T. Schneider (Editor)/*Acidification and its Policy Implications*

ACIDIFICATION EFFECTS IN THE AQUATIC ENVIRONMENT

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ABSTRACT

The emissions of sulfur in Europe have been reduced somewhat as compared to 10-15 years ago. This is reflected by reduced sulfate concentration in several lakes in Southern Scandinavia, but not necessarily by reduced acidity. The acid deposition still far exceeds what low buffered catchments can produce of bases. The soils are therefore under continuous degradation. Also nitrate concentration is increasing. For both sulfur and nitrogen the yearly deposition needs to be reduced by 70-80 % in order to stop further acidification of surface waters and to avoid a coming boom from nitrate acidification.

"Acidification of soil and water is a dynamic process which depends on fluxes of acidifying chemicals and on geochemical and biochemical reactions involving an exchange of protons in the whole ecosystem." (ref.1)

INTRODUCTION

Today it is accepted by the scientific community that atmospheric deposition of acidifying substances will affect surface waters. It is also accepted that in areas with high dry deposition of SO_2 and $(NH_4)_2SO_4$ these substances significantly contribute to the acidification.

The relations between emission, deposition and effects can be found by studying the actual pollution situation in Europe. The deposition range of acid varies from 0.1 Keq/ha in the most remote areas to 10 Keq/ha in the most polluted regions. The run off pattern of acid anions very closely reflects the emission pattern. The concentration ranges from 10 µeq/l in the most remote areas to above 1000 µeq/l in the central parts.

It is also accepted that in non calcareous areas the yearly weathering of basic substances (Ca, Mg, Na, K or HCO_3) will not increase at a great extent if acid load increases. Instead the soil or run off water will be acidified.

This means that water acidification will be most apparent in areas of low base content, whereas soil acidification will be predominant where the soil conditions are more favourable.

Accordingly, up till now water acidification has been most obvious in rather remote areas of Europe, as Scandinavia, where the soil conditions are naturally very poor. Here yearly production from weathering is only 0.1-0.4 Keq/ha whereas the acid load is in the range of 1 Keq/ha.

In Central Europe the gradual soil destruction is more apparent which causes increased leaching of hazardeous metals from the soil to the run off waters. But, simultaneously the alkalinities of streams and lakes have decreased during this century (ref.1).

Nevertheless acidification of poorly buffered lakes in sandy regions in Central Europe took place without being noticed by scientists for a long time (ref.2).

Now acidified lakes and small water bodies are observed all over Europe. In Scotland, England, Denmark, Western Germany, Eastern Germany, Poland, Czechoslovakia streams and lakes have undergone a significant degree of acidification. The freshwater acidification in the Alpine zones in Switzerland and Italy is less serious than in North Europe because of the more favourable geological environment. However, many alpine lakes and tarns are already suffering a deterioration. In Belgium and the Netherlands acidification has been proved to have taken place in poorly buffered, oligotrophic waters on mineral sandy soils, i.e. moorland pools, some small lakes and dune pools (ref.3).

HISTORICAL REVIEW

Perhaps the very first reports of acidification in Europe came as long ago as the early 1900s from Norwegian fisheries inspectors. Fish kills of Atlantic salmon were reported as early as in 1911 (ref.4). Several fish hatcheries had already installed limestone filters by the 1920s to treat acid hatchery water. Brown trout began disappearing from mountain lakes in the 1920s and 1930s, and, by the 1950s, barren lakes were reported from many regions in southernmost Norway. Also the salmon had essentially disappeared from several major rivers.

The doubling in sulfur emissions over the 1950-1970 period resulted in an approximate doubling of the acidity in precipitation measured at the European precipitation chemistry network stations in Southern Scandinavia over the same period. During the same period, the number of fish populations that have disappeared have increased tremendously (ref.5).

In Scandinavia, Norway, Sweden and Finland some 30.000 lakes and running waters of a total length of at least 200 000 km are affected by acidification.

ACIDIFICATION MOBILIZES TOXIC ALUMINIUM

When the amounts of acidic anions from the atmosphere (e.g. SO_4^{2-},NO_3^-) leaching through the soil approaches or exceeds the leachable amounts of basic cations, high concentrations of acidic cations (H^+, Al^{n+}) will be found in the run off. Elevated concentrations of aluminium is therefore exported in acidic waters in areas with high inputs of acidic substances. Pronounced temporal and spatial variations in concentration of aqueous aluminium have been reported in acidic surface waters as well. Pulsed inputs of NO_3^- are typically observed during snowmelt in sensitive areas (ref.6). The higher the acid load and the degree of soil acidification, the higher will the leaching of aluminium appear. In northernmost Scandinavia - the least polluted - but one of the most sensitive parts of Europe - the aluminium level does not reach 100 μg/l during snowmelt whereas Al-concentrations of 10.000 μg/l are found in Central Europe at a higher degree of acid load and soil acidification.

The toxicity of aluminium to fish has been known for at least 47 years. At pH 5 "the solutions remain toxic until the concentration falls to 0.07 mg; which represents the lethal concentration limit for aluminium"(ref.7).

Of the different forms of dissolved aluminium found in the acidic waters the inorganic fractions $Al(OH)^{2+}$ and $Al(OH)_2^+$ appear to be most toxic. It is not possible to specify absolute levels of toxicity. Investigations show that Atlantic salmon are killed during short acidic episodes, when pH decreases and the concentrations of ionic aluminium increase rapidly (ref.8). The fish kill is documented in controlled fish experiments combined with continuous monitoring of pH and daily water sampling (Fig.1). During a two-week period, four episodes with pH drops from 5.9 to 5.1 coincided with increased water flow due to rainfall and snowmelt, accompanied by dilution of calcium and substantial changes in aluminium-speciation (Fig.1). The concentration of ionic Al increased from 0 to 50 μg/l during the pH drops. These rapid changes in Al-speciation could be due to dissolution of previously precipitated Al on the river bed by episodic flushing of the river from acid snowmelt and storm events. Of the three year-

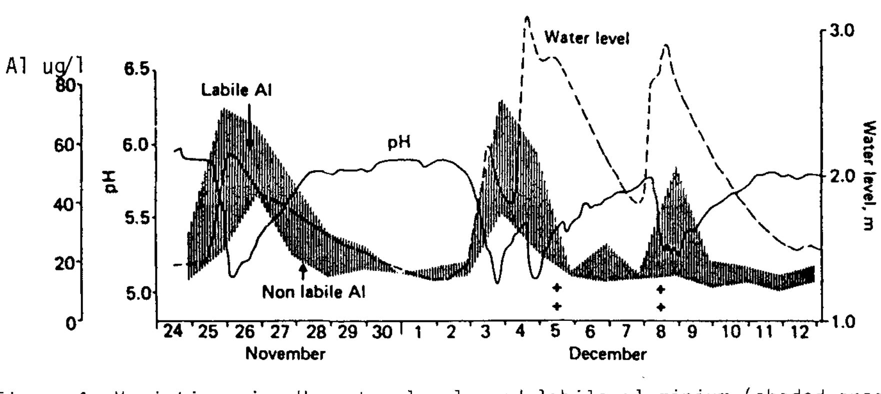


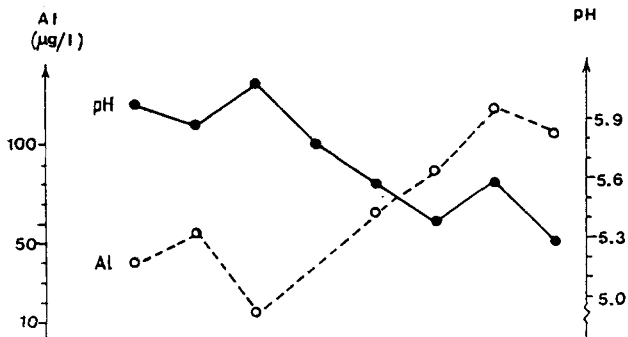
Figure 1. Variations in pH, water level, and labile aluminium (shaded area) in River Vikedalselva (southwestern Norway) Nov. 24 to Dec. 12, 1983. pH-curve is plotted on readings every second hour from a continuous pH monitor. Water levels are from 4 h readings of limnigraph records. Aluminium data are from daily samples. Times of death of salmon presmolts (1+) are indicated (+=1 fish)(ref.8).

classes of salmon (eggs to presmolts) only presmolts died, illustrating the higher sensitivity of salmon during smoltification (ref.9). Continuous monitoring of water chemistry and fish behaviour in waters subjected to acid episodes are considered a key to the understanding of biological responses to the acidification process.

EFFECTS OF ACIDIFICATION ON PRIMARY PRODUCTION

Phytoplankton

Most acid lakes have been oligotrophicated as a result of increased aluminium levels. An example is given in Fig. 2 illustrating the gradual acidification along with increased aluminium- and decreased phosphourus levels (a 1000 hectare. lake in Southwestern Sweden. The lake was limed at the fall of 1981. 1982-1985 pH raised to 6.5-7, the aluminium level was reduced to 30 µg/l and the phosphorus doubled to 4 µg/l (ref.11)).



År	1974	-75	-76	-77	-78	-79	-80	-81
Tot-P (µg/l)	5	4	3	3	4	2	2	2

Fig. 2. pH and levels of aluminium and total phosphorus in Lake Ömmern 1974-81, Sweden (August values).

Strongly acidified lakes generally have high levels of metals. The toxicity of these depends on the pH-value and concentration of humic compounds. The effect of aluminium is strongest at pH 5.2-5.8 whereas most other metals are more toxic near neutral pH-values (Table 1). According to the levels in the lakes and the toxic levels observed in biotests aluminium is probably the single most toxic metal in the acid environemnt. The visible effect of aluminium on algae may be enlarged cells, contorted cells and destroyed cell membranes. At a raised aluminium level (> 200 µg/l) the chloroplasts are destroyed (ref.10).

TABLE 1

Monoraphidium griffithii. Percentage growth reduction at the pH-values 4.8 5.5 and 6.5 at selected concentrations of manganese, aluminium, copper, zinc and cadmium (ref.10).

pH	4.8	5.5	6.5
Mn 2000 µg/l	0	0	11
Al 150 "	0	69	0
Cu 5 "	0	0	48
Zn 250 "	0	8	67
Cd 5 "	0	0	36
Mn + Cu + Zn + Cd	0	0	62

Macrophytes

A strong development of Juncus bulbosus and Sphagnum are reported from acidified lakes in Scandinavia. Investigations in the Netherlands show that more than 80 % of all naturally poorly buffered pools and lakes in heathland areas have been strongly acidified during the last decades. The pH-value is at present on an average of 3.8. In most cases the original vegetation has been replaced by submerged Juncus bulbosus or Sphagnum species. On these locations the CO_2 levels in the soil solution and the water layer have strongly increased.

Initial acidification of water leads to luxurious growth of these plants as a result of increased carbon dioxide and ammonium levels in the water layer (ref. 12).

The yearly production of Sphagnum and Juncus far exceeds the original of Lobelia, Isoëtes and Littorella which are now being overgrown. As the prodcution of Sphagnum is continuously accumulating and the decomposition of organic material is strongly reduced in the acid environment, the life length of most European low buffered and shallow lakes and ponds is now drastically shortened. Within a century many of them will be just swamps.

CONCLUSIONS ABOUT ACIDIFICATION EFFECTS ON AQUATIC ECOSYSTEMS

Progressive research during the last 20 years has revealed the deep influence from acidifying emissions on aquatic ecosystems. In almost whole Europe lakes and streams are exposed to increasing concentrations of acids or metals like aluminium leaching from the soil. The effects are found on all trophic levels.

Natural reserves and national parks are threatened or already destroyed and cannot fullfill their purposes to save and keep the original fauna and flora for coming generations.

EFFECTS OF REDUCED EMISSIONS OF SULFUR, PROGNOSIS

Several attempts have been made to make models and prognoses of the effects from reduced emissions on aquatic chemistry and biology.

There is a strong relationship between sulfur emission, deposition, sulfur in run off and loss of alkalinity. Therefore reduced emissions have to result in increased alkalinity of the surface waters. The question still open is the time scale involved including the effects of accumulated soil acidification. By applying empirical data and models it is possible to calculate the effects of different emission reductions.One example can be given.

The effects of a 50 percent reduction in deposition on the pH of two rivers in southern Norway that receive acid precipitation have been estimated. Figure 3 shows the estimated "preacidification" pH-values (pH_0), present pH-values (pH_t), and pH-values at 50 percent lower sulfate concentrations (pH_{-50}). For River Mandalselva, a 50 percent reduction in sulfur deposition does not appear to keep the pH above critical levels for fish (pH>5.0), while River Nidelva would offer the fish acceptable conditions.

River Mandalselva was subjected to acid episodes as early as the 1930s, and the salmon catch started to decline in the 1920s. The anthropogenic emissions of sulfur in the 1925-1950 period were fairly constant, at a level about half of those emitted today. Thus, Figure 3 indicates that the present-day water chemistry can be used to predict to which level the sulfate concentration must be reduced to obtain a given water quality (ref.5).

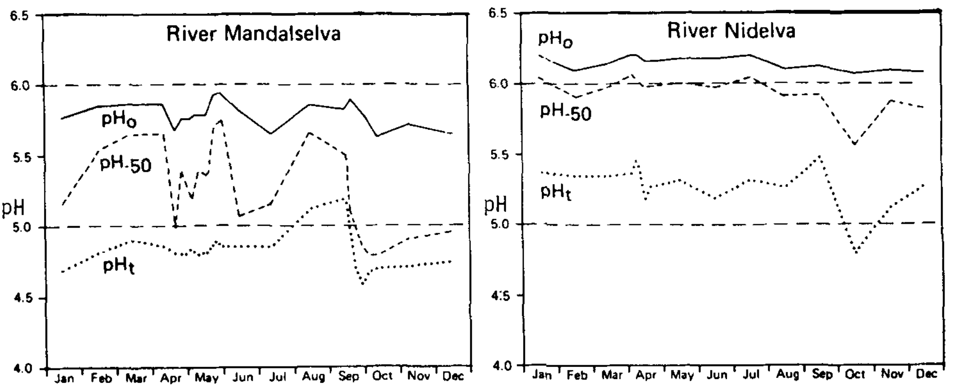


Fig. 3. Variations in present pH (pH_t), "past" pH (pH_0) and pH at 50 percent lower sulfate load (pH_{-50}) in the rivers Mandalselva and Nidelva in southernmost Norway. pH_0 and pH_{-50} are estimated using accepted principles of the relationships between sulfur deposition and sulfate concentration in run off and a slight reduced leaching of Ca+Mg (F-factor 0.2) at reduced SO_4^{2-}.

It has been proposed that emissions of sulfur in Europe be reduced 30 percent by 1993. Using the approach outlined with relationships between deposition and run off sulfur, it can be predicted that more than 20 % of the lakes now experiencing fisheries problems in Southern Norway should be able to support fish (ref. 13).

On the other hand, following the criterium that at least 80 % of the lakes in Southwestern Sweden should have a summer alkalinity, the present deposition level has to be reduced by 70-80 % in that area (ref.14).

EFFECTS FROM ALREADY REDUCED SULFUR DEPOSITION

The last decade´s sulfur emissions in Europe have been reduced by ~ 20 %. Local emissions in Sweden have reduced by ~60 % since 1970. Also sulfur deposition in precipitation has been reduced by ~20 % in South Scandinavia (ref.15). The investigations performed in lakes in Southwestern Sweden indicate a reduced sulfur content in lake waters by on the average 20 %. Often the reduction is coupled to an increased pH-value, as described by (ref.16).

Some comparisons of different lake water quality for the years 1947-52, 1976 and 1983 are given in Table 2 as mean values from some very dilute lakes, and some rather lime rich lakes. The naturally most low buffered waters were still very acid 1983. The well buffered lakes contain natural limestone (shells) and a reduced sulfur deposition will influence the weathering of limestone. The lake category between these extremes, is the one which is nowadays normally limed by "anthropogenic limestone" payed by the government. These lakes also show a reduced sulfur concentration by on the average 20 % (ref.17).

TABLE 2
Long term water quality changes in some lakes of Southwestern Sweden (ref.17) ($Ca + Mg^x$ and SO_4^x values mean non marine). meq/l

	Well buffered (n=6)				Low buffered (n=5)			
	$Ca+Mg^x$	Alk	SO_4^x	pH	$Ca+Mg^x$	Alk	SO_4^x	pH
1947-52	0.29	0.30	-	6.9	0.04	0.01	-	5.3
1974-79	0.56	0.24	0.31	7.0	0.11	0	0.22	4.3
1983	0.45	0.20	0.25	7.1	0.12	0	0.21	4.6

Concerning the time delay between sulfur decrease and pH-increase, one has to remember that even the present acid loadsin Southern Scandinavia (1-1.5 keq/ha·y) far exceed what most of the catchments can produce of bases (0.1-0.4 keq/ha·y), and that accumulated soil acidification is a present fact that will delay the stream water restauration.

CRITICAL LOAD FOR NITROGEN ON SURFACE WATERS

In contrast to sulfur the atmospheric nitrogen loading does not show declining trends. In Central Europe the yearly deposition of nitrogen compounds (NH_4-N, NO_3-N and Org-N) is in the order of 40-80 kg N per hectare, in Southern Sweden 20-30 kg N whereas in Northern Scandinavia total deposition is less than

5 kg. However, in most of Europe still 70-90 % of the deposited nitrogen compounds are stored in the soil. Therefore the accumulation will be considerable after some decades. The potential effects of the ongoing accumulation and leaching to the waters are discussed frequently and apparently in large areas this increased leaching has already begun. In soils of low base saturation the leaching has to be in the form of nitric acid and aluminium nitrate.

In River Mörrumsån (90 % of catchment area forested) in Southern Sweden the nitrate concentration has increased from less than 100 μg NO_3-N/l in 1965 to 300 μg/l 1985 (Figure 4).

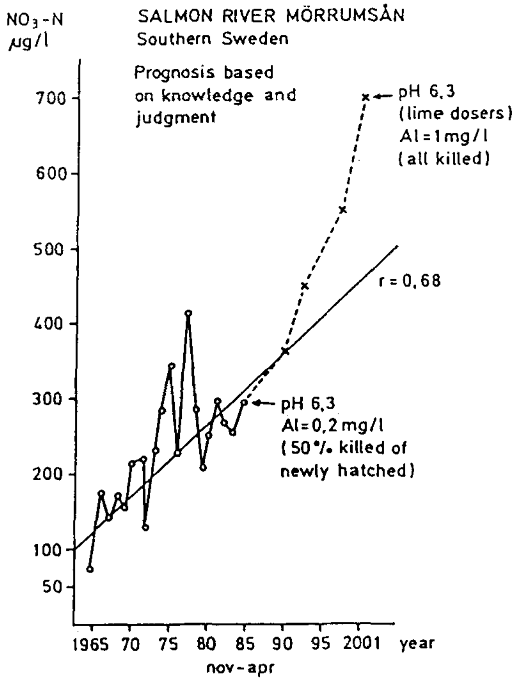


Fig. 4. The nitrate levels during winter season (nov-apr) has about trippled during the period 1965 to 1985. During the last winters the mortality of newly hatched salmon fry in the Mörrum Hatchery has been about 50 %, although pH is above 6. But the aluminium level is about 0.2 mg/l, which may cause problems during cold water season. A speculative prognosis for the year 2001 could give a 100 % mortality if nitrate increases to 700 μg/l and aluminium to 0.5-1 mg/l (ref.17).

A similar increase is shown in lakes from southern Sweden not effected by agriculture or forest fertilizers. Deep oligotrophic lakes now have high nitrate content even during late summer. During the last 10-20 years the nitrate concentration has increased by 50-100 %. The high nitrate level also indicates a severe phosphorus deficiency, which is connected to acidification as a decreased leaching of phosphorus in the acid environment.

To set up a critical load for the long term acceptable deposition of nitrogen as for sulfur is certainly a difficult task. Concerning the direct acidification effects from nitric acid during spates perhaps the same critical acidity as for sulfur in snow could be used i.e. pH 4.6-4.8.

But as at least half of nitrogen deposits as neutral but strongly acidifying ammonium the critical load should rather be expressed in terms of keq/ha. Increasing leaching of nitrate to surface waters are found in Scandinavia where total deposition exceeds 1 keq/ha (15 kg N/ha). This figure seems to be a rather conservative one, but still far less than the present deposition amount from the more polluted atmosphere further south.

NITROGEN AS EUTROPHICATION RISK

Concerning eutrophication even lower values should be needed if the natural ecosystem will persist. A total leaching of inorganic nitrogen of less than 0.1-0.2 kg per hectare is only reached where deposition of nitrogen is below 5 kg per hectare (i.e. about 2 kg as wet deposition). As for sulfur this level is exceeded by 5-10 times in Southern Scandinavia and Central Europe.

Recently, the eutrophication of the Baltic has focussed on the nitrogen deposition from the atmosphere. Available figures indicate that about one third of the nitrogen input comes as atmospheric deposition directly onto the Baltic surface.

This amount plays a significant role in the speeding up of the Baltic eutrophication. The present load on the Baltic from the atmosphere is estimated to 10 kg N/ha·y (ref.18). The critical load therefore should be set to a figure less than this.

LIMING OPERATION AS ALTERNATIVES

In attempts to combat acidification of lakes, streams or soils several national liming programmes have started . In Sweden, more than 4 000 lakes have been limed over the last few years. Much of the cost is met by the State: this year 110 million SEK is being spent on liming and follow up.

The biological effects are positive, although leaching of metals cannot be stopped from the soil as long as only waters are treated (ref.19).

The most commonly used materials are limestone powders of fractions 0-0.5 or 0-0.2 mm. These seem to be the most cost effective for lakes. By liming strategically along shores and on wetlands it is possible to retain alkalinity for several years even in lakes with very short retention times.

Liming running waters is more complicated than lakes as the dosing machines have to operate during high flows and low temperatures. Several high as well as low technological machines have been developed to combat these problems.

But the ongoing acidification will continue unless land is limed or the atmospheric acid load is decreased. Liming nationalparks and reserves in remote mountain areas is not a very attractive way to combat the present acidification. A preferable way is further emission reductions.

Most waters would become healthy if the total acid load from atmosphere gets lower than 0.3 keq/ha (0.5 g sulfur per m^2)and year. For the most sensitive waters the load has to be even less than 0.2 keq/ha (0.3 g S/m^2). In southern Scandinavia the actual load is 1.3 keq/ha (2 g S/m^2) and in Central Europe 3-7 keq/ha (5-10g S/m^2).

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