Chapter 6
Effects on Freshwater Ecosystems

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6.1. Evidence from water quality monitoring

The previous AMAP assessment of acidification of surface water in the Arctic focused on northern Fennoscandia and the Kola Peninsula (AMAP, 1998). There were no reports of acidified lakes and rivers in Arctic Canada and Alaska. Although lakes in some areas of North America were reported to be acid sensitive there were no indications of acidification.

The geographical extent of surface water acidification was based on national lake surveys in Finland, Norway, and Sweden between 1986 and 1990 (Henriksen *et al*., 1992). These surveys showed that the impacts from high levels of sulfur deposition were mostly limited to a distance of about 50 km from the large pollution sources. Nitrate concentrations were very low over the whole area, due to very low nitrogen deposition.

The border areas between Norway, Finland, and Russia were reported to be heavily polluted. Studies of lakes in the eastern parts of Finnmark in 1986 (Traaen, 1987) showed that the sulfate concentration had more than doubled since 1966 and was at the same stage of acidification as the most acidified lakes in southern Norway. Numerous small mountain lakes in the area were chronically acidic (pH<5). Even large lakes had little of their original buffering capacity left. Some small lakes, in particular at Jarfjordfjellet, were too acidic to support fish. Studies in 1987 to 1989 (Traaen, 1991) indicated that large areas in Sør-Varanger would become increasingly damaged, with a loss of fish stocks, if the acid deposition increased further.

On the Kola Peninsula acidified lakes were reported around the industrial centers, and along the northern and eastern parts of the peninsula. However, at Kola, pollution from nickel and copper was a bigger problem in lakes than acidification (Moiseenko *et al*., 1995).

An extensive inventory of small lakes in northern Finland between 1987 and 1991 showed that acidic and poorly buffered lakes were widely found in northeastern Lapland near the Norwegian and Russian borders. Sulfate concentrations here were generally higher than in other parts of Lapland (Kähkönen, 1996). A survey of small mountain lakes and brooks in northeastern Lapland in 1991 to 1993 found that the alkalinity of surface waters was lowest (mostly <50 µeq/L) in the Vätsäri area 40 to 50 km west of the Nikel smelter (Lappalainen *et al*., 1995).

Areas sensitive to acidification and areas possibly acidified by acid deposition were quantified by calculating the critical loads for acidification of surface waters (see Box). Sulfur was regarded as the only acidifying agent as nitrate concentrations in lakes and streams in this area were very low. Critical loads for northern Fennoscandia, the Kola Peninsula, and the Spitsbergen Archipelago (Henriksen *et al*., 1994; Lien *et al*., 1995) were very variable, ranging from <300 to >1300 mg S/m^2/yr. Most areas of Finland

Definitions, terms, and calculations

Water chemistry

The chemical composition of surface waters in an undisturbed ecosystem is mainly determined by the contribution of ions from weathering and ion exchange in the catchment and from atmospheric deposition. Atmospheric deposition is influenced by sea salts, soil dust, and long-range transported air pollutants. The chemical composition of precipitation depends on distance from the sea and anthropogenic pollution sources. It is modified by a number of processes when passing through a catchment. Such processes are biological (microbial activity, uptake by plants, release of ions through decomposition, etc.) and chemical (weathering, ion exchange, adsorption and desorption, redox processes, precipitation etc.). In general, bedrock composed of gneisses and granitic gneisses has low weathering rates, yielding waters with a low content of base cations and bicarbonate that consequently have a low buffering capacity toward acidification. Bedrock with a more basic character such as gabbro, greenstone, and schist has higher weathering rates and releases more base cations and bicarbonate, yielding surface waters with a higher buffering capacity. Biological processes usually result in modification of ion composition or removal of ions, while weathering gives a net contribution. The total sum of ions from deposition and weathering together with all the various processes occurring within a catchment determine the chemistry of the runoff water. Additional, but often similar, in-lake processes can further modify the ion composition.

Acidification and naturally acidified lakes

The pH of most natural, mineral-bearing waters falls within the range 6 to 9. pH 6 is a threshold value below which lake biology is detrimentally affected by acidification (Baker et al., 1990; Doka et al., 2003; Holt and Yan, 2003). pH in a lake is affected by several natural processes within the catchment, such as the rate of weathering and production of bicarbonate, mobilization and leaching of organic acids derived from humic substances (organic anions, typically indicated by dissolved organic carbon/ total organic carbon levels), and input of sulfate from natural sulfide-bearing minerals. Low weathering rates, high input of organic anions, and high input of natural sulfate help to depress pH in the lake or river. Large inputs of anthropogenically derived sulfur and nitrogen that exceed the critical loads for the lake can also depress the pH to biologically harmful levels. It is not obvious, by measuring pH only, if a low pH value in a water body is due to anthropogenic or natural processes.

Alkalinity

Alkalinity is a measure of the buffering capacity of water, or the capacity of bases to neutralize acids. Alkalinity is a measure of the water's ability to resist change in pH and to neutralize

acid inputs. Alkalinity is a more integrative indicator of lake acidification than pH. The most important buffering materials in natural waters in the Arctic are primarily bicarbonate (HCO_3^-) and organic acids. Waters with low alkalinity (<20 µeq/L) are very susceptible to changes in pH. Waters with high alkalinity (>200 µeq/L) are able to resist major shifts in pH. As increasing amounts of acid are added to a water body, the buffering capacity of the water is consumed, and the pH of the water decreases (acidification). At pH 5.5, only very weak buffering ability remains, and at pH levels below 4.5 there is no alkalinity left. Alkalinity is measured by titration. An acid of known strength (the titrant) is added to a volume of a treated sample of water. The volume of acid required to bring the sample to a specific pH level reflects the alkalinity of the sample. Alkalinity can be measured in the laboratory in many different ways, making it difficult to compare results from different investigations.

Acid neutralizing capacity

Calculated Acid Neutralizing Capacity (ANC) is an equivalent to measured alkalinity. ANC is an even more integrative and robust parameter than alkalinity in establishing good dose/response relationships between water chemistry and damage to the biological community. ANC is the parameter used as the critical chemical criterion for sensitive indicator organisms in surface waters within the international critical loads work. ANC is defined as (Reuss and Johnson, 1986): equivalent sum of base cations minus the equivalent sum of strong acid anions $ANC = ([Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+]) - ([Cl^-] + [SO_4^{2-}] + [NO_3^-])$*. Waters with low ANC (<50 µeq/L) indicate possible damage to biota.*

Biologically relevant chemistry

The ultimate goal of emissions control programs is biological recovery, or the return of sensitive species that have been eliminated during the course of acidification. An assessment of biologically-relevant chemical trends can only suggest that biological recovery is possible (or expected), not that it has occurred. When surface water trends are shown to be moving in the correct direction (e.g., decreases in sulfate, or increases in pH), they indicate improvement in the acid–base chemistry of lakes and streams. It is important to note that these improvements do not necessarily equate to recovery. The term 'recovery' implies that the chemistry has returned to some pre-acidified status, such as pre-industrial levels of sulfate or alkalinity; trends indicate only that surface waters are moving toward this recovered status, not that they have reached it. In the absence of good data on biological recovery, it is common to assume that biological recovery will eventually occur, after a sufficient time lag, when key chemical variables have recovered their pre-acidification levels. These key chemical variables are those that have direct toxic effects on biota (primarily hydrogen ion and aluminum) and those that ameliorate some of the toxic effects (primarily base cations like calcium). For these reasons, evaluations of chemical recovery are often focused on acidity (pH and alkalinity), aluminum, and base cations (calcium).

Non-marine concentrations

All calculations and presentations of sulfate and base cations (sum of Ca + Mg) in this work are non-marine fractions, i.e. the seasalt contributions have been subtracted from the total levels measured. For sulfate, what is left represents the natural background input from weathering (which is normally very low) and the anthropogenic contribution from deposition. For base cations the remaining fraction is derived from weathering. Non-marine fractions (denoted by an asterisk) of sulfate and base cations* in lake and river water are calculated (see below) under the assumptions that all chloride (Cl) is of marine origin (cyclic sea salts) and is accompanied by other ions in the same proportions as in seawater. Base cations* are in this assessment taken as the sum of non-marine Ca + Mg. All units are in µeq/L.*

$[Ca^*]$	=	$[Ca]$	-	0.037	·	$[Cl]$
$[Mg^*]$	=	$[Mg]$	-	0.198	·	$[Cl]$
$[SO_4^*]$	=	$[SO_4]$	-	0.103	·	$[Cl]$

Acid sensitive lakes and critical loads

Lake water chemistry gives information on sensitivity to acidification. An extremely sensitive lake typically has an alkalinity of <20 µeq/L, and a less sensitive lake from 20 to 50 µeq/L. A lake with an alkalinity of >200 µeq/L is considered to be insensitive to acidification. The concentration of base cations can also give an indication of the acid sensitivity of the water, as the base cation concentrations directly reflect the weathering rate and bicarbonate production rate within the catchment. Surface water with low concentrations of base cations (BC <100 µeq/L) indicates sensitivity to acidic atmospheric inputs. Concentrations of base cations from 100 to 400 µeq/L indicate moderate sensitivity and values >400 µeq/L indicate general insensitivity.*

To evaluate anthropogenic acidification of lakes, the water chemistry must be evaluated together with deposition input. This is done by calculating the critical load of acidity (CL_{Ac}) and the exceedance of the critical load based on atmospheric inputs of sulfur and nitrogen. The critical load concept is a method of estimating ecosystem sensitivity to acidic inputs (i.e., sulfur and nitrogen), and was used to prepare the two protocols to the LRTAP Convention for reducing emissions of sulfur and nitrogen in Europe: the Oslo Protocol in 1994 (UNECE, 1994) and the Gothenburg Protocol in 1999 (UNECE, 1999). Similarly, critical loads were used to guide the distribution of sulfur dioxide emissions reductions in southeastern Canada during the 1980s and 1990s (Jeffries, 1997). The CL_{Ac} is a property of the lake and its catchment and is primarily based on weathering rates in the catchment. Since weathering is a function of bedrock geology, the sensitivity to acidification of surface waters can also be determined from geological maps. Exceedance of critical loads compares the critical load with deposition – actual or expected. When the deposition is greater than the critical load the aquatic ecosystem is expected to become damaged.

The geographical extent of surface water sensitivity to acidification in the AMAP region can also be determined from a map prepared by the Stockholm Environmental Institute based on soil type, land cover, and soil moisture. This is mainly assumed to hold for assessment of soil sensitivity, but will in general also hold for surface water sensitivity.

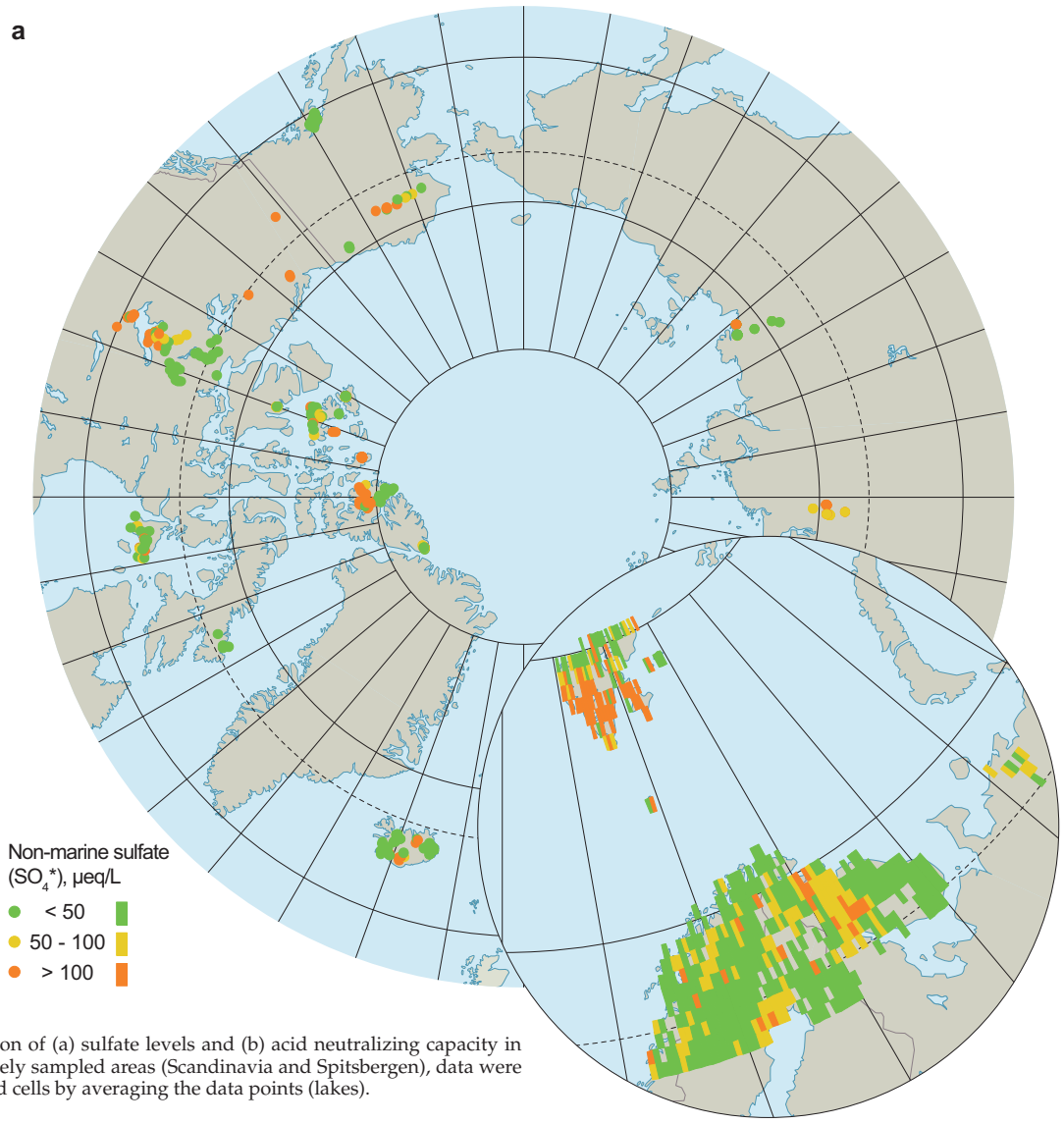


Figure 6.1. Distribution of (a) sulfate levels and (b) acid neutralizing capacity in arctic lakes. For densely sampled areas (Scandinavia and Spitsbergen), data were summarized into grid cells by averaging the data points (lakes).

and Norway near the smelters were quite sensitive, and critical loads for the Kola Peninsula were low. Exceedance of critical loads (based on 1990 sulfur deposition), which indicates possible surface water acidification, occurred in 70% of the county of Sør-Varanger in Norway. Critical loads were exceeded in 48% of lakes on the Kola Peninsula (Moiseenko, 1994). Small exceedances (based on 1990 sulfur deposition) were recorded in 5% of the ice-free area of Svalbard and Bear Island, but only in the northern parts (Lien *et al.*, 1995).

Long-term trends in surface water chemistry in Finland, Norway, Sweden, and on the Kola Peninsula, showed that between the mid-1980s and early 1990s, acidification had stabilized and may even have reduced slightly in some lakes. This was assumed to have resulted from decreased sulfur emissions in Europe. Some of the lakes and rivers had enough buffering capacity that they were not affected by high acid inputs.

6.1.1. **Current status**

The current status of acidification of surface waters in the Arctic has been determined from a compilation of regional and sub-regional lake surveys. Most were undertaken in northern Fennoscandia and the Kola Peninsula, but areas of Arctic Canada, northern Russia, Alaska, Iceland, and the Spitsbergen Archipelago were also covered. Since the previous AMAP assessment on acidification (AMAP, 1998) there has been one large lake survey in the arctic part of the Fennoscandian region. This was undertaken in 1995 and included the Kola Peninsula, the northern part of Fennoscandia, and Iceland (Henriksen *et al.*, 1997a,b; Skjelkvåle *et al.*, 2001c).

This assessment compiles data from several arctic regions. Sources of data and median values for key chemical variables for different arctic regions are summarized in Table 6.1. The geographical distribution of sulfate and acid neutralizing capacity (ANC) in arctic lakes is shown in Figure 6.1. It should be remembered that compiling data in this way means that the sample population is not a statistical subset of the overall lake population. Chemical data from 605 lakes within the Canadian Arctic were compiled for this assessment. Most of the data were collected in the 1990s (Table 6.1). The variables include: pH, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), alkalinity, sulfate (SO_4^{2-}), chloride (Cl^{-}), nitrate (NO_3^{-}), plus dissolved organic carbon (DOC) and specific conductance. Some datasets contained dissolved inorganic carbon (DIC) values rather than alkalinity, and in such cases, the latter was estimated by assuming that the DIC exists entirely as bicarbonate (HCO_3^{-}).

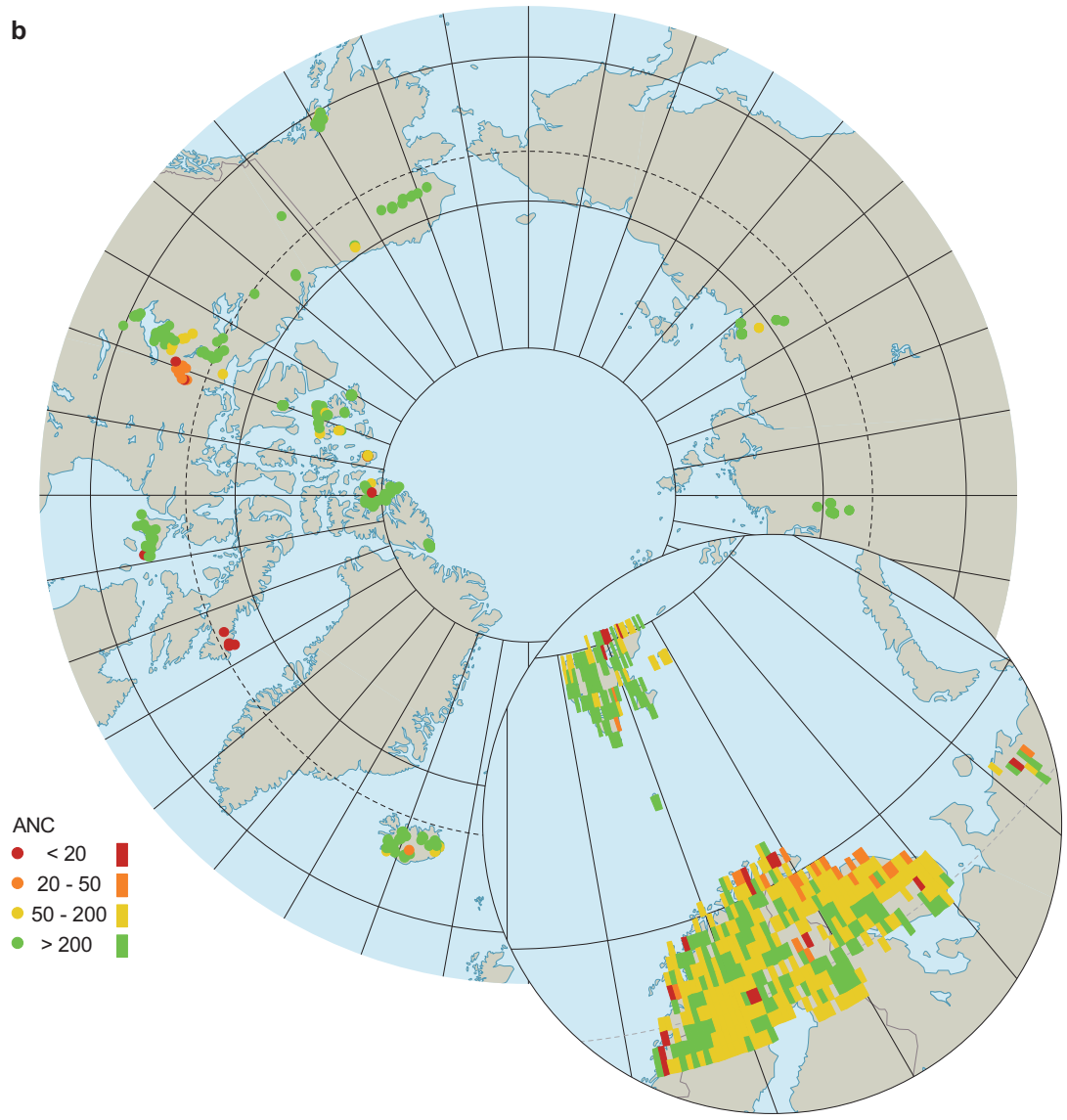


Table 6.1. Median values for a selection of key chemical variables including the calculated critical load of acidity CL_{Ac} and exceedance.

		n	% of total lake population	pH	BC*, µeq/L	Alkalinity, µeq/L	ANC, µeq/L	SO_4*, µeq/L	DOC, mg C/L	NO_3, µeq/L	CL_{Ac}, meq/m²/yr	% of area exceeded by sulfur deposition
Northern Russia [a]	Taymir area	23		7.97	490		445	80	4.0			
Northern Russia [a]	Pechora River basin	29		6.75	196		195	53	7.7			
Northern Russia [a]	Lena River basin	31		7.40	393		312	37	4.0			
Northern Russia [b]	Kola Peninsula	460	2.3	6.45	172	79	144	36	7.6	0.1	66	14
Finland [b]	Lapland	184	2.1	6.81	196	116	175	35	5.3	0.2	64	8
Norway [b]	Nordland, Troms and Finnmark	205	1.4	6.80	145	88	106	27	1.4	0.2	101	12
Sweden [b]	Norbotten	641	3.5	6.84	188	114	165	30	4.0	0.4	64	3
Iceland [c]		39	2.1	7.30	369	441	477	10	1.0	>0.1	546	0
Svalbard and Bear Island [c, d]		167	30	7.54	541	492	429	82	0.5	1.9	193	5
US, Alaska [e]	Kenai	59		6.88	101	96	144	3	6.4	0		
US, Alaska [f]	CABAL	22		7.79	457	459	448	89	4.7	0		
Canada [g]	Yukon (YK)	96		8.09	972	692	756	55	5.6	0.6		
Canada [g]	Northwest Territories (NT)	167		7.89	1866	1525	1519	83	3.0	0.7		
Canada [g]	Nunavut (NU)	3		7.90	1577	1200	1098	275	10.6	0.8		

CL_{Ac} is calculated by using the catchment dependent ANC_{limit} (Henriksen and Posch, 2001) and the Norwegian background sulfate concentration for all countries, except Sweden (Wilander, 1994). Exceedance CL is calculated with S-deposition from different sources, for each country year of deposition and name of the institute providing the deposition numbers are given: Norway (1990, NILU Norwegian Institute for Air Research), Sweden (1994, SMHI Swedish Meteorological and Hydrological Institute), Finland (1990, SYKE), Kola and Iceland (1992, EMEP European Monitoring and Evaluation Programme).

Data sources: [a] Duff *et al.* (1998); [b] Henriksen *et al.* (1997b); [c] Skjelkvåle *et al.* (2001c); [d] Lien *et al.* (1995), [e] Newell and Mitch (1992), Eilers *et al.* (1993); [f] Allen-Gil *et al.* (1997) [g] Nahanni (NT), Tuktoyaktuk (NT), Yellowknife (NT) and Wager Bay (NU) from Environment Canada, unpub. data; region between Coronation Gulf and Great Slave Lake (both NT and NU) from Rühland and Smol (1998), Rühland *et al.* (2003); region between southern YK and Tuktoyaktuk (NT) from Pienitz *et al.* (1997a,b); Wood Buffalo National Park (NT) from Moser *et al.* (1998); Melville Island (both NT and NU) from Bronwyn Keatley (Queen's University, unpub. thesis data); Prince Patrick Island (NT), Ellef Ringnes Island (NU) and Ellesmere Island (NU) from Antoniades *et al.* (2003a,b); Victoria Island and Axel Heiberg Island (NU) from Michelutti *et al.* (2002a,b); Baffin Island (NU) from Joynt and Wolfe (2001); Southhampton Island (NU) from Mallory *et al.* (2006).

6.1.1.1. **Northern Fennoscandia and the Kola Peninsula**

The Euro-Arctic Barents region consists of two major geological provinces: the northern part of the Precambrian shield and the Caledonian fold belt toward the north and west. Within the framework of European geology, the Norwegian, Swedish, Finnish, and Kola Precambrian is a part of the Fennoscandian or Baltic Shield. The Caledonian fold belt includes Precambrian and Paleozoic sediments. The Precambrian rocks are dominated by gneisses and granitic gneisses with low weathering rates, while the Caledonian and the Archean Karelian province also include rocks of more basic character with higher weathering rates (Lidmar-Bergström and Näslund, 2005).

The results from the 1995 Nordic Lake Survey were reported by Henriksen *et al*. (1997a,b), Henriksen (1998), and Skjelkvåle *et al*. (2001c) and form the basis of this section.

Lakes with relatively high concentrations of base cations are found in areas with basic/mafic rocks and metasediments; south-central Kola, central Finnmark, and central Lapland as well as scattered areas in the Swedish mountains. Low base cation concentrations, giving the greatest sensitivity to acidification, are found scattered all over the area and are most abundant in areas with bedrock composed of granite and granitic gneisses, i.e., the northern part of Kola, Norwegian coastal areas, the northeastern and southern parts of Lapland, and the western part of Norrbotten county. Northern Norway had the highest percentage of lakes with low concentrations of base cations; in Norway 40% of lakes had <100 µeq/L, while Finnish Lapland had only 10%. In Norrbotten and Kola respectively, 21 and 26% of lakes were acid sensitive. On the other hand, Norway also had the highest number of lakes with very high concentrations of base cations (11% of lakes had >500 µeq/L compared to 4 to 6% in the other countries).

Low alkalinity lakes (<20 µeq/L) were most abundant in the northern parts of the Russian Kola. Here, the higher content of organic matter in lakes in the eastern parts and the higher anthropogenic sulfate content in the western parts lowers the alkalinity. In the northern parts of the Nordic countries both the geological conditions and the precipitation amounts determine the alkalinity; depending on the weathering rate of the minerals in the soil and dilution by precipitation, respectively. In some regions with a high proportion of peatland, low alkalinity values in lakes are largely attributable to organic acidity. In general, low alkalinity lakes are rare in the northern Nordic countries and are scattered throughout the region as a whole.

Sulfate is considered to be the major acidifier of surface waters. High sulfate concentrations were most common in the western part of the Kola Peninsula, particularly around the smelters in Nikel and Monchegorsk. More than 10% of the lakes on the Kola Peninsula had >100 µeq/L non-marine sulfate (SO_4*). High concentrations were also found scattered around the whole Euro-Arctic Barents region. Most of these lakes probably had a significant input of sulfate from geological sources, reflecting the diverse geology of the area. The eastern Kola Peninsula represented the largest area with consistently low (<20 µeq/L) sulfate levels, reflecting the low sulfur deposition in this area.

Nitrate concentrations in the lakes of the Euro-Arctic Barents region were generally very low. More than 75% of lakes had <1 µeq/L NO_3. It was therefore concluded that nitrogen deposition was an insignificant acidifier of these lakes.

pH values of <5.5 were most abundant in the northern part of the Russian Kola (19% of lakes). Russian Kola also had the highest frequency of lakes with pH levels of <6.0 (28% of lakes), followed by northern Norway (14%), Norrbotten (7%), and Lapland (7%). In general, the lakes of the Euro-Arctic Barents region are less acid than lakes further south in these countries.

There was a pronounced west to east gradient in total organic carbon (TOC) concentrations. The coastal areas of Norway usually had <2 mg C/L, while lakes with >8 mg C/L were abundant in Norrbotten, Lapland, and the eastern parts of the Kola Peninsula. The topographically flat areas with peatland accumulation on the eastern Kola Peninsula and around Bothnian Bay are reflected in high TOC levels. However, despite the high proportion of peatland areas in the north, TOC concentrations in lakes in northern regions were found to be lower than in the countries as a whole, due to the colder climate, longer soil frost period, and lower peat decomposition rate (Kortelainen, 1993). Low TOC values in mountain lakes in the border area between Norway and Sweden are due to less organic soils in the catchments and high precipitation leading to dilution.

The estimated critical loads of acidity were exceeded in all countries. The highest percentage of exceeded lakes occurred in the Russian Kola and Norway, while Sweden had the lowest percentage of exceeded lakes. The calculations were based on sulfur deposition for 1990 (Finland and Norway), 1992 (Kola), and 1994 (Sweden) (see Henriksen *et al*., 1997a for full references of source data). In Norrbotten, the mean exceedance for 47 NILU-grids (95 percentile) using the FAB model with respect to deposition in 1990, 1997, and 2010 (in accordance with the Gothenburg Protocol) was 117, 38, and 31 eq/ha/yr, respectively.

6.1.1.2. **Iceland**

Iceland was created by volcanic activity along the Mid-Atlantic Ridge during the last 20 million years. The volcanic rocks in Iceland are predominantly mafic. Owing to the vesicular nature of the lava with glassy crusts, they weather readily. The lake water chemistry clearly reflects this geology. Results from the 1995 lake survey (Skjelkvåle *et al*., 2001c) showed that Icelandic lakes generally had high concentrations of base cations and high values of ANC and pH. Sulfate and nitrate concentrations were in general very low, due to low anthropogenic deposition of sulfur and nitrogen. High sulfate lakes were found in the active geological zones. Owing to the basic conditions of Icelandic lakes, they are not sensitive to acidification.

Owing to the high critical loads and the low sulfur deposition in Iceland, critical loads were not exceeded in any of the lakes studied. Hence, acidification of lakes is not a problem in Iceland.

6.1.1.3. **Svalbard and Bear Island**

The sedimentary rocks at Svalbard and Bear Island have a diverse mineralogy that includes limestone, dolomite, gypsum/anhydrite and shales containing phosphatic nodules, and yields waters with highly variable ionic composition. The lakes were sampled in 1990 to 1992 (Lien *et al*., 1995; Skjelkvåle *et al*., 2001c). High sulfate lakes were related to gypsum/ anhydrite in the soils and bedrock. In the northern parts of Svalbard some lakes were very acid sensitive, and in this area the critical loads were exceeded given the 1990 sulfur deposition (Lien *et al*., 1995).

6.1.1.4. New critical loads and exceedance calculations for the Euro-Arctic Barents region

Critical load calculations are used for assessment and policy work under the Convention on Long-range Transboundary Air Pollution (LRTAP) and the European Union and so are regularly updated (see section 5.4). This assessment focuses on data for northern Europe submitted to the Coordination Centre for Effects in 2004 (Hettelingh *et al.*, 2004) and new data for 104 lakes in the Kola region. The data on individual lake catchments are aggregated to the 'EMEP 50x50 km grid', which is used under the LRTAP Convention for deposition and exceedance calculations. Figure 6.2 shows the 5 percentile of the critical load of acidity on this grid system. Also shown are the critical loads for surface waters in Svalbard, which were computed and documented by Lien *et al.* (1995).

Exceedance of critical loads was calculated by combining the critical load maps with modeled deposition data, using the hemispheric Eulerian model DEHM (see section 3.7.4). Three emission/deposition scenarios were used in the calculations (see section 2.3): (i) 1990 emissions, (ii) the 'Current Legislation' scenario for 2010 (CLE 2010), and (iii) the 'Maximum technically Feasible Reduction' scenario for 2020 (MFR 2020). The same scenarios were used for calculating critical load exceedance for soils (see section 5.4).

Estimated exceedance of critical loads for the surface waters in northern Europe are shown in Figure 6.3 for the three emissions scenarios. The results indicate that implementation of presently agreed emissions reductions will reduce both the area and magnitude of exceedance substantially. However, the results also show that there is still clear exceedance of critical loads for surface waters in parts of the Kola region even after implementation of maximum technically feasible emissions reductions.

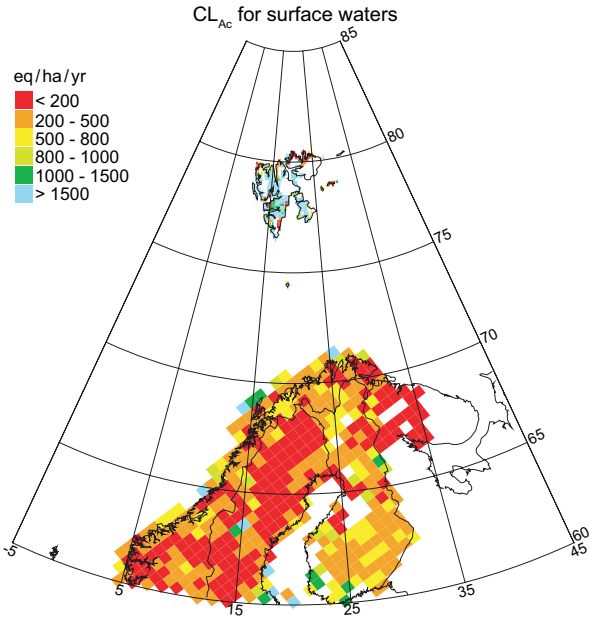


Figure 6.2. Critical loads of acidity for surface waters in northern Europe.

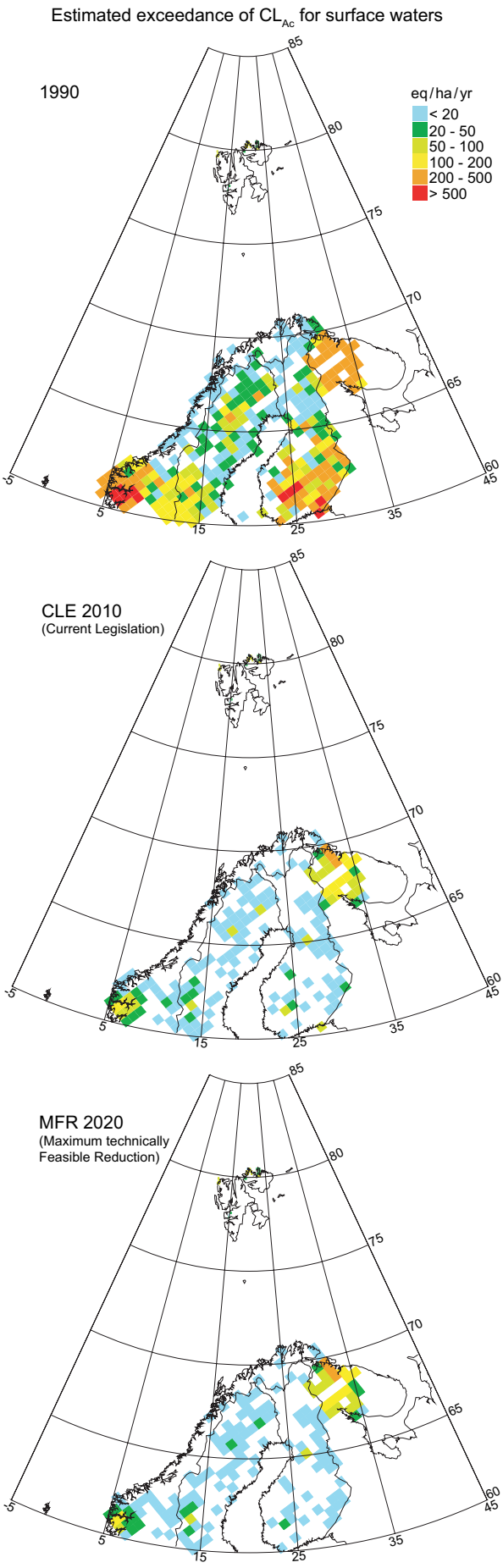


Figure 6.3. Estimated exceedance of critical loads of acidity for surface waters in northern Europe for three scenarios: 1990 emissions, Current Legislation for 2010 (CLE 2010), Maximum technically Feasible Reductions for 2020 (MFR 2020).

6.1.1.5. **Current status in Arctic Canada**

The area north of 60° N in Canada (the southern boundary of the AMAP domain) contains three politically defined territories: Nunavut, the Northwest Territories and the Yukon, plus the northernmost part of the province of Quebec. The area (more than 4 million km^2) comprises eight terrestrial ecozones spanning the boreal, taiga, arctic, and cordillera types that encompass the full spectrum of geological sensitivity to acidification. The largest expanses of acid-sensitive terrain (defined by a combination of bedrock and surficial geology) occur on Baffin Island and the continental mainland west of Hudson Bay. Most of the islands of the Arctic Archipelago have carbonate geology and so are not acid-insensitive.

Owing to the low solubility of the soils and bedrock characteristic of acid-sensitive terrain, associated surface waters are typically low in dissolved minerals and so the concentration of base cations indicates aquatic sensitivity. Fifteen percent of lakes investigated had base cation levels of <100 µeq/L, 20% of 100 to 400 µeq/L, and 65% of >400 µeq/L. The only extremely acid-sensitive lakes occur on Baffin Island and the central mainland straddling the border of Nunavut and the Northwest Territories. It should be noted, however, that the sample population excluded a large proportion of the acid-sensitive terrain.

Sulfur dioxide has long been acknowledged as the main air pollutant acidifying Canadian lakes (Jeffries, 1995, 1997) and is ultimately deposited on aquatic and terrestrial landscapes as SO_4. Sulfate deposition in the Canadian Arctic is very low (~3 meq/m^2/yr) so if atmospheric deposition is the main source of SO_4 in lakes, then lake concentrations should also be uniformly low. Figure 6.1 shows that lake SO_4 concentrations in Canadian arctic lakes are in fact spatially variable indicating the presence of geological sources in some areas, particularly Axel Heiberg Island.

Dissolved organic carbon levels in artic lakes exhibit a broad range in concentration (Table 6.1). Approximately 25% of lakes in Arctic Canada had substantial levels of DOC (>10 mg/L), which may contribute to some acidification by naturally occurring organic acids.

Lakes having alkalinity concentrations of <200 µeq/L have traditionally been considered sensitive to acidic deposition and 26% of the samples fell into this category. The spatial distribution of low alkalinity lakes tends to confirm the sensitivity interpretation using base cations. Unfortunately, there are no alkalinity data for Baffin Island lakes.

Of the lakes sampled, 251 had sufficient data to permit a calculation of critical loads for acidity (CL_{Ac}) using the Steady-State Water Chemistry Model (Henriksen and Posch, 2001) with an acid neutralizing capacity threshold value (ANC_{limit}) of 40 µeq/L. The median CL_{Ac} was 127 meq/m^2/yr and 8% of lakes had values of ≤10 meq/m^2/yr. The spatial distribution of three CL_{Ac} classes confirmed that the sample lakes mostly likely to acidify occur on Baffin Island and the central mainland. Whether or not the Steady-State Water Chemistry Model should be applied in a desert environment (annual surface runoff for almost all lakes was estimated to be 150 mm or less) merits further consideration.

6.1.1.6. **Naturally acidic lakes in Arctic Canada**

Most of the Canadian lakes fell within the pH range 6 to 9, which is assumed as the normal range for most natural, mineral-bearing waters. Only 3% of sample lakes had a pH of <6. Furthermore, only three of 605 lakes were strongly acidic, having a pH of <5. Two of the three strongly acidic lakes are on Axel Heiberg Island (pH 3.6 and 3.8) and both had extremely high SO_4 concentrations (Michelutti *et al*., 2002a). Schiff *et al*. (1991) used isotopic techniques to identify the source of the acid in the most acidic of these lakes (Colour Lake). They showed that oxidation of pyrite in the surrounding basin and oxidation of ferrous iron from an anoxic zone of the lake following spring ice-off and water column overturn caused the observed low pH and high SO_4 concentrations. It is not clear whether the arctic setting of these lakes is an important determinant in this acidification process. Certainly, lakes and rivers in temperate climates that are affected by acid mine drainage become acidic through similar processes. In natural temperate settings, however, acid generation by sulfide mineral oxidation tends to be self-limiting because the iron oxide weathering product coats the mineral surface rendering it less reactive. The occurrence of a naturally extremely acidic lake such as Colour Lake (and probably the other Axel Heiberg lake) is quite rare. Given the widespread occurrence of sulfide and to a lesser extent sulfate minerals, it seems reasonable to assume that some and perhaps even many lakes have been affected by acid-generating oxidation processes. The best evidence of this is probably the SO_4 data rather than the pH data. The third extremely acidic lake in the Canadian sample population was on Baffin Island (pH 4.66), but there are no SO_4 data to confirm oxidation of local sulfide minerals as the acid source.

A unique ecosystem acidification occurs at the Smoking Hills along the sea shore of Cape Bathurst in the Northwest Territories (70°14′ N, 127°10′ W; Havas and Hutchinson, 1983). Bituminous shales appear to have been burning for thousands of years thereby producing ground-level acidic fumigations that strongly influence the local tundra. Ponds in the area (not included in the data compilation described above) typically have pH levels of >8, but those within the fumigation zone have been acidified, sometimes to a pH of <2. The ponds exhibit elevated metal concentrations (aluminum, iron, zinc, nickel, manganese, and cadmium) and biota that are characteristic of acidic environments elsewhere. Biota in adjacent non-acidified ponds are typical of other arctic environments.

6.1.1.7. **Alaska**

There are very few lake or stream chemistry data available from acid-sensitive parts of the Alaskan arctic. The Kenai Lakes Investigation Project (Newell and Mitch, 1992; Eilers *et al*., 1993) characterized the major ion chemistry of over 800 lakes on the Kenai Peninsula from a statistical survey of 59 lakes in 1988. The results showed two groups of lakes: those with an alkalinity of <300 µeq/L (78% of lakes) and those with an alkalinity of >700 µeq/L. Low-alkalinity lakes had significantly lower concentrations of base cations and silica and significantly higher average concentrations of DOC than high-alkalinity lakes. Despite widespread acidic soils and bog vegetation, and resulting high DOC levels, none of the lakes sampled were acidic (minimum alkalinity 20 µeq/L).

The Chemistry and Biology of Arctic Lakes (CABAL; Allen-Gil *et al*., 1997) project sampled 22 lakes on the North Slope of Alaska in 1992 (D. Landers, U.S. Environmental Protection Agency, unpubl. data). The results showed only two lakes with an alkalinity of <200 µeq/L (minimum 156 µeq/L); none were considered to be acidified.

6.1.1.8. **Northern Russia, Siberia**

Lakes were sampled in three regions of Siberia, northern Russia, in 1993 to 1995 (Duff *et al*., 1998). The lakes were situated in the Pechora River basin, in the Yenisey River basin on the Taymir Peninsula, and in the Lena River basin. Only the lakes in the Taymir region were located in the same area as the large emissions source at Norilsk, but these were still around 200 km away. All the lakes (with the exception of a few in the Pechora River basin) were small, dilute, and oligotrophic with a neutral to slightly alkaline pH. Forested lakes near the mining center of Norilsk had higher concentrations of the major ions and metals; sediments in these lakes also had elevated metal concentrations (Blais *et al*., 1999). However, all the sample lakes in this area had ANC levels of >200 µeq/L and so were well buffered towards acidification. Some acidic lakes in the Pechora River basin had very high levels of organic carbon or high sulfate concentrations, probably due to geological sources.

6.1.2. **Temporal trends**

Temporal trends in water chemistry can be identified using data from regular monitoring over many years or from a series of repeated lake surveys. This assessment is based on both types of data but is limited to the Euro-Arctic Barents region (i.e., the northern part of Finland, Norway, Sweden and the Kola Peninsula of Russia). Data for other areas are not available.

The Euro-Arctic Barents region is affected by long-range transboundary air pollution and by emissions from industrial centers on the Kola Peninsula. Although the pollution exhibits relatively large year-to-year variations, it has still been possible to identify a general decrease in sulfur deposition and consistently low nitrogen deposition (see section 3.3).

6.1.2.1. **Lakes in Finland, Norway, and Sweden**

Acidification has been monitored in Finnish lakes since 1990. In northern Finland, there are estimated to be around 2100 small (4-100 hectare) headwater or seepage lakes susceptible to acidification (Forsius *et al*., 2003). A subset of 35 small forest or mountain lakes has been monitored annually in Finnish Lapland. In Norway, 24 lakes have been monitored on an annual basis since the 1986 lake survey (Henriksen *et al*., 1988). The monitoring is focused on areas of eastern Finnmark near the Russian border. The monitoring network includes six lakes in the Jarfjord area and 11 lakes in the county of Sør-Varanger. In addition there are six lakes in the counties of Nordland and Troms (SFT, 2005). In Sweden, eight 'reference' lakes have been sampled three to four times each year (Wilander, 1998).

The data from these 60 lakes for 1990 to 2004 were compiled to assess surface water trends in non-marine sulfate (SO_4*), non-marine base cations (Ca+Mg)*, alkalinity, ANC, and pH. The lakes were sub-divided into three groups based on geographical location: (1) Lapland, Finland, (2) eastern Finnmark, Norway, (3) northern Norway and Sweden (Figure 6.4). Trends for each lake and each variable were analyzed using the non-parametric tests given by Hirsch *et al*. (1982). These are equivalent to a non-seasonal Mann-Kendall trend test and the Sen slope estimator (cf. Helsel and Hirsch 1995). Trend slopes for each region were calculated using the same test, but in this case each lake was treated as a 'season'. The results give the direction of the trend from the trend slope. The detected trends are monotonic, i.e., proceed in only one direction.

Non-marine sulfate

Most sites showed a significant decrease in sulfate between 1990 and 2004 (Figures 6.4 and 6.5, Tables 6.2 and 6.3). The exception was a single site in northern Sweden (Abiskojaure) in which concentrations increased due to sulfur-containing minerals within the drainage basin. Lakes in eastern Finnmark near the emissions sources showed the most pronounced decrease with a trend slope of -1.4 µeq/L/yr (Table 6.3) based on concentration levels of 78 µeq/L in 1990 to 55 µeq/L in 2004 (representing a 30% decrease). Lakes in Finnish Lapland showed a trend slope of about -1.0 µeq/L/yr based on concentrations of 32 µeq/L to 18 µeq/L (a 43% decrease). Lakes in southern and central Lapland are more affected by long-range transported air pollutants from the south and so have benefited from the decrease in total European sulfur emissions. Lakes in northern parts of Norway and Sweden showed very slight decreases with an overall trend slope of -0.4 µeq/L/yr (Table 6.3) based on concentrations of about 20 µeq/L to 13 µeq/L (a 30% decrease).

Non-marine base cations

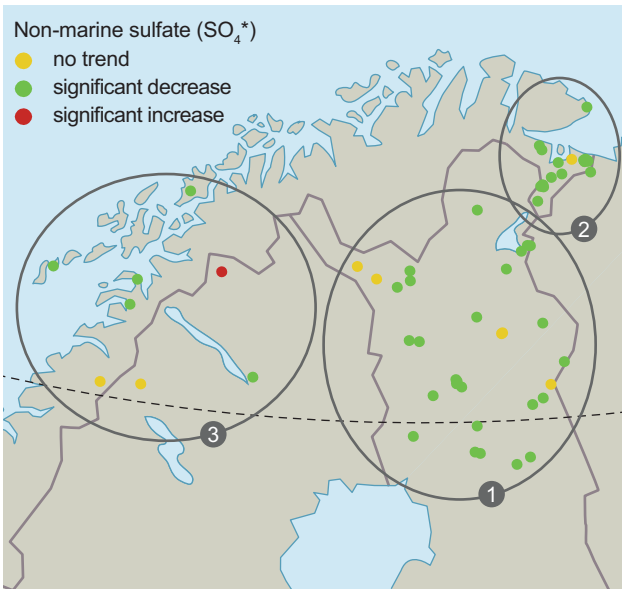
Base cations showed very small changes in concentration and the trends were both positive and negative (Figures 6.4 and 6.5, Table 6.3). Of the 60 lakes in this assessment, 25% had slightly significant increasing trends while 12% had significant decreasing trends. Trends for two of the three regions showed significant increases with average trend slopes of +0.5 µeq/L/yr for northern Norway and Sweden and +0.8 µeq/L/yr for Lapland. The increase in the first group was strongly dependant on the increase in a single lake (Lake Abiskojaure). Small changes and even increases in BC* concentrations compared to SO_4* con-

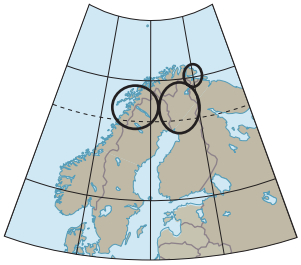
Table 6.2. Decrease in sulfate concentrations (µeq/L) between 1990 and 2004 for the three sub-regions. Values are calculated from linear regressions of average values.

	SO_4*, µeq/L		Change
	1990	2004	(%)
Lapland, Finland	32	18	-43
Eastern Finnmark, Norway	78	55	-30
Northern Norway and Sweden	20	13	-30

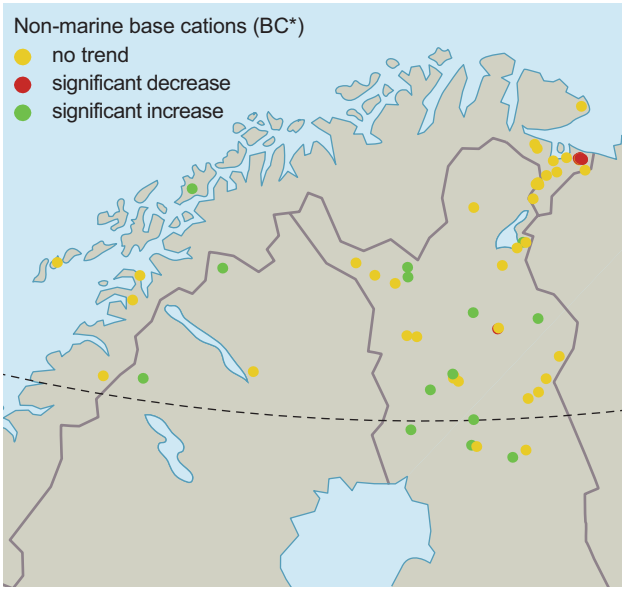
Table 6.3. Regional trends for 1990 to 2004. Values are median slopes with significant results (p<0.05) in bold. Units are µeq/L/yr.

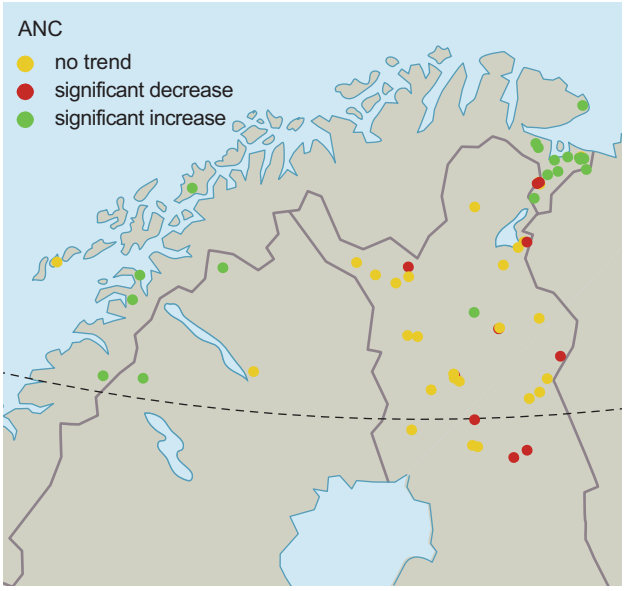
		Alkalinity		ANC		BC*		H^+		SO_4*	
	n	p	Theil slope	p	Theil slope	p	Theil slope	p	Theil slope	p	Theil slope
Lapland, Finland	35	**0.002**	**1.0**	**0.04**	**-0.3**	**0.006**	**0.8**	0.2	0.00	**0.0003**	**-1.0**
Eastern Finnmark, Norway	17	**0.004**	**0.3**	**0.0003**	**1.9**	0.05	-0.4	**0.0004**	**-0.04**	**0.0001**	**-1.4**
Northern Norway and Sweden	8	**0.007**	**0.9**	**0.001**	**1.6**	**0.007**	**0.5**	**0.002**	**-0.01**	**0.001**	**-0.4**

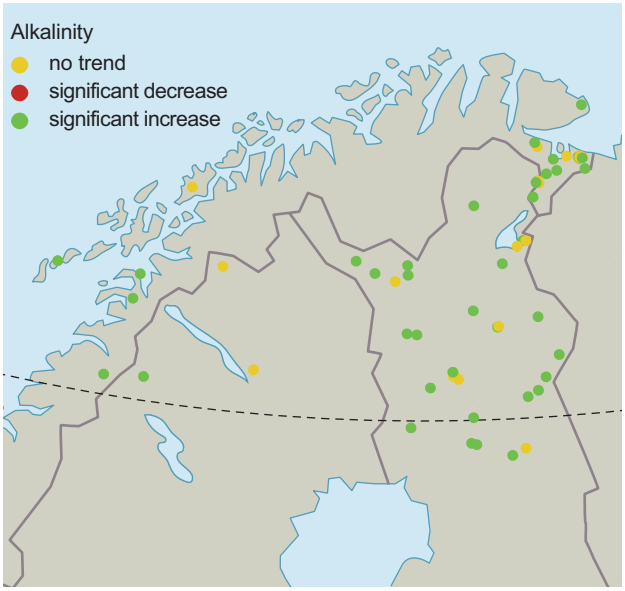




1 Lapland, Finland
2 Eastern Finnmark, Norway
3 Northern Norway and Sweden







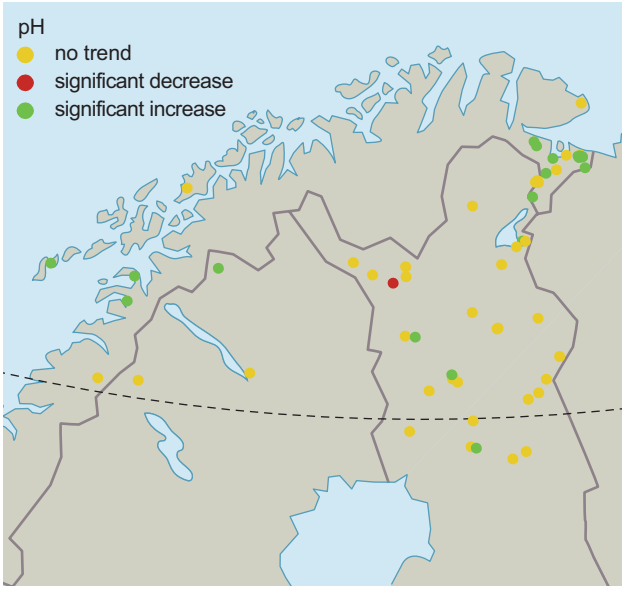


Figure 6.4. Trends in non-marine sulfate, non-marine base cations (Ca+Mg), alkalinity, acid neutralizing capacity, and pH across the Euro-Arctic Barents region for 1990 to 2004. Large circles denote the three sub-regions.

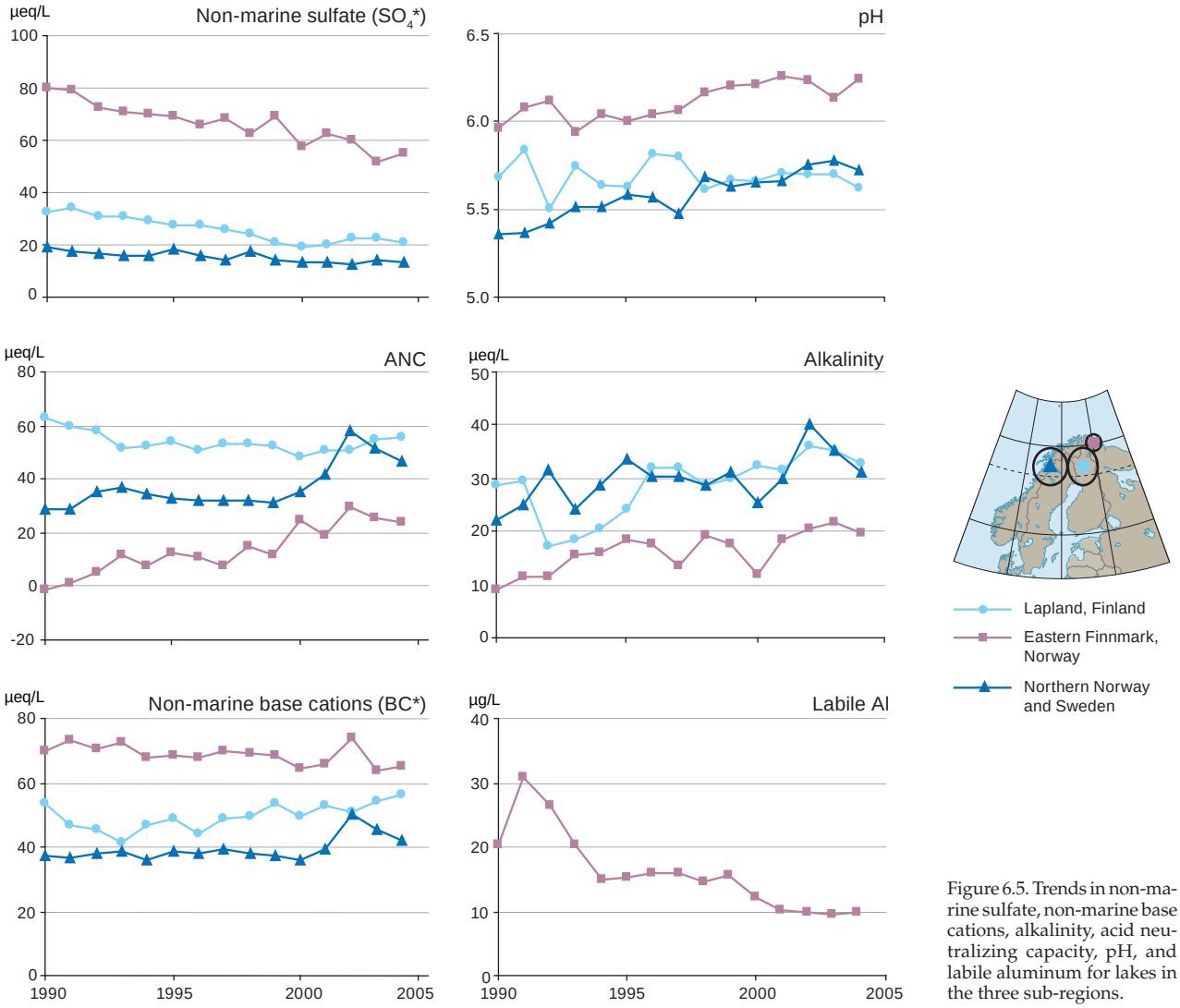


Figure 6.5. Trends in non-marine sulfate, non-marine base cations, alkalinity, acid neutralizing capacity, pH, and labile aluminum for lakes in the three sub-regions.

centrations enabled alkalinity to increase (see Figures 6.4 and 6.5). The median annual change in alkalinity ranged from +0.3 to +1.0 µeq/L/yr for the three regions (Table 6.3). The signs of chemical recovery are not reflected in the same way in calculated ANC (Figures 6.4 and 6.5). For Lapland, the median annual change in ANC was a decrease of -0.3 µeq/L/yr (Table 6.3). The small lakes in northern Finland are low ionic, dilute lakes (with BC* typically <100 µeq/L) that have had only modest impacts from air pollutants. Therefore, a high interannual variation in ion concentrations in these lakes reflects hydrological variations.

Alkalinity and pH

Increases in alkalinity are at an early stage and not really reflected in the pH values. In 37% of lakes, pH showed a significant increase (Figures 6.4 and 6.5, Table 6.3 (calculated as decrease in concentration of H^+)). This increase was most pronounced in eastern Finnmark. There is a large interannual variation in pH in lakes in eastern Lapland, due to variations in hydrology and natural organic acids. So a consistent and corresponding increase in pH cannot be expected. There is also pronounced seasonal variation, with the highest values in late summer and the lowest at the end of winter or at snowmelt.

Aluminum

There are few data on aluminum. In Finland, when sample pH was >6.2, the laboratories did not analyze aluminum. Moreover, at many sites inorganic bound aluminum was below the detection limit (<10 µg/L). The 1995 lake survey showed that a median value for lakes in northern Finland was <10 µg/L (with a 90 percentile of 10 µg/L), and the median in northern Norway was also <10 µg/L (90 percentile of 13 µg/L). Lakes in eastern Finnmark show a clear decrease from around 20 to 30 µg/L in the early 1990s to 10 µg/L in 2004 (Figure 6.5).

6.1.2.2. **Lakes on the Kola Peninsula**

A lake survey has been conducted every five years on the Kola Peninsula (1990, 1995, 1998, 2000, 2005). Six lakes with different atmospheric loads were chosen to illustrate long-term changes. Two are near (10 km) the large point sources at Nikel and Monchegorsk while the other four are over 80 km away (Figure 6.6).

Water quality in the two lakes near the point sources had improved, with decreased concentrations of sulfate (Figure 6.6), nickel, and copper. Base cation levels have also decreased at these sites. As the concentrations of sulfate, nickel and copper also decreased in the four lakes located

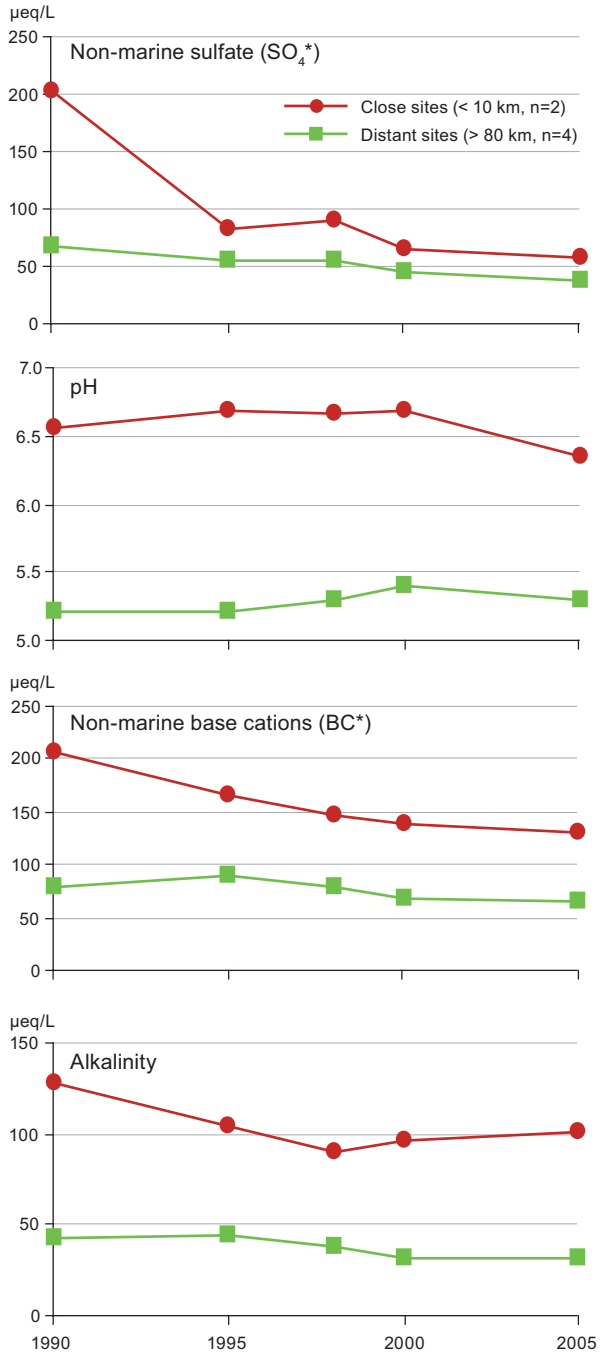


Figure 6.6. Trends in non-marine sulfate, alkalinity, non-marine base cations, and pH for lakes on the Kola Peninsula.

some distance from Nikel and Monchegorsk it appears likely that these decreases represent a decrease in regional sulfate and metal loads in the Kola North. There was no tendency for pH or alkalinity to increase despite the large decrease in sulfate.

6.1.2.3. **Swedish repeated lake survey**

In each of the Swedish lake surveys (1990, 1995 and 2000) 315 lakes were sampled in Norrbotten county. An evaluation using Theil's slope showed that SO_4 concentrations fell in 96% of lakes, which supports the results of other studies presented here. Alkalinity and ANC decreased in 91 and 69% of lakes, respectively. So this study shows no anticipated response of the lakes to the decreased sulfur deposition. Seven Norrbotten reference lakes studied several times each year also had decreasing trends for alkalinity, but in all seven the ANC increased (median 0.0015 meq/L/yr). A comparison of these two studies shows that changes observed on just a few occasions may be more indicative of variation between years than a trend. Trends, as evident from more intense monitoring, are very small and so surveys with few observations over time may be insufficient to identify the trends found using more intensive studies (Wilander, 1998).

6.1.2.4. **Concluding comments on trends**

Long-term monitoring indicates that lakes in the Euro-Arctic Barents region are recovering from acidification and that this is due to reduced sulfur deposition. However, even if the lakes have received acidic inputs and have consequently experienced a decrease in ANC, alkalinity, and pH, the lake water has not necessarily been acidified to a level at which visible damage to the biota can be expected. Lakes in eastern Finnmark near the non-ferrous metal smelters on the Kola Peninsula show the clearest signs of recovery due to reduced sulfur deposition. Other studies from the Finnish-Norwegian-Russian border area also show signs that lakes there are recovering from acidification. Surveys of small mountain lakes and brooks in northeastern Lapland in 1993 and 2000 found a significant increase in alkalinity and a decrease in sulfate concentrations. The increase in alkalinity was pronounced in the most acidic lakes (i.e., those with an alkalinity of <20 µeq/L) in 1993 (Lappalainen *et al.*, 1995; Tammi *et al.*, 2003b). The recovery of lakes further from these major pollution sources (that experienced only modest impacts from air pollutants) are affected by a high interannual variation in ion concentrations and so trends are not easily detected. Although the changes seen in Swedish surface waters are thus less pronounced than in northern Norway, they are still significant evidence of improvement in the Barents region.

6.2. Effects of acidification on arctic biota

The first AMAP assessment (AMAP, 1998) reviewed data on the effects of acidification on the freshwater biota of arctic surface waters. One of the key conclusions of the assessment was that arctic biota live in an extreme environment – the limited temperature range, ice-free season, and productivity of the Arctic produce biotic assemblages that may require very little additional stress before they are affected. The assessment also described those characteristics of arctic biota that make them especially sensitive to acidification. The assessment concluded that, while the taxa found in arctic waters are also likely to occur in sub-artic (and even temperate) waters, the number of different taxa in any one arctic lake or stream is relatively low – low taxa richness and low productivity create the potential for small changes in biotic assemblages to have relatively large ecosystem effects (Hobbie, 1984). Within the Arctic, the likelihood of low productivity and paucity of species increases with latitude. The assessment found that crustacean zooplankton may be absent from ultra-oligotrophic arctic lakes due to lack of food and that benthic invertebrate assemblages are generally dominated by chironomid larvae in lakes, and in flowing waters by the same sensitive insect taxa (e.g., mayflies) that dominate in northern temperate areas. The assessment also found that there are a small number of fish

species in most arctic waters – fish life spans may be very long (e.g., 25 to 40 years for Arctic char) due to slow growth and the slow accumulation of sufficient energy reserves for reproduction. Thus, arctic fauna is considered sensitive or vulnerable to anthropogenic alterations, including acidification (Hammar, 1989), principally because arctic assemblages occupy simple and labile ecosystems that undergo extreme climatic conditions and fluctuations.

Although there are relatively few (compared to temperate zones) published studies on arctic biota and acidification, research and monitoring prior to 1996 supports the characterization of arctic biota as susceptible to acidification (AMAP, 1998). The few documented effects include sensitive zooplankton (e.g., some species of *Daphnia*) being rare or absent from acidified lakes in the Jarfjord area of Norway (Nøst *et al*., 1992); there are no other reports of acidification effects on plankton in the Arctic. Also in the Jarfjord area, Nøst *et al*. (1992) reported low abundance of acid-sensitive mayflies (Ephemeroptera) in acidified lakes; in the Dalelva catchment (Norway) the loss of sensitive benthic invertebrate taxa was attributed to low pH and elevated aluminum concentrations (Bækken and Aanes, 1990). In the Murmansk region of Russia, the abundance of zoobenthos in small acidified lakes was as low as that in lakes contaminated by heavy metals (Yakovlev, 1992). In northeastern Finland, no acidification effects were reported for the benthos, with sensitive taxa (e.g., *Baetis rhodani*, *B. lapponicus*) found throughout the area. Many researchers concluded that fish populations in the Arctic were relatively unaffected by acidification (e.g., Erkinaro *et al*., 1992; Lappalainen *et al*., 1995; Nøst *et al*., 1992); deleterious effects of acidification on fish may only be found in the Jarfjord area of Norway (Hesthagen *et al*., 1992).

6.2.1. **Current status**

More recent data support the conclusions of the first AMAP assessment (AMAP, 1998), namely that acidification effects are rare. These data are all for the areas immediately adjacent to the Kola Peninsula – there continues to be no biological data for any acid-sensitive areas of the North American Arctic.

6.2.1.1. **Phytoplankton and periphyton**

Planktonic and epilithic diatoms are considered some of the best biotic indicators of acidification; the disappearance of acid-sensitive diatom species, and the dominance of acid-tolerant species, has long been used to quantify the long-term progression of acidification (see section 6.4). The current species composition of diatoms and chrysophytes can also be used to assess whether acidification has altered the current status of lakes and streams. There is currently no evidence of altered diatom assemblages due to acidification in the Arctic. Sorvari *et al*. (2002), for example, examined sediment cores from five lakes in Finnish Lapland and concluded that, although diatom assemblages have changed over the past two centuries, there was no evidence of changing diatom-inferred lake water pH. Similarly, Korhola *et al*. (1999) reported stable diatom assemblages from three lakes in northeastern Finnish Lapland, and concluded from their pH reconstructions that 'no substantial changes in the acidification status of lakes have occurred within the last century despite the very high local acidic deposition' (see also section 6.4).

Lakes in northeastern and northwestern Finnish Lapland have been studied for their contemporary phytoplankton fauna as a part of the European-wide project EMERGE (European mountain lake ecosystems: regionalization, diagnostics & socio-economic evaluation). One purpose of the project was to set the baseline of the ecological conditions of pristine mountain/arctic lakes in Europe for future monitoring. Even though the lakes do not appear to be anthropogenically acidified, variations in the species composition of phytoplankton indicate different responses and sensitivities to pH.

Phytoplankton were studied from 33 lakes in northern Finland as part of EMERGE. All the lakes had low biomass and low species numbers and are classified as oligotrophic or ultraoligotrophic from their chlorophyll a concentrations and phytoplankton biomass (Vollenweider and Kerekes, 1982). Most lakes were dominated by chrysophytes, which are characteristic of oligotrophic lakes with cool summer water temperatures, low alkalinity and conductivity, and neutral or slightly acid pH (Sandgren, 1988). Several lakes showed a pronounced dominance pattern, where only a few phytoplankton taxa contributed up to 80% of total phytoplankton biomass. This pattern is considered to be a consequence of stress, such as harsh climate (Willén, 2003). In the EMERGE study this pattern seemed to be more common in lakes with some additional stress (other than climate), such as high altitude or low pH. Although the studied lakes are widely distributed across Finnish Lapland, representing different environmental, altitudinal, and geomorphological settings, site-specific lake chemical properties (e.g., pH, conductivity, calcium, magnesium, sodium, alkalinity) seem to be the best predictors of species composition.

6.2.1.2. **Macroinvertebrates**

Data on benthic invertebrates from lakes and streams suggest that, while demonstrable acidification effects are rare, sensitive taxa are common in the Arctic, and the potential for subtle (or future) effects is high.

Nearly 400 small lakes and their inlet/outlet streams have been studied in northeastern Fennoscandia (Finnish Lapland, northern Norway, and the Murmansk region). Data collected between 1990 and 1997 suggest that both anthropogenic (mineral) and natural (organic) acidification have effects on the structure of benthic assemblages (Yakovlev, 1999). These effects (e.g., declines in species diversity, relative abundance and biomass in acid-sensitive invertebrates such as *Gammarus*, as well as snails, mayflies, and stoneflies) also vary strongly with natural abiotic factors of the landscape, including lake size, hydrological type, and morphology. Impoverished benthic fauna, typical of acidified lakes, was found in roughly 25% of the acid and/or humic lakes in central and northern Lapland, and attributed to decreased pH and the toxic effects of elevated aluminum (Yakovlev, 1999). Yakovlev (2000) also reported increased dominance of the benthos by predators, and a decrease in primary consumers, with decreasing pH in Fennoscandia. Both Yakovlev (1999) and Erkinaro *et al*. (2001) reported no observable acidification effects on macroinvertebrate assemblages in northernmost Finland.

Benthic assemblages may also be strongly affected by acidic episodes in the Arctic. Hämäläinen and Huttunen (1998) used a set of 17 test streams in northeastern Finland to construct a weighted averaging (WA) model predicting minimum pH from invertebrate assemblage data, and then

applied the WA model to an additional 37 streams in the region. They found that the predicted pH values correlated most closely with the minimum pH values observed during spring snowmelt. They also found a strong correlation with longitude, suggesting stronger effects (and lower minimum pH values) near the Kola region.

Midge larvae (chironomids; Diptera: Chironomidae) have been sampled extensively in the EMERGE lakes in Finnish Lapland. The composition of benthic littoral chironomid assemblages in this region appears to be strongly influenced by pH, but the assemblages do not exhibit signs of acidification. Nyman *et al*. (2005) found that the variation in chironomid communities of 50 shallow lakes across western Finnish Lapland was explained by the factors that are likely to respond to future climate change (e.g., sediment organic content, total organic carbon, pH, and mean July air temperature). These subarctic lakes are not anthropogenically acidified, but are highly vulnerable to multiple stresses caused by climate change and ultraviolet radiation (ACIA, 2004; Rautio and Korhola, 2002) (see section 6.5).

6.2.1.3. **Fish**

Recent data from acid-sensitive regions of the Arctic suggest little evidence of widespread effects on fish assemblages, but significant effects in some highly affected areas. Hesthagen *et al*. (1998) analyzed questionnaire data from 401 lakes (236 with Arctic char, 293 with brown trout) in northern Norway near the Russian border. They concluded that only three populations of Arctic char had been lost due to acidification, while three populations of char and eight of brown trout were reduced at least to some degree. This is consistent with the larger context of acidification (and recovery) in the Nordic countries; results from the project 'Fish status of Nordic Lakes' indicate that 'fish population losses were most frequent in the most highly acidified region of southern Norway and least common in eastern Fennoscandia' (Rask *et al*., 2000; Tammi *et al*., 2003a). Similarly, a study of 13 rivers in northernmost Finland found no signs of acid-induced failure in salmonid reproduction and/or recruitment (Erkinaro *et al*., 2001). Importantly, many studies of fish in acid-sensitive regions of the Arctic have focused on salmonids (e.g., Arctic char, brown trout) which may be relatively tolerant of low pH and elevated aluminum (Poléo and Bjerkely, 2000).

In a fish and water chemistry survey carried out in northeastern Finnish Lapland in 1991-1993, Lappalainen *et al*. (1995) found that the buffering capacities of small lakes and brooks were lowest in the Vätsäri area. The surface waters of the area consist of an exceptionally high number of small headwater lakes and brooks, which are sensitive to acidification due to the geochemistry of the local soil (Kähkönen, 1996). Owing to the relatively large differences in altitude over a short distance, natural obstacles to migration are common and fish populations in many lakes and brooks are isolated from each other. In some of the small lakes in the Vätsäri area, the alkalinity values were critically low in 1993, and studies revealed the first signs of acid-induced fish population damage in Finnish Lapland in local minnow (*Phoxinus phoxinus*) populations. In continuing this research and monitoring, special attention has been focused on the minnow and its reproduction because of the sensitivity of the species to acidification and its frequent occurrence in the study area (see section 6.2.2.2).

6.2.2. **Temporal trends**

6.2.2.1. **Invertebrates**

Temporal trend data are available for 12 arctic lakes in Norway (included in the Norwegian national monitoring program on long-range transported air pollution (SFT, 2005)). The microcrustacean assemblages of six lakes situated in Nordland and Troms counties were surveyed in 1999, and the data indicate no or only minor impacts of acidification. One of these lakes has been followed with annual sampling and shows no signs of changing acidification status. Six lakes in the eastern part of Finnmark (Varanger Peninsula) were surveyed in 2000 and 2004 (additional data are available for 1990 to 1997 for most of the lakes); these data indicate minor to moderate impacts of acidification in the microcrustacean communities.

Lake Dalvatn is an acid-sensitive lake in Finnmark that has been monitored for zooplankton since 1990. Signs of improvement in the acidification status of Lake Dalvatn are given by the increased abundance of the acid-sensitive cladoceran *Daphnia longiremis* (Figure 6.7). This species, which is absent in acidified lakes (Keller *et al*., 2002), was first recorded in Lake Dalvatn in 1996, and has been found each year since 1999 with increasing dominance. The presence of other acid-sensitive species of microcrustaceans has also increased in the last six years.

6.2.2.2. **Fish**

Tammi *et al*. (2003b) reported on fish data collected as part of a re-sampling of 20 lake and stream sites in the Vätsäri area of northeastern Finland in 2000; these were the same sites as were sampled in 1993 by Lappalainen *et al*. (1995),

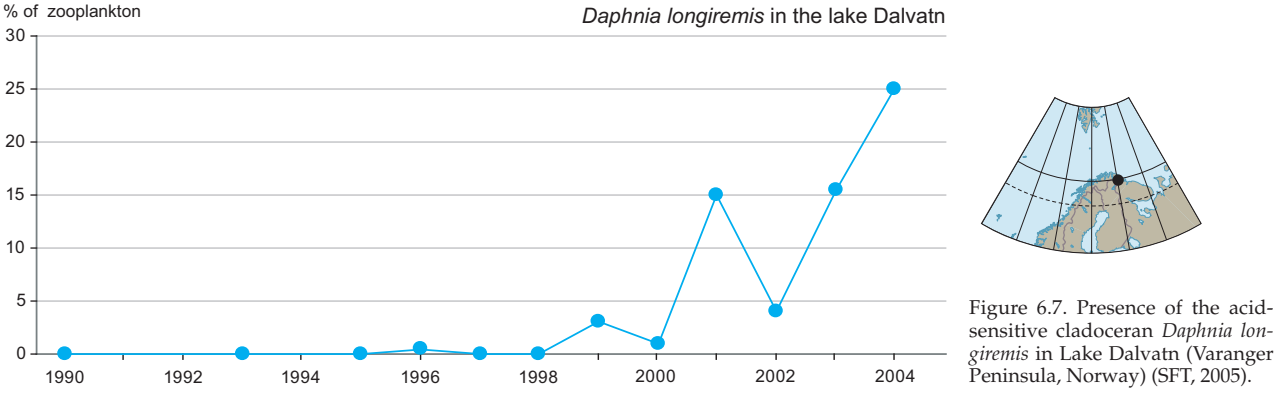


Figure 6.7. Presence of the acid-sensitive cladoceran *Daphnia longiremis* in Lake Dalvatn (Varanger Peninsula, Norway) (SFT, 2005).

who found evidence of acidification in the age-structure of minnow populations. Comparisons of the 1993 and 2000 data are shown for four sites in Figure 6.8. In all brooks and lakes, the alkalinity values were significantly higher, and the sulfate concentrations and conductivity values significantly lower, in 2000 than in 1993. The increased densities of minnow, and changes in the length distribution of the sampled fish, indicate reproductive success and recruitment of young fish at most sampling sites in the late 1990s. Although fish samples were taken in single years, the catches of electrofishing included several age-classes – the combined data on abundance and length distribution provided convincing evidence of the reproductive success of fish in the late 1990s. Despite the improvement in water quality, sparse minnow populations at some of the study sites appear to have disappeared completely during the 1990s. At these sites, the catch for 1993 consisted of only a few, rather large (60–80 mm) individuals and no minnows were found at all by electrofishing in 2000.

Lake Otervatn in eastern Finnmark has been monitored for water chemistry and brown trout populations (using benthic gill nets) since 1986 (Figure 6.9). The lake has shown a dramatic recovery in both acid/base status and brown trout populations over the last 20 years. Brown trout catch per unit effort shows a significant increase over time, and is significantly correlated with the observed increase in alkalinity. These data are strongly suggestive of recovery from acidification.

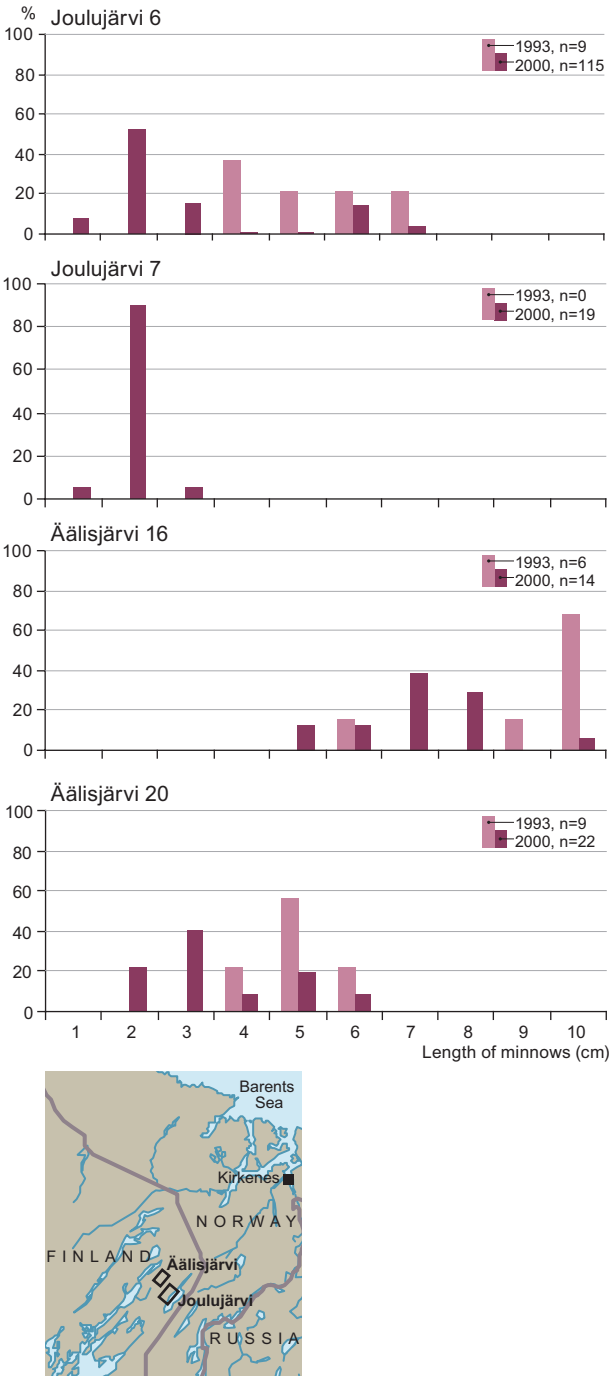


Figure 6.8. Length distributions of minnows caught by electrofishing in the Joulujärvi area (sites 6 and 7), and in the Äälisjärvi area (sites 16 and 20) in 1993 and 2000 (re-drawn from Tammi *et al.*, 2003b).

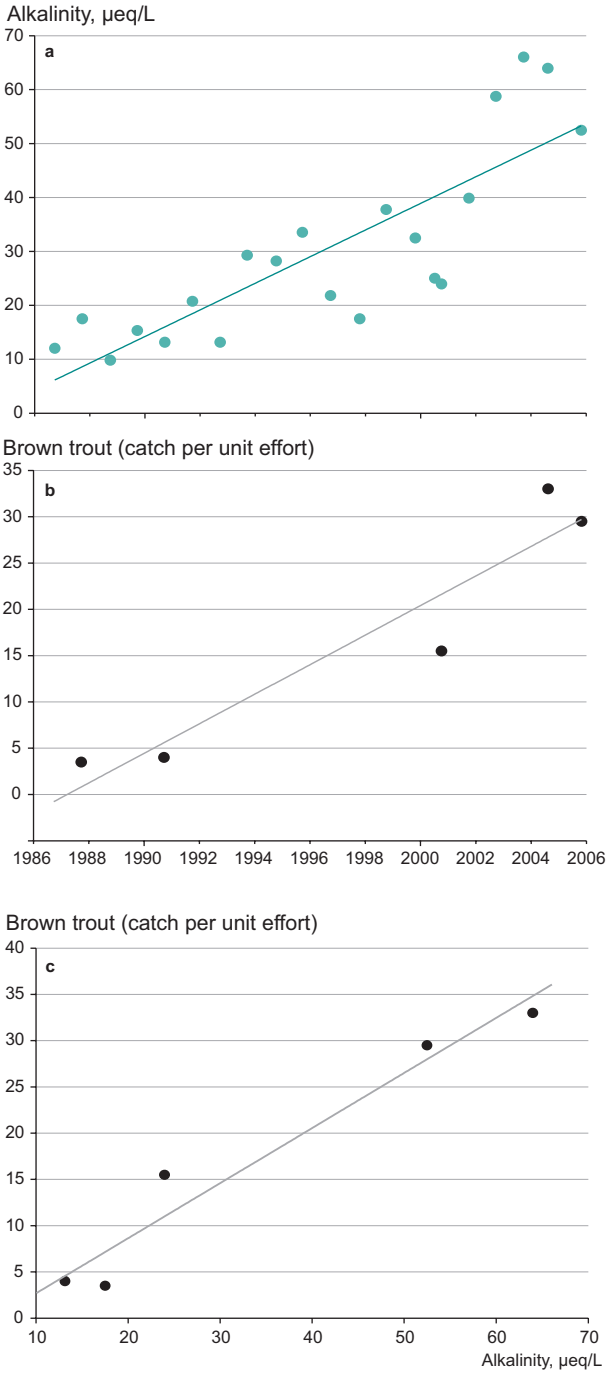


Figure 6.9. Data for Lake Otervatn in eastern Finnmark, showing (a) alkalinity (µeq/L) and (b) brown trout catch per unit effort (CPUE, expressed in number of fish caught per 100 m^2 of gill net area) since 1986, and (c) brown trout populations in relation to changes in alkalinity.

6.3. Episodic acidification

Episodic acidification of surface streams during spring floods is a ubiquitous phenomenon all over the world, including arctic regions. Acid episodes are especially dangerous in the Arctic; contaminants deposited from the atmosphere accumulate in the snowpack during the long polar winter and are released rapidly into drainage basins during the short spring flood in acidified polluted snowmelt waters that cause a sharp decrease in pH and alkalinity. Simultaneous pulses of protons and metals may lead to episodes with extremely strong toxic effects in streams and rivers. pH in rivers often drops during spring or rain floods under natural conditions because of base-flow dilution by atmospheric precipitation, although in some cases this phenomenon can be due to the leaching of natural organic acids from soils in forested or wetland catchments (Laudon and Bishop, 1999). However, this natural pH decline can also be dramatic and may affect biota. The accumulation of anthropogenic acids (SO_4, NO_3) in catchments abruptly intensifies the episodic acidification in flood periods. Arctic ecosystems are especially vulnerable to acid pulses during spring floods. After polar night, the vulnerability of arctic biota to acid and toxic impacts is much higher. Situations in which two or more stressors occur simultaneously, thereby multiplying the risk for aquatic life, are dealt with in more detail in section 6.5. Episodic pH decline has been observed in several arctic regions, for example, Sweden, Finland, and Russia (Kinnunen, 1992; Moiseenko, 1999; Laudon *et al.*, 2000; Moiseenko *et al.*, 2001).

How pH episodes form depends on the conditions of water formation. Catchments in the Arctic are mostly of the tundra or forest type, although hilly and mountainous catchments also occur. The mechanism of pH depression in surface waters is determined, as a rule, by the interaction of several factors capable of causing acidification. Published reports emphasize five factors that contribute to depressed ANC during flood time: (1) dilution from increased discharge; (2) H_2SO_4 and (3) HNO_3 derived from precipitation or natural sources; (4) organic acids derived from watershed soils or wetlands; and (5) HCl derived from 'salt-effect', i.e., reactions within catchment soils (e.g., Jeffrey *et al.*, 1992).

6.3.1. Acidic episodes in the Kola region

Acidic episodes have been studied in the Kola North, where a high level of anthropogenic sulfur deposition has been recorded. The decrease in pH during spring flood relative to the pre-episode period (i.e., the winter low-water period) was examined in 21 streams (Moiseenko, 1999; Moiseenko *et al.*, 2001). The decrease was most noticeable in streams where the pre-episode pH was high, while in streams that were chronically acidified (with pH values during the low-water period of <6) the pH drop was insignificant owing to the similarity between the chemistry of water in acidified streams and atmospheric precipitation (Figure 6.10). This is in general agreement with data collected in Europe and North America (Wigington *et al.*, 1992). The period of pH depression during spring flood in this part of the Arctic is short and rarely exceeds five to seven days.

Acidic episodes facilitate the discharge of metals into streams and rivers. It is well known that water acidification causes an increase in the concentrations of labile metal forms (Dillon *et al.*, 1988; Nelson and Campbell, 1991; Jeffries, 1997). In arctic regions, an abrupt drop in water pH in a short flood period is accompanied by a pulse of metals, especially in their ionic forms, and it is this that generates the greatest hazard for aquatic organisms. The leaching of metals during flood (2–3 weeks) can account for up to 75% of their total annual load (Moiseenko, 1999; Moiseenko *et al.*, 2001). Data on streams of the Kola North showed that in the periods of pH depression during floods, the total metal concentration increases in all types of creek, notwithstanding dilution by snowmelt water. The total concentration of aluminum in water increased by 50–88%. In the most acidified tundra stream studied, an increase in the concentration of its labile form was accompanied by a drop in the form bound with organic complexes.

6.3.2. Acidic episodes in the Dalelva catchment in eastern Finnmark, Norway

Dalelva is a small (3.2 km^2) undisturbed catchment dominated by heathland and mountains, in Jarfjord in eastern Finnmark, Norway (69°45′ N, 30°23′ E). Vegetation comprises birch forest to an elevation of about 150 m with heath and moorland above. Small lakes cover about 15% of the catchment. The catchment is usually covered with snow for six to seven months of the year, approximately from mid-October to late May, and receives relatively little precipitation (500–600 mm/yr). At the adjacent meteorological station (Lanabukt) about 45% of the annual precipitation was accumulated as snow during 1990 to 2000 (Kaste and Skjelkvåle, 2002). The extensive snow accumulation has a large impact on the seasonal runoff pattern, which is characterized by very low flow during winter and a distinct snowmelt flood in May to June.

The large seasonal variations in streamwater flow also have big impacts on water chemistry (Kaste and Skjelkvåle, 2002; SFT, 2005). During the long cold winters, when precipitation is accumulated as snow, the stream is dominated by baseflow with relatively high solute concentrations

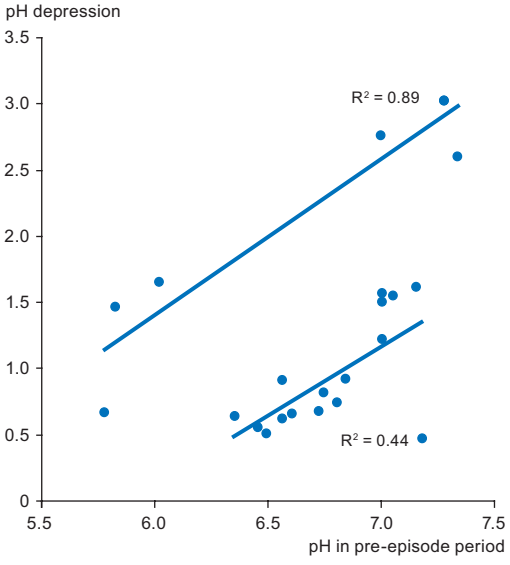


Figure 6.10. Water pH depression during spring flood versus pH during the low-flow period in streams of the Kola North. The upper line shows the relationship in streams where the minimum pH during high flow was <5, and the lower line where the minimum pH during high flow was >5.

(Figure 6.11). Concentrations of major ions and nitrogen compounds (not shown) tend to build up during winter and then decrease rapidly to initial levels at the start of the snowmelt flood. This dilution of base cations during snowmelt also causes a rapid decrease in streamwater pH, from the normal level of around 6.0 to 6.5, to values of around 5.5 (Figure 6.11). Sea-salts accumulated in the snowpack during winter are eluted from the snow in the early melting phase, resulting in an annual peak in chloride concentrations immediately before the onset of the main snowmelt flood (Figure 6.11).

After snowmelt, streamwater flow and solute concentrations return rapidly to normal summer levels. The Dalelva catchment usually experiences a short and intense growing season that lasts approximately four months. During summer, air temperatures can be relatively high and owing to the relatively low precipitation amounts, streamwater flow is usually very low at this time.

The overall water chemistry at Dalelva is characterized by relatively high concentrations of non-marine sulfate owing to industrial SO_2 emission sources on the Russian side of the border. During 1990 to 2000, however, streamwater concentrations of non-marine sulfate declined by 35% as a result of reduced SO_2 emissions (SFT, 2005). Dalelva is moderately affected by humic substances; average concentrations of total organic carbon between 2001 and 2003 were in the range 3.7 to 4.4 mg C/L. The greatest influence of total organic carbon is often associated with the onset of snowmelt. Streamwater concentrations of nitrate are relatively low, with annual peaks up to 70 to 100 µg N/L prior to snowmelt, and growing season values typically below 5 µg N/L.

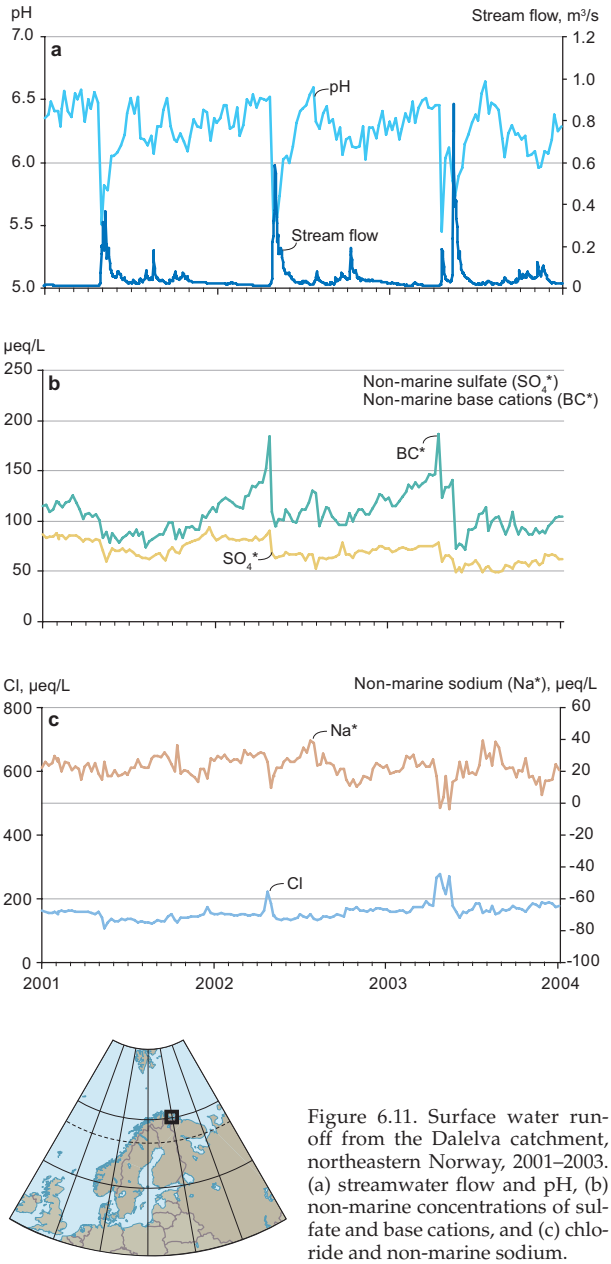


Figure 6.11. Surface water runoff from the Dalelva catchment, northeastern Norway, 2001–2003. (a) streamwater flow and pH, (b) non-marine concentrations of sulfate and base cations, and (c) chloride and non-marine sodium.

6.3.3. **Acidic episodes in northern Sweden**

A large, multi-investigator project in northern Sweden developed the Boreal Dilution Model (BDM) to quantitatively distinguish the natural and anthropogenic mechanisms that drive episodic decline of ANC and pH during hydrological events (Bishop *et al.*, 2000; Laudon *et al.*, 2000). The BDM identifies the anthropogenic component of episodic ANC decline (ΔANC_{poll}) from relative differences in the runoff dynamics of base cations and anthropogenic acid anions during episodes. Snow chemistry data are not used in the BDM. However, comparison of snow chemistry with the results from over 50 applications of the BDM in catchments from the alpine zone to the coast of northern Sweden sampled between 1991 and 1999 revealed a strong relationship between SO_4 in snow and the anthropogenic impact on the subsequent spring flood. This suggests an immediate and proportional response in spring flood acidification to changes in winter SO_4 deposition. Nitrogen is not a factor in the spring flood of this nitrogen-poor region (Laudon *et al.*, 2000).

Trends in anthropogenically driven episodic acidification were analyzed in five streams from northernmost Sweden between 1990 and 1999 using the BDM (Laudon and Hemond, 2002). Although there was no significant change in annual average stream water chemistry, the anthropogenically driven episodic acidification associated with spring flood runoff decreased by 40 to 80%. A strong correlation between winter SO_4 deposition and the anthropogenic component of episodic acidification in these five streams suggests that future reductions of acid deposition will further improve the spring flood acidification situation in northern Sweden. These results also indicate that reduced emissions of acid precursors have generated significant improvements in the surface water chemistry during episodes associated with spring runoff in northern Sweden.

While the data requirements of the BDM are too big for regional assessments, the correlation between snow SO_4 and ΔANC_{poll}, together with a relatively consistent amount of snowmelt in the peak of spring flood creates the basis for the more empirical 'one point BDM' (pBDM, Laudon *et al.*, 2004). This model uses widely available lake chemistry measurements, and can thus provide a more synoptic view of how human impact on spring melt ANC in northern Sweden has responded to changed SO_4 deposition. This is a region where many surface waters experience low ANC and pH in conjunction with hydrological episodes despite a relatively low annual acid deposition load. The largest episodic ANC declines and greatest biological effects in the region are associated with spring flood (Laudon *et al.*, 2000).

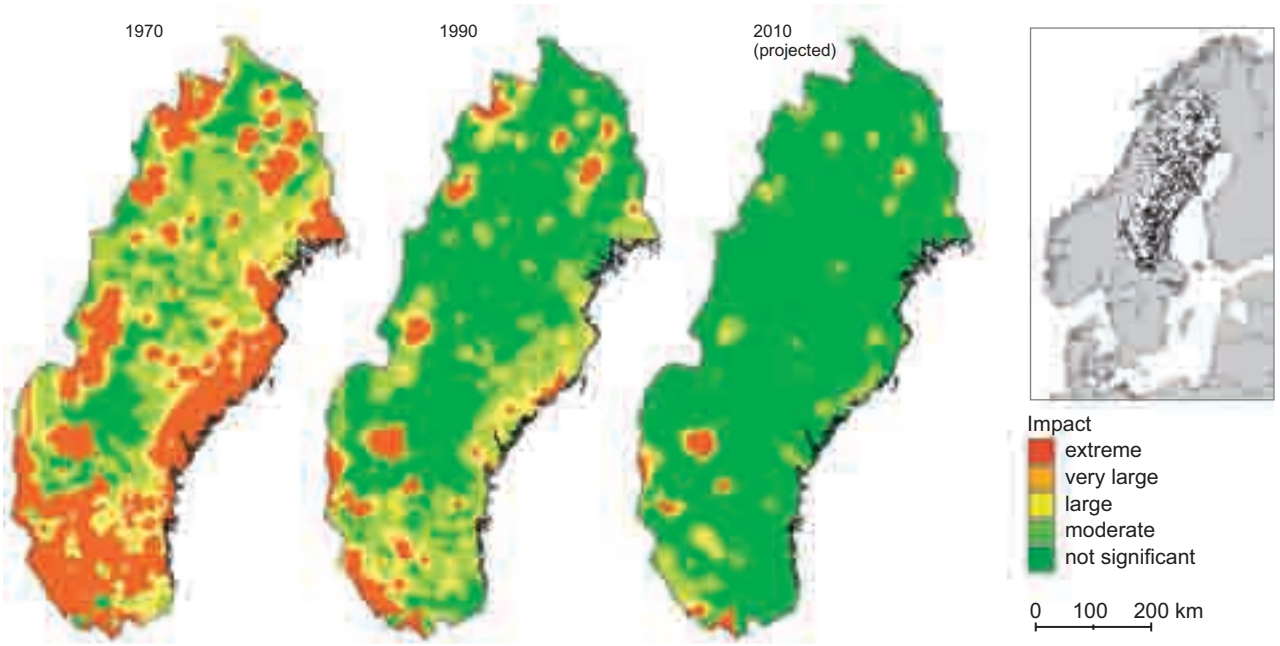


Figure 6.12. Intensity of anthropogenic episodic acidification in northern Sweden during the 1970 spring flood and the 1990 spring flood, and projected for the 2010 spring flood. Assessed using the acidification index of the Swedish Environmental Protection Agency and the pBDM model (Laudon and Bishop, 2002).

Sulfur deposition in northern Sweden peaked in 1970 (Mylona, 1996) and had declined by 65% by 1990 (S. Mylona, Norwegian Pollution Control Authority, unpubl. data). A further 55% reduction relative to the 1990 level is expected by 2010 in accordance with the 1999 Gothenburg Protocol to the LRTAP Convention. Winter chemistry data suitable for use in the pBDM was available for 1240 lakes sampled in conjunction with national monitoring (Figure 6.12). Application of the pBDM to these lakes using the 1990 and 2010 data projects a clear recovery (Figure 6.12, Table 6.4). In 1970, 54% of lakes in Sweden were subject to significant human impact (classes 3–5, Table 6.4). By 1990, only 14% of the lake population was more than moderately impacted by acid deposition during spring. By 2010 that number is projected to be 3%. Reductions in acid deposition have led to rapid and substantial chemical recovery from spring flood acidification in arctic waters, including 70 000 lakes and 1 000 000 km of watercourses in northern Sweden (Laudon and Bishop, 2002). These results are based on the strong correlation between SO_4 concentration in snow and the anthropogenic component of spring flood ANC decline (Laudon *et al*., 2004). Laudon *et al*. (2004) estimated that the 65% reduction in sulfur deposition between 1970 and 1990 reduced the area of acidified spring floods across 250 000 km^2 of northern Sweden by 75%.

A large and rapid reduction in the anthropogenic influence on spring flood acidity does not mean that spring ANC/pH decline disappears. A large spring flood ANC decline (equivalent to ca. 50%) is a natural feature of aquatic ecosystems in northern Sweden. The relative increase in organic acids during spring flood also contributes to a natural pH decline (Ivarsson and Jansson, 1995; Laudon *et al*., 1999).

The difficulties in assessing episodic acidification have contributed to the focus of previous acidification recovery assessments on changes in average lake conditions. The failure to account for an episodic response may greatly underestimate the immediate benefits of reducing acid deposition. Furthermore, since spring flood responds directly to snow acidity in this region that is not chronically acidified, delays in deposition reduction translate directly into recovery delays. Important as these results are for northern Sweden where large investments are made each year to remediate acidification in spring flood by liming, it is very likely that extensive regions in the boreal zones of North America, Europe and Asia may be similarly sensitive to changes in winter SO_4 deposition.

Table 6.4. Extent of anthropogenic acidification in northern Sweden (Laudon and Bishop, 2002).

			Percentage cover		
Acidification class	ANC_p / ANC_{pi}	Acidification index	1970	1990	2010
1	1.0 - 0.75	not significant impact	20	63	91
2	0.75 - 0.50	moderate impact	26	23	6
3	0.50 - 0.25	large impact	18	6	1
4	0.25 - 0.10	very large impact	7	1	1
5	<0.10	extreme impact	29	7	1
1-2			46	86	97
3-5			54	14	3

ANC_p: peak in ANC; ANC_{pi}: pre-industrial peak in ANC

6.3.4. Concluding comments on episodic acidification

In arctic regions, episodic acidification is a ubiquitous natural phenomenon during spring flood that has been intensified by acidic deposition. It develops swiftly due to the pollutants accumulated in the snowpack over winter being released rapidly into drainage basins during snow melt. The dominant factor in the acidification mechanism is the type of stream catchment. Replacement of hydrocarbonates by stronger acids and dilution are the most apparent and well-known factors and these affect acid episodes in all streams. In forest and wetland streams, organic acids also contribute strongly to pH decline. In remote coastal tundra areas, HCl is the dominating factor because of ion-exchange processes in catchments (adsorption of marine aerosol Na^+).

A general pattern in the behavior of metals induced by acidification is an increase in their concentration, redistribution toward the most toxic ionic form, and pulses of metals during the period of episodic acidification. An abrupt increase in the ionic form, which is the most toxic form for biological systems, together with low pH causes a toxic stress for water inhabitants. In polar regions, the maximum stress for biota occurs during spring flood periods, when pH is at a minimum and the concentration of ionic forms of metals is at a maximum.

A model based assessment on data from five streams in northern Sweden indicated that reduced emissions of acid precursors have generated significant improvements in surface water chemistry during episodes associated with spring runoff. Although there was no significant change in the annual average stream water chemistry at these sites, the anthropogenically driven episodic acidification associated with spring flood runoff decreased by 40 to 80% between 1990 and 1999. A regional scale model application indicated that the 65% reduction in sulfur deposition between 1970 and 1990 has reduced the area of acidified spring floods across 250 000 km^2 of northern Sweden by 75%. It is also likely that future reductions in acid deposition will further improve the spring flood acidification situation in this region.

The difficulties of assessing episodic acidification have contributed to many previous acidification recovery assessments having focused on changes in *average* lake conditions. The failure to account for an episodic response may greatly underestimate the immediate benefits of reducing acid deposition. Also, since spring flood responds directly to snow acidity in those northern regions that are not chronically acidified, delays in deposition reductions translate directly into recovery delays.

6.4. Evidence from paleolimnological studies

Monitoring of northern lakes often started after industrial pollution had been ongoing for tens of years. In the absence of long-term data on water quality, as is often the case in the Arctic and subarctic, paleolimnological reconstructions using microfossils preserved in lake sediments provide a powerful chronology of acidification history and recovery and a tool for separating anthropogenic impact from the natural pH succession. Microfossils are surprisingly accurate proxy sources for reconstructing past environmental conditions. Modern distributions of organisms that preserve well in lake sediments can be related to the hydrochemistry of the water body using a large set of lakes ('training set') and environmental optima and tolerance ranges for the individual species. These ecological optima and tolerance ranges can then be applied to fossil communities by means of mathematical calibration (transfer) functions, which enable changes in the hydrochemistry of a lake to be quantitatively determined from the fossil assemblages deposited in the sediment over a certain time period. In particular, the strong linkage between diatoms and lake-water pH has long been recognised (for a historical review, see Battarbee *et al*., 2001), which is why diatoms have been widely used as indicators in bio-monitoring present and past changes in the acidification status of surface waters. Using paleolimnological techniques, it is possible to obtain a temporal perspective on the lake ecosystems with regard to acidification (Smol, 1992).

In the previous AMAP assessment (AMAP, 1998), paleolimnological assessments of acidification in arctic Canada and Alaska showed that the lakes had been unproductive throughout their entire existence and that long-term natural acidification was still occurring. However, anthropogenically-induced acidity was reported to have affected the present-day acid-sensitive plankton species, invertebrates, and fish on the Kola Peninsula and in the neighboring areas of Finland and Norway (AMAP, 1998). Critical loads were reported to have been exceeded in large areas of northern Finland and Norway due to the low critical load values in these systems (the lakes in the region are characterized by a low buffering capacity and are sensitive to acidification, see section 6.1) and the influence of emissions from industrial areas on the Kola Peninsula. At present, the diatom-based pH-reconstructions cover extensive areas of arctic Fennoscandia, the Kola Peninsula, Siberia (Norilsk), Svalbard, and arctic Canada.

6.4.1. Millennial trends in lake acidification

6.4.1.1. Fennoscandia and the Kola Peninsula

Natural long-term acidification is a common feature of lakes in cold environments with thin soils and acid bedrock in the catchment. Most of the available pH reconstructions are based on changes in the subfossil diatom flora, since diatoms are very responsive to changes in acidity (e.g., Weckström *et al*., 1997; Bigler and Hall, 2002). Seppä and Weckström (1999) studied the acidification history of Lake Tsuolbmajavri, located just above the present pine treeline in northwestern Finnish Lapland. The current pH of the lake is around 7.4. Diatom-inferred pH (hereafter referred to as DI-pH) was observed to have decreased slowly and gradually throughout the Holocene (i.e., the last 10 000 years) (Figure 6.13). The periods of slightly more evident drops in DI-pH values were related to climate-driven changes in soil-forming processes and catchment vegetation patterns, for example the immigration of pine and the initiation of paludification. However, the influence of peatlands on the acidification status of lakes is probably less clear in northern Fennoscandia than in more southerly boreal environments owing to the less acidic nature of the mire vegetation and water in the northern rich fens (Korhola *et al*., 2002; Sjörs and Gunnarsson, 2002). A similar slow and gradually decreasing pH trend was reconstructed from another lake (Lake Toskaljavri) in the barren tundra region of Finnish Lapland (Figure 6.13), with a pH decrease of ca. 0.3 to 0.4 pH units during the Holocene (Seppä *et al*., 2002).

An even weaker trend in natural acidification was evident in data from Solovieva and Jones (2002), who studied the Holocene history of a small upland lake (Lake Chuna) on the Kola Peninsula (Figure 6.13). The lake water is currently dilute, clear and slightly acidic with a pH of around 6.4. The lake experienced slow natural acidification in the early Holocene, with the acid-base balance achieved about 4000 years ago after which there appeared to have been no further acidification. By applying the diatom models developed by Weckström *et al*. (1997) and Solovieva (2000), Grönlund and Kauppila (2002) recorded a similar slight trend of progressively declining DI-pH towards the present in Lake Soldatskoje, a small tundra site located in the northern coastal area of the Kola Peninsula. Similarly,

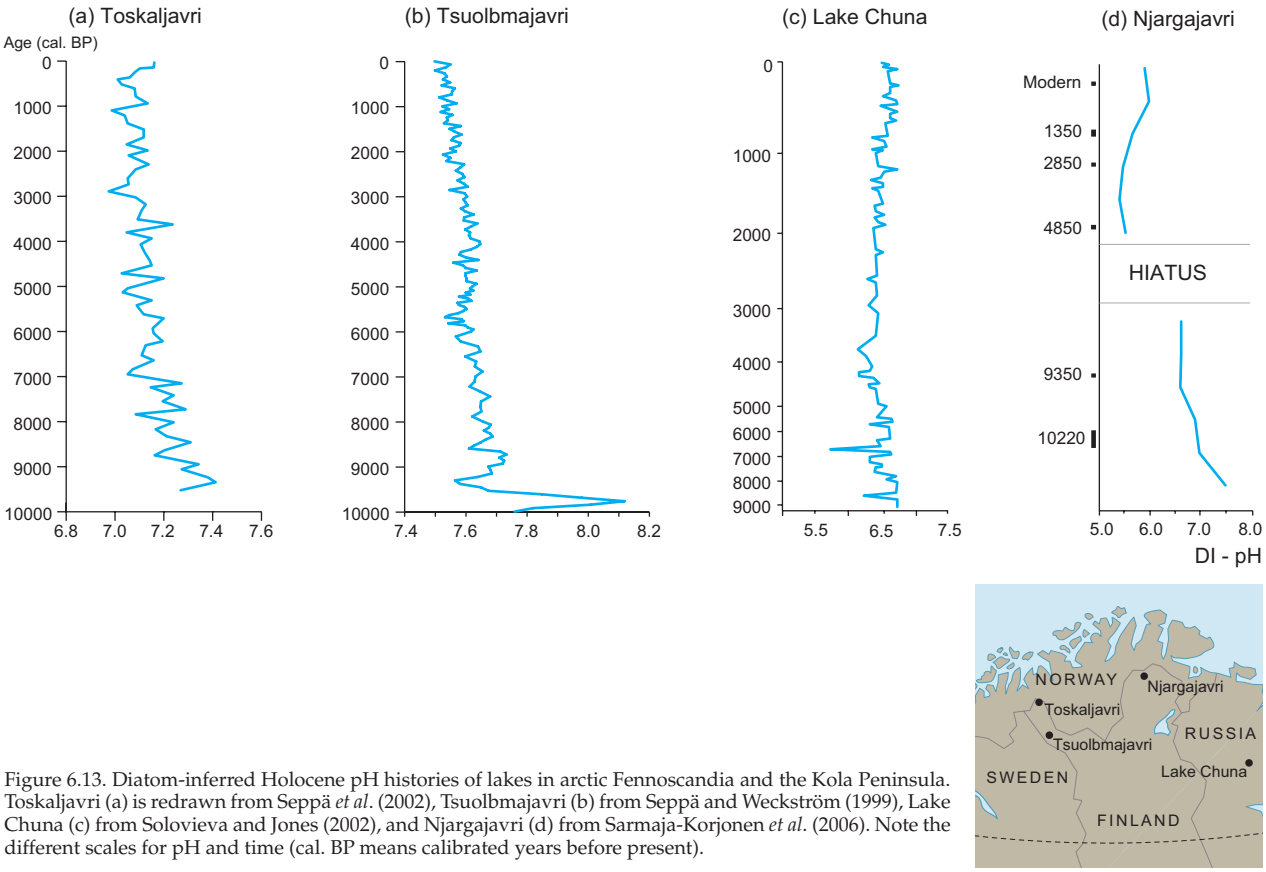


Figure 6.13. Diatom-inferred Holocene pH histories of lakes in arctic Fennoscandia and the Kola Peninsula. Toskaljavri (a) is redrawn from Seppä *et al*. (2002), Tsuolbmajavri (b) from Seppä and Weckström (1999), Lake Chuna (c) from Solovieva and Jones (2002), and Njargajavri (d) from Sarmaja-Korjonen *et al*. (2006). Note the different scales for pH and time (cal. BP means calibrated years before present).

Bigler *et al*. (2002a, 2003) found that two small subarctic lakes near Abisko in northern Sweden had gone through a slow long-term acidification during the Holocene from about pH 7.2 to 6.8 and 7.2 to 6.5, respectively. No evidence was found that changes in land-use or reindeer herding would have affected the acidity status of these lakes during the last 1000 years.

Korsman (1999) reconstructed the late Holocene pH history from five currently acidic lakes in northern Sweden using diatoms and reported a slight natural acidification trend beginning thousands of years ago as a result of soil-forming processes and natural changes in vegetation. One of these lakes is within the AMAP region. In a recent study, Sarmaja-Korjonen *et al*. (2006) reported relatively strong mid-Holocene acidification of around two pH units from 7.5 to 5.5 in Lake Njargajavri, a small shallow lake in Finnish Lapland (Figure 6.13). The reasons for the rapid decline in pH may be due to specific characteristics of this poorly buffered, acid (pH 5.3) and oligotrophic lake and its catchment that made the system particularly susceptible to climatically-induced changes in pH. Climate is known to modulate lake acidity through links between lake ice cover, primary productivity, and DIC dynamics (Wolfe, 2002, see section 6.5.1).

6.4.1.2. **Concluding comments on millennial-scale acidification**

Millennial-scale changes in lake water acidity in arctic Fennoscandia and the Kola Peninsula are mainly slow or non-existent during the Holocene. Excluding the initial transient alkaline period following deglaciation evident at some sites, Korhola and Weckström (2004) estimated that the long-term natural rate of pH decline in arctic lakes in this region has been around 0.005 to 0.01 pH units per 100 years, which is considerably less than the corresponding 0.01 to 0.02 pH units per 100 years in boreal lakes. Some arctic lakes may, however, be especially vulnerable to changes in climate, which can modulate pH.

6.4.2. **Recent acidification**

6.4.2.1. **Fennoscandia and the Kola Peninsula**

In 1990, critical loads for surface waters in northern Europe were exceeded almost everywhere. Henriksen *et al*. (1997a,b) reported that critical loads of acid deposition were exceeded in 50 to 70% of lakes on the Kola Peninsula and in the Norwegian–Russian border areas. Regional geochemical mapping from 1992 to 1998 demonstrated that although the local influence of industry on the Kola Peninsula can be seen, distance from the coast dominates the distribution of pH and sulfur trends in lake water at the regional scale (Reimann *et al*., 2000a).

A quick and efficient paleolimnological means to establish the extent of lake acidification at the regional level is the so called 'top–bottom approach'. From a number of lakes a single sediment sample is analysed (e.g., for diatoms) from the top of the sediment layer, to represent present-day conditions, with another taken from deeper down the core to represent pre-industrial conditions. By comparing these samples it is possible to estimate the extent of the change in species assemblages and thus the DI-pH values since pre-industrial times. This method was applied to 118 northern Swedish lakes (Korsman, 1999) and to 32 lakes around the smelters on the Kola Peninsula (Weckström *et al*., 2003). The results indicate that in the majority of the Swedish lakes DI-pH was unchanged, while on the Kola Peninsula the decrease in DI-pH occured only within the immediate vicinity of the smelters. These diatom data do not sup-

port the hypothesis of large-scale modern acidification in northern Sweden, nor the widespread acidification of arctic lakes due to sulfur pollution from the Kola smelting and mining industries. However, in four lakes out of 15 studied by Dauvalter (1997) in Finnish Lapland, acidification was postulated to have altered the geochemical cycling of potentially harmful metals by dissolution from sediments back to water or by reducing the adsorption of metals onto sedimenting particles.

In addition to these broad-scale top-bottom studies, several downcore pH reconstructions covering the past 200 to 300 years have been made for a number of individual lakes (see Figure 6.14). Collectively, these studies indicate that no substantial changes in DI-pH have taken place. The next paragraph summarises some of these studies.

Data from three small, potentially acid-sensitive (autumn alkalinity values of 20, 20, and 60 µeq/L) lakes, two in eastern Finnish Lapland 40 km west and 150 km southwest from the Nikel smelter and a reference lake in western Lapland, suggested no substantial changes in DI-pH despite the relatively high acid deposition in the east (Korhola *et al*., 1999) (Figure 6.14, lakes A-C). The other lakes (Figure 6.14, lakes D-N), dilute clearwater lakes with varying geology, were not chosen to evaluate their acidification history and so their sensitivity to acidification was not a major criterion for selection. Sorvari *et al*. (2002) did not find change in DI-pH over the last 200 years in five tundra lakes in northwestern Finnish Lapland (Figure 6.14, lakes H-L) investigated using high-resolution sediment sampling. Similarly, Weckström (Environmental Change Research Unit, University of Helsinki, unpubl. data) found no decrease in DI-pH in two lakes in western Finnish Lapland (Figure 6.14, M-N), in fact one even showed a slight increase in DI-pH since 1800 AD.

Sediments representing the industrial time of Lake Chuna, a small upland lake on the Kola Peninsula about 30 km from the Monchegorsk smelter, were studied by Moiseenko *et al*. (2000) and Ilyashuk and Ilyashuk (2001). Moiseenko *et al*. (2000) found that toward present times the acidobiontic diatom taxa (as well as abnormal forms of some diatom species) increased as species diversity decreased, these changes running in parallel with the start of heavy metal accumulation due to industrial development of the region. Ilyashuk and Ilyashuk (2001) studied changes in the subfossil benthic invertebrate (Diptera: Chironomidae) communities in the sediments of Lake Chuna. They concluded that compositional changes in the assemblages were due to inputs of airborne contaminants and climate change. According to their interpretation, the first changes that took place in chironomid communities around 1950 were caused by the decrease in pH and the accumulation of heavy metals in bottom sediments. In the uppermost sediment layers climate change may have lead to the decrease in the predominant species, to increased taxon evenness, and thus to an increase in species diversity over the last two decades. Solovieva and Jones (2002) studied the same lake using modern quantitative approaches but did not find any significant decline in DI-pH over recent decades/centuries. This discrepancy between the pH reconstructions for Lake Chuna from the two different diatom studies is still to be resolved. It may in part result from methodological differences in reconstructing pH. Nevertheless, over the last 100 years the sediments have accumulated some toxic elements (lead, nickel, copper, cobalt, and cadmium) despite their

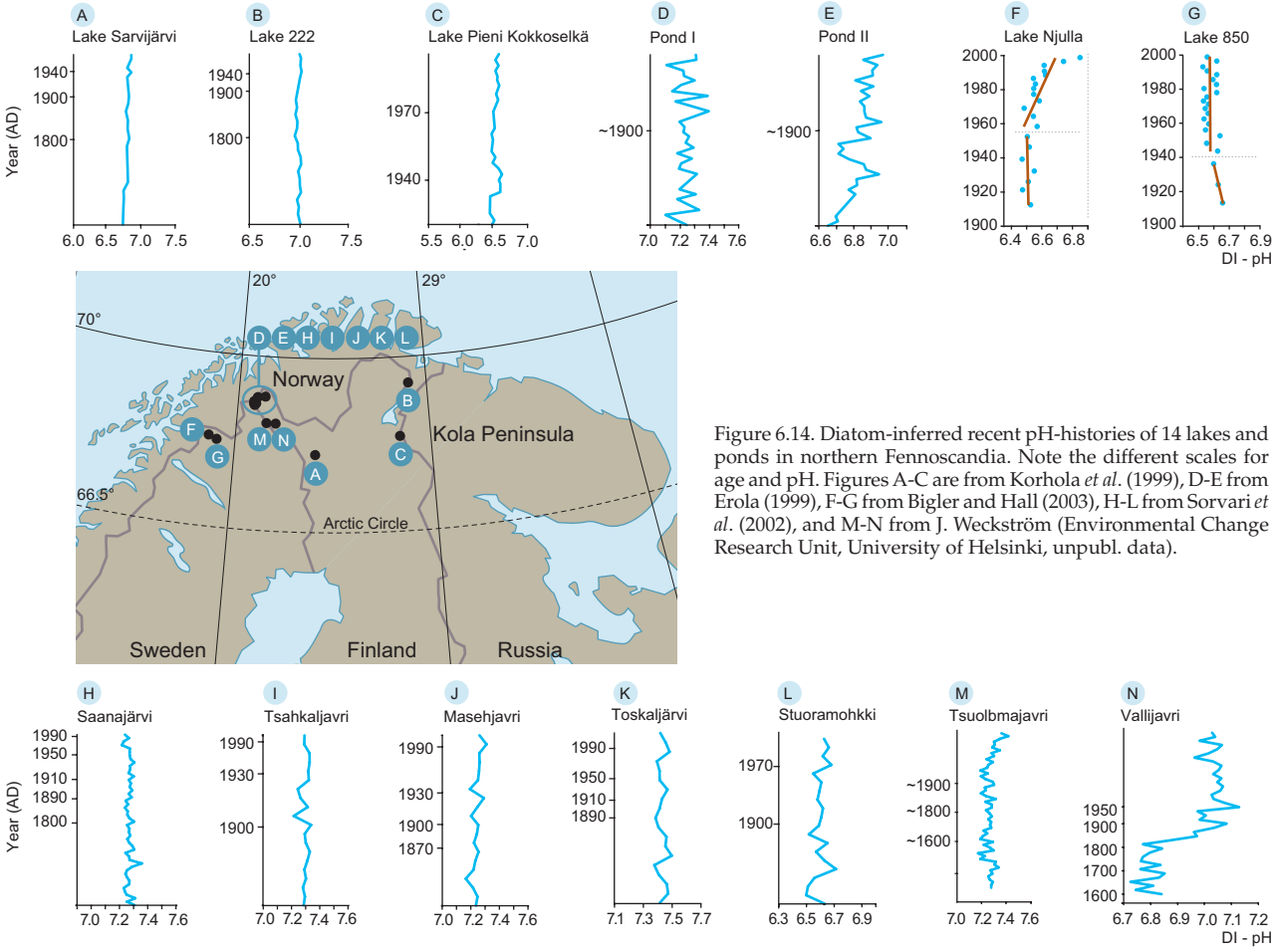


Figure 6.14. Diatom-inferred recent pH-histories of 14 lakes and ponds in northern Fennoscandia. Note the different scales for age and pH. Figures A-C are from Korhola *et al*. (1999), D-E from Erola (1999), F-G from Bigler and Hall (2003), H-L from Sorvari *et al*. (2002), and M-N from J. Weckström (Environmental Change Research Unit, University of Helsinki, unpubl. data).

low concentrations in water. The increasing appearance of deformations in diatom and chironomid specimens towards recent times may indicate that the accumulation of heavy metals has had an adverse effect on the lake biota.

In their study of two bays of Lake Imandra on the Kola Peninsula (Monche Bay in the near vicinity of the Monchegorsk copper-nickel smelter and Kunchast Bay, an internal reference site located about 90 km southwest from the smelter), Ilyashuk *et al*. (2003) found an increase in the metal contamination of the sediments in Monche Bay that was accompanied by marked changes in chironomid communities towards more toxic-tolerant species and a decline in diversity and total abundance. Also, the presence of increasingly frequent morphological deformities among the detritus-eating *Chironomus* and the decreased Benthic Quality Index (BQI) both served to indicate increasingly toxic conditions for the biota. At the reference site (Kunchast Bay) no obvious changes in chironomid communities were noted that could be connected to metal contamination and acidification. The mouthpart deformities of *Chironomus* may reflect a switch from non-genetic stress in midge larvae to an increasing amount of stress at genetic level under prolonged stress conditions (Ilyashuk *et al*., 2003).

Dauvalter and Rognerud (2001) studied the impact of heavy metals on the watershed of the Pasvik River, the largest river system in northern Fennoscandia. They found increased concentrations of heavy metals in recent sediment layers in the lower reaches of the river. This was presumably due to the atmospheric emissions of nickel, copper, cobalt, zinc, cadmium and mercury from the smelters and to wastewaters from tailing dams and mines. In the upper river reaches no significant changes in vertical distribution of heavy metals were apparent.

The geochemical and biological data from the Kola Peninsula suggest localized effects of pollution from the smelter industries within a few tens of kilometers from the actual emission sources. However, no precise dates were available for the sediment cores studied by Dauvalter and Rognerud (2001) and Ilyashuk *et al*. (2003) and the time resolution of the samples (1 cm sediment slices) was not high enough to allow estimates of any recovery.

6.4.2.2. **Siberia**

Using the top–bottom approach, Michelutti *et al*. (2001) found that diatom assemblages in the sediments of 17 lakes had experienced relatively little change since pre-industrial times in the Norilsk area, in Russian Siberia. Lakes seemed well buffered against acidification due to the surrounding alkaline bedrock and overlying glacial deposits. According to their investigations, the effects of the massive mining activities on the water quality of these lakes have been minimal, and the alkaline nature of the lake water has resulted in the incorporation of the insoluble metallic complexes into the lake sediments. However, the mining activities may have caused increased erosion, which had altered the species assemblages to some extent (Michelutti *et al*., 2001).

There is no evidence of widespread lake acidification during the industrial period in the Usa Basin of the East-European Russian Arctic according to the subfossil diatom assemblages studied by Solovieva *et al*. (2002). However, they did find evidence of alkalinization of the lakes due to atmospheric deposition, as shown by the increased DI-pH values towards the present. Similarly, Solovieva *et al*. (2005) did not find any detectable signs of acidification in two lakes within this region studying both diatoms and chironomids from the high-resolution sediment record extending back to about 1800.

6.4.2.3. **Svalbard**

Elevated levels of atmospheric contaminants such as spheroidal carbonaceous particles (from fossil fuel combustion), polyaromatic hydrocarbons, polychlorinated biphenyls, and possibly lead from both long-range and local sources are recorded in Svalbard lake sediments for the past 30 to 40 years (Rose *et al*., 2004). Lakes in Svalbard are potentially particularly sensitive to acid deposition as they are located on deep permafrost and there is little groundwater interaction (Betts-Piper *et al*., 2004). Exceedance of critical loads for acidity (Lien *et al*., 1995) also suggests that acidification effects are possible, but no ecological impacts on diatom (Jones and Birks, 2004) or chironomid (Brooks and Birks, 2004) assemblages from the lake sediments have been observed. Trends in DI-pH values in five Svalbard lakes have been stable over the past few centuries. However, top–bottom analysis of chrysophycean stomatocysts showed marked shifts in assemblages in most of the lakes studied. Lakes on granitic bedrock, which are presently acidic, may have become more acidic over time. On the other hand, lakes on carbonate bedrock that are presently alkaline appear to have increased their pH in recent times. These changes may be related to atmospheric contamination from local and remote sources, but climate change may also play a role (Betts-Piper *et al*., 2004).

6.4.2.4. **Concluding comments on recent acidification**

Broad-scale recent acidification of arctic lakes is not apparent through DI-pH reconstructions. This may be partly because most of the lakes studied are not particularly sensitive to acidification or are not located in areas of high deposition. Also, there are no accurately dated high-resolution DI-pH reconstructions from the near vicinity of the local emission sources to allow a paleolimnological evaluation of acidification status in these lakes. However, within a few tens of kilometers from the local emission sources there is clear evidence of the effects of metal accumulation on the lake biota as a function of time, as indicated by the increased proportion of deformed diatoms and chironomids towards the core top. As documented in a recent Arctic-wide study (Smol *et al*., 2005), climate change is already affecting lakes and ponds and their biota in arctic areas. This is evident from the marked recent change in algal and zoological paleolimnological indicators that is inconsistent with atmospheric acidification or nutrient input but instead indicates the widespread impacts of climatic change (e.g., Douglas *et al*., 1994; Sorvari *et al*., 2002; Michelutti *et al*., 2003).

6.5. Interaction between acidification and other environmental issues

Both the causes and effects of air pollutants are closely linked to other environmental problems and human activities. Many of the traditional air pollutants and green-

house gases have common sources. They interact chemically and physically in the atmosphere and cause a variety of interrelated environmental effects at different spatial scales (Swart *et al*., 2004; Table 6.5). Politically these different air pollutants and greenhouse gases have been treated separately; they also have different spatial and temporal scales. Others have a more local deposition pattern (e.g., many heavy metals) while others are spread over hundreds of kilometers or even globally (sulfur, greenhouse gases). The different spatial scale of each pollutant and its effects makes georeferenced modeling necessary, as this can handle different scales and resolutions simultaneously (van Rompaey, 1995 and references therein). There is also a need to seek synergies in emissions controls for air pollution and climate change to gain economic and political benefits (Swart *et al*., 2004). Furthermore, the projected climate change-related alterations in temperature, wind patterns, and precipitation can change the routes of contaminant entry and the locations and amounts of deposition in the Arctic (AMAP, 2002; Macdonald *et al*., 2003; ACIA, 2004).

Table 6.5. Impacts of various substances emitted to the air (redrawn from Seip and Aunan, 2002).

		Regional impacts		Local impacts		
	Climate change	Acidification	Ground level ozone	Health	Vegetation	Materials
CO_2	x					
CH_4	x		x			
SO_2	x	x		x	x	x
NO_x	x	x	x	x	x	x
NH_3	x	x		x	x	x
NMVOC[a]	x		x	x	x	?
PM[b]	x	x		x	x	x

[a] non-methane volatile organic compounds; [b] particulate matter

Climate warming, acid deposition, the effects of toxic chemicals, and increasing exposure to ultraviolet (UV) radiation are all regarded as widespread problems in northern ecosystems. In the past, climate warming, acidification, and UV radiation were treated as if they had distinct and separate effects on ecosystems. It is now clear that these major stresses caused by man's alteration of the atmosphere cannot be studied in isolation (Schindler *et al*., 1996; Schindler and Curtis, 1997). The recent Arctic Climate Impact Assessment (ACIA, 2004) concluded that the total impact of contaminants, excess UV radiation, and climate warming is greater than the sum of its parts. Thresholds of tolerance of biodiversity or of the structural and functional attributes of ecosystems to changes in atmospheric stressors are largely unknown (Freedman and Beauchamp, 1998). Multiple stresses, for example, concomitant changes in the atmosphere and land use, make these thresholds even more difficult to define.

This section summarizes the possible interactions between acidification and other environmental issues in high-latitude aquatic ecosystems in two key sectors: climate change and UV radiation, and heavy metals/contaminants.

6.5.1. Interactions concerning climate change and UV radiation

6.5.1.1. Anticipated changes in climate

The overarching stress on ecosystems in the future will be global climate change, which is projected to be greatest in the Arctic due to various feedback mechanisms (Chapman and Walsh, 1993; Overpeck *et al*., 1997). The Arctic is highly likely to be warmer and moister in future. According to the Arctic Climate Impact Assessment (McBean, 2005), the average surface temperature in the Arctic is currently increasing by approximately 0.09 ºC per decade and it is probable that there was an increase in arctic precipitation of 1% per decade during the past century. The Arctic Climate Impact Assessment projected (Kattsov and Källén, 2005) that the annual precipitation will increase by 7.5 to 18.1% by 2071-2090, depending on the model used. The projected increase is generally greatest in autumn and winter and smallest in summer. Temperature is projected to increase by 2.8 to 4.6 ºC in the Arctic (north of 60º N) by 2071-2090. Climate change will influence water quality by altering the balance between the atmospheric, terrestrial, and aquatic processes in watersheds, and the effects of human resource use on these processes. Among the most important physical and chemical changes projected for freshwater ecosystems are: increasing water temperatures, thawing permafrost, changes in ice cover on rivers and lakes, and increasing levels of contaminants (ACIA, 2004).

6.5.1.2. Anticipated changes in hydrology and water quality

Effects of increasing temperature and moisture on water quality

Murdoch *et al*. (2000) summarized some of the potential water quality effects of increasing temperature and changing moisture conditions. If air temperatures increase, fewer arctic lakes and streams will freeze to the bottom and lakes will have an increased number of ice-free days. In both cases these changes will increase nutrient cycling and productivity. A shallower depth of freezing in arctic lakes during warm years has been shown to cause increased productivity through a lengthening of the growing season. If sufficient nutrient sources are available, lakes in arctic and alpine regions will also experience increasing productivity as a result of more frequent mixing and deeper thermoclines with increases in temperature. Longer thaw seasons will enhance decomposition and greenhouse gas releases from northern wetlands and peatlands. Increased moisture is predicted to decrease permafrost thawing compared to warm-dry conditions, but increased erosion from high runoff may yield greater nutrient, DOC, and sediment loads from thawing permafrost terrain.

Dissolved organic carbon is derived from terrestrial vegetation, especially wetland vegetation. Concentrations in high latitude lakes are low. In small boreal lakes DOC is the most important determinant of thermocline depth (Perez-Fuentetaja *et al*., 1999). Changes in the levels of DOC are likely to be one of the most important changes of climate warming in surface waters (Schindler, 2001). The effects of climate change on treeline lakes are likely to be strong since shifts in vegetation cover near the treeline will affect DOC in lake waters as well as hydrology (Rouse *et al*., 1997). The projected increase in supply of organic material and nutrients will enhance primary production

in arctic freshwaters dramatically (Schindler, 1997; Hobbie *et al*., 1999; Flanagan *et al*., 2003).

Thawing permafrost increases the flow into groundwater, which can lead to the disappearance of water bodies in some areas but an increase the area of wetlands and small ponds in others. Longer ice-free periods and the northward advance of vascular plants will increase evapo(transpi)ration, leading to lower water levels. On the other hand, increased precipitation and cloudiness may counteract this. However, lakes, ponds, and wetlands are more likely to dry out during summer (Wrona *et al*., 2005). Earlier ice break-up affects supplies of nutrients, sediments, and water quality, but increases the amount of harmful UV-radiation during spring. These multiple stressors will impact on the aquatic biota at a time when they are having to compete with new species moving north from lower latitudes.

pH changes in high-latitude and high-altitude lakes

Thawing permafrost and a deepening of the active layer are very likely to increase geochemical weathering and nutrient release (Wrona *et al*., 2005). Warmer wetter conditions will also favor erosion and greater runoff of weathering products. This could increase the buffering capacity of lakes against strong acids.

As previously described, climate change probably alters the chemical properties of high-latitude lakes, potentially influencing their susceptibility to anthropogenic atmospheric deposition. A small change in temperature can have a profound impact on aquatic environments, especially in areas where the duration of snow and ice cover has a dominant role in determining ecosystem functioning. It has been suggested that climate (e.g., temperature and precipitation) indirectly controls the pH of oligotrophic alpine lakes (Psenner and Schmidt, 1992) as well as poorly buffered arctic lakes (Wolfe, 2002). In the Arctic, this is explained by dissolved inorganic carbon (DIC) dynamics, which are affected by lake ice cover and primary productivity (Wolfe, 2002). Thus DIC regulates the pH of dilute lakes. Globally, lakes are supersaturated by carbon dioxide (CO_2) and under prolonged ice conditions this situation is exaggerated, which leads to a decline in pH. With a warmer climate and longer ice-free season CO_2 supersaturation is eliminated and enhanced algal production further reduces limnetic CO_2, shifting the balance in inorganic forms of dissolved carbon away from CO_2 and toward HCO_3, resulting in an increase in pH (Wolfe, 2002). If the catchment to lake area ratio is small (e.g., < 10) in-lake processes become especially important in determining the lake pH status. Otherwise changes in the catchment, such as vegetation, land use, erosion, and weathering, would mainly drive changes in lake water quality.

Climate change may also affect the seasonality of the stress. A rise in algal productivity under warmer conditions may lead to larger seasonal fluctuations in pH as organic matter production influences the redox potential and consequently the acid-base equilibrium (Psenner and Schmidt, 1992), thus acting as an additional stress on the biota with pulses of strong acids into lakes in spring (see section 6.3). The relationship between climate and pH is, however, dependent on the unbuffered character of remote high-latitude lakes, which allows the direct control of pH by DIC dynamics. In general, it seems that a warmer and moister future climate would increase the alkalinity of arctic lakes.

At present, water below the winter ice in subarctic lakes is warmer than in lakes further south due to the rapid ice over. This sustains efficient decomposition on the sediment surface and causes anoxia in lakes (especially mesopolyhumic lakes) at the end of winter. Climate warming may remove this problem by shortening the ice-on period and increasing wind mixing in shallow lakes. On the other hand, increased production and DOC concentrations in shallow lakes may strengthen thermal stratification and sedimentation of organic matter to the bottom, thus increasing oxygen demand. Deep lakes are projected to be more strongly stratified. Changing the redox situation near the bottom will affect the alkalinity of the lakes.

Multiple stressors and effects on biota

The combined effects of multiple stressors may be antagonistic or synergistic, i.e., smaller than expected or larger than expected, respectively (Folt *et al*., 1999). The cumulative impacts of anthropogenic stressors on ecosystems are especially worrying in relation to a loss of biodiversity and to changes in ecosystem functioning (Sala *et al*., 2000; Schindler, 2001; Vinebrooke *et al*., 2004). When the critical load for multiple environmental stresses is exceeded, the ecosystem may change abruptly. Sala *et al*. (2000) projected very little change in biodiversity in arctic areas if the interactions between driving factors (land use, climate, nitrogen deposition, biotic exchange and atmospheric CO_2) are synergistic, and much change if the interactions are antagonistic.

For example, acidification typically shifts phytoplankton communities towards larger dinoflagellates and filamentous algae, while suppressing cyanobacteria and smaller chrysophytes and larger eukaryotic algae that are less well adapted to higher temperatures, suggesting that acidification and environmental warming have synergistic negative impacts on phytoplankton. It has been hypothesized that since acidification favors smaller zooplankton species, such as rotifers and certain copepods, the effects of several other stressors on zooplankton will be reduced in acidified lakes. For example, smaller zooplankton species experience lower metabolic costs per capita than larger species during warming, and are less vulnerable to UV radiation, visually feeding vertebrate predators, and pesticides. On the other hand, some planktonic crustaceans, which are UV-tolerant due to their ability to produce photo-protective pigmentation, are likely to face an increased risk of predation by visually feeding planktivorous fish, especially if large populations of alien sportfish are introduced into clear lakes (Vinebrooke *et al*., 2004). In their experiments on multiple stress effects on daphnids, Folt *et al*. (1999) concluded that effects of toxins and low food supply would probably be enhanced by thermal stress. Hypothesized antagonistic and synergistic effects of anthropogenic acidification and other major abiotic and biotic stressors on phytoplankton and zooplankton are shown in Table 6.6.

6.5.1.3. **Recovery from acidification in surface waters**

There is good documentation of a large-scale chemical recovery process from surface water acidification in Europe and North America (Stoddard *et al*., 1999; Forsius *et al*., 2001; Evans *et al*., 2001; Skjelkvåle *et al*., 2001a). Recovery is also documented in the northern regions (section 6.1.2). Modeling studies based on current emission reduction

Table 6.6. Hypothesized antagonistic (+) and synergistic (-) effects of major abiotic and biotic stressors (first column) and anthropogenic acidification on phytoplankton and zooplankton (redrawn from Vinebrooke *et al*., 2004).

	Phytoplankton	Zooplankton	Rationale
Elevated temperature	-	+	Acid-sensitive cyanobacteria are thermophilic; small acid-tolerant zooplankton (e.g., rotifers) experience lower metabolic costs than large acid-sensitive cladocerans.
Ultraviolet radiation	+	+	Acid-tolerant species must also be UV-tolerant as they experience elevated UV exposure during lake acidification and loss of UV-attenuating DOC. Small acid-tolerant rotifers show higher UV-tolerance than other zooplankton.
Eutrophication	-	?	Acid-sensitive cyanobacteria are better competitors for nutrients than other groups of phytoplankton.
Toxins	+	+	Acid-tolerant, small zooplankton species are more resistant to contaminants than large species.
Predation	+	-	Large, acid-tolerant phytoplankton (e.g., cyanobacteria, dinoflagellates) are less edible; smaller zooplankton are more susceptible to predatory invertebrates like *Chaoborus*, while pigmented UV- and acid-tolerant zooplankton are easily detected by introduced fish.

plans project further chemical recovery (Jenkins *et al*., 2003; Wright *et al*., 2005). Uncertainties in these scenarios are mainly related to the effects of climate change and future behavior of nitrogen in the ecosystem. Other uncertainties are related to the biological response.

Present-day climatic conditions are commonly assumed in model projections of future scenarios. However, as previously discussed large changes in climate are anticipated for the Arctic and the direction and degree of change may significantly affect the dynamics of terrestrial and aquatic ecosystems. Skjelkvåle *et al*. (2003) identified four key climate-related factors that may influence recovery from acidification: (a) increased frequency and severity of sea-salt episodes, (b) increased frequency and severity of drought, (c) increased turnover of organic carbon, and (d) increased mineralization of nitrogen. Although most empirical evidence is from boreal or temperate regions, it is likely that these processes are also relevant for most arctic environments.

Increased frequency and severity of sea-salt episodes

The 'sea-salt effect' in surface waters is important in areas receiving substantial inputs of sea-salts, in particular coastal areas of Norway, the United Kingdom and the United States. The sea-salt effect may temporarily increase the acidity of runoff. However, a prerequisite for the lake and stream acidification effect to occur from sea-salt episodes is that the catchment soil is acidic. Recent climate forecasts project a dramatic increase in the North Atlantic Oscillation index (see section 3.7.3) over the next 80 years, implying that warm, westerly conditions in winter may become more prevalent. A greater frequency and intensity of sea-salt episodes may therefore be expected in coastal surface waters. Sea-salt episodes may have important regional biological effects. Massive regional fish kills were reported for the first time after the episode in southwestern Norway during winter 1993 (Barlaup and Åtland, 1996). The fish deaths occurred in moderately acidified systems that suddenly became extremely acid.

Increased frequency and severity of drought

In parts of North America, the reduction and storage of sulfate in wetlands, and its subsequent re-oxidation and release, have been shown to have a major impact on runoff water quality and hence recovery (Dillon and LaZerte, 1992; Jeffries *et al*., 2003). Immobilization and re-mineralization of sulfur within soil organic matter are both important in European soils. Both stores of sulfur are sensitive to drought. Relationships between sulfate pulses and drought associated with El Niño events have been shown to occur in lakes in Ontario, Canada (Dillon *et al*., 1997). In the UK, large flushes of sulfate were widely observed in streams following a drought in 1995 (e.g., Harriman *et al*., 2001). Climate-regulated sulfur retention and release represent 'noise' within an overall recovery trend. Release of stored sulfur will delay recovery where pools are large. Also, sulfate flushes following drought (particularly if droughts become more severe with climate change) may continue to generate acidic episodes, despite improvements in baseline water quality. These drought-driven episodes may be more extreme or frequent in future climate scenarios and may, like sea-salt episodes, contribute to a delay in chemical and biological recovery in surface waters.

Increased turnover of organic carbon

Regional trends of increasing DOC concentrations over the last two decades have been documented across substantial parts of northern and central Europe (Evans and Monteith, 2001; Skjelkvåle *et al*., 2001a,b, 2005; Evans *et al*., 2005; Vuorenmaa *et al*., 2006) and eastern North America (Stoddard *et al*., 2003). For Canada the picture is less straightforward (Jeffries *et al*., 2003). The widespread occurrence of these trends indicates a regional cause and various hypotheses have been put forward to explain them. It has been proposed that these increases may be coupled to change in potential drivers, such as increasing temperature (Freeman *et al*., 2001; Hejzlar *et al*., 2003), changes in hydrological regimes (Tranvik and Jansson, 2002; Hejzlar *et al*., 2003), increasing atmospheric CO_2 concentration (Freeman *et al*., 2004), airborne nitrogen enrichment in soils (Findlay, 2005), or decreasing sulfur deposition (Stoddard *et al*., 2003; Evans *et al*., 2005; Vuorenmaa *et al*., 2006). More research is needed to establish the relative significance of the various drivers in the different regions.

Elevated DOC concentrations in surface waters have raised concerns that terrestrial carbon stores may be becoming unstable, with unpredictable consequences for the global carbon cycle and with complex consequences for surface waters. Recovery from acidification along with decreasing acid deposition is being partially offset by increasing organic acidity. Increasing DOC concentrations may also cause increased buffering of changes in pH, increased water coloration, and decreased visible light and UV-B

penetration within the water column (see sections 6.5.1.2 and 6.5.1.4). While increased organic acidity may delay chemical recovery from acidification in surface waters, the other factors may influence biological recovery.

Increased mineralization of nitrogen

Additional uncertainties with regard to nitrogen processes relate to the influence of climate (short and long term) on nitrate leaching, which may alter the long-term trend, or simply add 'noise' to the anthropogenic signal. Because internal ecosystem cycling of nitrogen greatly exceeds system inputs and outputs, any disturbance of this cycle has the potential to completely obscure the relationship between nitrogen deposition and runoff. Both in the UK and the US, large pulses of nitrate have been observed in surface waters following severe winters possibly as a result of soil freezing (Mitchell *et al.*, 1996; Monteith *et al.*, 2000). The frequency of such pulses may change in future in response to altered climate. Results from the CLIMEX project, where ambient air and soil temperature was increased over three years, show increased leaching of inorganic nitrogen, probably due to increased mineralization and nitrification rates in soils (Wright and Jenkins, 2001). Continued high deposition of nitrogen is likely to increase nitrogen saturation and generate increased nitrate concentrations in runoff, thereby delaying recovery due to reductions in sulfur emissions. Increased temperature due to climate change may increase nitrate in runoff and thereby contribute to delay in recovery. The role of nitrogen in acidification and recovery remains uncertain.

6.5.1.4. Impacts of DOC changes on UV radiation in lakes

Climate effects on exposure to UV radiation were discussed extensively by Wrona *et al.* (2005). Humic substances strongly absorb UV radiation and act as a screen, thus protecting organisms from its detrimental effects. Under normal conditions all wavelengths of solar radiation in freshwater ecosystems, including UV radiation, are attenuated to some degree by DOC (Schindler, 1999) and long term variation in underwater UV irradiance is primarily controlled by the amount of dissolved organic material. Long lasting ice cover has a similar protective role, protecting organisms from UV radiation during the most intensive radiation period in spring. Interactions between climate change and UV radiation potentially modify the underwater UV radiation regime via: (a) changes in stratospheric ozone levels, (b) changes in snow- and ice-cover duration, and (c) changes in DOC levels in natural waters (Wrona *et al.*, 2005). A reduction in snow and ice cover on the surface of rivers, lakes, or oceans is likely to increase the exposure of many organisms to UV radiation (Weatherhead *et al.*, 2005). On the other hand, UV penetration in dilute lakes that are presently within catchments dominated by tundra and forest-tundra may be significantly reduced if climate warming induces a northward shift in the treeline or increases in the density of forest cover, leading to increased DOC inputs (Pienitz and Vincent, 2000; Figure 6.15). Lakes with very high catchment to lake area ratios are likely to be most affected by vegetation changes in treeline areas (Pienitz and Vincent, 2000). Export of humic substances is related to climate and to the balance between production and decomposition. However, climatic as well as deposition impacts on DOC export are under debate (Evans *et al.*, 2002; section 6.5.1.3).

Thus, both acid precipitation and climate warming may enhance the exposure of aquatic organisms to increased UV radiation, which is usually attributed only to depletion of stratospheric ozone (Schindler *et al.*, 1996; Gorham, 1998; Schindler, 1999). Levels of DOC decrease rapidly when lakes become acidified. Lower pH values lead to increased protonation of functional groups and cause the dissolved materials to become hydrophobic and to settle out of the water column onto bottom sediments. Increased photodegradation also seems to occur. Acidification, climate warming, and stratospheric ozone depletion may thus act together in a 'three-pronged attack' of UV radiation on aquatic systems, particularly in dry conditions (Schindler *et al.*, 1996; Schindler, 1999; Figure 6.15).

6.5.2. Interactions concerning heavy metals/contaminants

In principle, the atmospheric transport routes for acidic compounds should be similar to the pathways of other contaminants, such as heavy metals. Trace metals can catalyze the oxidation of SO_2 to sulfate by sunlight (Kellogg, 1995). Acid precipitation contains a variety of trace metals. However, the deposition pattern of heavy metals is different from SO_2 in that they (usually) deposit within

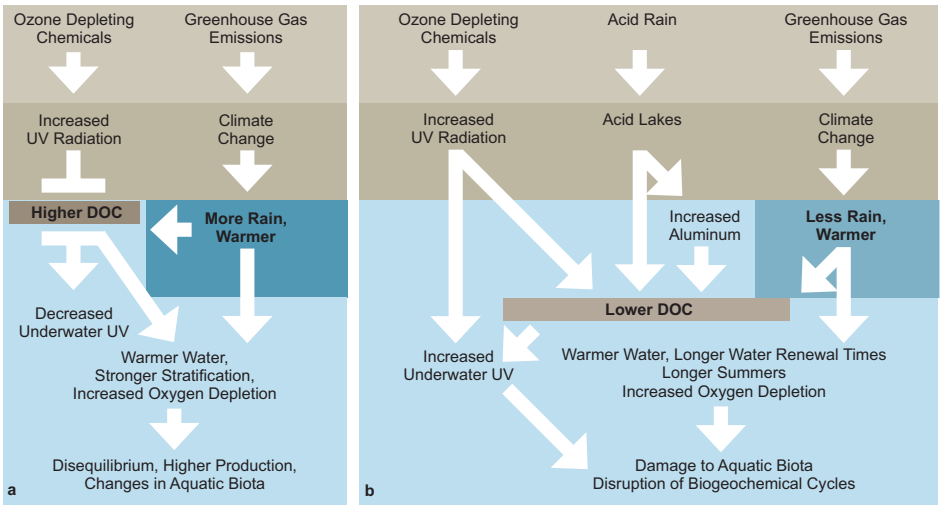


Figure 6.15. Climate warming will induce environmental changes in the Arctic that alter the exposure of aquatic organisms to the increasing levels of UV radiation caused by stratospheric ozone depletion: (a) a warmer wetter climate is likely to result in higher DOC levels in arctic lakes which, because humic substances strongly absorb UV radiation, will offset the effects of increased UV radiation from stratospheric ozone depletion (modified from Schindler, 1999), whereas (b) in arctic areas with a warmer drier climate the effects of stratospheric ozone depletion, acid rain, and climate warming can combine to increase the exposure of aquatic biota to UV radiation by causing a decrease in the DOC levels in lakes (redrawn from Schindler, 1999).

the immediate vicinity of the sources (mercury being a clear exception). Therefore, the interactive effects of metals and acid precipitation are especially visible locally near the emitters. The co-emissions of the smelters (base cations) may be adequate to prevent environmental acidification at the regional scale (e.g., Kashulina *et al*., 2003). The AMAP heavy metals assessment (AMAP, 2005) included little information on the potential interactions of heavy metals with other pollutants, for example sulfate, or the cumulative impacts of multiple pollutants. This section addresses potential interactions of heavy metal/contaminant pollution with other air pollution issues, including climate change. The complementary AMAP assessment on contaminant pathways (Macdonald *et al*., 2003) addressed recent global changes and their effects on the distribution of various contaminants.

6.5.2.1. **Processes in air**

Warming, increased precipitation, and thawing permafrost will increase the transport and deposition of contaminants to the Arctic. This was discussed in detail by Wrona *et al*. (2005) in relation to mercury and persistent organic pollutants. The timing of weather events also affects the transfer of contaminants to the Arctic. For example, snowfall occurring at the time of arctic haze would increase the transfer of contaminants to the ground at that time of year.

The northward movement of toxic metals and organic pollutants by cold condensation was confirmed by evidence from tree bark (Simonich and Hites, 1995) and lake sediments (Muir *et al*., 1995). Differential distillation, which pollutants undergo, allows them to be released in vapor form from warm areas and to re-condense in colder regions. However, Givelet *et al*. (2004) concluded that there is no evidence for the 'cold condensation hypothesis' and that the Arctic was not an important natural sink for mercury during pre-industrial times. Moreover, while the anthropogenic emissions of mercury are thought to have decreased by 30% in the past 20 years (Pacyna and Pacyna, 2002), there is evidence that mercury fluxes may have doubled over the past 100 years in the Arctic (Lockhart *et al*., 1995, 1998; Jackson, 1997) and that the average concentration of heavy metals has more than doubled on the Kola Peninsula over the last 20 years (Dauvalter, 2003). According to Givelet *et al*. (2004), springtime mercury depletion events are the chief mechanism for transferring atmospheric mercury to the arctic environment. Climate warming enhances mercury depletion events, which in turn increases the transfer of mercury into the food webs.

Synergistic interactions seem to occur between acidification, climate warming, and stratospheric ozone depletion that enhance the global mercury cycle (reviewed by Schindler, 2001). Global change and air pollutant levels influence the scale of mercury depletion (mercury transport and deposition from the air) (AMAP, 2002). The release of mercury to the atmosphere might be expected to increase as lakes become clearer (due to changes in DOC concentrations), particularly if increased methyl mercury is available due to warming lakes, and as reservoirs are constructed (Schindler, 1999).

6.5.2.2. **Processes in terrestrial areas**

Terrestrial processes have a key role in determining the impacts of heavy metals on surface waters. On the Kola Peninsula, direct exposure to SO_2 seems to be the main reason for ecosystem deterioration (Kashulina *et al*., 2003). The pine ecosystems there act as a biogeochemical barrier against metals by accumulating them in plant tissue and humus horizons (Goryainova and Nikonov, 1997). The function of forest ecosystems as a regulator of the cycles of these heavy metals (copper and nickel) is disrupted if the vegetation is lost (e.g., by acidification) and more toxic substances can then drain into watercourses.

Significant interactions between acidic rain and metal exposure were also observed in the lichen *Bryoria fuscesens* by Tarhanen *et al*. (1999). They established that although the metal load had a very important role in the decline of epiphytic lichen cover, acidic precipitation further disturbs the symbiosis between the photobiont and mycobiont of a lichen. Kashulina *et al*. (2003) concluded that the whole spectrum of emitted elements needs to be studied in the Kola region, in order to understand the effect of anthropogenic activities, including acidification.

6.5.2.3. **Processes in surface waters**

Changes in the timing of spring freshet, ice melt, and productivity are very likely to alter the efficiency of arctic lakes in capturing contaminants, for example mercury. Episodes of high contaminant levels are likely to occur in freshwaters when stored contaminants are released due to warming climate (Wrona *et al*., 2005). A wetter climate will expand the spatial extent of direct runoff to surface waters thus significantly increasing pollutant loads from point and non-point sources that are hydrologically isolated or filtered through groundwater aquifers under current flow conditions (Murdoch *et al*., 2000). Inundation of wetlands, riparian zones, and low-lying soils results in increased mobilization of trace metals and organic compounds from soils, increased mobilization and methylation of mercury, and greater anaerobic activity in saturated soils (sulfate reduction, denitrification) (Murdoch *et al*., 2000).

A change in flow patterns can alter the capability of a lake to receive and restore contaminants. At present, most of the contaminant load is carried through the lake surface layers under the ice before lake turnover and peak primary production and little is retained in the lake itself (Macdonald *et al*., 2000). In a warming climate the main runoff pulse may couple with lake mixing and primary production and hence cause more contaminants to be captured within the lake. In the case of acidifying compounds, lakes in catchments with thin soils, especially on slowly weathering bedrock, may thus face strong effects as the substances remain in the lake, rather than being carried rapidly through the lake.

Acidification and heavy metal contamination often work synergistically because the solubility of heavy metals in water increases as pH falls. As a result, heavy metals leach more quickly from contaminated soils in contact with acidic water. Dauvalter (1995) studied 15 lakes in Finnish Lapland. In four acidic lakes, the low pH had changed the geochemical cycling of potentially harmful metals by increasing desorption of metals from sediments back to water and/or decreasing the adsorption of metals onto settling sediment particles. Cadmium and nickel mobilization from sediments during acidification was observed by Nuorteva *et al*. (1987) and Fjeld *et al*. (1994).

Heavy metals are absorbed by plankton at the base of the food web and biomagnified to significant amounts at higher trophic levels. The influence of acidification and eutrophication on metal behavior must therefore be consid-

ered. It is well known that inorganic monomeric aluminum acts synergistically with pH to cause embryo mortality (e.g., Clark and Hall, 1985; Clark and LaZerte, 1985; Freda and McDonald, 1990; Blaustein *et al*., 2003). UV radiation also may affect the toxicity of contaminants (Wrona *et al*., 2005).

Water chemistry, especially acidity, and food web structure also affect mercury availability and uptake. Acidification can greatly enhance methylation, producing a higher proportion of bioavailable methylmercury (Miskimmin *et al*., 1992; Gilmour and Henry, 1991). Lake acidification is known to favor higher methylation to demethylation ratios, both directly and via effects on DOC (see references in Schindler *et al*., 1995). Climate warming alters the thermal conditions of lakes in a way that increases the methylation of mercury (Ramlal *et al*., 1993; Schindler *et al*., 1995). On the other hand, increased penetration of shortwave solar radiation due to decreases in DOC may cause increased conversion of methylmercury to elemental mercury, which is then released back to the atmosphere (Sellers *et al*., 1996). Once back in the atmosphere, mercury is susceptible to long-range transport and biomagnification in distant food chains (Schindler, 1999).

Future climate change, in interaction with other environmental problems, is thus thought to influence the distribution patterns and mobility of organic pollutants and toxic metals in freshwater systems and to lead to changes in the uptake and accumulation of these substances in freshwater food chains. This is one of the main hypotheses tested in an ongoing EU project EURO-LIMPACS (http://www.eurolimpacs.ucl.ac.uk/index.php).

Acidification of the oceans

Owing to increasing atmospheric CO_2 levels, CO_2 levels in the oceans have increased since pre-industrial times. Added CO_2 decreases the CO_3^{2-} (carbonate) ion concentration and makes the ocean more acidic. Ocean pH has decreased by 0.1 units, equivalent to a 30% increase in hydrogen ion concentration over the last two centuries (Caldeira and Wickett, 2003; The Royal Society, 2005). If global emissions of CO_2 continue to rise on current trends, then the average pH of the oceans could fall by 0.5 pH units by 2100 (a 0.5 unit decrease in ocean acidity means a three-fold increase in hydrogen ions). This could have substantial effects on the biological processes in surface oceans. Recent studies indicate that future undersaturation of aragonite and calcite, especially in polar oceans, may have potential biological impacts on calcifying organisms, especially shelled pteropods, the densities of which are high in cold water regions (Orr et al., 2005). Shell dissolution rates of pteropods increase in waters that have become undersaturated with aragonite (e.g., Byrne et al., 1984). Also, benthic calcareous organisms such as cold-water corals are in danger of becoming surrounded by water masses that are undersaturated with aragonite. Orr et al. (2005) suggested that some high latitude surface waters will probably become undersaturated within the next 50 years, leading to detrimental conditions for many organisms.

Abbreviations

*	of non-marine origin
1-D	one-dimensional
3-D	three-dimensional
Al	aluminum
AMAP	Arctic Monitoring and Assessment Programme
ANC	acid neutralizing capacity
AO	Arctic Oscillation
AOD	aerosol optical depth
BC	black carbon / base cation
C	carbon
Ca	calcium
C-horizon	parent material of soil
CH_4	methane
Cl	chloride
CL_{Ac}	critical load of acidity
CLE scenario	emissions scenario based on current legislation
CO	carbon monoxide
CO_2	carbon dioxide
Cu	copper
DEHM	Danish Eulerian Hemispheric Model
DIC	dissolved inorganic carbon
DI-pH	diatom-inferred pH
DOC	dissolved organic carbon
EANET	Acid Deposition Monitoring Network in East Asia
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
K	potassium
LRTAP Convention	Convention on Long-Range Transboundary Air Pollution
MFR scenario	emissions scenario based on maximum technically feasible reductions
Mg	magnesium
Mn	manganese
N	nitrogen
Na	sodium
NAO	North Atlantic Oscillation
N_2O	nitrous oxide
NH_3	ammonia
NH_4	ammonium
NH_4-N	ammonium nitrogen
Ni	nickel
NILU	Norwegian Institute for Air Research
nmVOC	non-methane volatile organic compounds
NO_2	nitrogen dioxide
NO_3	nitrate
NO_3-N	nitrate nitrogen
NO_X	nitrogen oxides
NO_X-N	nitrogen oxides nitrogen
NSR	Northern Sea Route
O-horizon	organic horizon of soil
S	sulfur
SO_2	sulfur dioxide
SO_4	sulfate
SO_4-S	sulfate sulfur
SO_X	sulfur oxides
UN ECE	UN Economic Commission for Europe
UV	ultraviolet
Zn	zinc

AMAP
Arctic Monitoring and Assessment Programme

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