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Metals in Scandinavian Surface Waters: Effects of Acidification, Liming, and Potential Reacidification

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ABSTRACT: This article is a state-of-the-art review about such metals as Al, Fe, Mn, Cu, Zn, Cd, Pb, Cr, Ni, Hg, and As in surface waters. It focuses on natural and anthropogenic sources, chemical properties and levels, and toxicity mechanisms of these metals to aquatic organisms, primarily fish and invertebrates. Organisms living in almost anoxic, sulfide-rich evironments are not incorporated into this study. This information is then linked to a Nordic Lake Survey implemented in 1995 on major chemistry and metals in Scandinavian surface waters to scale the problems of metals in Swedish and Norwegian surface waters. Because many acidified Swedish and Norwegian lakes also are limed, we also assess the risk of remobilization of metals because these waters reacidify due to reduced liming activity. The concentrations and chemical properties of metals in lakes relative to the biological effect levels suggest that the potential risks associated to both current and potential reacidified status of limed waters decreases in the order Al >> Cd > Pb in Swedish and Norwegian lakes. Also Hg, because of the organometallic forms such as methylmercury (MeHg), might be of concern, because it biomagnifies in the food chain and subsequently of great importance for top predators, including human beings. However, other factors than pH, such as changes in organic matter load from the surrounding soils due to natural climatic variations, are much more important for the Hg load and thereby the Hg concentrations in lakes than pH. The risks associated with other metals such as Cu, Fe, Mn, Ni, and Zn are very low and have to be considered only occasionally, because high concentrations are very rare in Norwegian and Swedish lakes. Less than 2% of the lakes have concentrations ≥ the lowest biological risk levels quoted in the two countries. Because primarily As is present as anions in surface waters, this element differs significantly from the cationic metals. Only a few lakes have high As concentration in relation to critical levels in Sweden, and high As concentrations are mainly related to agricultural areas and consequently high pH waters.

I. INTRODUCTION

Surface water acidification by atmospheric deposition of strong acids has impacted aquatic resources in large regions, particularly in North America and Northern Europe (e.g., Jeffries et al. 1986; Gunn 1986; Henriksen et al. 1989). A result is the loss of many fish populations, obviously with negative effects on other parts of aquatic ecosystems. The low pH itself may affect the biology, but the main toxic factor is the increased concentration of inorganic aluminium following soil and surface water acidification. Increased concentrations of other metals may also be a consequence of acidification, but will seldom cause harmful conditions to aquatic life. Exceptions are often related to very catchment-specific conditions or human activities such as mining.

Base addition has been widely practiced to mitigate surface water acidification in Sweden (Bengtsson et al. 1980; Hultberg and Andersson 1982; Svensson et al. 1995), Norway (Wright 1985; Sandoey and Romundstad 1995), Canada (Dillon and Scheider 1982), and the USA (Porcella 1989; Olem 1990, Smallidge et al. 1993). As the main base addition sources have been different types of limestone, the base addition strategy is commonly called liming. Besides increasing pH and the acid-neutralizing capacity of water (ANC), liming also reduces the concentration of toxic Al so that surface water ecosystems are again able to host a viable fish population. It is far more debateable to what extent liming has also reduced the concentration of other potential toxic metal species. Due to generally low concentrations, however, effects of liming on other metals have so far been less obvious. This is reasonable, because metals other than aluminium have only caused local damages directly related to point sources.

In Sweden, liming has achieved governmental subsidies since 1976, and so far 2.0 billion SEK has been used on different liming activities. In the last 5 years, approximately 200,000 tons of lime have been used in lakes (7500 objects), rivers (12,000 km), and on wetlands (1600 objects), corresponding to approximately 175 million SEK a year (SNV 1999). In Norway, about 2000 localities, ranging from small lakes to large salmon rivers, have been limed (Sandoey and Romundstad 1995), but so far regarding wetland and/or catchment liming only experimental projects have been conducted in Norway (Hindar et al. 1995, 1996).

Recently, the Swedish liming programme has been under official investigation, and a large financial reduction down to 80 million SEK a year was proposed (SOU 1996:53). However, the budget never reached such low levels, and for 1997 it was cut down to 140 million SEK. From 1998, there has also been a cutdown in the Norwegian liming program, from 119 million NOK in 1997 to 105 million NOK in 1998. Significantly, reduction in liming grants necessarily implies a shutdown of liming projects. Accordingly, concerns have been raised about the chemical and biological consequences of reacidification of earlier limed systems.

This report focuses on water chemical effects of reacidification of earlier limed objects, particularly regarding changes in the biogeochemical cycling of metals (Al, Fe, Mn, Cu, Pb, Zn, Cd, Cr, As, Hg). The subsequent goal is to evaluate the biological effects of the chemical changes in the coming years and try to give some advise concerning which limed objects might sustain the reacidification if liming terminates. Organisms living in almost anoxic, sulfide-rich evironments are not incorporated into this study.

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II. SURFACE WATER ACIDITY AND BIOLOGICAL EFFECTS

A. Surface Water Acidification

Smith (1852, 1872) first reported urban acid deposition. His work, however, was forgotten until a century later when the spread of acid deposition, largely sulfuric acid, became apparent far from urban sources (Barrett and Brodin 1955; Houghton 1955; Gorham 1955). The effects of acid deposition on lake pH were probably first described by Mackereth (1957) and Gorham (1957, 1958a) in England. Although Huitfeld-Kaas (1922), Dahl (1926), and Sunde (1926) claimed that acid freshwater caused mortality of salmon and trout, Dannevig (1959) was the first who correlated fish death in Norway with acidification of surface waters by acid deposition. The broad ecological consequences of long-range transport of acidifying air pollutants were first recognized by Odén (1968). From that time, acidification of surface waters has been reported as a major problem in large areas of the northern temperate regions. Common to all these affected areas is the following:

1. Low pH-buffering capacity in the catchment.
2. Large atmospheric inputs of directly (e.g., strong acids) and/or indirectly (e.g., various NH_4-N compounds) acidifying compounds.

The acidification of surface waters may also arise due to special conditions in the catchment, for example, aeration (oxidation) of sulfide-rich soils (Alasaarela 1982; Erviö and Palko 1984; Björkqvist and Weppling 1987). In addition, natural sources to soil and freshwater acidification exist (Ulrich 1980), mainly due to:

1. Nutrient uptake by plants.
2. Production of $CO_2$by plant roots and microorganisms.
3. Oxidation of N and S compounds.
4. Humification of organic substances.

The knowledge of the acidification phenomenon has increased tremendously since Odèn (1968) suggested that the increasing acidity of precipitation was responsible for the decline in fish populations. In the initial years of the acid precipitation science it was generally accepted that the deposition of acidic substances from the atmosphere into soil and aquatic systems was the dominant cause of surface water acidification (Wright and Gjessing 1976; Seip and Tollan 1978; Likens et al. 1979). Based on this assumption, Henriksen (1980) claimed that the acidification process could be described as a large-scale titration, where the effect of acid precipitation on a catchment could be compared with an acid titration of a hydrogen carbonate solution. Other scientists, especially Rosenqvist (1977, 1978, 1981, 1990), claimed that the main reason for the acidification of surface waters is the change in the biogeochemical buffering level of the catchment. The acidification thus is more dependent on the amount and intensity of the precipitation than its acidity during the acid flood episodes. Reeve and Fergus (1982) have shown that podzol soils can naturally create highly acidic clearwaters containing high amounts of inorganic dissolved aluminium. These observations were made in coastal Australia areas that do not receive acidic H_2SO_4 precipitation, but receive high amounts of neutral chloride salts from sea spray. The proposed mechanism is that sea salt cations (Na^+, Ca^{2+}, Mg^{2+}) are taken up by soils or vegetation and replaced by H^+ ions, resulting in acidic waters. This is also well known from Norwegian coastal areas (Hindar et al. 1994). The effect of neutral salt on soil and surface water acidification was reported earlier by several scientists (Wiklander 1975; Rosenqvist 1977; Skartveit 1980; Seip et al. 1989). Thus, "unpolluted rain" might also be responsible for acid-stressed aquatic systems.

The most significant biological consequences of soil acidification is the mobilization of aluminium from edaphic to aquatic environments (Magistad 1925; Scheider et al. 1975; Wiklander 1975; Wright et al. 1977; Dickson 1978; Cronan and Schofield 1979; Cronan 1980; Dickson 1980; Driscoll 1980; Driscoll et al. 1980; Vangenechten and Vanderborght 1980; Wright et al. 1980; Krug and Isaacson 1984; Mulder et al. 1989). Many scientists have stressed the importance of the biogeochemistry of the catchment for the surface water chemistry (Brosset 1979; Glover and Webb 1979; Overrein et al. 1980; Seip et al. 1980, 1989; Stuanes 1980; Ulrich 1980; Groeterud 1981; Johnson et al. 1981; Christophersen 1983; Reuss and Johnson 1985; Van Breemen and Mulder 1987; Mulder et al. 1990; Sullivan et al. 1990). Further, Sullivan et al. (1990) claimed that the role of catchment for neutralization of acidic input is more important than generally assumed. Similar conclusions were also made by Krug (1991) based on an extensive review of literature concerning the theories of the acidification of freshwaters. Model-based estimates of future chemical changes and biological responses therefore should be reevaluated in light of these results (Sullivan et al. 1990). A similar conclusion was also drawn in the final report from the Surface Water Acidification Programme (Mason 1990).

The interactions of acid rain and acid soils generally have been concerned with the major inorganic constituents of precipitation, soil, and leachate. The leaching of base cations from extremely acid soil materials therefore is often observed to be small relative to the H^+ additions of acid rain (Wiklander 1973; Abrahamsen 1980; Bache 1980; Smith 1981). Consequently, the release of Al by dissolution or exchange are considered to be the major acid neutralization processes (Ulrich et al. 1979; Mulder and Van Breemen 1987; Mulder et al. 1987), as dissolution of solid Al is a proton-consuming process. That means that a dissolved Al species, like Al^{3+}, acts as a mobile temporary proton sink, enabling acidity to be transported by this ion in large quantities in the draining water. The fate of these ions is determined by secondary reactions, like adsorption, complexation, and precipitation processes, during which protons are released again. These observations have led to the hypothesis that such soil materials are poorly buffered against H^+ addition (Overrein et al. 1980; Seip 1980).

The buffering capacity against H^+ in a catchment is also shown to be highly dependant on the mobility of the accompanying anions, mainly the strong acid anions Cl^-, SO_4^{2-}, and NO_3^- (Seip 1980; Reuss and Johnson 1985). In acid soils, the introduction of mobile anions, whether as salts or acids, can cause a sufficient increase in soil solution ionic strength to reduce the alkalinity of the soil solutions significantly. Within certain critical ranges this will lead to a switch from positive to negative alkalinity in the solution (Reuss and Johnson 1985). If Cl^-, which is the most mobile anion, predominates, a relatively fast acidification response will occur. The SO_4^{2-} ion is less mobile and the acidification effect by this ion is highly dependent on the sulfate retention in the catchment. This was already pointed out by Gorham (1958b). The effects of the NO_3^- ion on the acidification is difficult to evaluate. This ion is often totally resorbed by the vegetation, and effects of plant growth on soil acidification are difficult to quantify.

Most areas considered highly sensitive to acidification by acid rain often have high proportions of extremely acid, organic-rich lithic soils, and peats (Braekke 1976; Krug and Frink 1983). Even though Hedin et al. (1990) claimed that organic, acid-base systems have a very limited capacity to buffer inputs of strong mineral acids, several experiments in acid, organic-rich soils show that they are not poorly buffered. Treatments (additions of strong acid) more acidic than pH 4 are required to significantly reduce pH and significantly increase the quantity of cation leaching from these soils (Overrein 1972; Seip et al. 1979, 1980; Abrahamsen 1980; Abrahamsen and Stuanes 1980; Cronan 1980; Overrein et al. 1980; Smith 1981). Because cation exchange reactions predominate in the organic soil horizons, cation exchange reactions are important in regulating the solution chemistry. However, it is unreasonable to assume that cation exchange is the only mechanism by which soil organic matter influences solution chemistry. Very little is known about how the solubility and mobility of organic matter and its complexes are influenced by acid input and how such interactions influence cation flux and leachate acidity (Krug and Frink 1983). The results obtained by Krug and Isaacson (1984) indicate that soil organic matter buffers against strong acid additions by a number of other mechanisms than exchange of base-cations and aluminium for H^+. Complex changes in both the organic and inorganic composition of leachate are suggested (Ritchie and Posner 1982). The organic acid-buffering mechanism may be an alternative explanation to the observation that humic-colored lakes in Scandinavia are becoming clearer. This effect was previously attributed to precipitation of humic acid by iron and aluminium dissolved by acid rain (Almer et al. 1974; Dickson 1978).

B. Biological Effects of Acidification

The main toxic effect of acidification is the increased transfer of Al from edaphic to aquatic environments (e.g., Cronan and Schofield 1979; Dickson 1980; Seip et al. 1989) primarily by increased dissolution of solid Al pools and the increased mobilization of Al by cation exchange processes. Already more than 100 years ago, it was well known that Al might be present in toxic amounts in soils (e.g., Hartwell and Pember 1918; Magistad 1925; Hardy 1926) and aquatic environments (Penny and Adams 1863; Weigelt et al. 1885; Thomas 1915; Ebeling 1928; Oshima 1931; Ellis 1937, Sanborn 1945; Pulley 1950; Murdock 1953; Wallen et al. 1957; Jones 1964; Dickinson Burrows 1977). In general, these older studies have been performed under conditions where the Al concentration exceeded the solubility of Al and little attention has been given to the effects of precipitates. Furthermore, the studies have often been performed at pH levels where pH itself could have been the lethal factor. Recent concerns about the effects of soil acidification on the biogeochemistry of Al have broadened the scope of interest in Al toxicity, and the recent toxicity studies therefore have been performed at more relevant concentrations of Al, that is, at concentrations in agreement with values reported for many acidified surface waters (< 10 μmol Al L^{-1}).

Even though Al toxicity to fish was demonstrated almost 70 years ago (Ebeling 1928), Schofield (1977) was the first to report the link between acidic Al-rich freshwater and fish mortality. Similar results were obtained independently by Dickson (1978). From that time, numerous scientists have observed toxic effects of Al on many species of freshwater fish. Toxicity of Al has also been reported in oversaturated solutions where unstable inorganic Al chemistry is present, as after liming of acidic Al-rich waters (e.g., Dickson 1978). Lydersen (1992) found that generally, for all later corresponding studies, high toxicity in unstable Al chemistry water only occurs when pH is raised compared with the initial water pH. Thus, he concluded that there has to be a prehistory of lower pH for significant amounts of unstable toxic Al polymers to form. This was later supported by Oughton et al.

(1992) with the use of ^{26}Al tracer. They found that Al on gills of fish exposed to limed water only derived from Al present in the acidic water where Al primarily was present as an inorganic low-molecular-weight species prior to liming. Later studies have supported these observations and further concluded that the most toxic Al conditions exist soon after a pH increase in Al-rich acidic waters (Weatherley et al. 1991; Rosseland et al. 1992; Poléo et al. 1994; Lydersen et al. 1994a), and that the toxicity decreased by aging of the polymers (Lydersen et al. 1994a). Today, there is no doubt that the increased concentration of inorganic Al during soil and surface water acidification is the primary cause of fish kill in acidic freshwaters, and that highly toxic conditions may occur soon after a pH increase (e.g., by liming) of acidic Al-rich waters.

Al toxicity to aquatic organisms other than fish has also been reported. Several studies have demonstrated the toxicity of inorganic Al to amphibians (e.g., Clark and Hall 1985; Clark and LaZerte 1985; Cummins 1986; Leuven et al. 1986; Freda and McDonald 1990; Freda et al. 1990). Others have shown that Al has lethal and sublethal effects on several invertebrates (Correa et al. 1985; Malley et al. 1982; Malley and Chang 1985; Burton and Allan 1986; Fjeld et al. 1988). Fjeld et al. (1988) and McCahon et al. (1989) observed increased Al on gills of invertebrates (crayfish and zooplankton). Many have documented Al toxicity to different species of green algae (e.g., Helliwell et al. 1983; Folsom et al. 1986; Törnqvist 1989), while Gensemer (1991) showed Al toxicity to an acidophilic diatom.

It is mainly strong mineral acids (primarily H_2SO_4) through acid rain that most frequently have been the focus as the main cause of soil acidification and subsequently the dissolution of inorganic Al. This is understandable, because there is a co-occurrence in time and space between increased acid rain input and severe decline in many fish populations in large acid-sensitive areas of the northern hemisphere. Natural acidic water systems with a high concentration of inorganic Al also exist, despite minor or no impacts from acid rain (Krug 1991). These waters might contain both low and high concentrations of DOC. A major difference between these naturally acidic environments and the acid-rain-acidified environments, however, is the biological possibility of physiological adaptation. In natural acidic environments, the biology may have been adapted gradually to the water chemical changes through hundreds or maybe thousands of years. The significant changes in water chemistry during a few decades as a result of strong impacts from acid rain have proceeded too fast in relation to the time many aquatic organisms need to adapt. Accordingly, large biological effects have been documented as a result of acid rain impact.

III. LIMING STRATEGIES

Liming criteria in Norway and Sweden are different. In Norway negative biological effects have to be documented, and a target pH of 6.0 is defined as a

Table 1. Average values of pH, alkalinity, the sum of Ca and Mg and water colour before and after liming in 634 lakes in Sweden (table taken from Thörnelöf and Degerman 1991). Color is divided into lakes with color < 100 mg Pt L^{-1} before liming and > 200 mg Pt L^{-1} before liming. Groups have been compared with paired t-test

Parameter	Before liming	After liming	t-test
Average pH	5.83	6.42	$p < 0.001$
Lowest pH	5.67	6.20	$p < 0.001$
Average alkalinity (meq L^{-1})	0.05	0.15	$p < 0.001$
Lowest alkalinity (meq L^{-1})	0.03	0.11	$p < 0.001$
Average conductivity mS m^{-1}	4.9	5.2	$p < 0.001$
Average $Ca^{2+} + Mg^{2+}$ (meq L^{-1})	0.27	0.35	$p < 0.001$
Average colour (mg Pt L^{-1})	66.6	74.5	$p < 0.001$
Colour when pre-treatment colour < 100 mg Pt L^{-1}	46	62	$p < 0.001$
Colour when pre-treatment colour > 200 mg Pt L^{-1}	246	206	$p < 0.001$

proper liming goal, except in salmon rivers during the smoltification period (late winter and spring), when somewhat higher pH (up to 6.4 to 6.5) is recommended. Lakes with acid-neutralizing capacity, ANC > 20 µeq L^{-1} (ANC = Σ (Ca^{2+},Mg^{2+},Na^{+},K^{+}) - Σ(SO_4^{2-},$NO3^{-}$,Cl^{-}) are normally not limed in Norway, as well as humic lakes with high concentration of organic acids, that is, TOC > 6 to 8 mg C L^{-1}. In Sweden, not ANC but inorganic alkalinity has been used as a parameter for liming. Inorganic alkalinity in Sweden is defined as the amount HCl used (µeq L^{-1}) to reduce pH from actual pH down to pH = 5.4. In Sweden, lakes with pH < 6.0 and/or inorganic alkalinity < 50 µeq L^{-1} are defined as liming objects.

Inorganic alkalinity ≥ 100 µeq L^{-1} is the chemical goal for liming in Sweden. Negative biological effects do not have to be documented. By not taking the TOC and ANC status of the waters into consideration, it is most probable that naturally acidic humic-rich lakes with relatively high ANC are limed in Sweden (see Table 1). The average alkalinity of the 634 lakes in this table was 50 µeq L^{-1} prior to liming, which means that many of these lakes did not fulfill the Swedish liming criteria. Because the lowest alkalinity of these lakes was 30 µeq L^{-1}, none of the lakes would likely have been limed in Norway. The high color (average: 66 mg Pt L^{-1}) in many of the lakes indicates that ANC would have been much higher than the alkalinity. Information about Al, which is the most essential toxic compound in acid water, is lacking from most limed objects.

As criteria for liming, Norway, but not Sweden, has accepted the critical load for surface waters ($ANC_{CL} \leq 20$ µeq L^{-1}) used by the Nordic countries in the international negotiations on the reduction of Long-Range Transport of Atmospheric Pollutants (LRTAP). Obviously, Swedish liming and emission reduction measures are controlled by different critical load criteria (SNV 1998).

Reestablishing the chemical environment for natural recruiting fish populations was the primary goal for the initial liming activity in both countries. Today, the most important criterion for liming in Norway is to preserve biological diversity, and surface waters still containing original populations of acid-sensitive species have the highest priority (Sandoey and Romundstad 1995). In Sweden a corresponding future liming strategy is under development and will encompass both biological and chemical targets.

Except for a few projects, neither country incorporates Al and heavy metals in their liming programs. Thus, good documentation of the fate of these metals after liming or when limed waters reacidify is generally lacking.

Limestone powder ($CaCO_3$), or dolomite powder ($CaMg(CO_3)_2$), are the most common liming products used in Norway and Sweden. In a few Swedish lakes with low retention time, Na_2CO_3 has been used. Different fraction (particle size) is used for direct lake liming, for dosers on streams and rivers, and for wetland liming (Henrikson and Brodin 1995).

Lake liming: Liming directly into the lake is the most common method used in Sweden and Norway. The limestone is mixed with lake water and dispersed mostly from boat and helicopter. In winter limestone can be spread on ice using snowmobile. In Sweden, lake liming is used where the lake surface exceeds 10% of the catchment area. The normal dose is 10 to 30 g m^{-3}, and reliming is usually every 1 to 5 years or 2 to 4 turnover times. Limestone utilization for lake liming is normally from 50 to 80% (Svensson et al. 1995). In Norway and also in USA a certain amount of precipitated limestone on the surface of lake sediment is often wished, because this pool acts as a more slowly soluble source, which means that it take somewhat longer time until reliming is necessary.

River/stream liming: Continuous dosing of lime is used in running waters in both countries, and in Norway this activity has increased significantly during recent years as several acid salmon rivers are limed continuously. Limestone is added directly into the watercourse, dry or mixed with water, and is added in proportion to flow, water level, water speed, or pH. Limestone utilization is about 50 to 70%. Due to dissolution constraints, the liming site is generally several hundred meters upstream the target area.

Catchment liming: Wetland liming is often used in Sweden as a supplement to other liming, but has only been used in experimental scientific projects in Norway so far (Hindar et al., 1996). The limestone is dispersed on discharge areas, where groundwater reaches the surface and transports dissolved limestone to the surface waters. In Sweden, it is also common to lime waste areas of peatland, generally referred to as bogs (Abrahamson 1995). This strategy mitigates acid episodes during hydrological extreme episodes, like during snowmelt, where very acidic and sometimes metal-rich water flows through the lake in the uppermost 1 to 2 meters of the lake. This is a common situation in a limed lake where limestone is not continuously added like in running water. The method, however, involves undesired effects, such as significant changes in wetland flora and hydrology. Doses are 10 to 30 tons ha^{-1} wetland with duration > 2 years. Limestone utilization is 50 to 70% (Henrikson and Brodin 1995).

Terrestrial liming: In both Sweden and Norway, forest floor liming is practiced at an experimental level in some areas. So far, both positive and negative effects are documented on the aquatic and terrestrial ecosystems. Increased ANC and reduced Al concentrations are documented only in forest streams where both recharge and discharge areas have been limed (Staaf et al. 1996; Larsson and Westling 1997). Liming on exposed rocks has resulted in an almost total extermination of the original lichens and moss flora.

IV. LIMING EXPERIENCES

The main chemical purposes of aquatic liming are to increase pH and alkalinity of acidic/acidified waters. The dynamic nature of the neutralisation process results in both short- and long-term effects to the aquatic environment, and many effects of liming (both chemical and biological) may differ depending on the various types of aquatic systems limed. The knowledge of specific liming effects is very useful in order to evaluate the effects of reacidification, even though reacidification will never be a direct reverse chemical and biological process.

A. Duration

The amount of lime added is of course essential for the duration of liming, but the duration also depends on catchment specific hydrology, like, water pathways, water retention time within the catchment or lake, and the amount and quality of precipitation.

The downstream effects of liming running waters depends on the dose and the amount and quality of both upstream and downstream waters. If liming stops, running waters more or less reacidifies immediately and reach prelimed water chemical conditions very soon (hours to days), assuming no changes in the impact on the ecosystem within liming period.

Treatment longevity is normally much longer for direct lake liming. The time for reliming is highly dependent on the retention time of water in the lake. Alenäs et al. (1991) made a dilution curve expression of Ca, which seems to be a satisfactory approximation for many lakes, at least in southern Sweden:

$$C(t) = \exp^{-t/T}(Cs - Cb) + Cb$$

where

C(t): is the actual (Ca^{2+}) at time t; T: theoretical retention time; Cs: (Ca^{2+}) after liming; Cb: (Ca^{2+}) background.

This manifests the crucial importance of hydrology for reacidification. When lake liming is stopped water chemical effects therefore may last from weeks to a few years until the prelimed water chemical conditions are reestablished.

The effects of terrestrial liming may last for many years, depending on factors such as the type of terrestrial ecosystem limed, the amount of lime, the hydrological flow path, and residence time, etc. Estimates of treatment longevity indicates that watershed liming may be more effective on forested than morland areas. Three subcatchments (<20% of the total catchment) of Loch Fleet were limed to obtain a lake water quality of pH > 6, $Ca^{2+} > 2$ mg L^{-1} and inorganic aluminium (LAL) < 30 µg L^{-1}. Hydrochemical reactions were limited to the litter and upper 5 cm of the profile (Dalziel et al. 1994). The liming gave successful spawning of reintroduced trout, and the liming goals lasted > 5 years. The Loch Fleet liming project concluded that target water quality might last up to 15 years when forested areas are limed, and 7 years in morland areas. Studies of a number of terrestrial liming experiments (0.5 to 6 tonnes per hectare) in southern and central Sweden showed that an obvious and rapid effect on pH and alkalinity was only achieved if the discharge areas were treated (Warfinge et al. 1996).

B. Physical Effects (Transparency and Color)

Physical changes that may occur due to acidification or liming, typically include changes in transparency, color and thermal conditions. These changes are often interrelated. Regarding changes in transparency and color with pH, there are several works that link these changes to changes in primary production of lakes. In acidic, dilute Scandinavian waters, however, our opinion is that the primary reason for changes in transparency and color is the qualitative and quantitative changes in dissolved organic carbon (DOC) that occur as a result of changes in pH, aluminium, and calcium. Subsequently, changes in light attenuation may affect the primary production and the phytoplankton community of lakes.

Almer et al. (1974) reported a significant increase in transparency (from 3 to 10 m) in a Swedish westcost lake from 1943 to 1973, during a period when pH fell from 6.25 to 4.5. Similarly, Schofield (1972) compared transparencies measured from 1950 to 1953 with those measured in 1967 in 14 Adirondack lakes. Mean Secchi transparency increase from 5.6 to 8.3 m, while mean pH fell from 5.9 to 5.0. Almer et al. (1978) suggested that increased clarity in acidic lakes was attributable to precipitation of Al-organic complexes. Schnitzer and Kahn (1972) had reported previously that at low pH, high concentrations of Al and Fe would coagulate and subsequent precipitate humic acids. Schindler (1980) and Shearer et al. (1987) also reported increased transparency after acidification, but without any change in the concentrations of DOM, which means that a decrease in color (quality of DOM) is the most reasonable explanation.

Many studies have shown that liming acidic lakes causes changes in total organic carbon (TOC), color, and transparency. Liming may cause a decrease in TOC and color (transparency increase), apparently due to precipitation of humic matter (Dickson 1979; Hultberg and Anderson 1982; Yan and Dillon 1984), as Ca-organic precipitates or coprecipitation with other inorganic and organic metal complexes, where aluminium may play an important role. Several lakes in Sweden have responded in this manner (Hultberg and Anderson 1982), as did a lake in Adirondack Mountains (Driscoll et al. 1982). On the other hand, many scientists have documented a permanent increase in TOC (transparency decrease) after liming (e.g., Dickson 1979; Yan 1983; Wrigth 1985; Marcus 1988; Bukaveckas and Driscoll 1991), but the Secchi depth tends to return to pretreatment values as the lakes reacidify (Yan 1983; Bukaveckas and Driscoll 1991). The explanation mechanisms here include an increased phytoplankton growth (Hultberg and Anderson 1982), more dissociated organic acids, increased respiration rates in the sediment with release of organic substances, and simple pH-dependant light adsorption properties of humic substances (Hultberg and Anderson 1982; Yan 1983). Almer et al. (1978) further noted that the color of aqueous solutions was lowest at pH ≈ 4.8 with the addition of 1 mg Al L^{-1}, and found increases in color at both higher and lower pH. Others have reported unchanged concentrations of TOC after liming (Marcus 1988).

Changes in TOC, color, and transparency by liming and reacidification are probably due to several factors, where the relationships between the concentration of dissolved organic compounds (ligand) and potential complexing metals (primarily Ca^{2+} and Al^{n+}) are essential chemical factors besides renewal time of lakes as an essential physical factor. Thörnelöf and Degerman (1991) concluded that water color in Swedish lakes generally increased after liming of clearwater lakes (< 100 mg Pt L^{-1}), while it decreased in humic-rich lakes (> 200 mg Pt L^{-1}). In Norway, lakes with color > 100 mg Pt L^{-1} are relatively few, and are normally not limed.

Obviously, changes in transparency influence light penetration, with effects on heat budgets, and thermocline levels in lakes (Malley et al. 1982; Yan 1983; Bukaveckas and Driscoll 1991). These changes will of cause impact lake chemistry and biology. Deeper light penetration means that hypolimnetic O_2 may be depleted more rapidly because the hypolimnetic volume decreases as well as higher temperatures may increase the decomposition rates of the organic matter. However, this may be counterbalanced by earlier autumn turnover and because the trophogenic zone may extend into the hypolimnion, permitting O_2 genreation by photosynthesis.

From 1971 to 1995, a darkening of Swedish surface waters was documented (Forsberg and Löfgren 1988; Forsberg and Petersen 1990; Forsberg 1992; Wiederholm 1996; Löfgren 1997). The observations of Wiederholm (1996) are based on 169 reference lakes and 99 river stations all over Sweden, analyzed since 1971 (rivers) and 1984 (lakes). The data from Löfgren (1997) relies on 517 lakes in the county of Dalarna. In some cases the increase in color may be due to an increase in color-interfering elements such as Fe and/or Mn (Pennanen and Frisk 1984), but in most cases it is likely a result of an increased concentration of dissolved organic matter (DOM). An increase in DOM may rely on several factors such as increased precipitation, increased ground water level leading to increased runoff from superficial organic-rich soils (often with a high Fe content, Löfgren 1991), increased accumulation of litter and humic matter due to increased vegetation growth and larger areas with forest, simultaneously with more intensive catchment management (clear-cut, ditching, fertilizing). The assumption that increased DOM during the last 10 to 20 years is due to further acidification is contradictory to the clearing of lakes observed during the previous acidification period (Almer et al. 1974; Schofield 1972). If pH is important for the changes in DOM, it is more likely that DOM will increase if pH increases. This relies on the fact that weaker acids are able to dissociate at higher pH, which means that total amounts of organic acids will increase as pH increases. A pH increase will subsequently lead to a reduction in the concentration and cationic properties of important organic complexing cations as Al, which further may increase the possibility of DOM leakage. Increased greenhouse impact with higher air temperature further increases the mineralization rates and also contributes to a higher concentration of DOM. It is, however, difficult to assess how much of the observed changes are attributed to natural variations or anthropogenic impacts.

C. Major Chemical Effects

Direct liming of surface waters causes a substantial and spontaneous change of the water chemical conditions, primarily due to increased pH, an increase in alkalinity or acid-neutralizing capacity (ANC), and Ca^{2+} (or ionic strength). The subsequent effect of liming is the reduction in the concentration of inorganic aluminium forms (LAL), the primary toxic compounds in acid surface waters. In some cases also reductions in some other potential toxic metals (e.g., Fe, Mn, and Cd) occur after liming (Svenson et al. 1995), but the concentrations of these metals are normally far lower than the biological effect concentrations even before the waters are limed. Undesirable effects of direct watercourse liming are minor. Highly acute toxic water chemistry immediately after liming (mixing zone problems) are documented as a negative effect (Dickson 1983; Weatherly et al. 1991; Rosseland et al. 1992; Lydersen et al. 1994a); quantifying these effects are however, very difficult. Undoubtedly, positive liming effects on fish survival and fish production totally overshadowing these negative effects. Direct lake liming does not prevent episodic acidification of stream water and the near-shore region of the lake during snowmelt, a phenomenon critical for the development of fish population. Furthermore, direct surface water liming does not reduce the inputs of toxic Al forms and other metals to the limed surface water objects.

Watershed liming ($CaCO_3$) results in a gradual increases in pH, alkalinity (or ANC), and Ca^{2+} in the water column (Driscoll et al. 1996). This is in strong contrast to direct lake liming, which is characterized by abrupt changes following base additions and the subsequent rapid reacidification when liming stops. Driscoll et al. (1996) reported that the supply of ANC to draining waters was largely derived from dissolution of $CaCO_3$ from wetlands over the 3-year study period. Similar results was also reported from watershed liming around the Lake Roeynedalsvannet, Norway (Hindar et al. 1996). Relatively little dissolution occurred in freely draining upland soils (Warfvinge et al. 1996). Watershed liming eliminates the episodic acidification of stream water and the near-shore region of the lake during snowmelt. Watershed liming decreases the transport of Al to lake and running waters and increases the concentrations of dissolved organic carbon (DOC) and dissolved silica (H_4SiO_4) in stream and lake waters. Also, increased nitrification and increased concentrations of NO_3^- in soil and surface water are reported, but are low compared with the ANC increase. In contrast to direct lake liming, Ca^{2+} inputs from watershed liming were largely transported from the lake.

D. Biological Effects

The flora and fauna of acid waters normally consist of fewer species compared with more alkaline waters (Almer et al. 1974; Hultberg and Andersson 1982; Nyberg 1984; Jackson et al. 1990; Keller et al. 1992; Fjellheim and Raddum 1995). After liming, the numbers of species often increase, and many acid-sensitive species are able to recolonize and survive, and the fish production normally increases significantly.

Regarding primary producers in aquatic systems, no consistent positive effects of liming are reported for phytoplankton (e.g., Brettum and Hindar 1985; Yan and Dillon 1984; Bukaveckas 1988a). In addition, problems with increased growth of macrophytes are reported in limed lakes (Henrikson and Brodin 1995; Roelofs et al. 1995). This is assumed to be an effect of increased mineralization and decreased redox potential causing increased phosphorous and ammonium concentrations in sediment pore water. Thus, the interpretation of the effects of liming on lake primary production may be complicated by shifts in the relative importance of pelagic and littoral productivity.

Liming may sometimes have minor effects (Yan et al. 1977; Nyberg 1984) or negative effects (Yan and Dillon 1984; Henrikson et al. 1984, 1985; Ekström and Hörnström 1995) on zooplankton communities. Many factors may contribute to the different responses, including varying initial degree of damage, the variable time scale of the studies, the availability of recolonisation, and the degree of chemical changes. In addition, biological status whether fish are present or not before liming is implemented, may greatly affect the zooplankton response (Keller et al. 1992).

The most undesired effects of liming are primarily related to watershed liming, like vegetation damage on Sphagnum mosses on limed wetlands and the removal of lichen located on exposed rock after liming of more typically terrestrial ecosystems surfaces (Traaen et al. 1997). Liming on naked bedrock is not practiced in Norway and Sweden, while Sweden still practices wetland liming. Kreutzer (1995) has evaluated the effects of terrestrial liming. He concludes that the positive terrestrial liming effects discussed in the literature are

- Deacidification of soil and water
- Reduction in the mobility of toxic species of aluminium and heavy metals
- Increase in Ca and Mg supply
- Improvement of humus quality

These positive effects, however, have to be faced with real or potential negative effects such as:

- Increase in nitrate concentrations of the seepage water
- Reduction of the humus store
- Mobilization of organic metal-complexes such as Pb and Cu complexes
- Induction of boron deficiency
- Shallower root systems
- Induction of root rot

Similar conclusions were obtained by the expert group evaluating the Swedish forest-liming program (Staaf et al. 1996).

An increase in metal-organic complexes by liming may in the long run be harmful to aquatic life. On slopes where draining is controlled by subsurface flow, organically complexed metals may be translocated over some distance and leached into streams and lakes. There, toxic effects may arise when the metal ions are released by decomplexation or by decomposition of organic ligands. This effect may increase as the ligand/metal ratio change as the humus store decrease. Besides heavy metals, aluminium shows similar behavior because it also forms rather stable complexes in the humus layer. The high pH caused by liming may compensate for the decreasing humus store, to a certain degree, especially for these metals that easily precipitate at the actual soil pH.

Watershed liming (including wetland liming) is favorable when the main goal is obtaining a continuous high surface water quality, because watershed liming eliminates episodes when acidic water from snowmelt effects near-shore region of lakes, because of thermal stratification. This acidification is reported to cause problems for fish reproduction and other near-shore aquatic life (Hultberg 1977; Schofield and Trojnar 1980; Baker and Schofield 1982; Hasselrot et al., 1987;

Molot et al. 1990; Driscoll et al. 1996; Barlaup et al. 1998). However, terrestrial liming often causes many more negative ecosystem effects compared with direct surface water liming.

Despite the fact that species richness and diversity generally are similar in limed and circum-neutral reference lakes, it is important to be aware of the qualitative differences reported by Molot et al. (1990). They documented that the composition of the fauna did not resembled that of comparable neutral lakes, even 14 to 15 years after liming. The same phenomenon is focused on in Appelberg et al. (1995).

V. TIME TRENDS IN PRECIPITATION AND SURFACE WATER CHEMISTRY

Time trends and/or the currents status in precipitation and surface water chemistry are essential data to estimate the chemical conditions in limed acidified lakes, if liming terminates and the lakes undergoes reacidification. At present we have relatively good documentation on both current status and trends in water chemistry in Scandinavia.

A. Atmospheric Trends

The effects of sulfur on terrestrial and aquatic ecosystems were partly known by the beginning of the 20th century. European sulfur emissions increased steadily from 1880, only interrupted by the second World War, up to a maximum of nearly 60 million tonnes per year in 1975, followed by a steep decline (Figure 1). In Norway, the mean concentrations of sulfate (SO_4^{2-}) in precipitation have decreased by 39 to 58% at 11 precipitation stations during the period 1980 to 1996 (Toerseth and Manoe 1997). During the same period no significant changes have been recorded for nitrate (NO_3^-). For ammonia (NH_4^+) three stations show decreasing trends, one increasing, while the remaining stations show no significant changes. At 25 stations distributed all over Sweden the reduction in SO_4^{2-} has been approximately 50%, with relatively small differences in trends between the stations during the period 1983 to 1995. The sulfate deposition was at its maximum in the early 1970s (L. Granath MISU, personal comunication). A future deposition scenario for the next decade indicates that S-deposition will level out at slightly lower level than at present in Norway and Sweden (Figure 2).

Regarding trends of heavy metals, Norway has weekly wet-deposition data from three weather stations for Pb, Cd, and Zn back to 1978. These data (Figure 3) show a 60 to 80% concentration decrease of Pb in wet-deposition from 1978 to 1996, and a decrease of 70% for Zn and 50 to 80% for Cd during the same period (Toerseth and Manoe 1997). The concentrations of the same metals in wet-

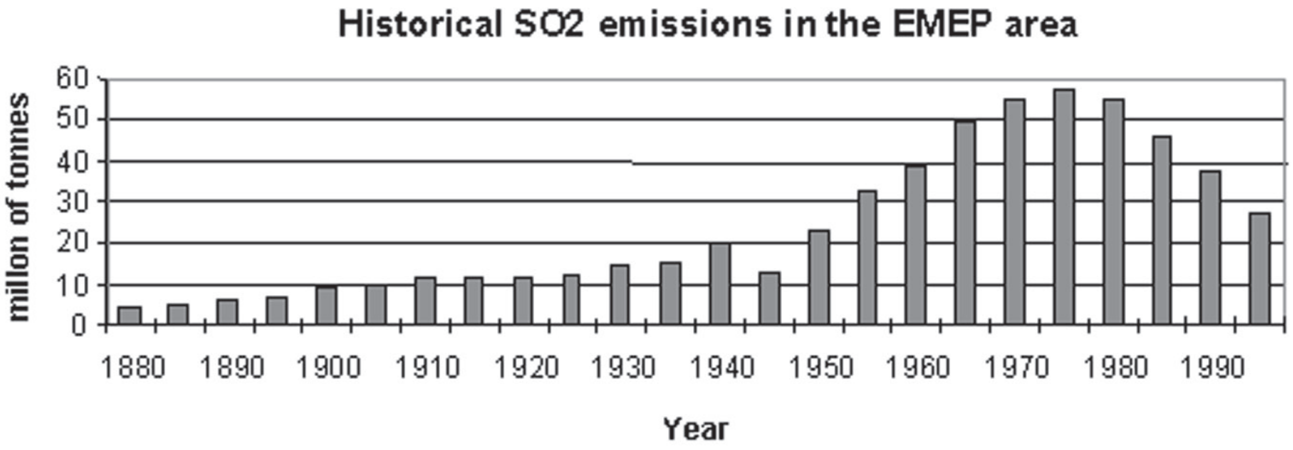


FIGURE 1. European sulfur emissions, 1880 to 1995. (Source of data: Mylona (1996) and UN-ECE, 1997a [from 1980].)

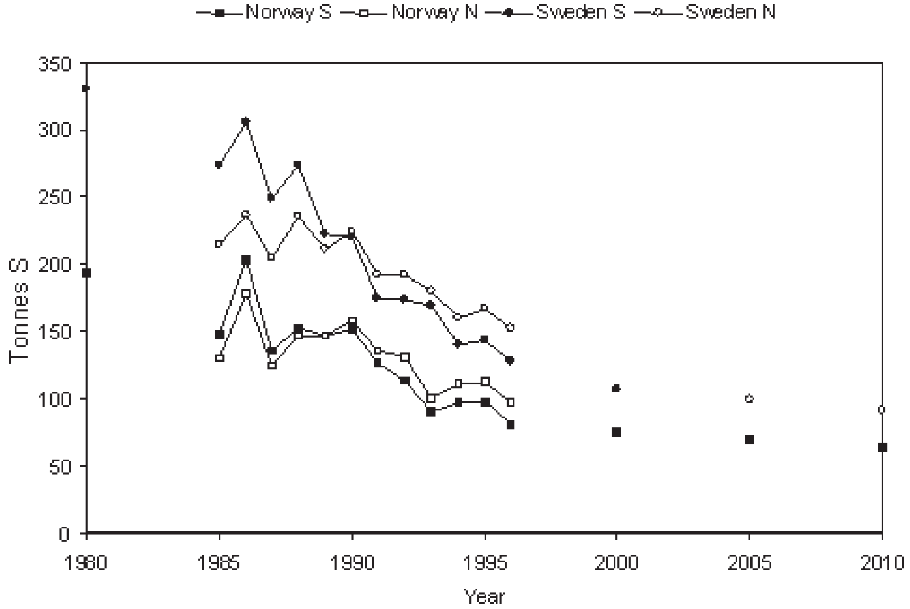


FIGURE 2. Trends in total deposition of S in Sweden and Norway from 1980 to 2010. Data are from (Mylona 1996; Berge 1997). Calculation of future deposition is calculated by Arne Semb (NILU), based on calculated emission of S from the most important contributing countries in Europe. 27% and 20% of the total S-deposition in Norway and Sweden are assumed being “unknown” sources. In the model predicting future emissions, these unknown sources are reduced to 7% and 5% for Sweden and Norway. Despite this, the emission trends seem to level out in the next decade.

deposition have also decreased significantly at four precipitation stations in Sweden during 1984 to 1995 (Table 2), that is, by 25 to 53% and 48 to 76% for Cd and Pb, respectively. For Zn, significant downward trends (23 to 35%) were only documented at Arup and Svartedalen in southwestern Sweden. For Cu, no significant trends could be detected at any of the Swedish stations.

B. Surface Water Trends

1. Trends in Europe, USA, and Canada

During the last 10 years international emission reduction measures in Europe and North America have resulted in a decrease in atmospheric sulfur deposition of up to 50% (Lückewille et al. 1997). Nitrogen deposition has stayed almost constant. Trend analyses on surface water chemistry in the 1980s and 1990s indicate that the reduction in sulfur deposition has led to an improvement in water chemistry and partly also to a recovery of the invertebrate fauna at many ICP Waters sites. Important results of the regional trend analyses of surface

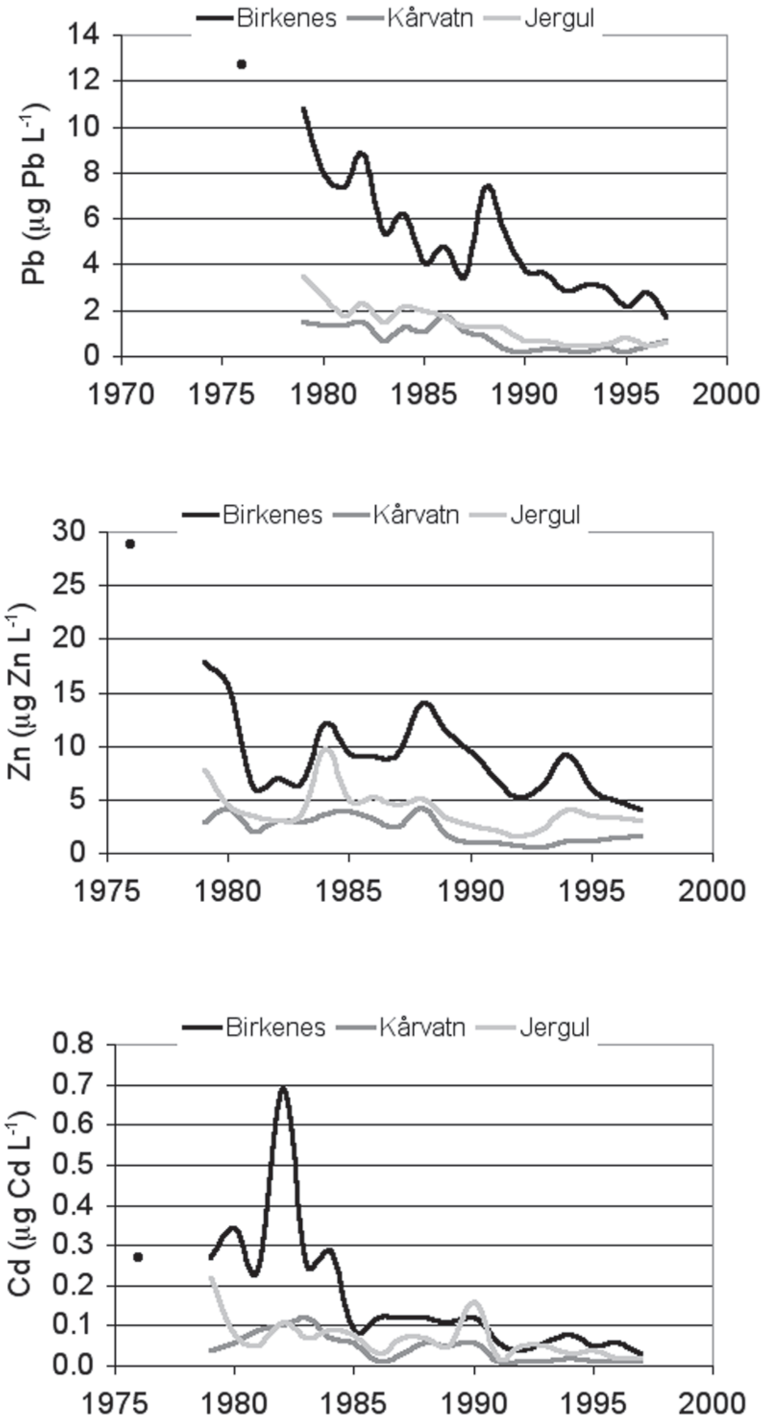


FIGURE 3. Concentrations Pb, Zn, and Cd and (µg L^{-1}) in wet deposition in Norway at Birkenes (south), Kårvatn (central), and Jergul (north) during 1976 to 1997.

Table 2. Trends (Seasonal Kendall test) in atmospheric deposition of metals (monthly concentrations) at different sites in Norway and Sweden during 1984 to 95. Data from IVL and NILU. —: negative trend; +: positive trend; nd: no data; — or +: p<0.05; — — : p<0.01; — — — : p<0.001

Site	Arup S Swe	Svartedalen SW Swe	Aspvreten SE Swe	Bredkälen Mid Swe	Birkenes S Nor	Kårvatn Mid Nor	Jergul N Nor
Zn	—	—			— —	— — —	—
Cu					nd	nd	nd
Cd	— —	—	—	—	— — —	— —	— —
Pb	—	—	— —	— —	— — —	— — —	— — —
Cr				+	nd	nd	nd
Ni		—	—		nd	nd	nd
V	— —	— —	— —	—	nd	nd	nd
Co					nd	nd	nd
As			—	—	nd	nd	nd
Mn	—		—		nd	nd	nd
Fe	— —	—	— —		nd	nd	nd

waters are that sulfate concentrations are decreasing at almost all ICP Waters sites, and in almost all cases the decreases in the 1990s are larger than in the 1980s (see Table 3).

The changes in sulfate concentrations cause changes in concentrations of other constituents in the water as well. Alkalinity is a measure of water quality. In general, high values are good and low values are acid-sensitive or acidified waters. An increase in alkalinity indicates improved water quality and recovery from acidification. In the Nordic countries (Finland, Sweden, Norway) alkalinity decreased in the 1980s (acidification), but increased in the 1990s (recovery). At many European sites (Italy, Germany, Netherlands, Denmark) alkalinity increased in the 1980s, and the rate of increase accelerated in the 1990s. The remaining regions (Adirondacks and Quebec, Midwestern North America, U.K.) show either no recovery or further acidification. Regions with declining sulfate that fail to show recovery in alkalinity in the 1990s (Adirondacks/Quebec, Midwestern North America) are characterized by strongly declining base cation concentrations. Trends in acidity (pH) detectable at a regional level are consistent with the alkalinity trends observed within each region.

Decreasing sulfate concentrations emphasize the importance of nitrate as the second important acidifying anion. Concentrations of nitrogen in surface waters show increases in almost all regions in the 1980s, although the variability in nitrogen trends are quite large from site to site. These increases have disappeared in the 1990s. It seems likely that regional-scale phenomena other than nitrogen deposition are responsible for the development in the 1990s (e.g., changes in climate or climate extremes). Future monitoring will evaluate such aspects.

Table 3. Results of regional trend meta-analysis for sulphate, nitrate, alkalinity, sum of base cations (SBC), and H^+. Slope values are $\mu eq\ L^{-1}\ yr^{-1}$. Regional trends that are significant at $p < 0.05$ are shown in bold. (Table is from Löckewille et al. 1997)

Region	Decade	SO_4^{2-}	NO_3^-	ALK	SBC	H^+
Adirondacks and Quebec	1980s	**-0.63**	**+0.46**	**-1.39**	**+0.39**	+0.00
	1990s	**-1.62**	**-1.57**	+0.53	**-3.41**	**-0.01**
Europe	1980s	**-1.26**	**+1.37**	**+2.50**	+0.00	-0.05
	1990s	**-4.50**	**-2.38**	**+7.94**	-6.25	-0.00
Midwestern North America	1980s	**-1.46**	+0.04	**+0.71**	+0.94	**-0.02**
	1990s	**-4.25**	-0.00	**-1.60**	**-4.79**	-0.00
Nordic Countries	1980s	**-0.83**	**+0.13**	**-1.41**	**-2.42**	**+0.01**
	1990s	**-2.95**	+0.01	**+2.50**	-0.05	**-0.15**
Atlantic North America	1980s	-0.00	+0.00	**+1.37**	-0.13	**-0.02**
	1990s	**-2.42**	-0.00	+1.14	-0.89	+0.01
U.K.	1990s	-0.01	**+0.17**	+0.15	-1.46	-0.14

2. Lake Chemistry Status of Northern Europe, 1995

In the autumn of 1995 regional lake surveys were conducted in the Northern European countries on the initiative by the environmental authorities in Sweden, Finland, and Norway (Henriksen et al. 1997). Previously, these countries have carried out nationwide lake surveys. The 1995 surveys were, however, coordinated with respect to lake selection, analytical methods, sampling techniques, and sampling period. The project was expanded to include Denmark, Russian Kola, Russian Karelia, Scotland, and Wales. The countries included in the Nordic Lake survey cover a geographic area of ca. 1,300,000 km^2. This is about 13% of Europe's total area, including the European part of Russia, and 28% of Europe not including Russia. The total number of lakes in the study area is ca. 155,000 and of these 5690 lakes are sampled in this survey, corresponding to 3.7% of the total lake population (> 4 ha) giving a sampling density of one lake per 244 km^2.

The results from the survey show that the lake water chemistry in the northern European countries, with the exception of Denmark, are dominated by low ionic strength (dilute) water, with low concentrations of nutrients (nitrogen and phosphorus compounds). This is due to underlying bedrock and deposits with low weathering rates that release small amounts of ions to the water, and catchments with low agriculture intensity and low population density.

There are, however, general differences in the lake water chemistry between the countries, due to differences in hydrology, precipitation chemistry, soil cover, and vegetation. From western Norway to eastern Finland there is a gradient from high to low precipitation (3500 mm yr^{-1} to 300 mm yr^{-1}), from mountainous areas with thin and patchy soils to forested areas and thick soils. This is reflected in lake water chemistry with low concentrations of base cations (Ca, Mg, Na, K), inorganic alkalinity (HCO_3^-), and total organic carbon (TOC) in the western areas to higher concentrations in the eastern areas. Median values for base cation concentrations are three times higher in Sweden, Finland, Scotland, and Wales than in Norway, and the TOC concentrations vary even more.

The sensitivity of a lake, with respect to acidification, can be roughly evaluated from the nonmarine base cation and alkalinity levels. An alkalinity value (or more exactly ANC) of 20 $\mu eq\ L^{-1}$ can be chosen as a reference value for very sensitive lakes (Henriksen et al. 1990). 40% of the lakes in Wales and 37% of the lakes in Norway had alkalinity less than 20 $\mu eq\ L^{-1}$. In Sweden and Russian Kola, the percentages are 14 and 16, respectively. The lowest percentage of such lakes was found in Finland (9%) and in Scotland (10%). In Denmark, there were three lakes with alkalinity $< 20\ \mu eq\ L^{-1}$. The lowest pH values were found in southern and western Norway and in southwestern Sweden. Lakes in these areas are influenced by acidification. There were also some low pH lakes scattered throughout Sweden, Finland, Wales, and the eastern parts of Russian Kola, and these lakes are mainly influenced by organic acids and are "naturally" acidic. Very high pH lakes were found in scattered regions in southern, eastern, and central Sweden and in the mountains along the border to Norway, and in Denmark. Such lakes always have high concentrations of base cations indicating high weathering rates of the minerals in the catchment. Low pH levels were found in lakes without alkalinity, where nonmarine sulfate, organic anions, or nitrate has replaced bicarbonate. In general, lakes with organic anions can be "naturally acidic". Such lakes have been "naturally acidic" most often for centuries or millennia, while lakes with high concentration of nonmarine sulfate and nitrate are acidified by antropogenic pollution. These anthropogenic affected lakes have sometime in the past (< 100 years ago) probably been nonacidic with bicarbonate (HCO_3^-) as the major anion. However, lakes in regions with naturally occurring pyrite, such as the clays around the Baltic seashore or in mineralized areas, may have high naturally occurring sulfate levels because of sulfide oxidation (e.g., Alasaarela 1982; Krug 1989; Laudon 1999). Precipitation events or especially sea salt episodes might induce low pH and acid-neutralizing capacity (ANC) due to chloride (Cl^-) mobility and the exchange of sodium by H^+ and Al^{n+} (Mulder et al. 1990; Hindar et al. 1994).

a. The Acidification Situation — Critical Load and Exceedances

The acidification situation in the countries can be quantified by calculating critical loads and their exceedances. The highest percentage (27%) of lakes with exceedances of critical load (CL) for S (CL for ANC = 20 $\mu eq\ L^{-1}$) was found in Norway, where the lakes with highest exceedances are also located. This is due to a combination of high S-deposition and very low critical loads, especially in the southernmost parts of Norway. Also, Russian Kola has a high percentage of lakes with the exceedance of critical load for S (17%). This is due to the high emission of S from the smelter industries in this area, and consequently high S-deposition in the areas near the factories. The critical load of S is exceeded in 9% of the lakes in Finland and Sweden. This implies that for about 6000 Swedish lakes and 3000 Finnish lakes the critical load of S-deposition was exceeded. Scotland and Wales showed the lowest percentage of exceedance, about 1% of the total lake population. This low figure can be explained by the high critical loads for the Scottish and Welsh lakes. For Denmark and Karelia the number of sampled lakes was too low to give reliable estimates.

3. Time Trends in Water Chemistry of Norwegian and Swedish Lakes and Monitoring Sites

The Norwegian lake survey (Skjelkvaale et al. 1996) shows a significant decrease in sulfate in lakes all over the country from 1986 to 1995. This decrease in sulfate has led to a significant improvement in lake water chemistry, manifested in higher neutralizing capacity (ANC) and pH, and a decrease in the concentration of toxic aluminium in the lakes (Table 4). Monitoring of 100 Norwegian lakes (sampled annually), 16 rivers (monthly sampling), and 4 field research sites confirm almost the same picture during the same time period (Skjelkvaale et al. 1997). In 70% of the Swedish reference lakes (188 lakes), the alkalinity has increased and as a median for all reference lakes, the increase was 1.4 μeq L^{-1} between 1983 and 1994 (Wilander 1997). Another study of chemical trends in 71 Swedish rivers (Löfgren and Fölster, 1998) documents different patterns in differ-

Table 4. Mean values of essential water chemical parameters in 485 lakes in Norway (N.) sampled both in 1986 and 1995. SO_4*: non-marine SO_4^{2-}; ANC: acid neutralising capacity, (CM)*: non-marine Ca^{2+} and Mg^{2+}; LAl: labile aluminium, i.e., the acute toxic Al forms. (Table is from Skjelkvaale et al. 1996)

	SO_4*			ANC		(CM)*		PH		LAl	
	μeq L^{-1}			μcq L^{-1}		μcq L^{-1}				μg L^{-1}	
Area	1986	1995	% change	1986	1995	1986	1995	1986	1995	1986	1995
Eastern N.	73	50	32	19	39	79	78	5.44	5.65	42	28
Southern N.	60	36	40	-28	-12	29	22	4.82	4.97	112	64
Western N.	30	23	25	-8	1	26	21	5.24	5.39	22	15
Mid N	16	12	25	17	26	32	30	6.09	6.15	4	1
Northern N.	47	42	11	24.5	43	73	75	6.45	6.52	0	0

ent parts of Sweden, with the most accentuated sulfur drop in rivers in southern Sweden.

The decreasing trends in atmospheric inputs of strong acid and heavy metals, and the subsequent distinct decrease in acidification status in surface waters, is important data in assessing the reacidification chemistry in surface water if the liming activity is reduced or will stop in certain bodies of water.

VI. PHYSICO-CHEMISTRY OF DISSOLVED ORGANIC CARBON

Dissolved organic matter (DOM) in surface waters primarily derives from the terrestrial ecosystem and is normally named humic matter, humic substances, or only humus. The formation of humic substances is primarily microbiological, where carbohydrates serve as the main microbial source of energy and carbon in the intracellular synthesis of protein and hemicellulose. Carbohydrates and proteins are more available for microorganisms and have a higher rate of chemical decomposition. Therefore, lignin is considered to be the most important source of humic compounds (Gjessing 1976). Lignin is modified during degradation, forming humic-like substances of high molecular weights. Further degradation of these compounds results in generation of humic and fulvic acids and various decomposition products (fats, amino compounds, and the gases CO_2, H_2, CH_4, N_2, NH_3 and H_2S). Also, autolysis of the microorganisms themselves (including fungi) represents a major source of humic-like substances. A significant part of dissolved humic material is organic acids, and much study has been conducted on these acids, particularly regarding their role in water pH, their pH-buffering capacity and metal-complexing properties. The metal-complexing properties of DOM is essential, because the acute toxicity of metals is normally significantly reduced or totally eliminated when the metals are complexed to organic compounds, often weak organic acids. Because DOM consists of an organic acid cocktail with numerous pK and CD values (Cronan and Aiken 1985; Kramer and Davies 1988; Ephraim et al. 1991), the speciation of DOM is, however, very complicated or almost impossible.

It has also been documented that high concentration of dissolved organic carbon (> 20 mg C L^{-1}) per se may cause toxicity to aquatic organisms (Petersen et al. 1986; Petersen and Persson 1987). The toxic compounds are evaluated to be within octhanol-extractable fractions of DOM. The toxic level of DOM does, however, occur at unrealistically high concentrations compared with most surface waters, even in Scandinavia.

Acidification may causes increased transparency of water (Almer et al. 1974; Schindler and Turner, 1982), decrease in water color (Dickson, 1978), and decrease in total organic carbon (TOC) or dissolved organic carbon/matter (DOC/DOM) in lakes (Davis et al. 1982). These physico-chemical effects can be or are often explained by two major processes:

1. The pH-buffering role of the organic acids of DOM
2. The pH-dependant dissolution of essential complexing cations (like Al^{n+}, Fe^{n+} and Ca^{2+}), or ionic strength

In Process 1, a decrease in pH leads to decreased dissociation of organic acids due to increased protonation. The acidification of a catchment therefore may cause decreased solubility of the weakest acids because they are totally protonated as a result of the H^+ increase. Thus, their abilities to be present as dissolved organic compounds are reduced.

In Process 2, acidification leads to increased concentrations of cations such as Al^{n+} and Ca^{2+} (e.g., Fuller et al. 1988; Hedin et al. 1990; Lydersen et al. 1996). Accordingly, more organic acids will precipitate as metal-humates.

Despite these fundamental chemical properties, several works are not able to document any effects on the concentration of DOM after a pH change (e.g., Fuller et al. 1988; Wright 1989; Hedin et al. 1990; Lydersen et al. 1996), while others have even reported increases in DOM by acidification (e.g., Krug and Isaacson 1984; McColl and Pohlman 1986). Forsberg and Petersen Jr. (1990) reported increase in DOM in Swedish lakes during the 15-year period 1971 to 1985, but the increase was not directly linked to acidification. They only concluded that lake processes as precipitation, ultraviolet light degradation, and microbial transformations, which normally removes some of the humic substances of incoming waters are no longer able to keep up with the increased concentrations of humus in many lakes throughout Sweden. Forsberg (1992) further documented that the main factor of increased humus in Swedish lakes was an increase in discharge due to increased precipitation during the 15-year period. However, 10 to 40% of the increase has to be explained by other processes. The assumed increased ground water level leading to increased superficial runoff through organic and Fe/Mn-organic-rich horizons, increased terrestrial primary production and thereby increased amounts of humic matter, and reduced amount of soil to absorb organic matter because of acidification are other important factors.

There are many explanations for these discrepancies. One is to evaluate the two major chemical processes (1 and 2) together, by considering that H^+ competes with metal ions for anionic binding sites of organics, while OH^- competes with organic anions for the cationic metal ions. As the pH decreases, the organic acids become less available for complexation because the organic acids are less dissociated, while metal cations become more available due to increased dissolution and/or increased cationic charge. An intermediate pH favors complexation between organic acids and metal ions as illustrated for aluminium in Figure 4. Thus, the pH, as well as the quality and quantity of inorganic and organic ions, are decisive for whether the acidification leads to a change in DOM in freshwater systems.

Regarding the quality and quantity of DOM, it is well documented that large vertical differences exist, depending on which soil horizon DOM derives from (e.g., Krug and Isaacson 1984; Easthouse et al. 1992). Acidification may cause

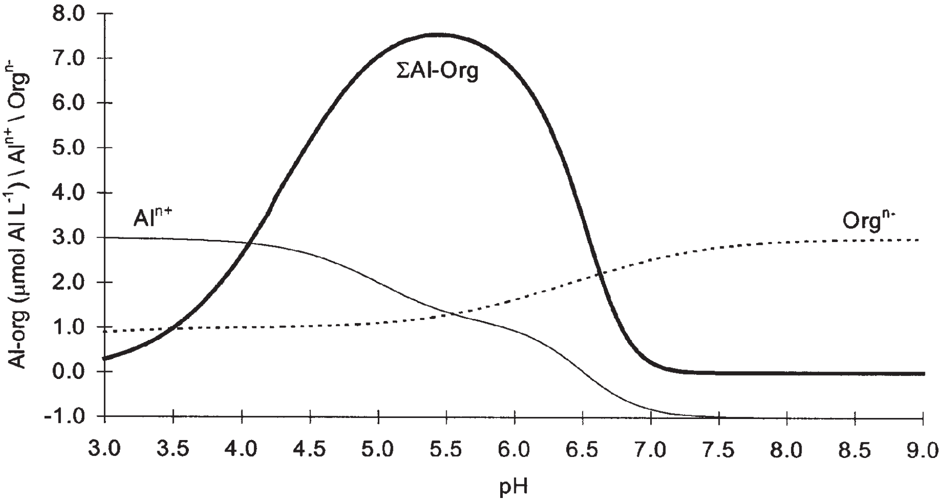


FIGURE 4. Concentration of organic Al complexes (μmol Al L^{-1}), average charge of Al and a triprotic organic acid (both in μeq L^{-1}) as a function of pH. Organic Al complexing constants, Al hydrolysis constants and pK values and CD values are those given in the Alchemi Version 4.0 program (Schecher and Driscoll 1987, 1988). Amounts of Al-Org are based on solution containing 500 μmol C L^{-1} and 10 μmol Al L^{-1}. (Figure taken from Lydersen [1998].)

complex changes in both the organic and inorganic composition of leachate (Stevensen 1982; Ritchie and Posner 1982) in addition to the two major processes already mentioned. For example, acidification has been shown to increase the solubility of organic matter from plant residues in *organic* soil horizons by hydrolysis of carbohydrates and amino acids (e.g., Stevenson 1982). On the other hand, acidification may cause reduced aqueous solubility of organic matter due to a combination of increased H^+ content of humic macromolecule and lower pH. This may increase the role of inter- and intramolecular hydrogen bonding in the macromolecules, which in turn may enhance aggregation of organic compounds (e.g., Hayes and Swift 1978; Ritchie and Posner 1982). Acidification may also increase the solubility of organic matter from *mineral* soil horizons by cleavage of metal ion-organic bonds or from disaggregation of metal-humic complexes (e.g., Ritchie and Posner 1982). This illustrates both the enormous complexity of DOM as well as the complexity of physico-chemical processes involved.

Evidence for significant changes in DOM primarily comes from studies with unrealistic high treatment levels of mineral acids. At more realistic experiments, only significant increases in base cations and Al^{n+} have been observed, with no accompanying changes in the concentration of DOM, neither in lake and stream waters (e.g., Fuller et al. 1988; Hedin et al. 1990; Lydersen et al. 1996) or in soil solutions (e.g., Fuller et al. 1988). The only general change in DOM due to acidification has been a certain and very often significant decrease in $[A^-]$, reflecting the acid-neutralizing capacity of DOM (Hedin et al. 1990; Lydersen et al.

1996). The same patterns were also observed by Wright (1989) after the removal of strong acids in precipitation, where no change in the concentration of DOM was observed, while [A^-] increased and base cations and Al decreased.

The unrealistically high levels of mineral acid often added in many experiments (e.g., Krug and Isaacson 1984) may, however, be an indicator of the tight interactions between inorganic and organic chemistry present, where the quality and quantity of organic and inorganic compounds in the different soil horizons, types and volumes of soil horizons, quantity and quality of precipitation, runoff pattern, temperature, origin of organic compounds, and stage of degradation/humification are all essential factors. The sum of all these factors gives the observed water chemistry, including the water pH. Accordingly, an essential part of the organic acids in solution have pKa values closely related to the pH of the actual water and thereby a significant pH-buffering role for each particular system. As mentioned earlier, fitted pKa values of organic acids on the basis of different surveys are therefore closely related to the pHs of the waters incorporated. The only exception is the assumption of an important strong acid organic fraction ($pKa < 3$), a fraction always totally deprotonated in most natural waters, that is, at $pH > 4$, and thereby with an acid strength equally to a strong mineral acid.

VII. BIOGEOCHEMISTRY OF METALS

Heavy metals and other trace metals in surface water systems and sediments primarily derives from terrestrial sources and/or from atmospheric dry and wet deposition. In remote unpolluted areas, the background concentrations of heavy metals are normally low, except in special metal-rich geological structures, which normally occur on a very local scale. While elements such as iron (Fe), manganese (Mn), and aluminium (Al) in surface waters primarily derives from terrestrial sources, elements such as cadmium (Cd), mercury (Hg), and lead (Pb) to a larger extent derives from atmospheric inputs, often well correlated with the general atmospheric pollution level at the actual site (Henriksen and Wright 1978; Rüling and Tylor 1984; Borg 1987; Steiness et al. 1989; Steinnes 1990; Rognerud and Fjeld 1993). A high atmospheric pollution level also normally means high impact from acid rain. Accordingly in areas with low acid-neutralizing capacity, acid rain causes soil and surface water acidification with subsequently increased concentrations of typically terrestrial derived metals, especially aluminium. The increase in inorganic aluminium is undoubtedly the main toxic factor to aquatic life, even though a low pH itself sometimes might affect terrestrial and aquatic biology.

Maximum atmospheric inputs of strong acids (primarily H_2SO_4 and HNO_3) and heavy metals (Pb, Cd, Cu, Ni, Cr, Hg, Zn) have increased significantly in the industrialized world (including Scandinavia) during the last century, even though a significant decrease has occurred during the last 2 decades. This is a direct result of reduced atmospheric emissions of SO_2 and particles. The inputs of both strong acids (sulfuric acid) and heavy metals reached a maximum in the Western world, in the 1970s before it culminated (e.g., Rühling and Tylor 1984). Besides the direct reduced inputs of metals from the atmosphere in the last 2 decades, less metals are be mobilized from terrestrial sources and lake sediments as the acidity of rain also has decreased during the same period. How fast the decline in heavy metals occurs depends of the actual metal loads at different sites and their actual soil and surface water acidity.

Increases in concentrations of metals are usually found in acidified surface waters. The increase is normally attributed to three main factors.

1. Increased industrial contamination of precipitation
2. Increased leaching from soils in the draining waters of the lake
3. Increased leaching from the lake sediments.

It would be impossible to distinguish the three sources of metal in areas where acid and heavy metals contamination from industrial emissions are widespread. It is also very difficult to make quantitative comparison between sites, because a lot of important factors vary from site to site. Some important variable factors are

- Quality (chemical forms) and quantity of metal sources
- Catchment (bogs, soil cover) and catchment hydrological characteristics (residence time, catchment/lake surface area)
- Climate
- Lake characteristic (area/volume ratio), and hydrological characteristic (residence time)
- Degree of pH changes
- Trends in atmospheric inputs
- Catchment prehistory (land use)
- Frequency of sampling

It is also important to underline that very few studies present reliable data on the aqueous concentrations of metals such as Cd, Pb, and Hg. This is principally due to difficulties in sampling and analyses of metals at the very low concentrations typical of freshwaters. This problem has not been fully appreciated, so that rigorous trace-metal-free sampling and collecting techniques have not been applied universally. As a result, Coale and Flegal (1989), who used a trace metal sampling technique for seawater in freshwater, and found the aqueous Cd and Pb concentration in Great Lakes to be 1 to 10% lower than earlier reported. With the same technique, Fitzgerald and Watras (1989) reported Hg concentrations in Wisconsin lakes to be 20- to 100-fold lower than previously estimated for lakes in this area. Accordingly, we should all be aware of this problem when evaluating and reviewing trace metal studies.

Because liming increases the pH of soil and surface water, often it has a strong impact on the dissolution (mobilization) and speciation of many metals, and thereby toxicity to aquatic biota. Liming often leads to a higher retention of many metals in the catchment or in the lake sediments. If liming terminates, and the water system undergoes reacidification, the reduced retention might increase the metal concentrations in the surface water.

For total concentrations of metals, lime additions may directly increase the inputs of heavy metals (like Cd), because the lime itself often contains trace amounts of such metals. Liming may also lead to an increase or to no effects on the total metal concentrations in surface water due to other effects that often are more important than pH. The most important factor is the concentration of dissolved organic carbon (DOC), which is highly important for the mobilization of metals from edaphic to aquatic environment. Thus, both pH and DOC are essential factors regarding mobilization of metals in surface waters. In addition, coprecipitation with Fe/Mn-oxides and the redox-potential (E_h) in soils, sediments, and hypolimnion of lakes might be important dissolution/precipitation factors.

The type of metal species present in aquatic environments is the most important factor regarding toxicity. Usually the most toxic forms are the inorganic cationic metal species, which at certain concentrations cause acute mortality, that is, within hours or few days. Erichsen Jones (1939), Ellis (1937), and others were pioneers studying the toxicity on fish exposed to salts of Pb, Zn, Cu, Cd, Hg, Ag, Au, Co, Ni, Cr, Mn, and Al. All of them described the similar lethal action. In every case, the metal exposure caused enhanced mucus secretion produced by the gills. They further described that the film of precipitate coats the gill filaments so that the water passing through the gill chamber does not reach the cells of the gill membranes, and the interlamellar spaces become filled with precipitate so that the normal movement of the gill filament is restricted or rendered impossible. Passage of water through the gill chamber is so restricted that much of the water taken in is expelled through the mouth instead of through the opercular apertures, often with such violence that the fish is propelled backward. The frequency and amplitude of the respiratory movements are greatly increased, but the efficiency of the respiratory system is so impaired that the fish dies from asphyxiation (hypoxia). Today, the same general mechanisms for acute metal toxicity are still valid. Thus, we feel it is highly relevant to repeat the conclusions drawn by these pioneers, just to underline the importance of doing literature reviews in the early phase of scientific studies, a routine too often forgotten or ignored today.

A. Aluminium (Al)

1. General Geochemistry

a. Sources

Aluminium is the most common metal in the Earth's crust, and is the major metal in rocks like granites and gneisses. Most common primary minerals of Al are aluminium-silicates like different feldspars and micas. Accordingly, a lot of aluminium is also present in secondary minerals or clays, which are weathering products of primary minerals. There are also younger precipitates of dissolved Al, like in the precipitation zone of podzolic soils. The most common Al-winning mineral for Al-metal production is bauxite, which is an oxidehydrate, $Al_2O_3.xH_2O$. Aluminium is widely used as construction material often alloyed by other elements like Mg, Zn, Si and Cu, because pure Al metal is very soft (like in Al foil). Metal-Al is also widely used as reduction agent, often-called aluminiumthermal reduction. In addition, $KAl(SO_4)_2.12H_20$ often called alum, is widely used in the color production industry, because Al-hydroxide precipitate from alum have a very large effective surface, and accordingly an effective binder of colored substances. Al-oxi(hydrox)ides are often used as carrier in tooth pasta, dynamite, tablets, etc. The major antropogenic sources of aluminium to surface waters derive from alum treatment of drinking water, sewage treatment, and pulp and paper processing (Neville et al. 1988).

Atmospheric inputs of aluminium is probably slight (Galloway et al. 1976). However, an internal report by Dickson (1980) documented periods and sites with significant atmospheric Al depositions. The highest deposition (< 1000 µg Al L^{-1}) was sometimes measured in a highly polluted area in Sweden (Solna), while the concentration in forest during wintertime was between 200 to 800 µg Al L^{-1}. In open less-polluted areas the concentration typically range from 40 to 150 µg Al L^{-1}. Because the pH of rain and snow typically ranged from pH 3.7 to 4.5, we assume that some of this Al might have been present in solution. Today the amount of Al derived from anthropogenic sources has likely decreased as the amount of particle emissions has also decreased significantly during recent years. In addition, the pH of rain has increased and the dissolution properties accordingly reduced. Thus, atmospheric sources of Al are primarily dry-deposition compounds, primarily from wind-driven transport of soil and industrial-derived particles. The dissolution of Al from these sources is not well documented, but it is unlikely that these sources play important role for the concentrations of dissolved Al in soil and surface waters.

High concentrations of Al in surface waters are primarily due to low water pH and or high concentrations of dissolved organic carbon. In the latter case most Al is present as organic complexed Al with minor effects on biology. In low pH waters with minor organic concentrations, dissolved inorganic Al compounds are present in higher concentrations. These compounds are highly toxic and are the main reason for the severe negative effects on aquatic life in most acidified surface waters.

b. Chemical Properties

Due to the redoxpotential of aluminium ($E_0 = -1.66$ V from $Al^{3+}(aq)$), it is reasonable to expect that Al will rapidly react with water and oxygen. However, in pure water and air this is not the case. The reason is that a thin oxide layer is quickly established at the metal surface, protecting the metal toward further reactions. This is the reason why pure Al metal will not dissolve in nitric acid, an acid with significant oxidation properties.

Al oxides have amphoteric properties and easily dissolve in both acids and bases. However, the solubility of oxides and silicates (the main Al solids in natural environments) is relatively low, and the solubility kinetics slow.

The aluminium present in ionic form in natural water can normally be expected to occur as the free aquo Al^{3+}, hydroxide-, fluoride-, and silicate-complexes, and as sulfate complexes in waters with low pH and high SO_4^{2-} concentrations (see Lydersen 1992). In waters of pH above 6, or in waters of high organic carbon content, the presence of these species are small, while polymerized hydroxides and Al organic aggregates of colloidal and subcolloidal size predominate.

The main processes controlling aluminium in soil and surface waters are

- Cation exchange reactions
- Adsorption/desorption reactions
- Dissolution and formation of amorphous aluminium structures, that is, more or less positively charged colloids and particles

These processes are the most rapid ones, and accordingly the most important. Rapid changes in concentrations of Al are mainly linked with changes in water flow rates and water pathways. Thus, rapid processes have to be involved.

The concentration and chemical forms of Al in soil and surface waters are highly dependent on pH, temperature (see Figures 5 and 6) and concentrations of inorganic and organic ligands. This is of major importance because the acute toxic forms of Al seem to be different inorganic monomeric and polymeric Al cations. This is reasonable because the gill surface seems to be the main target organ. Gills have significantly amounts of negative charge sites where aluminium has to compete with other cations. Thus, besides the concentration of Al in relation to other cations, the cationic properties of Al monomers and polymers are essential competition criteria for cation exchange success. Cation exchange success on the gill surface of aquatic organisms is decisive for Al toxicity. This is likely why higher Ca concentrations and/or higher ionic strength reduce the Al toxicity.

It has been observed repeatedly that the negative impacts of acidification on freshwater fish are most severe in low conductivity (i.e., low ionic strength) waters (Bua and Snekvik 1972; Leivestad et al. 1980; Grande and Andersen 1979; Brown and Lynam 1981; Hutchinson et al. 1989; Bulger et al.1993). Ca^{2+} is the predominant cation in most natural waters, and thus the concentration of Ca^{2+} is normally positively correlated with ionic strength. It is well documented that high concentrations of Ca^{2+} can reduce Al toxicity in fish (Brown and Lynam 1981; Brown 1983; Playle et al. 1989; Playle et al. 1993a, 1993b; Rosseland and Staurnes 1994). This mitigating effect has most often been attributed to Ca^{2+} *per se*, through its

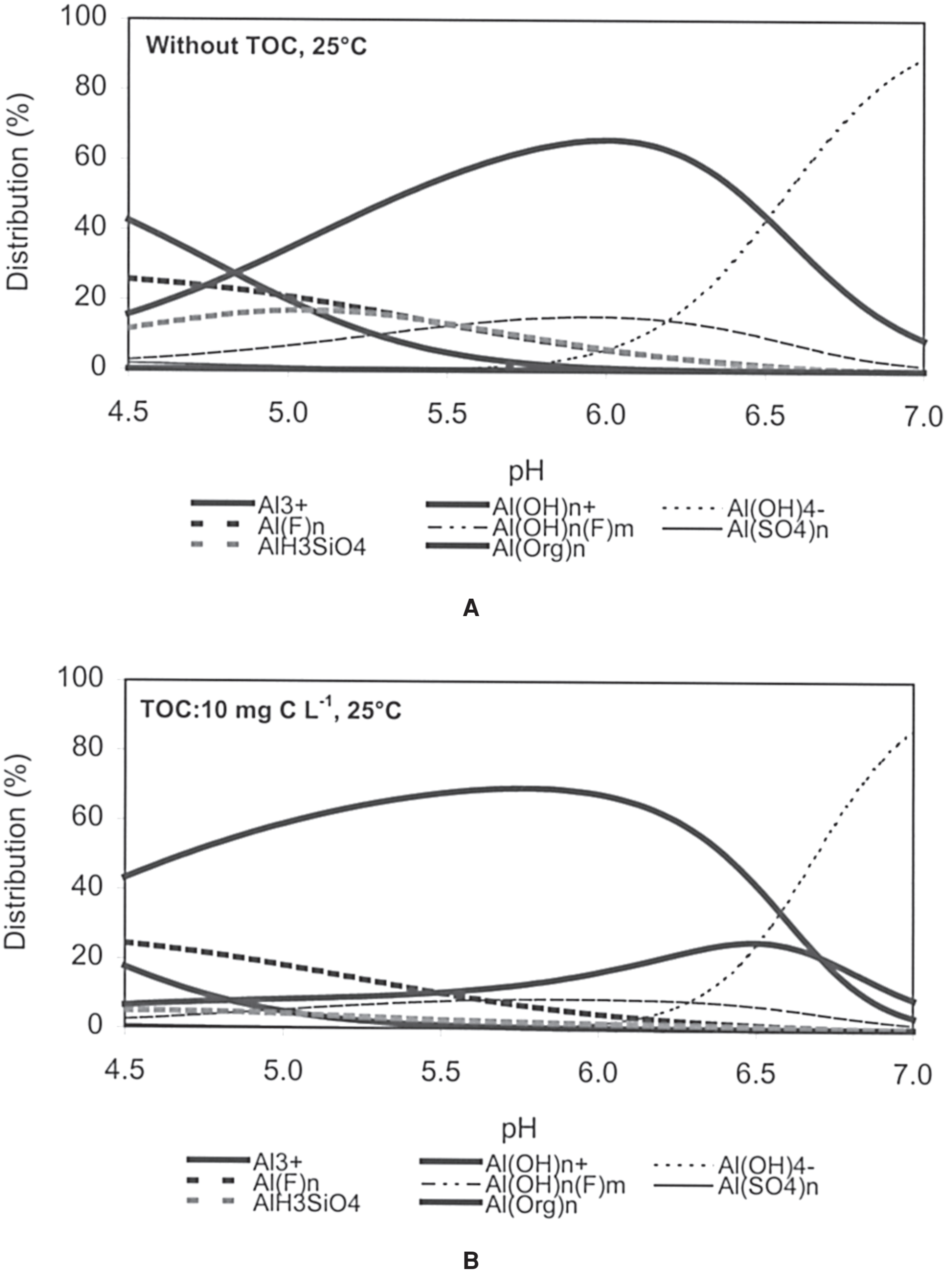


FIGURE 5. Distribution of major Al species in relation to pH at total organic carbon concentrations of 0, 10 and 20 mg C L^{-1}. Essential input conditions: 25°C; CO_2 and O_2 at equilibrium with partial pressure of air; [Al]: 10 μmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 μg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}. [F]: 3 μmol L^{-1}. [Si]: 50 μmol L^{-1}. Assuming triprotic acid according to Schecher and Driscoll (1987,1988), with pK_1:2.10; pK_2: 5.94; pK_3: 6.86.

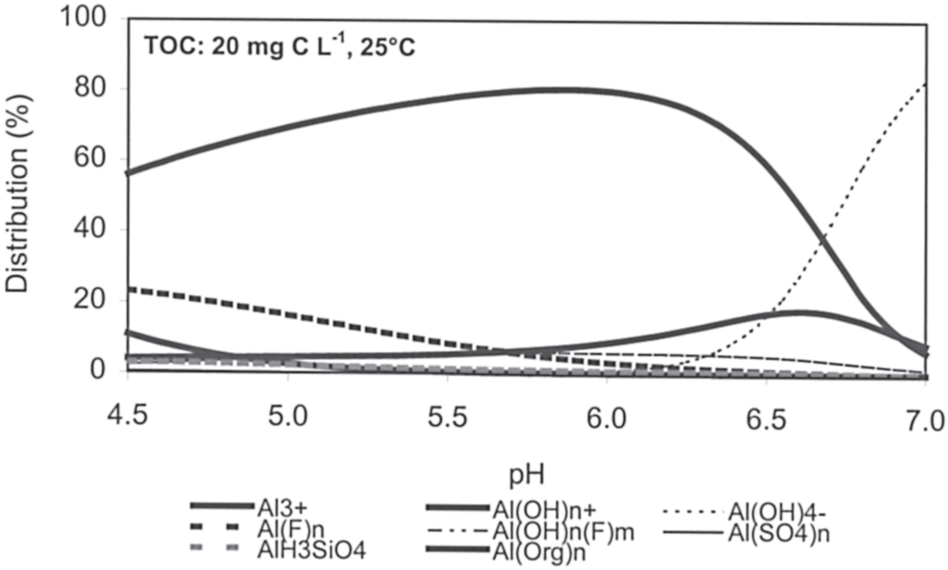


FIGURE 5C

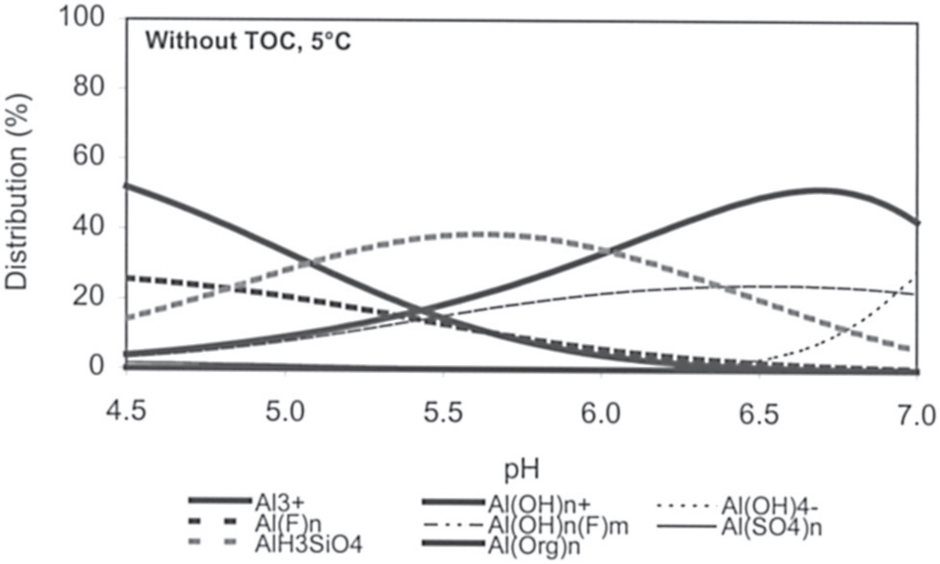


FIGURE 6A

FIGURE 6. Distribution of major Al species in relation to pH at total organic carbon concentrations of 0, 10, and 20 mg C L^{-1}. Essential input conditions: 5°C; CO_2 and O_2 at equilibrium with partial pressure of air; [Al]: 10 µmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 µg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}. [F]: 3 µmol L^{-1}. [Si]: 50 µmol L^{-1}. Assuming triprotic acid according to Schecher and Driscoll (1987,1988), with pK_1:2.10; pK_2: 5.94; pK_3: 6.86.

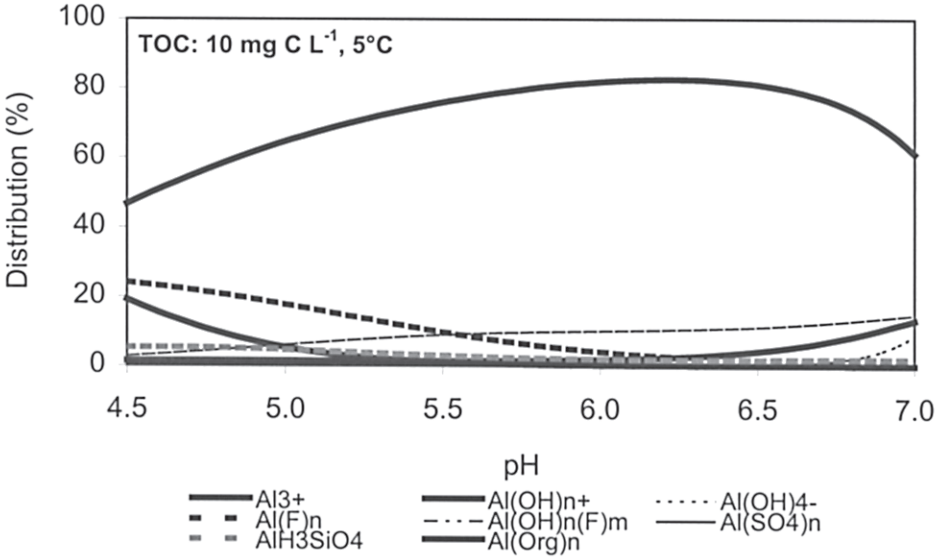


FIGURE 6B

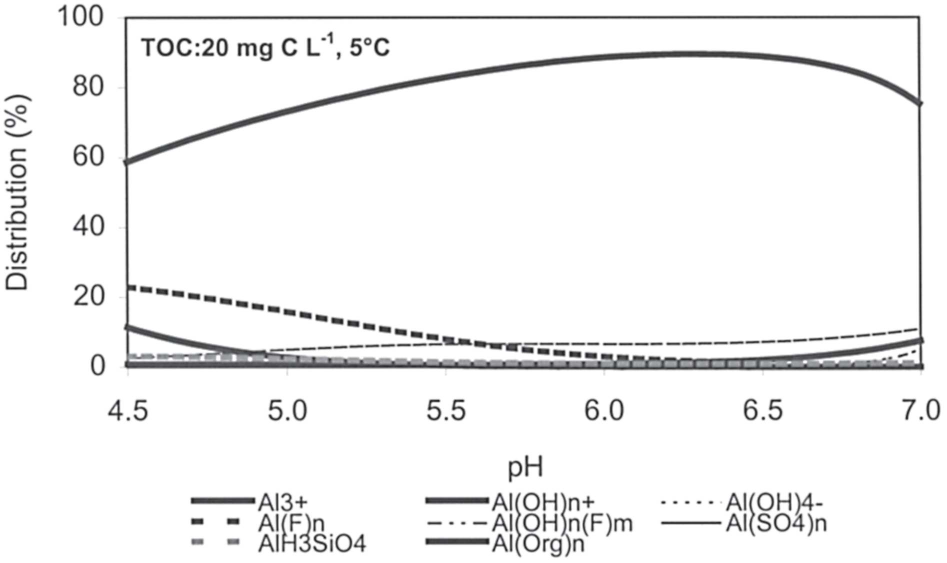


FIGURE 6C

effect on fish gill permeability. This is not surprising because Ca^{2+} is important in stabilizing biological membranes, maintaining the integrity of cell to cell junctions, and controlling ion and water permeability across epithelial tissues (Schoffeniels 1967; Oduleye 1975; Steen and Stray-Pedersen 1975; McDonald 1983). In accordance with this, early field survey investigations of acidic lakes in southernmost Norway indicated that the concentration of Ca^{2+} in the water was of the same importance for the fish population status as pH (Wright and Snekvik, 1978). Later, however, correspondent surveys indicate no correlation between water Ca^{2+} and fish population status (Muniz and Walloee 1990; Baker et al. 1993). Therefore, it is possible that the mitigating effects of Ca^{2+}, and base cations in general to some extent can be explained by the ionic strength of water. Ionic strength effects on metal toxicity has never been systematically tested in any of the above referred studies.

The reason to believe that ionic strength is important for the Al toxicity in fish is that the interaction between aqueous aluminium and the gill surface is central for the mechanism of acute Al toxicity in fish (Exley et al. 1991; Poléo 1995). The ionic strength (I) is defined as $I = 1/2\sum c_i \cdot z_i^2$, where ($c_i$) is the molar concentration and (z_i) the charge of an ion (i), and the sum is taken over all ions in the solution. Ionic binding is probably of major importance for the interaction between aluminium and the gill surface, and there are two main reasons to anticipate that the ionic strength could affect the interaction between them:

- The first reason is that cations may compete for the negatively charged sites on the gill surface. However, cation exchange can only take place if the association between the anion and cation is an ionic binding and not a covalent binding. Covalent binding is a too strong binding for cation exchange to occur. However, in natural water with numerous types of ligands and cations, numerous complexes with numerous binding strengths will be formed. This means that natural waters will contain discreet transition of binding types with different degree of ionic and covalent properties. At what binding strength cation exchange is able to take place is not well documented or defined in the literature.
- The second reason is based on the fact that increased ionic strength will reduce the rate of ionic binding between opposite charged molecules. The reason for this is enhanced competition between anions and the negatively charged gill surface for the cations. In other words, the layer above a surface in which dissolved ions can be influenced by its charge is dependent on ionic strength. In a medium of low ionic strength, this layer will extend further into the solution than in a medium of higher ionic strength. Due to this, the availability of cations that can bind to the gill surface by ionic bonds is higher in low ionic strength water than in high ionic strength water.

Thus, increased ionic strength may reduce Al toxicity by both reducing the ability of aluminium to bind to the gill by ionic bonds, and due to increased competition from base cations for negatively charged sites on the gill surface. Accordingly, it has been indicated that not only calcium, but also high water Na^+-concentrations, may reduce Al toxicity in fish (Brown and Lynam 1981; Booth et al. 1988; Dietrich et al. 1989, Lydersen et al. 2001). Lydersen et al. (2001) directly compared the ameliorating effect of equal equivalent addition of Ca, Na, and Mg on brown trout exposed to acute toxic Al water. They found no difference between the base cations regarding their properties of reducing Al toxicity. As far as we know, this is so far the only systematic ionic strength experiment conducted.

The gill surface is covered with a layer of protecting mucus, consisting of glycoproteins, mycopolysaccarides, amino acids (Fletcher et al. 1976, Van de Winkel et al. 1986, Lumsden and Ferguson 1994) and 95% water (Wold and Selseth 1977). The glycoproteins are rich in sialic acid with a pK_a value < 3 (Clamp et al. 1978). This means that at most fresh water pH's sialic acid is primarily negatively charged. This means that the fish gill similar to dissolved organic carbon (DOC) in water contains strong acid cation exchangers. An illustration of extreme cation exchange impact on surface water chemistry is sea salt episodes where high inputs of pH-neutral NaCl enter the catchment. A chemical description of a seasalt episode might be obtained by evaluating the concentration of Na relative to Cl. When the equivalent ratio of Na/Cl is less than that of seawater, the concentration of nonmarine Na is negative, which indicates that action exchange reactions have occurred. Divalent hardness metals (Ca^{2+} and Mg^{2+}) are concluded being much more successful in the competition compared with common monovalent cations such as Na^+ and K^+ (Pagenkopf 1983). However, to quantify this difference is very difficult because cation exchangers exhibit low or moderate preference for one cation species compared with another (Bolt 1979), a preference that is reduced further when the temperature is low (Boyd 1970), as in most natural waters. This means that the concentration of a cation often is more important than the type of cation concerning the possibility of taking part in cation exchange reactions. These facts have to a minor degree been evaluated in the ecotoxicological literature dealing with the Biotic Ligand Model (BLM). Therefore, this model is linked too much to laboratory experiments, where only a few cations and ligands are tested. As an example, if only Ca^{2+} is tested as competing cation for toxic metals, the ameliorating effect of calcium will be documented (e.g., Brown and Lynam, 1981; Brown, 1983; Playle et al., 1989; Playle et al., 1993a, 1993b; Rosseland and Staurnes, 1994). However, by not doing the same experiments with other base cations, one might not conclude that Ca^{2+} plays an unique ameliorating role.

2. Aluminium in Surface Water Systems

As well documented by the Swedish and Norwegian survey in 1995, there is a relatively significant negative relationship between total aluminium (RAL) or inorganic Al (LAL) and pH, especially at low concentrations of total organic carbon, TOC (Figures 7 and 9). This is as expected because the hydrolysis of Al predominates within the pH range 4.5 to 6.0, pH values common in acidic surface waters. The concentration of organic Al forms (ILAL) shows no significant relationship with pH, except for a certain tendency of higher ILAL at low pHs in higher TOC lakes (Figure 8).

For low TOC lakes the concentration of LAL really starts to increase at pH 5.5. At higher TOC concentrations there are far more lakes with higher LAL concentrations at pH > 5.5 compared with the lower TOC lakes (Figure 9). This might be due to analytical reasons, because more organic Al complexes may lose their Al to the strong cation exchange resin used in the fractionation method when the concentration of organic Al is high. Even though natural organic acids contains a continuum of acid functional groups, many of which display weak acid characteristics, it has been well documented that an important fraction of the organic acids have pK values < 3.0 (Munson and Gherini 1993; Ephraim et al. 1991; Leenheer et al. 1995). Accordingly, under most natural pH regimes of freshwaters (pH > 4), these strong organic acids are almost totally deprotonated and evaluated equal to a strong mineral acid. That means that high TOC concentrations may contribute to low water pH and thereby increased the dissolution of inorganic Al. The amounts of organic ligands and the Al-binding strength of the different functional groups are decisive for the amount of organic Al that might lose Al to the cationic resins used for analytical fractionation, that is, Amberlite, Dowex, etc. This is likely the case for the weakest organically associated Al complexes. Thus, weakly organically bound Al species might be important regarding Al toxicity, because the complexed Al might be transferred to negatively charged sites even on gill surfaces. The gill surfaces have strong cation complexing properties. No works so far are conducted in order to confirm these assumptions.

A regional lake survey from the Czech Republic shows decreasing Al concentrations at very low pH (pH < 4.2), suggested to be due to long time leakage of aluminium under chronic very acidic environments (Vesely and Majer 1996). This is probably the reason why pH also is extremely low, because the release of Al by dissolution or exchange are major acid neutralization processes (Ulrich et al. 1979; Mulder and Van Breemen 1987; Mulder et al. 1989), because the dissolution of solid Al is a proton consuming process. In Scandinavia, a decrease in Al due to long time leakage of aluminium under chronic very acidic environments is not common.

As shown (Table 7 and Figure 9) there are many lakes in Norway and Sweden with LAL concentrations higher than the expected toxic effect level, most at low pHs (Table 5 and Figure 11) and/or at medium to high TOC (Table 6 and Figure 12). Based on the Nordic survey in 1995, totally 76.9% and 80.7% of the Norwegian and nonlimed Swedish lakes have lower LAL concentrations than the assumed Critical Concentration (20 μg LAL L^{-1}) for Atlantic salmon (*Salmo salar*). Atlantic salmon is likely the most sensitive species in Norway and Sweden to

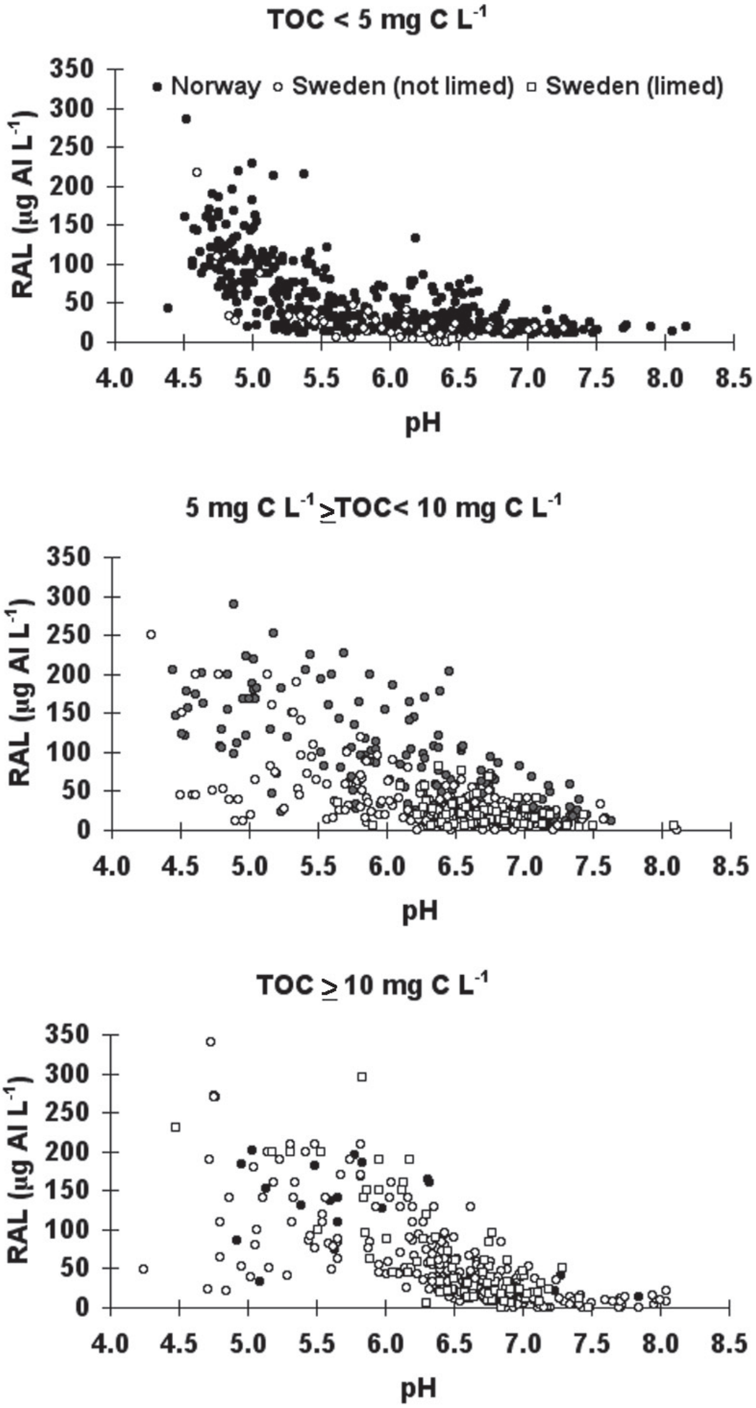


FIGURE 7. Total concentration of total dissolved aluminium (RAL) in Norwegian and Swedish nonlimed and limed lakes in relation to pH for 3 different TOC classes. (Data from Skjelvaale et al. [1996, 1999].)

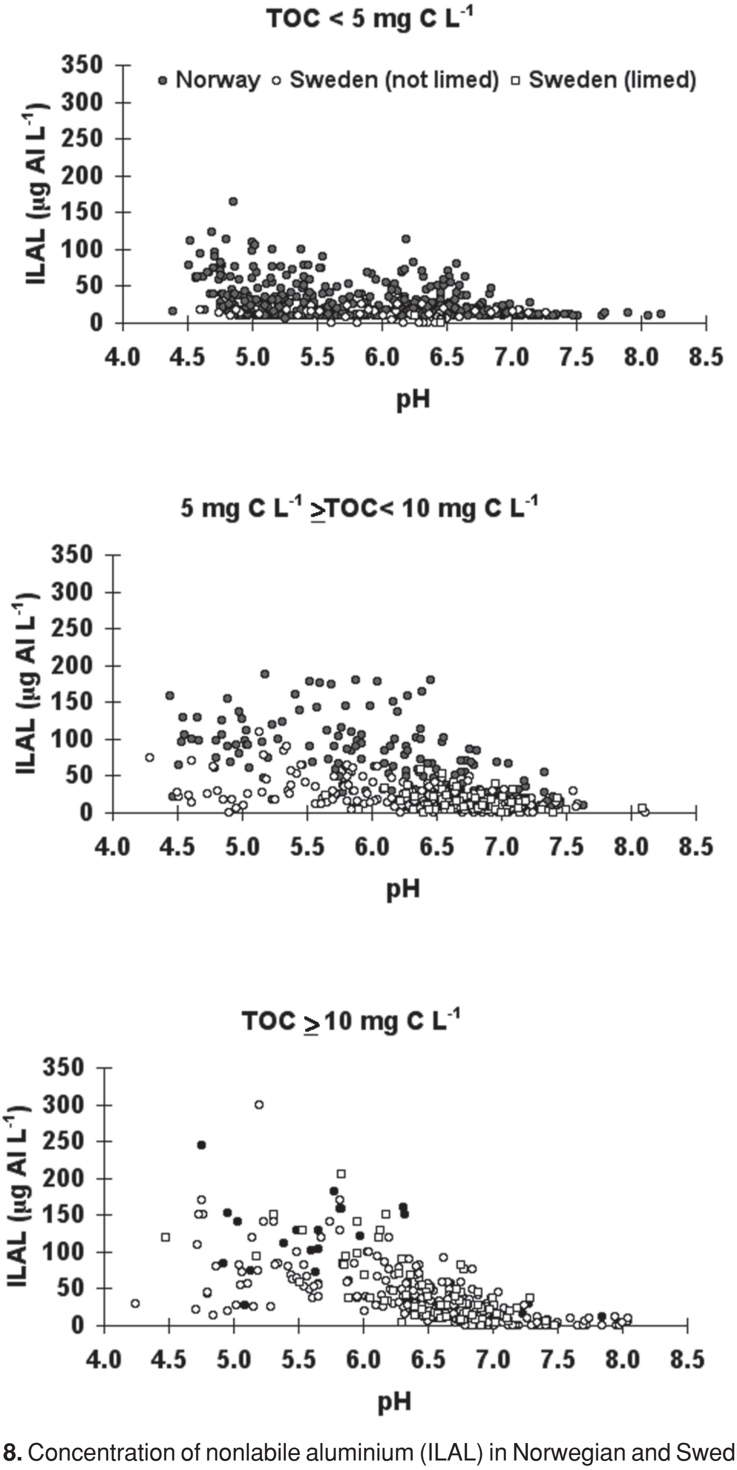


FIGURE 8. Concentration of nonlabile aluminium (ILAL) in Norwegian and Swedish nonlimed and limed lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

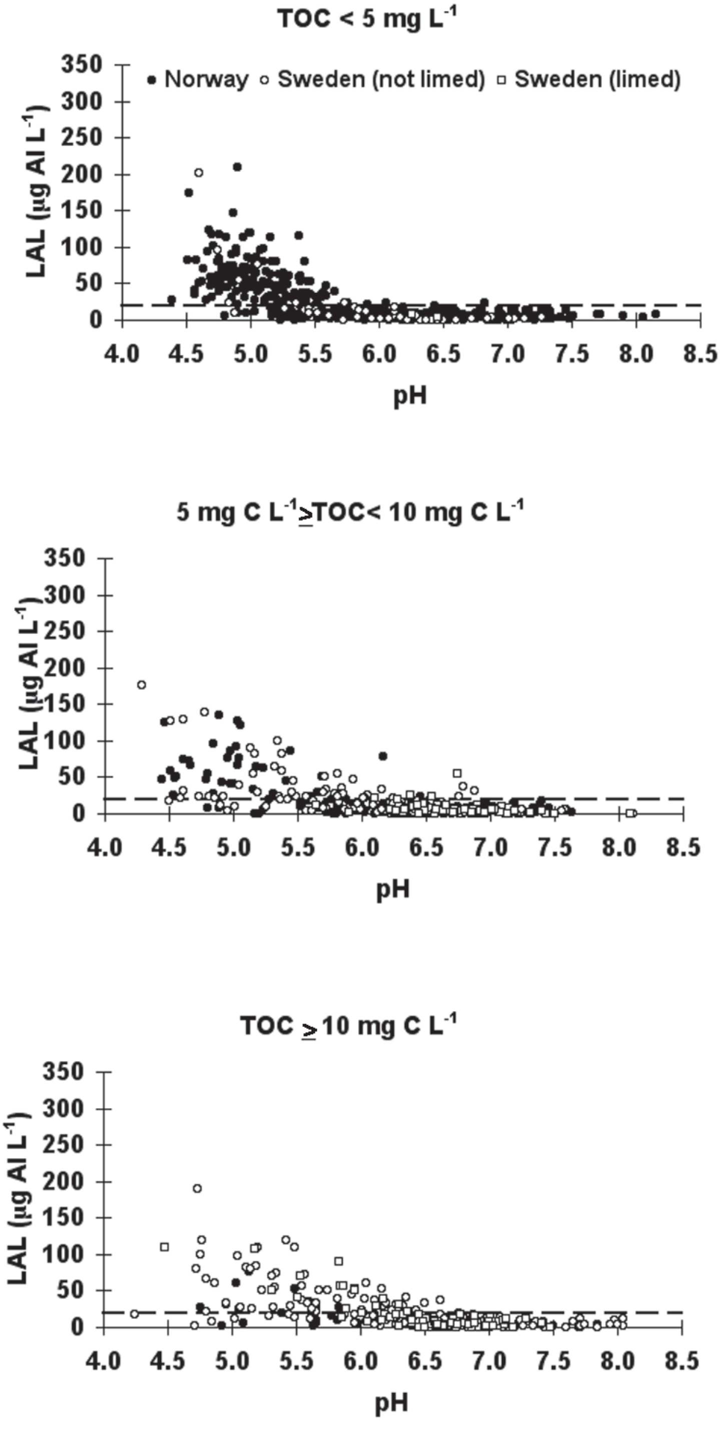


FIGURE 9. Concentration of labile aluminium (LAL) in Norwegian and Swedish nonlimed and limed lakes in relation to pH for three different TOC classes. Samples are from 1995. The dotted line indicates reported effects on aquatic organisms, LAL = 20 µg Al L^{-1}. (Data from Skjelkvaale et al. [1996, 1999].)

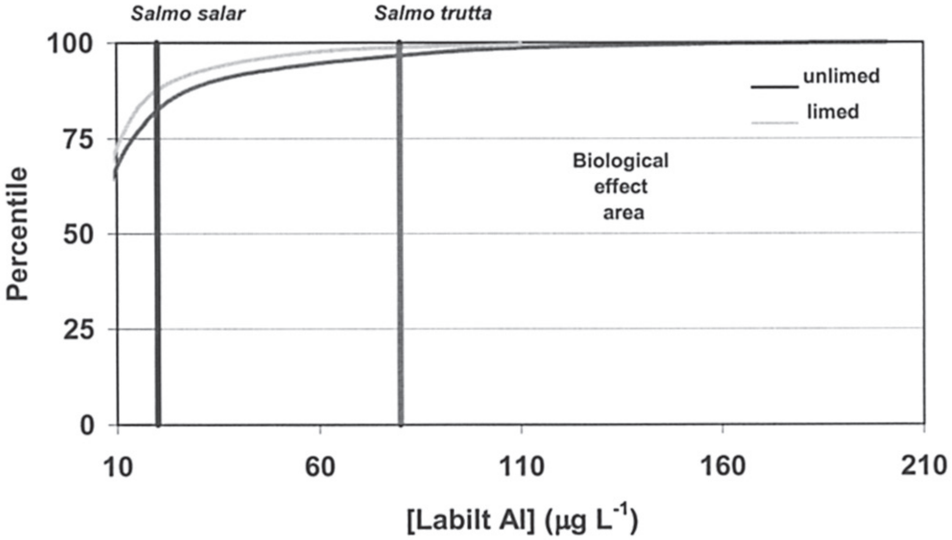


FIGURE 10. Percentile distribution of labile Al (LAL) in limed (n = 157) and not limed (n = 555) Swedish lakes. (Data from Skjelkvaale *et al*. [1996, 1999].)

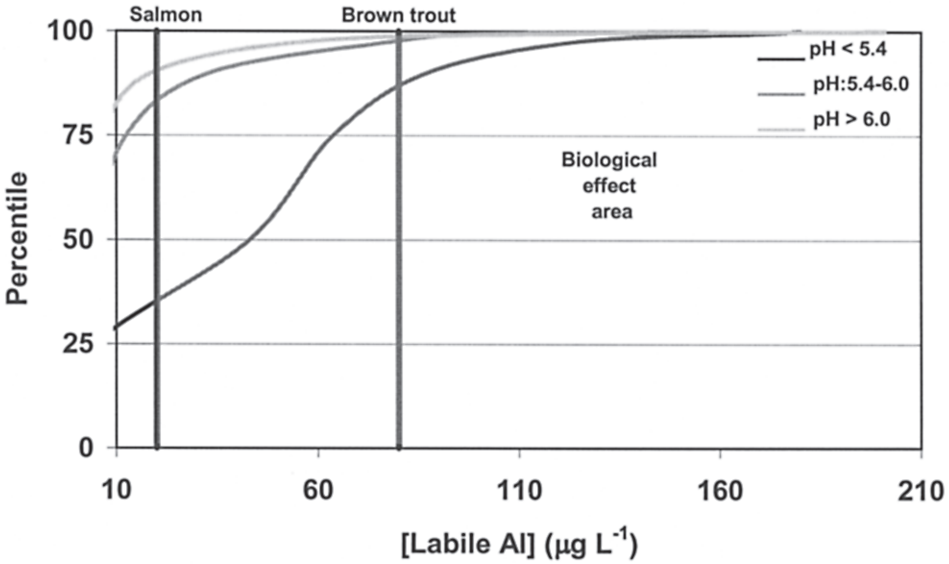


FIGURE 11. Percentile distribution of labile Al in Norwegian and Swedish lakes based on three pH classes. Data are from the Nordic Lake survey 1995. pH < 5.4, n = 242; 5.4 ≤ pH < 6.0, n = 199; pH ≥ 6, n = 1083. (Data from Skjelkvaale et al. [1996, 1999].)

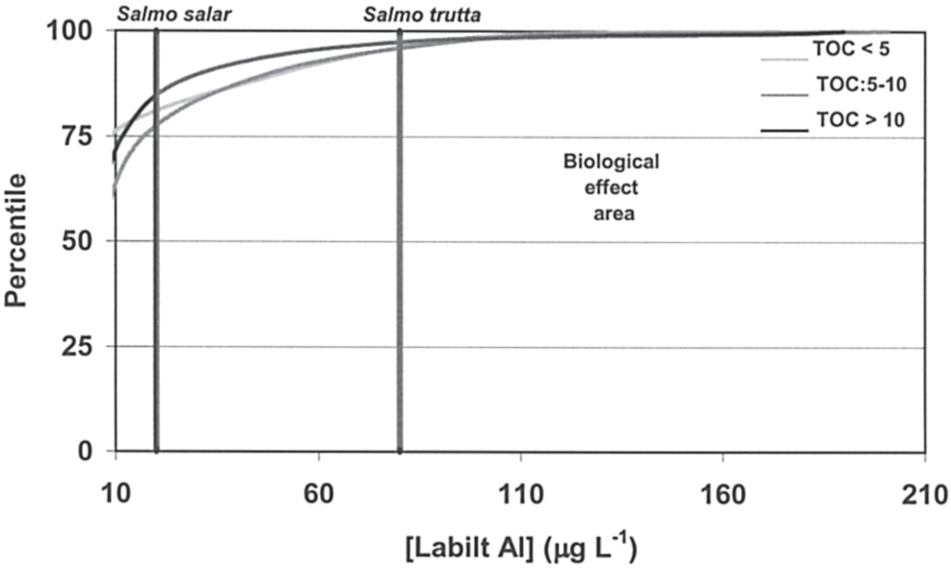
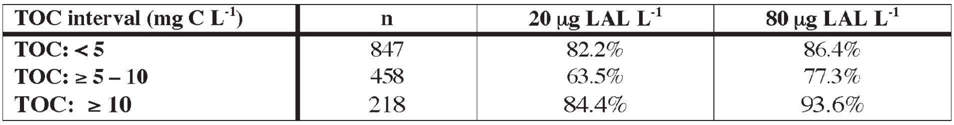


FIGURE 12. Percentile distribution of labile Al in Norwegian and Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). Data are from the Nordic Lake survey 1995. TOC < 5, n = 849; 5 ≤ TOC < 10, n = 459; TOC ≥ 10, n = 219. (Data from Skjelkvaale et al. [1996, 1999].)

Table 5. Percentage of non-limed lakes in Norway and Sweden (n = 1524) below the biological Critical Concentration (CC) level of labile aluminium within three pH classes. Labile aluminium (LAL) is the toxic fraction of Al. No CC levels are given for Norway or Sweden. Thus, the CC values for Atlantic salmon (*Salmo salar*) and brown trout (*Salmo trutta*) are tentative because of large tolerance variations within life-stages and strains of these species. CC-value: 20 µg LAL L^{-1} is for Atlantic salmon; 80 µg LAL L^{-1} is for brown trout. Independent of fish species we assume the LAL interval should represent the concentration range where biological effects should be expected in Nordic surface waters.

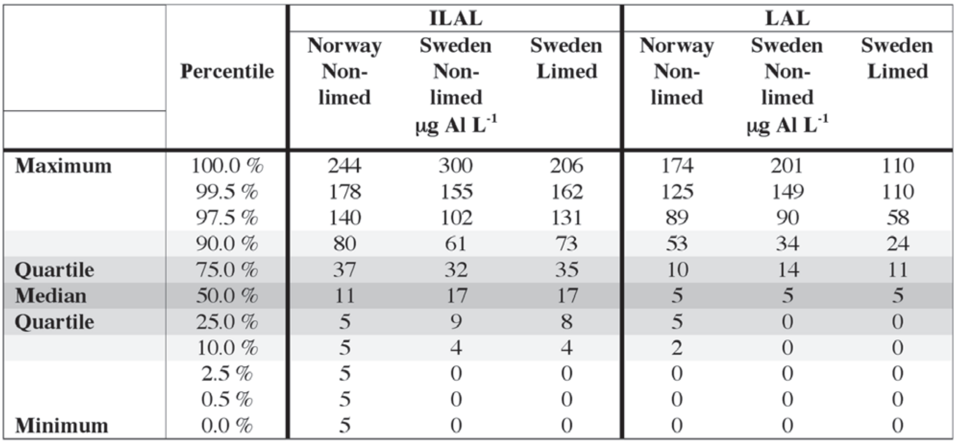
pH interval	n	20 µg LAL L^{-1}	80 µg LAL L^{-1}
pH: < 5.4	242	38.0%	47.1%
pH: ≥ 5.4 - 6.0	199	89.9%	93.5%
pH: ≥ 6.0	1983	90.7%	96.4%

Tabel 6. Percentage of nonlimed lakes in Norway and Sweden (n = 1524) <u>below</u> the biological CC-level of labile aluminium within three TOC classes (mg C L^{-1}). TOC < 5 (n = 847); 5 ≤ TOC < 10 (n = 458); TOC ≥ 10 (n = 218). (See Table 5 for further explanation).



TOC interval (mg C L^{-1})	n	20 µg LAL L^{-1}	80 µg LAL L^{-1}
TOC: < 5	847	82.2%	86.4%
TOC: ≥ 5 – 10	458	63.5%	77.3%
TOC: ≥ 10	218	84.4%	93.6%

Table 7. Percentile distribution of dissolved organic Al (or nonlabile Al, termed ILAL) and dissolved inorganic Al (or labile Al, termed LAL) in Norwegian and Swedish surface waters, based on the Nordic Lake survey in 1995. Norway: n = 969; Sweden, nonlimed: n = 555; Sweden, limed: n = 157. Values < 10 µg Al L^{-1} are below the detection limit for the Norwegian method.



		ILAL			**LAL**		
	Percentile	**Norway Non-limed**	**Sweden Non-limed µg Al L^{-1}**	**Sweden Limed**	**Norway Non-limed**	**Sweden Non-limed µg Al L^{-1}**	**Sweden Limed**
Maximum	100.0 %	244	300	206	174	201	110
	99.5 %	178	155	162	125	149	110
	97.5 %	140	102	131	89	90	58
	90.0 %	80	61	73	53	34	24
Quartile	75.0 %	37	32	35	10	14	11
Median	50.0 %	11	17	17	5	5	5
Quartile	25.0 %	5	9	8	5	0	0
	10.0 %	5	4	4	2	0	0
	2.5 %	5	0	0	0	0	0
	0.5 %	5	0	0	0	0	0
Minimum	0.0 %	5	0	0	0	0	0

acidification and aluminium. For lakes lower than pH 5.4, only 38.0% of the nonlimed Swedish and Norwegian lakes have LAL concentrations < 20 μg LAL L^{-1}, while 90% of lakes with higher pHs have LAL concentrations < 20 μg LAL L^{-1} (Table 5). About 80 to 85% of the low TOC lakes (< 5 mg C L^{-1}) and high TOC lakes (≥ 10 mg C L^{-1}) have LAL concentrations < 20 mg Al L-1, while only 64% of the medium TOC lakes (≥ 5 to 10 mg C L^{-1}) fell within this category (Table 6). The same pattern is also present for the same TOC classes in light of the upper Critical Concentration boarder for LAL, that is, 80 μg Al L^{-1}.

For limed Swedish lakes in this survey, 86.0% of the lakes have LAL < 20 μg LAL L^{-1}. This means that about 15% of limed lakes in Sweden have not achieved optimal water chemical conditions for Atlantic salmon. Because roach (*Rutilus rutilus*) is also rather sensitive, we assume suboptimal conditions for this species also in the same lakes. The reason why some limed lakes have LAL concentrations above Critical Concentration might be medium to high TOC concentrations, slow precipitation kinetics of LAL, and/or simply the reduced effect by time in objects that are not continuously limed.

a. Experimental Acidification

Successive acidification (2-year intervals) of the clearwater (TOC: 2 to 4 mg C L^{-1}) Little Rock Lake, USA, from pH ≈ 6.1 to pH 5.6, 5.1 and 4.7 by H_2SO_4 (Breezing et al. 1993), showed a significant increase in aluminium after acidification the lake to pH 5.1. A further increase in Al was observed after acidification to pH 4.7. At pH 5.6 the increase in Al was not significant. The lake has no outlet or inlet and receives 98 to 100% of its water from precipitation directly on the lake surface. Thus, the metals primarily derive from internal lake sources. Because the lake has a mean depth of 3.8 m and presumably a long residence time, distinct effects of acidification should be revealed. Hall et al. (1987) showed significant quantities of Al mobilized from stream sediments at pH values encountered during natural acidic episodes. Al was gradually mobilized at pH 5.3 to 5.0, and Al concentrations greatly increased at pH 4. Acidification experiments is normally conducted in running water, with acidification down to 4.0 and lower (Hall et al. 1980; Armoured et al. 1987; Henriksen et al. 1988a; Ferrier et al. 1992). These conditions are significantly more severe than normally present under natural hydrological events, because of *too* low pH and discharge. By also conducting the acidification experiments under unrealistic low flow conditions, the sediment surface/water volume is at its highest. This significantly overestimates the role of sediment surfaces to mobilize aluminium under episodic condition when the discharge normally is high.

Kahl and Norton (1983) recorded a certain increase (up to 12%) in the concentration of Al in water close to the sediments by acidifying the waters above sediments (taken from different depths) from pH 5.24 to 5.89 down to pH ≈ 5.0.

By acidifying down to pH 4.0, however, they documented significantly increases in the concentration of Al derived from sediments. By assuming biannual dilution of this water (two turnovers) with the total lake volume, and a lake water residence time of 6 months, the maximum increase of Al in the lake was from 75 μg Al L^{-1} to 237 μg Al L^{-1}.

b. Liming

Liming normally causes a decrease in aluminium (Yan 1983; White et al. 1984; Wright 1985; Marcus 1988; Driscoll et al. 1989; Gloss et al. 1989; Alenäs et al. 1991), primarily due to a decrease in the dissolved inorganic Al species that are rather pH sensitive. This is well illustrated in the clear water lake, Lake Lysevatn, where Al fell from 170 to 20 μg Al L^{-1} when lake pH increased from 5.0 to 5.5 to about pH 7 after liming (Alenäs et al. 1991). Liming a low TOC lake in Canada from pH 4.8 to 7.0 caused a decrease in total Al from 480 μg Al L^{-1} to 310 μg Al L^{-1} 1 to 4 months after liming (White et al. 1984). Similar slow removal of Al is also reported from Norway (Wright and Skogheim 1983).

After the liming of 20 mildly acidic lakes, Marcus (1988) observed a higher total concentrations of Al in two lakes, lower in four lakes, and unchanged concentrations in 14 lakes. That liming not necessarily causes decrease in total concentration of Al is biological less important, because a reduction in the main toxic forms (inorganic Al forms) normally occurs by liming. This means that the concentration of organic Al forms and/or high molecular weight Al forms often increase by liming. The relative decrease in Al after liming is often largest in lakes with low concentrations of organic matter (Johannessen and Skogheim). Decreases in organic Al forms are less common (Wright, 1985; Johannessen and Skogheim, 1985; Driscoll et al. 1989).

The liming of acidified systems undoubtedly reduce the concentrations of toxic Al species.

c. Reacidification

An extreme increase in Al after reacidification of a limed lake nearby Gothenburg, Sweden was reported by Dickson et al. (1995). This lake was also extremely acidic before liming (pH 4.0), and returned to pH 4.5 and 500 μg Al L^{-1}, 3 years after liming ceased. Campbell and Tessier (1987) and Driscoll et al. (1989) reported that the degree of organic Al complexation decreases only slightly, especially over the pH range from 7 to 5. At lower pH the transformation of organic Al to inorganic Al is somewhat higher (e.g., Driscoll et al. 1989; Lydersen et al. 1993), and toxic levels of inorganic Al may occur during reacidification even in high TOC waters.

The concentrations of LAL in the acidified limed objects incorporated in the 1995 Swedish survey (Figure 9) indicate no dramatic effects of reacidification other that what should be expected due to the reacidified pH level. Thus, enhanced remobilization of LAL (metal bomb theory) from the catchment, the lake sediment, and/or the streambed should not be expected when a limed object reacidifies. Similarly, Hindar and Lydersen (1995) concluded that reacidification of limed objects, will not contribute to any dramatically increase in the concentration of Al. The concentration of inorganic Al will relatively fast be as before liming or lower. Lower concentrations of LAL are expected because the amount of acidifying compounds in precipitation has decreased significantly during recent years. This has caused a significant reduction in LAL in most acidified surface waters in Norway (see Table 4).

Reacidification of earlier limed objects may also cause lower LAL concentrations during a certain period due to lasting effects of the liming itself. This effect may last for day/weeks after liming has stopped in running waters, from months to years in lakes, and for many years in some terrestrial limed objects.

3. Biology and Toxicity

a. Toxic Species

i. Acute Toxic Species

Many attempts to relate toxicity to levels of Al in aquatic systems have met with variable degree of success, probably due to insufficient understanding of the importance of Al speciation when assessing its biological availability and toxicity. The toxicity of Al is highly dependent on the Al species present where pH, ionic strength, type of ligands, and water temperature are essential factors. Based on present knowledge, it is reasonable to conclude that *acute* Al toxicity is primarily related to inorganic Al chemistry, at least for aquatic gill organisms, while organic Al complexes per se have at least *no acute* biological effect. Nevertheless, organic Al complexes might represent a potential toxic pool, because the equilibrium between inorganic and organic Al species may change due to other physicochemical factors. A relevant example is acid episodes related to sea salt events (see Hindar et al. 1994), where Na^+ ions are able to cation exchange for H^+ and inorganic Al (Al^{n+}) complexed to organic sites.

Today it is well accepted that acute Al toxicity is primarily related to cationic and thereby predominantly inorganic Al forms, both positively charged monomers and polymers (see Lydersen 1992; Poléo 1995). Numerous cationic polymers are known being highly acute toxic to fish (Biesinger and Stokes 1986; Goodrich et al. 1991; Scott Hall and Mirenda 1991). The physiological and pathological descriptions of fish exposed to many different cationic electrolytes are almost identical to the description of Al toxicity to fish (e.g., compare Biesinger and Stokes 1986 with Rosseland et al. 1992 and/or Poléo et al. 1994). Cationic polyelectrolyte studies conclude that the lowest-molecular-weight polymers (e.g., Goodrich et al. 1991) and the cationic polymers with highest positive charge densities (Scott Hall and Mirenda 1991) are the most toxic. This agrees well with the chemical and biological relationships in the Al toxicity study reported by Lydersen et al. (1994a). There is good evidence that the toxicity of cationic polymers can be eliminated by addition of an anionic polymer (Biesinger and Stokes 1986). Accordingly, as also proposed by them, natural humic acids and clays might be used for detoxifying cationic Al polymers. pH changes may also reduce or eliminate the cationic properties of aluminium. An example is liming where the cationic properties of monomeric and polymeric Al is significantly reduced or almost eliminated. Accordingly, the Al toxicity is eliminated.

ii. Nonacute Toxic Species

Several works have demonstrated that complexation of Al with citrate essentially eliminates toxic effects of Al to fish (e.g., Baker and Schofield 1980, 1982; Driscoll et al. 1980; Fivelstad and Leivestad 1984). Skogheim et al. (1986) found that the toxicity of Al to salmon was significantly reduced when Al was complexed to humic material. The same conclusion was drawn for stream invertebrates when organic substances where added to the water (Burton and Allan 1986). Later, Lydersen et al. (1990) and Witters et al. (1990) both observed no toxic effect of Al (within 10 days) when complexed to humic substances, even at relatively high Al organic concentrations (> 7 to 8 μmol L^{-1}).

There are several plausible reasons why organic Al complexes exhibit no acute toxic effect to aquatic gill organisms. Both the gill surface and DOC act as complex acid cation exchange resins. Accordingly, they compete for cations present in solution. In other words, more Al is able to bind to gill surfaces in solution with no or low concentrations of DOC. In waters with high concentrations of DOC, however, a major part of Al is already complexed to DOC when it enters into surface waters where the gill organisms normally live. Accordingly, the strength of the cation exchanger present on the gill surface is decisive to which extent Al ions complexed to DOC are able to resist this competition. Lydersen et al. (1990) cation exchanged water from a natural DOC rich lake with high Al concentrations with the use of a strong acidic Amberlite IR-120 resin, according to the procedure described by Driscoll (1984). The fish were then exposed to the eluate. Even though this is an operational technique, most likely the predominant part of the Al present in the eluate is Al organic complexes that have passed through the cation exchanger and still kept their Al complexed to DOC. Because no fish died (during 10 days of exposure) when exposed to the eluate, it is reasonable to conclude that Al organic complexes have no acute toxic effects on fish. The reason why this analytical cation exchange procedure has been shown to be so applicable to distinguish between toxic and nontoxic Al forms has to be related to the cation exchange properties on the surface of fish gills.

There may also be other possible reasons why DOC may eliminate Al toxicity. Karlsson-Norrgren et al. (1986) concluded that even though humic substance additions reduced or totally inhibited gill lesions among brown trout exposed to Al at pH 5.5, there was no significant difference in bioaccumulation compared with control fish exposed to Al without added humic substances. The reduced or eliminated toxicity of Al to fish in the presence of dissolved organic carbon could potentially result from the changed coordination chemistry of the Al bound to the gill surface (Wilkinson et al. 1993). On the other hand, binding of organic acids at the gill surface itself can be expected to induce physiological effects due to modifications in the structure, fluidity, or permeability of the gill membrane, which may contribute to increased tolerance toward Al toxicity (Visser 1982).

b. Target

Already in 1939, Erichsen Jones concluded that in case of all the metal ions other than the alkali and alkaline earth metals, the reactions responsible for the death of fish (stickleback) take place outside the body, and the most toxic metals are those with the lowest solution pressure. Toxicity of metals is often linked to the free-ion activity and the surface complexation of these free-ions at biological interfaces as gill surfaces. At the gill surface the most toxic metals precipitate the gill secretions. This is the fundamental mechanism for acute metal toxicity, both with respect to Al and many other cationic metals.

The gill surface is covered with a layer of protecting mucus, consisting of glycoproteins, mycopolysaccarides, amino acids (Fletcher et al., 1976, Van de Winkel et al. 1986, Lumsden and Ferguson 1994), and 95% water (Wold and Selseth 1977). The glycoproteins are rich in sialic acid with a pK_a value < 3 (Clamp et al. 1978). This means that at most fresh water pH's sialic acid is primarily negatively charged. Regarding metal complexation, sialic acid denotes a family of more than 20 natural derivatives of neuramine acid and acid amino sugar in pyranose form with nine C atoms. (Schauer 1985). Unsubstituted neuraminic acid does not occur in nature. The amino group of neuramine acid is substituted either by an acetyl or glycolyl residue, and the hydroxyl groups may be methylated or esterified with acetyl, lactyl, sulfate, or phosphate groups (Schauer 1985). This is of interest because metal cations in class A (like Al) beside fluoride form complexes preferentially with ligands having oxygen as donor atom. Among the oxygen-containing organic ligands the complex stability increase in the order $OH > RO^{-} > RO_2^{-}$ (Stumm and Morgan 1981). In addition, the most stable metal organic chelates are those that form five-membered rings, that is, the stability of organic Al complexes decreases for acids in the order oxalic > malonic > succinic as the ring size of the chelate increases from 5 to 6 to 7 (Stumm and Furrer 1987).

The properties of mucus or mucin include bacterial adherence (Krovacek et al. 1987), reduction in drag or friction (Rosen and Cornford 1971), attraction of heavy metals (e.g., Cu^{2+}: Lauren and McDonald 1985; Cd^{2+}: Verbost et al. 1987; Spry and Wood 1985; Al: Booth et al. 1988; Exley et al. 1991; Rosseland et al. 1992; Wilkinson and Campbell 1993), and the attractions of ions (Handy 1989).

The physiological role of gill mucus in osmoregulation and gas exchange may be of particular relevance for fish (Ultsch and Gros 1979). The presence of an "unstirred layer" influencing ionoregulation over the lamellar surface is generally accepted (Randall et al. 1991), but both the thickness and the composition of this layer remain controversial. Handy and Eddy (1991), however, suggested that the lamellae of unstressed rainbow trout lacked a mucus coat, but that was contradictive to the results obtained by Lumsden et al. (1994), and they used a much more sensitive technique. In addition, the mucous secretion varies a lot (Randall et al. 1991), there are pH gradients close to the gill surface (Playle and Wood 1989), and the gill surface itself is shown to vary over time (Chretien and Pisam 1986). In addition, the chemistry of the actual complexing metal, like Al, exhibit large variations depending on the concentrations of essential ligands (e.g., F^-, H_4SiO_4 organic anions), pH, and temperatures. This strongly demonstrates the physicochemical complexity of both the metal and the actual ligands involved in chemical/biological interactions.

Under the mucus layer is the gill membrane, which is a phospholipids membrane with a lot of metal complexing phosphate groups. Based on Stumm and Morgan (1981), the stability of Al with respect to inorganic oxide complexes are $PO_4^{3-} \gg SO_4^{2-} \gg ClO_4^-$. This means that Al is able to bind strongly to the phosphate groups at the gill surface.

Thus, Al particles can be both present on the gill membrane (in mucus) and in membrane bound particles, within the epithelial cells of gills. Youson and Neville (1987) also confirmed this through X-ray microanalysis of aluminium-exposed rainbow trout.

i. Fish

The main cause of fish death in dilute acid freshwaters seems to be the disturbance of respiratory gas transfer and/or ion-regulation (e.g., McDonald et al. 1984; Neville 1985; Neville and Campbell 1988; Poléo 1995; Withers et al. 1996). At pH above 6.0 and Al present in inorganic forms, the main cause of fish death is hypoxia (Neville 1985), mostly caused by the high concentration of polymerized Al on gill surfaces. No significant ion loss is observed. Cameron (1976) and McDonald et al. (1984) also support this. At pH between 4.0 and 4.5, the electrolyte loss seems to be the main cause of death (Neville 1985; McDonald et al. 1984), due to the high H^+ concentration. At intermediate pH values, between 4.5 and 6.0, a combination of the two mechanisms seems to be the cause of death (Neville 1985). When Al is present in toxic concentrations, the highest mortality rates are observed within this intermediate pH regime, most severely at pH 5.2 to 6.0. Thus, a combination of loss of electrolytes and hypoxia seems most harmful to fish. Lydersen et al. (2001) indicate that the mortality is less acute when leakage of plasma ions is the predominant physiological problem compared with hypoxia that normally is the main mechanism when mortality occur within hours or few days.

Aluminium is likely the most investigated metal regarding chemical forms and toxicity to fish. Despite so, there is very difficult to assess Critical Concentrations of inorganic aluminium (the primary toxic Al fraction). This is because Critical Concentration differs a lot due to variation in many physico-chemical (as pH, water temperature, ionic strength, etc.) and biological factors. Based on present literature the biological response of Al to fish depends highly on:

- **The fish species** (Rosseland 1980; Rosseland and Skogheim 1984; Hutchinson et al. 1989; McCahon et al. 1989)
- **The life stage of fish** (Baker 1982; Baker and Schofield 1982; Rosseland and Skogheim 1984; Cleveland et al. 1986; Gunn 1986; Hutchinson et al. 1989; McCahon et al. 1989; McCormick et al. 1989; Ingersoll et al. 1990b)
- **The fish strain** (Rosseland and Skogheim 1987; Ingersoll et al. 1990a; Dalziel et al. 1995)

Almer et al. (1974) and Bergquist (1991) have studied the relative sensitivity of fishes in Scandinavia to acid freshwater. These studies only focus on water pH, and not inorganic aluminium, the primary toxic compound in acidic waters. Ask et al. (1995) showed that the concentration of inorganic aluminium (labile Al, LAL) was essential in determining whether populations of different fish species were affected by acid precipitation. Focused on labile aluminium, Poléo et al. (1997) reported relative sensitivity among common Scandinavian fish species to acute aluminium challenges to be in the following order:

Atlantic salmon (*Salmo salar*) > roach (*Rutilus rutilus*) > minnow (*Phoxinus phoxinus*) > *perch (Perca fluviatilis*) > greyling (*Thymallus thymallus*) > brown trout (*Salmo trutta*) > Artic char (*Salvelinus alpinus*) >> Crucian carp (*Carassius carassius*).

Crucian carp shows almost no sensitivity to inorganic Al challenges normally found in natural acidic freshwater (Poléo et al. 1995).

Even though there is a considerable range in the sensitivity to aluminium among fish species, it is generally accepted that salmonid fish are the most sensitive group, particularly at the early gill-breathing stages in their life (Schofield 1977; Baker and Schofield 1982; Cleveland et al. 1986). The embryo is the life stages least sensitive to aluminium (Leivestad et al. 1987), while the smoltification period of Atlantic salmon likely is the most sensitive stage within all Scandinavian fish species.

There are also studies from Norway indicating large strain differences toward aluminium/acidification (Dalziel et al. 1995). The strains that naturally have survived in the most acidified areas of Norway seem to be the most tolerant, indicating adaptation as an important mechanism.

In addition, different toxicity responses may occur depending on whether the studied fish are caged or free-swimming (Schofield and Trojnar 1980; Ingersoll et al. 1990a). Further, pulses of acidic/aluminium- rich water with low calcium water or ionic strength (which often take place in nature) may lead to a lower toxicity response compared to that obtained by a continuous exposure (Mount et al. 1990).

Based on literature review, it is reasonable to assume a Critical Concentration of inorganic Al (LAL) within the range 20 to 80 μg Al L^{-1}, where sublethal effects occur at the lowest concentrations. The effects of sublethal Al concentration are reduced hatchability, reduced larval feeding behavior, reduced swimming capacity, slower growth, and general poorer condition.

ii. Bioaccumulation

A lot of studies confirm that the internal bioaccumulation and tissue distribution of aluminium differ markedly from the patterns observed for methyl-Hg, Cd, and Pb. Aluminium concentrations in the blood and the internal organs of fish (heart, liver, kidney, stomach, muscle, gonads, and intestine) are much less than those in the gills (see Spry and Wiener 1991). Thus, bioaccumulation of aluminium is minor, so that the toxicity is external, that is, at the gill surface. Accordingly, the toxicity to aluminium is primarily a threat to fish and other aquatic organisms at their gill-breathing stages.

iii. Invertebrates

Generally, aquatic invertebrates are not as sensitive to aluminium as fish. The most sensitive organisms seems to be the cladocerans, and the most tolerant appear to be the molluscs. Similar to fish, aquatic invertebrates are most sensitive to the soluble inorganic cationic forms of aluminium (Havas and Likens 1985). Aluminium toxicity to freshwater invertebrates is species specific and highly variable. Insect larvae in freshwater are fairly tolerant of chronic exposures to elevated concentrations of aluminium and low pH (Havas and Hutchinson 1982). In general, concentrations of inorganic Al < 100 μg Al L^{-1} do not cause acute toxicity to invertebrates. Invertebrates are often reported being more sensitive to a low pH than the aluminium conditions (see Wren and Stevensen 1991). However, reported effect pH is often in the pH range: 3.5 to 4.5. This is irrelevant for this evaluation report, because it is not of current interest to stop liming water bodies where the reacidification pH is expected to be that low. The effect on invertebrates is also reported at pH < 5. This was reported for *Daphnia magna* (Havas 1985), a cladoceran primarily present in small ponds and surface waters of good water quality and no fish. Accordingly, also this information is irrelevant for this evaluation report.

As for fish species, there is no evidence that aluminium biomagnifies in aquatic systems. Similar to fishes, the main effects of aluminium is adsorption and accumulation of the metal primarily in the respiration structure of aquatic insects. Although data are scarce, there are species-specific differences in the bioaccumulation of aluminium, which may contribute to the variability of aluminium concentrations in zooplankton among lakes (see Wren and Stevensen 1991). Regarding pH and aluminium accumulation, many studies document decreasing whole body aluminium with decreasing pH in blackflies, mayflies (Hall et al., 1988), caddisfly (Otto and Stevensen 1983), crayfish (Malley et al. 1987), Daphnia (Havas 1985), unionid clams (Servos et al. 1987), and a chironomid (Young and Harvey 1988). Other studies with clams and benthic insects showed no relationship between water pH and tissue aluminium concentrations (Sadler and Lynam 1985; Servos et al. 1987; Armoured et al. 1988). These studies generally contradict the findings of Nyholm (1981), which suggested aluminium concentrations were higher in invertebrates from acidified waters.

4. Reacidification — Biological Risk

As stated above, neither Sweden, Norway, nor most other countries have assessed Critical Concentrations of aluminium to aquatic organisms. This is a puzzle to most of us dealing with Critical Concentrations for many other metals where the knowledge about concentration and biological effects is far less, but critical concentrations given.

Canadian water-quality guidelines recommended a total Al concentration < 5 µg Al L^{-1} to protect aquatic life (CCREM 1987). There is no good evidence that such low a concentration is needed to protect aquatic environments in Norway and Sweden. This low concentration is further at, or lower than, the detection limit for the most used Al analytical methods. Furthermore, 5 µg Al L^{-1} is very close to the lowest solubility concentration at equilibrium with different solid Al forms within the actual pH range of natural waters.

Based on present knowledge, we assume the smoltification stage of Atlantic salmon to represent the most sensitive biological stage in Scandinavian surface waters, with LAL as the overshadowing toxic compound. In this evaluation report we assume all surface waters with inorganic aluminium (LAL) concentrations < 20 µg Al L^{-1} to be harmless for all aquatic life, including the most sensitive species and life stages. Accordingly, it is no doubt that reacidification of earlier limed water bodies and catchments might cause negative effects on the aquatic life. As shown (Figures 9 and 11), reacidified pH should not be lower than 5.4 to avoid too large ecological effects.

Even 14% of the limed Swedish lakes in the 1995 survey (Figure 10) had higher LAL concentrations than < 20 µg Al L^{-1}. Accordingly, this survey indicates that about 15% of limed lakes in Sweden have not achieved optimal water chemical conditions for Atlantic salmon. Because roach is also rather sensitive, we assume suboptimal conditions also for this species in the same lakes. However, if these water bodies never have hosted these species, somewhat higher LAL concentrations should be accepted. The reason why some limed lakes have LAL concentrations above lowest Critical Concentration of LAL might be medium to high TOC concentrations in the actual waters, slow precipitation kinetics of LAL, and/or simply that the objects need to be relimed.

Because acute Al toxicity is primarily related to inorganic Al species, it is of major interest that a decrease in inorganic Al (Al_i) and accordingly an increase in organic Al forms (Al_o) seems to occur in many surface waters during recent years (see Figure 13). This is a result of declining SO_2 emission and thereby reduced inputs of SO_4^{2-} (see also Section V).

B. Iron (Fe)

1. General Geochemistry

a. Sources

About 4.7% of the Earth's crust is iron (Fe), and the only metal present in higher amounts is aluminium. Iron is a common metal in many silicate minerals,

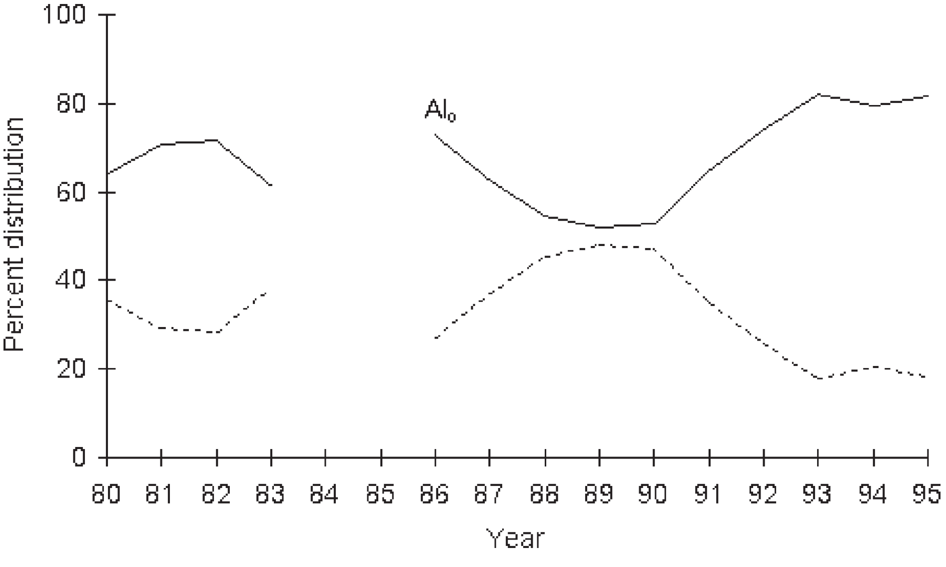


FIGURE 13. Distribution between inorganic Al (Al_i) and organic Al (Al_o) in Lake Langtjern during 1980 to 1995. During this period, no significant change in RAl ($Al_i + Al_o$) has occurred, while SO_4^{2-} in runoff has decreased by ≈ 40%, which further has caused an increase in ANC and a slight increase in pH. TOC in Lake Langtjern has not changed. Average weighted TOC is 9.1 ± 1.1 mg C/L. (Figure is from Lydersen 1998.)

but the most important Fe-winning minerals are the Fe oxides, but siderite ($FeCO_3$) and Fe sulfides are also used. The widely use of Fe is first of all due to the large amounts of this metal present on Earth, and Fe sources will likely never become a limited factor for human consumption. Iron is first of all used in construction material (different steel types) and in numerous alloys. Most used Fe oxides are hematite (Fe_2O_3) and magnetite (Fe_3O_4) and wurtsite ($Fe_{1-y}O$). It is not uncommon that oxides have no well-defined stoichiometric composition, but wurtsite exhibits "abnormal" stoichiometric deviations. The y value may vary from 0.05 to 0.15 depending on equilibrium conditions. This means that 5 to 15% of Fe^{2+} is lacking, and this deficit of positive charges is compensated by trivalent Fe^{3+} ions. Both Fe^{2+} and Fe^{3+} ions are also present in magnetite, where 2/3 of the Fe ions are Fe^{3+}.

In Norway large hematite sources are present in Dunderlandsdalen (Norway), while magnetite is the main mineral in South-Varanger in the county of Finmark. A very rich magnetite area is present in Norrland (Sweden), like in the Kiruna mining area.

The iron associated with atmospheric sources constitutes a negligible fraction of the inputs to both large (Salmons and Forstner 1984) and small (Davison et al. 1980) lakes. However, iron may be present in high concentrations (200 μ*M*) in fogwater and due to photochemical processes and low pH (3 to 7), it may be mainly present as Fe(II) (Behra and Sigg 1990). Despite so, the atmospheric inputs of Fe are minor compared with the catchment-derived sources, but might appreciably affect the chemistry of surface microlayers of water bodies.

High concentrations of iron in surface water is normally due to draining of mining areas or iron pickling wastes, as well as complexed to organic matter, primarily derived from areas with low redox potential as in bogs. High concentrations are also common under strongly anaerobic conditions in hypolimnion of many lakes with substantial oxygen consumption as a result of significant degradation of organic matter.

b. Chemical Properties

Iron is a transition metal and is capable of existing in more than one valence state. In inorganic water solutions, the monomeric form of iron is the aquo ions Fe^2+ and Fe^{3+}. Reduced (FeII) and oxidized (FeIII) are among the most electron active ions of the redox reactants in natural water systems. All of the oxygenation reactions of Fe^{2+} to Fe^{3+} are exergonic and capable of supplying energy. Accordingly, many of these reactions serve as an energy source for many microorganisms. Fe (II) is oxidized to Fe (III) under standard conditions at Eh_7 of ≥ 100 mV.

Because the oxidation potential of the transition of ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron fall within the range found in natural waters, the concentration of iron primarily depends on the redox potential, water temperature, and the concentration of organic ligands present. Within the pH range of Nordic freshwaters (4.5 to 7.0) pH is less important, except regarding the oxidation rate from Fe^{2+} to Fe^{3+} (see below).

Ferrous iron is stable in anoxic water. In freshwater it exists almost exclusively as a simple hydrated aquo ion. Even at pH 8, hydroxo and sulfate complexes typically account for $< 4\%$ of the solution species present (Davison 1979). Fe^{2+} is very soluble with respect to most inorganic ions, but siderite ($FeCO_3$), amorphous iron sulfide (FeS) and vivianite ($Fe_3(PO_4)_2 \bullet 8H_20$) can be formed. The solubility products for these phases in freshwater are such that for most conditions Fe^{2+} can reach concentrations of 0.1 mmol L^{-1} ($\approx$ 5.6 mg Fe L^{-1}) before the solubility product is exceeded. Literature values of solubility products may also be inappropriate to freshwaters, as the kinetics of solid phase formation is often slow, and the measurement of soluble species (e.g., by filtration) may include colloidal forms. Fe(II) is also present in lattice of clay minerals (Hilton et al. 1986), but in this form it is unavailable for reactions in solution.

In well-oxygenated waters Fe(III) is the stable oxidation state. This acid cation is completely hydrolyzed at neutral pH, with its stability being controlled by amorphous iron hydroxide (Jones et al., 1974). At pH 7, $Fe(OH)_3$ is the dominant species, having a concentration of 5×10^{-10} to 5×10^{-12} mol L^{-1} (Baes and Mesmer 1976), that is, almost neglectable concentrations (0.03 to 0.0003 μg Fe L^{-1}). In lakes, ferric ion has been found to be present as amorphous particles, which are negatively charged due to adsorption of humic substances (Tipping et al. 1981).

It is well known that redox transformations dominate the chemistry of both iron and manganese in anoxic and oxic waters and sediments. While it is substantially true that ferrous iron (FeII) ions predominates in anoxic water, and Fe(III) mainly occur in well-oxygenated systems, there are many exceptions to this rule.

There is a tendency for the reduced phase (Fe^{2+}) to lose electrons and transform to an oxidized state, which means that free ions in reduced (Fe^{2+}) and oxidized (Fe^{3+}) state can exist together (Wetzel 1975). Furthermore, not all the filterable iron in anoxic water is Fe^{2+} ions, as there can be appreciable concentrations of colloidal particles (see Davison 1993). The larger particles found in oxygenated waters cannot be represented by any simple oxyhydroxide. They are usually poorly crystalline and of various size and reactivity. Oxide particles appear to be able to exist in anoxic waters with iron sulfide that may have formed by reaction of reactive oxides with sulfide (S^{2-}). Amorphous iron (FeIII) is also present in highly reducing sediments where only Fe (II) would be expected. In lake water, Fe(II) is often oxidized in the absence of oxygen. Nitrate (Balistrieri et al. 1992) and manganese oxides (De Vitre et al. 1988) have been suggested as possible oxidants.

Like the presence of Fe(III) under anoxic conditions, Fe(II) is found in well-oxygenated waters. The rapid rate of oxidation of iron at neutral pH restricts presence of Fe (II) in oxic waters to more acid waters (see Pankow and Morgan 1981; Davison 1993). While a predicted half-life of pH 7 is about 30 min, the half time at pH 5 is predicted to be 200 days. Therefore, if Fe(II) is produced within acid lake water it should be sufficiently persistent to be measurable.

Relatively high levels of organic matter is shown being able to stabilize Fe^{2+}, but organic matter is also able to reduce the oxyhydroxides to their reduced forms. Furthermore, humic acids, especially those derived from *Sphagnum* mosses of bogs, have a low Eh of about 350 mV (Visser 1964), and their reducing properties lead to a metal enrichment by complexing and adsorption to acid organic molecules (Szilàgyi 1973). These reactions are photosensitive and can be accelerated by sunlight. Depending on the prevailing conditions photochemical reactions can be responsible for both the oxidation and reduction of iron in natural waters. The lifetime of the divalent ions (FeII and MnII) depend on their kinetics of oxidation, and so Fe(II) is less likely to persist than Mn(II). This difference in oxidation rates is probably the most noticeable difference in the redox chemistry of the two metals. Interactions of particulate iron are more dependent on humic material than those of particulate manganese, and iron, unlike manganese, plays an important role in the sulfur cycle.

Fe^{3+} forms stronger complexes than Fe^{2+} with various organic substances. Experiments at low pH (pH: 3) suggest that organic is bound to the surface of the iron oxide, allowing a surface (Fe(III) center to be reduced to Fe (II) (Sulzberger et al., 1989). As Fe(II) bonds are weaker than Fe(III) bonds, Fe is released into solution. Thus, naturally occurring organic may increase the initial rate of dissolution.

The release of Fe and Mn from sediments is not as straightforward as it once seemed. Undoubtedly, there are times when Fe(II) and Mn(II), formed at depth within sediment, diffuse upward and are released into anoxic overlying waters. Generally, however, it is the sediment-water interface that supplies the reduced forms from rapid reduction of oxyhydroxide particles that have settled from the water column. These reduced forms are released whether the overlying water is oxic or anoxic, but they can only be easily measured in the latter case. Regarding Mn, it can soon be depleted from the sediment surface and, if *in situ* dissolution of sinking particles occurs within the water column, the net diffuse flux can be from overlying water to interstitial water.

Many metals, like Cu and As ions, are shown to be adsorbed by and coprecipitated with ferric hydroxide precipitates (e.g., Lundgren and Dean 1979). Later studies indicate that trace metals adsorbed to Fe oxyhydroxides are probably less important in the overall pathway of these elements than was once thought (Davison 1993).

As shown, besides redox conditions of water, the solubility and availability of iron (both FeII and FeIII) is greatly altered when organic compounds are present (see Figure 14). These high concentrations of soluble organically complexed Fe are directly related to the high concentrations of humic acids (Shapiro 1957; Gjessing 1964), tannic acids (Hem 1960), and other lignin derivatives. The theoretical Fe concentration with no organic present is almost zero ($< 0.03\ \mu g\ Fe\ L^{-1}$) within the pH range 4.5 to 7.0. Therefore, it is unlikely that acidification (reduced pH) will have important impact on the Fe level of most surface waters. The typical range

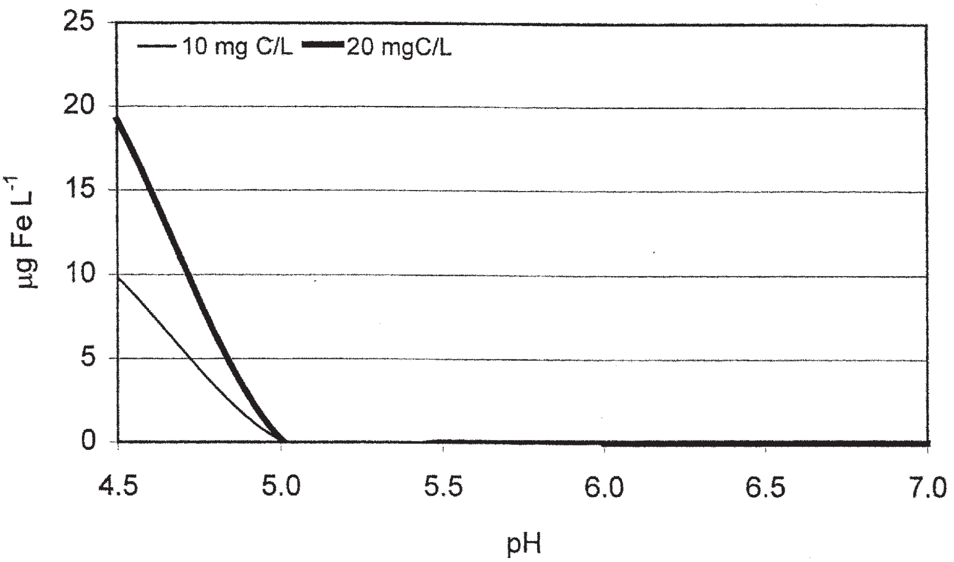


FIGURE 14. Concentration of iron (Fe) in relation to pH at citrate concentrations of 0, 10, and 20 mg C L^{-1}. Essential input conditions: CO_2 and O_2 at equilibrium with partial pressure of air; [Fe_{tot}]: 1 µmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 µg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

of total iron found in oxygenated surface waters of pH 4.5 to 7.0 is about 50 to 200 µg Fe L^{-1}, and high Fe concentrations are almost closed linked to the concentration of organic matter present.

2. Iron in Surface Water Systems

Fe concentrations in lakes are normally significantly positively correlated with TOC (Borg 1983, 1987; Verta et al. 1990, Vesely and Majer 1996), but often also negatively correlated with pH (Verta et al., 1990, Vesely and Majer 1996). During spring melt Borg (1986a) reported extremely high Fe concentrations in some mountain streams in central Sweden, simultaneously with a dramatic pH decline (pH 7.3 to 4.3) and TOC increase (2.5 mg C L^{-1} to 12 mg C L^{-1}). The extreme mortality of brown trout (*Salmo trutta*) during this episode was difficult to relate to one single metal, but a substantial increase was also recorded for Al and Mn. However, regarding concentration of dialyzable Mn, Fe, and Al (assumed to be low molecular inorganic species), the concentration changes were minor. No metal analysis on fish gills was conducted. The high Fe, Mn, and Al concentrations were mainly a result of metal deposits precipitated in the stream bed during low-flow periods, and flushed out during high-flow events (Borg 1996a). We assume that the simultaneous occurrence of high Fe and Mn reflects metal mobilization under reduced conditions in the soils, with subsequent oxidation and precipitation in the streambed. This is likely because the dialyzable metal-fraction (dissolved species) were very low both during high and low flow.

Borg (1987) found higher concentration (two times) of Fe during wintertime compared to summertime, and explained this by higher sedimentation rates during the summer.

Nordic surveys confirm that many Scandinavian surface waters contain high concentrations of total Fe (Tables 8, 9), and > 10% of lakes in Finland and Sweden have Fe concentrations > 1000 μg Fe L^{-1} (Table 9). The Nordic survey in 1995 (Table 9) shows that median Fe concentrations in Norway, Sweden, and Finland are 52, 159, and 312 μg Fe L^{-1}, while median Fe concentration for limed Swedish lakes was 284 μg Fe L^{-1}. The generally higher Fe concentrations in the limed Swedish lakes (Figure 16 and Table 9) cannot be explained by different TOC or pH values between the two categories of lakes. While median TOC and pH in nonlimed Swedish lakes were 7.30 mg C L^{-1} and 6.88, the corresponding values for limed lakes were 7.70 mg C L^{-1} and 6.83. The tight correlation between TOC and Fe concentrations is well illustrated in Figure 15 and 18. While the median concentrations of Fe in nonlimed Swedish and Norwegian lakes with TOC ≥ 10 mg C L^{-1} is 522 μg Fe L^{-1}, the total Fe-concentration in lakes within the TOC classes 5 to 10 mg C L^{-1} and TOC < 5 mg C L^{-1} are 185 and 34 μg Fe L^{-1}, respectively. Regarding pH, it was minor differences in concentrations of Fe between the different pH classes (Figure 17), but somewhat higher Fe concentrations are normally present in the highest pH class (pH > 6.0). This, in addition to the much higher concentrations of total Fe in limed Swedish lakes compared with nonlimed, indicates that more Fe is complexed to organic carbon in limed lakes compared with nonlimed Swedish lakes. One explanation for this is increased deprotonation of organic acids at higher pH.

a. Experimental Acidification

Successive acidification (2-year intervals) of the clearwater (TOC: 2 to 4 mg C L^{-1}) Little Rock Lake, USA, from pH ≈ 6.1 to pH 5.6, 5.1, and 4.7 by H_2SO_4 (Brezonik et al. 1993), showed an increase in Fe when the lake was acidified to pH 5.6 and 5.1, that is, from about 10 to 15 μg Fe L^{-1} before acidification to 30 and 65 mg Fe L^{-1} as pH decreased to 5.6 and 5.1. Acidification to 4.7 resulted in a certain decrease from that observed at pH 5.6, that is, 50 μg Fe L^{-1}. Andersson et al. (1978) observed a certain decrease in the concentration of Fe above the sediment both when water pH was lowered from 5.4 to 5.0 or down to pH 4.0. The decline in Fe at this pH was likely due to coprecipitation with humic compounds because both color and TOC decreased at this pH. Several others have drawn the same conclusion.

A minor increase in mobilization of Fe from sediments (enclosure experiments) occurred during the first months after pH was lowered from 6.7 to 6.8 to

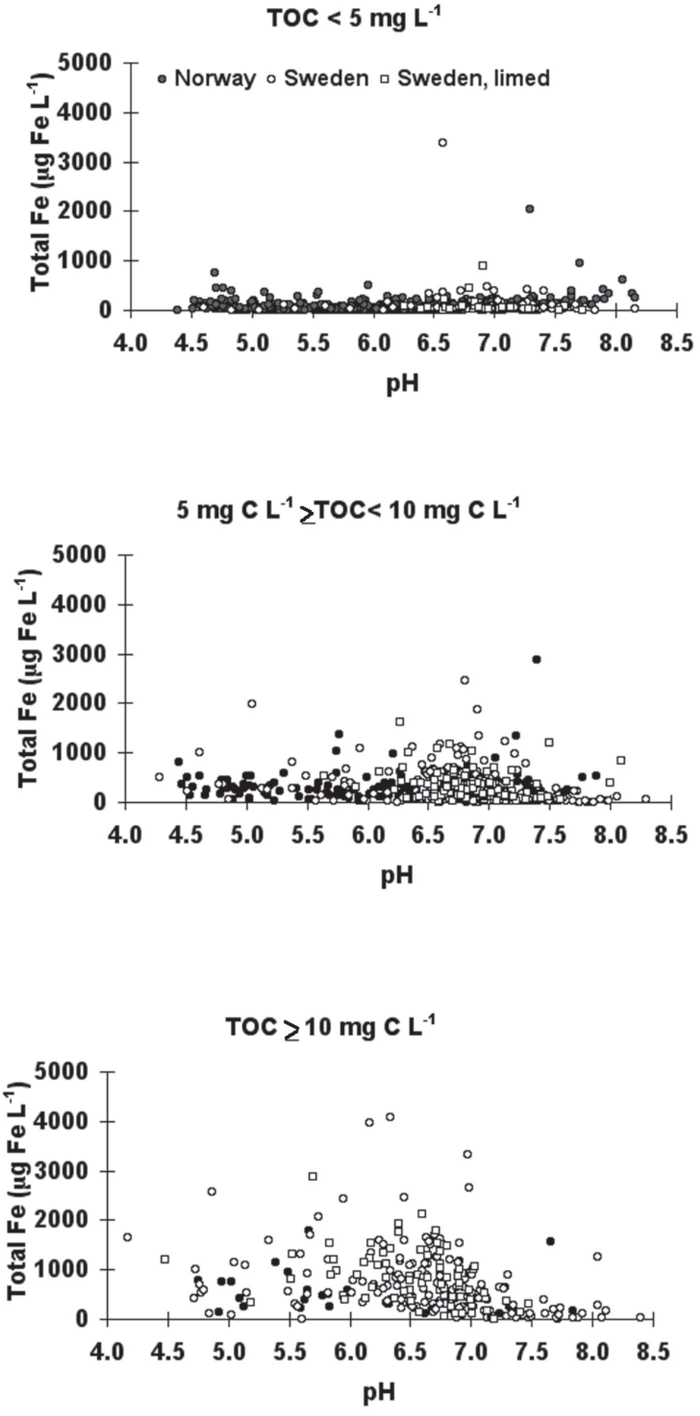


FIGURE 15. Total concentration of iron (Fe) in Norwegian and Swedish (non-limed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

Table 8. Concentrations of Fe (μg Fe L^{-1}) in Nordic surface waters and in the Czech Republic. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min – Max	Mean (±)
Finland south[1]	95	n.r.	n.r. – 1400	270 ± 272
Finland, north[1]	384	n.r.	n.r. – 2600	384 ± 424
Sweden, south[2]	20	n.r.	50 – 2200	616 ± 597
Sweden, north[2]	18	n.r.	40 – 2600	416 ± 601
Sweden, north[3]	56	n.r.	10 – 1520	364 ± 350
Czech[4]	5363	n.r.	n.r.	80

[1] Verta et al. (1990), based on samples from autumn 1987.

[2] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden,south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[3] Borg (1987), based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}.

[4] Vesely and Majer (1996), based on data collected between 1984 and 1992.

Table 9. Percentile distribution of Fe (μg Fe L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462

Fe	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	7680	10149	7616	3900
	99.5 %	1374	7854	6733	3539
	97.5 %	595	3318	1775	2400
	90.0 %	291	1118	1108	1200
Quartile	75.0 %	135	497	617	730
Median	50.0 %	52	159	284	312
Quartile	25.0 %	17	41	100	99
	10.0 %	8	19	39	32
	2.5 %	3	8	14	9
	0.5 %	1	3	2	2
Minimum	0.0 %	0	1	1	2

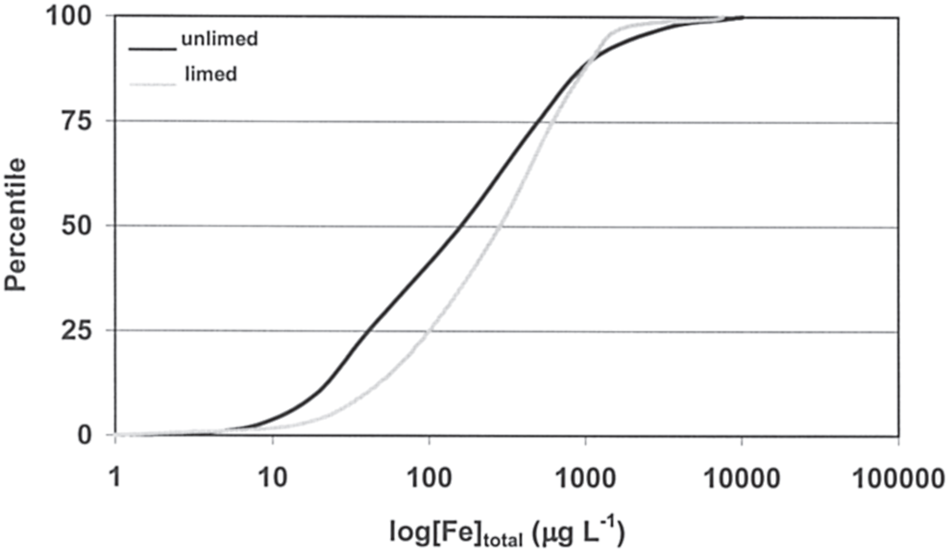


FIGURE 16. Percentile distribution of total Fe in limed (n = 261) and not limed (n = 820) Swedish lakes. Data are from the Nordic Lake Survey, 1995. (Data from Skjelkvaale et al. [1996, 1999].)

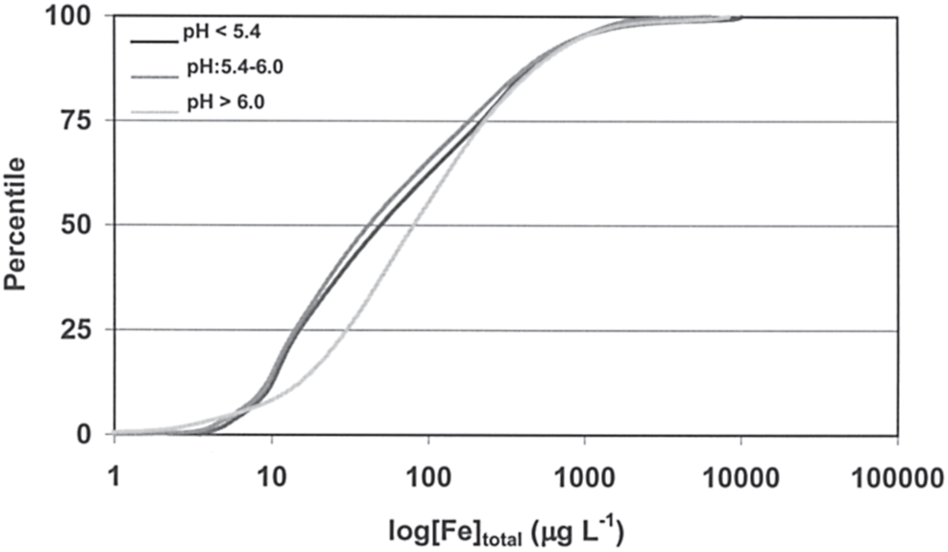


FIGURE 17. Percentile distribution of total Fe in Norwegian and Swedish lakes based on 3 pH classes. Data are from the Nordic Lake Survey, 1995. pH < 5.4, n = 250; 5.4 ≥ pH < 6.0, n = 204; pH ≥ 6, n = 1090. (Data from Skjelkvaale et al. [1996, 1999].)

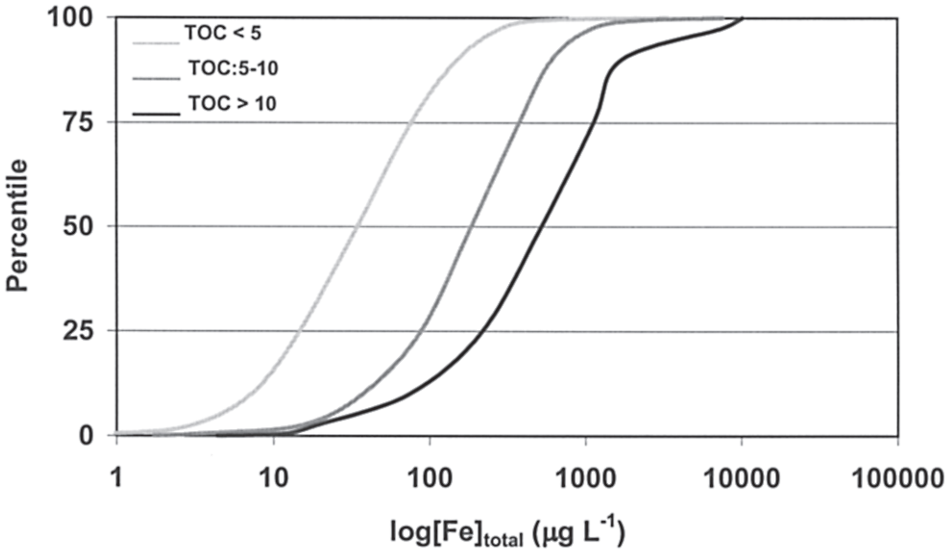


FIGURE 18. Percentile distribution of total Fe in Norwegian and Swedish lakes based on three TOC classes (TOC: mg C L^{-1}). Data are from the Nordic Lake Survey, 1995.TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale et al. [1996, 1999].)

either pH 5.7 or 5.1 (i.e., from 5 to 10 µg L^{-1} to 20 to 25 µg L^{-1}) from a sandy sediment in Lake 223 (Schindler et al. 1980). This fits well with the observations made by Tipping (1981), who noted that in the adsorption of aquatic humic substances by iron hydroxides, the extend of adsorption decreased with increasing pH. Because many heavy metals to a large degree are associated with Fe-humic precipitates, the effects of pH changes on adsorption and precipitation of such compounds might be essential for the distribution of trace metals between water column and the sediments. The increase in Fe by pH lowering reported by some authors is, however, minor.

b. Liming

After liming of 20 lakes, most of them mildly acidic lakes, Marcus (1988) observed no significant changes in the concentration of Fe in 19 lakes, and a significant increase in one. Generally, it was a tendency of higher concentrations after liming. The prelimed mean concentrations of Fe (n =113) was 30 µg L^{-1}, while the postlimed mean (n = 112) was 50 µg L^{-1}. Prelimed pH of the lakes varied from 4.44 to 6.99, with a mean pH of 5.51.

Liming of a low TOC lake in Canada (from pH 4.8 to about pH 7) caused a significant increase in the concentration of Fe in lake water from 230 µg L^{-1} to 450 μg L^{-1} (White et al., 1984). This variation in Fe concentration was due to the fact that the water color varied from 0.5 to 30 mg Pt L^{-1}.

Roelofs et al. (1995) documented strong increases in the concentrations of Fe (and Mn) in sediment pore water of limed lakes in southwestern Norway. This was primarily due to a decrease in the redox potential as a result of increased mineralization after liming.

Borg et al. (1995) showed that watershed liming strongly reduced the Fe (as well as Mn, Al, Zn, Cd, and Pb) leakage to eight highly metal-rich mountain streams in central Sweden. The mean Fe concentration decreased from 2451 to 756 μg Fe L^{-1} after liming. In our opinion, this liming effect is mainly a result of more rapid Fe and Mn oxidation kinetics in the soils due to increased soil pH, and less coupled to the stream water pH.

Liming of a wetland in Dalarna, Central Sweden, did not reduce the Fe concentration significantly. Before liming the median Fe concentration was 545 μg L^{-1} in the outlet stream (see Section VII.F.3 and Table 25).

c. Reacidification

Because iron mainly behaves as a conservative element bound with mineral particles and strongly associated with organics, pH changes within natural water pH levels have minor effects on the concentrations and speciation of Fe. Regarding oxidation of ferrous iron (FeII), this oxidation is much slower at lower pH, with a predicted half-life at pH 5 of 200 d, compared with 30 min at pH 7 (Davison 1993). However, Fe(II) may be stabilized in well-oxygenated waters by organic material (Shapiro 1964; Koenings 1976), and even produced by organic reduction processes (McMahon 1969). Thus, it is unlikely that significant changes in the Fe concentrations of lakes will occur during reacidification of limed objects, leading to harmful effects on aquatic biota.

Cessation of terrestrial or wetland liming in areas with reduced conditions in soil and high concentrations of Fe (II) in soil and groundwater before liming would most certainly regain high Fe concentrations in the surface waters, due to the reduced precipitation kinetics of Fe at lower pH.

3. Biology and Toxicity

There are no critical concentrations assessed neither in Norway, Sweden, nor other countries regarding Fe in surface waters. However, it is likely that high concentrations of Fe related to the oxidation of reduced iron deriving from natural springs, after, for example, ditching or land upheavel of sulfide-rich sediments (e.g., from the Littorina Sea period), may lead to harmful conditions for aquatic life (e.g., Alasaarela 1982).

One should avoid using total Fe to assess toxicity levels, because Fe is strongly complexed to organics and thus normally very significantly correlated to TOC/DOC. A cation exchange method similar to what normally used in the Al fractionation (e.g., Driscoll 1984) should be performed to separate dissolved nontoxic organic Fe complexes from dissolved cationic inorganic Fe complexes, which likely represent the acute toxic Fe-forms. In addition, small particles of inorganic Fe might be harmful, because they are assumed to have a direct physical effect by clogging the pores in the egg membranes (Sykora et al. 1972). We assume that negative effects of iron on aquatic life may occur at concentration of 50 to 100 µg Fe L^{-1}, but this level highly depends on the types of Fe species present.

a. Fish

With very few exceptions, toxicity information is limited to moderately hard waters or soft waters, and the few studies in softwater (Amelung 1982; Brenner and Cooper 1979) are also conducted in relative ionic-rich waters compared with most Norwegian and Swedish lakes. These studies do not suggest any variations in the toxicity of iron in relation to pH. However, other literature information suggests that the toxicity of dissolved iron may be dependent on pH (Decker and Menendez 1974). At pH values close to 7, a tentative environmental quality standard (EQS) of 300 µg L^{-1} is suggested for both *Salmo gairdneri* and *Salvelinus fontinalis* (Mance and Campbell, 1988). In the latter case the EQS value might need to be considerably lower (i.e., 40 µg L^{-1}) at pH values below 6.5. However, these low concentrations have to be inorganic iron that undergoes hydrolysis and precipitation under the given pH and E_h conditions and not humic-complexed iron.

On the basis of literature information, there are no reported differences between the susceptibilities of salmonids and non-salmonids species, but it is reported that the sensitivity differs from life stage to life stage and most sensitive life stage varies among species. For *Salvelinus fontinalis* the most sensitive life stage seems to be the adult, while in contrast it is the eggs and larvae *of Pimephales promelas* that are reported being the most sensitive to iron (Mance and Campbell 1988).

From the lowest adverse effect concentration a tentative EQS value of 500 µg L^{-1} as an annual average concentration of total iron might be suggested (Mance and Campbell 1988). This tentative value is based on laboratory data. Field data document that such standards would be unjustifiably restrictive. A study of brown trout (*Salmo trutta*) population indicates that a healthy population was present at total concentration of 710 µg Fe L^{-1}, while at an iron concentration of 2390 µg L^{-1}, the biomass was reduced by a factor of six (Scullion and Edwards 1980). There was also evidence of reduced hatching and larval survival. Another field study with brown trout showed that normal hatching of caged eggs and survival of alevins occurred at concentrations of

110 μg L^{-1} dissolved iron and 310 μg L^{-1} total iron (Geertz-Hansen and Mortensen 1983). At mildly contaminated sites, there was an effect on egg viability at dissolved iron of 230 μg L^{-1} and 580 μg L^{-1}, with total Fe concentrations of 460 μg L^{-1} and 820 μg L^{-1}.

b. Invertebrates

Whether dissolved or particulate iron, the literature indicates that the majority of invertebrate species tested are more tolerant than fish. The exception by an order of magnitude is the mayfly *Ephemerella suvaria* for which a 96-h LC_{50} of 320 μg Fe L^{-1} has been reported (Warnick and Bell 1969). Assuming a safety factor of 10, this will require an EQS value of approximately 50 μg Fe L^{-1} in aquatic systems hosting this species. The remaining toxicity data on aquatic insects suggest a value above 1000 μg Fe L^{-1} of total iron. Of possible greater importance than the direct effect of iron concentration is the physical effect of precipitated iron smothering the natural substrate with fine particulate ferric hydroxide (ochre). This can eliminate the benthic biota because of the change in substrate type or alter the biota to one that is dominated by burrowing oligochaetes and chironomid larva (Hoehn and Sizemore 1977). This might be a combined effect of precipitation and the reduction in dissolved oxygen as ferrous iron is oxidized to ferric iron.

4. Reacidification — Biological Risk

Redox potential and the concentrations of dissolved organic carbon totally overshadow the effects of a certain reduction in pH if liming terminates. Accordingly, we do not assume any significant negative effects to aquatic biota when a limed surface waters undergo reacidification.

In areas with very high Fe concentrations and/or Mn concentrations, like in organic-rich ecosystems such as bogs and wetlands, changes in the concentrations of these metals may vary a lot due to variation in the water level. This might cause changes in both the amount of dissolved organic carbon and/or the redox potential. This occurs because new areas are exposed to air or covered by water as the water level changes. If the water level changes are man-made so that concentrations of typically redox-sensitive metals such as Mn and/or Fe increase, liming might to a certain degree increase the amounts of metal retained in the wetland areas, because nce higher pH may speed up the precipitation process to a certain extent. This pH effect is likely more enhanced for Fe compared with Mn, but the effect of the pH increase also depends on flow patterns through these wetlands, residence time of water and time of the year, the latter primarily related to Mn, because biology plays a more important role for the mobility of this element than Fe.

C. Manganese (Mn)

1. General Geochemistry

a. Sources

Important manganese (Mn) minerals are oxides and oxyhydroxides, such as pyrolusite (MnO_2), manganite MnO(OH), and hausmanite (Mn_3O_4). Mn is also present as manganese spar, or rhodochrosite ($MnCO_3$) and braunite, $3Mn_2O_3{\bullet}MnSiO_3$. Divalent manganese (MnII) is also present in many rock-forming minerals, where it replaces Fe(II) in the crystal lattice. Thus, olivine, pyroxene, hornblende, biotite, chlorite, serpentinite, and magnetite may all contain appreciable amounts of Mn(II), typically 0.05 to 0.5%, although there is generally much more iron (Wedepohl 1980).

Concentrations and nodules in which Fe and Mn are concentrated relative to the soil matrix are common in some soils, and they result from dissolution-precipitation processes of these elements in the soil solution. They are typical of hydromorphic soils of humid temperate climates, particularly in soils with impeded internal drainage. Their highest concentrations and largest sizes appear in horizons that are subjected to seasonal water logging, under conditions in which there is only a slow removal of the end product of weathering. In the first stage Mn becomes mobile by reduction. It is then concentrated in various forms and during drying out of the soil under aerobic conditions it is reoxidized and precipitates around local nuclei. Fe undergoes a similar process, but Mn appears to be concentrated first, associated with, and followed by Fe at a stage where Mn is nearly exhausted (Schwertmann and Fanning 1976). The following four properties are discernible: (1) concretions and nodules have higher Fe and lower Mn concentrations in the outer layers than in the core (Blume and Schwertmann 1969); (2) the ratio of concentration in the nodules to concentration in the whole soil is generally much greater for Mn than for Fe (Taylor et al. 1964); (3) the larger concretions contain higher Mn/Fe ratios than the smaller ones (Phillipe et al. 1972); (4) with increasing depth there is a general trend for the Mn/Fe ratio in the concretions to increase. Correspondingly, nodules in lake sediments do not form under highly anoxic conditions at the deepest sites of lakes, where Mn is easily reduced at the sediment surface and returned to overlaying water. Rather they form in more shallow water, where Mn oxidation processes are more important. The necessary Mn(II) is probably supplied by local reduction, release from phytoplankton, and by convective transport from the deeper reducing sites (Carignan and Lean 1991). Studies of the more known Mn nodules in oceans have shown that they form by different mechanisms under different conditions (Salomons and Forstner 1984).

The contribution of Mn from direct atmospheric deposition onto the lake surface is usually negligible (Eisenreich 1980).

b. Chemical Properties

Manganese (Mn) has three oxidation states of importance to aquatic chemistry, Mn(II), Mn(III), and Mn(IV). Mn^{3+} is generally thermodynamic unstable in aqueous solutions under normal conditions, and Mn^{4+} compounds are insoluble at most environmental pH values. Similar to iron, ionic divalent Mn^{2+} predominates at low redox potentials and pH. Some forms of oxidized Mn will be in equilibrium with Mn^{2+} under oxidation conditions of high pH and E_h, and some forms of Mn^{2+} may be in equilibrium with $MnCO_3$ under reducing conditions and low pH.

Manganous ions, Mn(II), are stable in anoxic waters where they are present as simple hydrated aquo ions, Mn^{2+}. Between pH 6 and 8 the aquo ion accounts for > 95% of the solution species. Even in hard water at pH 9, the aquo ion accounts for 62% of the solution species, while most of the remainder being the soluble $MnCO_3$ complex (Turner et al. 1981). Complexation by humic material is also thought to be unimportant (Chiswell and Mokhtar 1986). Manganese is very soluble with respect to most inorganic ions and in certain environments, such as interstitial waters (Robbins and Callendar 1975), it is possible to exceed the solubility product of rhodochrosite ($MnCO_3$). Besides Mn^{2+} ions, low molecular labile Mn species also includes weak complexes with organic ligands (Davison et al., 1988). A certain low-molecular-weight fraction is also nonelectroactive and is thought to comprise small colloidal Mn species, which may or may not be organically associated (Knox and Turner 1980; Laxen et al. 1984; De Vitre et al. 1988)

In well-oxygenated waters Mn(IV), such as MnO_2, is the thermodynamic stable form, but due to kinetic limitations a range of metastable oxidation products often predominates in natural waters. In the absence of any biological material, Mn(II) is oxidized much more slowly than Fe(II). Solutions of Mn(II) at pH 8.4 and free from catalysts have been shown to be stable for years (Diem and Stumm 1984). However, direct measurements of the rate of removal of Mn(II) from lake waters have shown that the half-life is typically 1 to 100 days (Chapnick et al. 1982; Tipping et al. 1984; Kawashima et al. 1988). It is little doubt that this is due to microbial catalysis. Today, several mechanisms of microbial oxidation are known. Freshwater organisms, *Pseudomonas* sp., have been implicated in manganese oxidation, likely through energy-yielding enzymatic reactions (Kepkay and Nealson 1987; Adams and Ghirose 1988). Mn (II) can also be oxidised extracellularly. *Leptothrix discophora* SSI, a freshwater bacteria, has been shown to excrete one or more Mn oxidation proteins that in association with acidic exopolymers catalyzes the oxidation of Mn(II) (Adams and Ghiorse 1987, 1988). Furthermore, even surfaces of dormant spores of bacteria are shown to have sped up the oxidation (Rosson and Nealson 1982). This highly biological-dependent oxidation of Mn(II) is likely the main reason for the normally higher manganese concentrations in lakes during winter compared with summer when the temperature and bacterial activity are higher.

Many metals, such as Zn and Ni ions, are shown to be adsorbed by and coprecipitated with manganese oxyhydroxides (e.g., Lundgren and Dean 1979). Later studies indicate that trace metals adsorbed to Fe oxyhydroxides are probably less important in the overall pathway of these elements than was once thought (Davison 1993).

There are a lot of work demonstrating the large removal of Mn^{2+} by the outflow of the lake, that is, 70 to 90% of the input (Dean et al. 1981; Davison et al. 1982), even in well-oxygenated water, but the lake depth is relatively essential. Within a given lake it has been shown that the concentration of Mn in the sediment increases as the depth of the overlying water increases (Delfino et al. 1969; Takamatsu et al. 1985a). Accordingly, the change in Mn concentration with depth in long sediment cores has been used to assess historical changes in water depth (Takamatsu et al. 1985a). For shallow waters, where most of the Mn is lost from the system, but most of the Fe is retained, the Fe to Mn ratio in the sediments tends to be 50:1, which is similar to the world-wide ratio in sediments (Wedpolhl 1980).

Although the background levels of Mn in major rivers is usually < 10 μg Mn L^{-1}, the concentration can vary considerably and is very dependent on local conditions (Salomons and Forstner 1984). The proportion of particulate Mn may vary from 0 to 100%, attributed to the origin of sources. Weathering processes that produce suspended material produce a high proportion of particulate Mn, while soluble Mn(II) compounds are leaching from oxygen-deficient soil and ground waters (see Davison, 1993).

2. Manganese in Surface Water Systems

High concentrations of manganese (Mn) in surface waters are normally present in high TOC and/or low pH lakes (Borg 1986a; Borg 1987; Verta et al. 1990) and is normally well correlated with iron (Fe). Even though it might often be a good correlation between concentration of Mn and organic carbon, the complexation of Mn by humic material is thought to be unimportant (Chiswell and Mokhtar 1986). The TOC/Mn relationship has been attributed to other indirect factors, like there being less organic carbon permanently added to the sediment when there is a high rate of microbial degradation of organic material at the sediment surface. High microbial activity will be associated with particularly pronounced reducing conditions, providing a rich supply of electrons capable of reducing and releasing manganese. As a result, less manganese is retained within the sediments (Hilton et al. 1985). Humic substances with phenolic and carboxyl groups, oxalate, pyruvate, and fatty acids are all capable to reducing many metal oxides, and many of these compounds readily reduce Mn oxides. These and other reductants (like Fe(II), S(-II)) are thought to be involved in a four-step process: (1) adsorption of reductant; (2) electron transfer at surface; (3) release of oxidized organics; (4) release of Mn(II). The rate of reduction increases with the concentration of reductant and H^+

concentration. Thus, the highest Mn concentration should be expected in shallow (see comments above), acidic, high TOC lakes. There are also some indication that reductive dissolution of Mn by fulvic and humic acids is enhanced by light (see Wait et al. 1988), but the effect of light was larger at pH 7 compared with pH 4.

During spring melt (Borg 1986a) reported very high Mn concentrations in some mountain streams in central Sweden, simultaneously with a dramatic pH decline (pH 7.3 to 4.3) and TOC increase (2.5 mg C L^{-1} to 12 mg C L^{-1}). Vesely and Majer (1996) reported an increase in Mn by decreasing pH, but Mn tended to decrease again at very low pH (pH < 4.2), likely as a result of long time leakage under chronic very acidic environments. Correspondingly, Young and Harvey (1992) reported very low concentrations of Mn in sediments of acid lakes, consistent with a poor supply.

Nordic surveys confirm that many Scandinavian surface waters contain high concentrations of total Mn (Tables 10, 11), and ≈ 10% of lakes in Finland and Sweden have Mn concentrations > 100 µg Mn L^{-1} (Table 11). The Nordic survey in 1995 (Table 11) shows that median Mn concentrations in Norway, Sweden, and Finland are 3.2, 14.5, and 17.5 µg Mn L^{-1}, while median Mn concentration for limed Swedish lakes was 23.3 µg Mn L^{-1}. As for Fe, the generally higher Mn concentrations in the limed Swedish lakes (Figure 20) cannot be explained by different median TOC or pH values between the two categories of lakes. The tight correlation between TOC and Mn concentrations is well illustrated in Figure 22. While the median concentrations of Mn in nonlimed Swedish and Norwegian lakes with TOC ≥ 10 mg C L^{-1} is 30.8 µg Mn L^{-1}, the total Mn concentration in lakes within the TOC classes 5 to 10 mg C L^{-1} and TOC < 5 mg C L^{-1} are 15.2 and 2.5 µg Mn L^{-1}, respectively. Regarding pH, it was minor differences in concentrations

Table 10. Concentrations of Mn (µg Mn L^{-1}) in Nordic surface waters and in the Czech Republic. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min – Max	Median/ Mean (±)
Finland[1]	153	0	2 – 380	21
Finland south[2]	95	n.r.	n.r. – 280	41 ± 33
Finland, north[2]	26	n.r.	n.r. – 290	26 ± 24
Sweden, south[3]	16	n.r.	8 – 553	195 ± 238
Sweden, north[3]	17	n.r.	2 – 149	42 ± 49
Sweden, north[4]	56	n.r.	1 – 88	19
Czech[5]	5363	n.r.	n.r.	80

[1] Tarvainen et al.,1997 based on samples from 1990-1992.

[2] Verta et al., 1990 based on samples from autumn 1987.

[3] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden, south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[4] Borg (1987) based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

[5] Vesely and Majer, 1996, based on data collected between 1984 and 1992.

Table 11. Percentile distribution of Mn (μg Mn L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462

Mn	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	326.7	697.4	3530.8	2600.0
	99.5 %	103.0	475.3	382.1	312.7
	97.5 %	58.9	285.3	268.8	154.8
	90.0 %	23.8	90.5	78.0	78.0
Quartile	75.0 %	9.0	43.2	46.2	35.0
Median	50.0 %	3.2	14.5	23.3	17.5
Quartile	25.0 %	1.3	5.0	10.8	6.4
	10.0 %	0.5	1.9	4.7	2.0
	2.5 %	0.2	0.6	1.8	1.0
	0.5 %	0.1	0.2	0.3	0.2
Minimum	0.0 %	0.0	0.0	0.1	0.0

of Mn between the different pH classes (Figure 21) This very well illustrates the close relationship between Mn and dissolved organic carbon, but in contrast to Fe this is not because of strong Mn-complexing properties to organics, but the fact that many organic compounds are able to reduce Mn or keep Mn reduced even at aerobic conditions. Because Mn(II) is relatively soluble, this explains the tight correlation between TOC and Mn. With or without minor amounts of TOC, the reduction capacity is much lower, and oxidized Mn(IV) will stay oxidized under aerobic conditions. Thus, the almost insoluble MnO_2 will be formed and the concentration of dissolved Mn will be low.

a. Experimental Acidification (Including Mining)

Successive acidification (2-year intervals) of the clearwater (TOC: 2 to 4 mg C L^{-1}) Little Rock Lake, USA, from pH ≈ 6.1 to pH 5.6, 5.1, and 4.7 by H_2SO_4 (Brezonik et al. 1993) showed a significant increase in Mn by decreasing pH. From a background concentration of Mn of ≈ 10 μg Mn L^{-1}, Mn increased successively to 30, 50, and 80 μg Mn L^{-1} because pH decreased to 5.6, 5.1, and 4.7, respectively. This was interpreted to be due to increased solubility of manganite.

Only a certain increased mobilization of Mn from a sandy sediment in Lake 223 (enclosure experiments) was observed during the first months after pH was lowered from 6.7 to 6.8 to pH 5.7, but a strong increase was observed when pH was lowered to 5.1 (Schindler et al. 1980). At pH 5.1, the concentration of Mn in overlaying water reached 150 to 200 μg L^{-1}, but leveled out at about 100 μg L^{-1}. Some high values in the control enclosures (25 μg Mn L^{-1}) indicated relatively high background concentrations.

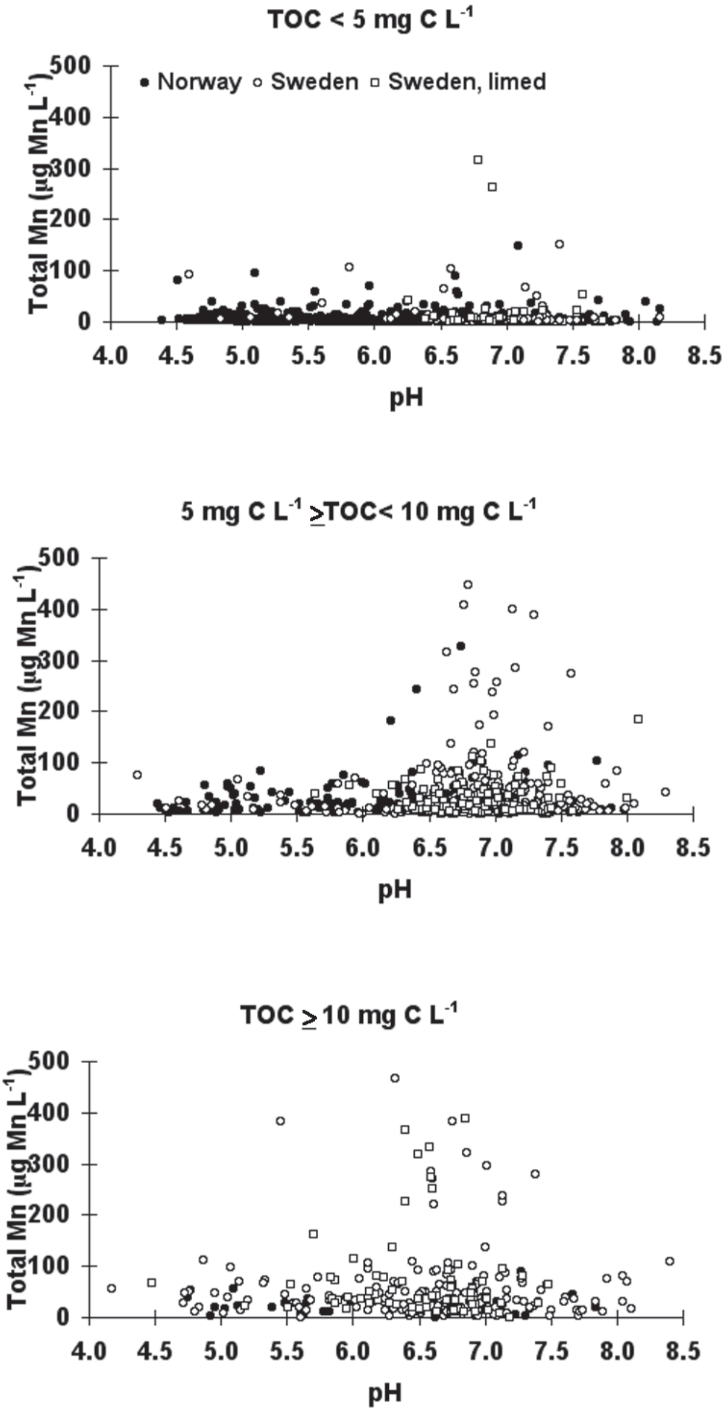


FIGURE 19. Total concentration of manganese (Mn) in Norwegian and Swedish (non-limed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

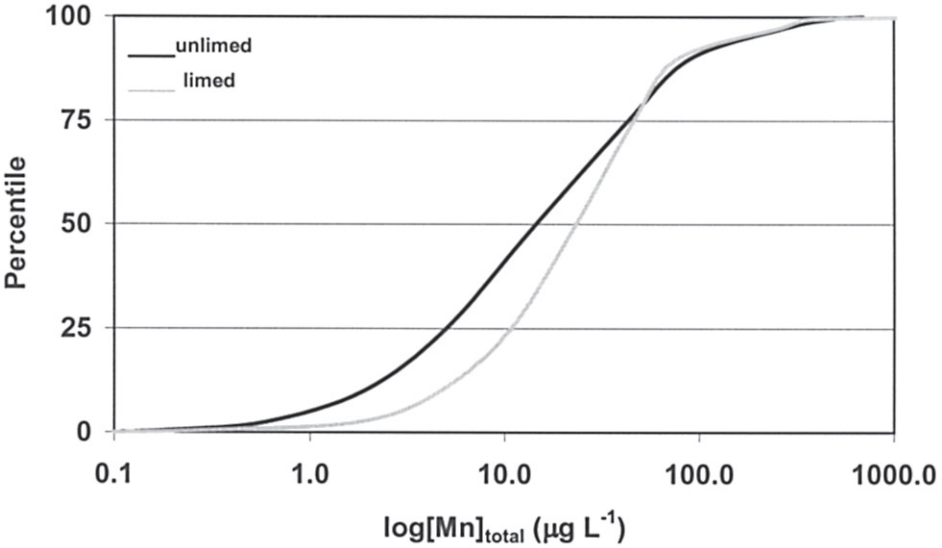


FIGURE 20. Percentile distribution of total Mn in limed (n = 261) and not limed (n = 820) Swedish lakes. Data are from the Nordic Lake Survey, 1995. (Data from Skjelkvaale et al. [1996, 1999].)

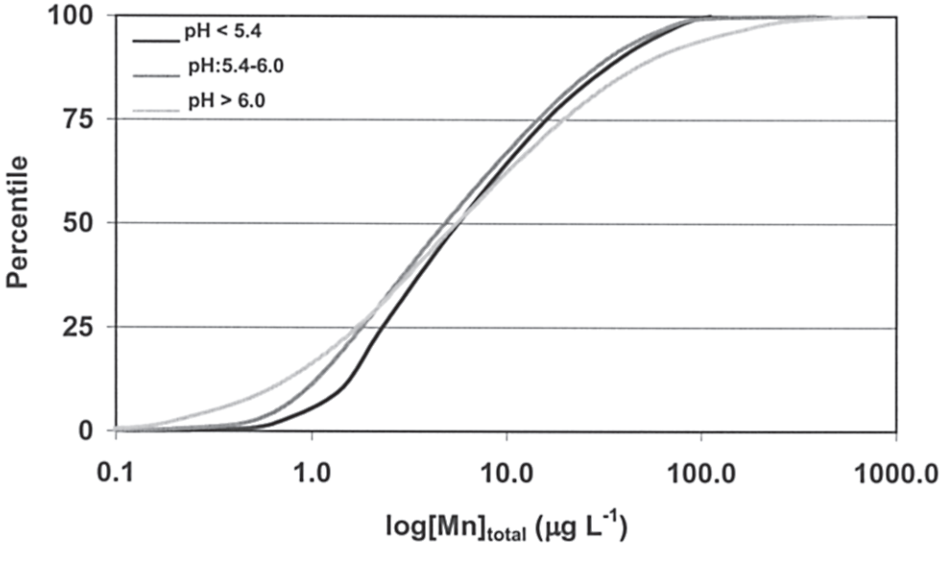


FIGURE 21. Percentile distribution of total Mn in Norwegian and Swedish lakes based on 3 pH classes. Data are from the Nordic Lake survey 1995. pH < 5.4, n = 250; 5.4 ≥ pH < 6.0, n = 204; pH ≥ 6, n = 1090. (Data from Skjelkvaale et al. [1996, 1999].)

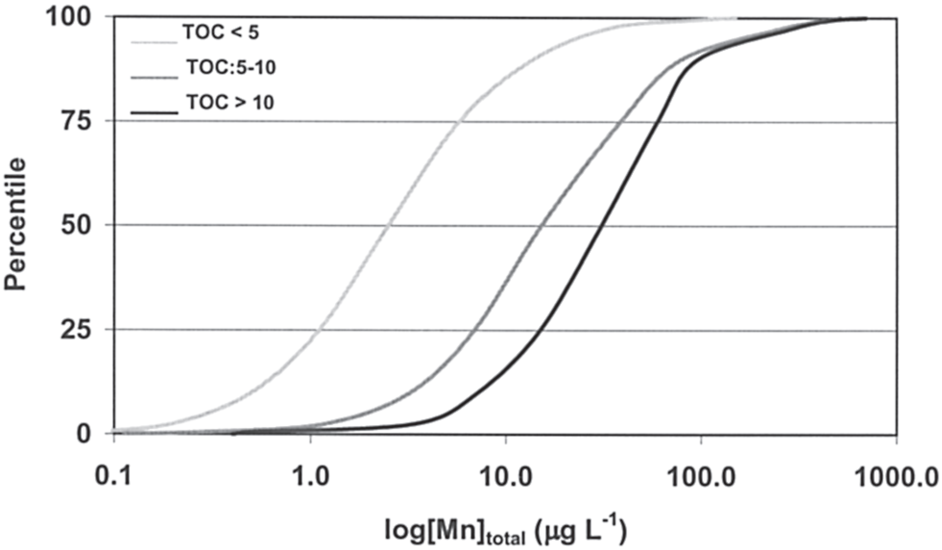


FIGURE 22. Percentile distribution of total Mn in Norwegian and Swedish lakes based on three TOC classes (TOC: mg C L^{-1}). Data are from the Nordic Lake survey 1995. TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale et al. [1996, 1999].)

Particulate metal speciation in surficial sediments from Loch Dee, Scotland, also documented relatively easily mobilizing Mn during acid conditions (Williams 1993). They also explained the increments of total Mn (and Co) in the upper 5 cm as an accumulation of secondary oxides and adsorbed species, consistent with precipitation from the interstitial pore waters across a sedimentary redox front. This means an upward migration of mobile Mn^{2+} (under anaerobic conditions) and subsequent accumulation in the aerobic interfacial sediment due to precipitation of Mn^{4+} oxides. Several have shown that Mn is also very easily mobilized from the catchment under acidic conditions (e.g., Dillon et al. 1988; Bryant et al. 1997), often attributed to the stability decrease of Mn oxides/hydroxides with decreasing pH. This often means that less Mn is precipitated in acidic lakes (White and Driscoll 1987a; Young and Harvey 1992).

Kahl and Norton (1983) recorded small changes in the concentration of Mn in water close to the sediments by acidifying the waters above sediments (taken from different depths) from pH 5.24 to 5.89 down to pH≈ 5. One of the sediment cores showed a certain increase, which by assuming biannual dilution of this water (two turnovers) with the total lake volume, and a lake water residence time of 6 months resulted in an increase of Mn by maximum 3.9µg Mn L^{-1}, that is, from 20.0 to 23.9 µg Mn L^{-1}. Another sediment core was unaffected by the pH lowering, while two cores showed a minor decreasing concentration of Mn above the sediments. Andersson et al. (1978) also documented a significant decrease in Mn in a similar experiment when pH was lowered from 5.40 to 5.00. Both Andersson et al. (1978)

and Kahl and Norton (1983) documented significantly increases in the concentration of Mn derived from sediments when water pH was lowered to 4.00. These experiments suggest that there are a critical pH for Mn mobilization at pH ≈ 4.8.

Besides dissolution of inorganic Mn sources, it is also shown that Mn has a very low stability constant for fulvic acid complexes, tested at both pH 3.5 and pH 5.0 (Schnitzer and Skinner 1966, 1967).

b. Liming

After liming of 20 lakes, most of them mildly acidic lakes, Marcus (1988) observed no significantly changes in the concentration of Mn in the lake water, but there was a tendency of lower concentrations after liming. The prelimed mean concentrations of Mn (n = 113) was 60 μg L^{-1}, while the postlimed mean (n = 105) was 30 μg Mn L^{-1}. Prelimed pH of the lakes varied from 4.44 to 6.99, with a mean pH of 5.51. Liming of a low TOC lake in Canada (from pH 4.8 to about pH 7) reduced the concentration of Mn in lake water from 250 μg L^{-1} to 200 μg L^{-1} (White et al. 1984). Liming of a wetland in Dalarna, Central Sweden, did not reduce the Mn concentration significantly. Before liming the median Me concentration was 24 μg L^{-1} in the outlet stream (see SectionVII.F.2 and Table 25). Roelofs et al. (1995) documented strong increases in the concentrations of Mn (and Fe) in sediment pore water of limed lakes in southwestern Norway. This was primarily due to a decrease in the redox potential as a result of increased mineralization after liming. Consequently, the concentration of dissolved organic matter increased as well as the concentration of total nitrogen and phosphorous. The concentration of nitrate in pore water decreased after liming, while the ammonium increase was so strong that the total concentration of nitrogen increased.

c. Reacidification

There are little data on the mobilization of Mn during the reacidification of earlier limed systems, but if Mn is present in large amounts in the soil and or lake sediments, an increase in Mn will likely occur under reacidification. If reacidified pH is not < 5, we assume that the increase will be relatively small, at least in light of biological effect concentrations.

3. Biology and Toxicity

There is very limited literature dealing with manganese toxicity. Nyberg et al. (1995) assumed Mn (Mn^{2+}) being the main toxic compound for brown trout mortality during springmelt in two mountain streams in central Sweden. However, very high concentrations of Fe were present in both streams during these episodes, while inorganic Al was low. Their data indicated that labile inorganic Mn (primarily Mn^{2+}) about 50 μg L^{-1} may be toxic for brown trout, even at pH 5.5 to 6. Wetland liming reduced the mortality even during the episode, but the mortality was not totally eliminated. A similarly high mortality was reported by Borg (1986a) during very high Mn concentrations in some mountain streams in the same area. This occurred simultaneously with a dramatic pH decline (pH 7.3 to 4.3) and a TOC increase from 2.5 mg C L^{-1} to 12 mg C L^{-1}. The extreme mortality during this episode was difficult to relate to one single metal, but an extreme increase in Fe and a substantial increase in Al was simultaneously observed. In both these studies, it is difficult to eliminate rapid polymerization of Fe, when reduced iron (Fe^{2+}) enter into surface water and undergoes oxidation ($FeOH_3$). This process is very fast, and accordingly difficult to reveal analytically. Thus, Fe polymerization may also be an important mortality factor, similar to the well-known extreme toxicity under Al polymerization conditions (e.g., Rosseland et al. 1992; Lydersen et al. 1994a).

4. Reacidification — Biological Risk

The concentration of Mn in surface water and the subsequent efflux are highly dependent on the concentration of Mn^{2+}. Low concentration of oxygen (low E_h), low pH, and high TOC (reductant) increases the possibility of high Mn^{2+} concentrations. The highest Mn concentration should be expected in shallow acidic, high TOC lakes. However, chronically acidified lakes may have very low Mn concentrations because of long time leakage both from sediments and poor catchment supply. Accordingly, reacidification of limed lakes may cause increases in Mn, primarily as aqueous Mn^{2+}. However, due to the very weak complexing properties of Mn^{2+}, we assume this ion not being particularly harmful to aquatic gill organisms. If the Mn oxidation processes are going to cause toxic conditions similar to oxidation of Fe and hydrolysis of Al, we will assume that this is a larger problem when the lakes are limed, because these processes are likely more enhanced at higher pH.

In areas with very high Mn concentrations and/or Fe concentrations, like in organic-rich ecosystems such as bogs and wetlands, changes in the concentrations of these metals may vary significantly due to variation in the water level. Because areas will be exposed to air or covered by water as the water level changes, the amount of dissolved organic carbon, the redoxpotential, and pH may change significantly depending on the actual ground water level. If these water level changes are man-made (“unnatural”) so that concentrations of typically redox-sensitive metals as Mn and/or Fe increase, liming might to a certain degree increase the amounts of metal retained in the wetland areas, because higher pH may speed up the precipitation process to a certain extent. These pH effects are likely more enhanced for Fe compared with Mn, but the effect of the pH increase also depends on flow patterns through these wetlands, residence time of water, and time of the year, the latter primarily related to Mn because biology plays a more important role for the mobility of this element than Fe.

In areas with no clear man-made reasons for water level changes, the ecosystem should be kept untouched, that is, no liming should be recommended. In areas where such ecotypes are uncommon, one should consider natural protection, even though high concentrations of metals like Mn and Fe are present.

D. Zinc (Zn)

1. General Geochemistry

a. Sources

The principle ores of Zn are sulfides such as spalerite and wurtzite, but about 96% of zinc discharged into the global environment is the result of human activity (Leonard and Gerber 1989). Major sources of anthropogenic Zn discharges to the environment include electroplates, smelting and ore processors, draining from active and inactive mining operations, domestic and industrial sewage, combustion of fossils fuels and solid wastes, road surface runoff, corrosion of Zn alloys and galvanized surfaces, and erosion from agricultural soils (see Eisler 1993).

An investigation of 360 samples from the mor layer of Swedish forest soils showed Zn concentrations within the range 14 to 149 mg kg^{-1} dw, with a median concentration of 55 mg kg^{-1} dw. There was no north-south gradient to be seen in the Zn concentrations. However, elevated levels were found in the mineralized area called Bergslagen in central Sweden, where mining activities and metal production have been pursued for centuries, and around the metal industries along the southern and northeastern coast. A typical north-south gradient was found in the Zn content, but it mainly reflects the differences in mor layer thickness and the redistribution of soil derived metals to the mor layer by root uptake and litterfall (Andersson et al. 1991). A similar survey in 1981 of 841 localities in southern Norway showed a large influence by long-range atmospheric transport. The general level of Zn in Norwegian soils is about 30 mg kg^{-1} dw in the humus layer (Steinnes et al. 1989).

In soils, Zn forms relatively stable complexes with dissolved organic acids in the A horizon. However, the Zn leached from soils is to a large extent originating from the mineral phase in the B horizon. The leaching from this layer is very susceptible to changes in the soil acidity, with larger amounts lost at lower pH (Bergkvist et al. 1989). Mass balance calculations indicate that Zn is lost in significant quantities from acidic forest soils (Bergkvist 1987; Bergkvist et al.

1989; Aastrup et al. 1995a). However, retention processes seem to greatly reduce the high Zn concentrations below the B horizon and in ground water discharge areas in acidified forest soils in southern Sweden. Thus, there is a large translocation of Zn in the soil profile both vertically and horizontally. As yet, this retention is efficient and the Zn concentration increase only moderately in the stream water (Löfgren 1999).

Scandinavian moss analysis in 1995 showed elevated Zn concentrations in the vicinity of large point sources such as the metal smelters in Rönnskär (Sweden) and Odda (Norway). Generally, the Zn concentration in moss was approximately 20 mg kg^{-1} dw in areas not affected by local pollution. There was only a slight contribution from long-range transport, most obvious in southern Norway and southwest Sweden (Rühling et al., 1996). In Norway, Zn in wet deposition has decreased by 70% from 1978 to 1996 (Toerseth and Manoe 1997). In Sweden Zn concentration in wet deposition has decreased by 23 to 35% during 1984 to 1996. Bredkälen in the subalpine are a in central Sweden, however, shows an increase in Zn during this period by a factor 1.7.

In groundwater in Sweden the median Zn concentration is 10 $\mu g\ L^{-1}$, which is higher than for running waters (4.1 $\mu g\ L^{-1}$) and lakes (1.0 in northern and 2.2 $\mu g\ L^{-1}$ in southern Sweden), respectively (Alm et al. 1998; Ledin et al. 1989). The median background concentration in groundwaters (pH>6) is considered to be 3 $\mu g\ L^{-1}$, but the concentration range is large (0.8 to 30 $\mu g\ L^{-1}$) due to differences in Zn content in soil and bedrock (Ledin et al. 1989). The Zn concentration in groundwater varies with pH, with higher levels at lower pH. Median concentration at pH<5 is 25 $\mu g\ L^{-1}$ compared with 10 $\mu g\ L^{-1}$ and 4 $\mu g\ L^{-1}$ in the pH intervals 5.5 to 6 and 6.5 to 7, respectively (Aastrup et al. 1995a).

Most of the Zn introduced into aquatic environment precipitates into lake sediments, but less at low pH. Young and Harvey (1992) showed that Zn was primarily present in inorganic fractions of sediments: (1) the easily reducible fraction of surficial oxic lake sediments (which mean easily exchangeable and bound to oxides of Mn) and (2) the reducible fraction (bound to oxides of Fe). Only small amounts of Zn were recovered in the organic fractions. 40 to 60% of leachable Zn was present in the easily reducible fraction in sediments of circumneutral lakes, while 20 to 40% was found in the same fractions in the sediments of the acidic lakes. This agrees well with other findings (e.g., Campbell et al. 1985; Tessier et al. 1985, 1989). Despite this, relatively more Zn is associated with organic fractions in relation to the more easily reducible fractions in sediments of acidic lakes (pH 5.0 to 5.6) compared with circumneutral lakes, pH 6.4 to 6.5. These organic Zn fractions, likely coprecipitated with Fe-humic compounds, are relatively strongly bound at low pH (Young and Harvey 1992). Tessier et al. (1989) predicted a model of Zn derived from sediments from Fe and Mn oxyhydroxides, and assumed that most of the mobile Zn should be present in the water column at pH < 5, and in the surficial sediments at pH > 7. Within the intermediate pH range (5.5 to 6.5) changing pH should have a pronounced effect on the partitioning of Zn between the water column and the sediment. Williams (1993) showed that dissolution of Zn (and Cd) from sediments increased at low pH, and that $ZnCO_3$ is not an actual species under acidic conditions ($pH < 7.0$).

Based on studies in relatively few unpolluted lakes ($n = 133$), the sediment Zn concentrations varied between 130 to 430, 130 to 380, and 59 to 330 g Zn kg^{-1} dw (10-90 percentiles) in southern, central, and northern Sweden, respectively (Alm et al. 1998). In northern Sweden, the concentrations are close to the natural background levels (Johansson 1989). Decreased metal concentrations toward the sediment surface in acidified lakes may be attributed to a reduced metal sedimentation due to reduced adsorption on precipitating particles or desorption or dissolution from already sedimented materials (Dauvalter 1995). Laboratory studies on the long-term, pH-induced release of metals from the sediments to overlaying water indicate that the sediments can retain Zn at $pH>3$ (Arafat and Nriagu 1986).

Dissolved zinc rarely exceeds 40 µg L^{-1} in Canadian rivers and lakes, very comparable with the situation in Scandinavia. Higher concentrations are usually associated with zinc-enriched ore deposits and anthropogenic activities.

b. Chemical Properties

Because Zn ligands are soluble in neutral and acidic solution, Zn is readily transported in most natural waters. However, Zn oxide, the compound most commonly used in industry, has a low solubility in most solvents (Elinder 1986). Zinc mobility in aquatic systems is a function of the composition of suspended material and bed sediments, dissolved and particulate iron and manganese concentrations, pH, salinity, concentrations of complexing ligands, and the concentration of Zn. In freshwater, Zn is most soluble at low pH and low alkalinity; 10 mg Zn L^{-1} at pH 6 declines to 6.5 mg Zn L^{-1} at pH 7, and 0.65 mg Zn L^{-1} at pH 8. In water, the free zinc ion thought to coordinate with six water molecules to form octahedral aqua ion $Zn(H_2O)_6^{2+}$ in the absence of other complexing or adsorbing agents. In freshwater Zn exists almost exclusively as the aquo ions at pH between 4 to 7 (Campbell and Stokes 1985). In freshwater at pH 6, the dominant forms of Zn are the free ion (98%) and $ZnSO_4$ (2%). Normally, almost 90% of inorganic zinc in surface waters is the free ion and the remainder species are $ZnHCO_3^+$, $ZnCO_3$, and $ZnSO_4$. The concentration of other species primarily depends on the concentration of metal-complexing dissolved organic compounds (Figure 23) and the presence of inorganic adsorbing agents as mineral particles, clays and hydrous oxides of manganese, iron and silicon. Increased pH increases the zinc sorption to particles, while increased ionic strength reduces the adsorption of zinc due to competition with other cations. Correspondingly, increased ionic strength and/or decrease in pH (Figure 23) may increase the proportion of free zinc in relation to organic-bound zinc, at least if pH decrease below 5.5 to 5.0.

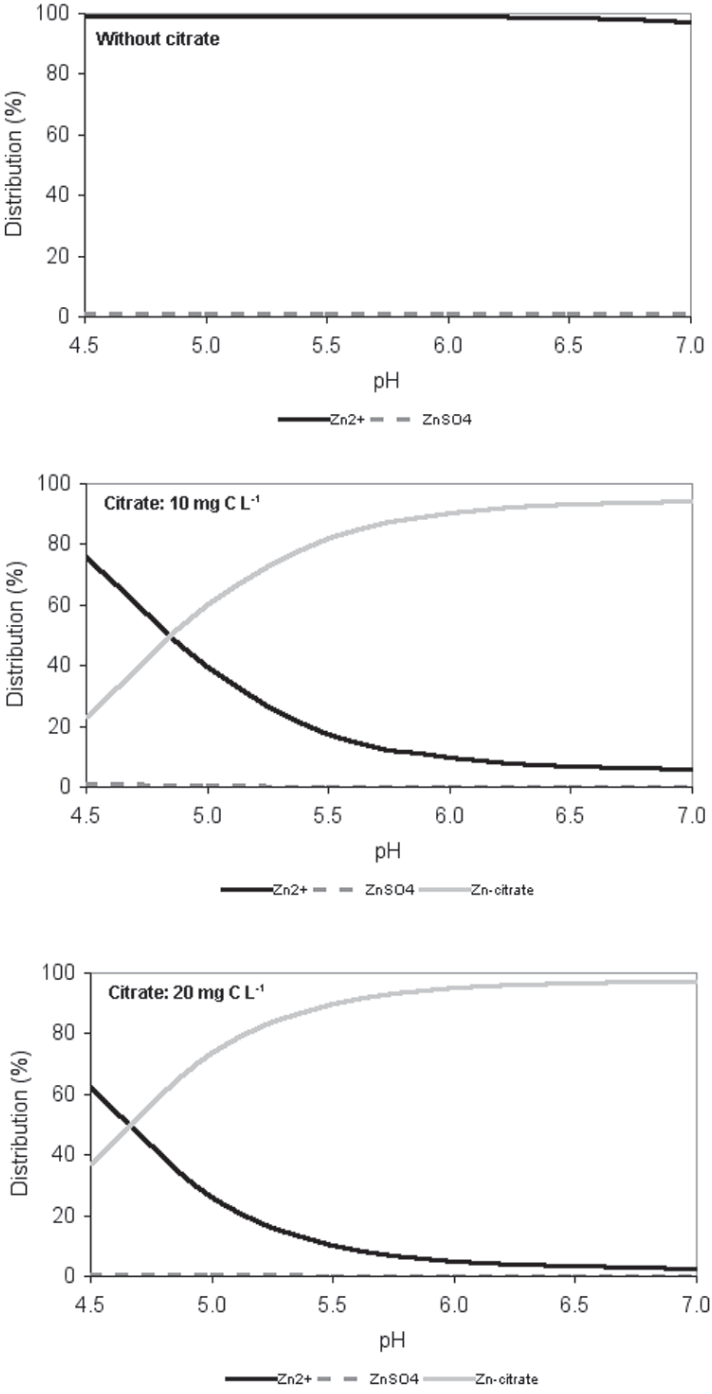


FIGURE 23. Distribution of major Zn species in relation to pH at citrate concentrations of 0, 10 and 20 mg C L^{-1}. Essential input conditions: 25°C; CO_2 and O_2 at equilibrium with partial pressure of air; [Zn]: 1 µmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 µg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

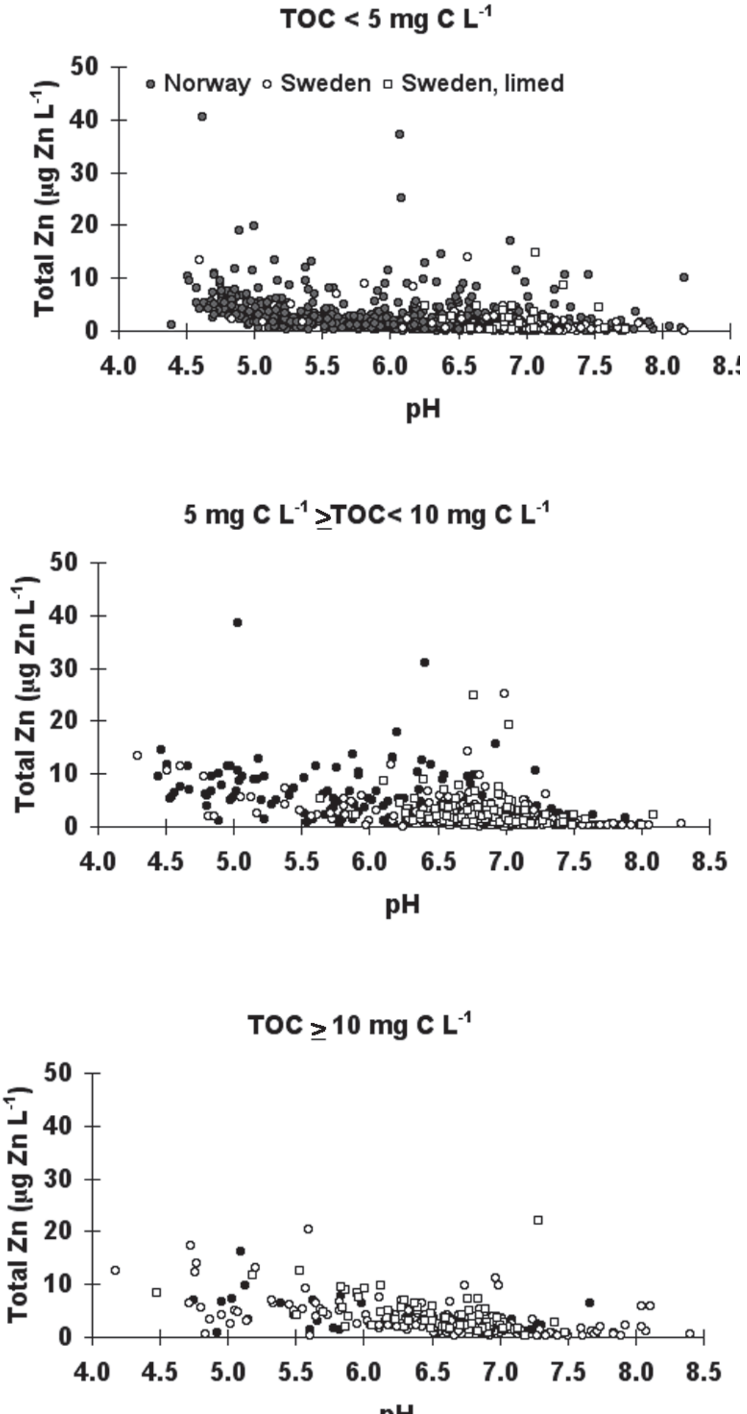


FIGURE 24. Total concentration of zinc (Zn) in Norwegian and Swedish (non-limed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

Zinc-oxide/hydroxide is, like aluminium, also soluble at very high pH, forming Zn $(OH)_4^{2-}$ ions (zincate). Generally, Zn release from sediments is enhanced under conditions of high dissolved oxygen, low salinity, and low pH.

2. Zinc in Surface WaterSystems

High Zn concentrations in surface water are seldom correlated with bedrock or till geology (Tarvainen et al. 1997; Alm et al. 1998), but high values are more likely to occur in acid surface waters, both due to increased solubility by decreasing pH (where acid rain plays an important role) and increased inputs of Zn by an increased influence of air pollutants (Henriksen and Wright 1978; Borg 1987; Verta et al. 1990; Johansson et al. 1995a). This is also confirmed by increase in Zn during snowmelt (e.g., Kahl and Norton 1983).

Based on a regional survey in the Czech Republic, Vesely and Majer (1996) found that Zn (and Cd) were independent of pH within the pH range 5.4 to 6.0, but on both sides the concentrations increased by decreasing/increasing pH.

Significant negative relationship between Zn and pH has been reported frequently (e.g., Borg 1983; Borg 1987; Brezonik et al. 1993; Johansson 1995b), but this pH relationship was found to be less evident in northern Swedish watercourses (Johansson et al. 1995b). Johansson et al. (1995b) also documented large differences in the concentration of Zn between rivers and streams in southern and northern Sweden. In the northern streams, the concentration of Zn (and Cd) was about half the concentrations present in southern streams at same pH level. They also documented higher concentrations and larger concentration variations in streams compared with rivers, which also should be expected. Indications of higher Zn concentrations in southern Sweden and Finland compared with northern water systems are also present in Table 12. The highest Zn concentration recorded by Johansson et al. (1995b) was about 60 μg Zn L^{-1}, within a pH variation range 4.0 to 7.5, based on > 2000 samples collected from 23 large rivers and 13 small streams in 1990. The highest concentration recorded during the Nordic Lake survey in 1995 (Table 13) were 55 μg Zn L^{-1} in Finland (n = 462), 427 μg Zn L^{-1} in nonlimed Swedish lakes (n =5 59), 56 μg Zn L^{-1} in limed Swedish lakes (n = 261) and 139 μg Zn L^{-1} in Norwegian lakes (n=1985). However, almost 90% of all Nordic lakes investigated had concentrations of total Zn < 5 μg Zn L^{-1}, This means that almost all lakes fell in the categories: *Very low* or *Low* according to the Norwegian and Swedish classification systems (Table 14).

The pH-dependent relationship between Zn and pH is likely because a large portion of Zn is often present in easily ion-exchangeable fractions in soils and sediments, and thus sensitive to pH changes (Tylor and McBride 1982; Dillon et al. 1988; Brezonik et al. 1993, Williams 1993). Accordingly, concentrations of Zn should also be sensitive to episodic ionic strength variations (sea salt episodes), especially under acidic conditions. Elevated concentrations of Zn have been docu-

Table 12. Concentrations of Zn (µg Zn L^{-1}) in Nordic surface waters and in the Czech Republic. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	152	4	< 0.70 – 14.3	3.58
Finland south[2]	60	n.r.	n.r. – 28.1	5.6 ± 4.4
Finland, north[2]	112	n.r.	n.r. – 20.1	2.5 ± 2.6
Sweden, south[3]	15	n.r.	4 – 25	11 ± 5
Sweden, north[3]	18	n.r.	< 2 – 20	7 ± 6
Sweden, north[4]	56	n.r.	< 0.4 – 8.5	2.2
Czech[5]	5363	n.r.	n.r.	<10

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

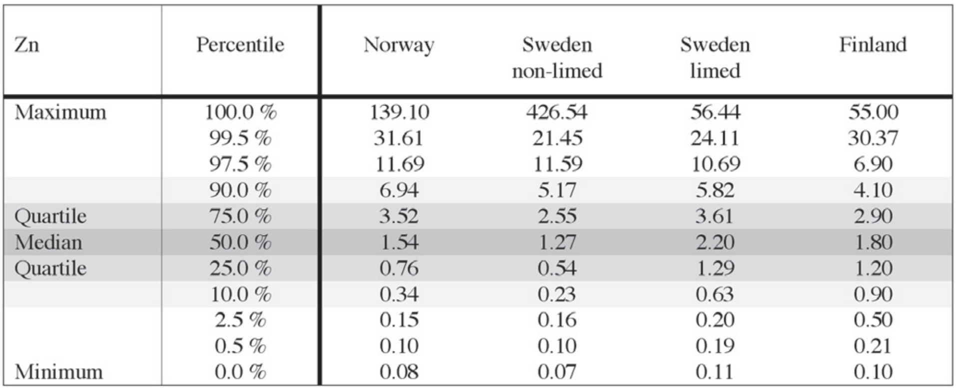
[2] Verta et al. (1990), based on samples from autumn 1987.

[3] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden, south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[4] Borg (1987). based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour

[5] Vesely and Majer (1996), based on data collected between 1984 and 1992.

Table 13. Percentile distribution of Zn (µg Zn L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462



Zn	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	139.10	426.54	56.44	55.00
	99.5 %	31.61	21.45	24.11	30.37
	97.5 %	11.69	11.59	10.69	6.90
	90.0 %	6.94	5.17	5.82	4.10
Quartile	75.0 %	3.52	2.55	3.61	2.90
Median	50.0 %	1.54	1.27	2.20	1.80
Quartile	25.0 %	0.76	0.54	1.29	1.20
	10.0 %	0.34	0.23	0.63	0.90
	2.5 %	0.15	0.16	0.20	0.50
	0.5 %	0.10	0.10	0.19	0.21
Minimum	0.0 %	0.08	0.07	0.11	0.10

Table 14. Classification of concentrations of Zn in surface waters (μg L^{-1}), the upper (0 to 1 cm) of lake sediments (mg kg^{-1} dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Zn (Sweden 1991)	≤ 1	1 - 5	5 - 15	15 – 75	> 75
Zn (Sweden, 1998)[1]	≤ 5	5 - 20	20 - 60	60 – 300	< 300
Zn (Sweden, 1998)[2]	≤ 1	1 - 5	5 - 15	15 - 150	< 150
Zn (Norway, 1997)	< 5	5 - 20	20 - 50	50 – 100	> 100
Sediment					
Zn (Sweden, 1991)	≤ 70	70 – 175	175 - 300	300 – 1000	> 1000
Zn (Sweden, 1998)[3]	≤ 150	150 – 300	300 - 1000	1000 – 5000	> 5000
Zn (Norway, 1997)	< 150	150 – 750	750 - 3000	3000 – 9000	> 9000

[1] Based on risks of biological effects

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96)

[3] Based on distribution in Swedish lakes with and without local emissions.

mented in small streams in southern Sweden, caused by ion exchange in soils due to deicing salt applications on roads (Löfgren 2001). Besides low pH, an increase in SO_4^{2-} significantly increases both the solubility and mobility of Zn, due to formation of dissolved $ZnSO_4$ complexes (Lindsey 1979). This is of interest because SO_4^{2-} deposition in Scandinavia is reduced by about 50% in the most air-polluted areas mainly during the last decade.

At very low pH ($pH < 4.2$), the concentrations of Zn is reported to decrease again, as a result of long time leakage under chronic very acidic environments (Vesely and Majer 1996).

None of the above-mentioned surveys have recorded significant relationship between concentration of Zn and TOC/DOC. However, covariation with color, TOC, Fe, and pH ($p < 0.01$) was found in a survey of 118 streams in the county of Dalarna in central Sweden (Alm et al. 1998). There was co-linearity between pH and humus, reducing the possibility to interpret the casual relationship. Similarly, by dividing the 1995 surveyed Nordic lakes into TOC and pH classes, there is a clear tendency of increasing Zn concentrations by decreasing pH (see Figure 26), while the tendency of increasing Zn by increasing TOC is very weak (Figure 27). For Norwegian and Swedish lakes with $pH < 5.4$, median Zn concentration is 4.10 μg Zn L^{-1}, while the corresponding concentrations in pH class: 5.4 to 6.0 and pH class > 6 are 2.00 and 1.05 μg Zn L^{-1}, respectively. For the TOC class > 10 mg C L^{-1}, the median concentration is 2.16 μg Zn L^{-1}, compared with the medium (TOC: 5 to 10 mg C L^{-1}) and low (TOC < 5 mg C L^{-1}) classes, with 1.66 and 1.18 μg Zn L^{-1}, respectively (Figure 27). Other factors like the amount of atmospheric zinc deposition and local geology are also highly essential for the Zn concentration in surface waters.

Based on the regional survey in 1995, the median concentrations of Zn in Norway, Sweden, and Finland are 1.54, 1.27, and 1.80 μg Zn L^{-1}, respectively,

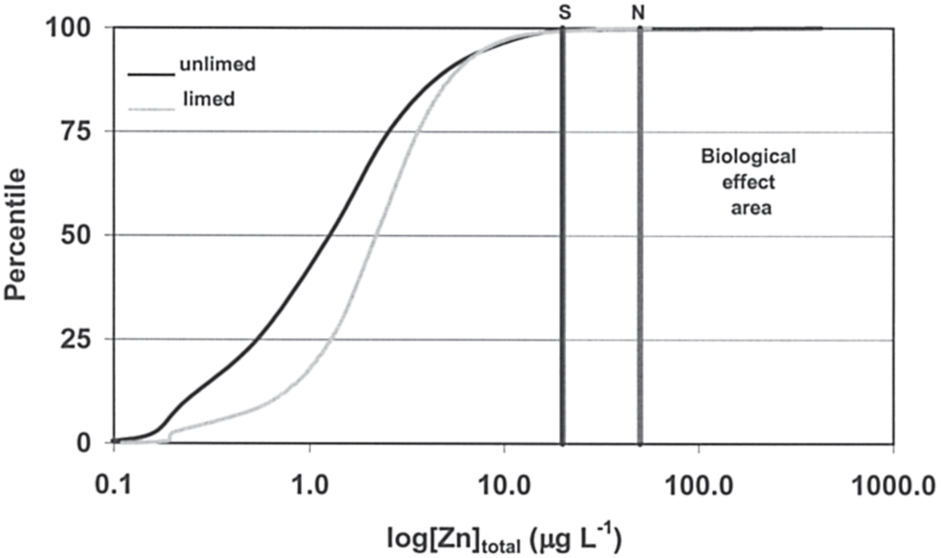


FIGURE 25. Percentile distribution of total Zn in limed (n=261) and not limed (n=820) Swedish lakes. S and N show the assessed critical concentrations for aquatic life in Norway and Sweden. (Data from Skjelkvaale et al. [1996, 1999].)

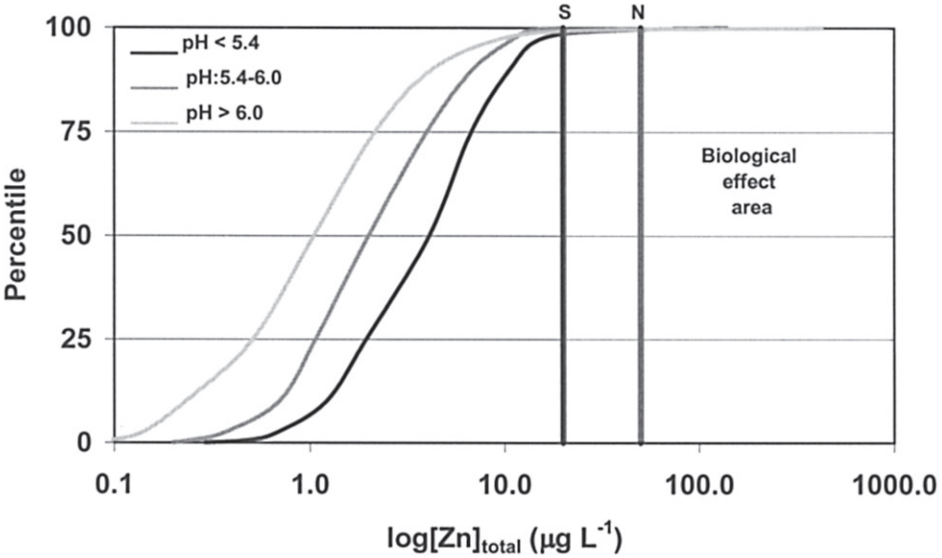


FIGURE 26. Percentile distribution of total Zn in Norwegian and Swedish lakes based on three pH classes. Data are from the Nordic Lake survey 1995. pH < 5.4,n=250; 5.4 ≤ pH <6.0, n=204; pH ≥ 6, n=1090. (Data from Skjelkvaale et al. [1996, 1999].)

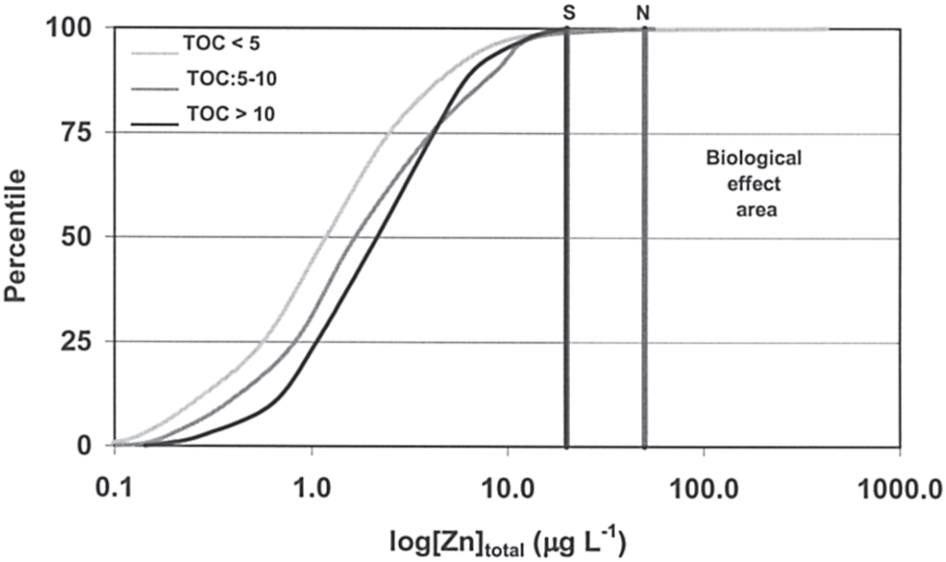


FIGURE 27. Percentile distribution of total Zn in Norwegian and Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥10, n = 202. (Data from Skjelkvaale et al. [1996, 1999].)

while the median concentration of limed Swedish lakes are the highest, that is, 2.20 µg Zn L^{-1} (Figure 25). The higher concentrations in limed Swedish lakes compared with nonlimed Swedish lakes is likely because many of the limed lakes were relatively acidic before limed and situated in southern and central Sweden where the Zn deposition has been high.

a. Experimental Acidification

Minor increases in mobilization of Zn from sediments (enclosure experiments) were recorded during the first months after the lake pH was lowered from 6.7 to 6.8 to pH 5.7 (Schindler et al. 1980). A decrease in pH to 5.1, however, resulted in an increase in Zn from 5 to 50 µg L^{-1} up to above 300 µg L^{-1}. Some high values in the control enclosures (80 to 90 µg Zn L^{-1}) indicated relatively high background concentrations of Zn at this site.

Kahl and Norton (1983) recorded a certain increase of Zn in water close to the sediments (from different depths) by acidifying the waters from pH 5.24 to 5.89 down to pH ≈ 5. However, by assuming two complete circulation periods during a year and a lake water residence time of 6 months, the Zn-enriched water will be diluted by the total lake volume twice a year. Accordingly, the lake concentration of Zn will only increase by maximum 1.3 µg Zn L^{-1}, that is, from 30 to 31.3 µg Zn L^{-1}. Accordingly, acidification down to pH 4.0 will contribute to a maximum increase of 4.9 µg Zn L^{-1}.

b. Liming

After liming of 20 lakes, most of them mildly acidic lakes, Marcus (1988) observed no significant changes in the concentration of Zn in 15 lakes, a significant decrease in 4 lakes, and an increase in 1. Evaluated together, there was a significant ($p \leq 0.05$) lower concentration of Zn after liming. The pre-limed mean concentrations of Zn ($n = 113$) was 30 μg L^{-1}, while the postlimed mean ($n = 112$) was ≈ 0 μg L^{-1}. Prelimed pH of the lakes varied from 4.44 to 6.99, with a mean pH of 5.51.

Liming of a low TOC lake in Canada (from pH 4.8 to about pH 7) reduced the concentration of Zn in lake water from 30 μg L^{-1} to 10 μg L^{-1} (White et al. 1984).

Liming of wetlands in *Dalarna*, Central Sweden, did not reduce the Zn concentration significantly ($p > 0.05$). Before liming the median Zn concentration was 5.3 μg L^{-1} in the outlet stream (see Section VII.F.2 and Table 25).

c. Reacidification

Concentrations of Zn increased from 10 μg Zn L^{-1} to 50 μg Zn L^{-1} during a 3-year reacidification period of a limed lake nearby Gothenburg, Sweden (Dickson et al. 1995). This lake was extremely acidic before limed (pH 4.0), and returned to pH 4.5 3 years after liming. In addition, the atmospheric deposition of Zn in this area was very high at that time (1977), that is, the concentration of Zn in snow pack was 180 μg Zn L^{-1}.

3. Biology and Toxicity

a. Toxic Species

Zn is an essential micronutrient involved in the enzymatic processes. Therefore, and within certain limits, the organisms can regulate uptake and removal of this element.

Within normal surface water pH, dissolved Zn consists primarily of the toxic aquo ion ($Zn(H_2O)_6^{2+}$) and some different organic and inorganic complexes. At high pH, other toxic species like $ZnCO_3$ and $ZnHCO_3^+$ and $ZnSO_4$ might be present to some extent, and at very high pH $Zn(OH)_4^-$ may form. The concentration of organic zinc complexes depends on the concentration of dissolved organic carbon present. Organic Zn complexes are likely not acute toxic, but they are relatively unstable, and may liberate Zn^{2+} due to dissociation under reducing conditions (Spear 1981) or by the substitution of other cations by cation exchange processes (Löfgren, 2001). Accordingly, Zn organic complexes may represent a potential toxic pool under extreme chemical changes when the metal is transformed to inorganic forms. This situation is similar for many organic bond heavy metals. The

Zn^{2+}-ion predominates over other dissolved species and is suspected of being most toxic. Because the aquo ion concentration decreases under conditions of high alkalinity, the bioavailability and toxicity of Zn to aquatic organisms are highest under conditions of low pH (low alkalinity). Furthermore, the toxicity and bioavailability increase by decreasing concentration of dissolved oxygen and elevated temperatures (Weatherly et al. 1980). Water hardness is the principal modifier of acute toxicity in acidic waters, because aquo Zn (Zn^{2+}) predominates and $ZnCO_3$ (also toxic) is low under acidic conditions.

The effects of excess zinc in natural resources are modified by numerous variables, especially by interactions with other chemicals. Interactions frequently produce radically altered patterns of accumulation, metabolism, and toxicity, some of which are beneficial to the organism, whereas others are harmful. Many factors modify the lethal properties of Zn to fish. Zinc is more toxic under conditions of comparatively low dissolved oxygen concentrations, high sodium concentrations, decreased loading of organic complexing agents (Spear 1981), and low pH. It is also shown that increased concentrations of other metals may both enhance or reduce the toxicity of zinc, as is also the case for many other metals. A high concentration of Zn may also have an antagonistic role in moderating the toxicity of other much more toxic metals. This was assumed by Lindeström (1988) who studied a mining-influenced Swedish lake with Zn, Cd, and Cu concentrations of 600 to 2000 μg Zn L^{-1}, 2 μg Cd L^{-1}, and 25 μg Cu L^{-1}, with a presumable normal fish and bentic invertebrate fauna.

b. Target

Zinc has its primary metabolic effect on zinc-dependent enzymes that regulate RNA and DNA. Low-molecular-weight proteins, metallothioneins, play an important role in zinc homeostasis and in the protection against zinc poisoning in animals. Zn is a potent inducer of metallothioneins. The pancreas and bone seem to be primary targets of zinc intoxication in birds and mammals, while gill epithelium is the primary target site in fish. Signs of Zn poisoning in fish include hyperactivity, followed by sluggishness. Before death, it is described that fish swim to the surface, were lethargic and uncoordinated, showed hemorrhaging at the gills and base of fins, shed scales, and had extensive body and gill mucus (Bengeri and Patil 1986). High metal precipitation within mucus and epithelial layers of the gills is assumed to be the main cause of Zn toxicity (Everall et al. 1989a,b). Thus, acute Zn poisoning in fish generally is attributed to the blockade of gas exchange across the gills, causing hypoxia at the tissue level. Tissue hypoxia in fish is a major physiological change before death once the gas exchange process at the gill is no longer sufficient to meet its oxygen requirements (Grobler et al. 1989). This mechanism may likely be similar even for other aquatic gill organisms.

Chronic exposure often leads to increased concentrations of Zn on the outer surface of bones (Joyner and Eisler 1961) and in the erythrocyte membranes (Bettger et al. 1987) and may affect the development of eggs and produce larvae with cellular disruption in the brain, muscle, and epidermis (Somasundaram 1985; Somasundaram et al. 1985).

c. Fish

Freshwater fish are more sensitive to Zn than marine species, and embryos and larvae are the most sensitive developmental stages.

Acute concentrations for fish are reported from Zn ≥ 66 μg L^{-1} (EPA 1987). Effects are lethal or sublethal for most species in the concentration range 50 to 325 μg Zn L^{-1}, but as low as 5 to 10 μg Zn L^{-1} has been reported (Sayer et al. 1989) for brown trout (*Salmo trutta*) in acidic waters (pH 4 to 6).

Limited tolerance was observed in freshwater fish preexposed to sublethal levels of Zn (Spear 1981; Heath 1987; Woodall et al. 1988; Anadu et al. 1989; Hobson and Birge 1989). In one case, rainbow trout acclimatised to 50 μg Zn L^{-1} for 21 days were as much as five times more tolerant to subsequent zinc exposures than nonacclimatized trout. This was, however, not the case if the fish were preexposed to 100 μg Zn L^{-1}. Acclimatization to zinc also produced tolerance to Cu and Cd in trout (Anadu et al. 1989). The mechanism to account for this phenomenon is unknown, but several theories are proposed. One is increased metallothionein synthesis (Woodall et al. 1988), although Hobson and Birge (1989) dispute this. Another theory claims that high mortality during preexposure may have caused the selection of more zinc-tolerant individuals (Spear 1981), and tolerance may be limited to strains capable of increased zinc excretion. There is good evidence that links exist between genetic mechanisms and metal resistance, particularly regarding different tolerances of acidic Al-rich water between brown trout strains (Dalziel et al. 1995).

Chronic effects may lead to significant adverse effects on growth, reproduction, and survival for sensitive freshwater species at nominal water concentrations between 10 to 25 μg Zn L^{-1} (Eisler 1993). Reproductive impairment seems to be one of the more sensitive indicators of zinc stress in freshwater teleosts, and effects are evident in the 50 to 340 μg Zn L^{-1} range (Spear 1981). In some cases, reproduction was almost totally inhibited at zinc concentrations that had no effect on survival, growth, and maturation of these same fish (Brungs 1979). Behavioral modifications, such as avoidance, are reported to occur as low as 5 to 6 μg Zn L^{-1} (EPA 1987).

d. Aquatic Invertebrates

Acute concentrations are reported for aquatic invertebrates from Zn ≥ 32 μg Zn L^{-1}. Arthropods are found to be the most zinc-sensitive groups among the many tested invertebrates (Eisler 1993). However, freshwater insects, including many species of mayflies, damselflies, stoneflies, and caddisflies, are relatively tolerant to Zn, with LC_{50} values usually > 1.33 mg Zn L^{-1}. Despite this, no species is adversely affected at concentrations between 30 to 37 µg Zn L^{-1}.

e. Bioaccumulation

Fish can accumulate zinc from both the surrounding medium and from their diet. In freshwater fish, bioconcentration values for whole invidious are reported between 51 and 500 times, but are strongly influenced by dose, duration of exposure, water chemistry, and several biological factors as species, life stage, and if the fish exposed have been starved or newly fed (see Eisler 1993). Bioamagnification through various trofic levels has not been reported.

f. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

It is very common that a large deviation exists between toxic values reported based on laboratory experiments and what is observed out in nature. Very often relatively higher critical concentrations are reported from nature compared with exposure experiments in laboratories. Effects are lethal or sublethal for most species in the range 50 to 325 µg Zn L^{-1}, but as low as 5 to 10 µg Zn L^{-1} is reported from laboratory experiments (Sayer et al. 1989). The classification system of Norwegian freshwaters primarily related to salmonids (Table 15) based on natural observations assess no effects on biota or no limitations for human consumption of fish at concentration < 30 µg Zn L^{-1}. Maximum annual acceptable 50 and 95 percentiles in concentrations of dissolved Zn (< 0.45 µm) for salmonids based on EIFAC criteria (Alabaster and Lloyd 1982) at a hardness of 10 mg $CaCO_3$ L^{-1} are 10 and 30 µg Zn L^{-1}. Lithner (1989) reported the lowest known effect at 15 µg Zn L^{-1}, while Alm et al. (1998) assumed risks of biological effects at 20 µg Zn L^{-1} in sensitive Swedish waters.

The critical concentrations of Zn in Norwegian and Swedish freshwaters are 50 µg Zn L^{-1} and 20 µg Zn L^{-1}, respectively (Table 16). According to the Nordic lake survey in 1995, only 0.7% of the Norwegian and nonlimed Swedish lakes, 1.1% of the limed Swedish lakes, and 0.6% of the Finnish lakes have Zn concentration above the critical concentration for surface water in Sweden, that is 20 µg Zn L^{-1}. Correspondingly, maximum 0.4% of all surveyed lakes in the three countries has higher Zn concentrations than the critical concentration in Norway (50 µg Zn L^{-1}). The median concentration of Zn in Nordic lakes is generally 10-fold lower than the assumed biological effect concentrations in Sweden.

Table 15. Classification system of Zn (µg L^{-1}) in Norwegian freshwaters primarily related to salmonids (UN-ECE 1997b). Class 1: No effects on biota or no limitations for human consumption of fish. Class 2: Some sensitive species may be affected, but no effects on fish. Little ecosystem effects. Class 3: Effects on salmonids, reduced number of species with a dominant of tolerate species. Class 4: No salmonids and serious effects also on many other species. The structure of the ecosystem is completely destroyed

Class 1 Very Low	**Class 2** Low	**Class 3** Medium	**Class 4** High
< 30 µg L^{1}	30 – 60 µg L^{1}	61 – 100 µg L^{1}	> 100 µg L^{1}

Table 16. Critical concentrations of Zn at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997); Sweden (Alm et al. 1998)

	Freshwater µg L^{-1}			Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
		Acute	Chronic			
The Netherlands	6.6			480	16	
United Kingdom[1]	8 - 50					
Germany[2]		120	110			
EU[1]	30					
Canada	30			123	200	
Sweden	**20**			**1050**		
Denmark	110				100	
Norway	**50**					
Finland					90	

[1] Range means that values depend on water hardness; [2] Hardness dependent criteria (100 mg $CaCO_3$ L^{-1} is used).

A proposed effect-related sediment criteria for heavy metals in Canada (Smith et al. 1996) assume a biological effect level of Zn in sediments at 315 mg kg^{-1} dw.

4. Reacidification — Biological Risk

We might assume only minor changes in concentrations of Zn during reacidification of limed water bodies. In low TOC lake small effects will likely occur if the reacidified water pH is > 5.0. Increases in total Zn may occur at higher pH in higher TOC lakes, but because the Zn-organic complexes likely will predominate even in the reacidifed water body, we should not expect serious biological effects due to altered Zn concentration and changes in Zn species when most limed water bodies reacidify. Because Zn also seems to be relatively mobile in acid soil and surface waters, the catchment pool of easily mobile Zn in acid rain-impacted areas is likely relatively small. Although laboratory experiments suggest that some trace metals could be remobilized from lake sediments at low pH, field studies indicate that sediment porewaters are not sufficiently acidic for metal remobilization to occur (Nelson and Campbell 1991). In addition, the atmospheric deposition of Zn has decreased significantly during the last decade. In Norway, Zn in wet-deposition has decreased by 70% from 1978 to 1996 (Toerseth and Manoe 1997), and by 23 to 35% since 1984 in southwestern Sweden (see Section V.A). Furthermore, the concentration of Zn in most surface waters surveyed in Scandinavia shows concentrations far below critical loads. Thus, changes in the concentration or speciation of Zn due to reacidification will not cause any effect on aquatic life in almost all Scandinavian lakes.

E. Cadmium (Cd)

1. General Geochemistry

a. Sources

Cadmium (Cd) is a relatively rare metal, usually present in small amounts in zinc ores (due to many chemical similarities with Zn), and is commercially obtained as an industrial byproduct of the production of Zn, Cu, and Pb. Major uses of Cd are electroplating, in pigment production, and in the manufacture of plastic stabilisers and batteries. Anthropogenic sources of Cd includes smelter fumes and dust, the products of incineration of Cd-bearing materials and fossil fuels, fertilizers, limestone (due to liming of different ecosystems), and municipal wastewater and sludge discharge. Concentrations are most likely highest in the localized regions of smelters or in urban areas (Hammons et al. 1978; Hutton 1983), but also in areas highly affected by long-range transported air pollutants. Even so, human activity has not, at present, had a measurable impact on the global, or even hemispheric cycling of the metal. This is in marked contrast to lead, where human activities have enhanced lead concentrations in recent ice cores from Greenland and the Antarctic, as well as in surface waters from mid-ocean sampling locations (Zoller 1984). However, Cd emissions from anthropogenic sources may still make a significant contribution to the overall atmospheric burden of Cd at local and regional scales. The size of the particles involved in Cd transport is one key factor in determining local accumulations.

Volcanic action is considered to be a major natural source of atmospheric Cd. Other natural sources include ocean sprays, forest fires, and the release of metals-enriched particles from terrestrial vegetation. These sources are difficult to quantify. Only in the case of release from vegetation are the quantities likely to be significant on a global scale. Also, certain carboniferous shales found in various parts of the world are enriched with Cd.

An investigation of 360 samples from the moor layer of Swedish forest soils showed Cd concentrations within the range 0.19 to 3.05 mg kg^{-1} dw, with a median concentration of 0.64 mg kg^{-1} dw. The Cd concentrations exhibited a north-south gradient with higher levels in the south. Elevated levels were also found around the metal smelter in Rönnskär at the northeastern coast. This geographical gradient was even more pronounced in the Zn content (Andersson et al. 1991). A similar survey in 1981 of 841 localities in southern Norway showed large influence by long-range atmospheric transport. The general level of Cd in Norwegian soils is about 0.2 mg kg^{-1} dw in the humus layer (Steinnes et al. 1989).

In soils, Cd forms relatively stable complexes with dissolved organic acids in the A horizon. However, the Cd leached from soils is to a large extent originating from the mineral phase in the B horizon. The leaching from this layer is very susceptible to changes in the soil acidity, with larger amounts lost at lower pH (Bergkvist et al. 1987). Mass balance calculations indicate that Cd is lost at significant quantities from acidic forest soils (Bergkvist et al. 1987), but almost balanced Cd fluxes have also been reported (Aastrup et al. 1995a).

Scandinavian moss analysis in 1995 showed a marked south-north concentration gradient of Cd, reflecting a significant contribution from long-range transport. Elevated Cd concentrations were also found in the vicinity of large point sources such as the metal smelters in Rönnskär (Sweden) and Odda (Norway) and in pronounced agricultural areas. In areas not affected by local pollution in southern and northern Scandinavia, the Cd concentration in moss was approximately 0.3 and 0.2 mg kg^{-1} dw, respectively (Rühling et al. 1996). In Norway, Cd in wet deposition has decreased by 50 to 80% from 1978 to 1996 (Toerseth and Manoe 1997). In Sweden Cd concentration in wet deposition has decreased by 25 to 53% during 1984 to 1996.

In groundwater in Sweden, the median Cd concentration is 0.03 µg L^{-1} (Ledin et al. 1989), which is higher than for running waters (0.01 µg L^{-1}, Alm et al. 1998) and lakes (0.01 µg L^{-1}, see below). The median background concentration in groundwaters (pH>6) is considered to be 0.002 μg L^{-1}, but the concentration range is large (0.003 to 0.1 μg L^{-1}) due to differences in Cd content in soils and bedrock (Ledin et al. 1989). The Cd concentration in groundwater varies with pH, with higher levels at pH<5. Median concentration at pH<5 is 0.10 μg L^{-1}, compared with 0.003 μg L^{-1} in the pH intervals 5 to 8 (Aastrup et al. 1995b).

Based on studies in relatively few unpolluted lakes (n = 133), the sediment Cd concentrations varied between 1.6 to 5.0, 0.6 to 2.6, and 0.2 to 1.7 g Cd kg^{-1} dw (10 to 90 percentiles) in southern, central, and northern Sweden, respectively (Alm et al. 1998). In northern Sweden, the concentrations are close to the natural background levels (Johansson 1989). Decreased metal concentrations toward the sediment surface in acidified lakes may be attributed to a reduced metal sedimentation due to reduced adsorption on precipitating particles or desorption or dissolution from already sedimented materials (Dauvalter 1995). Laboratory studies on the long-term, pH-induced release of metals from the sediments to overlaying water indicate that the sediments can retain Cd at pH>4 (Arafat and Nriagu 1986).

Reported background levels of Cd in uncontaminated surface water range from ≈ 0 to 0.2 μg Cd L^{-1}. According to Moore and Ramamoorthy (1984), the level of dissolved Cd in freshwaters generally ranges from 0.01 to 0.5 μg Cd L^{-1}.

b. Chemical Properties

Cd is only present as a divalent cation, and in low alkalinity freshwater systems, the free aquo ion, Cd^{2+}, predominates across the pH range 4.5 to 7.0 (Figure 28), while in higher alkalinity water the $CdCO_3$ complex is also of major importance. In high-salinity water (like in seawater), chloride complexes predominate, and both uncharged negatively and positively charged complexes are present in significant amounts (Turner 1987). While zinc oxide/hydroxide is acidic, Cd oxides/hydroxide are alkaline, and the Cd oxides are not soluble at high pH like the amphoteric Zn and Al oxides/hydroxides.

Adsorption and desorption processes are likely to be major factors controlling the concentration of Cd in natural waters and tend to counteract changes in the concentration of Cd ions in solution. Adsorption and desorption rates of Cd are generally rapid on clay, silica, and humic material. Low pH and high E_h (Khalid et al. 1981) as well as high concentrations of dissolved organic matter (Gardiner 1974) all contribute to increased Cd mobility in low ionic surface waters. The dominant dissolved form of Cd in low organic surface waters are the free and bioavailable Cd^{2+} ion, but in organic-rich surface waters the comparatively nonbioavailable Cd organic complexes may contribute a significant portion of dissolved Cd (Figure 28).

Besides Cd organic precipitates, $CdCO_3$ may contribute a major part of Cd in sediments. Under anoxic conditions CdS may form, and this sulfide complex has a very low solubility, much lower than the corresponding ZnS. Accordingly,

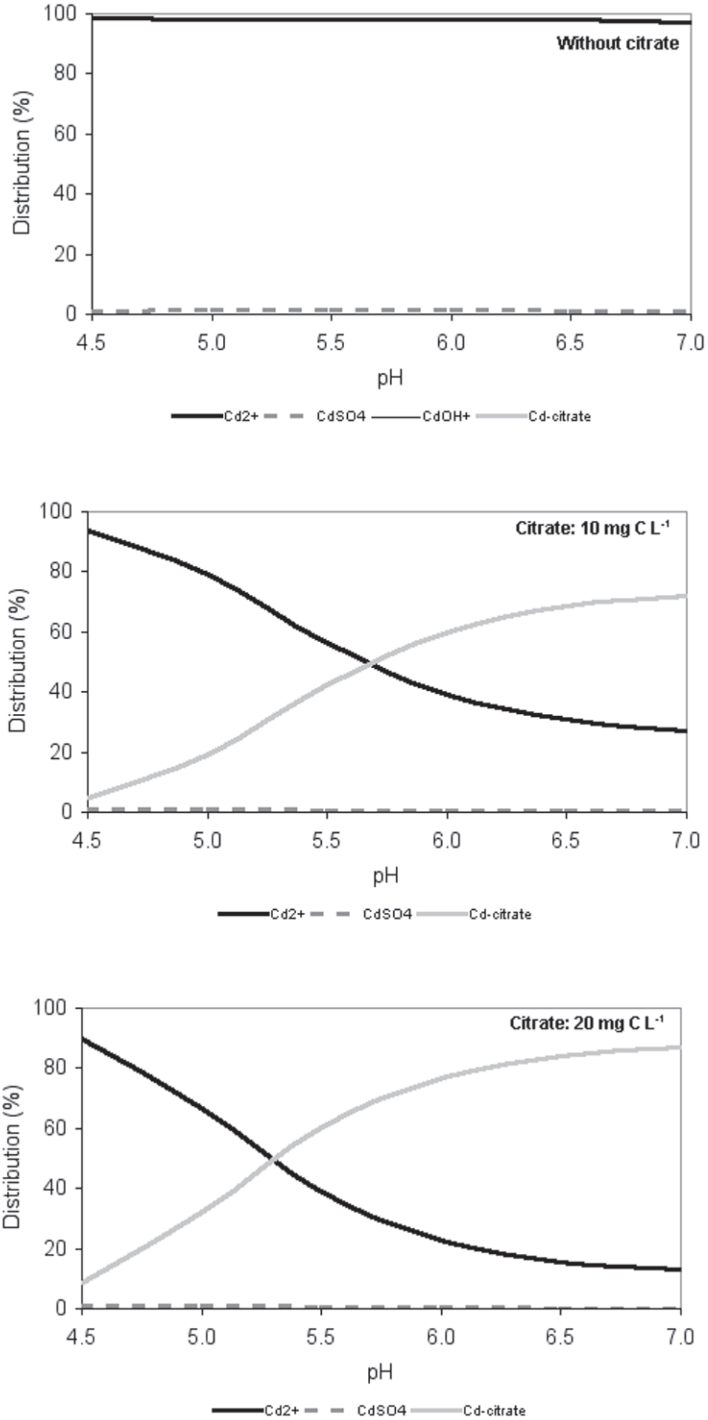


FIGURE 28. Distribution of major Cd species in relation to pH at citrate concentrations of 0, 10 and 20 mg C L^{-1}. Essential input conditions: CO_2 and O_2 at equilibrium with partial pressure of air. [Cd]: 0.05 μmol L^{-1}: [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 μg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

during anaerobic conditions, like in the hypolimnion of many lakes, a marked decrease in the dissolved fraction may occur, with a corresponding increase in the suspended fractions (Shepard et al. 1980).

It is possible that significant amounts of Cd are transferred from the sediments into rooted aquatic macrophytes and later released into the water after macrophyte death, particularly in heavily contaminated systems (Mc Intosh et al. 1978).

2. Cadmium in Surface Water Systems

Cadmium concentrations in Sweden, Norway, and Finland are generally low (see Tables 17 and 18). In Finland, the highest concentrations of Cd are often found along the Finnish west coast in acid waters with relatively high ionic strength, and often with a significant positive relationship between Cd and Zn (Tarvainen et al. 1997). Johanson et al. (1995a) found a gradually decreasing concentrations of heavy metals, including Cd, toward the north in Sweden. Combinations of atmospheric input and soil acidification are the two major factors determining the Cd levels in Finnish (Verta et al. 1990) and Swedish surface waters (Borg 1983; Borg 1987; Johansson 1995a,b). Borg and Andersson (1984) reported a significant

Table 17. Concentrations of Cd (μg Cd L^{-1}) in Nordic surface waters and in the Czech Republic. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	152	6	0.03 – 0.13	0.04
Finland south[2]	89	n.r.	n.r. – 0.13	0.03 ± 0.03
Finland, north[2]	104	n.r.	n.r. – 0.13	0.02 ± 0.02
Sweden, south[3]	19	n.r.	0.005 – 0.12	0.04 ± 0.03
Sweden, north[3]	16	n.r.	0.004 – 0.09	0.04 ± 0.03
Sweden, east[4]	12	n.r.	0.029 – 0.11	0.06 ± 0.03
Sweden, s.east[4]	27	n.r.	0.009 – 0.094	0.04 ± 0.02
Sweden, s.west[4]	9	n.r.	0.005 - 0.12	0.04 ± 0.04
Sweden, north[5]	56	n.r.	0.007 – 0.036	0.014
Czech[6]	5363	n.r	n.r.	0.04

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

[2] Verta et al. (1990), based on samples from autumn 1987.

[3] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden, south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[4] Borg and Andersson (1984), oligotrophic forest lakes, sampled during 1980-1983. East: lakes south of Stockholm, TOC: 7.4 ± 2.0 mg C L-1, pH: 5.1 - 6.9; S.east: Småland, TOC: 6.6 ± 2.8 mg C L-1, pH: 4.6 - 6.7. TOC: 7.4 ± 2.0 mg C L-1, pH: 5.1 - 6.9; S.west: Halland/Småland, TOC: 10 ± 4.6 mg C L-1, pH: 4.7 - 6.5.

[5] Borg (1987) based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

[6] Vesely and Majer (1996), based on data collected between 1984 and 1992.

Table 18. Percentile distribution of Cd (μg Cd L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462

Cd	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	1.072	0.540	0.271	0.230
	99.5 %	0.174	0.310	0.257	0.085
	97.5 %	0.114	0.167	0.096	0.030
	90.0 %	0.058	0.055	0.045	0.030
Quartile	75.0 %	0.030	0.022	0.024	0.020
Median	50.0 %	0.014	0.010	0.013	0.011
Quartile	25.0 %	0.007	0.005	0.008	0.006
	10.0 %	0.004	0.003	0.005	0.003
	2.5 %	0.002	0.001	0.003	0.002
	0.5 %	0.001	0.001	0.002	0.001
Minimum	0.0 %	0.000	0.001	0.001	0.001

negative correlation between pH and Cd concentrations in Swedish lakes, but this pH relationship was found to be less evident in northern Swedish water courses (Johansson et al. 1995b). Johansson et al. (1995b) further documented large differences in the concentrations of Cd between rivers and streams in southern and northern Sweden. In northern Swedish streams, the concentration of Cd (and Zn) was about half the concentrations present in southern streams at same pH level, and also somewhat lower in the northern rivers compared with southern rivers. They also documented higher concentrations and larger concentration variations in streams compared with rivers, which also should be expected.

The higher concentrations of aqueous Cd often observed in many acidified lakes may be a result of decreased removal of atmospherically deposited metals from the water column by sedimentation at low pH (Dillon et al. 1984; Borg et al. 1989). A literature review by Nelson and Campbell (1991) also concluded that the decreased retention of Cd in acidic lakes appears to be due to a decrease in sedimentation, rather than Cd remobilization from the sediments. A diffusive flux could contribute to the subsurface maximum in Cd concentrations often observed in sediments from acidified lakes. Borg and Johansson (1989) compiled data from regional surveys of atmospheric deposition, terrestrial runoff, and soils to estimate metal budgets for a hypothetical Swedish lake. They calculated that 70 to 95% of Cd leaves the catchment by runoff. Accordingly, for lakes with high catchment/ lake surface area, the catchment may contribute to the majority of Cd to the lake: further the retention time of Cd is short, which means that Cd has low ability of accumulate, at least in acidic soils. They further concluded that the main source of Cd from the catchment derives from atmospheric deposits. Accordingly, it is highly important that the Cd deposition has decreased significantly during the last decade.

The trofic status of lakes may further influence metal availability, because typically oligotrofic lakes have lower sedimentation rates than the more productive lakes.

Young and Harvey (1992) found that 50 to 75% of leachable Cd from sediments were adsorbed to oxides of Fe in acidic lakes, while 40 to 60% was in this fraction in lakes at circumneutral pH. Furthermore, 25% of leachable Cd was present in the organic fraction in acidic lakes, while 10 to 20% was present in that fraction in lakes of circumneutral pH. Williams (1993) showed that dissolution of Cd (and Zn) from sediments increased at low pH. Stepwise artificial acidification of a lake from 6.1 to 5.6, 5.5, and 4.6 showed no effect on the concentration of dissolved Cd (Mach and Brezonik 1989). Regarding remobilization from sediments, the reacidification pH is essential. Thus, it is of interest that LaZerte (1986) concluded that once Cd is deposited it is not readily released from aerobic sediments, except at very high acidity, $\text{pH} < 4.0$. Borg and Andersson (1984) found that the major part of Cd was present in a dialyzable fraction ($\text{MW} < 2.4$ nm), 60 to 100% at pH 6.0 to 4.5, 10 to 60% at pH 7.0 to 6.0. The concentration of dialyzable Cd was negatively correlated with pH, while no such correlation was found for TOC.

Borg (1987) found that higher concentrations of Cd normally are present during winter-time compared to summer-time, and explained this by higher sedimentation rates during the summer.

The highest Cd concentration recorded by Johansson et al. (1995b) was about 0.1 μg Cd L^{-1}, within a pH variation range 4.0 to 7.5, based on > 2000 samples collected from 23 large rivers and 13 small streams in Sweden during 1990. The highest concentration recorded during the Nordic surveys (Table 18) were 0.23 μg Cd L^{-1} in Finland, 0.54 μg Cd L^{-1} in nonlimed Swedish lakes, 0.27 μg Cd L^{-1} in limed Swedish lakes and 1.07 μg Cd L^{-1} in Norwegian lakes. However, almost all investigated lakes (>95%) fell into the following categories: *Very low* to *Medium* according the Norwegian and Swedish classification systems (Table 19).

Table 19. Classification of concentrations of Cd in surface waters (μg L^{-1}), the upper (0 to 1 cm) of lake sediments (mg kg^{-1} dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Cd (Sweden, 1991)	≤ 0.01	0.01 - 0.05	0.05 - 0.1	0.1 - 0.3	> 0.3
Cd (Sweden, 1998)[1]	≤ 0.01	0.01 - 0.1	0.1 - 0.3	0.3 - 1.5	> 1.5
Cd (Sweden, 1998)[2]	≤ 0.005	0.005 - 0.03	0.03 - 0.06	0.06 - 0.6	> 0.6
Cd (Norway, 1997)	< 0.04	0.04 - 0.1	0.1 - 0.2	0.2 - 0.4	> 0.4
Sediment					
Cd (Sweden, 1991)	≤ 0.2	0.2 - 0.7	0.7 - 2.0	2 - 5	> 5
Cd (Sweden, 1998)[3]	≤ 0.8	0.8 - 2.0	2.0 - 7	7 - 35	> 35
Cd (Norway, 1997)	< 0.5	0.5 - 2.5	2.5 - 10	10 - 20	> 20

[1] Based on risks of biological effects.

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96).

[3] Based on distribution in Swedish lakes with and without local emissions.

By dividing the 1995 surveyed Nordic lakes into TOC and pH classes, it is clear that pH plays an important role for the concentration of Cd in surface waters (see Figures 29 and 31), most likely due to the link between high atmospheric inputs of strong acids and Cd and low surface water pH. For Norwegian and Swedish lakes with pH < 5.4, median Cd concentration is 0.030 μg Cd L^{-1}, while the corresponding concentrations in pH class: 5.4 to 6.0 and pH class > 6 are 0.014 and 0.010 μg Cd L^{-1}, respectively. Thus, because Norway has the highest number of acidic lakes and also the largest area of strong acid rain impact, it is expected that Norwegian lakes generally have the highest Cd concentrations (Table 18). Based on the regional survey in 1995, the median concentrations of Cd in Norway, Sweden, and Finland are 0.014, 0.010, and 0.011 μg Cd L^{-1}, respectively, while the median concentration in limed Swedish lakes is 0.013 μg Cd L^{-1} (Figure 30). The higher concentrations in limed lakes compared with nonlimed Swedish lakes is likely because many of the former lakes were relatively acidic before treated.

The concentration of TOC in lakes seem to have minor to no effects on the Cd levels in surface waters (Figure 32). As for Zn local geology influences the concentrations in several surface waters.

a. Experimental Acidification

The experimental lake acidification reported by Brezonik et al. (1993) showed a high negative correlation between Cd (and Zn) and pH. Like Zn, Cd is associated primarily with ion-exchangeable fractions, and thus relatively sensitive to pH changes. Accordingly, concentrations of Cd should also be sensitive to episodic ionic strength variations (sea salt episodes), especially under acidic conditions. Elevated concentrations of Cd have been documented in small streams in southern Sweden, caused by ion exchange in soils due to deicing salt applications on roads (Löfgren, 2001).

b. Liming

Liming of a forested catchment in Norway so far has shown minor changes in heavy metals in runoff, including Cd (Atle Hindar, personal communication). Liming of a wetland in Dalarna, Central Sweden, did not reduce the Cd concentration significantly ($p > 0.05$). Before liming the median Cd concentration was 0.029 μg Cd L^{-1} in the outlet stream (see Section VII.F.2 and Table, 25).

c. Reacidification

The concentration of Cd increased from 0.05 μg Cd L^{-1} to 0.4 μg Cd L^{-1} during a 3-year reacidification period of a limed lake nearby Gothenburg, Sweden (Dickson

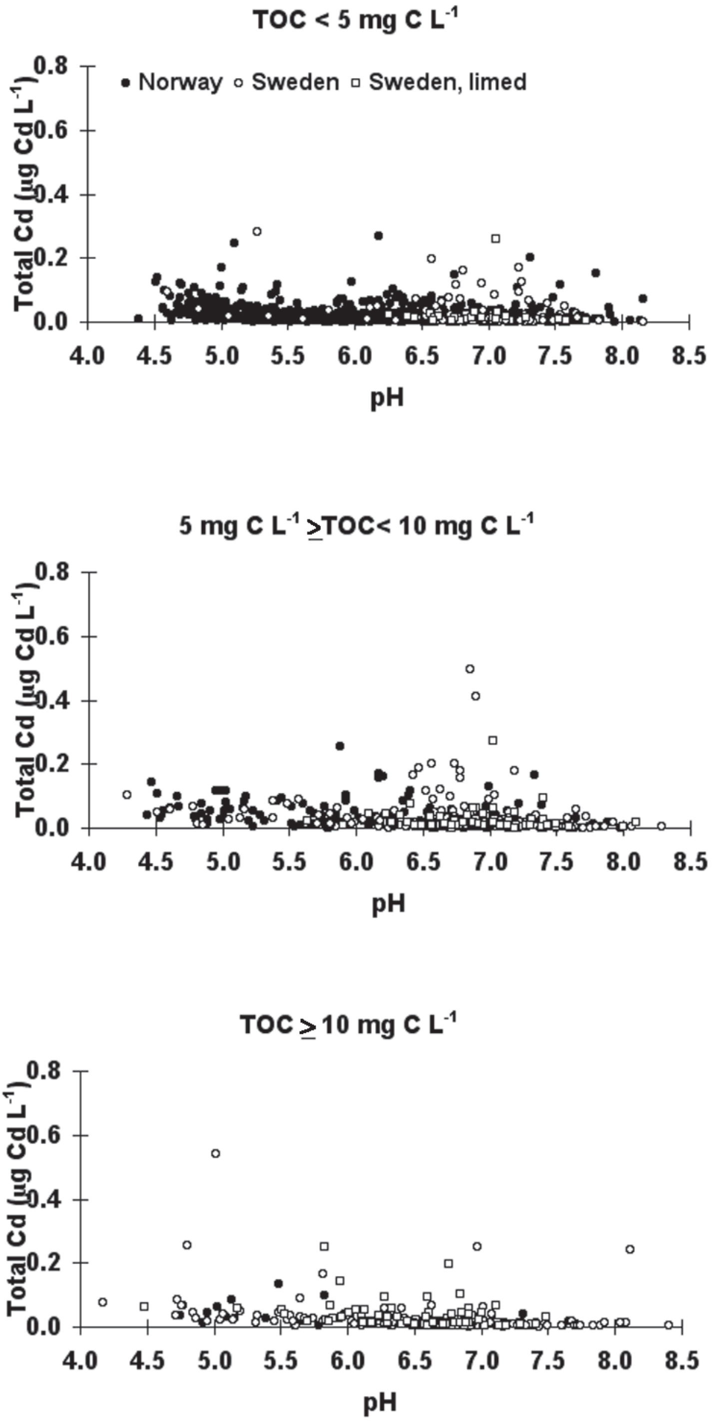


FIGURE 29. Total concentration of cadmium in Norwegian and Swedish (non-limed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

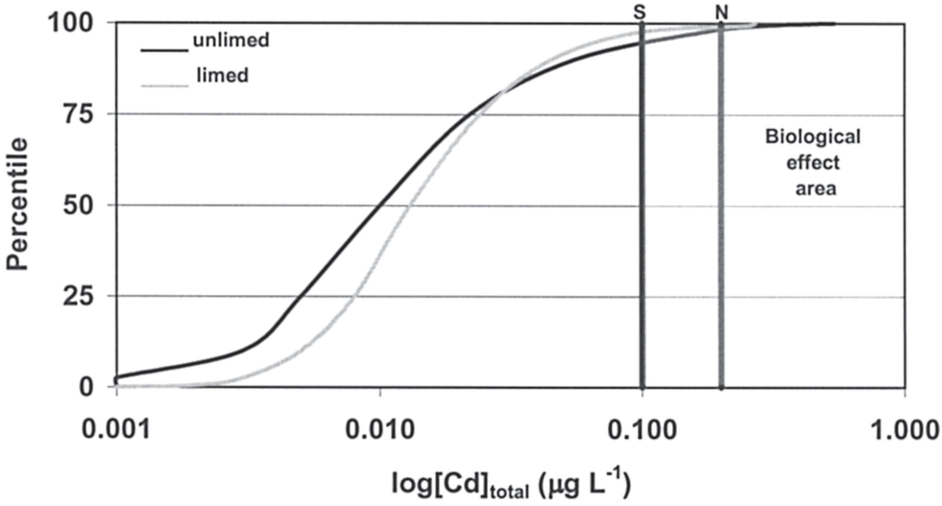


FIGURE 30. Percentile distribution of total Cd in limed (n = 261) and not limed (n = 820) Swedish lakes. S and N show the assessed critical concentrations for aquatic life in Norway and Sweden. (Data from Skjelkvaale et al. [1996, 1999].)

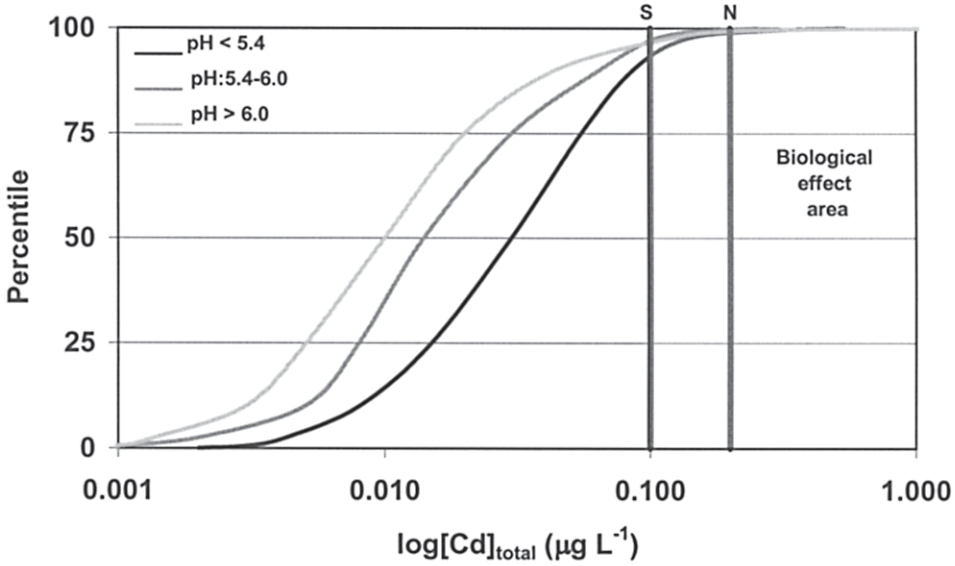


FIGURE 31. Percentile distribution of total Cd in Norwegian and Swedish lakes based on three pH classes. pH < 5.4, n = 250; 5.4 ≤ pH < 6.0, n = 204; pH ≥ 6, n = 1090. (Data from Skjelkvaale *et al*. [1996, 1999].)

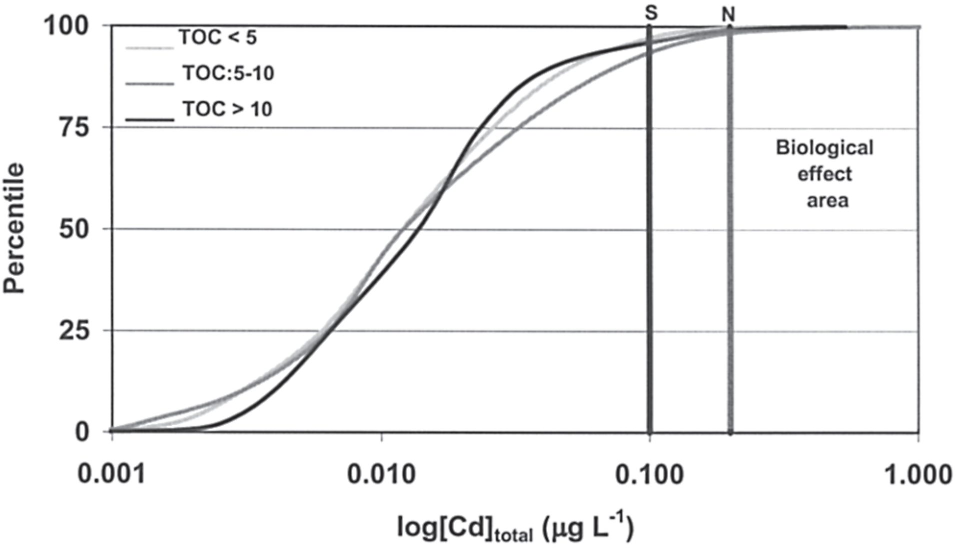


FIGURE 32. Percentile distribution of total Cd in Norwegian and Swedish lakes based on three TOC classes (TOC: mg C L^{-1}). TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale *et al.* [1996, 1999].)

et al. 1995). This lake was extremely acidic before limed (pH 4.0), and returned to pH 4.5 3 years after liming. In 1977 the concentration of Cd in the snowpack from this area was measured to be 1.4 µg Cd L^{-1}, documenting highly air-polluted conditions. Thus, these data are very extreme, and cessation of liming in such lakes is not recommended.

3. Biology and Toxicity

a. Toxic Species

The availability of Cd to living organisms depends on numerous factors, including adsorption desorption rates, pH, E_h, and the concentrations modifying compounds, like other cations (including other heavy metals) and organic complexes.

The dominant inorganic form of cadmium at low ionic strength within actual pH 4.5 to 7.0 is the free readily available Cd^{2+} ion. The inorganic Cd^{2+} have acute toxic effects, but might also bioaccumulate under chronic exposure. Organic Cd complexes, which are comparatively nonbioavailable, make up the other significant fraction of total dissolved Cd. Organic Cd complexes are likely not acute toxic, but they are relatively unstable and may liberate Cd^{2+} by the substitution of other cations by cation exchange processes (Löfgren, 2001). Accordingly, Cd organic complexes may represent a potential toxic pool under extreme chemical changes when the metal is transformed into inorganic forms. This situation is similar for many organic bond heavy metals.

b. Target

The exact mechanism of acute Cd poisoning is unknown, but among teleosts it depends in part of exposure period, concentration on Cd, the water temperature, and salinity (e.g., Hughes 1973; Chapman 1978; Chapman and Stevens 1978; Finlayson and Verrue 1982; Roch and Maly 1979). Because Cd concentrations are at highest on gills during short exposures, the gills seem to be the primary site of damage and accumulation. This is the same acute toxicity pattern as reported for many metals.

The bioconcentration factor (BCF) of Cd (and Pb) by fish typically increases with increasing exposure concentration in water. Under conditions of low Cd concentrations and prolonged exposure, the concentration of Cd on liver and kidney is shown to gradually increase. Roberts et al. (1979) found a (BCF) of 260 for gills, 17 for liver, and 26 for kidney after 2 weeks exposure to 9 μg Cd L^{-1}. At slightly higher ambient Cd levels (10 μg Cd L^{-1}) and exposure for 3 months, the BCF values were substantially higher: 1740 for gill, 4900 for liver, and 740 for kidney. Besides accumulation in kidney and liver, accumulation in the gastrointestinal tract has been reported (Benoit et al. 1976; Harrisson and Klaverkamp 1989; Norey et al. 1990). The degree of bioaccumulation may locally show large individual variations within a water system, often associated with proximity to industrial and urban areas, or point sources.

Biomagnification through various trofic levels suggests that only the lower trofic levels exhibit biomagnification, while fish showed no or much less change in body burden when fed on Cd-contaminated cladocerans for 4 days (Ferard et al. 1983). Later studies conclude that unlike Hg, Cd, and Pb do not biomagnify in aquatic foodwebs (e.g., Campbell and Stokes 1985; Hodson 1986). This may indicate that the major Cd source is aqueous Cd, not through the diet.

Where mechanisms of acclimation to metals have been explored, induction of the protein metallothionein is the most commonly invoked mechanism. This protein is involved with the metabolism of the essential metals Zn and Cu. The ability of metallothionein to bind metals in group Ib (Cu, Ag) and IIb (Zn, Cd, Hg) might play some role in acclimation, but even this is unclear (Hamilton et al. 1987a,b). Roch et al. (1986) used hepatic metallothionein to predict a no-effect concentration for Cd of < 0.2 μg L^{-1} for rainbow trout in a mixture of Zn, Cu, and Cd at a hardness of 25 mg Ca L^{-1} (as $CaCO_3$). Aqueous Cd concentrations in low-alkalinity lakes are normally less than the maximal no-effect concentration of 0.2 μg Cd L^{-1}.

c. Fish

As with many other metals, salmonids seem to be the most sensitive taxonomic group (family) to cadmium in freshwater, but data are not sufficient to rank other taxa. Acute toxic levels of Cd in low ionic waters normally range from 0.5 to 3.0 μg Cd L^{-1}. A single study by Cusimano et al. (1986) indicated that the toxicity of aqueous Cd decreased significantly by decreasing pH, that is, LC_{50} at < 0.5 μg Cd L^{-1} at pH 7, 0.7 μg Cd L^{-1} at pH 5.7, and 28 μg Cd L^{-1} at pH 4.7. Brezonik et al. (1993) showed less Cd on fish gills and fish tissue of yellow perch (*Perca flavescens*) in an acidified basin compared with the control basin.

When the concentration of aqueous Cd is high and acute toxicity occurs, the toxic mechanism is gill damage, as for most other inorganic free metal ions. Cadmium, however, has a systemic mode of action at lower Cd concentrations, producing hyperactivity and eventual muscle tetanus (Benoit et al. 1976; Roch and Maly 1979).

Chronic tests with several fishes indicate that the chronic effect concentrations are very similar to the LC_{50} values. The survival and growth of early life stages, exposed for periods as long as 60 days, indicate that effect or maximum acceptable toxicant concentrations range from about 0.40 to 6.7 μg Cd L^{-1} for salmonids and higher for other fishes tested. Atlantic salmon (*Salmo salar*) exposed to soft water showed decreased growth when exposed to 0.47 μg Cd L^{-1} (Rombough and Garside 1982). When eggs of Atlantic salmon was exposed to 1 to 5 μg Cd L^{-1}, the mortality was slightly higher compared with fish exposed to Cd-free control water across the pH range 4.5 to 6.8 (Peterson et al. 1985). The accumulation of Cd by eggs was 10-fold higher at pH 6.8 water compared with pH 4.5 water. The relationship between pH and Cd accumulation was complex, however, because newly hatched fry had higher Cd concentrations at pH = 4.5 and 5.0 than at pH 6.8.

The reported concentrations of aqueous Cd that produce biochemical effects are highly variable, and often higher than concentrations that cause acute lethality. The lowest reported concentrations of aqueous Cd causing biochemical changes is about 1 μg Cd L^{-1}, which resulted in altered cycling of sex steroids and premature testicular regression in brook trout of soft water (Sangalang and Freeman 1974). Why often higher Cd concentration is reported to have chronic effects than the acute Cd concentration should be good evidence for a certain adaptation, at least to relatively low Cd concentrations.

d. Invertebrates

Acute toxicity of Cd to freshwater invertebrates normally range from 7 to 34,600 μg Cd L^{-1}. Cladoceran are particularly sensitive to Cd. Chronic effects have been documented in the concentration area 0.28 to 3.0 μg Cd L^{-1}, both in the laboratory (Biesinger and Christensen 1972; Chapman et al. 1980) and in the field (e.g., Marshall et al. 1981, 1983; Lawrence and Holoka 1987; Winner 1988). Chronic effects are reduced growth and survival.

Available data suggest that the Cd accumulation in invertebrates undergoes biphasic response to water pH. Decreasing pH from approximately 7.0 to 5.5 increases Cd uptake, while a further decrease below pH 5.5 reduces Cd uptake. Cd toxicity is markedly reduced in the presence of organic complexing material. Low hardness increases the toxicity, but low pH generally reduces the Cd toxicity both to invertebrates and other aquatic biota.

e. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

The classification system of Norwegian freshwaters primarily related to salmonids (Table 20) based on natural observations, assess no effects on biota or no limitations for human consumption of fish at concentration < 0.2 μg Cd L^{-1}. Maximum annual acceptable 50 and 95 percentiles in concentrations of dissolved Cd (< 0.45 μm) for salmonids based on EIFAC criteria (Alabaster and Lloyd 1982) at a hardness of 10 mg $CaCO_3$ L^{-1} are 0.3 and 0.6 μg Cd L^{-1}. Lithner (1989) reported lowest known effect at 0.1 μg Cd L^{-1}.

The critical concentrations of Cd in Norwegian and Swedish freshwater are relatively similar, that is, 0.2 μg Cd L^{-1} in Norway and 0.1 μg Cd L^{-1} in Sweden (Table 21). According to the Nordic lake survey in 1995, 3.4% of the Norwegian, 4.5% of the nonlimed Swedish, 2.3% of the limed Swedish, and 0.6% of the Finnish lakes have Cd concentration above the critical concentration for surface water in Sweden. Correspondingly, only 0.5% (Norway), 1.4% (nonlimed Sweden), 1.1% (limed Sweden), and 0.2% (Finland) have higher Cd concentrations than the critical concentration in Norway. However, 4.5% and 2.3% of nonlimed and limed Swedish lakes have Cd concentrations higher than the biological effect concentrations for Sweden, while about 50% of all Swedish lakes have 10-fold lower concentration than the biological effect concentration.

Table 20. Table classification system of Cd (μg L^{-1}) in Norwegian freshwaters primarily related to salmonids (UN-ECE 1997b). Class 1: No effects on biota or no limitations for human consumption of fish. Class 2: Some sensitive species may be affected, but no effects on fish. Little ecosystem effects. Class 3: Effects on salmonids, reduced number of species with a dominant of tolerate species. Class 4: No salmonids and serious effects also on many other species. The structure of the ecosystem is completely destroyed

Class 1 Very Low	**Class 2** Low	**Class 3** Medium	**Class 4** High
< 0.2	0.2 - 0.5	0.6 – 1	> 1

Table 21. Critical concentrations of Cd (µg L^{-1}) at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997), Sweden (Alm et al. 1998)

	Freshwater µg L^{-1}			Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
		Acute	Chronic			
The Netherlands	0.34			29	0.76	0.05
United Kingdom[1]					3	
Germany[2]		3.9	1.1			
EU[1]	1.0					
Canada[1]	0.2 - 1.8			0.6	1.4	
Sweden	**0.1**			**2.4**		
Denmark	5				0.3	
Norway	**0.2**					
Finland					0.3	

[1] Range means that values depend on water hardness; [2] Hardness dependent criteria (100 mg $CaCO3\ L^{-1}$ is used).

A proposed effect-related sediment criteria for heavy metals in Canada (Smith et al. 1996) assume a biological effect level of Cd in sediments at 3.5 mg kg^{-1}dw, while the national critical concentrations for Canada and Sweden are 0.6 and 2.4 mg kg^{-1} dw, respectively (Table 21).

4. Reacidification — Biological Risk

The main toxic Cd form in freshwaters is the aqueous free metal ion Cd^{2+}. This ion is the only important inorganic species across the actual pH range 4.5 to 7.0. Cadmium toxicity is markedly reduced in the presence of organic complexing material (Wren and Stevenson 1991). Cd concentrations < 0.1 µg L^{-1} are not considered to be harmful to aquatic organisms, but values between 0.1 to 1.0 µg Cd L^{-1} may disturb reproduction among certain species. Concentrations > 1 µg Cd L^{-1} is found to be toxic for several aquatic organisms

The main source of Cd to surface water systems is direct atmospheric inputs, both to the catchment and directly on the lake surface. Higher concentrations of Cd in acidic lakes do not appear to be due to Cd remobilization from sediments, but rather by a decreased sedimentation. Because the retention time for Cd is normally relatively short, particularly in acidified systems, the atmospheric load is decisive for the lake concentration. Therefore, it is important that the atmospheric inputs of Cd have decreased in most areas of Scandinavia during recent years. In Norway, Cd in wet deposition has decreased by 50 to 80% from 1978 to 1996 (Toerseth and Manoe 1997). There is no good evidence for increased Cd in lakes after a reacidification of a limed catchment. Because Cd is not very sensitive within the actual pH range (down to pH 5.0 to 5.5), we assume minor effects in Cd concentrations in surface water when a limed catchment reacidify to pH 5.0 to 5.5, as long as the atmospheric inputs does not increase.

Many lakes in Norway and Sweden are relatively close to the critical loads of 0.1 µg Cd L^{-1}, so minor increases may have biological consequences. On the other hand, some studies indicate a certain adaptation to a certain Cd level, while several studies have documented an increased tolerance for Cd at lower pH compared with higher. Accordingly, if a certain increase in Cd occurs after a limed water body undergoes reacidification, the higher Cd tolerance at lower pH may compensate for this increase. Because the Cd level in a certain amount of Norwegian and Swedish lakes are close to or higher than the lowest biological risk concentration, the Cd level should be evaluated in each lake before an eventual cessation of liming.

F. Copper (Cu)

1. General Geochemistry

a. Sources

Copper (Cu) is a relatively common trace element in nature, and it is the 28th most common element in the Earth's crust. The average Cu concentration in the Earth's crust is estimated to be 50 to 70 mg Cu kg^{-1}, but it varies considerably between different bedrocks (Thornton 1979; Ledin et al. 1989; Steinnes 1990). Granites and gneisses, which dominate in Scandinavia, exhibit relatively low concentrations (4 to 30 mg Cu kg^{-1}) compared with basic, eruptive bedrock as basalt (30 to 160 mg Cu kg^{-1}) or different types of shale (18 to 200 mg Cu kg^{-1}). Limestone and sandstone exhibit low Cu concentrations (<1 to 20 mg Cu kg^{-1}, Thornton 1995). However, locally in mineralized areas the Cu content can be very high. In ore used for mining, the Cu concentrations generally exceed 1500 mg Cu kg^{-1}. In known deposits, potentially available for mining, Cu is mainly bound to sulfides (90%) and oxides (9%) and only rarely as pure metal (<1%, Landner and Lindeström 1998).

In society, Cu is used mainly to manufacture products used for electrical power transmission (cables, transformers, engines, etc.), in buildings (tubes, roofs, etc.), in vehicles (tires, brake shoes, etc.), for agricultural application (fertilizers, pesticides, wood preservatives, etc.), and for applications in the chemical industry (pigments, catalysts, developers, etc.).

In soils, Cu concentrations are generally in the range of 10 to 100 mg kg^{-1} dw, depending on the composition of the mother material (Krauskopf 1972). An investigation of 360 samples from the mor layer of Swedish forest soils showed Cu concentrations within the range 3 to 36 mg kg^{-1} dw, with a median concentration of 6.3 mg kg^{-1} dw. There was no north-south gradient to be seen in the Cu concentrations, mostly because the elevated levels in southwestern Sweden due to contribution from long-range atmospheric deposition were counterbalanced by large domestic emissions in the northeastern part of the country. Elevated levels were found in the mineralized area called Bergslagen in central Sweden, where mining activities and metal production have been pursued for centuries, and around the metal industries along the southern and northeastern coast. A typical north-south gradient was found in the Cu content, but it mainly reflects the differences in mor layer thickness (Andersson et al. 1991). A similar survey in 1981 of 841 localities in southern Norway showed little influence by long-range atmospheric transport. However, in the most southern part of the study area the Cu concentrations were strongly influenced by air pollution from the Cu-Ni smelter in Kristiansand. The general level of Cu in Norwegian soils is about 10 mg kg^{-1} dw in the humus layer (Steinnes et al. 1989).

In soils, Cu form stable complexes with dissolved organic acids in the A horizon. These complexes are vertically transported to the upper part of the B horizon, where they are precipitated and accumulated together with Fe and Al oxyhydroxides. Soil-derived Cu is transported to surface waters mainly as metal–humus complexes (Bergkvist et al. 1989). Acidification experiments in pine forest soils in southern Norway indicate that the ambient level of acid deposition is insufficient to increase the mobility of heavy metals accumulated in natural surface soils over time periods less than about 15 years (Berthelsen et al. 1994).

Scandinavian moss analysis in 1995 showed elevated Cu concentrations in the vicinity of large point sources such as the metal smelters in Rönnskär (Sweden), Kristiansand (Norway), and the Kola peninsula (Russia). Generally, the Cu concentration in moss was approximately 4 mg kg^{-1} dw in areas not affected by local pollution. There was only a slight contribution from long-range transport, most obvious in southern Norway and southwest Sweden (Rühling et al. 1996). Mass balance calculations indicate that Cu is accumulated in forest ecosystems (Bergkvist et al. 1989; Aastrup et al. 1995a). For Cu, no significant wet deposition trends could be detected at any of the four Swedish stations.

In sediments, Cu is efficiently retained due to the formation of stable complexes with negatively charged organic compounds (Nriagu and Coker 1980; Håkansson et al. 1989). In oxic sediments in clearwater lakes, Cu adsorption to Fe and Mn oxyhydroxides is an efficient retention process also at low pH ($pH \approx 4.8$, Belzile and Morris 1995). However, studies of 39 Canadian lake sediments have shown that the apparent equilibrium constants for Cu ($\log K_{Cu}$) adsorbing on mainly Fe oxyhydroxides are linearly correlated to pH ($\log K_{Cu} = apH + b$, $a \approx 1$, $r^2 = 0.75$), indicating reduced Cu solubility in the pore water at increased pH (Tessier 1992). In anoxic sediments, precipitation of Cu sulfide may ultimately constitute a major sink for Cu (Belzile and Morris 1995). Cu in sediments is not particularly mobile under neither oxic nor anoxic conditions (LaZerte 1986; Landner and Lindeström 1998). Based on studies in relatively few unpolluted lakes (n = 133), the sediment Cu concentrations varied between 16 to 38, 10 to 34, and 7 to 27 g Cu kg^{-1} dw (10 to 90 percentiles) in southern, central, and northern Sweden, respectively (Alm et al. 1998). In northern Sweden, the concentrations are close to the natural background levels (Johansson 1989). Decreased metal concentrations toward the sediment surface in acidified lakes may be attributed to a reduced metal sedimentation due to the reduced adsorption on precipitating particles or the desorption or dissolution from already sedimented materials (Dauvalter 1995).

b. Chemical Properties

Copper occurs in four valance stages. Metallic copper, Cu(0), is chemically rather inert and dissolves very slowly at oxic and slightly acidic conditions. Monovalent Cu(I) is very labile in aqueous solutions and disproportionates to Cu(0) and Cu(II) at oxic conditions. The Cu^+ ion can be stable if covalent bound to strong organic complexes or if precipitated in insoluble salts and oxides such as CuCl (pK = 6.76) and Cu_2O (pK = 15). The divalent form is the normal valance stage in oxic, aqueous environments and many of the Cu(II) compounds, such as copper sulfate ($CuSO_4$, pK = –2), are soluble in water. However, copper oxide (CuO, pK = 20.5) and copper pyrite ($CuFeS_2$, pK = 97.6) are very insoluble. The Cu^{2+} ion forms strong complexes with hydroxide and organic ligands such as humic and fulvic acids (Figure 33). Biomolecules, such as sulfur or nitrogen-containing amino acids and proteins, can form extremely strong Cu(II) complexes and are used by organisms to assimilate, store, and excrete metals. Metallothionein, which is a protein with a large content of the sulfur-containing amino acid cysteine, is used by many organisms to regulate their Cu level. Cu(II) is also readily adsorbed by clay particles and by Fe and Mn oxyhydroxides. Trivalent copper, Cu(III), is strongly oxidizing and extremely labile, and it is not known to occur in natural environments (Landner and Lindeström 1998).

Most of the selectivity differences for metals to form complexes with ligands might be explained by the ionic characteristics like polarizability, hydration conditions, and the ability to form stable organo-metallic complexes. However, Cu^{2+} is an exception. According to polarizability and hydratisation energy the degree of selectivity to organic complexes for classic divalent metals should be as follows: $Pb^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} \approx Ni^{2+} > Cu^{2+}$. However, based on Jahn-Tellers theorem (Phillips and Williams 1966), Cu exhibit the strongest asymmetry in coordinate positions around the Cu^{2+} ion, which means that two ligands have larger binding lengths. Thus, H_20 molecules associated in these positions are far easier to remove, which may explain the strong binding between Cu and organic complexes. Also the thickness of the water layer around the metal ions might be important for binding strengths, because a negative correlation exists between the thickness of the water layer and ionic selectivity. According to these properties, Thiele and Schacht (1959) made this rank: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$.

In soil, the combined information from different investigations suggests bonding strength for divalent ions within the pH range 3.5 to 5 approximately according to the sequence $Hg^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+} \approx Cd^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$, and for trivalent ions $Fe^{3+} = Cr^{3+} > Al^{3+}$ (Andersson et al. 1991). In peat and humic acids

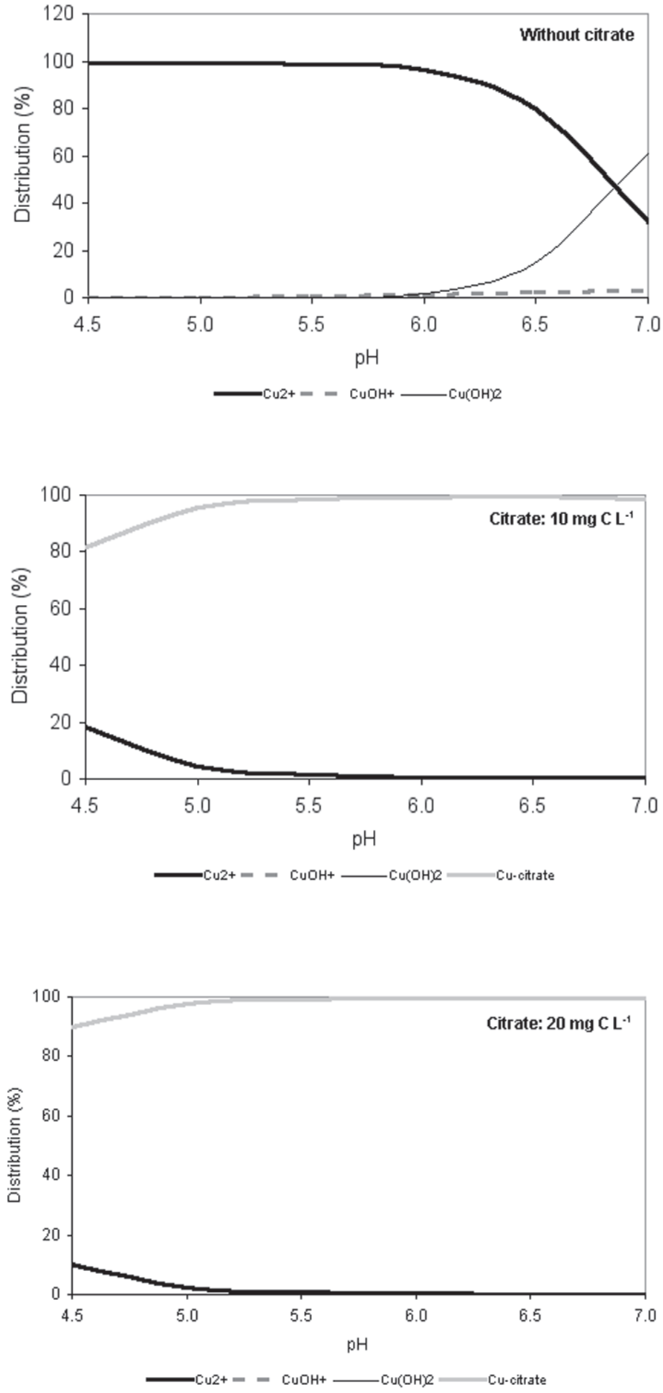


FIGURE 33. Distribution of major Cu species in relation to pH at citrate concentrations of 0, 10, and 20 mg C L^{-1}. Essential input conditions: 25°C; CO_2 and O_2 at equilibrium with partial pressure of air; [Cu]: 0.1 µmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 µg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

fractionated from the peat, the same sequence for divalent ions is mainly $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ in the pH range 3 to 4.6. The adsorbed quantities of metal ions increase with increasing base saturation and increased decomposition of the peat due to dissociation of acid functional groups and the increased content of carboxyl groups, respectively (Krogstad 1982).

According to the literature dealing with the most essential factors essential for bonding strength, divalent cations might be ranked as follows: $Hg^{2+} \approx Pb^{2+} > Cu^{2+} >> Cd^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$. This means that Hg, Pb, and Cu have the strongest association to organic compounds among these metals. Metals with medium bonding strength to organics are Cd, Ni, Co, Zn, Mn, while Ca and Mg exhibit the weakest bonding strength.

The stability constants (pK values) for Cu complexes with humic and fulvic acids have been reported to be in the range 6 to 8. The reported pK_1 values for water- or soil-derived fulvic acids generally fall within the range 5.5 to 7.0 and the pK_2 values in the range 3.8 to 5.4 (Borg and Johansson 1989), which agrees well with the values found for Cu organic complexes in 10 lake waters in northern Sweden ($pK_1 = 5.4$ to 6.4, $pK_2 = 4.2$ to 5.0). The potential binding capacity of the organic compounds in these waters was in the range 64 to 2200 µg Cu L^{-1} (Borg and Johansson 1989), which is extremely high compared with the total concentrations found in Scandinavian freshwaters.

2. Copper in Surface Water Systems

Generally, elevated Cu concentrations are found in surface waters in agricultural areas. This might be caused by naturally higher Cu concentrations in the clays or as a result of Cu accumulation caused by fertilizer use (Tarvainen et al. 1997; Alm et al. 1998). In southern Finland, till geochemistry is reflected in the Cu distribution in water (Tarvainen et al. 1997), while this pattern not was found in northern Finland or in the County of Dalarna in central Sweden. Locally, Cu mineralization areas are common in both these regions (Tarvainen et al. 1997; Alm et al. 1998).

Acidity and the amount of humic substances in the water influenced the distribution of Cu in Finnish streams, but lakes and running waters in Sweden did not show this pattern. Actually, Alm et al. (1998) conclude that acidification does not seem to influence the Cu concentrations in Swedish surface waters. As for mosses, high concentrations were found in some waters around industries with large atmospheric Cu emissions (Tarvainen et al. 1997; Alm et al. 1998). However, the Cu concentrations in surface waters in Sweden, Norway, and Finland are generally low (Table 23) according to the classification systems in Sweden and Norway (Tables 26 and 27). Data obtained in 1980 to 1992 indicate that the median Cu concentration in Scandinavian surface waters was below 1 µg Cu L^{-1} (Table 22). This agrees well with the national lake surveys in 1995 showing median values

Table 22. Concentrations of Cu (µg Cu L^{-1}) in Nordic surface waters and in the Czech Republic. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	151	6	< 0.11 - 4.30	0.31
Finland south[2]	89	n.r.	n.r. - 2.60	0.38 ± 0.37
Finland, north[2]	156	n.r.	n.r. - 3.01	0.43 ± 0.36
Sweden, south[3]	20	n.r.	0.3 - 1.0	0.68 ± 0.23
Sweden, north[3]	17	n.r.	0.25 - 2.66	0.90 ± 0.65
Sweden, east[4]	12	n.r.	0.25 - 0.79	0.38 ± 0.15
Sweden, s.east[4]	28	n.r.	0.16 - 1.60	0.58 ± 0.33
Sweden, s.west[4]	9	n.r.	0.34 - 0.95	0.65 ± 0.23
Sweden, north[5]	56	n.r.	0.1 - 2.0	0.51
Czech[6]	5363	n.r.	n.r.	0.8

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

[2] Verta et al. (1990), based on samples from autumn 1987.

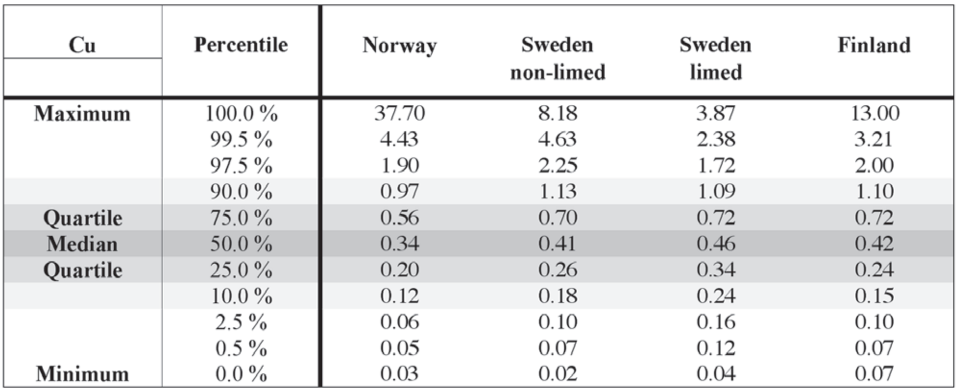
[3] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden, south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[4] Borg and Andersson (1984), oligotrophic forest lakes, sampled during 1980-1983. East: lakes south of Stockholm, TOC: 7.4 ± 2.0 mg C L^{-1}, pH: 5.1 - 6.9; South-east: Småland, TOC: 6.6 ± 2.8 mg C L^{-1}, pH: 4.6 - 6.7. TOC: 7.4 ± 2.0 mg C L^{-1}, pH: 5.1 - 6.9; South-west: Halland/Småland, TOC: 10 ± 4.6 mg C L^{-1}, pH: 4.7 - 6.5.

[5] Borg (1987) based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

[6] Vesely and Majer (1996), based on data collected between 1984 and 1992.

Table 23. Percentile distribution of Cu (µg Cu L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462



Cu	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	37.70	8.18	3.87	13.00
	99.5 %	4.43	4.63	2.38	3.21
	97.5 %	1.90	2.25	1.72	2.00
	90.0 %	0.97	1.13	1.09	1.10
Quartile	75.0 %	0.56	0.70	0.72	0.72
Median	50.0 %	0.34	0.41	0.46	0.42
Quartile	25.0 %	0.20	0.26	0.34	0.24
	10.0 %	0.12	0.18	0.24	0.15
	2.5 %	0.06	0.10	0.16	0.10
	0.5 %	0.05	0.07	0.12	0.07
Minimum	0.0 %	0.03	0.02	0.04	0.07

Table 24. Classification of concentrations of Cu in surface waters ($\mu g\ L^{-1}$), the upper (0-1 cm) of lake sediments ($mg\ kg^{-1}$ dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Cu (Sweden, 1991)	≤ 0.3	0.3 - 1.0	1 - 2	2 - 5	> 5
Cu (Sweden, 1998)[1]	≤ 0.5	0.5 - 3.0	3 - 9	9 - 45	> 45
Cu (Sweden, 1998)[2]	≤ 0.5	0.5 - 1.0	1 - 3.5	3.5 - 35	> 35
Cu (Norway, 1997)	< 0.6	0.6 - 1.5	1.5 - 3	3 - 6	> 6
Sediment					
Cu (Sweden, 1991)	≤ 10	10 - 25	25 - 50	50 - 150	> 150
Cu (Sweden, 1998)[3]	≤ 15	15 - 25	25 - 100	100 - 500	> 500
Cu (Norway, 1997)	< 30	30 - 150	150 - 600	600 - 1800	> 1800

[1] Based on risks of biological effects.

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96).

[3] Based on distribution in Swedish lakes with and without local emissions.

Table 25. Median concentrations and probability of concentration difference (ANOVA test) between two adjacent streams, before (August 1994-September 1995) and after liming (October 1995-January 1998) in the Skidbågsbäcken area, Dalarna, central Sweden. n.s.: not significant

Parameter	**Before liming**			**After liming**		
	$SK1_{ref}$	**$SK2_{non\text{-}limed}$**	**ANOVA**	**$SK1_{ref}$**	**$SK2_{limed}$**	**ANOVA**
pH	4.29	4.30	n.s.	4.42	6.78	$p < 0.0001$
TOC ($mg\ L^{-1}$)	15.5	15.4	n.s.	12.9	14.4	$p < 0.05$
Cu ($\mu g\ L^{-1}$)	0.20	0.24	n.s.	0.22	0.33	n.s.
Pb ($\mu g\ L^{-1}$)	0.63	0.70	n.s.	0.47	0.51	n.s.
Zn ($\mu g\ L^{-1}$)	4.8	5.3	n.s.	3.9	3.3	n.s.
Cd ($\mu g\ L^{-1}$)	0.023	0.029	n.s.	0.020	0.020	n.s.
Al ($\mu g\ L^{-1}$)	201	209	n.s.	171	153	n.s.
Fe ($\mu g\ L^{-1}$)	783	545	n.s.	644	370	n.s.
Mn ($\mu g\ L^{-1}$)	19	24	n.s.	17	28	n.s.

Table 26. Classification system of Cu (μg L^{-1}) in Norwegian freshwaters primarily related to salmonids (UN-ECE 1997b). Class 1: No effects on biota or no limitations for human consumption of fish. Class 2: Some sensitive species may be affected, but no effects on fish. Little ecosystem effects. Class 3: Effects on salmonids, reduced number of species with a dominant of tolerate species. Class 4: No salmonids and serious effects also on many other species. The structure of the ecosystem is completely destroyed

Class 1 Very Low	**Class 2** Low	**Class 3** Medium	**Class 4** High
< 3	3 – 15	16 – 30	> 30

Table 27. Critical concentrations of Cu (μg L^{-1}) at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997) and Sweden (Alm et al. 1998)

	Freshwater μg L^{-1}			Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
		acute	chronic			
The Netherlands	1.1			37	3.5	
United Kingdom[1]	0.5 - 12					
Germany[2]		18	11			
EU[1]	5					
Canada[1]	2 - 4			36	63	
Sweden	**3**			**120**		
Denmark	12				30	
Norway	**3**					
Finland					32	

[1] Range means that values depend on water hardness; [2] Hardness dependent criteria (100 mg $CaCO_3$ L^{-1} is used).

of 0.34 µg Cu L^{-1} (Norway), 0.41 µg Cu L^{-1} (nonlimed Swedish lakes), 0.46 µg Cu L^{-1} (limed Swedish lakes), and 0.42 µg Cu L^{-1} (Finland). This survey also showed that > 97.5% of the lakes had less than 3 µg Cu L^{-1} (Table 23), which is assumed to be the level for biological effects in sensitive waters (Alm et al. 1998).

The Cu concentrations in 126 unpolluted groundwater aquifers in Sweden sampled in 1985 to 87 varied between 0.05 to 9 µg Cu L^{-1}, with a median value of 1 µg L^{-1} (n = 543). The concentrations showed no correlation with pH in the interval 4.5 to 7.5, and the Cu levels were undersaturated with respect to sparingly soluble hydroxides, carbonates, or sulfates (Ledin et al. 1989). In another study, based on more observations (n = 1203), a slight pH dependency was found with somewhat higher Cu concentrations (median ≈ 1.5 µg Cu L^{-1}) at pH<5.5 (Aastrup et al. 1995b). Obviously, the Cu concentration in groundwater is determined by other factors than pH as long as pH is above 5.5.

Figure 34 shows the total Cu concentrations in Norwegian and Swedish nonlimed and limed lakes in relation to pH within three TOC classes. The percentile distributions of total Cu for three TOC classes of Swedish and Norwegian lakes (Figure 37) show that high TOC lakes generally have the highest Cu concentrations. While median Cu concentration in the lowest TOC class (< 5 mg C L^{-1}) was 0.31 µg Cu L^{-1}, the median Cu concentrations in the medium (5 to 10 mg C L^{-1}) and high TOC class (> 10 mg C L^{-1}) were 0.46 and 0.56 µg Cu L^{-1}, respectively. There is no evident difference in Cu concentrations between pH classes (Figure 36). If there were any pH effect, it seems to be that there were higher Cu in the highest pH classes. The difference between limed and nonlimed lakes in Sweden (Figure 35) was very small, and the few reacidified limed lakes (limed lakes with pH < 6) did not show higher Cu concentrations than the nonlimed at the same pH interval (Figures 34 and 37). Almost 90% of all investigated lakes fell in the categories *Very low* to *Low* according the Norwegian and Swedish classification systems (Table 24).

In 1984 and 1985, metal dynamics during acid episodes related to snowmelt (pH drop from about 7 to 4.4 to 5.5) was investigated in two brooks mainly draining peat-dominated wetlands in the subalpine area of Härjedalen, central Sweden. It showed moderately elevated Cu concentrations simultaneously with the pH drops. However, Cu, Zn, Pb, and Cd concentrations were probably all far too low (0.06 to 0.52 µg Cu L^{-1}) to explain the acute toxic effects on caged trout in this study (Borg 1986a).

In 1996, the County Administration Board of Dalarna performed a similar study of the effects of acid surges in 13 small streams in northern Dalarna, draining forests, bogs, and alpine areas. In nine of the streams the general pattern was similar to that found in Härjedalen, with low concentrations during base flow ($pH_{base\ flow}$: 6.1 to 7.4, (Cu): 0.03 to 0.22 µg L^{-1}, Acktjärnsbäcken, Figure 38) and somewhat elevated levels during the only slightly acidic episodes ($pH_{episodes}$: 5.1 to 6.4, (Cu): 0.11 to 0.44 µg L^{-1}). However, three streams situated in the subalpine region, close to the mountain of Fulufjäll, Sweden, exhibited

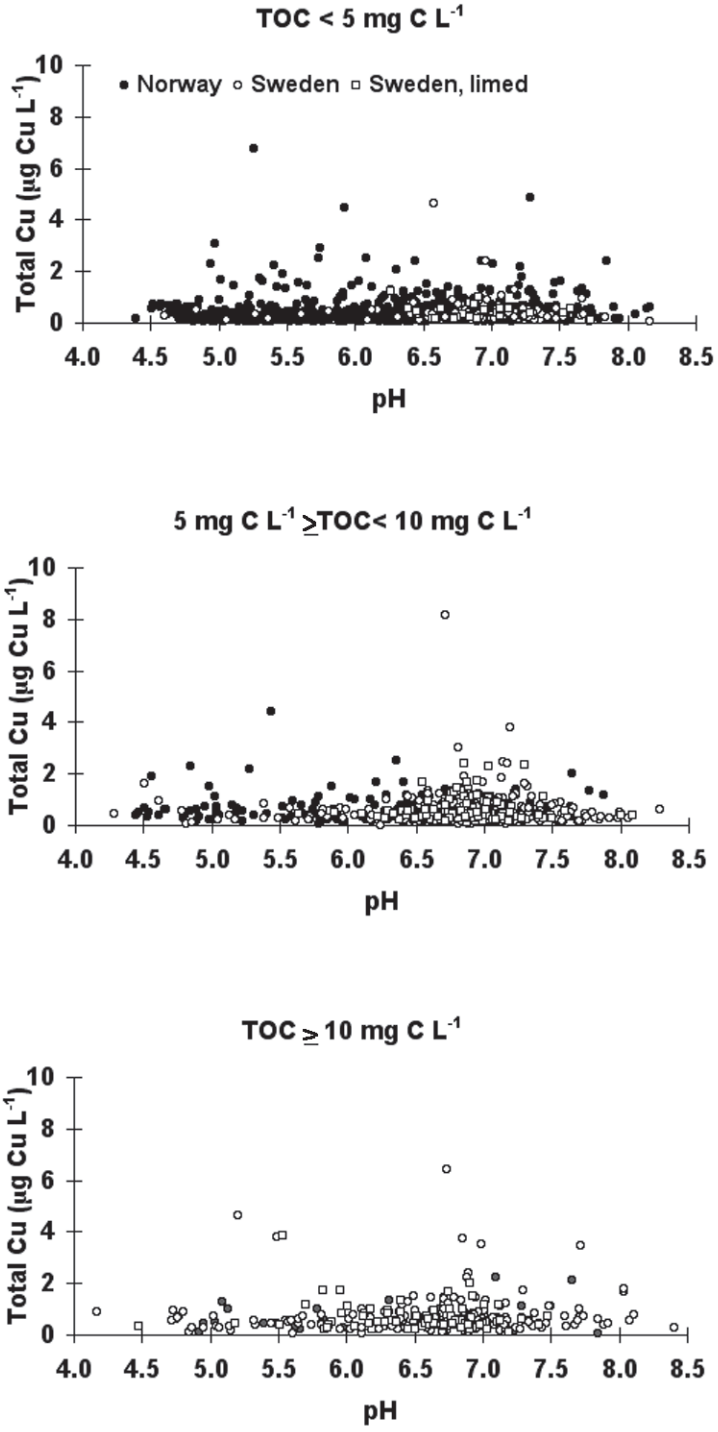


FIGURE 34. Total concentration of copper in Norwegian and Swedish (nonlimed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

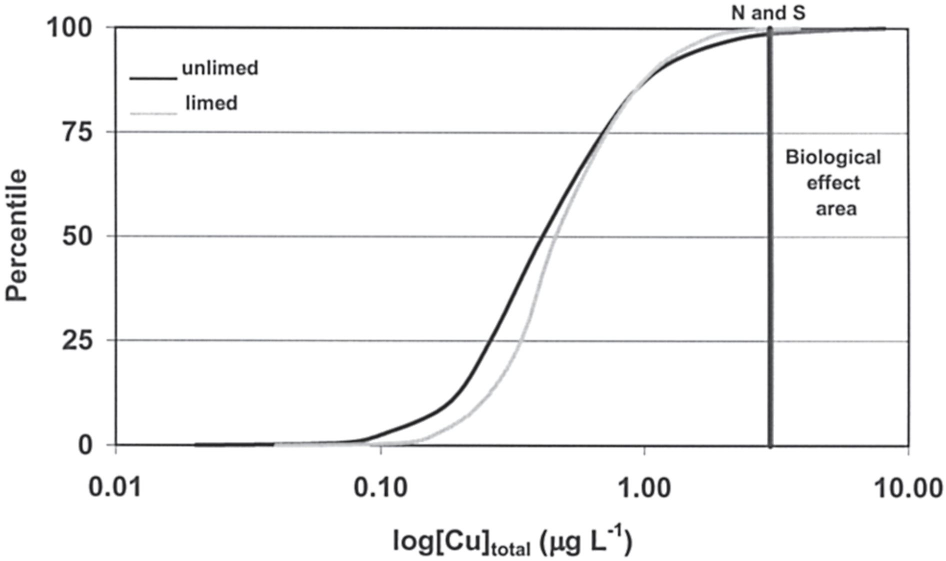


FIGURE 35. Percentile distribution of total Cu in limed (n = 261) and not limed (n = 820) Swedish lakes. S and N show the assessed critical concentrations for aquatic life in Norway and Sweden. (Data from Skjelkvaale et al. [1996, 1999].)

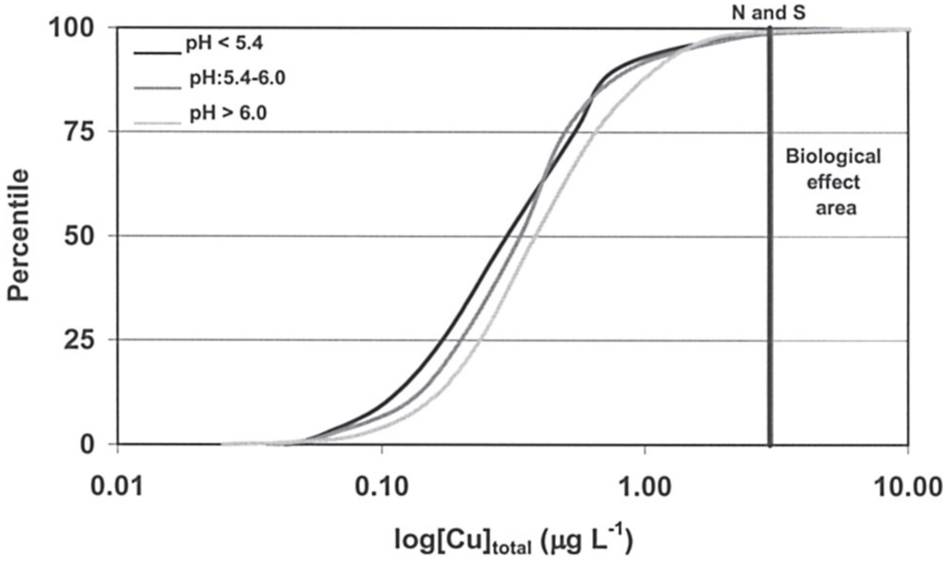


FIGURE 36. Percentile distribution of total Cu in Norwegian and Swedish lakes based on three pH classes. pH < 5.4, n = 250; 5.4 ≤ pH < 6.0, n = 204; pH ≥ 6, n = 1090. (Data from Skjelkvaale *et al*. [1996, 1999].)

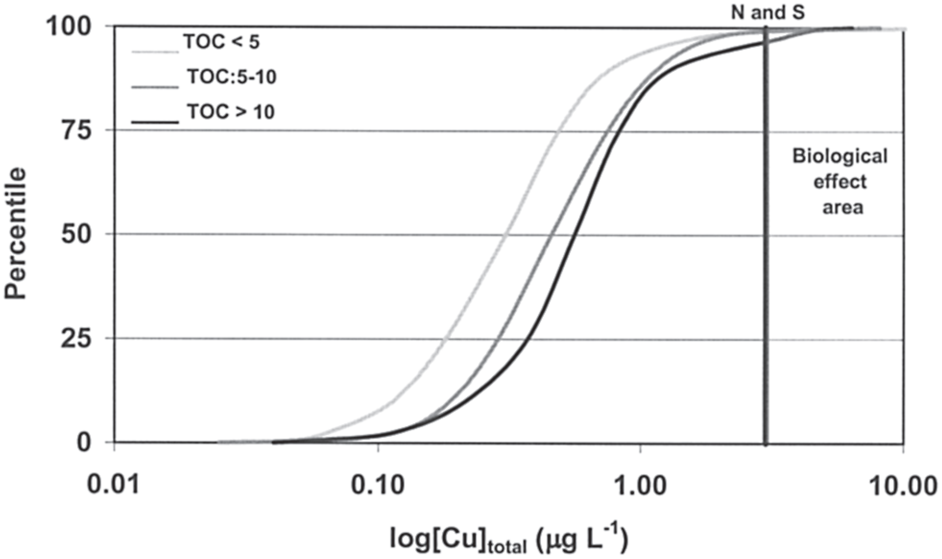


FIGURE 37. Percentile distribution of total Cu in Norwegian and Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale *et al*. [1996, 1999].)

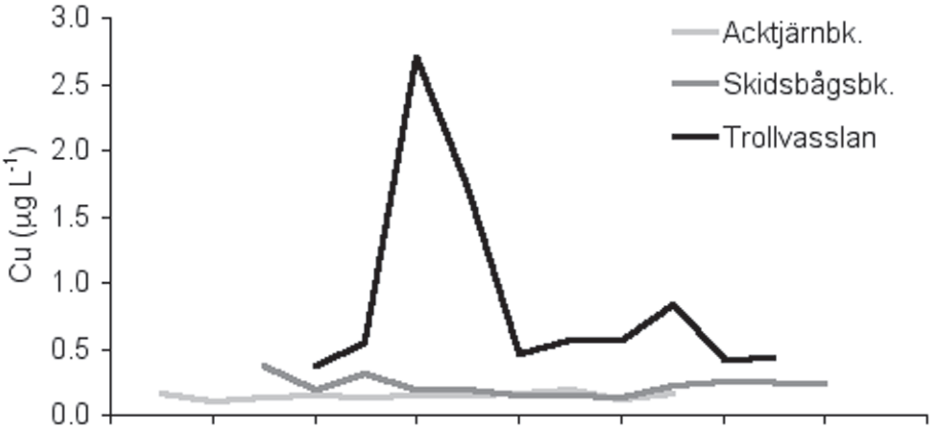


FIGURE 38. Total Cu concentration during snowmelt in April 1996 in three streams in northern Dalarna, central Sweden.

relatively high Cu concentrations during snowmelt (pH: 5.9 to 6.4, (Cu): 0.86 to 2.70 μg L^{-1}, Trollvasslan, Figure 38). The bedrock in this area is dominated by sandstone, but a layer of diabase reaches the soil surface at the mountain slopes. The increased Cu concentrations are probably a result of this diabase layer rather than an effect of decreased pH. In the permanently acid stream Skidbågsbäcken, the Cu concentrations slightly decreased at snowmelt (pH: 4.3 to 4.5, (Cu): 0.13 to 0.38 μg L^{-1}, Figure 38).

a. Experimental Acidification

Williams (1993) showed that acidification has minor effects on the dissolution of Cu from sediments. Young and Harvey (1992) found that up to 90% Cu in the sediments was present in the organic fractions of lake sediments, but contrary to the other metals studied (Zn, Cd, and Ni), the concentration of Cu associated with organics was positively correlated with pH. A high degree of Cu associated to organic fractions of sediments is well known (e.g., Campbell et al. 1985).

b. Liming

Unfortunately, many studies of liming effects on metal concentrations do not report any results for Cu and the available data therefore are meager. Liming of a low TOC lake in Canada (from pH 4.8 to about pH 7) reduced the concentration of Cu in lake water from 5 μg L^{-1} to 0.6 μg L^{-1} (White et al. 1984). However, the lake liming of Lake Hovvatn in Norway did not show any effects on the Cu concentrations (Wright 1985). The County Administration Board of Dalarna has studied the water chemistry in a limed stream (SK2, wetland liming) and an adjacent reference stream (SK1) since 1994. Sphagnum peat soils dominate both drainage areas and the SK2 wetlands were limed in 1995 and 1997. From Table 25 it is evident that there were no differences in the metal concentrations between the two streams either during the reference or the treatment periods. The wetland liming increased pH from 4.4 to 6.8 in the treated stream. Throughout the investigation period the Cu concentration varied in the ranges of 0.04 to 1.43 μg L^{-1} and 0.02 to 1.50 μg L^{-1} at SK1 and SK2, respectively.

Laboratory studies (Krogstad 1982) indicate that liming of Sphagnum peat increases the potential for metal adsorption due to increased dissociation of acid functional groups at higher base saturation and increased mineralization, yielding a higher content of carboxyl groups. Cu was after Pb the most efficiently adsorbed metal regardless of base saturation level and biological degradation. Hg was not incorporated in this study.

c. Reacidification

No data are available!

3. Biology and Toxicity

Copper is an essential element for all organisms, and it functions as a component in many metalloenzymes and proteins. The mono- and divalent redox couple Cu(I)/Cu(II) is an important electron transfer system active in photosynthesis and respiration. Cu is also essential for metabolic functions such as protein synthesis and lignification. At higher concentrations, Cu is toxic to vascular plants and very toxic to algae, fungi, and vertebrates. However, it is only moderately toxic to most mammals. In aquatic systems, the Cu^{2+} ion and its cationic hydroxide complexes are considered to be most toxic.

a. Toxic Species

In water, the toxic forms are mainly coupled to the Cu(II) ion, either as free Cu^{2+} ions or as ionic hydroxide complexes ($Cu(OH)^+$, $Cu_2(OH)_2^{2+}$). The uncharged $Cu(OH)_2^0$ might also be somewhat toxic, while the carbonate complexes seem to be relatively harmless. Mixtures of Cu and other trace metals (e.g., Zn, Hg, and Ni) might increase the toxicity in an additive way (Balsberg et al. 1981). The toxicity is reduced by increased water hardness (Ca + Mg), alkalinity, and pH due to decreased Cu permeability across gill membranes and the formation of less toxic hydroxides and carbonate complexes in water (Spear and Pierce 1979). Experiments with rainbow trout show that the gill permeability (Ca + Mg level) is the predominant reducing factor for the toxicity at concentrations below 12 to 28 mg Ca + Mg L^{-1}. At higher Ca+Mg levels increased alkalinity and pH is the main detoxifying factor (Balsberg et al. 1981). In soft waters, complexation with organic matter (humus) greatly reduces the Cu toxicity (Erickson et al. 1996). The excretion of extracellular organic components from bluegreen algae has also been shown to reduce the Cu toxicity (McKnight 1980). In soft waters with low pH, complexation by humus is the predominant detoxifying factor. However, Marr et al. (1999) have shown that Cu bound to organic complexes may be available to fish, and that acute toxicity of Cu is determined by the binding affinities of organic acids relative to Cu binding affinity of fish gill.

b. Target

In plants, metals are assimilated both actively and passively. Essential metals such as Cu are mainly actively assimilated through the roots (Folkesson 1982).

Invertebrates assimilate Cu directly through the cells at the body surface, while fish can assimilate Cu both through the gills and the intestines. The metal is rapidly adsorbed on the cell surface. Transport of Cu through the cell membrane by a protein carrier release from this carrier inside the cell membrane, and transfer of Cu to another carrier-protein in the cytoplasm are slower processes. Excess amounts of essential metals are in plants to some extent stored in vacuoles, while invertebrates use granulocytes in the cytoplasm for this accumulation. Mammals use a special sulfur-rich protein (metallothionein) for these transport and storage processes. Among vertebrates, metallothionein proteins are common in gills, liver, kidney, and intestines. These metal-regulating systems are also used for the excretion of excess amounts of metals (Owen 1981).

The need of Cu and the ability to excrete Cu varies between organisms. Generally, the Cu contents are higher at lower trophic levels, showing that Cu is not biomagnified in the food web. Plants, algae, and invertebrates have higher Cu concentrations than fish in both contaminated and pristine environments (Landner and Lindeström 1998).

The most important toxic mechanism of Cu in green plants and algae seem to be the reduction of the electron transport in the cytoplasts, creating the formation of free radicals (Fernandes and Henrique 1991). Many other effects can also occur at the cell physiological level, for example, hindered or reduced cell division (Flemming and Trevors 1989). However, algae have the possibility to regulate their sensitivity to Cu, within certain limits, by the excretion of extracellular chelating agents. Toxic effects of Cu on phytoplankton are documented in oligotrophic lakes at concentrations above 0.7 to 7 μg L^{-1} (Balsberg et al. 1981). Cu has also been used as a pesticide in hypertrophic lakes at concentrations of 5 to 10 μg Cu L^{-1}. The result has often been a shift from a Cyanobacteria to a green algae-dominated system (Flemming and Trevors 1989). The effects of Cu on algae in complex plankton communities (phyto and zooplankton) often seem to be the result of changed zooplankton grazing (Landner and Lindeström 1998). Structural and functional changes have also been documented in periphyton communities with additions of 2.5 and 5 μg Cu L^{-1} in oligotrophic streams (Balsberg et al. 1981).

Some marine zooplankton species are very sensitive to Cu, while limnic species seem to be more tolerant with effect levels in soft clear waters above 3.5 to 6 μg L^{-1} (Landner and Lindeström 1998).

The reduced ability to compete with other species seems to be of a larger ecological significance than lethal death for benthic fauna. Such effects have been documented within and between fauna groups such as *Trichoptera*, Ephemeridae, and Chironomidae (Clements et al. 1989a, b).

In fish, the most sensitive parameters responding to Cu toxicity are behavior, growth, and enzymatic activity, with the lowest recorded effect concentration at approximately 4 μg L^{-1} (Spear and Pierce 1979; Mance 1987). At higher concentrations, effects have been observed on reproduction, osmoregulation, biochemistry, smell, and respiration (Spear and Pierce, op. cit.). Acute toxic solutions of Cu (as for many other metals) cause increased mucus formation in fishes. The excess coagulates over the entire body and is particularly prominent over the gills. Thus, it interferes with the respiratory function with hypoxia as a cause of death (e.g., Aronson 1971; NRCC 1973; McDonald and Wood 1993).

Regardless of trophic level, physiological stress influencing the competition between species should be expected as the most common toxic effect of Cu at the concentration levels generally found in Scandinavian waters. Lethal effects might occur locally in the most polluted environments downstream point sources.

c. Fish

For salmonids, the lowest observed lethal concentration level for Cu in soft waters in America is reported to 10 µg L^{-1}, while avoidance behavior was detected at 4 µg L^{-1} (Mance 1987). Juvenile individuals of rainbow trout and Atlantic salmon tested in soft waters (12 to 14 mg L^{-1} $CaCO_3$) and at neutral pH usually have a 96-h LC_{50} value in the range of 18 to 25 µg L^{-1}. Most other freshwater fish species have considerably higher tolerance levels for Cu. The critical level for negative effects on the fish communities in 27 Norwegian rivers (3 to 30 mg Ca L^{-1}, pH ≈ 7), polluted by a mixture of metals from mine effluents, corresponds to a concentration of 20 µg Cu L^{-1}. All rivers keep stocks of salmonids, for example, *Salmo salar* and/or *Salmo trutta*. No synergistic or additive effects could be traced between Cu, Zn, and Cd, and Cu seemed to be the most toxic metal (Grande 1991).

The Cu toxicity to fish decreases with increasing ionic strength and/or complexation to organic ligands, for example, humic compounds (Brown et al. 1974; Spear and Pierce 1979; Welsh et al. 1993). However, recent findings show that Cu bound to organic molecules with an affinity to Cu lower than the Cu affinity to fish gills may in combination with free Cu ions cause toxicity (Erickson et al. 1996; Marr et al. 1999). The stability constant for fish gills have been determined to $pk_{Cu} = 7.25$ to 7.5 for rainbow trout, brook trout, and fathead minnow (Playle et al. 1993; MacRea et al. 1999a,b). Estimates of median lethal concentration thresholds were found to be in the range 7.9 to 8.6 µg Cu L^{-1} (Cu^{2+} and Cu bound to two low-affinity organic ligands) at varying equivalent concentrations of organic matter (0 to 16 mg DOC L^{-1}, Marr et al. 1999).

d. Invertebrates

Aquatic invertebrates display great interspecies variability in sensitivity to Cu. The lowest LC_{50} values for sensitive benthic fauna in soft inland waters ($CaCO_3$<50 mg L^{-1}) is reported to be 8 µg L^{-1} for the crustacean *Gammarus pseudolimnaeus*. However, another common crustacean, *Asellus* spp., is very tolerant to Cu (LC_{50}>1200 µg L^{-1}, Mance, 1987). Different strains of *Daphnia magna* show very large differences in Cu sensitivity (EC_{50} = 11 to 71 µg L^{-1}), and the toxicity effect is lowered after preexposure to Cu (10 µg L^{-1}), indicating the ability to excrete excess Cu (Correa and Ojeda 1997). The presence of organic matter derived from algal and daphnid blooms reduced the Cu-induced mortality in *Daphnia magna* (Meador 1991).

Leland et al. (1986) reported on changes in the macroinvertebrate communities at Cu concentrations as low as 5 µg L^{-1}. The effect was greater on herbivores and detritivores than on predators. In streams in central Sweden with elevated metal concentrations, Malmqvist and Hoffsten (1999) found reductions of taxonomic richness for total macroinvertebrates, mayflies, stoneflies and combined EPT (Ephemeroptera, Plecoptera and Trichoptera), but not for that of Trichoptera or total abundance or biomass. The Cu concentrations were in the range 1 to 35 µg L^{-1}, but Zn might also have contributed to the effects.

As for fish, low water hardness and alkalinity substantially enhance the toxicity of Cu to aquatic invertebrates. However, lethal toxicity to aquatic invertebrates generally occurs at concentrations that exceed ambient concentrations. Therefore, Cu toxicity to invertebrates, even in acidic waters, is mainly coupled to physiological stress factors rather than lethal effects.

e. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

Maximum annual acceptable 50 and 95 percentiles in concentrations of dissolved Cu (< 0.45 µm) for salmonids based on EIFAC criteria (Alabaster and Lloyd 1982) at a hardness of 10 mg $CaCO_3$ L^{-1} are 1 and 5 µg Cu L^{-1}. The classification system of Norwegian freshwaters primarily related to salmonids (Table 26) based on natural observations assess no effects on biota or no limitations for human consumption of fish at concentration <3.0 µg Cu L^{-1}. Lithner (1989) reported lowest know effect at 2 µg Cu L^{-1}. Alm et al. (1998) assume the risk of biological effects in sensitive Swedish waters at 3 µg Cu L^{-1}. The critical concentration of Cu in freshwater is 3 µg Cu L^{-1} both in Norway and Sweden (Table 27).

Based on the Nordic lake survey, 0.7% of Norwegian lakes, 1.6% of nonlimed Swedish lakes, 0.4% of limed Swedish lakes, and 0.9% of Finnish lakes have concentrations > 3 µg Cu L^{-1}. The median values of Cu in the Nordic lakes are about 10 times lower than the assumed biological effect concentration.

A proposed effect-related sediment criteria for heavy metals in Canada (Smith et al. 1996) assume a biological effect level of Cu in sediments at 197 mg kg^{-1} dw.

4. Reacidification — Biological Risk

There are no indications of increased internal flux of Cu from the sediments due to the large buffering capacity and high adsorption potential of Cu even at low pH. On the other hand, the sedimentation of Cu might be somewhat lower in low pH lakes. The Cu concentrations in most Scandinavian surface waters are, however, low to very low. Therefore, it is unlikely that reduced sedimentation due to the reacidification of limed lakes will significantly increase the concentration of Cu in most surface waters. This conclusion is supported by the observation that the few reacidified limed lakes in Sweden do not show higher Cu concentrations than the rest of the lake population.

The ambient level of acid deposition is probably insufficient to increase the mobility of Cu accumulated in most natural soils and lake sediments. Therefore, it seems reasonable to believe that no significant increases are to be expected if limed lakes reacidify. We might assume only minor or no changes in concentrations of Cu during reacidification of limed water bodies, regardless whether the treatment was performed as forest, wetland, lake, or stream liming.

G. Lead (Pb)

1. General Geochemistry

a. Sources

Among many Pb-containing minerals, galena (PbS), angeleside ($PbSO_4$), and cerusite ($PbCO_3$) are the most abundant. Galena, the primary form of Pb in natural state, is often associated with sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and other sulfur salts (May and McKinney 1981).

About 50% of the domestic Pb consumption is used in storage battery manufacture, and until recently (about 1980) about 20% was used in the manufacture of gasoline antiknock additives such as tetramethyl-Pb (TML) and tetraethyl-Pb (TEL). Pigments and ceramics account for about 6% of total consumption, and metallic Pb products, Pb-containing alloys, paint, solder, and ammunition constitute other minor use categories (EPA 1980).

The massive increases of Pb into the atmosphere by emission from automobiles have had a measurable impact on the global or the hemispheric cycling of the metal. Enhanced Pb concentrations are documented even in recent ice cores from Greenland and the Antarctic, as well as in surface waters from mid-ocean sampling locations (Zoller 1984). The significant reductions in the use of TML and TEL because gasoline antiknock additives have caused significant decreases in the atmospheric inputs of Pb since the early 1980s. In Norway, Pb in wet deposition has decreased by 60 to 80% from 1978 to 1996 (Toerseth and Manoe 1997). In Sweden Pb concentration in wet deposition has decreased by 48 to 76% during 1984 to 1996.

Typical background levels of Pb in uncontaminated surface waters is ≈ 0.2 μg Pb L^{-1} (Trefry and Presley 1976). According to Edgington and Robbins (1976) and

Lodemann and Buckenberg (1973), the level of dissolved Pb in freshwaters generally ranges from 0.1 to 1.5 μg Pb L^{-1}.

b. Chemical Properties

Lead occurs in four valence states: elemental (Pb^0), monovalent (Pb^+), divalent (Pb^{2+}), and tetravalent (Pb^{4+}), where all forms are environmentally important, except possibly Pb^+. In nature inorganic Pb occurs mainly as Pb^{2+} and only oxidizes to Pb^{4+} under strong oxidation conditions. Few simple compounds of Pb^{4+} other than PbO_2 are stable. Some Pb salts are relatively soluble in water (Pb acetate, Pb nitrate, and Pb chloride), whereas others are sparingly soluble (Pb sulfate, Pb sulfide, and Pb oxide). The solubility increases by increasing temperature. Of the organic Pb forms, TEL and TML are the most stable and the most important because of their widespread use. Both undergo photochemical degradation in the atmosphere to elemental Pb and free organic radicals, although the fate of automotive organo-Pb has yet to be fully evaluated.

Lead chemistry is complex. In water, Pb is most soluble and bioavailable under conditions of low pH, low organic carbon concentrations, low turbidity, and low concentrations of salts of Ca, Fe, Mn, Zn, and Cd (Eisler, 1988a). The solubility of Pb is low in water, except in areas of local point source discharge (Harrison and Laxen 1981; Scoullos 1986). Besides local sources (geology, mines), the major source of lead (Pb) are emissions from boats and vehicle traffic, a problem that has been significantly reduced during the last 2 decades due to the use of unleaded gasoline. Lead and its compounds tend to concentrate in the water surface microlayer (i.e., the upper 0.3 mm), especially when surface organic materials are present in thin films (Demayo et al. 1982). Organic Pb compounds are generally of anthropogenic origin and are found mostly in the aquatic environment as contaminants. However, some organic Pb complexes form naturally, and their formation may be affected by man-made organic Pb compounds (Nriagu 1978).

In surface water inorganic Pb exists in four dissolved (labile) forms, Pb^{2+}, $PbOH^+$, $PbSO_4$, and $PbCO_3$, but within the pH range 4.5 to 6.5 Pb^{2+} is the only significant inorganic specie present (Figure 39). In addition, Pb is bound in colloids and particles (Benes et al. 1985). The labile forms represent a significant part of the Pb input from washout of atmospheric deposits, whereas particulate and colloidal bound Pb are common in urban runoff and ore-mining effluents (Benes et al. 1985).

The solubility of Pb compounds is pH dependent, and range from about 10 g Pb L^{-1} at pH 5.5 to less than 1 μg Pb L^{-1} at pH 9.

Several studies have confirmed the immobility of Pb and the association of Pb with organic matter in acidifying soils. Dissolved Pb has been found to be positively correlated with dissolved organic carbon (Driscoll et al. 1988), and Bergkvist (1987) found that the B horizon was a sink for Pb. Furthermore, LaZerte et al.

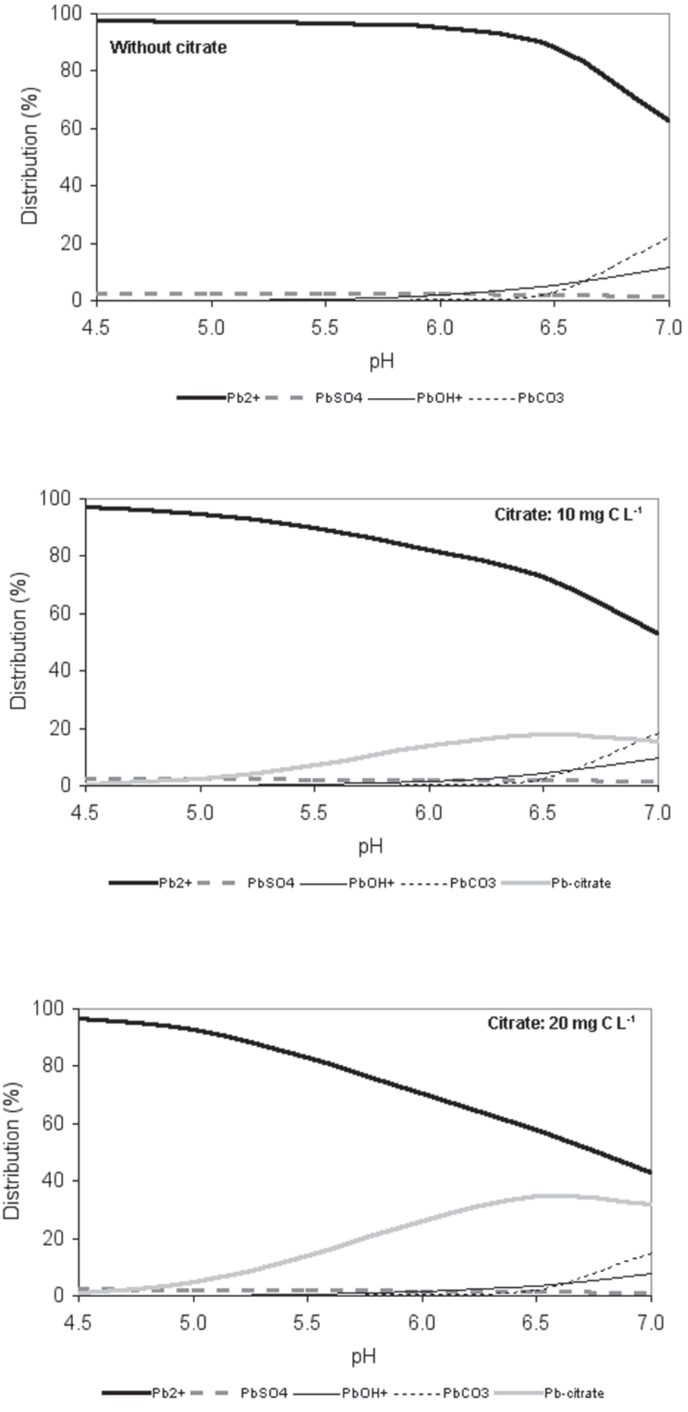


FIGURE 39. Distribution of major Pb-species in relation to pH at citrate concentrations of 0, 10 and 20 mg C L^{-1}. Essential input conditions: 25°C; CO_2 and O_2 at equilibrium with partial pressure of air. [Pb]: 0.01 μmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 μg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

(1989) found that organic matter controlled Pb transport. This is somewhat contradictory to the Pb-complexing properties to citrate shown in Figure 39. However, a lot of studies of complexing properties of Pb to specific organic complexes and natural organic peat and humic material confirm the very strong association with Pb. The order of decreasing selectivity of metals to organic complexes are normally: $Hg^{2+} \approx Pb^{2+} > Cu^{2+} >> Cd^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$ (see Stumm and Morgan 1981; Krogstad 1982). Most of the selectivity differences might be explained by ionic characteristics as polarizability, hydration conditions, and the ability of forming stable organo-metallic complexes.

Most Pb entering natural waters is precipitated to the sediment bed as carbonates or hydroxides (May and McKinney 1981). Lead is readily precipitated by many common anions, while desorption replacement by other cations is extremely slow (Boggess 1977). In some acid lakes the deposition of particulate Pb was strongly correlated with the deposition of aluminium and carbon, especially under periods of increasing pH (White and Driscoll 1987b). Precipitation of sparingly soluble Pb compounds are not a primary factor controlling the concentration of dissolved Pb in stream waters. Migration and speciation of Pb were strongly affected by water flow rate, that is, increasing flow rate resulting in increased concentrations of particulate and labile Pb, while colloidal forms decreased. At low flow, Pb was rapidly removed from the water column by sedimentation (Benes et al. 1985).

In the sediments, Pb is mobilized and released when pH decreases suddenly or by significant ionic composition changes (Demayo et al. 1982). However, there was no significant release of Pb from dredged soils suspended in estuarine waters of different salinity for 4 weeks (Prause et al. 1985). Some Pb^{2+} in sediments may be transformed to tetraalkyl-Pb compounds, including TML, through chemical and microbial processes. There is also a possibility of methylation of ionic Pb *in vivo* by fish and other aquatic biota, but the mechanisms are unclear (May and McKinney 1981). Methylation of Pb in sediments was positively related to increasing temperatures, reduced pH, and microbial activity, but seems to be independent of Pb concentration (Demayo et al. 1982). In general, the concentration of tetraalkyl-Pb in sediments is low, representing < 10% of total Pb (Chau et al. 1980).

Unfortunately, the little direct information available about speciation of Pb as well as many other metals has seriously limited our understanding of metal transport and removal mechanisms.

2. Lead in Surface Water Systems

In Finland, higher median concentration of Pb was found in lakes compared with streams, which is relatively uncommon for most heavy metals (Tarvainen et al. 1997). The concentration of Pb in Finnish surface waters was positively correlated with TOC (Tarvainen et al. 1997; Verta, 1990). Pb was found to increase by decreasing pH in surface waters in the Czech Republic (Vesely and Majer 1996), and in Finland (Verta 1990). Both a positive correlation between water color and Pb, and a negative correlation between pH and Pb, were reported in Swedish wood lakes (Borg 1983). In other Swedish lakes with somewhat lower color, located almost in the same latitude area, only a positive correlation between color and Pb was found (Borg 1987). The links between acidification and the concentration of Pb in Swedish rivers and lakes was also reported to be weak by Johansson et al. (1995b). Henriksen and Wright (1978) noted that it was impossible to distinguish between "acidification + mobilization" and "acidification + concomitant increased atmospheric loading" as potential explanations for the observed inverse relationship between aqueous Pb and lake pH in Norwegian lakes.

Borg and Andersson (1984) found that only a minor part of Pb was present in a dialyzable fraction (MW < 2.4 nm). Even at pH < 5, only 10 to 25% was dialyzable Pb. The highest dialyzable concentration of Pb was found in the lowest TOC waters, and in these clearwater lakes a certain but significant negative correlation was found between pH and dialyzable Pb.

Borg (1987) found that higher concentrations of Pb normally are present during wintertime compared with summertime, and explained this by higher sedimentation rates during the summer.

The increase in aqueous Pb in acidified lakes may result partly from decreased removal of atmospherically deposited metals from the water column by sedimentation at low pH (Dillon et al. 1984; Borg et al. 1989). The trofic status of lakes may further influence metal availability, because oligotrofic lakes typically have lower sedimentation rates than the more productive lakes. Once deposited, however, Pb is not readily released from aerobic sediments, except at very low pH (pH < 4.0, LaZerte 1986).

Campbell and Tessier (1987) reported an increase in Pb (and Cu) by decreasing pH, reaching a maximum level about pH 6, and decreases abruptly at lower pH. This is likely because these metals form strong carbonate complexes.

Many studies have shown that Pb is strongly accumulated in the topsoil, often causing an insignificant contribution from the watershed to the surface water (Bergkvist 1987; Blais and Kalff 1993; Brännvall et al. 1997). Thus, the major source is atmospheric inputs direct onto the lake surface (Brezonik et al. 1993; Renberg et al. 1994). Mobilization of lead from the watershed is also found to be minimal even under severe acidification (Vesely and Majer 1996). They and others (Borg and Andersson 1984) suggest this being both due to strong association with organics and sorption on Fe oxyhydroxides and aluminium (White and Driscoll 1987b).

Lead sediment profiles from acidic lakes typically indicate that acidification has little effect on Pb accumulation in the sediments (Norton et al. 1981; Nelson and Campbell. 1991). This has also been confirmed by laboratory experiments on surface sediments, where Pb release from sediments did not occur above pH 3

(Davis et al. 1982). Even the transport of Pb (but also Hg) within the lake and lake watershed is relatively unaffected by acidification. This insensitivity to acidification is presumably due to the strong affinity of humic matter for Pb and Hg. During recent decades atmospheric deposition of Pb has declined dramatically since the 1970s. As a result, studies (e.g., Renberg 1985) have reported decreased Pb concentrations in the uppermost sediment strata for Pb, and even for both Zn and Cd.

Borg and Johansson (1989) compiled data from regional surveys of atmospheric deposition, terrestrial runoff, and soils to estimate metal budgets for a hypothetical Swedish lake. They calculated that 30 to 35% of Pb leaves the catchment by runoff. In contrast to the mobility of Cd, atmospherically deposited Pb (and Hg) accumulated in the surficial soil layers. The transport of these two metals was primarily associated with humic matter and was relatively unaffected by acidification. This is also documented in an acidic lake near Oslo, Norway (Figure 41) where Pb markedly increased during snowmelt, with TOC as the most explainable factor. However, turbidity was not measured, so this increase may either be due to an increase in organic Pb and/or inorganic Pb colloids or particles. An increase in total Pb during snowmelt was also reported earlier (e.g., Abrahams et al. 1989).

Surface water surveys during 1980 to 1992 in Finland, Sweden, and the Czech Republic (Table 28) show mean values of Pb in surface waters between 0.1 to 0.7 μg Pb L^{-1}, with maximum concentrations from 0.7 to 2.0 μg Pb L^{-1}. The highest concentrations recorded during the much larger Nordic survey in 1995 (Table 29) were 2.8 μg Pb L^{-1} in Finland, 7.5 μg Pb L^{-1} in nonlimed Swedish lakes, 12.9 μg Pb L^{-1} in limed Swedish lakes, and 15.0 μg Pb L^{-1} in Norwegian lakes. However, only about 2.5% of the lakes in these countries have Pb concentrations > 2 μg Pb L^{-1}, and about 90% of the lakes fell in the categories *Very low* and *Low* according to the Norwegian and Swedish classification systems (Table 30).

The Swedish and Norwegian lake surveys in 1995 (Figure 40) show relatively clear relationships between Pb concentrations in surface waters and both pH (Figure 43) and TOC (Figure 44). Dividing the lakes into three pH classes, the median concentration of Pb in the lowest pH class (pH < 5.4) was 0.66 μg Pb L^{-1}, while in the medium pH class (pH: 5.4 to 6.0) and highest pH class (pH ≥ 6.0), median Pb concentrations were 0.27 and 0.11 μg Pb L^{-1}, respectively.

Dividing the Swedish and Norwegian lakes into TOC classes, the median Pb concentration in the lowest TOC class (TOC < 5 mg C L^{-1}) was 0.13 μg Pb L^{-1}, while the medium TOC class (TOC: 5 to 10 mg C L^{-1}) and highest TOC class (TOC ≥ 10 mg C L^{-1}) exhibited median values of 0.17 and 0.32 μg Pb L^{-1}, respectively. The positive correlation between TOC and Pb was expected, but the even more distinct relationship between pH and Pb was not expected, based on pure chemical evaluations only. The strong pH relationship with Pb is primarily due to the very close link between atmospheric inputs of strong acids and Pb. This means that the negative relationship between Pb and pH in lakes is not causal.

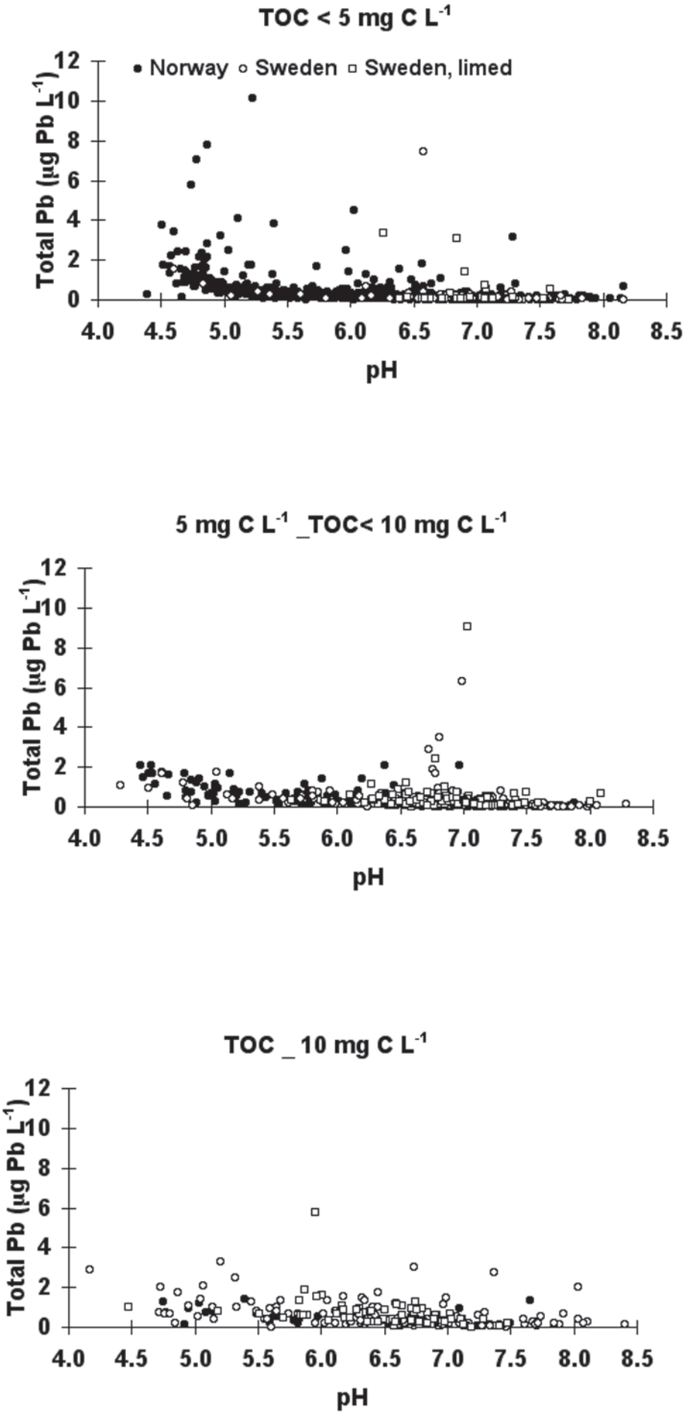


FIGURE 40. Total concentration of lead Norwegian and Swedish (nonlimed and limed) lakes in relation to pH for three different TOC-classes. (Data from Skjelkvaale et al. [1996, 1999].)

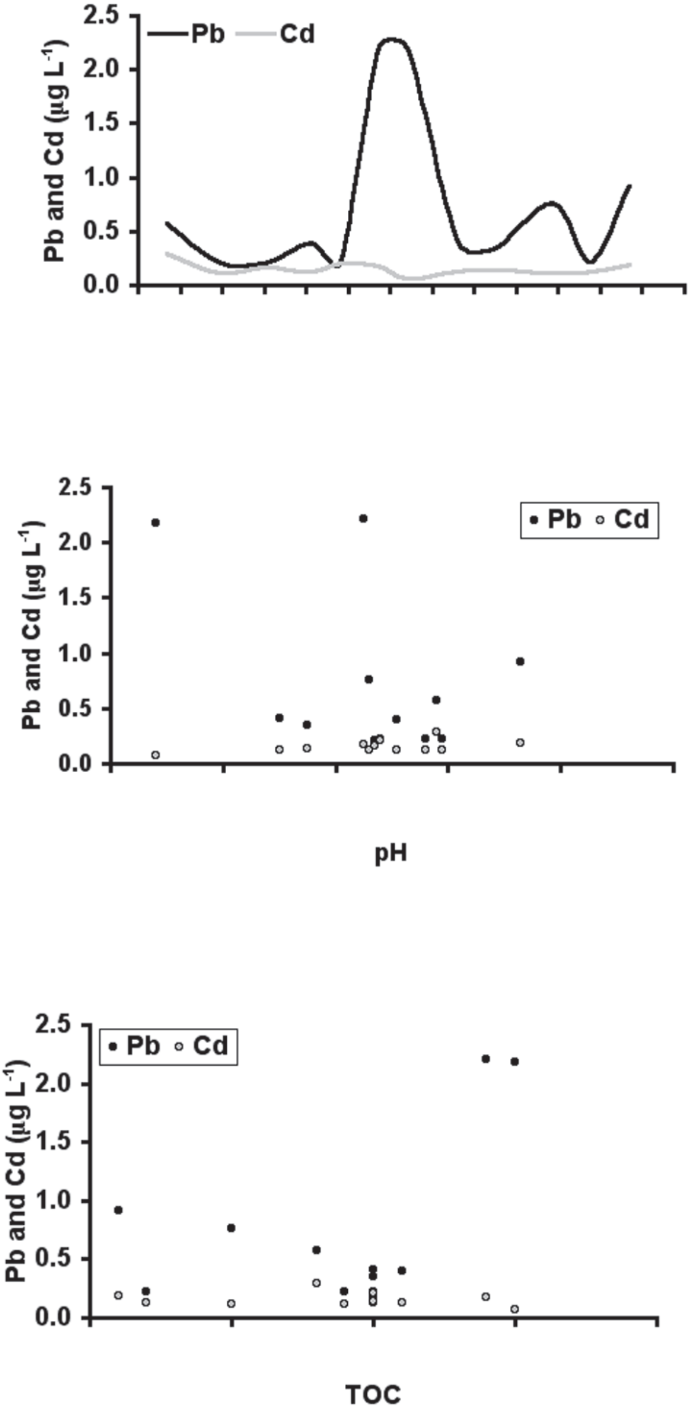


FIGURE 41. Seasonal variations in Pb and Cd in an acidic low TOC lake in Norway (Lake Nepptjern), and relationships to both water pH and concentration of total organic carbon (TOC).

Table 28. Concentrations of Pb (μg Pb L^{-1}) in Nordic surface waters and in the Czech Republic. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	152	1	<0.03 - 2.00	0.33
Finland south[2]	89	n.r.	n.r. - 0.89	0.13 ± 0.15
Finland, north[2]	86	n.r.	n.r. - 0.72	0.12 ± 0.14
Sweden, south[3]	7	n.r.	0.3 - 1.1	0.67 ± 0.32
Sweden, north[3]	10	n.r.	0.2 - 1.1	0.42 ± 0.25
Sweden, east[4]	12	n.r.	0.2 - 0.8	0.43 ± 0.19
Sweden, s.east[4]	28	n.r.	0.02 - 1.9	0.40 ± 0.36
Sweden, s.west[4]	7	n.r.	0.3 - 1.1	0.69 ± 0.30
Sweden, north[5]	56	n.r.	0.1 - 0.8	0.27
Czech[6]	5363	n.r.	n.r.	0.40

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

[2] Verta et al. (1990), based on samples from autumn 1987.

[3] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden,south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[4]) Borg and Andersson (1984), oligotrophic forest lakes, sampled during 1980-1983. East: lakes south of Stockholm, TOC: 7.4 ± 2.0 mg C L-1, pH: 5.1 - 6.9; S.east: Småland, TOC: 6.6 ± 2.8 mg C L-1, pH:

[5] Borg (1987), based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

[6] Vesely and Majer (1996), based on data collected between 1984 and 1992

Table 29. Percentile distribution of Pb (μg Pb L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (See Skjelkvaale et al. 1999). Norway: n = 985; Sweden, non-limed: n = 559; Sweden, limed: n = 261; Finland: n = 462

Pb	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	14.969	7.469	12.920	2.780
	99.5 %	7.098	3.501	8.053	1.548
	97.5 %	2.097	1.782	1.751	0.899
	90.0 %	0.868	0.767	0.845	0.560
Quartile	75.0 %	0.420	0.349	0.459	0.300
Median	50.0 %	0.174	0.152	0.270	0.140
Quartile	25.0 %	0.086	0.059	0.125	0.060
	10.0 %	0.047	0.031	0.083	0.030
	2.5 %	0.023	0.016	0.047	0.021
	0.5 %	0.012	0.008	0.022	0.017
Minimum	0.0 %	0.004	0.003	0.016	0.014

Table 30. Classification of concentrations of Pb in surface waters (μg L^{-1}), the upper (0-1 cm) of lake sediments (mg kg^{-1} dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Pb (Sweden, 1991)	≤ 0.2	0.2 - 1.0	1 – 2	2 - 5	> 5
Pb (Sweden, 1998)[1]	≤ 0.2	0.2 - 1.0	1 – 3	3 - 15	> 15
Pb (Sweden, 1998)[2]	≤ 0.1	0.1 - 0.4	0.4 - 1.2	1.2 - 12	> 12
Pb (Norway, 1997)	< 0.5	0.5 - 1.2	1.2 - 2.5	2.5 - 5	> 5
Sediment					
Pb (Sweden, 1991)	≤ 5	5 - 30	30 – 100	100 - 400	> 400
Pb (Sweden, 1998)[3]	≤ 50	50 - 150	150 – 400	400 - 2000	> 2000
Pb (Norway, 1997)	< 50	50 - 250	250 – 1000	1000 - 3000	> 3000

[1] Based on risks of biological effects.

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96).

[3] Based on distribution in Swedish lakes with and without local emissions.

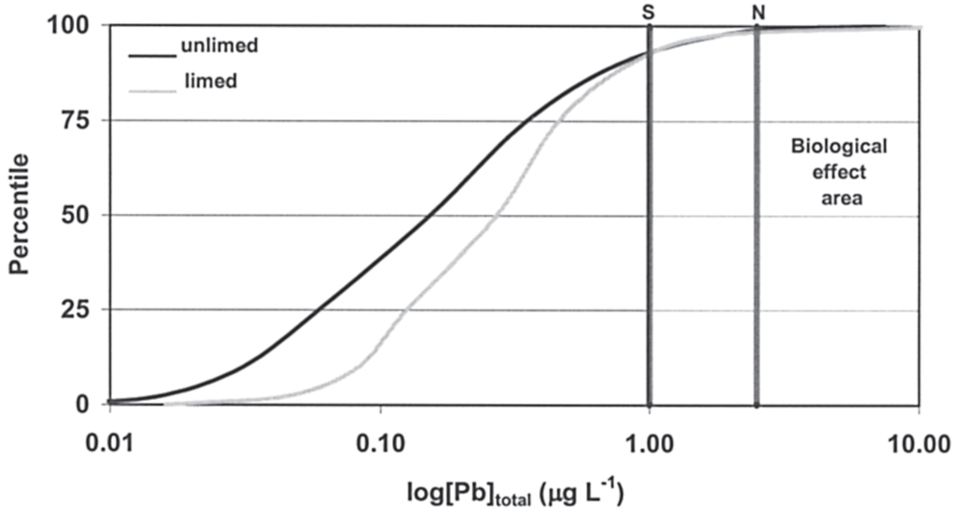


FIGURE 42. Percentile distribution of total Pb in limed (n = 261) and not limed (n = 820) Swedish lakes. S and N show the assessed critical concentrations for aquatic life in Norway and Sweden. (Data from Skjelkvaale et al. [1996, 1999].)

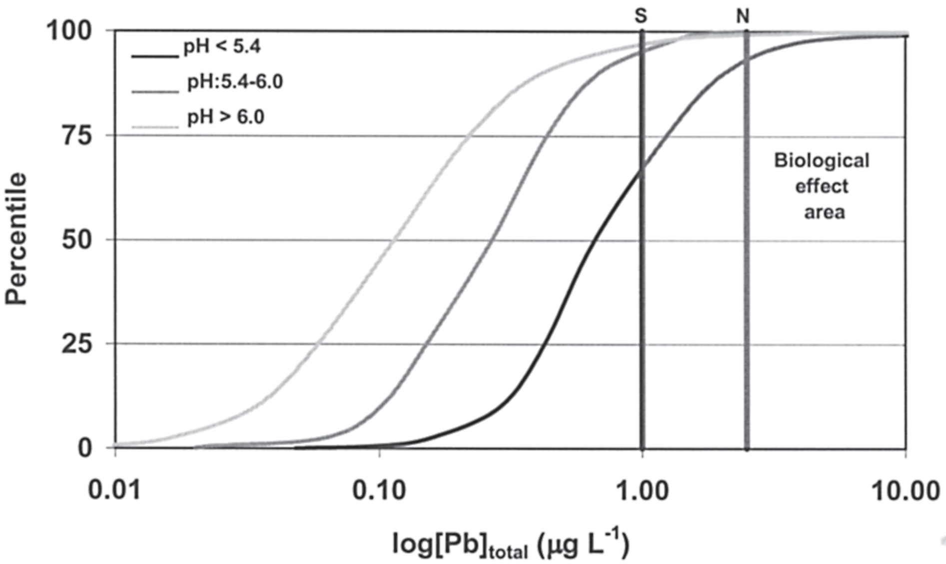


FIGURE 43. Percentile distribution of total Pb in Norwegian and Swedish lakes based on three pH classes. pH < 5.4, n = 250; 5.4 ≤ pH < 6.0, n = 204; pH ≥ 6, n = 1090. (Data from Skjelkvaale *et al*. [1996, 1999].)

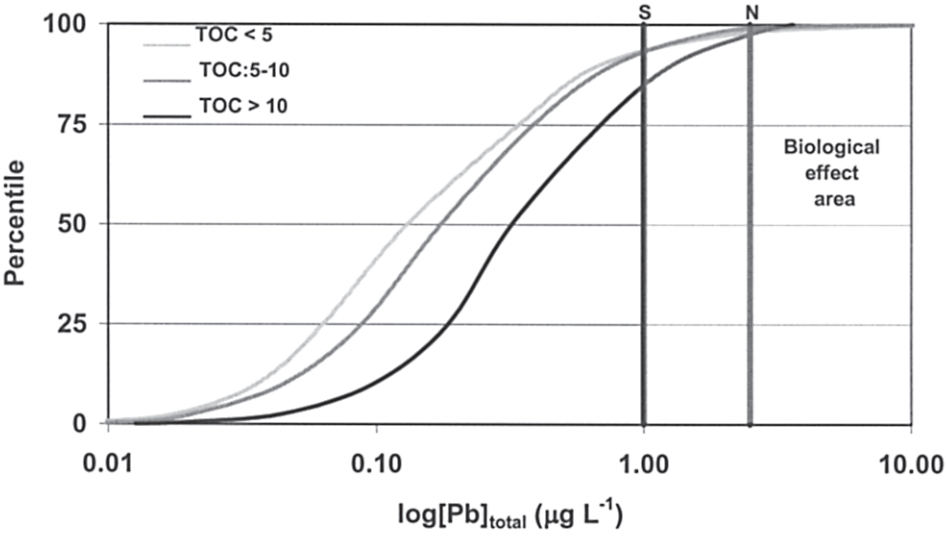


FIGURE 44. Percentile distribution of total Pb in Norwegian and Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale *et al*. [1996, 1999].)

Limed lakes in Sweden normally have higher Pb concentrations than nonlimed Swedish lakes, that is, median Pb concentration in limed lakes is 0.27 μg Pb L^{-1} compared with 0.15 μg Pb L^{-1} in nonlimed Swedish lakes (Figure 42). The tendencies of higher heavy metal concentrations in limed Swedish lakes are also documented for Pb (Table 29). This indicates that many lakes in the most air-polluted areas in Sweden are limed, but also that liming is not very effective for precipitation/retention of many heavy metals, especially the metals with strong complexing properties to organics. The survey also documents that several of the limed lakes in Sweden are under reacidification but do not show any extreme increase in Pb. Thus, it is unlikely that significant changes in the concentration of Pb will occur, especially if medium acidic ($pH > 5$), limed lakes reacidify.

A proposed effect-related sediment criteria for heavy metals in Canada (Smith et al., 1996) assumes a biological effect level of Pb in sediments at 91 mg kg^{-1}dw, while the national criteria in Sweden and Canada are 60 and 35 mg kg^{-1}dw, respectively.

a. Experimental Acidification

Stepwise (biannually) artificial acidification of a lake from 6.1 to 5.6, 5.5, and 4.6 showed no effect on the concentration of dissolved Pb (Mach and Brezonik 1989). Williams (1993) showed that acidification has a certain effect on dissolution of Pb from sediments. Kahl and Norton (1983) recorded no changes in the concentration of Pb in water close to the sediments by acidifying the waters above sediments (taken from different depths) from pH 5.24 to 5.89 down to $pH \approx 5.0$. By acidifying down to pH 4.0, however, they documented significantly increases in the concentration of Pb derived from sediments. By assuming biannual dilution of this water (two turnovers) with the total lake volume, and a lake water residence time of 6 months, a pH decrease to 5.0 should only (as a maximum) cause a concentration increase in the lake from 0.40 μg Pb L^{-1} to 0.74 μg Pb L^{-1}.

b. Liming

After liming of 20 lakes, most of them mildly acidic, Marcus (1988) observed no significant changes in the concentration of Pb in eight lakes, significant decreases in six lakes, and significant increases in six. Evaluated together, no significant change in the concentration of Pb was observed after liming. Prelimed pH of the lakes varied from 4.44 to 6.99, with a mean pH of 5.51. Liming of a low TOC lake in Canada (from pH 4.8 to about pH 7) had no effect on the concentration of Pb in lake water (White et al. 1984). Total concentration was 2 μg Pb L^{-1}.

Liming of a wetland in Dalarna, Central Sweden, did not reduce the Pb concentration significantly ($p > 0.05$). Before liming, the median Pb concentration was 0.70 $\mu g\ L^{-1}$ in the outlet stream (see Section VII.F.2 and Table 25).

c. Reacidification

No data are available!

3. Biology and Toxicity

Lead adversely affects survival, growth, reproduction, development, and metabolism of most species under controlled conditions, but its effects are substantially modified by numerous physical, chemical, and biological variables. In general, organic complexed Pb compounds are more toxic than inorganic Pb compounds, and the younger, immature organisms are most susceptible. Food chain biomagnification of Pb is negligible (e.g., Campbell and Stokes 1985; Hodson 1986). Unlike methylmercury, Pb as Cd does not accumulate appreciably in the skeletal muscle tissue of fish (e.g., Benoit et al. 1976; Holcombe et al. 1976; Bollingberg and Johansen 1979; Harrison and Klaverkamp 1989). Thus, contamination of fish with Cd and Pb is generally not considered a significant health risk to human consumers.

a. Toxic Species

In water, the toxic forms are within the dissolved Pb fraction. Some organic Pb compounds are in general more toxic than inorganic Pb compounds to aquatic environments. Ethyl derivatives are more toxic than methyl derivatives, and the toxicity increased with increasing degree of alkylation. Tetraethyl-Pb (TEL) is the most toxic (Chau et al. 1980). TEL was 10 times more effective than tetramethyl-Pb (TML) in reducing oxygen consumption by coastal marine bacteria (Marchetti 1978). TML chloride was 20 times as toxic as $Pb(NO_3)_2$ to freshwater algae (Wong et al. 1978)

Alkyl-Pb compounds accumulate more readily by freshwater teleosts than inorganic Pb compounds. Increased Pb accumulation with decreasing pH has been observed in laboratory studies (Hodson et al. 1978; Merlini and Pozzi 1977), a pattern opposite that reported for Cd. Particulate organic carbon has been shown to decrease Pb uptake by fish (Hodson et al. 1979), presumably through adsorption. The effects of DOC on toxicity, which is likely more relevant in many Nordic lakes, has not been examined.

Among the inorganic Pb species, the most bioavailable and toxic forms are thought to be Pb^{2+}, $PbCl^+$, and $PbOH^+$. Complexation with CO_3^{2-} will reduce the concentrations of Pb^{2+}, but this is of minor importance in lakes with $pH < 6.5$.

b. Target

Acute toxic solutions of Pb (as for many other metals) cause increased mucus formation in fishes. The excess coagulates over the entire body and is particularly prominent over the gills. Thus, it interferes with the respiratory function with hypoxia as cause of death (e.g., Aronson 1971; NRCC 1973). Thus, we assume the cationic Pb compounds as the main acute toxic species, as long as the concentration of TEL and TML often is low in surface waters.

As Pb is adsorbed from the water, the blood cell concentration increases and the erythrocyte enzyme, delta amino levulinic acid dehydratase (ALAD, part of the haemoglobin synthetic pathway), is inhibited. This inhibition is specific for Pb intoxication and may cause anaemia. The most profound physiological effects of Pb intoxication occur in the nervous system, not in the blood-forming tissue, and appear as a darkening in the caudal region (black tail) and eventually as a bending of the spine (lordoscoliosis). This is initially reversible, but later it becomes permanent.

Pb also interferes with chlorophyll formation in plants by inhibiting the conversion of coproporphyrinogen to proporphyrinogen by competing with iron, inhibits allantoise formation in annelids, inhibits alpha-glycerophosphate dehydrogenase activity in trout, increases glutamic oxalacetate transaminase activity in *Daphnia*, affects neural and hormonal systems that control activity of metabolic rates in fish, interacts with polar sites of glycoproteins in epidermal mucus of fish, and may inhibit vitamin C and tryptophan metabolism (Wong et al. 1978).

Elevated concentrations of Pb are normally found in blood, bone, gill, liver, and kidney. The toxicity of Pb is found to be higher under conditions favoring rapid growth. Thus, the concentration of Pb is more dependent of growth rate than fish size.

Even though a higher concentration of Pb is found in organisms exposed to high concentrations of Pb, the Pb concentration is observed to decrease markedly with increasing trofic levels, within both detritus-based and grazing aquatic food chains (e.g., Wong et al. 1978; Vighi 1981). The residence time of Pb in aquatic biota seems to be related to the route of administration, with Pb values of 9 days by waterborne routes and 40 days by diet (Vighi 1981).

c. Fish

Acute toxicity, 4-day LC_{50} for Pb, were reported to be 700 μg L^{-1} for Atlantic salmon at 11 mg L^{-1} hardness (Grande and Andersen 1983), 1170 μg L^{-1} in rainbow trout at 28 mg L^{-1} hardness (Davies et al. 1976), 4100 μg L^{-1} for brook trout at 44 mg L^{-1} hardness (Holcombe et al. 1976), and 2100 μg L^{-1} for fathead minnows at 44 mg

L^{-1} hardness (Spehar and Fiandt 1986). Only that of Grande and Andersen (1983) had a hardness typical for low-alkalinity lakes. Davies et al. (1976) found that 14-day (LC_{50}) was lower than the 4-day LC_{50}. For rainbow trout, the threshold value was 200 $\mu g\ L^{-1}$ in soft water (30 mg L^{-1} as $CaCO_3$), and mortality occurred between exposure days 5 and 14, rather than within the more usual 4 days (Sprague 1969). Although alkalinity may be the most significant abiotic factor influencing lead toxicity, Ca^{2+} probably exerts a biotic effect, because high dietary calcium reduces uptake of dietary Pb and aqueous calcium reduce uptake in some tissues (Varanasi and Gmur 1978). Despite so, no experiments have really focused on the likely ameliorating effect of dissolved organic carbon, and the likely ameliorating effect of higher ionic strength of water in general. Both these factors should be essential for acute toxicity of metals as long as the main target organ is the gill with ion exchange processes as the most likely mechanism involved at the gill surface.

Tetramethyl-Pb (TML) was acutely toxic to rainbow trout at 3.5 $\mu g\ L^{-1}$ (Wong et al. 1981).

Chronic effects, based on laboratory studies, suggest effects in sensitive aquatic organisms of about 5 to 10 μg Pb L^{-1}. Effect (5% of the fish) and no-effect concentrations for black tails in rainbow trout in a 19-month exposure were 7.6 and 4.0 μg Pb L^{-1} at 28 mg L^{-1} hardness as $CaCO_3$ (Davies et al. 1976). Later life stages of trout were 2- to 5-fold less sensitive than trout initially exposed as larvae (Davies et al. 1976) or juveniles (Hodson et al. 1979). Brook trout also exhibited black tail in a three-generation life-cycle test, but effect concentrations were much higher (Holcombe et al. 1976).

Exposures of early life stages of several species in soft water affected hatching success, mortality, and growth at Pb concentrations ranging from 83 to 253 μg Pb L^{-1} (Sauter et al. 1976).

Whitefish species *(Coregonus aspius* and *C. widegreni*) from lead-contaminated, soft water lakes in northern Sweden showed signs of lead intoxication, such as ALAD inhibition, elevated blood glucose, and depressed plasma sodium concentrations, but no overt symptoms (Haux et al. 1986). Concentrations of Pb in liver tissue were also quite high. Concentrations of aqueous Pb were quite variable, ranging form 1.5 to 41 μg Pb L^{-1}. The exposure history of the whitefish was unfortunately unknown.

Concentrations of Pb > 10 $\mu g\ L^{-1}$ are expected to provide severe long-term effects on fish and fisheries (Demayo et al. 1982). The accumulation of Pb by fish typically increases with increasing exposure concentration in water. The effects are most pronounced at high water temperature and low pH, in soft water, in younger stages, and after long exposures.

d. Invertebrates

Aquatic invertebrates display great interspecies variability in sensitivity to Pb. The minimum invertebrate 48-h LC_{50} was 248 μg Pb L^{-1} for the water flea *Ceriodaphnia dubia* (Spehar and Fiandt 1986). Mackie (1989) determined that the

96-h LC_{50} of Pb to different invertebrate species ranged from 10 µg Pb L^{-1} at pH 5 for the sideswimmer *Hyalella acteca* to > 60000 µg Pb L^{-1} for the damselfly, *Enallagma* sp. Therefore, short-term effects of Pb should not be a problem under normal environmental conditions.

The lowest concentrations reported for chronic effects are the adverse effect on daphnia (*Daphnia magna*) reproduction at 1 µg Pb^{2+} L^{-1} (Berglind et al. 1985) and Wilson (1982), who observed a significant reduction in the phototaxic response of zooplankton exposed to Pb levels ranging from 1.3 to 4.7 mg Pb L^{-1} over a 16-day period. Furthermore, a high bioconcentration factor was measured in freshwater algae at 5 µg Pb^{2+} L^{-1} (Vighi 1981). However, Pb is not shown to biomagnify as Hg.

In summary, low water hardness and alkalinity substantially enhance the toxicity of Pb to aquatic invertebrates. However, toxicity to aquatic invertebrates generally occurs at concentrations that exceed ambient concentrations. Therefore, direct Pb toxicity to invertebrates, even in acidic waters, is unlikely. Lead does not readily bioaccumulate or biomagnify in aquatic biota, but there is limited evidence to suggest that reduced pH increases Pb uptake by invertebrates. This could enhance food chain transfer of lead in acidified ecosystems.

e. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

The classification system of Norwegian freshwaters primarily related to salmonids (Table 31) based on natural observations assess no effects on biota or no limitations for human consumption of fish at concentration < 1.0 µg Pb L^{-1}. Lithner (1989) reported the lowest known effect at 1.5 µg Pb L^{-1}. The critical concentrations of Pb in Norwegian and Swedish freshwater are 2.5 µg Pb L^{-1} in Norway and 1.0 µg Pb L^{-1} in Sweden (Table 32).

According to the Nordic lake survey in 1995, 8.5% of the Norwegian, 7.0% of the nonlimed Swedish, 6.5% of the limed Swedish, and 1.7% of the Finnish lakes have Pb concentration above the critical concentration for surface water in Sweden. Correspondingly, only 1.6% (Norway), 1.8% (nonlimed Sweden), 1.9% (limed Sweden), and 0.2% (Finland) have higher Pb concentration than the critical concentration in Norway. As for Cd, where also a certain amount of lakes have so high concentrations of Pb that biological effects should be expected, it is important to do analytical fractionation of these metals in these lakes. Organic Pb is assumed to be the most toxic, but the most acute toxic forms of metals are generally the inorganic forms. Most organic Pb compounds in surface water will be bound to humic material. This may accumulate in the long run, but will likely not be as acute as inorganic cationic Pb compounds.

Table 31. Classification system of Pb (µg L^{-1}) in Norwegian freshwaters primarily related to salmonids (UN-ECE 1997b). Class 1: No effects on biota or no limitations for human consumption of fish. Class 2: Some sensitive species may be affected, but no effects on fish. Little ecosystem effects. Class 3: Effects on salmonids, reduced number of species with a dominant of tolerate species. Class 4: No salmonids and serious effects also on many other species. The structure of the ecosystem is completely destroyed

Class 1 Very Low	**Class 2** Low	**Class 3** Medium	**Class 4** High
< 1	1 - 5	6 – 15	> 15

Table 32. Critical concentrations of Pb (µg L^{-1}) at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997), Sweden (Alm et al. 1998)

	Freshwater µg L^{-1}			Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
		acute	Chronic			
The Netherlands	11			4700	55	0.5
United Kingdom[1]	4 - 25				500	
Germany[2]		83	3.2			
Canada[1]	1 - 7			35	70	
Sweden	**1.0**			**60**	**30 – 60**	
Denmark	3.2				50	
Norway	**2.5**					
Finland					38	

[1] Range means that values depend on water hardness; [2] Hardness dependent criteria (100 mg $CaCO_3$ L^{-1} is used).

4. Reacidification — Biological Risk

The main toxic forms of Pb are in the dissolved fractions, with some Pb organic compounds such as tetraethyl- and tetramethyl-Pb as the most toxic. The most bioavailable and thereby likely most acute toxic inorganic forms of Pb in mildly acidic freshwaters are Pb^{2+}, $PbCl^{+}$, and $PbOH^{+}$. Even though the toxicity of Pb complexed to natural organic acids has not been examined, it is likely that Pb associated with organic acids are less toxic or even not toxic to aquatic life, a common situation for many other heavy metals.

Main source of Pb to surface water systems is direct atmospheric inputs, both to the catchment and directly on the lake surface. Due to the strong association of Pb to natural organic compounds, Pb is primarily transported to surface waters as Pb organic complexes. Within normal pH values of surface waters, pH has minor effects on both the transport of Pb to surface waters and the sedimentation of Pb in lakes. Accordingly, the most important factor for the Pb concentrations in surface waters are the atmospheric inputs, an input that has decreased significantly during the last years. In Norway, Pb in wet deposition has decreased by 60 to 80% from 1978 to 1996 (Toerseth and Manoe 1997). Already in 1995 Renberg reported decreased Pb concentrations in Swedish lake sediments. A reacidification of limed water bodies will likely have no or minor effect on the Pb concentrations in water as long as the reacidification pH is > 5. Significant Pb release from sediments will likely not occur above pH 3 (Davis et al. 1982).

Based on the toxicity criteria in Sweden and Norway, only a few lakes have Pb concentrations that might have negative effects on aquatic life. An increase in Pb by reacidification of limed lakes is likely not a problem in most Swedish and Norwegian lakes.

H. Nickel (Ni)

1. General Geochemistry

a. Sources

Nickel (Ni) is an essential element to plants, bacteria, humans, and other mammals (Farago and Cole 1988; Nieboer et al. 1988). However, Ni is toxic at higher concentrations to most plants and fungi. It is moderately toxic to mammals, but can induce allergic effects in humans. Ni compounds and probably also metallic Ni are carcinogenic to humans (Aito and Tomatis 1990).

The contribution of Ni to the environment arises from both natural and anthropogenic sources. Among the former are parent bedrock and deposits enriched of Ni the most important. Man-made sources include smelting of nickeliferous ores, metal refining, burning of coal and petroleum products, disposal of waste, sewage and sludge, and fertilizer applications. The pollution effect of human activities is generally local, but air emissions have dispersed Ni over large regions.

In igneous bedrock, Ni is most abundant in the ultrabasic and basic suites. Gabbro and diabase have an average content of 208 mg Ni kg^{-1}, compared with 104 mg Ni kg^{-1} for basalt. Rocks such as granite and pegmatite have a low average Ni content of 13 mg kg^{-1}. Sedimentary rocks such as sandstone and limestone are also low in the Ni content (10 to 12 mg kg^{-1}), while shales exhibit somewhat higher values (60 to 85 mg kg^{-1}). The average Ni content in metamorphic rocks such as gneisses and quartzites is low (15 to 20 mg kg^{-1}), while serpentines are extremely high (1500 mg kg^{-1}). Nickel deposits occur as lenses or veins in or near mainly ultrabasic and basic igneous rocks. In these deposits, the Ni metal is associated with other elements such as Co, Fe, Cu, Pb, Zn, As, Sb, and S. Generally, the Ni concentrations in these deposits vary in the range <0.5 to 2%, but some may contain up to 20% (Boyle and Robinson 1988).

The global average Ni content in soil is estimated to be 35 to 40 mg kg^{-1} dw. Arctic tundra, brown earth soils, and podzols developed on intermediate and acidic rocks and most tills vary relatively little from the average. Soils developed on basic and ultrabasic rocks exhibit wide variations from the average and may contain up to 2.4% Ni. Soils in the vicinity of Ni deposits are generally enriched in Ni (Boyle and Robinson 1988). In the soil profile, Ni tends to follow iron with an accumulation in the B horizon. Nickel can also be enriched in the mor layer due to the relatively strong adsorption to humus. In general, however, the largest amount of Ni is concentrated in the hydrolysate and oxidate components of soils, including clay minerals, which are marked accumulators of Ni (Boyle and Robinson 1988). Increased soil acidity increase the release of Ni from the soil profile at least through the B horizon. The solubility of Ni increases rapidly if pH decreases to 4.0 to 4.5 in the B horizon. Soil solution concentrations of Ni were generally higher in brown forest soil than in podzol. Mass balance calculations indicate that acidic forest soils can lose significant quantities of the element (Bergkvist et al. 1989).

Scandinavian moss analysis in 1995 showed elevated Ni concentrations in the vicinity of large point sources such as the metal smelters in Vargön and Rönnskär (Sweden), Årdal and Kristiansand (Norway), and the Kola peninsula (Russia). Generally, the Ni concentration in moss was < 2 mg kg^{-1} dw in areas not affected by local pollution in Fennoscandia. The contribution from long-range transport was low (Rühling et al. 1996).

In unpolluted stream and river sediments, the Ni concentrations generally are in the range of 1 to 150 mg kg^{-1} dw, but with values up to 1000 mg kg^{-1} dw in the vicinity of nickeliferous deposits (Boyle and Robinson 1988). The Ni concentrations in surface sediments (0 to 1 cm) from 29 unpolluted lakes in central and northern Sweden did not show any geographical gradient. The concentrations varied between 3.6 to 21 mg Ni kg^{-1} dw (10 to 90 percentiles), with a median concentration of approximately 8 mg Ni kg^{-1} dw. The Swedish, preindustrial concentration of Ni is estimated to approximately 10 mg Ni kg^{-1} dw, which indicates a low accumulation of Ni due to long-range atmospheric transport. Locally, the preindustrial Ni concentration can be much higher due to geological anomalies. Areas with postglacial clay generally show elevated Ni concentrations in the preindustrial sediments (Alm et al. 1998).

In sediments, Ni is efficiently retained due to sorption to inorganic compounds such as hydrous oxides of iron and manganese and clay mineral complexes or to organic compounds such as different humic complexes (Boyle and Robinson 1988). Young and Harvey (1992) found that Ni was predominantly recovered from the extractable inorganic portion of the sediments, but 25 to 75% of leachable Ni was found to be associated with the organic sediment fraction, while < 25% was present in this fraction in the lakes with circumneutral pH.

b. Chemical Properties

Ni exists in four oxidation stages: Ni(0), Ni(II), Ni(III), and Ni(IV). The first two are the most common in nature, while the divalent form is the only oxidation stage found in natural freshwaters. Ni(II) is stable to oxidation under most natural conditions in contrast to Fe(II), which Ni(II) in other chemical aspects it is remarkably similar. Atomic radii, covalent radii, Me^{2+} ionic radii, and electronegativity are essentially identical for these two metals as well as for Co, which is the third metal in the Fe triad. These similarities make Ni to substitute for Fe and Co in a large number of compounds. Ni salts of chloride, sulfate, and nitrate are soluble, while Ni oxide is soluble only under acid conditions. Ni hydroxides, sulfides, arsenides, arsenates, silicates, are almost insoluble.

Ni(II) forms stable complexes with organic ligands (Figure 45) such as carboxylates, fulvates, and humates (Boyle and Robinson 1988). The bonding strength for divalent ions in peat and humic acids fractionated from the peat follows the sequence Pb^{2+} $Cu^{2+}>Cd^{2+}>Zn^{2+}>Ni^{2+}>Co^{2+}$ in the pH range 3 to 4.6 (Krogstad 1982).

2. Nickel in Surface Water Systems

Generally, elevated Ni concentrations are found in surface waters in agricultural areas in Sweden and along the Finnish coast. This might be caused by naturally higher concentrations in clay and fine fractions of till, formation of stable inorganic complexes with sulfates in sulfate-rich coastal waters, or high atmospheric inputs (Tarvainen et al. 1997; Alm et al. 1998). In eastern Finland, till geochemistry is reflected in the Ni distribution in surface waters. Neither till chemistry nor the high atmospheric deposition from the Kola Peninsula in Russia was reflected in the Ni concentrations in northern Finland (Tarvainen et al. 1997).

Both acidity and the amount of humic substances in water were shown to influence the distribution of Ni in 256 Finnish headwater lakes in 1987 (Mannio

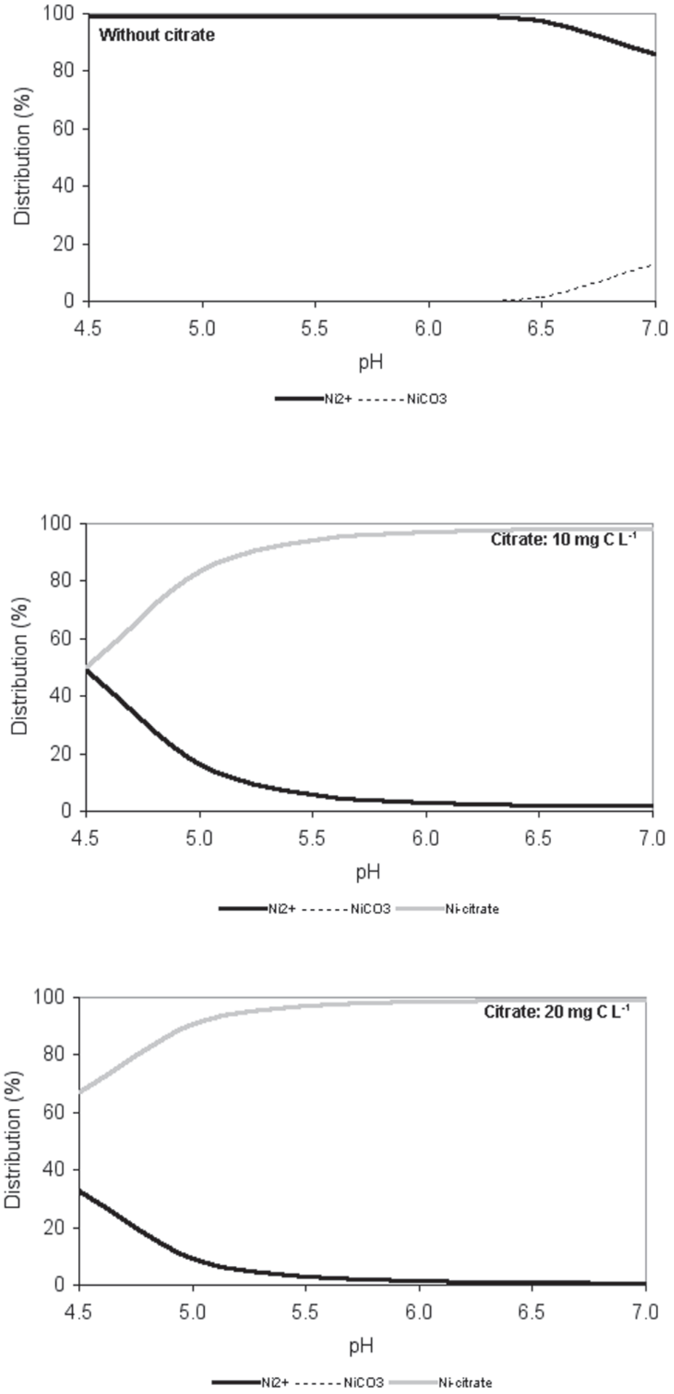


FIGURE 45. Distribution of major Ni species in relation to pH at citrate concentrations of 0, 10, and 20 mg C L^{-1}. Essential input conditions: 25°C; CO_2 and O_2 at equilibrium with partial pressure of air; [Ni]: 0.1 µmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 µg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

et al. 1993), but a similar survey of 116 lakes in 1992 only showed a correlation with organic matter (Mannio et al. 1995). The 1990 Finnish stream survey (1165 sampling points, Tarvainen et al. 1997) showed negative correlation between pH and Ni, positive correlation between nickel, and the amount of both humic substances and sulfate. The lake survey in Sweden (in 1995) also showed positive covariations between the concentrations of Ni and sulfate and Ni and organic matter. In contrast to Finland, however, this survey showed a positive covariation with pH (Alm et al. 1998). This is likely because of high pH and Ni concentrations in agricultural areas.

Data obtained in 1980 to 1992 and from the Nordic Lake survey in 1995 show that median Ni concentration in Swedish, Finnish and Norwegian surface waters was < 0.5 µg Ni L^{-1} (Table 33, Table 34). The Ni concentrations in these surface waters are generally *low* according to the classification systems in Sweden and Norway (Table 35).

Figure 46 shows the total Ni concentrations in Norwegian and Swedish nonlimed and limed lakes in the 1995 lake surveys and in relation to pH for three different TOC classes. From the percentile distribution of these TOC classes (Figure 49), it is evident that TOC is positively correlated with Ni. While median concentration of the Swedish and Norwegian lakes was 0.21 µg Ni L^{-1} for the low TOC lakes (TOC < 5 mg C L^{-1}), the corresponding median values for medium TOC lakes (TOC: 5 to 10 mg C L^{-1}) and high TOC lakes (TOC ≥ 10 mg C L^{-1}) were 0.41 µg Ni L^{-1} and 0.58 µg Ni L^{-1}, respectively.

There is no significant correlation between pH and concentration of Ni (Figure 48) in the Swedish and Norwegian lakes. While the median concentration of Ni in low pH lakes (pH < 5.4) was 0.22 µg Ni L^{-1}, the median concentration in the medium pH lakes (pH: 5.4 to 6.0), and high pH lakes (pH ≥ 6.0) were 0.20 µg Ni L^{-1} and 0.33 µg Ni L^{-1}. This, however, indicates generally higher Ni concentrations in

Table 33. Concentrations of Ni (µg Ni L^{-1}) in Nordic surface waters. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	152	0	0.06 - 2.10	0.38
Finland south[2]	89	n.r.	n.r. - 5.31	0.40 ± 0.60
Finland, north[2]	156		n.r. - 2.64	0.25 ± 0.38
Sweden, south[3]	6	n.r.	< 0.9 - 1.2	< 1.0
Sweden, north[3]	10	n.r.	< 0.9	< 0.9
Sweden, north[4]	56	n.r.	< 0.2 - 1.0	≤ 0.42

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

[2] Verta et al. (1990), based on samples from autumn 1987.

[3] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden,south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[4] Borg (1987), based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

Table 34. Percentile distribution of Ni (µg Ni L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462

Ni	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	7.047	10.169	11.082	47.600
	99.5 %	3.644	3.927	2.231	14.706
	97.5 %	1.589	2.604	1.192	2.848
	90.0 %	0.712	1.295	0.849	1.296
Quartile	75.0 %	0.433	0.700	0.609	0.640
Median	50.0 %	0.244	0.404	0.435	0.360
Quartile	25.0 %	0.127	0.209	0.260	0.210
	10.0 %	0.071	0.102	0.169	0.140
	2.5 %	0.034	0.046	0.096	0.040
	0.5 %	0.021	0.032	0.041	0.037
Minimum	0.0 %	0.006	0.010	0.028	0.023

Table 35. Classification of concentrations of Ni in surface waters (µg L^{-1}), the upper (0-1 cm) of lake sediments (mg kg^{-1} dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Ni (Sweden, 1991)	≤ 1	1 - 5	5 - 10	10 - 50	> 50
Ni (Sweden, 1998)[1]	≤ 0.7	0.7 - 15	15 - 45	45 - 225	> 225
Ni (Sweden, 1998)[2]	≤ 0.3	0.3 - 1	1 - 2.5	2.5 - 25	> 25
Ni (Norway, 1997)	< 0.5	0.5 - 2.5	2.5 - 5	5 - 10	> 10
Sediment					
Ni (Sweden, 1991)	≤ 10	10 - 30	30 - 75	75 - 300	> 300
Ni (Sweden, 1998)[3]	≤ 5	5 - 15	15 - 50	50 - 250	> 250
Ni (Norway, 1997)	< 50	50 - 250	250 - 1000	1000 - 3000	> 3000

[1] Based on risks of biological effects.

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96).

[3] Based on distribution in Swedish lakes with and without local emissions.

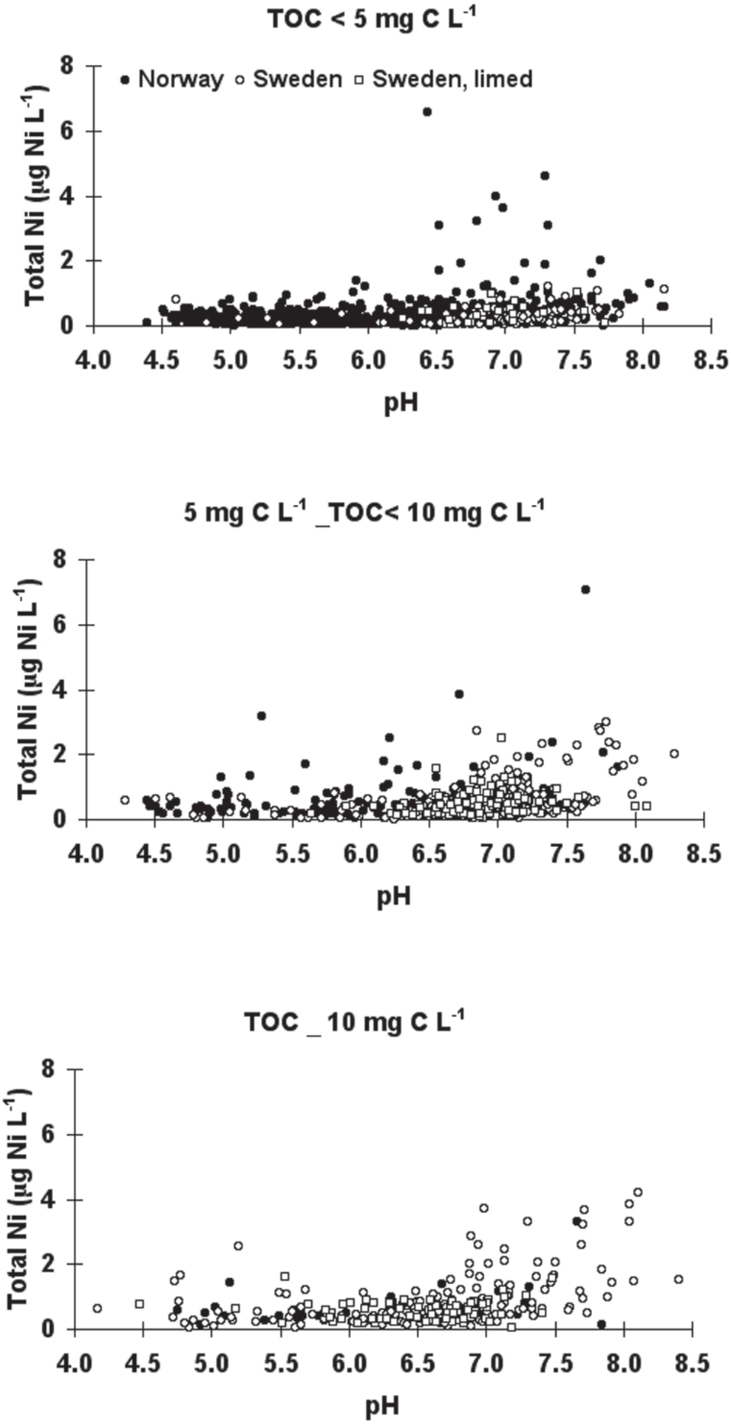


FIGURE 46. Total concentration of nickel in Norwegian and Swedish (nonlimed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale *et al*. [1996, 1999].)

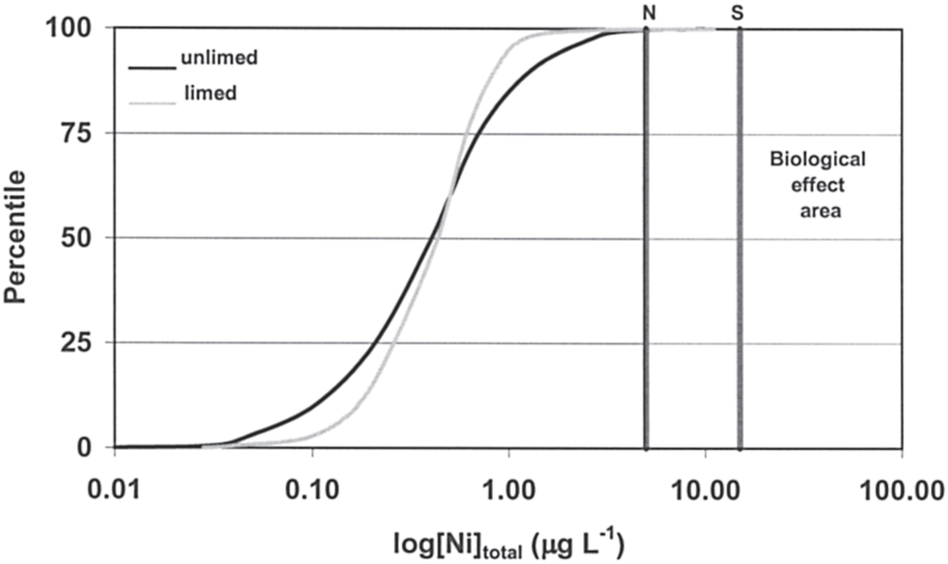


FIGURE 47. Percentile distribution of total Ni in limed (n = 261) and not limed (n = 820) Swedish lakes. S and N show the assessed critical concentrations for aquatic life in Norway and Sweden. (Data from Skjelkvaale *et al*. [1996, 1999].)

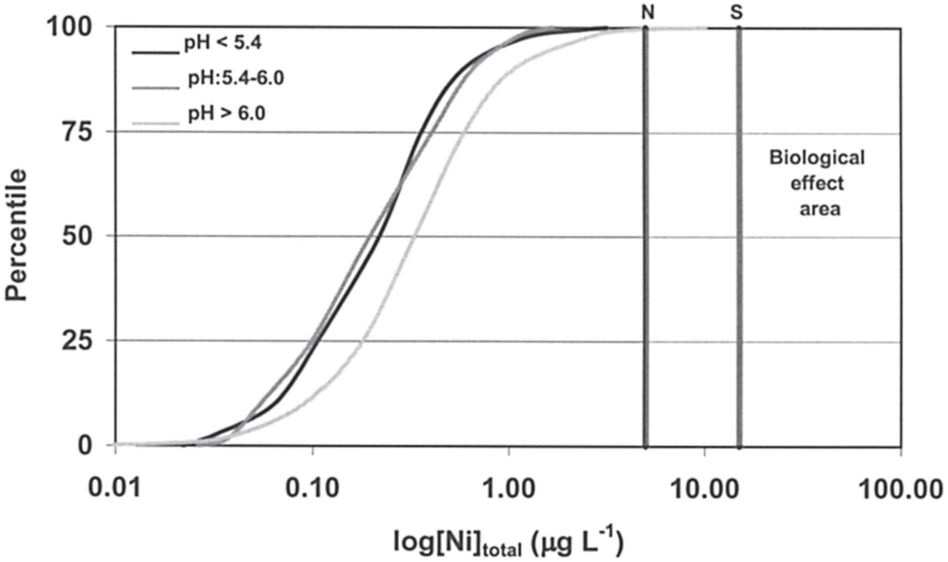


FIGURE 48. Percentile distribution of total Ni in Norwegian and Swedish lakes based on three pH classes. pH < 5.4, n = 250; 5.4 ≤ pH < 6.0, n = 204; pH ≥ 6, n = 1090. (Data from Skjelkvaale *et al*. [1996, 1999].)

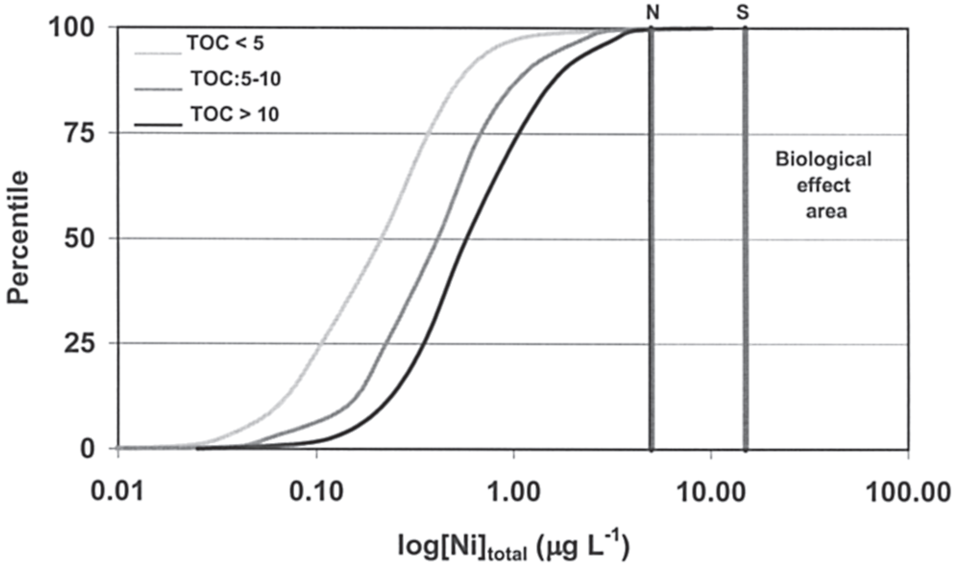


FIGURE 49. Percentile distribution of total Ni in Norwegian and Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale et al. [1996, 1999].)

the highest pH class. As mentioned above, this is likely because of high pH and Ni concentrations in agricultural areas.

The difference between limed and nonlimed lakes in Sweden was very small (Figure 47), and the few reacidified limed lakes (limed lakes with pH<6) did not show higher Ni concentrations than the nonlimed at the same pH interval (Figure 46).

A proposed effect-related sediment criteria for heavy metals in Canada (Smith et al. 1996) assume a biological effect level of Ni in sediments at 36 mg kg^{-1}dw.

a. Experimental Acidification

Long-term laboratory studies of the acidification effect on the mobilization of metals from sediments collected in two neutral lakes in the heavily metal polluted Sudbury area in Canada showed that Ni is strongly bound to the sediments down to a very low pH (pH ≈ 3). A similar threshold value has been found for sewage sludge (Arafat and Nriagu 1986). Acidified lakes usually remain net metal sinks, but retain less of the metals than more neutral lakes (LaZerte 1986).

b. Liming

In peat, the adsorbed quantities of Ni ions increase with increasing base saturation and increased decomposition, due to dissociation of acid functional groups and increased content of carboxyl groups, respectively (Krogstad 1982).

c. Reacidification

No data are available!

3. Biology and Toxicity

Lithner (1989) reported lowest known effect at 23 µg Ni L^{-1}. Alm et al. (1998) assume risk of biological effects in sensitive Swedish waters at 15 µg Ni L^{-1}. Grande and Andersen (1983) reported maximum acceptable toxicant concentration for Atlantic salmon of 50 µg Ni L^{-1} or somewhat lower. As for most metals, it is also documented that the toxicity of Ni decreases as the hardness increases (Birge and Black 1980; EPA 1986). The literature study by EPA (1986) concluded that TOC seems to be of minor importance for Ni toxicity variations, and that toxicity of Ni is related to the dissolved concentration of Ni.

a. Target

The mechamisms of toxicity are varied and complex (Mushak 1980). As with many other heavy metals, significant effects occur at cell membranes and membraneous tissues, such as gills. In fish, hematological effects such as hyperglycemia, lymphopenia, and erythrocytosis have been reported in association with nickel intoxicication (Agraval et al. 1979; Gill and Pant 1981; Chaudhry 1984; Chaudhry and Nath 1985).

b. Fish

The most sensitive life stage for fish regarding Ni exposure is the first stadium, because Ni affects hatching progress and causes a delay in hatching and increased mortality in embryos (Grande and Andersen 1983). Regarding fish age, Nebeker et al. (1985) reported that rainbow trout were more sensitive when 12 months old than when 3 months old. They reported reduced weight of rainbow trout at Ni concentration of 35 µg L^{-1}, while a decrease in survival was reported at concentrations of 134 µg Ni L^{-1}.

c. Invertebrates

Lazerva (1985) reported growth effects on *Daphnia magna* at 10 µg Ni L^{-1}, and predicted effects on population productivity at 5 µg Ni L^{-1}. Nickel appears being quite toxic to freshwater algae, with concentrations as low as 50 µg L^{-1} producing significant effects (EPA 1986). The acute 1 h concentration of Ni according to EPA formula for Ni toxicity is about 60 μg Ni L^{-1} at a hardness of 2.5 mg $CaCO_3$ L^{-1}, a hardness typical for dilute Norwegian freshwaters.

d. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

The Nordic Lake survey in 1995 shows that no lakes in Sweden and Norway and only three lakes in Finland had Ni concentrations > 15 μg Ni L^{-1}, which is assumed to be the biological effect level in sensitive Swedish waters (Alm et al. 1998). Even in relation to the lowest effect level according to the Norwegian critical load assessment (5 μg Ni L^{-1}, see Table 37), only one Norwegian lake, two Swedish nonlimed lakes, one Swedish limed lake, and five Finnish lakes had Ni concentration above this level. Referring to salmonids, concentrations < 10 μg Ni L^{-1} is assumed to have no effect according to another Norwegian classification system (Table 36).

4. Reacidification — Biological Risk

We might assume only minor or no changes in concentrations of Ni during the reacidification of limed water bodies. The ambient level of acid deposition is probably insufficient to increase the mobility of Ni accumulated in most natural surface soils and the atmospheric deposition of Ni has decreased. Therefore, it seems reasonable to believe that the influx of Ni to surface water will not increase or change dramatically compared with present status. Furthermore, there are no indications of an increased internal flux of Ni from the sediments due to the large buffering capacity and high adsorption potential even at low pH. On the other hand, the sedimentation of Ni might be somewhat reduced due to a decreased pH in the water phase. The Ni concentrations in most Scandinavian surface waters are, however, low to very low and there are no indications that a reduced sedimentation drastically could increase these levels. This conclusion is supported by the obser-

Table 36. Classification system of Ni (μg L^{-1}) in Norwegian freshwaters primarily related to salmonids (UN-ECE 1997b). Class 1: No effects on biota or no limitations for human consumption of fish. Class 2: Some sensitive species may be affected, but no effects on fish. Little ecosystem effects. Class 3: Effects on salmonids, reduced number of species with a dominant of tolerate species. Class 4: No salmonids and serious effects also on many other species. The structure of the ecosystem is completely destroyed

Class 1 Very Low	**Class 2** Low	**Class 3** Medium	**Class 4** High
< 10	10 - 30	31 - 100	> 100

Table 37. Critical loads of Ni (μg L^{-1}) at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997), Sweden (Alm et al. 1998)

	Freshwater μg L^{-1}			Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
		acute	chronic			
The Netherlands	1.8			9.4	2.6	
United Kingdom[1]	8 – 40					
Germany[2]		1400	160			
Canada[1]	25 – 150			18		
Sweden	**15**			**180**		
Denmark	160				10	
Norway	**5**					
Finland					40	

[1] Range means that values depend on water hardness; [2] Hardness dependent criteria (100 mg $CaCO_3$ L^{-1} is used).

vation that the few reacidified limed lakes in Sweden do not show higher Ni concentrations than the rest of the lake population. The effect of ceased liming on the Ni concentrations therefore would be minimal regardless whether the treatment was performed as forest, wetland, lake, or stream liming.

I. Chromium

1. General Geochemistry

a. Sources

Chromium (Cr) is a relatively common element in nature and at the trivalent form Cr(III) it is as an essential element in mammals by maintaining efficient glucose, lipid, and protein metabolism. In aquatic organisms, no biological function is known for Cr. The hexavalent form, Cr(VI), is toxic to organisms due to the oxidative power of these compounds (Eisler 1986).

In granites and gneisses, the Cr concentrations are in the range of 3 to 100 mg kg^{-1}dw. Basic, eruptive bedrock such as basalt and serpentine are rich in Cr with levels up to 3000 mg kg^{-1}dw. In soils, the Cr concentrations are generally below 100 mg kg^{-1}dw, but the levels depend on the composition of the mother material (Balsberg-Paahlsson et al. 1982). An investigation of 360 samples from the mor layer of Swedish forest soils showed Cr concentrations within the range 0.7 to 22 mg kg^{-1}dw, with a median concentration of 2.5 mg kg^{-1}dw. Chromium showed a typical north-south gradient, with double as high concentrations in the south. However, the high levels found in the south were partly explained by the Cr content in the mineral fraction, indicated by the negative correlation to the loss on ignition

(Andersson et al. 1991). Thus, the Cr concentrations in the mor layer are to a minor extent influenced by atmospheric deposition, while soil uptake and internal cycling are the dominating pathway for the accumulation (Bergkvist 1987; Andersson et al. 1991). However, Scandinavian moss analysis in 1995 showed elevated Cr concentrations in the vicinity of large point sources such as iron and steel mills. Generally, the Cr concentrations in moss are <1 mg kg^{-1}dw in areas not affected by local pollution (Rühling et al. 1996). Mass balance calculations indicate that Cr is accumulated or almost at balance in forest ecosystems (Bergkvist et al. 1987).

In soils, Cr form stable complexes with dissolved organic acids in the A horizon. These complexes are vertically transported to the upper part of the B horizon, where precipitation/accumulation occurs together with Fe and Al.

In sediments, Cr is mainly present in its trivalent form, and it is efficiently retained there due to the formation of stable complexes with negatively charged organic and inorganic compounds. Cr(III) in sediments is not particularly mobile under neither oxic nor anoxic conditions (Eisler 1986).

b. Chemical Properties

In natural waters, Cr occurs in trivalent and hexavalent forms. The latter can only exist in water with little organic matter due to the rapid reduction to Cr(III). Other reduced compounds such as Fe(II) and sulfides have the same effect as organic matter on Cr(VI). The hexavalent form is the dominating Cr ion in seawater. Opposite from the reduction of Cr(VI), the oxidation of Cr(III) is very slow in oxic water, but increases somewhat with increasing pH and temperature (Eisler 1986). In pure water, the hexavalent forms occur either as chromate (CrO_4^{2-}, pH > 6.5), hydrochromate ($HCrO_4^-$, pH < 6.5), or dichromate ($Cr_2O_7^{2-}$, very low pH). These ions are highly soluble and thus mobile in aquatic environments. In water without organic ligands, the trivalent forms occur (7.9.1) either as Cr^{3+} (pH < 5.5), $Cr(OH)^{2+}$ (pH < 6.5) or $Cr(OH)_2^+$ (pH > 4.5). Cr(III) hydroxides begin to precipitate at pH ≈ 5.5 to 6.0. However, Cr(III) forms stable complexes with negatively charged organic and inorganic compounds, and it is very unlikely that uncomplexed Cr(III) is to be found when anionic or particulate compounds are present in the water. Thus, the citrate complexing properties (Figure 50) is somewhat misleading, because the model assumes the precipitation of Cr(III). Even though a somewhat higher Cr(III) is able to stay in solution at very high concentrations of organic matter (citrate).

Clay particles, humus colloids, and Fe and Mn oxyhydroxides coprecipitate Cr into the lake sediments. Ion exchange due to increased salinity or the addition of strong chelates (EDTA) does not seem to increase the mobility of Cr in sediments (Balsberg-Påhlsson et al. 1982). Low pH favors Cr(III) retention under anoxic conditions (Eisler 1986). Under anoxic conditions, Cr does not form sulfides, such as Cu, Pb, Cd, Zn, etc.

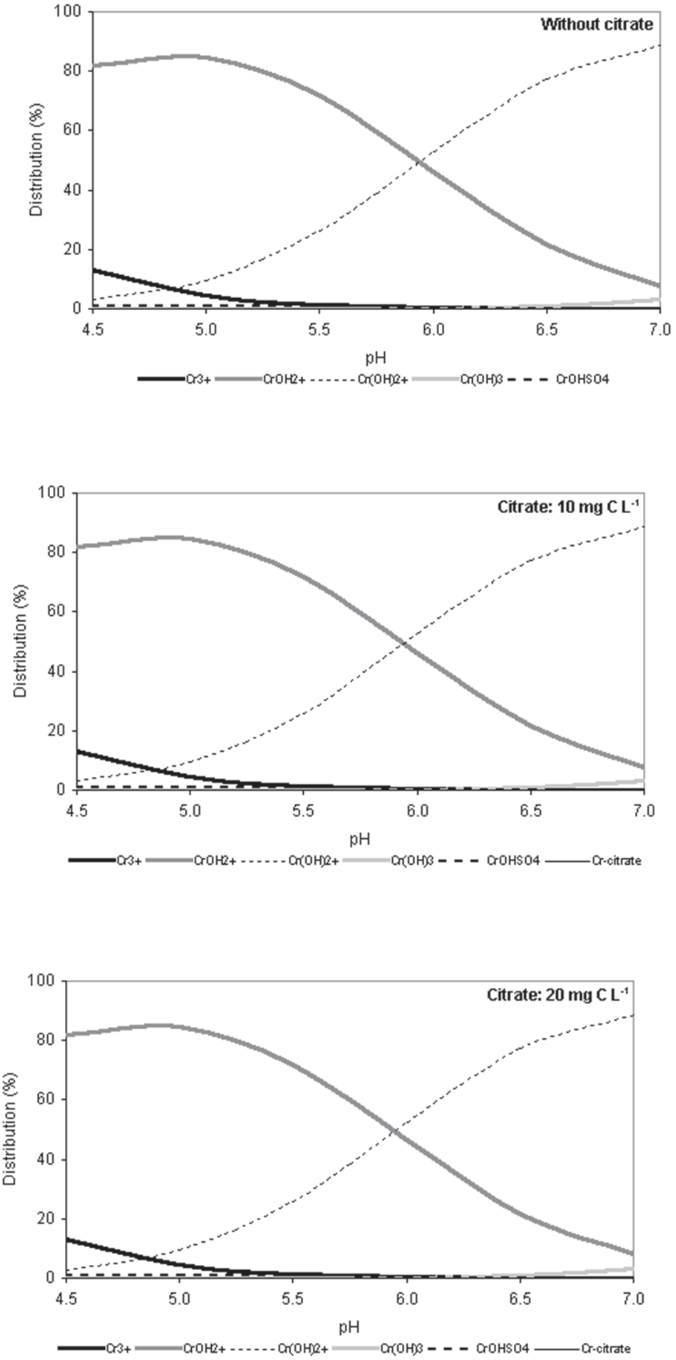


FIGURE 50. Distribution of major Cr species in relation to pH at citrate concentrations of 0, 10, and 20 mg C L^{-1} for the redox-pair Cr^{2+}/Cr^{3+}. At input conditions of CO_2 and O_2 at equilibrium with partial pressure of air, Cr^{2+} is negligible. Other input conditions: 25°C; [Cr]: 0.1 μmol L^{-1}; [SO_4^{2-}]: 5 mg L^{-1}; [Cl^-]: 2 mg L^{-1}; [NO_3^-]: 30 μg L^{-1}; [Ca^{2+}]: 3 mg L^{-1}; [Mg^{2+}]: 0.75 mg L^{-1}; [Na^+]: 2 mg L^{-1}; [K^+]: 0.25 mg L^{-1}.

2. Chromium in Surface Water Systems

According to More and Ramamorthy (1984), typical levels of dissolved Cr in unpolluted surface waters are 1 to 2 µg Cr L^{-1}. Based on this and the surface water classification systems (Table 40), the Cr concentrations in lakes in Sweden, Norway, and Finland are very low (Table 38 and Figure 51). More than 95% of the Scandinavian lakes were classified as *Very low* or *Low* (according to Table 40), and about 97.5% of the lakes in Scandinavia had Cr-concentrations < 1 µg Cr L^{-1} (Table 39). Only three nonlimed lakes (two Swedish and one Norwegian) had Cr concentrations > 5 µg L^{-1}. Cr concentration of 5 µg Cr L^{-1} is the proposed risk level for biological effects in sensitive Swedish waters (Table 42) and for salmonids in Norwegian freshwaters (Table 41). Highest Cr concentrations are generally found in Finland (median value: 0.27 µg Cr L^{-1}), while the lowest values normally are present in Norway (median value: 0.07 µg Cr L^{-1}). The differences between limed and nonlimed Swedish lakes are small, that is median value in limed Swedish lakes of 0.18 µg Cr L^{-1} and 0.15 µg Cr L^{-1} in nonlimed lakes. The reacidified limed lakes (pH < 6) did not show higher Cr concentrations than the nonlimed at the same pH interval (Figure 51).

Dividing the Swedish and Norwegian lakes into pH classes (Figure 53), the lowest pH class (pH < 5.4) exhibited the lowest Cr concentrations, with a median value of 0.069 µg Cr L^{-1}, while the median values in the medium pH class (pH: 5.4 to 6.0) and highest pH-class (pH ≥ 6.0) were 0.076 µg Cr L^{-1} and 0.087 µg Cr L^{-1}, respectively. The strong association between Cr and organic matter is also well illustrated in this survey (Figure 54). While the median Cr concentration in the Swedish and Norwegian low TOC lakes (TOC < 5 mg C L^{-1}) was 0.054 µg Cr L^{-1}, the median Cr-values for the medium TOC lakes (TOC: 5 to 10 mg C L^{-1}) and high TOC lakes (TOC ≥ 10 mg C L^{-1}) were 0.14 µg Cr L^{-1} and 0.27 µg Cr L^{-1}, respectively. Limed lakes generally have somewhat higher Cr concentrations than nonlimed, but the difference is rather minor (Figure 52).

Table 38. Concentrations of Cr (µg Cr L^{-1}) in Nordic surface waters. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	152	0	0.01 - 1.40	0.21
Sweden, south[2]	7	n.r.	0.11 - 0.35	0.21 ± 0.08
Sweden, north[2]	10	n.r.	0.09 - 0.33	0.18 ± 0.08
Sweden, north[3]	56	n.r.	< 0.1 - 0.6	≤ 0.19

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

[2] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden,south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[3] Borg (1987), based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

Table 39. Percentile distribution of Cr (µg Cr L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Concentrations < detection limit are imputed (see Skjelkvaale et al. 1999). Norway: n = 985; Sweden, nonlimed: n = 559; Sweden, limed: n = 261; Finland: n = 462

Cr	Percentile	Norway	**Sweden** non-limed	Sweden limed	Finland
Maximum	100.0 %	6.137	27.679	1.156	2.830
	99.5 %	2.028	2.239	0.775	1.698
	97.5 %	0.889	0.930	0.613	1.095
	90.0 %	0.282	0.499	0.423	0.639
Quartile	75.0 %	0.135	0.285	0.282	0.430
Median	50.0 %	0.069	0.146	0.175	0.270
Quartile	25.0 %	0.035	0.048	0.097	0.180
	10.0 %	0.017	0.026	0.043	0.100
	2.5 %	0.008	0.010	0.021	0.029
	0.5 %	0.004	0.007	0.011	0.009
Minimum	0.0 %	0.001	0.003	0.008	0.007

Table 40. Classification of concentrations of Cr in surface waters (µg L^{-1}) and the upper (0 to 1 cm) of lake sediments (mg kg^{-1} dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters. n.r.: not reported

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Cr (Sweden, 1991)	≤ 0.4	0.4 - 2.0	2 - 5	5 - 20	> 20
Cr (Sweden, 1998)[1]	≤ 0.3	0.3 - 5.0	5 - 15	15 - 75	> 75
Cr (Sweden, 1998)[2]	≤ 0.1	0.1 - 0.4	0.4 - 1.1	1.1 - 11	> 11
Cr (Norway, 1997)	< 0.2	0.2 - 2.5	2.5 - 10	10 - 50	> 50
Sediment					
Cr (Sweden, 1991)	≤ 10	10 - 25	25 - 75	75 - 300	> 300
Cr (Sweden, 1998)[3]	≤ 10	10 - 20	20 - 100	100 - 500	> 500
Cr (Norway, 1997)	n.r.	n.r.	n.r.	n.r.	n.r.

[1] Based on risks of biological effects.

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96).

[3] Based on distribution in Swedish lakes with and without local emissions.

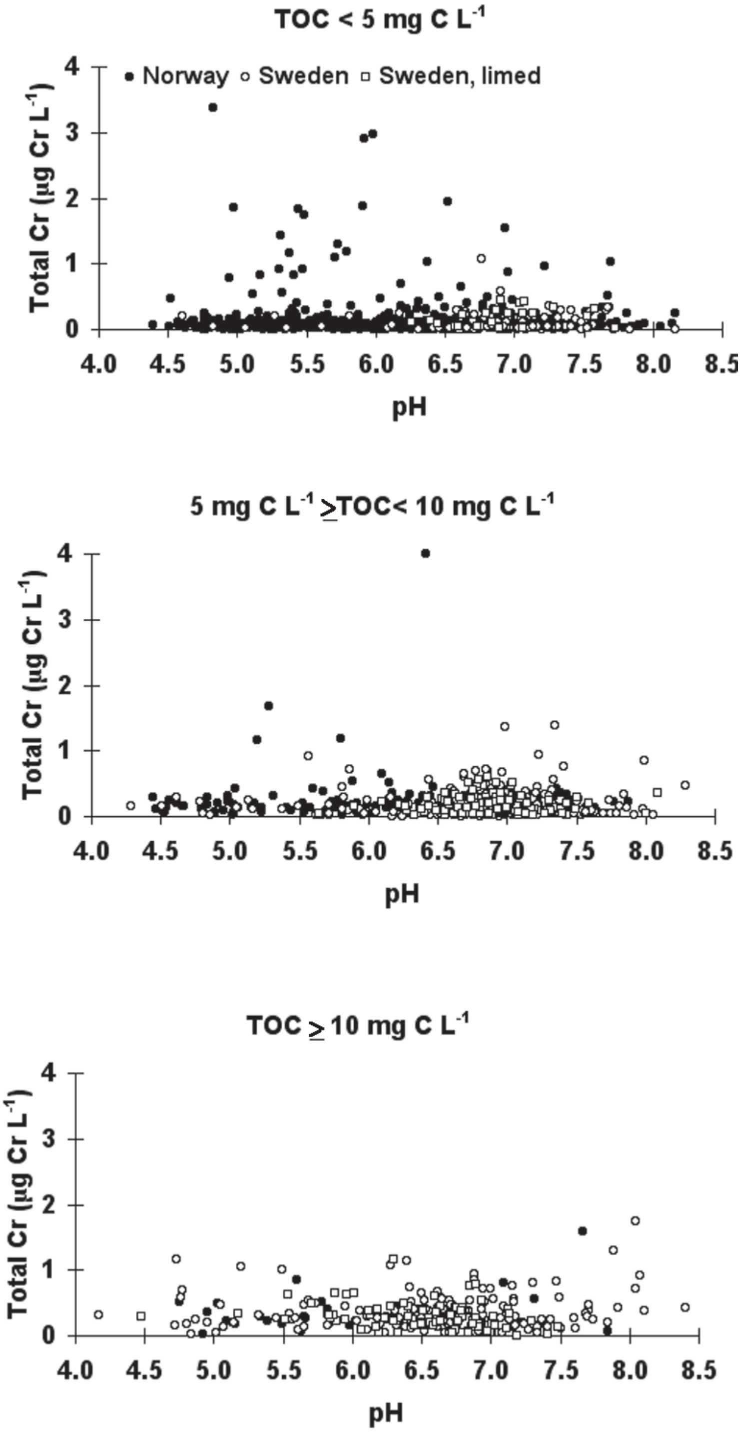


FIGURE 51. Total concentration of chromium in Norwegian and Swedish (nonlimed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

Table 41. Classification system of Cr (µg L^{-1}) in Norwegian freshwaters primarily related to salmonids (UN-ECE, 1997b). Class 1: No effects on biota or no limitations for human consumption of fish. Class 2: Some sensitive species may be affected, but no effects on fish. Little ecosystem effects. Class 3: Effects on salmonids, reduced number of species with a dominant of tolerate species. Class 4: No salmonids and serious effects also on many other species. The structure of the ecosystem is completely destroyed

Class 1 Very Low	**Class 2** Low	**Class 3** Medium	**Class 4** High
< 5	5 – 15	16 – 40	> 40

Table 42. Critical loads of Cr (µg L^{-1}) at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997), Sweden (Alm et al. 1998)

	Freshwater µg L^{-1}	acute	chronic	Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
The Netherlands	8.5			1620	3.8	
United Kingdom[1]	2 - 20					
Germany[2] CrIII/CrVI		1700/16	210/11			
Canada[1]	2 - 20			37	64	
Sweden	**5**			**120**		
Denmark CrIII/CrVI	10/ -				- / 2	
Norway	**10**	**16 - 40**	**5 - 15**			
Finland					80	

[1] Range means that values depend on water hardness; [2] Hardness dependent criteria (100 mg $CaCO_3$ L^{-1} is used).

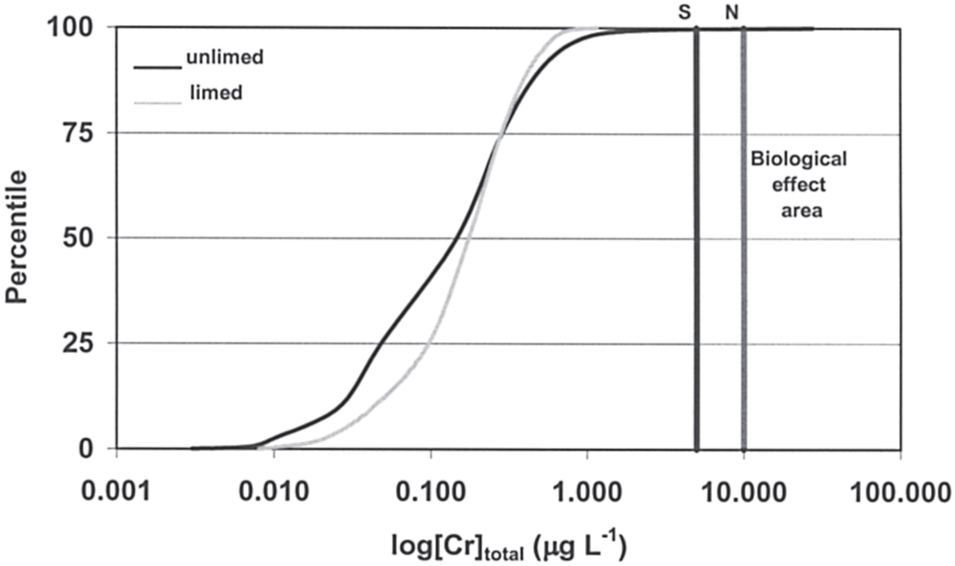


FIGURE 52. Percentile distribution of total Cr in limed (n = 261) and not limed (n = 820) Swedish lakes. S and N show the assessed critical concentrations for aquatic life in Norway and Sweden. (Data from Skjelkvaale *et al*. [1996, 1999].)

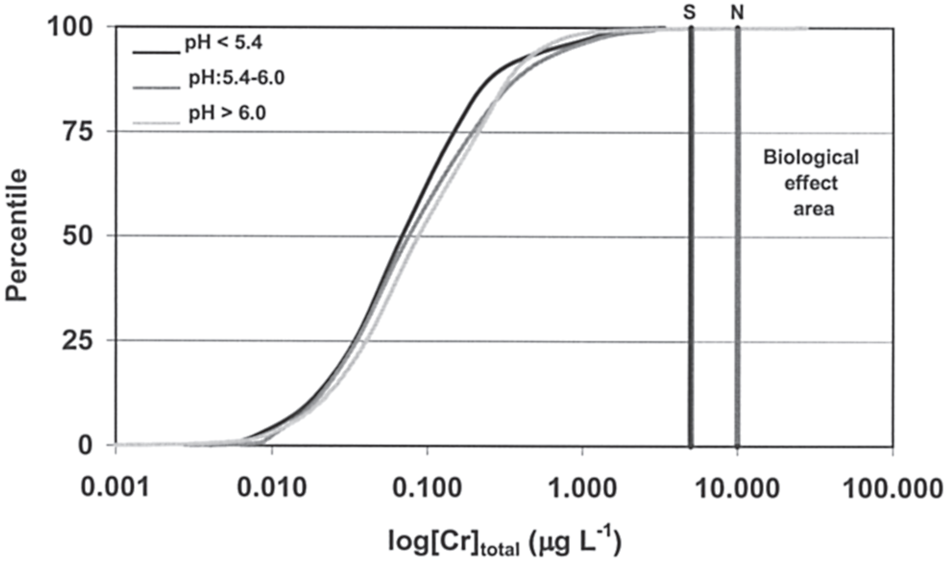


FIGURE 53. Percentile distribution of total Cr in Norwegian and Swedish lakes based on three pH classes. $pH < 5.4$, $n = 250$; $5.4 \leq pH < 6.0$, $n = 204$; $pH \geq 6$, $n = 1090$. (Data from Skjelkvaale *et al*. [1996, 1999].)

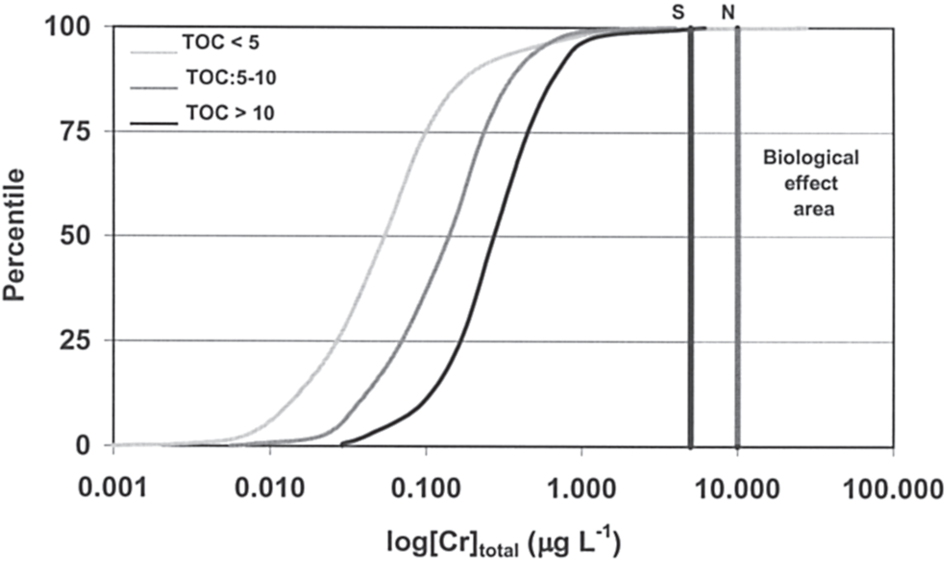


FIGURE 54. Percentile distribution of total Cr in Norwegian and Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). TOC < 5, n = 915; 5 ≤ TOC < 10, n = 427; TOC ≥ 10, n = 202. (Data from Skjelkvaale *et al.* [1996, 1999].)

The close relationship between Cr and organic matter is confirmed by Bergkvist et al. (1987). They claimed that soil-derived Cr is transported to surface waters mainly as metal-humus complexes Accordingly, elevated Cr concentrations are generally found in humic surface waters and in areas with high Cr concentrations in the soil due to local geology. As for mosses, high concentrations are found in some surface waters around industries with large atmospheric Cr emissions (Tarvainen et al. 1997; Alm et al. 1998).

In Sweden, the highest Cr concentrations were found in lowland rivers and lakes having high nutrient concentrations. The origin is probably natural and connected to the geochemistry of the postglacial clay, frequently abundant in these areas. The Cr concentrations did not covariate with pH or the humus concentration (measured as absorption at 420 nm on filtered water, Alm et al. 1998). Also in Finnish Lapland, the distribution of Cr in surface waters reflected the geochemistry distribution pattern, while elsewhere high Cr concentrations were found in brown-colored, humic lakes. Based on results from 38 Swedish forest lakes sampled in March to April 1980, Borg (1983) found a significant positive correlation between color and Cr. No such significant correlation was found during June to August 1980 in another lake survey of 59 northern Swedish forest lakes (Borg 1987). Besides high concentrations of organic compounds (TOC), decreasing pH tends to increase the Cr concentrations in Finnish surface waters (Tarvainen et al. 1997). A correlation between pH and Cr has not been found in Swedish lakes (Borg 1983; Borg 1987; Alm et al. 1998).

A proposed effect related sediment criteria for heavy metals in Canada (Smith et al., 1996), assume a biological effect level of Cr in sediments at 90 mg kg^{-1}dw.

a. Experimental Acidification

No data are available!

b. Liming

No data are available!

c. Reacidification

No data are available!

3. Biology and Toxicity

Relatively little is known about the relation between concentration of total Cr in an aquatic environment and biological effects. However, the toxicity of Cr to aquatic biota is significantly influenced by abiotic variable such as hardness, temperature, pH, salinity, and biotic factors as such species, population variations, and life stage (Eisler 1986).

a. Target

Under laboratory conditions, Cr is found to be mutagenic, carcinogenic, and teratogenic to a wide variety of organisms, and Cr(VI) has the greatest biological activity (Eisler 1986). However, information is minor on the biological effects of water-soluble inorganic and organic Cr (III) compounds.

Studies with perfused gills showed that the transfer of Cr was directly coupled with the transfer of oxygen from the external solution to the internal perfusion medium, and that this transfer was significantly more rapid at pH 6.5 than at higher pH (Van der Putte and Pärt 1982). The accumulation of Cr seems to be highest in gill, liver, kidney, and digestive tracts, after the transfer of rainbow trout to Cr-free media (Van der Putte et al. 1981).

Besides reported reduced survival, reduced fecundity, increased locomotion activity, increased chromosomal aberrations in gills, reduced disease resistance, and reduced salinity tolerance in migration salmon are reported after Cr exposure (see Eisler 1986). Thus, it is very difficult to find a well-defined or most sensitive target organ for Cr.

b. Toxic Species

Toxic effects of Cr seem to be largely related to the strong oxidation action of Cr(VI), and all biological interactions of Cr(VI) seem to result in reduction to Cr(III) and subsequent coordination to organic molecules (Langard and Nordseth 1979).

c. Fish

Among sensitive fish species, Cr (VI) concentrations between 16 to 21 μg L^{-1} has been reported to reduce the growth of rainbow trout and chinook salmon fingerlings during exposures of 14 to 16 weeks, and altered plasma cortisol metabolism in rainbow trout after 7 days. Lithner (1989) reported lowest know effect at 2 μg Cr L^{-1}. Alm et al. (1998) assume risk of biological effects in sensitive Swedish waters at 5 μg Cr L^{-1}. Grande and Andersen (1983) reported maximum acceptable toxicant concentration of hexavalent chromium for Atlantic Salmon of ≈ 10 to 100 μg Cr L^{-1}, while Eisler (1986) recommended lowest effect concentration of Cr(VI) to be ≈10 μg Cr L^{-1} and ≈ 30 μg Cr L^{-1} for Cr (III).

The most sensitive stadium for fish regarding hexavalent Cr exposure seems to be the yolk-sac fry and swim-up fry stages (Grande and Andersen 1983). Benoit et al. (1976) studied the effects of hexavalent Cr on two closely related salmonids, brook trout (*Salvelinus fontinalis*) and rainbow trout (*Salmo gairdneri*). This water was only somewhat harder than in the study by Grande and Andersen (1983), but they found a much higher maximum acceptable toxicant concentration, that is, 200 to 350 μg Cr(VI) L^{-1}. Because of minor ionic strength differences between the two studies, this may indicate that Atlantic salmon is much more sensitive to hexavalent Cr. As for most metals Cr seems to be more toxic in ionic poor waters (See EIFAC 1983).

d. Invertebrates

As for fish, most invertebrate studies has mainly been conducted with Cr(VI), and large variations in sensitivity are reported. Reduced survival and fecundity are reported for the cladoceran *Daphnia magna* at a concentration of 10 μg Cr(VI) L^{-1} (EPA 1980). LC_{50} values for *Bryozoa*, *Gammarus* sp., *Chironomus* sp., and *Tanytarsus* sp. are reported to be 0.7 to 1.6 mg Cr(VI) L^{-1}, 0.07 to 3.2 mg Cr(VI) L^{-1}, and 11 to 60 mg Cr(VI) L^{-1} (Balsberg-Paalsson et al. 1982). *Ephemeroptera* seem to be very sensitive to Cr(VI), and a more or less complete extinction of these species occurred in a subalpine stream in the pre-Alps, when polluted to a concentration of approximately 0.1 mg Cr(VI) L^{-1} (Ramusino et al. 1981).

Exposure to Cr(III) at different calcium concentrations has revealed LC_{50} values for *Daphnia magna* in the range 17 to 51 mg Cr(III) L^{-1}, with the lowest value at lowest ionic strength (44 to 55 mg L^{-1} $CaCO_3$). At the same calcium level, LC_{50} values for *Gammarus* sp., *Ephemerella* sp., and *Hydropsyche* sp. are reported to be 3 mg Cr(III) L^{-1}, 2 mg Cr(III) L^{-1}, and 64 mg Cr(III) L^{-1}, respectively. Eggs of *Lymnea* sp. have the lowest reported LC_{50} value (0.2 mg Cr(III) L^{-1}, Balsberg-Paalsson et al. 1982). Obviously, the Cr toxicity is higher at lower ionic strength also when considering invertebrates.

e. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

The Nordic Lake survey in 1995 shows that only one unlimed lake in Sweden (Cr: 28 µg L^{-1}) and one Norwegian lake (6.1 µg L^{-1}) had Cr concentrations > 5 µg Cr L^{-1}, which is assumed to be the biological effect level in sensitive Swedish surface waters (Table 42) and the criterion level for noneffect in Norwegian salmonid waters (Table 41). According to the other Norwegian classification system (Table 42), biological effects are not expected to occur at < 10 µg Cr L^{-1}. Only one unlimed Swedish lake was above this concentration (Table 39).

4. Reacidification — Biological Risk

We might assume only minor or no changes in concentrations of Cr during reacidification of limed water bodies. In a few low TOC freshwaters the Cr concentrations might increase, but hardly above the biologically critical level of 5 µg Cr L^{-1}. No changes are expected to occur in medium or high TOC waters.

J. Mercury (Hg)

The properties of Hg differ from the other metals in many aspects. The most toxic Hg species are, for example, organometallic forms such as methylmercury (MeHg), which biomagnifies in the food chain and is of greater concern for the human health and other top predators rather than for the limnic organisms in general. Both abiotic and biotic processes in which proton reactions are involved affect the bioaccumulation of Hg. Actually, very few chemical and biological processes in nature are independent of pH. This section does not aim to give a complete literature review on all possible pH-dependent processes coupled to the

Hg dynamics in surface waters. More comprehensive reviews on that subject have been published (e.g., Winfrey and Rudd 1990; Nelson and Campbell 1991; Gilmour and Henry 1991; Spry and Wiener 1991; Lindqvist 1991; Rudd 1995; Siegel and Siegel 1997). Instead, it is focused on the empirical findings that give indications of possible changes in the bioavailability of Hg in limed surface waters subjected to reacidification.

1. General Geochemistry

a. Sources

Igneous and sedimentary rocks are usually low in Hg (average content 1 to 12 μg kg^{-1}). However, bituminous shales might have higher levels (32 to 340 μg kg^{-1}) and sulfide ores may have exceptionally high concentrations. The mineral soils have the same content as the parent material, generally in the range of 2 to 8 μg kg^{-1}dw. As part of the pedogenic process, Hg has been transferred from the root zone to the organic topsoil layer (mor layer). In addition, atmospheric Hg deposition has been accumulated in the raw humus layer. According to different estimates, 65 to 76% and 73 to 92% of the Hg content in mor in northern and southern Sweden, respectively, could be attributed to anthropogenic derived, atmospheric Hg emissions. Dominating point sources for these Hg emissions have been chloralcali factories, waste incineration plants, coal and peat combustion, and metal smelters (Lindqvist 1991).

As a result of the high affinity to organic material, Hg is mainly bound to the organic matter in the mor and B horizons (Lindqvist 1991; Schuster 1991; Aastrup et al. 1991; Munthe et al. 1998) or in peat (Ek 1986). Regional surveys of total Hg concentrations (Hg-tot) in forest soils (humus layer) and lake sediments (Laag and Steinnes 1978b; Nilsson et al. 1989; Johansson et al. 1995a) show a positive correlation between total Hg concentrations and the total amount of atmospheric Hg deposition. Accordingly, higher concentrations of Hg are normally present in southern Scandinavia. However, a very week south-north gradient in total Hg was found in mosses collected in Scandinavia in 1995 (Rüling et al. 1996). This is likely a result of the less pronounced atmospheric deposition gradients during the 1990s (see below).

The transport of humus organic Hg complexes from soil to surface water occurs when the groundwater level reaches the organic-rich soil layers (Aastrup et al. 1991; Meili et al. 1991; Johansson and Iverfäldt 1995; Bergbäck and Johansson 1996), that is, during short high-flow periods. Therefore, the mobility of Hg is to a large extent coupled to the dynamics of dissolved organic matter (Iverfeldt and Johansson 1988; Mierle 1990; Meili et al. 1991c; Meili 1994; Bishop et al. 1995).

Budget calculations for small catchments in Sweden and Finland indicate that the drainage basin is the main source of total Hg in surface runoff (Aastrup et al.

1995a; Munthe et al. 1998; Lee et al. 1998). This conclusion is supported by Borg and Johansson (1989), who tried to estimate metal budgets for a hypothetical Swedish forest lake, based on regional data from surveys of deposition, terrestrial runoff and soils. They estimated terrestrial runoff, of Hg to contribute with 66 to 76% of total Hg load. However, atmospheric Hg deposition can be important in clear water and seepage lakes (Meili 1991c; Porcella 1994).

During the 1990s, the atmospheric deposition of Hg has declined by 50% over southern Scandinavia compared with the late 1980s (Bergbäck and Johansson 1996). Therefore, Hg pools in soils are likely more important for Hg in runoff today compared with the estimates made by Borg and Johansson (1989). This is also supported by the results from the roof project in Gårdsjön (Sweden), where no clear effect of total Hg in runoff was observed 4 years after an approximately 50% removal of atmospheric inputs (Munthe et al. 1998). However, the reduction in atmospheric Hg may cause a decline of Hg in runoff in the years to come, as suggested by Lindqvist (1991) and Hultberg et al. (1994).

Budget calculations for small catchments in Sweden and Finland indicate that the drainage basin is an important source not only for total Hg, but even for methyl mercury (MeHg). It is concluded that riparian peat, mires, and wet organic soil are more important than atmospheric MeHg deposition for the discharge of MeHg from the catchments. These soils are suggested to contribute with *in situ* production of MeHg (Munthe et al. 1998; Lee et al. 1998).

b. Chemical Properties

At redox and pH conditions of natural soil systems, Hg can occur in three oxidation states Hg(0), Hg_2^{2+}(I), and Hg^{2+}(II). The most important ligands for increased mobility are hydroxides, chlorides, and organic anions. High affinity to sulfur-containing functional groups seems to explain the strong binding to organic matter. The solubility of HgS is extremely low under reduced conditions like in sediments. Other mechanisms than solubility equilibrium seem to determine the concentration of Hg in soil solutions. The most likely explanations are formation of organic complexes and adsorption to solid surfaces (Schuster 1991).

Numerous adsorption studies have been performed with Hg and humus in order to estimate the chelating properties of the organic material. However, the concentrations generally have been high compared with natural levels in surface waters, but more relevant for soil or sediments.

From measured equilibrium constants and relevant surface water concentrations of carboxylic acid groups (70 μeq L^{-1}) and chloride ions (30 μeq L^{-1}) but high Hg concentrations (160 ng L^{-1}), it has been calculated that almost 40% of the Hg is complexed by humic substances at pH 3, and that humic complexes dominate Hg speciation up to pH 5 (Lövgren and Sjöberg 1989). It has also been shown that the adsorption of Hg on oxide surfaces (like alum) is greatly enhanced by complexation of fulvic acids (≥ 1 mg C L^{-1}) in the pH interval 2 to 9 (Xu and Allard 1991).

The mobility of inorganic mercury (Hg) within watersheds and lakes is very insensitive to changes in pH due to the high affinity to humic matter (Nelson and Campbell 1991; Lindqvist 1991).

Mercury in sediments seems to be tightly bound to organic matter or sulfides and will not dissolve by lowering of pH (Nelson and Campbell 1991). However, benthic fauna might redistribute sediment bound Hg to the fish population (Parkman 1993). A negative correlation between lake pH and total Hg concentrations in the sediments was demonstrated in a survey of 18 lakes in Finland. This relationship was interpreted as being due to more efficient sedimentation with organic matter at low pH (Rekolainen et al. 1986). Reduced evaporation of elemental Hg at low pH has been put forward as an alternative explanation for this pattern (Rada et al. 1993). Laboratory studies indicate that the pore water concentrations of Hg decrease at decreasing pH due to dissolution of iron sulfide and subsequent precipitation of Hg sulfide (Ramlai et al. 1985).

2. Mercury in Surface Water Systems

Generally, the total Hg concentrations in remote, unpolluted lakes are in the range of 1 to 10 ng L^{-1}. Median levels are 2 and 4 ng Hg L^{-1} in northern and southern Sweden, respectively (Meili et al. 1991; Alm et al. 1998). As for the other metals, there are no data from the national lake and stream surveys. The classification of surface waters, sediments, and fish with respect to Hg concentrations are presented in Table 43 and Table 44.

Due to the strong affinity to humus, a positive correlation is found between organic matter and total Hg. Therefore, humic lakes generally exhibit higher Hg concentrations than clear water lakes (Nelson and Campbell 1991; Lindqvist 1991). The sometime reported negative correlation between total Hg concentration and pH in surface water is likely a causal artefact due to the intercorrelation between humic compounds and pH (Meili et al. 1991; Lindqvist 1991).

3. Bioaccumulation of Methylmercury in Fish

Numerous regional lake surveys have shown that the Hg levels in fish vary considerably between lakes in restricted areas with similar atmospheric Hg loading. In Swedish lakes the Hg concentrations in fish vary with a factor >10, while the bulk deposition varies with a factor of < 4 (Lindqvist 1991). Because Hg in fish mainly appear in the form of MeHg, it is evident that the bioavailabilty of the loaded Hg is more important than the loading itself, at least in a shorter-term perspective. Annual Hg load to headwater lakes often exceeds the total Hg pool in

Table 43. Classification of concentrations of Hg in surface waters (μg L^{-1}), the upper (0 to 1 cm) of lake sediments (mg kg^{-1} dry weight), and concentration of Hg (mg kg^{-1} fish fillet wet weight) in *pike (Essex Lucas* L.) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
Hg (Sweden)					
Hg (Norway)	< 0.002	0.002 - 0.005	0.005 - 0.01	0.01 - 0.02	> 0.02
Sediment					
Hg (Sweden, 1991)	≤ 0.05	0.05 - 0.15	0.15 - 0.3	0.3 - 1.0	> 1.0
Hg (Sweden, 1998)[1]	≤ 0.15	0.15 - 0.3	0.3 - 1.0	1 - 5	> 5
Hg (Norway)	< 0.15	0.15 - 0.6	0.6 - 1.5	1.5 - 3	> 3
Fish					
Hg (Sweden, 1991)	≤ 0.25	0.25 - 0.5	0.5 - 0.75	0.75 - 1	> 1
Hg (Sweden, 1998)[2]	≤ 0.2	0.2 - 0.5	0.5 - 0.75	0.75 - 1	> 1
Hg (Norway)	< 0.2	0.2 - 0.5	0.5 - 1	1 - 2	> 2

[1] Based on distribution in Swedish lakes with and without local emissions.

[2] Based on human health risk at fish consumption and on distribution in Swedish lakes.

Table 44. Critical limits of Hg at different ecosystem levels in some countries, according to UN-ECE (1997b), Norway (SFT 1997)

	Freshwater μg L^{-1}	Acute	Chronic	sediment	Soil mg kg^{-1}	fish
The Netherlands	0.23			26	1.9	0.5
The Netherlands[1]	0.01			1.1	0.37	
United Kingdom					1	
US-EPA		2.4	0.012			
Canada	0.1			0.17	6.6	
Sweden				**0.6**	**0.2-0.3**	**0.5**
Denmark	1				0.1	
Norway	**0.01**					
Finland					0.2	

[1] Methyl-Hg

the water column by a factor > 20. Both the atmospheric deposition and the drainage water loading separately are large enough to supply the entire MeHg content in the water column, including biota (Meili 1991b). Therefore, rapid transformation processes rather than input loading seem to determine the MeHg concentrations in surface waters. This indicates that the MeHg cycling is ultimately determined by ambient chemical conditions, the configuration of detritial organic matter, microbial activity, and the relationship between primary and heterotrophic production at low trophic levels (Lindqvist 1991).

Table 45 shows the range of Hg in different compartments of eight Swedish headwater lake ecosystems located in the boreal forest region. It is evident that the bioaccumulation is very large (>1000-fold magnification) between the lake water and most organisms. There are also much higher concentrations of Hg in top predators compared with their prey, demonstrating the biomagnification of Hg.

Budget calculations by Meili (1991b) indicate that more than half of the MeHg pool in the water column is tied up in the fish population. Generally, fish accumulate Hg mainly from the feed (> 90%) and less through the direct uptake from water. Thus, the crucial factors for the MeHg concentration in fish are the food web structure. Furthermore, increased numbers of trophical levels increase the biomagnification. Thus, the trophic level and Hg level of predominant prey are essential factor for the Hg concentrations in top predators (Spry and Wiener 1991; Lindqvist 1991; Parkman 1993; Parkman and Meili 1993, 1997).

Meili (1991c) showed that the trophic transfer (seston, zooplankton, small zooplanktivorous fish, and piscivorous fish) of MeHg from one trophic level to next results in a fairly constant enrichment factor of ≈ 3.3 between adjacent levels, irrespective of lake type, trophic level, animal size, or age. This study was based on four Swedish oligo-mesotrophic forest lakes (pH 5.2 to 7.6). Meili (1991c) replaced traditional concentration units by a ratio of MeHg and nitrogen (MeHg/N), and differences in the MeHg/N ratio at the microseston base of the food web could explain the variation in food web contamination in neighboring lakes of different character.

Table 45. Range of Hg in different compartments of eight Swedish headwater lake ecosystems in the boreal forest region. (Modified from Lindqvist 1991)

Compartment	Range	Unit
Lake water Hg-total	0.8-10	ng L^{-1}
Lake water MeHg	0.04-0.8	ng L^{-1}
Sediment	0.08-0.3	mg kg^{-1} dw
Zooplankton	0.07-0.7	mg kg^{-1} dw
Macroinvertebrates	0.02-6	mg kg^{-1} dw
Roach (small)	0.4-2	mg kg^{-1} dw
Roach (large)	0.4-4	mg kg^{-1} dw
Perch (small)	0.2-2	mg kg^{-1} dw
Perch (large)	0.6-6	mg kg^{-1} dw
Pike (small)	1-5	mg kg^{-1} dw
Pike (large)	3-15	mg kg^{-1} dw

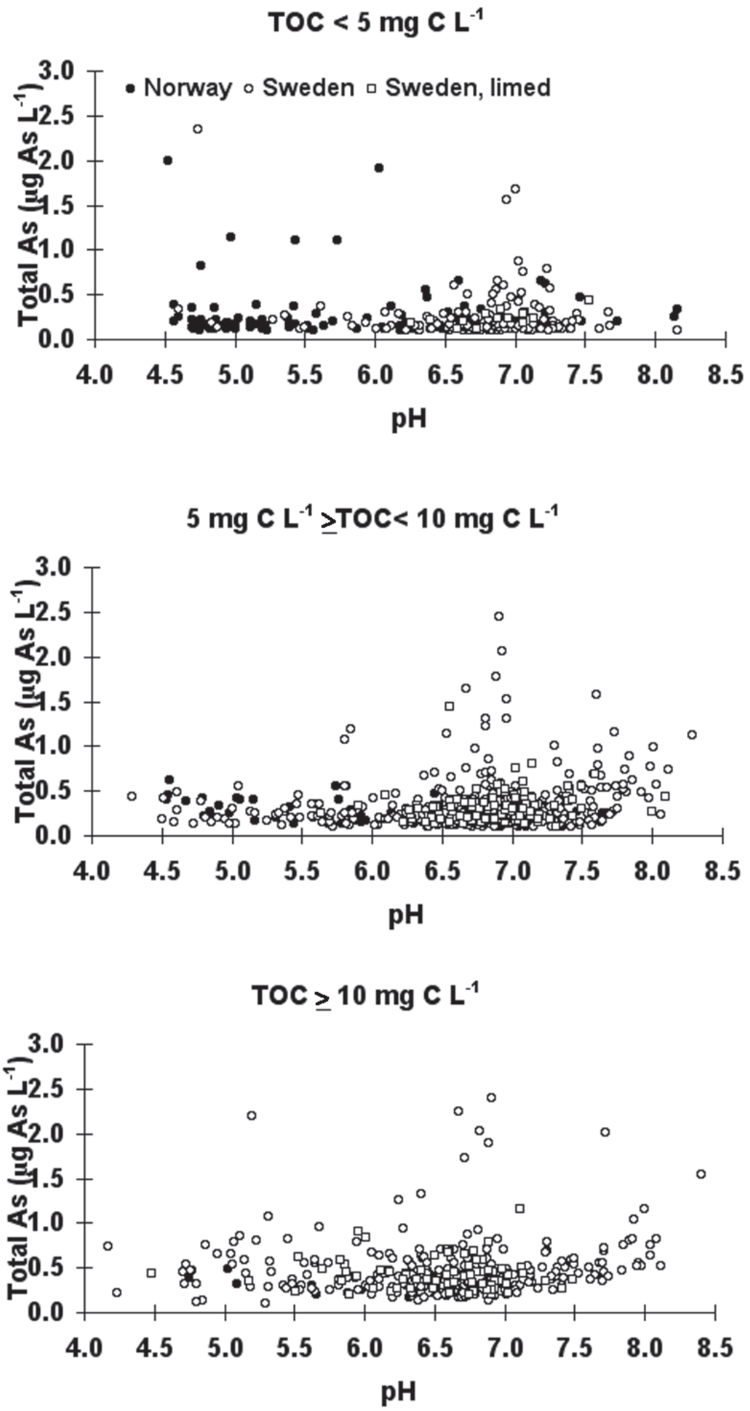


FIGURE 55. Total concentration of arsenic in Norwegian and Swedish (nonlimed and limed) lakes in relation to pH for three different TOC classes. (Data from Skjelkvaale et al. [1996, 1999].)

Many studies point out lake pH, alkalinity, calcium, water retention time, humus loading, and productivity as important factors, influencing the variation in the bioaccumulation of MeHg in fish (Håkansson et al. 1990; Verta 1990; Spry and Wiener 1991; Lindqvist 1991; Haines et al. 1994). However, there is a large degree of co-linearity between pH and these factors, which makes it uncertain to what extent pH alone affects the MeHg content in fish (Meili 1991a, b).

No simple relationship was found between pH and lake water MeHg concentrations in five nearly pristine seepage lakes in Wisconsin, USA, and neither did the partitioning of MeHg between water and seston and water and fish show any relationship with pH. This indicates that pH does not affect the specific rates of MeHg uptake by biota (Bloom et al. 1991).

Based on model calculations and empirical data from Swedish forest lakes, Meili (1991a) predicted total Hg concentration in lake water (23 lakes, summer concentrations in the ranges of 2 to 6 ng Hg L^{-1}, pH 5.0 to 7.0, water color 15 to 250 mg Pt L^{-1}, total phosphorus 6 to 42 $\mu g\ L^{-1}$) and MeHg in 1-kg pike (31 lakes, 0.5 to 2 mg Hg kg^{-1} muscle tissue) with reasonable accuracy (±1.5 of observed values). The model predicted concentrations, pool sizes, flux rates, and turnover times of Hg in the biogeochemical cycle, including atmosphere, forest soils, surface runoff, lake waters, and aquatic biota. Regional data on acid deposition, air temperature and surface runoff, and local data on the trophic status with respect to humus and nutrient concentrations were used to run the model. For most lakes, the predicted total Hg concentration in water was dominated by the contribution of Hg from the catchment. Similarly, the model calibrations indicated that Hg in atmospheric deposition was much less bioavailable (23%) than Hg from the catchment. Regional differences such as the growth rates of forests, geographic temperature gradients, lake productivity, and humic content seem to be more important for the variability of both total Hg in water and MeHg in pike. No improvement of the prediction was obtained by including lake water pH in the model. However, acidification may have indirect effects on factors as the productivity of aquatic biota or the configuration of organic matter (Meili 1991a).

a. Experimental Acidification

Experimental acidification, from pH 6.1 to pH 4.6, was tried in the seepage Little Rock Lake, USA. The lake was divided into two parts by a plastic barrier. However, the single effects of pH on the MeHg concentrations in water, seston, and fish were not possible to evaluate because only the acidified basin developed thermal stratification, anoxia, and sulfide-rich bottom water with high MeHg concentrations. The redoxcline interface corresponded to a layer with the presence of green sulfur bacteria. However, both treated and nontreated basins showed similar seasonal MeHg dynamics (Bloom et al. 1991).

b. Liming

The effects of lake liming and other pH-affecting treatments have been studied within different Swedish research projects (e.g., Håkansson et al. 1991; Meili 1995). The evaluations, however, generally have been based on a limited number of lakes or a limited period of time after treatment. Recently, a more comprehensive evaluation has been performed on the effects of liming on the MeHg concentrations in pike (Andersson and Lundberg 1996). The study includes 140 Swedish lakes without local Hg emission sources that were investigated during the period 1981 to 1987 and 1988 to 1995. Only lakes with a minimum of 3 years between the fishing occasions were selected.

The results show that the MeHg concentrations in pike have declined by approximately 20% between the two periods in the entire lake population ($n = 140$) as well as in the limed ($n = 39$) and nonlimed ($n = 48$) lakes. Reduced atmospheric Hg input especially during the 1990s and climatic variations have been suggested to explain this decline (Andersson and Lundberg 1996).

The two populations of limed and nonlimed lakes were not biased considering geographical distribution, time of sampling, or pH. The limed lakes had pretreatment pH similar to the nonlimed lakes. Analysis of two subpopulations of 20 lakes from each of the two categories, within pH range $5.5 \leq pH \leq 6.3$ before treatment, showed the same decline in both groups. However, there were statistical indications ($p < 0.1$) that five overlimed lakes had a larger decline than the nontreated (Andersson and Lundberg 1996). Obviously, increased pH due to lake liming has very little effect on the MeHg concentration in pike. Other factors seem to be more important than acidity for in-lake variations between years.

Of the studied lakes, some catchments had been wetland limed ($n = 18$) and soil limed ($n = 4$). None of these subgroups exhibited any decline in MeHg concentration in pike, which indicates that bioavailable Hg was mobilized from the catchment due to liming (Andersson and Lundberg 1996).

c. Reacidification

No information are available.

4. Reacidification — Biological Risk

A decreased pH due to ceased surface water liming should not be expected to significantly affect the total Hg concentrations in lakes and streams due to changed internal processes such as increased losses from sediments. Factors other than pH, such as changes in organic matter load from the surrounding soils due to natural climatic variations, are much more important for the Hg load and thereby the Hg concentrations in lakes. The ceasing of the liming of wetlands and forest soils might reduce the Hg load to surface waters as a result of a diminished mineralization and production of water-soluble humus–Hg complexes at lower pH. Similarly, a decreased pH due to ceased surface water liming would not be expected to change the MeHg levels in limnic organisms significantly, except in some very sensitive systems where increased MeHg concentrations in pike and other top predators could be foreseen. In these systems, the productivity or the food web structure has to change as the water bodies undergo reacidification. One scenario is that the top-predator prey becomes more piscivorous, for example, if the stock of fish eating perch increase. Lakes that lost or significantly reduced the roach population during acidification, but regained it as a result of liming, might behave in this way.

The number of lakes sensitive to reacidification and changes in trophic structure are unknown, but considering that approximately 60% of the limed lakes were not especially acidic (pH >5.5) before limed (Wilander et al. 1995), and the fact that atmospheric sulfur deposition is significantly reduced (50%) since the 1980s, the number of sensitive lakes are today reduced. Sensitive lakes are located primarily in the most heavily acidic influenced areas in Scandinavia.

The ceasing liming of wetlands and forest soils are not to be expected to have any negative effect on the MeHg concentrations in fish and other aquatic organisms. It is more likely that some positive effects might occur, because a reduced input of bioavailable Hg from the catchment is to be expected.

K. Arsenic (As)

1. General Geochemistry

a. Sources

Arsenic (As) naturally occurs as sulfides and as complex sulfides of Fe, Ni, and Co. Soil arsenic levels are normally elevated near arseniferous deposits and in mineralized zones containing gold, silver, and sulfides of lead and zinc. Secondary iron oxide formed from the weathering of pyrite act as scavengers of As. Pyrite, as, for example, pyrite shale, is a known carrier of As and may contain up to 5,600 mg kg^{-1}. Rönnskärsverken in Sweden has been the world-leading producer of As. Almost all or 97% of the As produced enters the end-product manufacture as arsenic trioxide (As_2O_3). More than 80% of this substance is used to manufacture products with agricultural application (pesticides, wood preservatives, medicine, etc.). Besides agricultural areas, man has modified the As cycle mainly by causing localized high concentrations around mining industries, metal smelters, coal-fired power plants, and pesticide factories (Eisler 1988b).

Scandinavian moss analysis in 1995 showed elevated As concentrations in the vicinity of large point sources such as the smelter in Rönnskär (Sweden) and industries at Årdal (Norway). However, in Norway the As distribution was dominated by atmospheric long-range transport with elevated concentrations (≈1 mg kg^{-1}dw) at the southern coast. In remote areas not affected by local pollution and with low long-range transport, the As concentrations in moss varied between 0.2 to 0.6 mg kg^{-1}dw in both Norway and Sweden (Rühling et al. 1996).

In soils, inorganic As is more mobile than organic As, and thus poses greater leaching into surface water and groundwater. The trivalent As species are more soluble and mobile than the pentavalent As forms. Soil microorganisms may metabolize arsenic into volatile As derivatives and depending on conditions, up to 60% may be volatilized (Eisler 1988b). In groundwater, elevated concentrations of As is mainly found in areas with As bearing minerals and at $pH > 6.5$. At low pH, As is bound to the soil particles (Aastrup et al. 1995b). In most soil systems, the chemistry of As to a large extent becomes the chemistry of arsenate. Estimated half-time of arsenic in soil is about 6.5 years (Woolson 1975).

In sediments, As is retained efficiently due to the sorption to inorganic compounds such as hydrous oxides of iron and manganese or due to the formation of arsenic sulfides. Small amounts of As might be methylated and volatilized to the atmosphere. Arsenic in sediments is not particularly mobile under either oxic or anoxic conditions (Eisler 1988b; Landner 1998).

b. Chemical Properties

In freshwater, As occurs in both inorganic and organic forms, as well as in dissolved and gaseous states. The chemical forms of As depend on E_h, pH, organic content, suspended solids, microbial activity, etc. Primarily, As exists as dissolved anionic species and particles account for a small fraction of the total amounts (Maher, 1985). At oxic conditions, the pentavalent As(V) species tend to be the most common, generally in the form of arsenic acid, H_3AsO_4 ($pKa_1 = 2.25$, $pKa_2 = 6.77$, $pKa_3 = 11.6$). At low redox potentials and with hydrogen sulfide present, arsenic sulfide ($As_2S_3(s)$, AsS_2^-) and trivalent arsenious acid (H_3AsO_3, $pKa = 9.23$) tend to be more abundant (Thanabalasingam and Pickering 1986). In reduced environments, such as sediments, arsenate (AsO_4^{3-}) can be reduced to arsenite (AsO_3^{3-}), which might be microbially methylated to compounds that volatilize to the atmosphere (Eisler 1988b).

Arsenates are readily sorbed by colloidal humic material under conditions of high organic content, low pH, low phosphate, and low mineral content (Thanabalasingam and Pickering 1986). Arsenates also coprecipitate with, or adsorb on, iron oxyhydroxides and form insoluble precipitates with calcium, sulfur, aluminium, and barium compounds (Eisler 1988b; Landner 1998). Polyvalent anions, such as phosphate, can displace arsenates sorbed on humic compounds or on metal oxyhydroxides (Thanabalasingam and Pickering 1986). Dissolved methylated arsenicals, such as methylarsonic acid (MAA) and dimethylarsinic acid

(DMAA), are during the summer produced in the surface euphotic zone by phytoplankton (Maeda 1994).

Arsenate is more strongly adsorbed to sediments than other As forms. One reason for that is the coprecipitation with iron oxyhydroxides and the adsorption onto manganese oxide surfaces (Aggett and Roberts 1986; Takamatsu et al. 1985b). The mobility of As in lake sediments and its release to the overlaying water is related partly to seasonal changes. These sediment-water interactions exhibit large similarities with the phosphorus (P) dynamics, with the release of As (or P) during anoxic conditions and/or at high pH (Aggett and O'Brien 1985). However, the relatively insoluble arsenic sulfide may accumulate in sediments and thereby remove As from the aqueous environment more or less permanently (Eisler 1988b). Arsenate reaches adsorption maximum for iron, manganese and aluminium hydroxides, and clay minerals at pH values between 4 and 7, while adsorption of arsenite increases with pH, reaching a maximum at pH about 9 (Landner 1998). Generally, As is immobilized in sediments as long as the overlaying water remains aerobic. Traces of methylated arsenicals are present in freshwater sediments (Maeda 1994).

2. Arsenic in Surface Water Systems

A regional lake and stream survey in Finland showed that variations in As concentrations in freshwaters and upper soil layers are heavily dependent on the local geology (Tarvainen et al. 1997), an observation also made in Norway (Laag and Steinnes 1978a) and Sweden (Alm et al. 1998). In some areas, however, impacts from air pollution may be significant (Laag and Steinnes 1978a; Rosen and Lithner 1986; Vesely and Majer 1996; Tarvainen et al. 1997; Alm et al. 1998). Vesely and Majer (1996) found an increase in median As concentrations by decreasing pH based on a large data base of surface waters from the Czech Republic. They also found that As is strongly accumulated in the topsoil, even under conditions of severe acidification. They suggest this being both due to a strong association with organics and sorption on Fe-oxyhydroxides. Precipitation of As into stream and lake sediments by Fe- and Mn-oxyhydroxides is also reported to be significant in Finnish surface waters (Tarvainen et al. 1997).

Concentrations of As in 10 major rivers in the southwestern United States ranged from 0.15 to 0.45 μg As L^{-1} (More and Ramamorthy 1984). High As concentrations occurred in both high and low TOC lakes and at all pH levels.

Borg (1983, 1987) reported a positive correlation between As and water color in forest lakes in southern and middle Sweden. Borg (1986b) also showed (in a study in August 1986 of 10 lakes around Rönnskärsverken) that the dialyzable fraction, which is supposed to be directly bioavailable, was dependent on the pH value and the humus content. The highest dialyzable As concentrations were found in lakes with low humus content and pH > 7 and lowest in a humic-rich lake with pH 5.9.

The As concentrations in lakes in Sweden, Norway, and Finland (Table 46 and Table 47) were generally *Low* to *Very low* according to the Swedish classification system for surface waters (Table 48). More than 95% of the lakes were classified into these two categories. The concentrations were generally below 1 μg As L^{-1}. Only three lakes in the Nordic survey in 1995 (two in Sweden, one in Norway) exhibited As concentrations > 5 μg L^{-1}, which is proposed to be the critical concentration level for biological effects in sensitive Swedish freshwaters (Table 49).

In Norway, high As concentrations seem to be more abundant in low TOC lakes with pH values < 6 (Figure 55). In contrast, Sweden high As concentrations were more frequent at neutral or high pH in both medium and high TOC lakes. Limed Swedish lakes generally show lower As concentrations than nonlimed Swedish lakes (Figure 56), that is, median As concentration in limed lakes of 0.091 μg As L^{-1} compared with 0.268 μg As L^{-1} in nonlimed lakes. Thus, liming might have an effect on As concentrations. Dividing the Swedish lakes in pH-classes (Figure 57), there are minor differences. Median As concentration in pH class: < 5.4 was 0.278 μg As L^{-1}, while the median concentrations in pH class: 5.4 to 6.0 and pH class: ≥ 6 were 0.246 μg As L^{-1} and 0.202 μg As L^{-1}, respectively. The differences were more significant with respect to the TOC status of lakes (Figure 58). While median concentrations of As in low TOC lakes (< 5 mg C L^{-1}) was 0.097 μg As L^{-1}, it was 0.220 μg As L^{-1} and 0.415 μg As L^{-1} in medium TOC lakes (5 to 10 mg C L^{-1}) and high TOC lakes (≥ 10 mg C L^{-1}), respectively. This means that TOC is essential for the As concentration in Swedish lakes. The reduced As-concentration in limed lakes might be due to the improved conditions for precipitation of As organic and/or As inorganic compounds at higher pH, besides geological differences. If differences in geology, acid-sensitive soils, and bedrock (e.g., granite, gneiss) should be more common in the already limed areas, and such soils and bedrock should generally contain low As concentrations compared with most other minerals and rocks. However, the concentrations of As in Swedish lakes are generally lower than the critical concentration level for biological effect. Accordingly, positive biological effects of reduced As concentrations because of liming are unlikely.

a. Experimental Acidification

No data are available!

b. Liming

No data are available!

Table 46. Concentrations of As (µg As L^{-1}) in Nordic surface waters. N_T: number of analyses; N_L: number of results below the analytical detection limit. n.r.: not reported

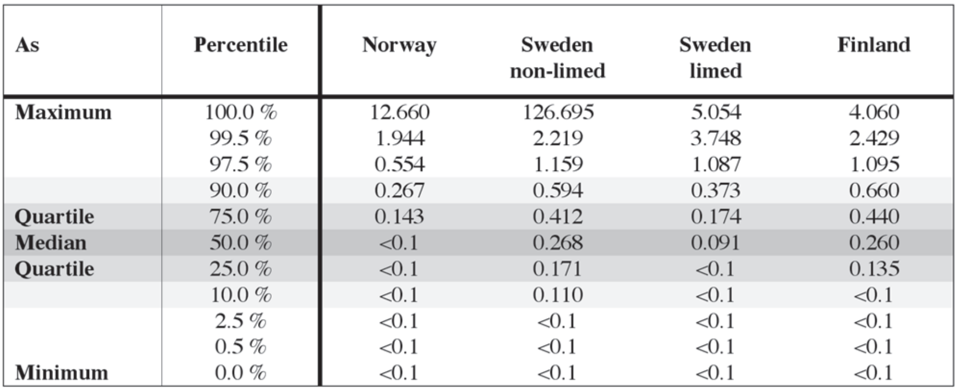
	N_T	N_L	Min - Max	Median/ Mean (±)
Finland[1]	152	0	0.08 - 5.20	0.33
Sweden, south[2]	20	n.r.	0.10 - 0.36	0.19 ± 0.06
Sweden, north[2]	17	n.r.	0.11 - 0.40	0.22 ± 0.07
Sweden, north[2]	56	n.r.	0.06 - 1.2	0.25

[1] Tarvainen et al. (1997), based on samples from 1990-1992.

[2] Borg (1983), woodland lake samples from March-April 1980. Mean lake colour 95 ± 70 mg Pt L^{-1} (Sweden,south), 65 ± 55 mg Pt L^{-1} (Sweden, north).

[3] Borg (1987), based on summer and winter samples of 59 lakes sampled in 1980. Mean lake colour was 42 ± 25 mg Pt L^{-1}. Mean values are without ± SD, since the data only are presented in a figure.

Table 47 Percentile distribution of As (µg As L^{-1}) in Nordic surface waters, based on the Nordic Lake survey in 1995. Norway: n = 514; Sweden, nonlimed: n = 1105; Sweden, limed: n = 281; Finland: n = 463



As	Percentile	Norway	Sweden non-limed	Sweden limed	Finland
Maximum	100.0 %	12.660	126.695	5.054	4.060
	99.5 %	1.944	2.219	3.748	2.429
	97.5 %	0.554	1.159	1.087	1.095
	90.0 %	0.267	0.594	0.373	0.660
Quartile	75.0 %	0.143	0.412	0.174	0.440
Median	50.0 %	<0.1	0.268	0.091	0.260
Quartile	25.0 %	<0.1	0.171	<0.1	0.135
	10.0 %	<0.1	0.110	<0.1	<0.1
	2.5 %	<0.1	<0.1	<0.1	<0.1
	0.5 %	<0.1	<0.1	<0.1	<0.1
Minimum	0.0 %	<0.1	<0.1	<0.1	<0.1

Table 48. Classification of concentrations of As in surface waters (µg L^{-1}), the upper (0 to 1 cm) of lake sediments (mg kg^{-1} dry weight) in Swedish (SNV 1991; Alm et al. 1998) and Norwegian (SFT 1997) freshwaters. n.r.: not reported.

	1 Very Low	2 Low	3 Medium	4 High	5 Very High
Surface water					
As (Sweden, 1991)	≤ 0.2	0.2 - 1.0	1 - 2	2 - 10	> 10
As (Sweden, 1998)	≤ 0.4	0.4 - 5.0	5 - 15	15 - 75	> 75
As (Sweden, 1998)[1]	≤ 0.1	0.1 - 0.4	0.4 - 1.4	1.4 – 14	> 14
As (Norway, 1997)[2]	n.r.	n.r.	n.r.	n.r.	n.r.
Sediment					
As (Sweden, 1991)	≤ 5	5 – 15	15 - 75	75 - 250	> 250
As (Sweden, 1998)[3]	≤ 5	5 – 10	10 - 30	30 - 150	> 150
As (Norway, 1997)	≤ 5	5 – 25	25 - 100	100 - 200	> 200

[1] Based on risks for biological effects.

[2] Based on distribution in Swedish lakes (1995) and rivers (1989-96).

[3] Based on distribution in Swedish lakes with and without local emissions.

Table 49. Critical concentrations of As (µg L^{-1}) at different ecosystem levels in some countries, according to UN-ECE (1997b).

	Freshwater µg L^{-1}			Sediment mg kg^{-1}	Soil mg kg^{-1}	Fish mg kg^{-1}
		acute	chronic			
The Netherlands	24			160	4.5	
United Kingdom	50				600	
Germany AsIII/AsV		360/190	850/ -			
Canada	50			6	12	
Sweden	**5**			**60**		
Denmark	4				2	
Finland					13	

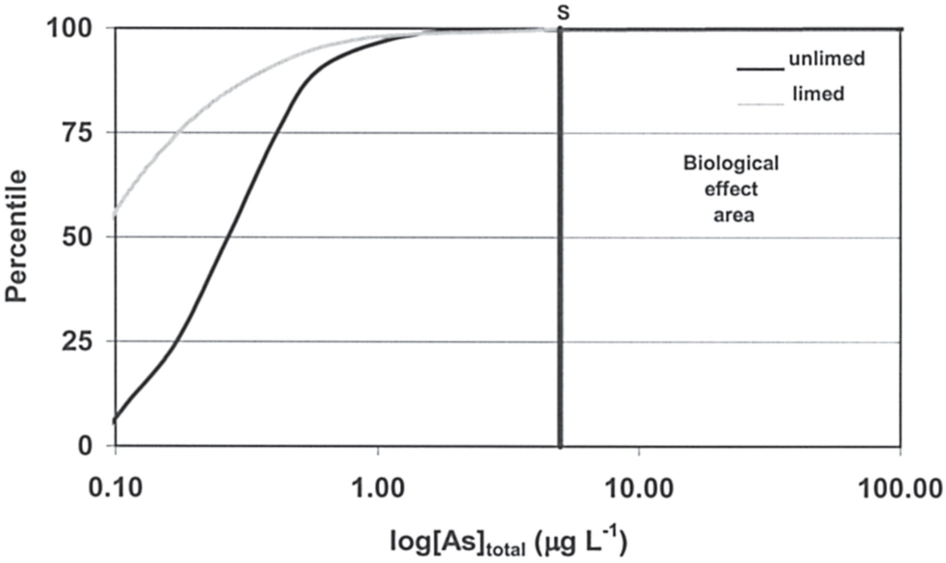


FIGURE 56. Percentile distribution of total As in limed (n = 261) and not limed (n = 1124) Swedish lakes. S shows the assessed critical concentrations for aquatic life in Sweden. (Data from Skjelkvaale *et al*. [1996, 1999].)

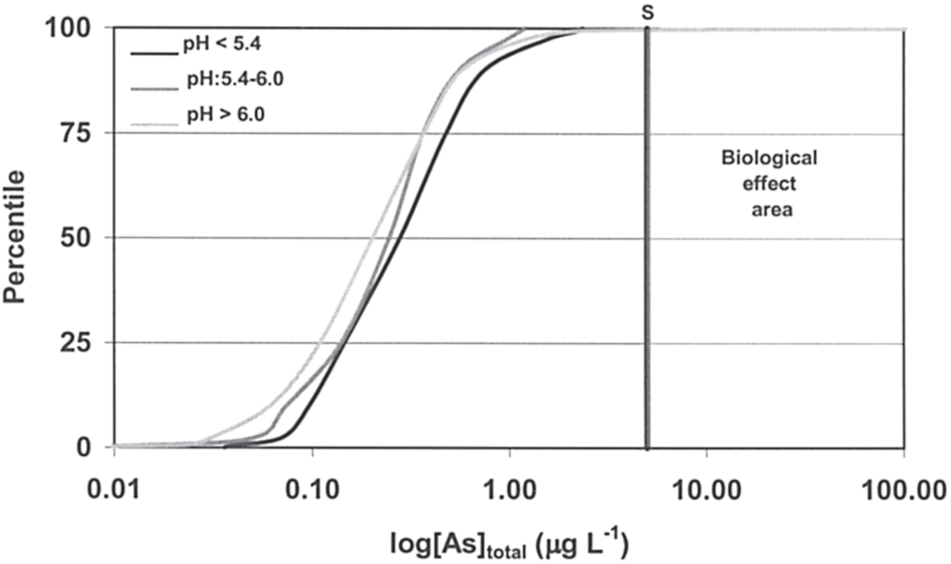


FIGURE 57. Percentile distribution of total As in Swedish lakes based on 3 pH classes. pH < 5.4, n = 63; $5.4 \leq pH < 6.0$, n = 71; $pH \geq 6$, n = 990. (Data from Skjelkvaale *et al*. [1996, 1999].)

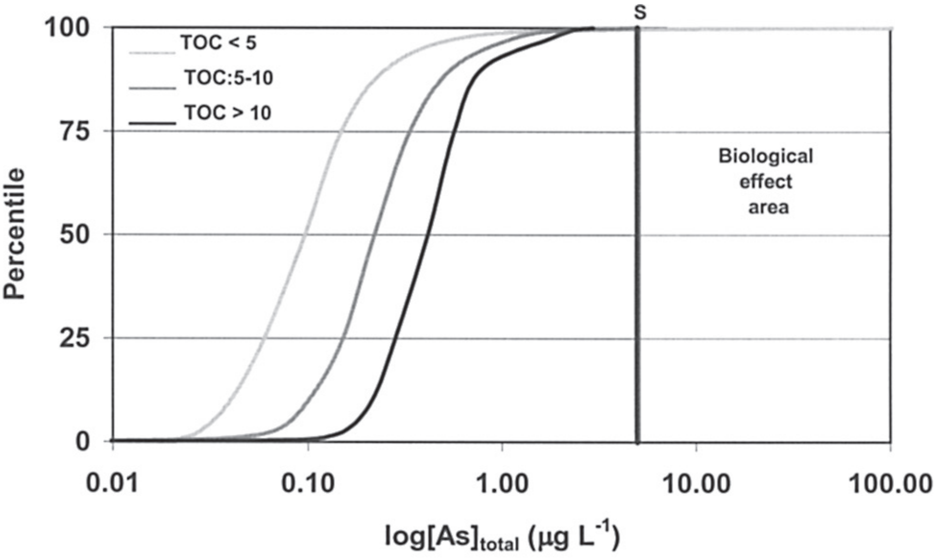


FIGURE 58. Percentile distribution of total As in Swedish lakes based on three TOC classes (TOC in mg C L^{-1}). TOC < 5, n = 352; 5 ≤ TOC < 10, n = 508; TOC ≥ 10, n = 264. (Data from Skjelkvaale *et al.* [1996, 1999].)

c. Reacidification

No data are available!

3. Biology and Toxicity

a. Toxic Species

Regarding toxic species, it is a general trend in the literature that inorganic arsenicals are more toxic than organic arsenicals, and trivalent forms are more toxic than pentavalent forms. The toxicity appears to be directly related to the solubility in water and body fluids, that is, the highest solubility implies the highest toxicity (Eisler 1988a). The mechanisms of As toxicity differ considerably among As species, although signs of poisoning appear similar for all arsenicals (Woolson 1975; NRCC 1978; Pershagen and Vahter 1979). The toxicity of As is significantly modified by numerous abiotic factors such as water temperature, pH, E_h, organic content, phosphate, suspended solids, etc.

Generally, early developmental stages are the most sensitive to arsenic exposure, and there are large interspecies differences (Eisler 1988b; Lithner 1989). Some aquatic life seem to be affected at water concentrations of 19 to 48 µg As L^{-1}, the more sensitive being some marine algae who showed reduced growth (EPA

1985). However, the most sensitive organisms seem to be natural, phosphorus-limited phytoplankton communities, showing reduced photosynthesis at arsenate concentrations as low as 0.2 µg L^{-1}. Arsenate has antimetabolic properties to phosphate and interferes in the phosphorylation process and reduces the ATP production (Lithner 1989).

Arsenic is accumulating in many organisms, but there is no evidence for biomagnification along the food chain (Woolson 1975; Hallacher et al. 1985; Hood 1985).

A proposed effect-related sediment criteria for heavy metals in Canada (Smith et al. 1996) assume a biological effect level of As in sediments at 17 mg kg^{-1}dw.

b. Target

The primary toxic mode of inorganic As^{3+} is through reactions with sulfhydryl groups of proteins and subsequent enzyme inhibition. Inorganic pentavalent arsenate does not react as readily as As^{3+} with sulfhydryl groups, but may uncouple phosphorylation (Howard et al. 1984, EPA 1985). Several other As species (arsenite, arsenic acids, organoarsenical etc) indirectly affect and react with the sulfhydryl groups of tissue proteins and enzymes (see Eisler 1988b). Methylation of As (unlike methylation of Hg) greatly reduces toxicity and is a true detoxifying process (Woolson 1975).

c. Fish

As^{3+} concentrations down to 40 µg As L^{-1} have been reported (EPA 1985) to cause 50% death or malformation in developing embryos in 7 days for the narrow-mouther toad (*Gastrophryne carolinensis*). Fishes seem to be somewhat less sensitive, but a LC_{50} value (13 days exposure) of 50 µg As L^{-1} has been documented for newly hatched fry of *Esox masquinongy* (Lithner 1989). Lowest reported effect concentration is 100 µg As^{5+} L^{-1} for gold fish (*Carassius auratus*) and 130 µg As^{3+} L^{-1} for rainbow trout (NRCC 1978; EPA 1985).

d. Invertebrates

Invertebrates seem generally less sensitive to As compared with fish (Eisler 1988b). Maximum acceptable toxic concentration seems to be ≈ 500 to 600 µg L^{-1} (As^{3+} and As^{5+}, EPA 1985). Phytoplankton algae seem to be the most sensitive freshwater species regarding As toxicity, with reported effects down to 0.2 µg As^{5+} L^{-1} (Lithner 1989).

e. Toxicity Levels in Relation to Water Chemical Status in Sweden and Norway

Lithner (1989) reported the lowest known effect at 0.2 µg As L^{-1} in the form of arsenate. Alm et al. (1998) assume the risk of biological effects in sensitive Swedish waters at 5 µg As L^{-1}. This is lower than the effect concentrations applied in most other European countries (Table 49) and USA (Eisler 1988b).

The Nordic Lake survey in 1995 (Table 47) shows that only one nonlimed lake (127 µg L^{-1}) and one limed lake in Sweden (5.1 µg L^{-1}) and one Norwegian lake (13 µg L^{-1}) had As concentrations > 5 µg As L^{-1}. Regarding the effect level reported by Lithner (1989, 0.2 µg As L^{-1}), more than 50% of the nonlimed Swedish lakes and more than 10% of the Norwegian lakes exceeded this level (Table 47).

4. Reacidification — Biological Risk

We might expect some increase in the concentrations of As during reacidification of limed water bodies, but significant increase is unlikely as long as pH does not drop to very low levels (pH < 4). The concentration of As in surface waters is likely lower in acid-sensitive areas compared with areas with soil and bedrock with higher acid neutralizing capacities. As long as liming has been conducted primarily in the most acid-sensitive areas, the background concentrations of As is low in the limed lakes. Thus, if a certain increase in As occurs during reacidification of these limed lakes, the concentrations will still be far below critical concentrations for aquatic life in almost all limed lakes.

VIII. METALS IN SURFACE WATERS IN NORWAY AND SWEDEN — A SYNTHESIS

A. Chemical Properties and Speciation of Metals

The fate of metals within the catchment is very important for the loading and chemical forms entering surface waters. Normally, only analyses of total metal concentrations are conducted, except for aluminium, where a certain fractionation is rather common. Accordingly, thermodynamic models are used widely for metal speciation, including aluminium. The value of the information from these models is, however, limited because they only estimate the percentage distribution of metal forms. The metal complexation strength is the crucial factor for geochemical and biological reactivity, and thereby the aquatic load of metals and the subsequent toxicity to biota. Thus, most important for the load is the amount of water-soluble metal forms normally with the free metal ions as the most relevant fraction regarding acute toxicity. Acute toxicity of metal-organic complexes is negligible, but certain metal-organic forms of metals such as Pb and Hg may have sublethal and lethal effects, but normally after longer time of exposure.

According to literature dealing with the most essential factors for bonding strength of metal complexes (see Stumm and Morgan 1981; Krogstad 1982), the adsorption of trivalent metal ions to soil organic material in the pH interval 3.5 to 5.0 might be ranked as follows: $Fe^{3+} = Cr^{3+} > Al^{3+}$. In the same pH interval, the adsorption of divalent cations might be ranked: $Hg^{2+} \geq Pb^{2+} > Cu^{2+} >> Cd^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$. In peat and humic acids fractionated from the peat, the sequence for divalent ions is mainly: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ in the pH range 3.0 to 4.6. The adsorbed quantities of metal ions increase with increasing base saturation and increased decomposition of the peat due to dissociation of acid functional groups and increased content of carboxyl groups, respectively (Krogstad, 1982). This means that Fe, Cr, Hg, Pb, and Cu have the strongest association to organic compounds among these metals. Metals with medium bonding strength to organics are Al, Cd, Ni, Co, Zn, Mn, while Ca and Mg exhibit the weakest bonding strength. In organic-free medium, the most toxic heavy metals should be expected among the metals with the strongest association to organics. As soon dissolved organic compounds are present, likely metals with medium bonding strength to organics are more important for the toxicity, because they normally will have higher proportions of free metal ions.

Heavy metals such as Hg, Pb, and Cd are acute toxic at very low concentrations compared with physico-chemical properties evaluated above. A likely reason for this is that these metals are nonessential to organisms and the organisms, therefore have restricted mechanisms “to handle” these metals.

B. Relationships between Metal Concentrations, pH, and TOC

A redundancy analysis (RDA analysis), that is, a linear, multivariate method for describing more than one dependent variable in relation to several independent variables (see ter Braak 1994) has been applied to evaluate trace metal concentrations in Swedish and Norwegian lakes against TOC and H^+. Lake chemistry data used are from Skjelkvaale et al. (1999). The RDA biplot (Figure 59) shows that the two independent variables are fairly orthogonal, and that they align closely with the RDA axes. The first RDA axis reflects a strong positive relationship between TOC and all the metals included in the analysis, but particularly Fe and Mn. The second RDA axis indicates a strong positive association between H^+ and Cd, Zn, and Pb, and perhaps a negative association with Ni. The strong association between H^+ and Pb is somewhat unexpected, due to large documentation in literature of strong associations between Pb, and organic compounds. A problem with Cd, Pb and Zn is the important atmospheric inputs of these metals and the close relationship between atmospheric inputs of strong acids and these metals. This is likely the causal factor for the relationship between these metals and pH.

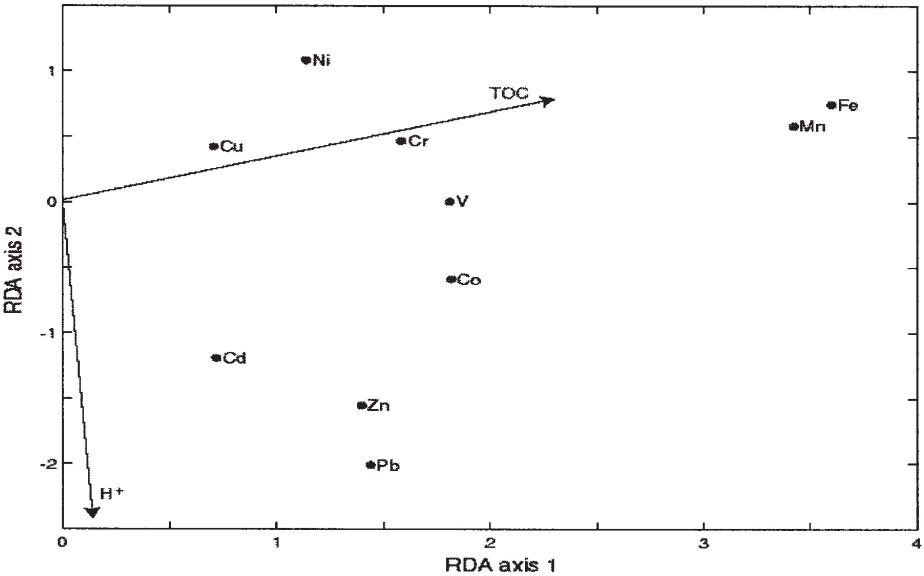


FIGURE 59. Redundancy analysis of trace metal concentrations against TOC and H^+ (arrows) for Swedish and Norwegian lakes based on the 1995 surveys. All variables are log transformed. Trace metal concentrations below the detection limit are estimated according to Skjelkvaale *et al.* (1999).

The effects of sulfate reduction to sulfide and the subsequent reduction in dissolved metal concentration in water (and thereby also the metal toxicity) as metal-sulfides precipitate are well known. This has been formalized in the Acid Volatile Sulfide model (e.g. Ankley et al., 1996). However, because sulfate reduction takes place at a very low redoxpotential ($E_h \approx 100$ mV), most fishes and animals focused on in this review cannot sustain these low oxygen levels. Thus, we have in minor degree focused on metal-sulfide chemistry. Of course, formation of metal-sulfide occurs in many of the Nordic lakes, but in recent decades it is pH not E_h changes in surface waters that have caused severe biological damage in many Nordic surface waters.

Inasmuch as the RDA analysis indicates that Cd, Zn, and Pb are the most pH sensitive, they are likely the most important metals with respect to reacidification effects. Inorganic Al is not included in the RDA analysis and should be added to this list, because it is the most important element in acidic surface waters.

The results from the RDA analysis agree well with the results from the evaluations of how the concentration of each metal covaries with pH and TOC within different TOC classes and pH classes.

Concentration levels, pH dependency and toxicity all point to Pb, Cd, and Al as the main metals to be concerned about when dealing with the reacidification of limed lakes. In complement to Pb, Cd, and Al, methyl mercury (MeHg) is important due to the high levels in fish, which influences the prerequisites for human consumption.

C. Remobilization of Metals from Sediments

A literature review by Nelson and Campbell (1991) concluded that although laboratory experiments suggest that some trace metals could be remobilized from lake sediments at acidic pH, field studies indicate that sediment pore waters are not sufficiently acidic for metal remobilization to occur. Furthermore, pH in sediments is not likely less than the water column pH due to the internal alkalinity production in the sediments. Studies of epilimnetic sediments from eight lakes (pH range 4.2 to 7.0) in Canada showed that pore water pH increased by sediment depth in the six lakes with a $\mathrm{pH} < 6.5$. The alkalinity (Gran titration in the pH range 4.2 to 3.5) in the sediments increased by greater than one order of magnitude above the water column values. The alkalinity increase started within 2 cm of the sediment-water interface and corresponded to an alkalinity flux out of the sediment of 0.4 to 510 meq m^{-2} yr^{-1} in the lakes with a $\mathrm{pH} < 6$ in the bottom water (Schiff and Andersson 1986). Alkalinity might also be produced by sulfate reduction in sediments, increasing the pH and reducing the metal concentrations (Belzile and Morris, 1995).

The concentrations of LAL in the reacidified limed lakes included in the 1995 Swedish lake survey indicate no dramatic reacidification effects, other than what is expected due to the reacidified pH level. Similarly, Hindar and Lydersen (1995) concluded that reacidification of limed objects will not contribute to any dramatic increase in the concentration of Al. The concentration of inorganic Al will relatively rapidly return to preliming levels or lower. LAL concentration lower than prelimed concentrations is likely because the amount of acidifying compounds in precipitation has decreased significantly during recent years (Skjelkvaale et al. 2001). This has caused a significant reduction in LAL in most acidified surface waters in Norway. Accordingly, this is probably the case also in areas of Sweden where the deposition of strong acids is the main cause of surface water acidification.

Lead sediment profiles from acidic lakes typically indicate that acidification has little effect on Pb accumulation in the sediments (Norton et al. 1981; Nelson and Campbell 1991). This has also been confirmed by laboratory experiments on surface sediments, where Pb release from sediments did not occur above pH 3 (Davis et al. 1982). Even the transport of Pb (and also Hg) within the lake and lake watershed is relatively unaffected by acidification. Regarding remobilization from Cd from sediments during reacidification, LaZerte (1986) concluded that once Cd is deposited it is not readily released from aerobic sediments, except at very low pH ($\mathrm{pH} < 4.0$).

D. Biological Effects of Metals

In this report, critical levels (CL) of heavy metals are evaluated for both fish and invertebrates. Because invertebrates generally are more metal tolerant compared with most fishes, primarily compared with the salmonids, we have focused primarily on CL of heavy metals on sensitive fish species. Furthermore, as most aquatic invertebrates, like the fishes are gill breathing, and the mechanisms of metal toxicity are linked primarily to processes at the gill surfaces, we have also chosen to focus on fish when describing the metal toxicity on aquatic organisms.

Based on the literature review, the general trend is that the main cause of acute metal toxicity to fish is the disturbance of respiratory gas transfer and/or ion regulation. A combination of loss of blood electrolytes and hypoxia seems most harmful. There are reasonable indications that the mortality is less acute when leakage of plasma ions is the predominant physiological problem compared with hypoxia, which normally causes mortality to many aquatic organisms already within hours or days of exposure.

The most acute toxic metals precipitate on the gill surfaces. Thus, the primary target organ of acute metal toxicity to aquatic organisms is the gill. Because the mucus on gills and the gill surfaces contain strong acid cation exchanging compounds, binding to the gills by cation exchange is the predominant mechanism of acute metal toxicity. Thus, acute toxicity of metals is normally linked to the free metal activity, and the toxic power of different metals is normally a combination of concentration and strength of metal complexation to biological interfaces such as gill membranes.

Both the gill surface and dissolved organic matter are strong acidic cation exchangers. Accordingly, there will always be a competition between the two cation exchangers for metal complexation. Because higher concentration of dissolved organic matter reduces the concentration of free metals in water, it also reduces the possibility of the metals to bind to negatively charged sites at gill surfaces. Thus, dissolved organic carbon is an important metal detoxificant in aquatic systems. However, in humus-rich waters with high concentrations of weakly bound metals, the capacity and strength of cation exhcange at gill surfaces might theoretically extract metals from humus to gills and thereby cause toxic effects. This phenomenon needs further evaluation.

Increased ionic strength may also reduce metal toxicity, because it normally means elevated concentrations of harmless cations, such as base cations. These base cations compete with the free toxic metal ions, and thereby reduce the possibility of toxic metal forms to bind to gill surfaces.

High valence and small ionic radii are relatively important competition factors in cation exchange processes. However, this preference is significantly reduced when the temperature is low as in most Scandinavian waters. This temperature effect is often overlooked in soil and surface water chemistry.

Both pH and temperature are important factors for the toxicity, because these parameters may change the metal speciation and the dissociation of complexing compounds, both of which influence the metal complex strength. Temperature is also directly important for the toxicity as the biological metabolism is very temperature dependent, that is, higher temperatures give higher metabolism. For aquatic gill organisms, higher metabolism means higher respiration frequency. Further, this means that lethal hypoxia and blood plasma ion levels occur earlier at high temperature.

E. Critical Levels of Aluminium

Unfortunately, the lack of metal speciation seriously limits our understanding of metal transport, removal mechanisms, and toxicity. Aluminium is the most investigated metal, where most data from the natural environment exist regarding the different chemical forms of the metals and their toxicity to biota. Nevertheless, it has been very difficult to assess critical concentrations of inorganic aluminium (the primary toxic Al fraction, LAL) because it differs widely due to variation in many physico-chemical variables such as pH, water temperature, TOC, and ionic strength. Furthermore, the toxic level differs significantly according to several biological factors such as species, life stage, and tolerance differences between strains of species.

The Swedish and Norwegian lake surveys in 1995 (Henriksen et al. 1998; Skjelkvaale et al. 1999) and earlier surveys (Henriksen et al. 1988b, 1989; Lien et al. 1996) show that inorganic aluminium is the only metal at concentrations with presumably biological consequences at a regional/national scale. This is why aluminium is the metal most focused on regarding chemical forms and toxicity to fish and invertebrates in acidified systems. Only a very few surface waters have the concentration of other metals at levels above or close to the lowest biological risk levels (LBRL).

Almer et al. (1974) and Bergquist (1991) have studied the relative sensitivity of fishes in Scandinavia to acid freshwater. These studies only focus on water pH, and not inorganic aluminium, the primary toxic compound in acidic waters. Rask et al. (1995) showed that the concentration of inorganic aluminium (labile Al, LAL) was essential in determining whether populations of different fish species were affected by acid precipitation. Focusing on labile aluminium, Polèo et al. (1997) reported relative sensitivity among common Scandinavian fish species to acute aluminium challenges to be in the following order:

Atlantic salmon (*Salmo salar*) > roach (*Rutilus rutilus*) > minnow (*Phoxinus phoxinus*) > perch *(Perca fluviatilis*) > greyling (*Thymallus thymallus*) > brown trout (*Salmo trutta*) > arctic char (*Salvelinus alpinus*) >> crucian carp (*Carassius carassius*).

Even though there is a considerable range in the sensitivity to aluminium among fish species, it is generally accepted that salmonids are the most sensitive group, particularly at the early gill-breathing stages in their life (Schofield 1977; Baker and Schofield 1982; Cleveland et al. 1986). The embryo is the life stages least sensitive to aluminium (Leivestad et al. 1987), while the smoltification period of Atlantic salmon likely is the most sensitive stage within all Scandinavian fish species (Staurnes et al. 1993).

There are also studies from Norway indicating large strain differences toward aluminium/acidification (Dalziel et al. 1995). The strains that have survived naturally in the most acidified areas of Norway seem to be the most tolerant, indicating adaptation as an important mechanism.

In addition, different toxicity responses may occur depending on whether the studied fish are caged or free-swimming (Schofield and Trojnar 1980; Ingersoll et al. 1990a). Further, pulses of acidic/aluminium-rich water with low calcium concentration or ionic strength may lead to a lower toxicity response compared with that obtained by a continuous exposure (Mount et al. 1990).

Based on our literature review, it is reasonable to assume a critical concentration of inorganic Al (LAL) within the range 20 to 80 μg Al L^{-1}, where sublethal effects occur at the lowest concentrations. Effects of sublethal Al concentration are reduced hatchability, reduced larval feeding behavior, swimming capacity, slower growth, and general poorer condition.

F. Concentration Levels in Norwegian and Swedish Surface Waters

The concentration of metals in Swedish and Norwegian lakes are generally *very low* to *low* according to the freshwater classification systems in the two countries (Table 50). A very limited number of lakes have metal concentration above or close to concentrations where biological effects are expected. Only inorganic aluminium (LAL) in surface waters seems to be a regional problem for aquatic life in both countries.

The population of limed Swedish lakes generally shows somewhat higher concentrations of heavy metals than the nonlimed lakes. This may indicate that many of the most acidified lakes are already limed, but also that liming likely has marginal effect on the total concentrations of heavy metals.

The limited number of reacidified limed lakes do not show elevated concentrations compared with levels expected from the ambient pH level. In addition, the concentrations of heavy metals are generally far from the lowest effect levels (except for inorganic aluminium). Thus, heavy metals will not cause any severe biological effects during reacidification of limed waters.

Regarding labile aluminium (LAL), we assume the most sensitive aquatic species to be Atlantic salmon (*Salmo salar*), with reported effects about 20 μg Al L^{-1} (Staurnes et al. 1995). Because roach (*Rutilus rutilus*) seem to be the second most sensitive fish species in Nordic waters (Poléo et al. 1997), we assume the same risk level for this species. Accordingly, many lakes in Norway and Sweden (Table 51) have LAL concentrations above the lowest biological risk level (LBRL) for LAL. Most of these lakes have low pH and/or at medium to high TOC.

Table 50. Concentrations (percentiles and lowest biological risk levels in μg L^{-1}) of heavy metals and arsenic in Swedish and Norwegian nonlimed lakes in 1995. The lowest biological risks levels (LBRL) used are based on the lowest assumed effect criteria in Norway (SFT 1997) and Sweden (Alm et al. 1998). Data are from Henriksen et al. (1998) and Skjelkvaale et al. (1999)

	Pb	Cd	Cu	Zn	Ni	Cr	Fe	Mn	Co	As[a]
Maximum	14.97	1.07	37.7	426.5	10.2	27.7	10149	697	3.15	5.05
90%	0.82	0.057	1.04	6.34	0.92	0.38	557.9	51.4	0.203	0.373
75%	0.39	0.028	0.62	3.11	0.53	0.20	221.5	17.9	0.097	0.174
50%	0.16	0.012	0.37	1.43	0.29	0.08	71.2	5.4	0.049	<0.1
25%	0.08	0.006	0.22	0.69	0.15	0.04	23.8	1.8	0.023	<0.1
10%	0.04	0.003	0.14	0.29	0.08	0.02	9.8	0.7	0.010	<0.1
Minimum	0.00	0.000	0.02	0.07	0.01	0.00	0.1	0.0	0.001	<0.1
LBRL	>1	>0.1	>3	>20	>15	>5	no	no	no	>5

a: Sweden only.

Table 51. Percentile distribution of dissolved inorganic Al (LAL) in Norwegian and Swedish surface waters, based on the Nordic Lake survey in 1995. Norway: n = 969; Sweden, non-limed: n = 555; Sweden, limed: n = 157. Values < 10 μg Al L^{-1} are below the detection limit for the Norwegian method. Suggested lowest biological risk level (LBRL) of 20 μg LAL L^{-1} is related to Atlantic salmon, based on the work by Staurnes et al. (1995). (Data are from Henriksen et al. [1998] and Skjelkvaale et al. [1999])

Percentile	Norway Non-limed	LAL Sweden Non-limed μg Al L-1	Sweden Limed
Maximum	174	201	110
99.5 %	125	149	110
97.5 %	89	90	58
90.0 %	53	34	24
75.0 %	10	14	11
50.0 %	5	5	5
25.0 %	5	0	0
10.0 %	2	0	0
2.5 %	0	0	0
0.5 %	0	0	0
Minimum	0	0	0

G. Metal Concentrations in Relation to Critical Levels

Table 52 shows the percentage of nonlimed lakes in Norway, Sweden, and Finland, and limed Swedish lakes below the lowest biological risk levels (LBRL) for different metals, according to the Norwegian and Swedish LBRL criteria (SFT, 1997; Alm et al., 1998). Excluding Cd, Pb, and Al, very few lakes (<2%) have heavy metal concentrations > LBRL. Regarding Cd, Pb, and Al, 5%, 7%, and 19% of the nonlimed Swedish lakes have concentrations > LBRL (according to the Swedish LBRL criteria for Cd and Pb). The differences are small between limed and nonlimed lakes, even though liming seems to decrease the exceedance to 2% and 14% of the lakes for Cd and Al, respectively, while the percentage of lakes > LBRL are almost equal for Pb in limed and nonlimed Swedish lakes. In Norway the percentage amounts of nonlimed lakes above the same LBRL values are somewhat higher for Al and Pb compared with the Swedish lakes, while somewhat lower for Cd.

Table 52. Percentage of nonlimed lakes in Norway (n = 985), (n = 985), Sweden (n = 820, n = 1124 for As), and Finland (n = 462), and limed Swedish lakes (n = 261) below the lowest biological risk levels (LBRL) according to Norwegian (SFT 1997) and Swedish criteria (Alm et al. 1998). The concentration for Al is labile aluminium (LAL), the toxic fraction of Al. No LBRL values for LAL are established in Norway or Sweden. Thus, the tentative LBRL values for Atlantic salmon (20 μg Al L^{-1}) and brown trout (80 μg Al L^{-1}) are according to the studies by Staurnes et al. (1995) and Lydersen et al. (1994b). The LAL interval 20 to 80 μg Al L^{-1} therefore should represent the concentration range where biological effects should be expected in Nordic surface waters

Element	Country	LBRL $\mu g\ L^{-1}$	%			
			Norway Non-limed	Sweden Non-limed	Sweden Limed	Finland Non-limed
Zn	Norway	50	99.8	99.6	99.6	99.8
	Sweden	20	99.3	99.3	98.9	99.4
Cd	Norway	0.2	99.5	98.6	98.9	99.8
	Sweden	0.1	96.6	95.5	97.7	99.4
Cu	Norway	3.0	99.3	98.4	99.6	99.1
	Sweden	3.0	99.3	98.4	99.6	99.1
Pb	Norway	2.5	98.4	98.2	98.1	99.8
	Sweden	1.0	91.5	93.0	93.5	98.3
Ni	Norway	5	99.8	99.6	99.6	98.9
	Sweden	15	100	99.8	100	99.4
Cr	Norway	10	100	99.8	100	100
	Sweden	5	99.9	99.6	100	100
As	Norway					
	Sweden	5	99.8	99.8	100	100
Al	*Atlantic salmon*	*20*	*76.9*	*80.7*	*86.0*	*n.a.*
	Brown trout	*80*	*95.5*	*91.4*	*92.4*	*n.a.*

IX. CONCLUSIONS ON BIOLOGICAL RISKS OF METALS

Based on the literature study and compared with the preliming period, it is unlikely that enhanced remobilization of inorganic aluminium (LAL) or other toxic metals (metal bomb hypothesis) from the catchment, the lake sediment, and/or the streambed will occur when limed waters reacidify. Rather, the concentrations in surface waters are expected to be lower than before liming started, because of reduced atmospheric inputs of both strong acids and metals as Cd, Pb, Hg, and Zn during the last 10 to 20 years. The high alkalinity in many Swedish lakes before liming was initiated (Table 1) indicates that the number of waters with high concentrations of heavy metals should be relatively limited. This conclusion is supported by the Nordic Lake Survey in 1995 (Skjelkvaale et al. 1999).

The concentrations in lakes relative to the biological effect levels, as well as the chemical properties of the different metals, suggest that the potential biological risks associated to the reacidification of limed lakes decrease in the order Al>>Cd>Pb in Norwegian and Swedish freshwaters. The risks associated with Fe, Mn, Zn, Cu, Cr, and Ni are very low and do not have to be considered except in waters with known concentrations > lowest biological risk level (LBRL). However, such waters are most certainly very rare. Hg is very special, because it biomagnifies and constitutes a problem to mainly human health and top predators such as mammals and birds. Considering the large amounts of waters with Hg levels in fish above the health limit, this is a significant problem in Scandinavian waters. However, present knowledge indicates that neither liming nor a future reacidification of limed waters would greatly change the Hg concentrations in fish. Because As is primarily present as anions in surface waters, this element differs significantly from the cationic metals. Only few lakes have high As concentrations in relation to critical levels in Sweden, and high As concentrations are mainly related to agricultural areas and consequently high pH waters.

Aluminium has the largest potential to cause biological damage due to reacidification of limed waters. There is no difference in risk assessment between running waters and lakes except that the highest aluminium concentrations are expected in small headwater streams and lakes. We might also expect temporarily higher concentrations of toxic heavy metal species in headwaters, but the same ranking of metals with respect to toxicity is expected regardless of time period and system. The risk with aluminium is mainly coupled to the pH decrease and less to the liming technique used to maintain circumneutral pH. Terrestrial liming has the potential to reduce the aluminium load from soils, but as yet the technique has been used in very restricted areas and is of less quantitative importance.

Therefore, aluminium is the metal that should set the limit for judging the risk of biological damage due to the reacidification of limed surface waters. A plan for the cessation of liming should use fish sensitivity to aluminium as a strategy to reduce the biological damage caused by reacidification. Such a strategy would reduce the biological damage on most other organisms as well.

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