40% of the total variance in the log-normal dataset.

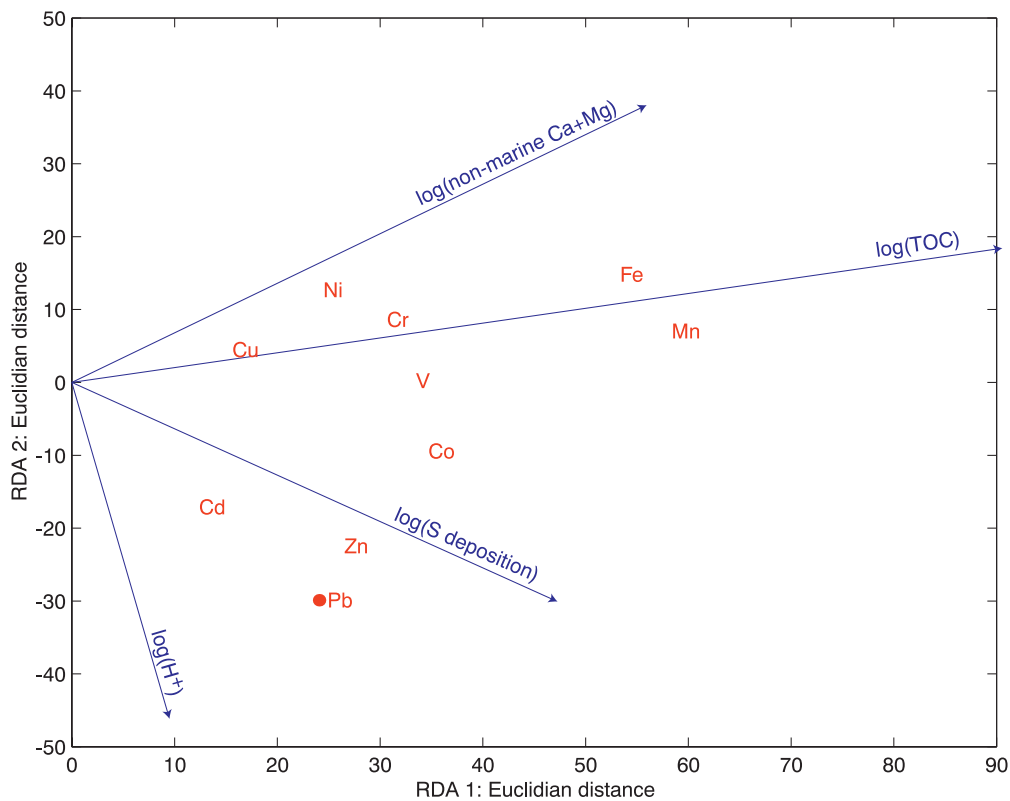
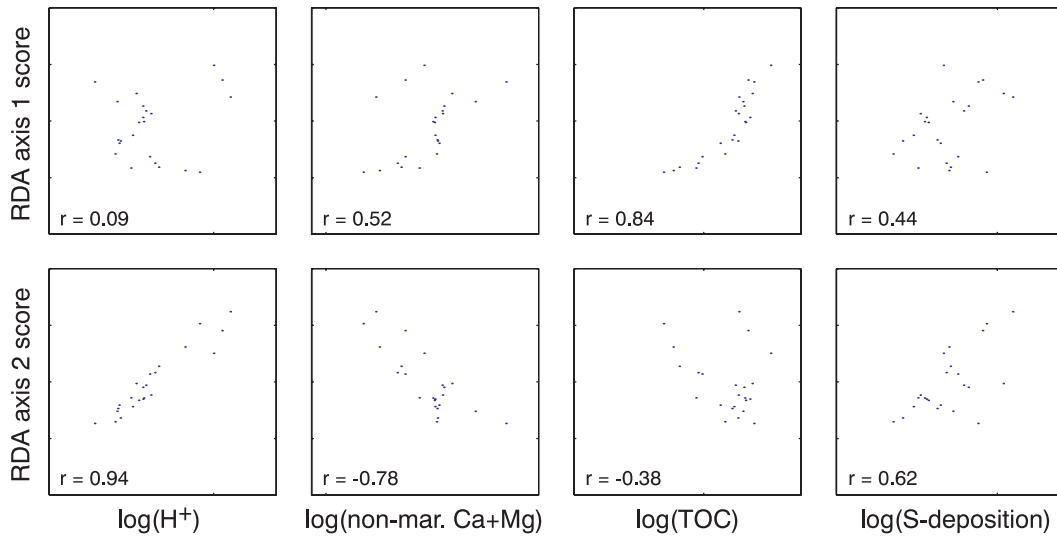


Figure 4.3 Output of the RDA . All variables are log-transformed.

Upper panel: Biplot of each of the explanatory variables (H^+ , non-marine Ca+Mg, TOC and S-deposition) against score on RDA-axis 1 and 2.

Bottom panel: RDA-ordination diagram. Dependent variables are indicated by points, whereas the independent variables are indicated by arrows (vectors). Vectors pointing roughly in the same direction indicate that the variables are positively correlated, vectors crossing at right angles indicate near-zero correlation, and vectors pointing in opposite directions indicate high negative correlation. The length of the vectors indicates the importance of the variables in the analysis; the longer the vectors the more confident one can be about the inferred correlation.

The scores from RDA-axis 1 and RDA-axis 2 (Figure 4.4) show very distinct geographical patterns. RDA-axis 1 show a gradient from low loading (blue) in Norway in the mountain areas, to high loading (yellow and red) in eastern Norway, southern Sweden and Finland. This correlates very well with the regional

picture of TOC (see Figure 1.1). RDA-axis 2 shows a gradient from high score in southern Norway, along the Swedish west coast, decreasing north and eastwards. This axis is defined by H^+ , and is describing acidification, which again is strongly related to long-range transported air pollutants.

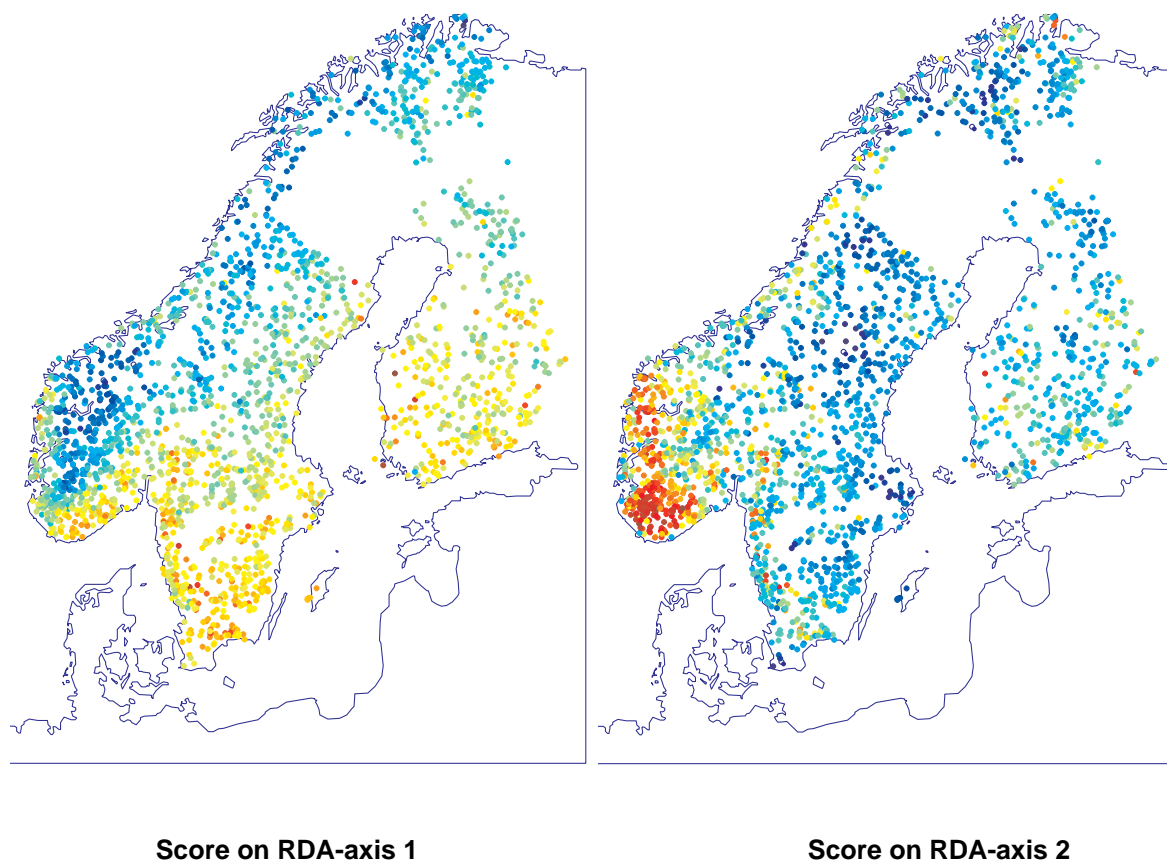


Figure 4.4 Loading of RDA-axis 1 and RDA axis 2 for each single lake in the investigated dataset. Red and orange values indicate high score while green and blue indicates low score.

4.3 Ecoregions – physical geographical region

Mostly due to the large variation in climate, the Nordic countries are covered by very different vegetation, from nemoral deciduous forest in south, to alpine zones in mountainous areas. The Nordic countries are divided into 76 physical geographical regions (eco-regions) (NMR, 1984). These 76 regions can be joined to 11 major zones (Table 4.3, Figure 4.5).

All the lakes in the imputed dataset were coded to one ecoregions. The percentiles for each of the elements in each region are shown in figure 4.6 and the median value for each element in each region are shown in table 4.3.

The difference in heavy metal distribution between the regions was tested statistically with one-way ANOVA. Due to the high number of observations, many of the regions

showed statistical significant differences, even if the differences in distribution are very small. However, there are some patterns that can be detected. In general, the alpine regions (Arcto-alpine and Alpine) and the Northern Boreal region show the lowest or low median values for all the heavy elements, while the South Boreal, Boreo-Nemoral and Nemoral regions in general show the highest or high median values for all heavy metals. Fe and Mn show the largest range in median value from the highest median values in Middle Boreal zone to the lowest values in the Alpine zone; Fe differs by a factor of 16 and Mn by a factor of 75.

The highest median values of Pb and Cd are found in the southernmost zones (Nemoral, Ocean South Boreal and Boreo-Nemoral) where we also find the highest input of long-range transported air pollutants.

Table 4.3 50-percentile for each of the elements in each of the eco-regions. Unit: $\mu\text{g/l}$

Ecoregion	n	Pb	Cd	Zn	Cu	Ni	Co	Mn	Fe	Cr	V
		$\mu\text{g/l}$									
Nemoral zone	43	0.38	0.012	2.48	0.52	0.59	0.145	59.8	167	0.27	0.30
Ocean South Boreal	222	0.26	0.015	1.84	0.30	0.22	0.055	3.6	35	0.07	0.11
Boreo-Nemoral zone	390	0.28	0.015	2.68	0.63	0.61	0.113	31.2	196	0.22	0.27
South Boreal zone	333	0.20	0.012	2.16	0.54	0.42	0.052	23.1	300	0.24	0.24
Ocean M Boreal zone	24	0.12	0.011	0.86	0.40	0.22	0.049	1.5	48	0.06	0.12
Middle Boreal zone	402	0.19	0.012	1.78	0.35	0.30	0.060	16.0	429	0.19	0.21
N-S Boreal zone	155	0.17	0.014	2.01	0.37	0.30	0.052	7.5	102	0.07	0.11
North Boreal zone	185	0.06	0.007	0.90	0.25	0.26	0.030	3.0	86	0.11	0.10
Alpine zone	414	0.13	0.011	1.14	0.29	0.17	0.031	2.2	26	0.05	0.07
Arcto-alpine zone	121	0.05	0.008	0.47	0.29	0.30	0.028	0.8	47	0.07	0.08



Figure 4.5 Simplified map showing location of the ecoregions (after NMR, 1984)

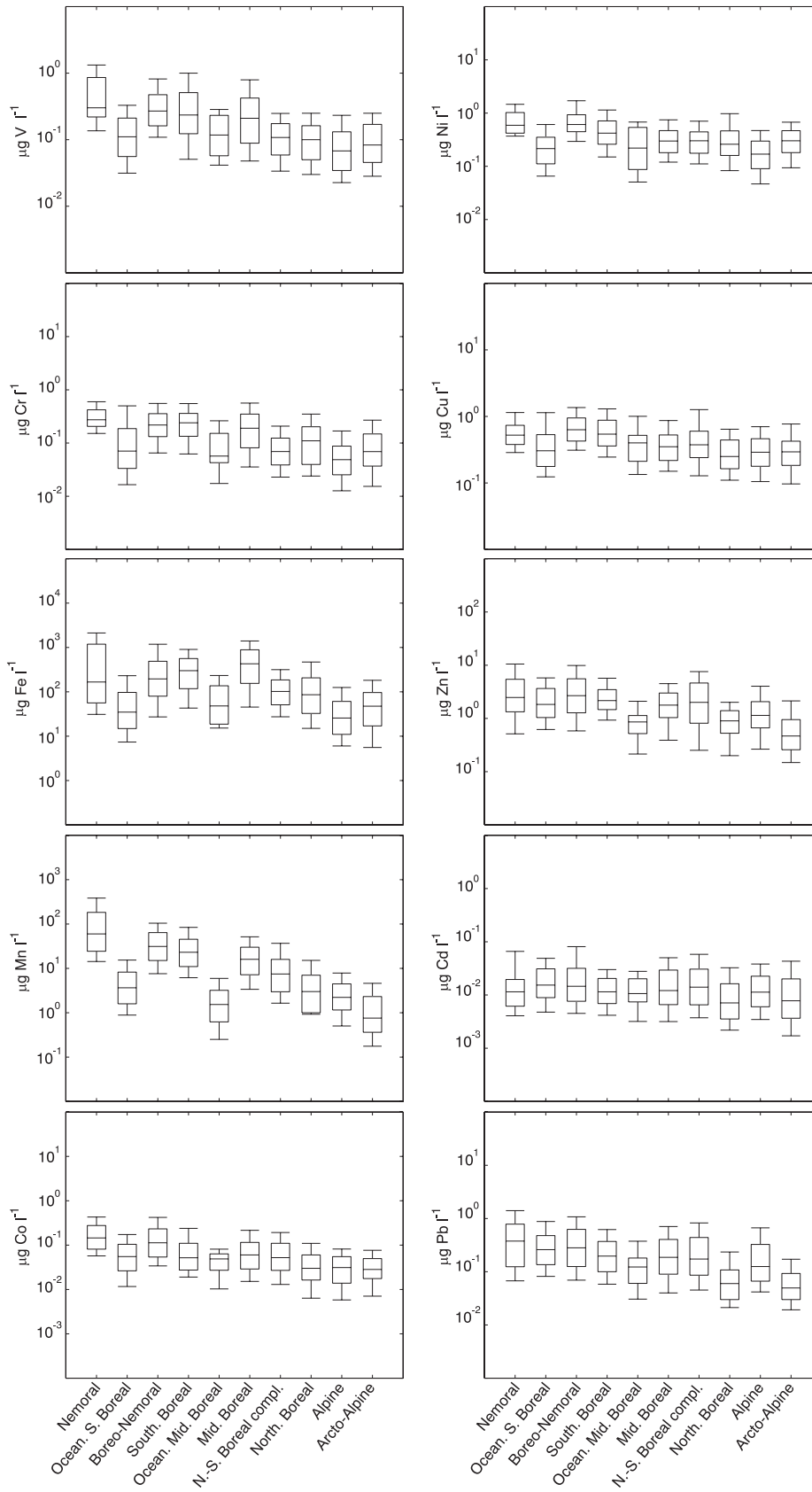


Figure 4.6 Percentiles (0.5, 25, 50, 75, 99.5) of all the elements in the different eco-regions.

5. Risk assessment

All forms of life depend on the availability of right amounts on essential metals: not too much, not too little. Too high concentrations of heavy metals have adverse effects on biota. There is an extensive work going on the international level (Umweltbundesamt 1998) to decide on toxic levels of heavy metals for aquatic and terrestrial biota. The aim of this work is to set critical limits or pollution classes for heavy metals of interest. This may be an important tool for national environmental management and also for the international work under the Heavy metal Protocol under the UN/ECE Convention on Long range transboundary Air Pollution (see textbox 5.1)

The five countries involved in this project (Finland, Norway, Sweden, Denmark and Russia) have at present five different systems for classifying levels of harmful effects of heavy metals (Table 5.1). In Finland, and Russia, effect-based critical limits for water have not been set. In Finland, the drinking water directive of the EU has been adopted as a decision of the Council of State. In Norway, Sweden and Denmark effect-based limits have been set for surface water. Denmark operates with one critical limit, while Norway and Sweden operate with five pollution classes from “very low” to “very high”. The

Norwegian and Swedish classification system (SFT, 1997, Naturvårdsverket, 1999) are based partly on data from the lake survey in 1995 and partly on knowledge of biological effects (Lithner, 1989) and international agreed limits (Umweltbundesamt, 1998, Alm *et al.* 1999). The division between the classes “very low” and “low” are based on the 75-90 percentile in the statistical reference material from the 1995 survey, while in the classes “high” and “very high” there are usually known biological effects. In Sweden a concentration has been set where adverse effects on biota might occur in sensible waters (SEPA 1999, Alm *et al.* 1999). In this report these concentrations has been used as the "critical limits"

In Norway and Sweden, the “critical limits” for each of the elements are set according to present knowledge of adverse effects of heavy metal pollution. In the background literature for the Swedish classification systems (Alm *et al.* 1999), it is stressed that the limits must be used with caution, as knowledge about adverse effects is limited. Most dose-effect relationships between heavy metals and effects on biota have been made in laboratory, and the applications of laboratory results to field conditions are usually not straight forward.

Textbox 5.1 The Aarhus Protocol on Heavy Metals.

The Aarhus Protocol on Heavy Metals (UN/ECE, 1998) aims at regulation and reduction of emissions of particularly Cd, Pb and Hg to the atmosphere.

Press release on the 1998 Aarhus Protocol on Heavy Metals

The Executive Body adopted the Protocol on Heavy Metals on 24 June 1998 in Aarhus (Denmark). It targets three particularly harmful metals: cadmium, lead and mercury. According to one of the basic obligations, Parties will have to reduce their emissions for these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). The Protocol aims to cut emissions from industrial sources (iron and steel industry, non-ferrous metal industry), combustion processes (power generation, road transport) and waste incineration. It lays down stringent limit values for emissions from stationary sources and suggests best available techniques (BAT) for these sources, such as special filters or scrubbers for combustion sources or mercury-free processes. The Protocol requires Parties to phase out leaded petrol. It also introduces measures to lower heavy metal emissions from other products, such as mercury in batteries, and proposes the introduction of management measures for other mercury-containing products, such as electrical components (thermostats, switches), measuring devices (thermometers, manometers, barometers), fluorescent lamps, dental amalgam, pesticides and paint.

There are many factors that influence on the concentration level at which harmful effects can be expected. Usually, only the free or inorganic bound form of the element is regarded as potentially toxic to aquatic biota, and complexation significantly reduces the concentration of the free and thus toxic metal ion. Organic matter is a strong complexing agent in natural waters, and in the presence of organic matter, higher concentrations of total metal can be tolerated without adverse effects

on organisms. This complexation is particularly strong for Cu and Pb, and decreases in importance for Ni, Zn and Cd. Further there are other factors such as pH and hardness that affect concentration of free metal ions and thus reduce toxicity.

The differences in classification of pollution between Sweden and Norway (Table 5.1) illustrate the difficulties of setting critical limits.

Table 5.1. Classification of pollution levels with regard to heavy metals for Norway (SFT, 1997) and Sweden (Naturvårdverket, 1999), and national guidelines for critical limits for heavy metals in surface waters for Norway, Sweden, Denmark and Russian Kola.

	Classification					"Critical limit"
	Very Low I	Low II	Medium III	High IV	Very High V	
Pb						
Norway	<0.5	0.5-1.2	1.2-2.5	2.5-5	>5	2.5
Sweden	≤ 0.2	0.2-1	1-3	3-15	>15	1
Denmark						3.2
Russia						100
Cd						
Norway	<0.04	0.04-0.1	0.1-0.2	0.2-0.4	>0.4	0.2
Sweden	≤ 0.01	0.01 - 0.1	0.1 - 0.3	0.3 - 1.5	> 1.5	0.1
Denmark						5
Russia						5
As						
Norway	-	-	-	-	-	-
Sweden	<0.4	0.4-5	5-15	15-75	>75	5
Denmark						4
Russia						50
Zn						
Norway	<5	5-20	20-50	50-100	>100	50
Sweden	<5	5-20	20-60	60-300	>300	20
Denmark						110
Russia						10
Cu						
Norway	<0.6	0.6-1.5	1.5-3	3-6	>6	3
Sweden	<0.5	0.5-3	3-9	9-45	>45	3
Denmark						12
Russia						1
Ni						
Norway	<0.5	0.5-2.5	2.5-5	5-10	>10	5
Sweden	<0.7	0.7-15	15-45	45-225	>225	15
Denmark						160
Russia						10
Cr						
Norway	<0.2	0.2-2.5	2.5-10	10-50	>50	10
Sweden	<0.3	0.3-5	5-15	15-75	>75	5
Denmark						10
Russia						1

5.1 How many lakes in the Nordic countries are polluted by heavy metals?

The percentage of the lake populations in the five pollution classes is calculated with regard to the Swedish classification system for pollution classes (Table 5.1 and results in Table 5.2). Class IV and V are lumped together because the number of lakes in class V is very few. The estimation of the percentage is uncertain since high concentration lakes are in the “tail” of the concentration distribution. The exact percentage should be interpreted with caution, but the value still gives a good indication of the dimension of the level.

Finland, Norway and Sweden

The percentage of lakes above the critical limit (class III+IV+V) for Pb is 6.2% in Sweden and 7.2% in Norway. For Cd the percentage is 3.5% in both Sweden and Norway. For Finland the numbers are 2.15% for Pb and ~ 0% for Cd. Most of the lakes above the critical limit for Pb are situated in southern parts of Norway and Sweden (Figure 5.1) and are clearly influenced by long-range transported air pollutants. Lakes with Cd concentrations above the critical limit show a slightly different geographical picture than Pb (Figure 5.2). In addition to a cluster of high concentration lakes at the southeastern coast of Norway, there are also some lakes with concentrations above critical limit scattered throughout the country. For Sweden, most of these lakes are scattered in the central parts of the country. The cluster of high Cd lakes in southern Norway and possible also in southern Sweden is most probably a result of deposition of long range transport of Cd or by increased leaching of Cd due to acidification. The lakes with high Cd concentrations scattered throughout the countries are most probably a result of natural conditions (e.g bedrock geology) in the catchment in addition to effect of increased deposition of Cd and acidifying substances (Bergbäck and Johansson, 1996). There is still accumulation of Pb in soils due to anthropogenic deposition (Bergbäck and

Johansson, 1996), and this may have an influence on lake water by increased concentrations of Pb in the years to come. Cd does not accumulate in upper soil layers, due to mobilisation caused by acidification. Cd is transported to deeper soil layers and this may cause increase in surface water Cd in the future (Bergbäck and Johansson, 1996).

The percentage of the lake population with Zn above the critical limit (Class III+IV+V) ranges from 0.5% in Finland to 1% in Sweden. This means only 2 lakes in Finland, 8 in Norway and 7 in Sweden. The percentage of the lake population with Cu above the critical limit (Class III+IV+V) ranges from 0.3% in Finland to 1.4 % in Sweden. This means only 4 lakes in Finland, 8 in Norway and 10 in Sweden. The percentage of the lake population with As, Cr, and Ni above the critical limit (Class III+IV+V) ranges from 0-0.5% of the lakes in Finland, Norway and Sweden. Lakes with concentrations for Zn, Cu, As, Cr and Ni above the critical limit are found scattered throughout the countries and the high concentrations are most probable due to natural conditions or in some cases local pollution sources.

Denmark

The number of studied Danish lakes is only 19 and the classification of the lakes in the pollution classes is therefore only indicative. For most elements the Danish lakes show largely the same distribution with regard to the percentage of lakes in the pollution classes as for the lakes in the Finland, Norway and Sweden. The only element that shows a totally different pattern is Zn. Half of the Danish lakes have Zn values above the critical limit. This may be due to influence from fertilizers.

Russia

The Kola lakes were analysed only for Zn, Cu and Ni. No lakes show Zn-values above the critical limit, while the percentage of lakes above the critical limit for Cu is 5.5% and Ni is 9.7 %. This is due to the high emission of Cu and Ni from industry in this area.

Table 5.2. Percentage of lakes in Finland, Norway, Sweden, Denmark and Russian Kola in the different classes of pollution levels set by Sweden (Naturvårdsverket, 1999) (see Table 5.1).

		I	II	III	IV+V
		Very Low	Low	Medium	High and very high
Pb	Finland	57.0 %	40.9 %	2.1 %	0.0 %
	Norway	61.9 %	31.0 %	6.1 %	1.0 %
	Sweden	56.9 %	36.9 %	4.9 %	1.3 %
	<i>Denmark</i>	16%	63%	11%	11%
	Russian Kola	-	-	-	-
Cd	Finland	43.7 %	56.2 %	0.1 %	0.0 %
	Norway	41.9 %	54.7 %	3.3 %	0.1 %
	Sweden	48.8 %	47.8 %	3.0 %	0.4 %
	<i>Denmark</i>	21%	68%	11%	0%
	Russian Kola	-	-	-	-
As	Finland	68.5 %	31.5 %	0.0 %	0.0 %
	Norway	95.3 %	4.5 %	0.2 %	0.0 %
	Sweden	69.9 %	29.8 %	0.1 %	0.2 %
	<i>Denmark</i>		100%	0%	0%
	Russian Kola	-	-	-	-
Zn	Finland	92.4 %	7.1 %	0.5 %	0.0 %
	Norway	87.0 %	12.3 %	0.5 %	0.2 %
	Sweden	89.0 %	10.0 %	0.8 %	0.2 %
	<i>Denmark</i>		50%	50%	0%
	Russian Kola	96.9%	3.1%	0%	0%
Cu	Finland	62.8 %	36.9 %	0.3 %	0.0 %
	Norway	73.1 %	26.4 %	0.3 %	0.2 %
	Sweden	66.8 %	31.8 %	1.4 %	0.0 %
	<i>Denmark</i>		95%	5%	0%
	Russian Kola	19.2%	71.1%	8.4%	1.3%
Ni	Finland	77.7 %	21.8 %	0.4 %	0.1 %
	Norway	90.4 %	9.6 %	0.0 %	0.0 %
	Sweden	82.1 %	17.9 %	0.0 %	0.0 %
	<i>Denmark</i>	11%	89%	0%	0%
	Russian Kola	44.3%	50.2%	2.9%	2.6%
Cr	Finland	52.1 %	47.9 %	0.0 %	0.0 %
	Norway	89.8 %	10.2 %	0.0 %	0.0 %
	Sweden	79.9 %	19.8 %	0.1 %	0.2 %
	<i>Denmark</i>		100%	0%	0%
	Russian Kola		-	-	-

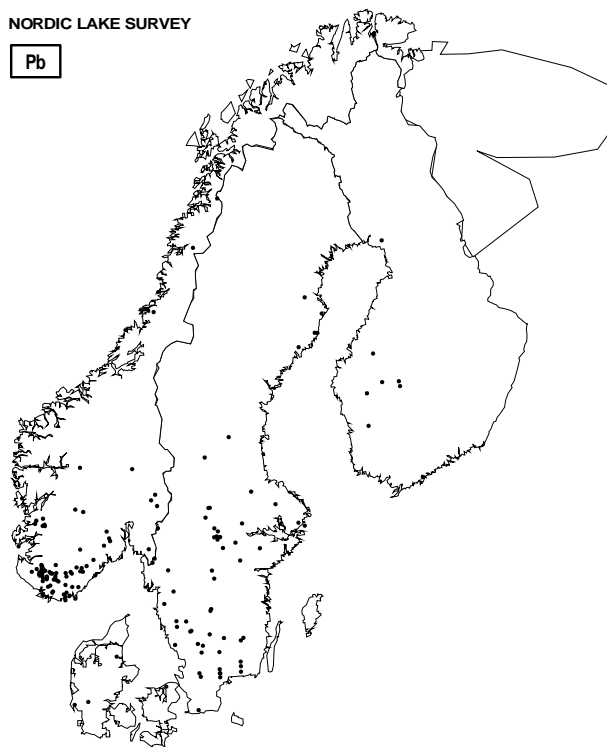


Figure 5.1 Lakes in the Nordic countries with Pb above the Swedish critical limit of 1 µg/l for assumed ecological effects.

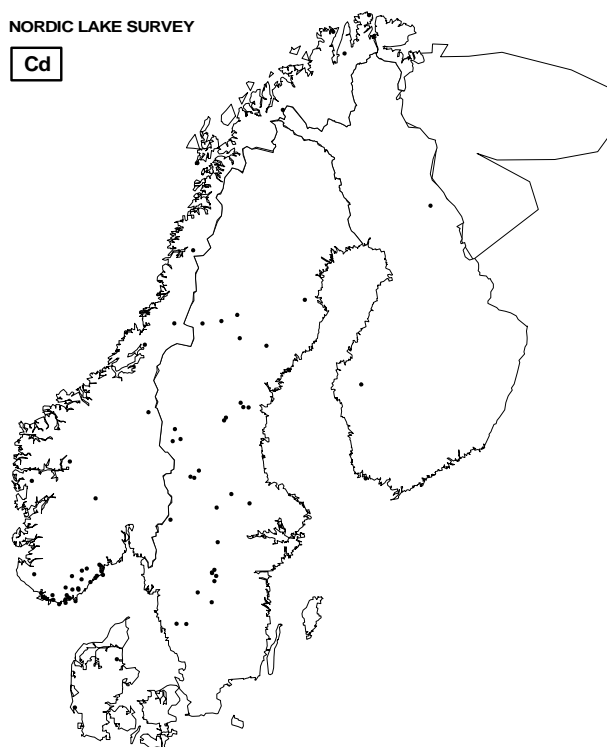


Figure 5.2 Lakes in the Nordic countries with Cd above the Swedish critical limit of 0.1 µg/l for assumed ecological effects.

5.2 What is the dimension of heavy metal pollution in Nordic lakes

Only Pb and Cd show a significant percentage of lakes with concentrations above a critical limit (set by Sweden and used in this report). Most of these lakes are situated in southernmost parts of Norway and Sweden influenced by high inputs from long-range transported air pollutants. However we have very limited information about eventually synergetic effects on biota of stress from acidification and high concentrations of one or more heavy metals.

In Russian Kola, a significant percentage of the investigated lakes show values above the critical limit for Cu and Ni (as set by Sweden). This is however a “local” problem due to large smelters in the area. Half of the investigated Danish lakes show values above the critical limit for Zn.

Hg is not included in the Nordic Lake Survey, but from other work (Lindquist *et al.* 1991, Verta *et al.* 1990) it is demonstrated that Hg in fish has increased substantially, and that this is a large environmental problem.

The results shown here indicate that heavy metal pollution in lakes is a minor ecological problem on a national level in the Nordic countries. Certain areas are however influenced by long-range transport leading to increases in heavy metal concentrations in lakes above limits set by environmental authorities in Norway and Sweden. Since effects of acid rain already put a stress on aquatic biota in areas affected by high deposition of Cd and Pb, this may be an important environmental problem in these areas.

The present work gives the status of heavy metals for *lakes* in the Nordic countries. There is, however, indication that especially in small running waters there may be higher levels of heavy metals than in lakes (Alm *et al.* 1999), and thus, the ecological problem of heavy metals may be larger for running water than for lake water.

The environmental target for heavy metals in lakes could be that the concentrations should not increase in surface water in the future, as the safety margins for many lakes are very small with regards to effects on biota. In addition acidification must decrease to prevent a continued leakage of heavy metals due to acidification.

6. Discussion

The regional distributions of the heavy metals show that many have strong gradients in concentration, from high levels in the south to low levels in the north, or alternatively low levels in the west to higher in the east. For some metals both patterns are present.

The levels and distributions of heavy metals in Nordic lakes are controlled by several factors of which the following are the most important:

- anthropogenic sources
 - direct deposition from long-range air pollution
 - indirect effects of long-range air pollution by increased leaching due to acidification
 - local point sources
- water chemical conditions – particularly levels of TOC
- bedrock geology

Of the anthropogenic sources, the contribution from long-range transported air pollutants directly through deposition or indirectly through increased mobilisation due to acidification contributes to the main large-scale patterns of heavy metals in the Nordic countries. Local point sources must have extreme emissions, like the smelter industry at the Kola peninsula, to influence the regional levels of heavy metals in lake waters. There is no sign of regional increase in any heavy metal concentration in lakes around any of the known point sources in Norway, Sweden and Finland. These point sources however, may contribute to heavy pollution locally by e.g. wastewater discharge directly into rivers or lakes.

Soil and surface water pH and the concentration of total organic carbon (TOC) are important factors for the mobilisation of metals from the catchment to runoff water. These factors are also dominant for sedimentation rates of heavy metals in lakes, and for remobilization of metals from sediments. In addition, co-precipitation with Fe/Mn-oxides and the redox-potential in soils and sediments are important for dissolution

and precipitation reactions. Comparison of maps of heavy metals and TOC in lakes shows that TOC explains much of the large-scale variation in heavy metal concentrations in lakes. This was confirmed by the statistical analyses, which show that about 40% of the total variance in the data is explained by variance in TOC and pH (where TOC is the most important of the two).

The bedrock and overburden is an important source of heavy metals in lake water. Metals are released during weathering, and both the content of metals in minerals and the weathering rate are important factors. In some areas small group of lakes show high concentrations of a specific element relative to other lakes in the vicinity. This is interpreted as a geochemical influence from the bedrock and overburden.

With some exceptions, the varying concentrations of TOC in the lakes are more important for controlling heavy metal concentrations than the content in the bedrock and overburden itself. Also the influence of long-range transport is more important for the regional patterns for some of the heavy metals than the mineralogy of bedrock and overburden.

Although the elements show different regional patterns and concentration levels the 11 elements can be grouped into 3 groups, based on the geographical distribution patterns and the results from the statistical analyses:

1. Pb, Cd, Zn, (Co)
2. Fe, Mn, (As, Cr, V)
3. Cu, Ni, As, Co, Cr, V

Pb, Cd, Zn (Co)

The regional pattern of this group is largely dominated by the impact of long-range transported air pollutants, either by elevated deposition or indirectly by increased leaching due to acidification, which in turn is caused by long-range transported air pollutants.

Pb is extremely tightly bound to humic substances, and on the average, more than 90% of deposited Pb is retained in the catchment (Borg and Johanson, 1989). Therefore, elevated concentrations of Pb seen in southern Sweden and Norway are mostly due to direct deposition of Pb on the lake surface. The pattern of Pb in southern Norway is very similar to the deposition map, with the highest concentrations 40-50 km inland from the coast, in areas with highest orographic precipitation.

Mobilisation of Cd in soils is positively related to pH in soil solution (Bergkvist, 1986). Cd is therefore mobilised and elevated in acidified regions, compared to non-acidified regions. The correlations between Cd on H⁺ and S-deposition as shown in the statistical analysis are clearly related to the causal relationship between high S-deposition and low pH in lake waters. In addition, Cd is a component in long-range transported air-pollutants.

The sources of Pb and Cd in polluted air are somewhat different. Cd is released from coal burning, which is more pronounced in eastern Europe, whereas Pb comes from leaded gasoline and central Europe is the most important source. Therefore Cd is transported with winds from south east, and this is reflected in the deposition pattern, with higher deposition levels on western parts of southern Sweden and eastern parts of southern Norway. Similar northward decreasing pattern is seen also in other matrix, e.g. snow (Roos and Granat 1986, Verta *et al.* 1990), moss (Rühling and Steinnes, 1998), bulk deposition (Kulmala *et al.* 1998) and lake sediments (Johansson 1989, Verta *et al.* 1989, Rognerud *et al.* 1998).

Although most of the present atmospheric lead is long-range transported, the denser traffic and road network in the more populated southern regions in Nordic countries contributes to the elevated Pb levels in lakes. There is no information on the distances of the studied lakes from nearest roads. Therefore we are unable to distinguish the effect of short-range transported from long-range transported Pb.

Zn shows very much of the same pattern as Cd, and these two elements behave very similarly both with regard to deposition pattern and mobilisation due to acidification of humic layers in soils (SEPA, 1993, Borg and Johansson, 1989).

Co is not a long-range transported element, but acidification leaches Co (Alm *et al.* 1999). This explains why the regional pattern of Co concentration in lakes resembles that of Pb, Cd and Zn. Finland has many scattered high Co lakes due to acid conditions caused by high humic content.

Fe, Mn (As, Cr, V)

The regional pattern of group 2 is largely dominated by the TOC content in lakes. There is a clear positive relation between Fe and Mn on TOC-levels in lakes. Both Fe and Mn are strongly correlated to organic matter, but in two different ways. Fe and Mn are released from Fe/Mn-oxides in bog areas where the redox-potential are so low that Mn and Fe are reduced to Fe²⁺ and Mn²⁺. In the surface water Fe is strongly bound to humic substances, while Mn is free.

When Fe and Mn oxides are dissolved, other trace metals which have been adsorbed on the oxide particles are dissolved as well. This explains why all the elements plot positive on the RDA-axis 1 ("TOC-axis"), which means that all elements have a positive relation to TOC in the lakes.

As a consequence of the different TOC levels, median value for Fe and Mn for the total lake population in Finland is respectively 8 and 10 times higher than the median values for the total Norwegian lake population.

As, Cr and V have a regional distribution similar to those of Fe and Mn. The median value for As, Cr and V for the total lake population in Finland is 6, 4 and 3 times higher respectively than the median values for the total Norwegian lake population, illustrating the east-west gradients for all these elements. For Cu, Ni and Co and also Pb, Cd and Zn this factor is < 1.

Cu, Ni, (As, Cr, V)

While the two first groups are identified by very clear characteristics, the third group containing Cu, Ni, As, Co, Cr and V are not clearly influenced by one single factor.

Cu and Ni show very similar concentration distributions, and these are also the elements with least geographical gradients. One obvious exception is the area around the smelter industry on the Kola peninsula where the Cu and Ni concentrations in lakes are very high. The median value for Ni is about the same in Kola as in Finland, Norway and Sweden, while the median value for Cu is about two times higher.

As, Cr and V are partly dissolved in connection with dissolution of Fe and Mn-oxides, but some of them also show a clear influence from bedrock geology. Lakes with high concentrations of As, Cr and V are located in the Hardangerfjorden area at the

west coast of Norway. Lakes with high concentrations of As and V are found in an area stretching from central west Finland to in central north Sweden. The lake water content of these elements is influenced by the bedrock geochemistry.

With exception of the smelters at Kola and Rönnskär in Sweden it is not possible to detect any clear influence from other point sources in the Nordic countries on lake water content of heavy metals on a regional scale.

These findings fit well with the output of the statistical analyses. The RDA analysis points to TOC as an important explanatory factor for Fe and Mn, and to a lesser degree for Cr and V. H^+ is the most important explanatory factor for Pb, Cd and Zn and to a lesser degree also for Co. Cu and Ni cannot be explained very well with either of these two variables. (As was not treated in the statistical analysis).

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Appendix A. Multiple imputation of missing data

by Tom Andersen, NIVA

Multivariate statistical methods are frequently hampered by missing data. Data may either be missing due to random factors (such as accidents during sample collection or processing) or due to censoring (i.e., non-random deletion of values above or below certain limits). Typically, results from chemical analyses will be left-censored by the detection limit of the actual analytical method. Until recently, missing data have been treated mainly by *ad hoc* practices, such as listwise deletion for randomly missing values, or substitution by some fixed value (like, zero or some factor proportional to the detection limit) for left-censored data. Substituting censored values with zeros will underestimate the means and overestimate the standard deviations compared to the true distribution, as well as cause numerical problems for any variable for which it is natural use a logarithmic scale. On the other extreme, substituting censored values with the detection limit will overestimate means and underestimate standard deviations. Using other factors proportional to the detection limit will only be an improvement under special conditions (for example, 0.5 times the detection limit will give unbiased means and standard deviations when the underlying distribution is uniform).

Recent advances in theoretical and computational statistics, however, have produced a new generation of flexible procedures with a sound statistical basis. These procedures involve **multiple imputation** (Rubin 1987), a simulation technique that replaces each missing datum with a set of $m > 1$ plausible values drawn from their predictive distribution. The m versions of the complete data are analyzed by standard complete-data methods, and the results are combined using simple rules to yield estimates that formally incorporate missing-data uncertainty.

A practical way of implementing multiple imputations is based on the principle of **data augmentation**. Assume that we have an incomplete data set which can be described by a parametric data model. If we knew the missing values, then estimating the model parameters would be straightforward. Similarly, if we knew the parameters of the data model, then it would be possible to obtain unbiased predictions of the missing values. This interdependence between model parameters and missing values suggests an iterative method where we first generate imputations of the missing values under assumed values of the model parameters, and then use these augmented data sets to generate new estimates of the model parameters. The procedure of alternately simulating missing data and parameters creates a Markov chain that eventually stabilizes or converges in distribution (Tanner & Wong 1987). The distribution of the missing data stabilizes to a predictive distribution – the exact distribution, in fact, that one needs to draw from to create proper multiple imputations.

The multivariate normal (MVN) distribution is known to be fully parameterised by the expectation vector (ξ) and the covariance matrix (Σ). furthermore, maximum likelihood estimates of these parameters are easily computed as means and covariances from any uncensored data set (i.e., the relevant complete-data method is well known and easy to implement). In order to start the imputation process for a censored, n -dimensional, MVN distribution, we first compute the means and covariances from a data set where all the censored values are substituted by their corresponding detection limits, and use this as our initial estimate for the parameters of the underlying distribution. This estimate will obviously be biased, but serve as starting point for the iteration. Given current estimates for the parameters of the MVN distribution, we can easily generate pseudorandom numbers with the same distribution. Pseudorandom numbers drawn from a MVN with parameters ξ and Σ are conveniently generated as $x = Cz + \xi$, where C is the Choleski factorization of Σ (i.e., $CC' = \Sigma$) and z is a n -vector of independent, pseudorandom normal variates with zero mean and unit variance (see, e.g., Tong 1990).

Usually, a large number of the observations in a data set will be only partially censored, i.e., at least one variable will be above the detection limit. Given that there is an underlying correlation structure among the variables, the information contained in the uncensored part of a given record may strongly influence the distribution of the censored part. In other words, it would be desirable to utilise as much as possible of the information contained in the uncensored variables when generating plausible values for the censored variables. Such a mechanism can be implemented by utilising some well-known properties of the marginal distributions of the MVN (Tong 1990). Any observation vector x can be permuted by an orthogonal linear transformation P into a partition $\begin{bmatrix} x'_1 & x'_2 \end{bmatrix}' = Px$ such that x_1 contains the (left)-censored elements, while x_2 is uncensored part. Due to the invariance of the normal distribution under linear operators, Px will be MVN with expectation $P\xi$ and covariance matrix $P\Sigma P'$. The conditional distribution of x_1 given x_2 will also be MVN with expectation $\xi_{1|2}$ and covariance $\Sigma_{1|2}$. If we partition the permuted expectation and covariance as

$$\begin{bmatrix} \xi_1 \\ \xi_2 \end{bmatrix} = P\xi \quad (1)$$

$$\begin{bmatrix} \Sigma_{11} & \Sigma_{12} \\ \Sigma_{21} & \Sigma_{22} \end{bmatrix} = P\Sigma P', \quad (2)$$

then the conditional expectations and covariances will be given by the projections

$$\xi_{1|2} = E(x_1 | x_2) = \xi_1 + \Sigma_{12}\Sigma_{22}^{-1}(x_2 - \xi_2) \quad (3)$$

$$\Sigma_{1|2} = \text{Cov}(x_1 | x_2) = \Sigma_{11} - \Sigma_{12}\Sigma_{22}^{-1}\Sigma_{21} \quad (4)$$

Thus, for every observation record with censoring we can use the conditional distribution given by (1) – (4) to impute plausible values for the censored variables. In order to be a valid imputation for the the censored variables, one must resample the conditional distribution until the generated values are within the censoring limits (i.e., below the actual detection limit for the present case). This procedure is repeated so that m different data sets are generated in each imputation step. The multiple imputation estimate of the MVN distribution parameters is then computed as the average of the means and covariances across these m data sets (Rubin's rule). The updated MVN distribution parameters can then be fed back to the imputation step, leading to an iterative sequence that converges to a predictive distribution for the censored values.

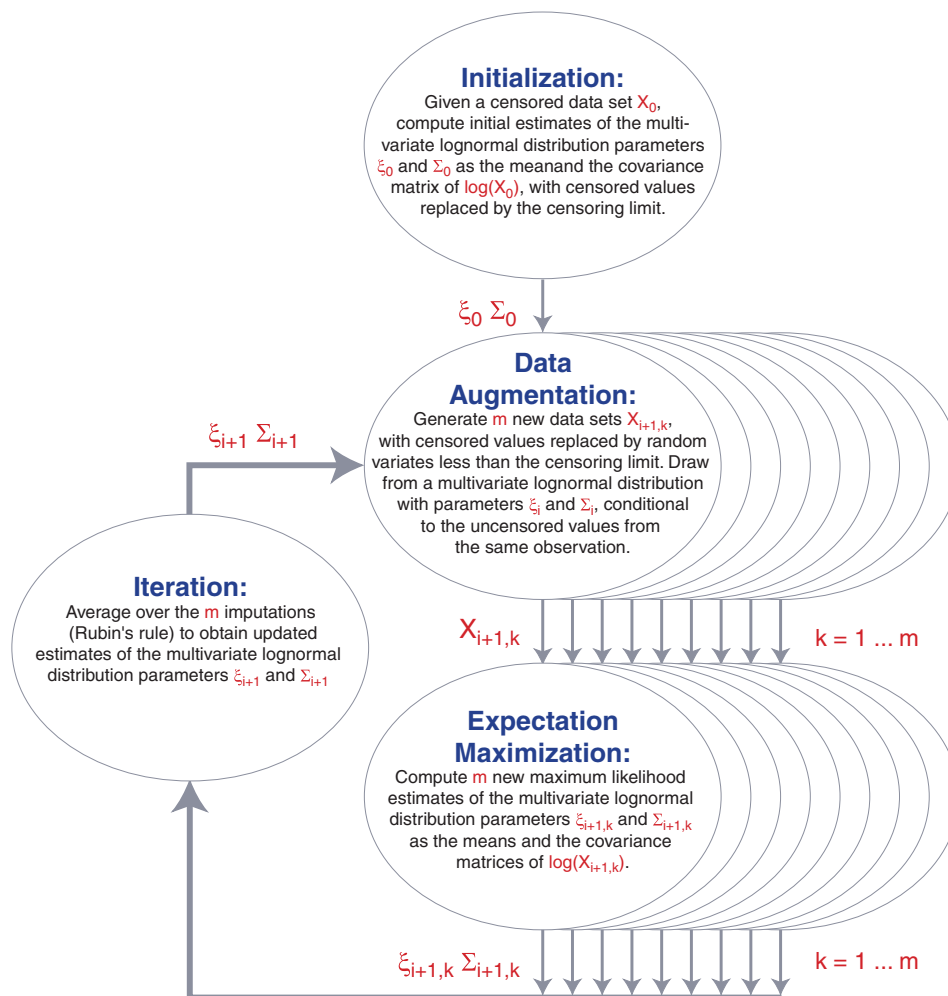


Figure A1. Outline of the multiple imputation algorithm for estimating distributional parameters from left-censored, multivariate lognormal data.

In the present case, involving (left-censored) trace metal concentrations from a large number of lakes in the Nordic countries, there is strong empirical support for assuming that the underlying distributions are close to log-normal. In other words, that the log-transformed data set would be well approximated by a multivariate normal distribution, thus constituting a parametric model for the data set.

The major steps of the corresponding multiple imputation algorithm for such a data set is illustrated in figure A1. The actual implementation used 10 imputations per iteration for a total of 40 iterations, which took ca 36 h of CPU time on a reasonably fast PC running Matlab 5.2 (The MathWorks, inc., Natick, Mass.) under Windows NT 4.0. Figure A2 shows that the univariate distributions changed very little after only 5 iterations, thus the algorithm converged considerably faster than expected (Figure A2). Furthermore the imputation process produce the expected pattern of decreasing means and increasing standard deviations, and this effect becomes more dramatic with increasing degree of censoring (Figure A2).

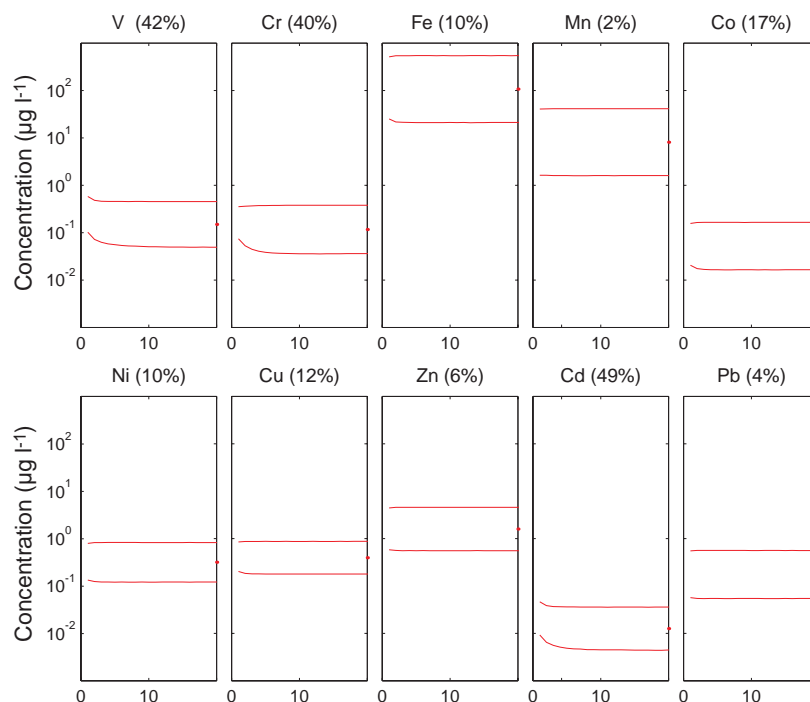


Figure A2. Iteration history for the multiple imputation algorithm. Means and standard deviations for the 10 trace elements during the first 20 iteration steps in the estimation of multivariate lognormal distributional parameters from left-censored data. Numbers in parentheses refer to overall frequency of censoring for a particular element.

More details of the changes in correlation structure are shown by the trajectories of the two first principal components of the covariance matrix during the imputation process (Figure A3). Also here, the major changes were isolated to the first 5 iterations, while variations between imputations were practically negligible after convergence. The large apparent change in the 5th iteration is exaggerated by a reflection of the principal component scores on the second axis at that particular stage. The two strong clusters, comprised of Fe/Mn and Zn/Cd/Pb, are preserved throughout the iteration history, although both clusters become more well-defined in the converged distribution. Among the other elements, there is a distinct reorganization where both V and Cr move away from their initial position close to Cu and Ni, and associate more directly with Co in the converged distribution.

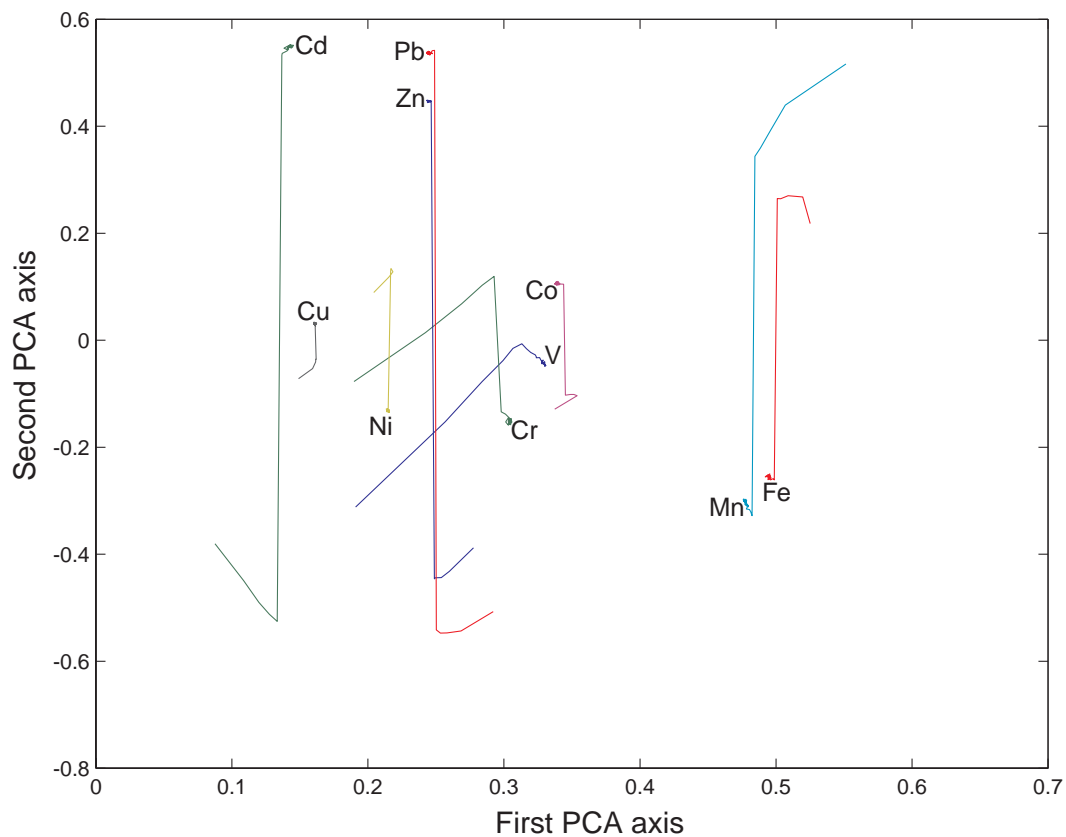


Figure A3. Principal component scores of the 10 trace elements on the two first eigenvalue axes of the covariance matrix as function of multiple imputation iteration history.

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