5 Acidification of rivers and lakes

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5.1 Introduction

Acidification of water implies a pH reduction. The pH reduction can be due to anthropogenic activities (e.g. burning of fossil fuels) but also to natural processes (e.g. presence of organic acids). It is important to separate these two causes of low pH as the ecological impact of elevated H^+ will vary. This difference is to a large extent due to the interaction between acid rain and the mobilisation of aluminum (Al). Al interacts with metal sensitive tissues such as the gills of fish and invertebrates and will impair physiological processes in both plants and animals affecting growth and reproduction (Gensemer and Playle, 1999). While low pH will aggravate the effects of Al, increased concentrations of e.g. calcium (Ca), increased ionic strength and the presence of various organic and inorganic ligands will act to reduce toxicity (see reviews in: Rosseland and Staurnes, 1994; Gensemer and Playle, 1999). The ecological effect depends on exposure intensity, the species and life stages exposed, exposure duration and the possibility for post-exposure recovery of a sub-lethal exposure. As toxicity is related to both H^+ and Al, acidification is a combined stressor. The two toxicants must be interpreted in combination, but also separately. While some species are mainly H^+-sensitive, others are mainly Al-sensitive (Gensemer and Playle, 1999). The ecological effect depends as such on the relative contribution of the prime toxicants and how these act in concert. Due to the combined action of H^+ and Al, the pH-limits restricting organisms in naturally acidic water-bodies are normally lower than the limits restricting the same species in water having elevated concentrations of Al. pH limits restricting organisms are further influenced by all confounding factors giving rise to a large variability in the response surfaces.

The most obvious biological impacts of acidification are related to changes in the composition and abundance of invertebrate and macrophyte periphyton communities and the reduction or extinction of fish populations (Raddum and Fjellheim, 1984; Farmer, 1990; Rosseland and Staurnes, 1994; Gensemer and Playle, 1999). The community structure changes from one supporting acid sensitive organisms to one supporting acid tolerant organisms. Only few of these changes are acidification specific, as similar changes can be related to a variety of pressures.

Annex V of the WFD outlines both the physico-chemical and biological elements to be included. The chemical elements are pH, alkalinity and acid neutralising capacity. All three are related to the true toxic components: hydrogen activity and Al. The annex does not detail how naturally acidic sites should be separated from sites being acidic due to anthropogenic activity. The biological elements: macrophytes and phytobenthos, phytoplankton, benthic invertebrates and fish are largely assessed using species composition and abundance with the addition of age structure for fish.

5.2 Sources of acidification

Acidification can be brought about by "acid rain", but also by activities such as draining of wetlands and mining activities (Hyne and Wilson, 1997). These latter sources of acidification have only local effects, while acid rain, being trans-boundary, has regional and global effects. Acid rain mainly results from the burning of fossil fuels and the subsequent emission of sulphur dioxide and nitrogen oxides into the atmosphere. In addition, ammonia from agricultural activities contributes locally to acid loading through the nitrification process. In air and in contact with water the oxides are transformed into sulphuric and nitric acids. These acids can be transported over large distances, before being deposited as "acid rain". In Europe, acidification has a negative impact in water bodies with a low alkalinity, i.e. in non-calcareous catchments.

The cause and effect chains linking acid rain to acid water were first established in the 1950s. Acidification became an international issue around 1970 (Almer, 1974). Since then, focus has changed from pH being regarded as the main factor for environmental change prior to 1980 to include the toxicity of Al mobilised at low pH values. Focus has also changed from "proving" effects and establishing causal relationships in the 1980's to the present day focus on recovery or the lack of recovery following deposition reductions (Skjelkvåle *et al.*, 2003). Although water quality has improved, episodes can still be detrimental and hinder the reestablishment of acid sensitive species. In addition, recolonisation rates are low in regions heavily impacted by acid rain.

Owing to the reduced emission of sulphuric compounds in Europe there has been a substantial reduction in the atmospheric deposition of acidity since the 1970s. However, there has been no significant decrease in nitrogen deposition (Alewell *et al.*, 2001). These trends are visible in the changes in wet deposition of sulphur and nitrogen over southern Norway (Figure 5.1). Future effects relating to the deposition of N represent an uncertainty. The reduction in acid loading will initiate a recovery process, the rate of which is related to changes in the deposition of acids, but also to local variations in soil properties e.g. weathering rates (Skjelkvåle and Wright, 1991). Future changes in water quality will also depend on climate change, where sea-salt episodes, elevated temperature and the mobilisation of organic matter will all contribute to changes in acidification.

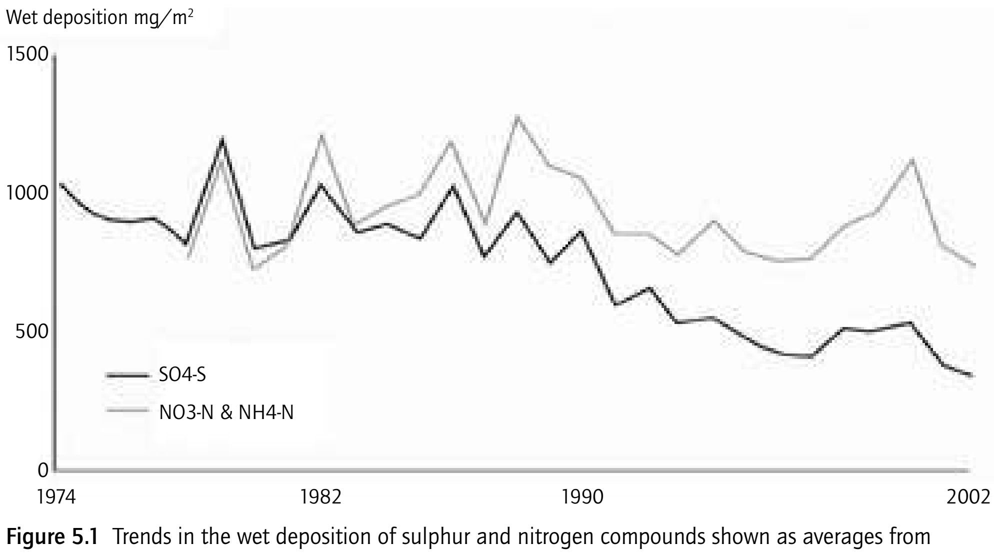

Figure 5.1 Trends in the wet deposition of sulphur and nitrogen compounds shown as averages from 7 representative sites in southern Norway.

5.2 Impacts on water quality

Key chemical water quality elements

The chemical impact acid rain has on surface water quality is well known. The immediate effect of acidification is a reduction in pH and alkalinity and an increase in Al. In acid water, Al is present in a number of forms and toxicity is related to the labile/cationic or inorganic form of Al (LAl). The concentration of LAl depends on many water chemistry properties, including pH and the presence of various organic (e.g. TOC) and inorganic (e.g. Si, F) ligands. The impact of acid precipitation on pH and metal concentration in water bodies depends on the watershed geology and vegetation, primarily the content of limestone, but also on the content of humic matter in the surface waters.

The changes in water quality can be summarised into changes in alkalinity or acid neutralizing capacity (ANC_{cb}). ANC_{cb} is calculated as the $\sum$base cations - $\sum$anions (Reuss and Johnson, 1986) and can be modeled (see later). Based on the empirical relationship between ANC_{cb} and the biological status established for various organism groups (Raddum and Fjellheim, 1984; Bulger *et al.* 1993; Lien *et al.*, 1996; Raddum and Skjelkvåle, 1995; Juggins *et al.*, 1995; Kroglund *et al.*, 2002), ANC_{cb} is commonly used to hind- and forecast changes in water quality and associated changes in biological status. The use of ANC_{cb} as a surrogate for the true toxic components is possible due to the close relationship between ANC_{cb} and pH and LAl. (Figure 5.2 and 5.3). An ANC_{cb} threshold of 20 μeq l^{-1} is currently considered as an indicator of water quality limits identifying good ecological status mandated by the WFD. However, the relationship between ANC_{cb}, water quality and biological health is not straightforward. The relationship between ANC_{cb}, pH and LAl is affected by TOC (Figure 5.2 and 5.3). In high TOC waters, pH is lower and LAl is higher for a given ANC_{cb} value than the relationship observed in low TOC waters. To protect the biological community, the ANC_{limit} must therefore be set higher in water containing organic matter than in clearwater systems (Lydersen *et al.*, 2004). The current ANC_{limit} is to a large extent based on clearwater lakes. The higher ANC_{limit} needed to protect organisms in high-TOC waters can be considered contradictory to the generally accepted view that organic matter reduces Al-related toxicity. Organic matter reduces the toxicity of total-Al, but the increased H^+-activity permits more Al to remain present in toxic form. Although the relative concentration of LAl to total-Al decreases with increased TOC, this does not say that toxicity is negligible. Current ANC_{cb} limits will not protect fish in more organic rich sites.

An index based on ANC_{cb} is preferable to those based on H^+ and LAl. While ANC can be modelled using knowledge regarding process-based relationships, H^+ and LAl are more difficult to model. Al is fractionated and analysed using a large variety of protocols where the reported concentrations are not comparable. Furthermore, correct determination of the free metal concentration is difficult due to its sensitivity to changes in pH and temperature. Downstream of the confluence of acid and more neutral waters LAl will polymerize into lesser or non-toxic forms of Al. As unstable forms can persist for hours, extensive areas of the river can be under the influence of this ongoing polymerizing process. Dose-response relationships that are based on *in situ* fractionation of Al (within seconds after sampling) yield better and different relationships from those based on traditional stored water samples (Kroglund *et al.,* 2001).

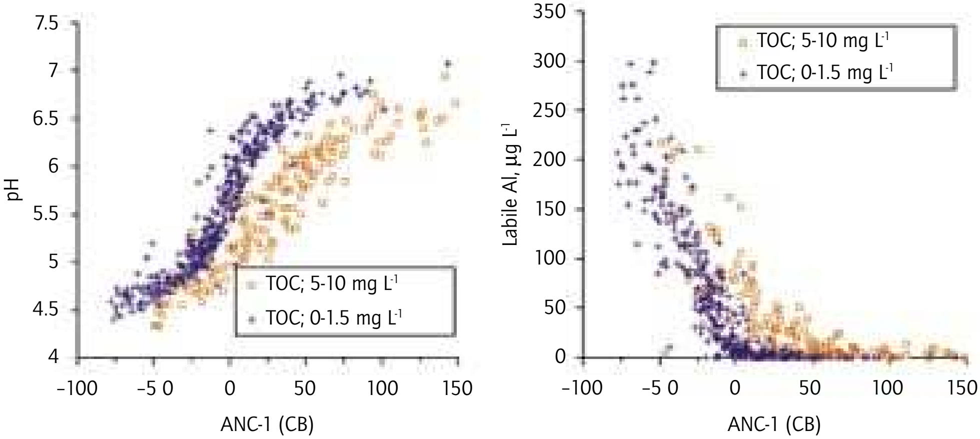

Figure 5.2 Relationships between pH (a) and labile aluminium (b) and ANC (∑base cations - ∑anions) for Norwegian lakes having low (<1.5 mg C/l) and high (>5 mg C/l) organic content (Data from the Norwegian 1000-lakes survey in 1986).

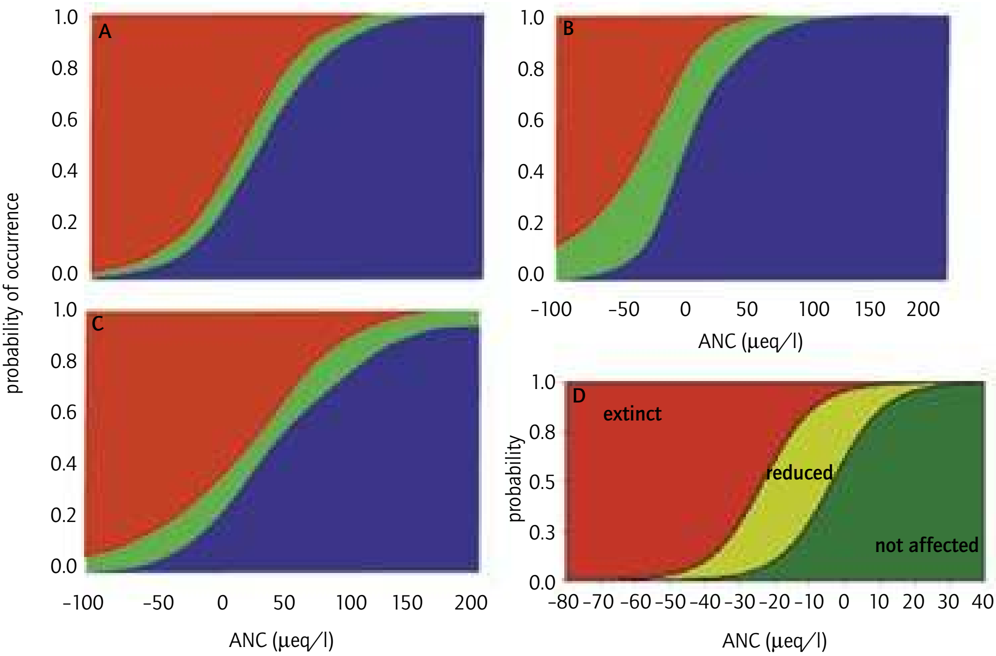

Figure 5.3 Response curves showing the relationship between ANC and the probability of occurrence of (A) the diatom Achnanthes minutissima, (B) the mayfly Baetis rhodani and (C) non-impoverished macroinvertebrate assemblage and (D) brown trout. Figures redrawn from Juggins *et al.* (1995) and Lien *et al.* (1996).

Due to the combined action from H^+ and LAl, it is important not to confuse natural acidic conditions with anthropogenic acidification. While both are associated with a low pH, elevated levels of Al in its toxic form are mainly found as a result of anthropogenic acidification. Water bodies acidified by natural processes can have a low pH due to a high content of organic (humic) matter and following oxidation of sulphide rich soils. Naturally acidic water bodies can as such have a "high ecological status" despite having a low pH restricting the diversity of the biological community.

5.3 Water quality and biological modelling

There are numerous models based on chemical criteria. Most models rely on the critical load concept. Critical load is defined as the maximum amount of a pollutant that can be deposited on an ecosystem without having adverse effects (Nilsson and Grennfelt, 1988). Application of the critical load approach involves the identification of a key organism (or organisms) to be protected and the "critical limit" with respect to a water quality indicator. With respect to acidification, the model should be able to relate changes in deposition to the indicator status. Figure 5.3 shows examples of relationships between a water chemistry indicator (ANCcb) and the probability of occurrence of different types of species and species groups.

Several chemical parameters or indices are being used as water quality indicators; e.g. pH, Al, alkalinity, Ca/H+ ratio and ANCcb which is the preferred indicator. Changes in water quality that have no biological implication are to be interpreted as acceptable. As the chemical and biological sensitivity to acidification varies according to bedrock and soil type the critical load varies accordingly (Figure 5.4).

Critical loads, and if those are exceeded, are calculated using various static models, such as the steady-sate water chemistry model (SSWC) and the first-order acid balance model (FAB; Posch *et al.*, 1997). Steady-state models indicate that something will happen in the future if, for example, pollution is reduced but does not indicate the timescale of recovery.

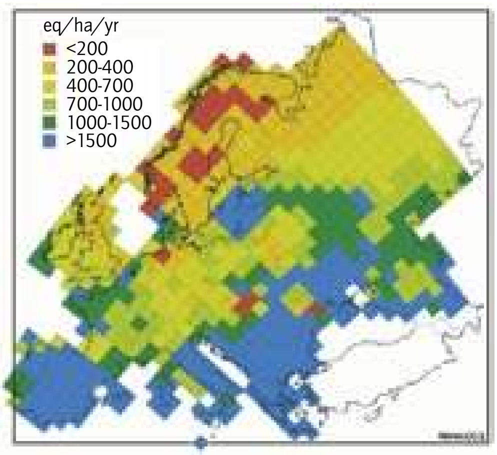

Figure 5.4 Critical loads for acid deposition. Red indicates high sensitivity, blue low. (Source: The Swedish NGO Secretariat on Acid Rain[1])

[1] http://www.acidrain.org/acidification.htm

Geochemistry and soils play a central role in the response of forests, lakes and rivers to acid rain. Dynamic, process-based models integrate and interpret theoretical knowledge from soil science and hydrochemistry with results from experiments and monitoring. Response times are related to factors such as mineral and organic matter content, weathering rates etc; all properties that are more or less unique for an individual site. Because of the complex nature of interactions, dynamic models are used to predict the rate of change over time. Experimental data from ongoing experiments (long time-series) are used to validate these models. The main dynamic model used in acidification studies is the MAGIC model.

At present there are no dynamic models for biological responses to acidification except for a model developed for Atlantic salmon in Canada (Korman *et al.*, 1994). There are several non-dynamic models based on the relationship between species composition and abundance and water chemistry (see chapter on individual organism groups).

5.4 Macrophytes and attached algae

Aquatic plants are not only impacted because of reduced pH and elevated Al, but also by the change in inorganic carbon speciation. The importance of inorganic carbon as a key element in the build up of organic material is often overlooked in acidified ecosystems. Carbon is the main structural element and is needed in much larger quantities than nitrogen and phosphorus during primary production (Redfield, 1958). The speciation of inorganic carbon changes with acidification; from bicarbonate (HCO_3^-) to free carbon dioxide (CO_2) in acid water (Wetzel, 1983). This change in the relative proportions of inorganic carbon species causes extensive changes in the species composition of freshwater primary producers, because some species use bicarbonate to produce organic material, while others use carbon dioxide. This is increasingly being acknowledged as the main cause for changes in species composition and diversity when a water body becomes acidified (Figure 5.5).

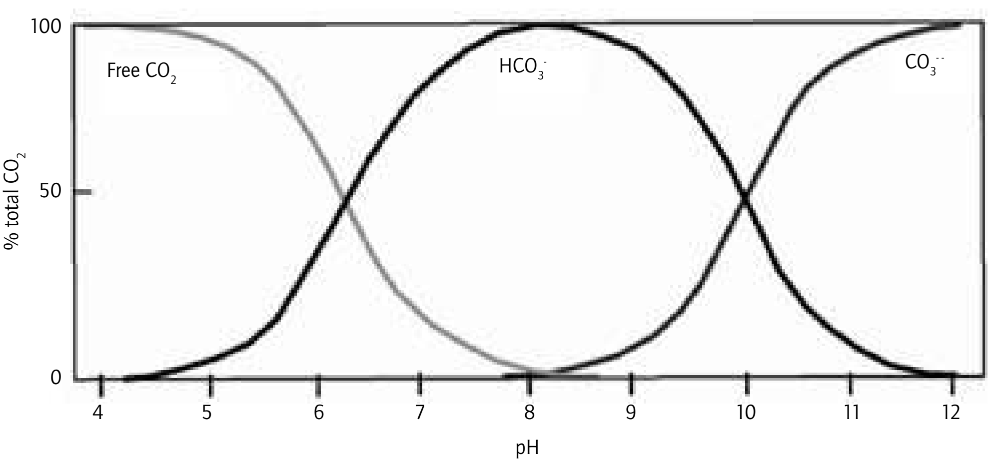

Figure 5.5 Relation between pH and the relative proportions of inorganic carbon species of CO_2 ($+H_2CO_3$), HCO_3^- and CO_3^{--}. Slightly modified from Wetzel (1983).

Some of the structural changes caused by acidification are well documented:

- Species composition change, partly because of a change in carbon source
- Species diversity decreases
- Vegetation biomass may increase.

In addition to the effect of a lower pH and change in carbon source, the increased atmospheric deposition of nitrogen compounds may increase the availability of this nutrient and increase the N/P ratio. This may lead to P-limitation of plant growth in the water and cause a shift towards species requiring a higher N availability. The phosphorus content in acidified Nordic rivers is usually low, generally less than 5 μg/l P, and the N/P ratio was around 20-40 prior to the increase in N deposition. Today, N/P ratios around 100-200 are common in these rivers. Some attached algae, mosses and macrophytes are reported to be particularly common in waters with such elevated N/P ratios (Lindstrøm *et al.*, 2004).

Many species of benthic algae, bryophytes and macrophytes have well defined tolerance limits of acidity (Lindstrøm *et al.,* 2004). Surprisingly, many taxa were found to tolerate a pH <5.0 and were classified as acid-tolerant (Table 5.1). Some even seemed to profit from acidification and increased significantly in frequency and biomass in markedly acidified rivers (pH <5.0). In contrast, a large number of taxa were never found below pH 6.5 and some were even limited to rivers with a pH permanently above 7.0. Different requirements concerning carbon source is probably the main reason for these differences.

During acidification aquatic vegetation undergoes a change in species composition and a decline in diversity. The study by Lindstrøm *et al.* (2004) demonstrated that the impact on regional diversity was more pronounced than at a given locality. The distribution of species according to their tolerance of low pH values is shown in Figure 5.6. Acidity-tolerant algae increased in frequency and occurred in most of the acidified rivers.

River acidification may be accompanied by an increase in plant biomass and occasionally one or more species occurs in mass abundance. The most common and striking phenomenon is the proliferation of filamentous green algae covering most of the riverbed. These mats/clouds usually consist of Zygnemales, mainly one or a few species within the genera *Mougeotia* and *Zygogonium*. However, plant biomass is not a useful indicator of acidification.

Table 5.1 Tolerance limits for acidity for 205 taxa of freshwater vegetation based on large datasets collected in Norway (Lindstrøm *et al.*, 2004).

Vegetation type	Total number of taxa assessed	Acid tolerant pH < 5	Weakly acid sensitive pH > 5	Moderately sensitive pH > 5.5-6.0	Strongly sensitive pH > 6.5
Benthic algae	127	34	8	36 (divided in 2 groups)	49
Macrophytes	70	12	9	28	29
Bryophytes	11	5	3	3	Not assessed
Total	208	51	20	67	78

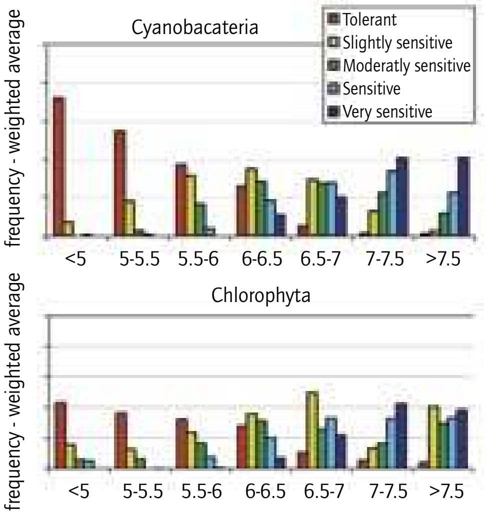

Figure 5.6 Changes in the frequency of five acid-sensitivity classes of benthic algae along a pH-gradient. Data based on benthic cyanobacteria and chlorophyta found in 768 algal samples collected in Norwegian rivers (Lindstrøm *et al.*, 2004).

Critical limits

Lindstrøm *et al.* (2004) showed the relationship between an index based on the presence of acid-sensitive attached algae (Index of Acid Sensitivity) and the pH values of Norwegian rivers (Figure 5.7). They concluded that the index showed that a pH > 6.3 was needed to ensure that the algal community was not impacted by acidification. They also concluded that the algal community had a substantial probability of being impacted if the pH was less than 5.6. In reference lakes that have a naturally low pH, the community structure resembles that of an acidified lake. The variability observed within the pH range 5.6 to 6.3 could have been caused by episodes, but could also have been due to toxic properties of Al being present in anthropogenically acidified water, but absent in waters having a naturally low pH (Gensemer and Playle, 1999).

Combined impacts of acidification and eutrophication on macrophytes

Aquatic macrophytes are intrinsically linked to lake water and sediments through their roots and leaves and individual species are sensitive to physical and chemical changes in these media. Several studies document significant alterations of macrophyte assemblages in recent decades as a result of gross reductions in pH in low alkalinity lakes. This has been due to high inputs of acidifying substances from the atmosphere (mostly sulphur and nitrogen; Hornung, 1997) or from the drainage basin (Farmer, 1990; Riis and Sand-Jensen, 1998; as cited in Vestergaard and Sand-Jensen, 2000). Eutrophication is caused by enhanced inputs of nutrients and is generally more of an issue in lowland environments with higher population densities and more intensive agriculture. In upland regions eutrophication can potentially be associated with atmospheric deposition of nutrients, primarily nitrogen compounds.

The pressures of eutrophication and acidification combined are, therefore, most likely to be significant in predominantly rain-fed, oligotrophic, low alkalinity lakes. These lakes are poor in (calcium) bicarbonate and nutrients (Roelofs *et al.,* 2002). Acidification and eutrophication cause changes in

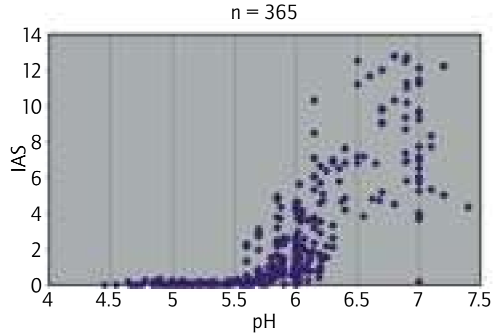

Figure 5.7 Index of Acid Sensitivity (IAS) as function of pH-gradient. Data based on attached algae collected from rivers in Norway (Lindstrøm *et al.*, 2004).

N, P and C budgets, with particularly apparent impacts on macrophyte community composition. Nutrient-poor, low alkalinity lakes can have highly diverse plant communities, in which isoetid species dominate (*Lobelia dortmanna*, *Littorella uniflora* and *Isoetes* spp.). During the 20th century, however, isoetid vegetation in lowland lakes has declined greatly and become threatened in many European countries and North America (Smolders *et al.*, 2002), with particularly devastating declines in the Netherlands, northern Germany and Belgium (Arts, 2002). This provides important warnings for other countries/regions, not least in the context of the EU Habitats Directive, and highlights the need to focus on macrophyte responses to combined eutrophication-acidification pressures.

Alkalinity and transparency appear to be the most influential drivers of macrophyte species composition (Vestergaard and Sand-Jensen, 2000). The macrophyte composition of low alkalinity lakes is very different from that of acidic or alkaline waters (Brouwer *et al.*, 2002). Isoetid species are most common in low alkalinity, oligotrophic lakes, as a consequence of the restricted availability of inorganic carbon within the water layer (Sand-Jensen and Sondergaard, 1979). The change in ammonium availability and inorganic carbon budgets as a consequence of acidification causes changes from isoetid macrophyte species to more acid-tolerant species such as *Juncus bulbosus* and *Sphagnum* spp in western European lakes (Arts, 2002). Enrichment with phosphate can then lead to a luxurious growth of more loosely-attached or free-floating macrophytes in shallow waters, and to plankton blooms and lavish growth of epiphytes in larger deeper waters (Roelofs, 1983).

The Northern Ireland Lake Survey quantified macrophyte species – environmental relationships from over 500 lakes using Generalised Additive Models (GAM) and Canonical Correspondence Analysis (CCA; Heegaard *et al.*, 2001). Nutrient concentrations appeared influential in 'explaining' species distribution, but were highly correlated with alkalinity/pH and altitude. A DCA ordination diagram with regressions of different physico-chemical environmental variables was used to classify vegetation types from an extensive set of 600 surface waters in The Netherlands (Smolders *et al.*, 2002).

The relationship between macrophytes and acidity in lakes has received relatively little attention in the scientific literature despite macrophyte assemblages showing clear changes over a broad gradient. These changes can often be related to acidity and other parameters, including nutrient availability. However, there have been few attempts to develop relevant classifications for these two pressures acting together. For a better understanding of the successional differences within low alkalinity macrophyte assemblages further research and cooperation is needed, in which vegetation, physico-chemical and atmospheric deposition data are integrated (Arts, 2002).

5.5 Benthic invertebrates

Indices and metrics

Ecological assessment indices based on macroinvertebrates have been developed during the last 2-3 decades in several countries where acidification of rivers and lakes has been recognised as a significant problem. Acidification indices in Europe are primarily based on the presence or absence of indicator species. However, many of these indicator species are tolerant species commonly observed both in acidified and not acidified water.

Within the EU project AQEM[2] the acidification assessment tools used by the different countries participating in the project were:

- France: A French biotic index of acidification (B.I.A) has been proposed to assess the acidification in streams of Les Vosges Mountains. The method uses a multimetric approach and the index has 10 classes that vary from 0 (unaffected) to 9 (strongly acidified; Guerold *et al.* 1995; 1999).
- Germany: German acidification index (Braukmann, 1992).
- Sweden: Medin's acidification index, a multimetric index with 5 classes based on macroinvertebrate data from humic rich rivers in Sweden (Henrikson and Medin, 1986).
- Norway: Raddum's index, based on data from clear, low conductivity rivers in Norway. Each taxon is given a score corresponding to a pH interval and to an acidification class in the index system (Raddum and Fjellheim, 1984; Lien *et al.,* 1996). The Raddum index has also been used on a European scale (Raddum and Skjelkvåle, 1995; Raddum, 1999) and is being further developed (Bækken and Kjellberg, 2004).

The aforementioned indices should be harmonised to derive an index suitable for use at a European scale.

Impacts of acid water

The concepts of critical load and critical limit of acidifying compounds have been crucial to the study of biological effects (Nilsson, 1986). The "critical limit" is usually defined in relation to the effect acidification has on the most sensitive species. This implies that the limit may vary across Europe depending on the species composition and their local adaptations. The critical limit for ANC_{cb} is often placed within the range 20 to 50 μeq/l. The French B.I.A index observed impoverished macro-invertebrate communities at ANC values between 50 and 100 μeq/l. However, severe loss of taxa was only observed below mean values of 50 μeq/l (Guerold *et al.,* 1999). Some of this variability in ANC limits is related to the presence of organic matter.

Turnbull *et al.* (1995) in N-E Scotland concluded that even though critical loads provide a good predictor of biotic status, it is not as sensitive a parameter as pH or alkalinity. Many acidification indices are related to pH. For the Nordic indices, the lower limit for the class of intolerant species is pH 5.5. In the French IBA index, unaffected streams were found only where mean pH values were above 6.5. The most significant change in the IBA index values occurred between pH 6.5

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[2] http://www.aqem.de.

and 5.5, a pH interval that has not received much attention in the Nordic indices (Guerold *et al.,* 1999). While these various indices give good predictions on a local scale, they are inadequate to predict subtle, but ecologically important changes on a regional scale.

Humic substances

In general, data from the Nordic countries indicate a higher tolerance to low pH at high levels of TOC (total organic carbon). It is generally assumed that humic substances detoxify the water making metals and in particular Al less bio-available. It has been shown experimentally that humic substances may reduce the toxic effect of low pH on the mayfly *Baetis rhodani* and the crustacean *Gammarus lacustris* (Bækken and Aanes, 1990). Using pH as the indicator avoids some of the difficulties in interpretation as discussed for the relationship between ANC_{cb}, pH and LAl.

Natural acid water

Parts of Europe, in particular the northern countries, have regions with naturally acid water due to organic acids. These may be wrongly regarded as temporarily or permanently acidified by anthropogenic sources and be incorrectly proposed for remediation by liming (Warfvinge *et al.,* 1995; Kortelainen and Suakkonen, 1995). Dangles *et al.* (2004) found that the taxonomic richness of macroinvertebrates as well as the breakdown rate of leaf litter in naturally acid streams was not significantly different from circum-neutral streams. Basing an index on pH will not separate anthropogenically impoverished sites from sites having low species richness due to natural causes.

General toxicity of aluminium and heavy metals

It is difficult to isolate the effects of low pH from associated chemical changes. Labile Al has been shown to be toxic to a number of macroinvertebrates and is certainly the most important toxic metal in acidified water. However, it has proven difficult to give general guidelines for Al (Herrmann, 2001). The concentration of Al varies substantially over a year and biological effects depend on the timing, duration and intensity of an episode rather than on average concentrations. Biological effects also depend on the differences in sensitivity between species, strain and life stage. Water chemistry sampled at the time of a survey may not be representative of the water quality episode that had the biological effect. Furthermore, some of the variability will be related to biotic interactions, where the presence of fish and/or invertebrate competitors and predators can have a gross impact on community assemblage. Although many studies have identified impoverished communities when LAl is in the range of 0.1 to 0.3 mg/l, many exceptions exist.

There are numerous experimental studies investigating the effects Al and other metals have on macroinvertebrate health (reviewed by Mance, 1987; Gensemer and Playle, 1999). In general these studies show responses related to metal concentrations, but tolerance will vary between species and life stages (Figure 5.8). As Al has an effect experimentally, it is most likely that Al also has an effect within individual water bodies, despite this being difficult to prove. As there is a close relationship between pH and LAl, LAl cannot be disregarded as the cause for population responses in anthropogenically acidified lakes.

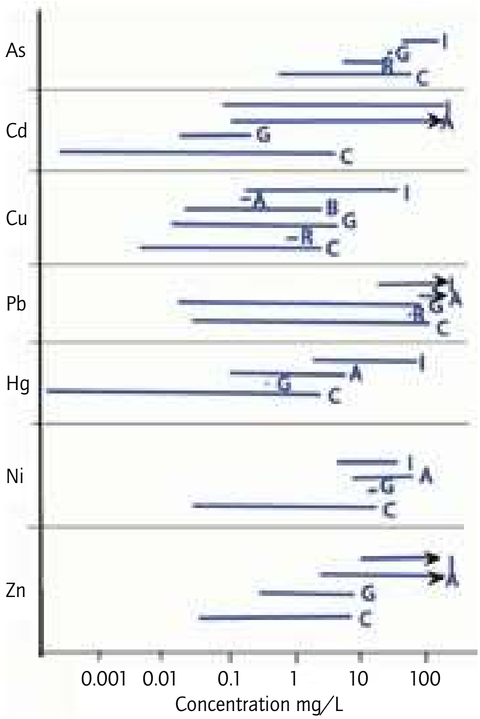

Figure 5.8 The range of observed adverse effect concentrations for freshwater invertebrates (main taxa) from laboratory tests. A: annelids, B: bivalves, C: crustaceans, G: gastropods, I: insects R: rotifers; (after Mance, 1987).

5.6 Fish

Fish are generally more sensitive to Al than to the pH reduction *per se*. For example, while Atlantic salmon are unaffected by H^+ concentration down to pH values lower than 5.4 (Lacroix and Townsend, 1987; Fivelstad *et al.*, 2004), in the presence of bio-available Al the species is extinct in rivers having average pH values lower than 5.5 while its abundance is reduced when the pH is lower than 5.9. Many of the currently acidified rivers have a background (historic) pH level that today would indicate toxic conditions. Based on such observations, it is concluded that pH alone does not give a satisfactory prediction of fish population status (Kroglund *et al.,* 2002). Therefore, understanding the interaction between pH and Al, but also between Al and fish and Al and other water quality constituents is fundamental to the understanding of the mechanisms controlling population changes.

Sensitivity to acidification varies between species, life stages and strains. Where Atlantic salmon (*Salmo salar*), brown trout (*Salmo trutta*), roach (*Rutilus rutilus*) and Arctic char (*Salvelinus alpinus*) are more sensitive than perch (*Perca fluviatilis*). While acid-sensitive fish species have declined the most, even populations of more acid-tolerant species are affected in some regions of Europe (Rask and Tuunainen, 1990; Rask *et al.,* 1995). Within Europe, the number of populations affected runs into thousands. In addition, an even higher number of populations have suffered reduced viability, i.e. show a non-healthy status. Compared to the number of lakes that have lost their fish populations, fish kills are rare. In most lakes and rivers, the effects of acidification are only observed as changes in fish species composition and/or abundance (Rask and Tuunainen, 1990; Hesthagen *et al.,* 1999; Tammi *et al.,* 2003). The fact that fish kills are rare events, despite populations being lost, suggests that density reductions occurs at life stages where kills are not easily observed (e.g. egg and fry) and that density reduction is a gradual event (e.g. more related to fish health and susceptibility to diseases, predation etc) rather than an acute event. Fish kills have been observed under extreme conditions and examples of total fish loss have been recorded in Norway, Scotland and Wales (Hindar *et al.,* 1994). Fish kills (*Salmo salar*) were observed in several Norwegian rivers in the years between 1910 and 1920, kills that were most likely due to acidification and sea salt episodes (Hindar *et al.,* 1994; 2004). Despite massive fish kills, it took more than 40 years for the various affected populations to go extinct. This illustrates that linking dose to response is not necessarily a straightforward process.

The alteration or loss of fish populations is not caused by food shortage. Bottom-up relationships are therefore only of minor importance in acidified systems (Rosseland and Staurnes, 1994; Gensemer and Playle, 1999). Fish population health is mainly related to Al, where the activity of H^+ will enhance toxicity. Since Al is not vital to any aquatic biota, the species have not evolved any defense mechanism specific for this metal. Al exercises its toxic properties by being accumulated onto the fish gill affecting both tissue function and properties (Rosseland *et al.,* 1994; Gensemer and Playle, 1999). The accumulation is directly related to the concentration of *in situ* fractionated Al (Gensemer and Playle, 1999). The relationships are poor when based on water samples where the dynamic nature of Al has been stabilised through ageing (Kroglund *et al.*, 2001). Al is accumulated onto the mucus layer surrounding the gill, onto cell walls and is over time transported inside the cell. The toxic role and effect depends on the concentration, exposure duration and the location where the Al is accumulated. As the speciation and hence toxicity of Al is dynamic, Al does not fit directly into biotic ligand models as these assume that the metals are present in a free, and stable form (Chapman *et al.,* 2003). Al characteristics are more dynamic in rivers than in lakes, and more at pH levels around 5.6 to 6.2 than at pH levels lower than 5.2. The probability for errors is as such related to pH and to water retention time.

The most exhaustive studies have been performed on salmonids. A water quality that has no appreciable effect on Atlantic salmon fry and smolt production can still have a large effect on the seawater survival of the postsmolt. Concentrations of LAl that are "below" the analytical certainty can impair enzyme activities essential for hypoosmoregulation (Kroglund and Finstad, 2003). Due to this analytical uncertainty, salmon health is best related to Al accumulated onto the gills. The present day reduction in Atlantic salmon catches across Europe and the North Atlantic could therefore be due to acidification related causes in addition to other pressures.

5.7 Summary

Acidification is caused by atmospheric deposition of nitrogen and sulphur compounds which reduces the pH in water bodies with low alkalinity. Reducing the pH has an impact on the chemical water quality through increasing concentrations of toxic Al and heavy metal species as well as changing the CO_2-bicarbonate equilibrium. A high nitrogen deposition can alter the nutrient balance of freshwaters (e.g. N:P ratio).

The biological impacts have been demonstrated for fish, invertebrates and plants in rivers and lakes. The impact increases when pH is lowered below 6.5. The specific impacts also depend on the concentration of aluminium and total organic carbon (TOC or humus). Naturally acidic water bodies generally have a more diverse flora and fauna compared to anthropogenically acidified water bodies with the same pH level.

There are still several major knowledge gaps that need to be filled for successful implementation of the WFD. Further work is needed on the relationship between atmospheric loading and the resulting chemical water quality in different types of catchments. It is necessary to develop quantitative metrics for biotic elements in water bodies susceptible to acidification, and to describe ecosystem effects of reductions in acid precipitation. Chemical and biological indices must be harmonised. Models currently in use are flawed with respect to their ability to identify dose-response relationships.

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