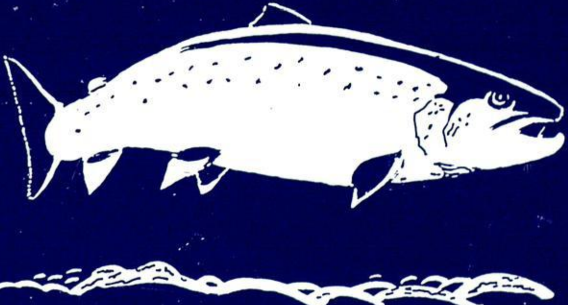
ATLANTIC SALMON TRUST

ATLANTIC SALMON FEDERATION

ACIDIFICATION OF FRESHWATERS: THE THREAT AND ITS MITIGATION

Bensinger Liddell Memorial Fellowship
1989/90

R. NORTH



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Price £3.00
May 1991

Atlantic Salmon Trust

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ISBN 1-870875-12-5

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1975-1977:	Research Associate with Severn-Trent Water Authority, Studying effects of river regulation on coarse angling.
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1989-present:	Fisheries Scientist with National Rivers Authority, Severn-Trent Region. Involved in salmon-pass installation in Upper Severn Area, responsible for fisheries biological work in general together with specific investigations into topics including acidification of salmonid spawning streams.

CONTENTS

1 INTRODUCTION

The life cycle of the Atlantic salmon (*Salmo salar* L.) occupies two distinct aquatic environments. Spawning by adults and the development of juvenile life stages occurs in the headwaters of river systems while the major growth period to pre-spawning adult takes place in the sea. This dual phase life cycle requires great physiological changes, firstly to adapt the seaward-migrating juveniles (smolts) to the switch from fresh to salt water and subsequently the pre-spawning adults must undergo the reverse adaptation upon re-entry to freshwater. Migration is an integral part of the salmon's life cycle, involving accurate navigation over great distances between the estuary of the natal river and the chosen marine feeding grounds.

The complexity of this life cycle renders the salmon vulnerable to the effects of many factors which may influence the survival of individual fish or entire populations. Exploitation of the adult fish by commercial or sport fishermen takes place in marine and freshwater environments and if unrestricted may threaten salmon stocks. Interference with migration of either adults or smolts can have disastrous effects upon populations in particular river systems. Creation of water or hydro-power dams have in the past frequently prevented access of adult salmon to their spawning grounds and led to the elimination of fisheries in only a few years [115]*. With power generating dams there is the additional hazard of mortality of migrating smolts as they pass through turbines. Fish pass facilities and screens on turbine intakes reduce this problem but the growing prospect of power-generating tidal barrages on major estuaries such as that of the Severn, which also receives the Wye, is likely to pose massive difficulties for the salmon and other migratory species.

Within the freshwater environment, the salmon, together with resident fish species, must tolerate whatever conditions occur in streams, rivers and lakes if they are to survive. Water quality, the sum of chemical and physical components, will determine whether or not a species of fish is able to exist in a given water body and, beyond that, will govern the abundance and productivity of the population. Changes in water quality can bring about the growth, decline or extinction of fish populations and can result from natural events or human activity.

Changes in water quality induced by human activity are unfortunately usually environmentally detrimental and are covered by the general term of pollution. Pollution of freshwaters most often results from the introduction of a contaminant at a localised point. The effects of river pollution decrease with distance downstream from the contaminant source through dilution and deactivation and individual events may cause only limited damage to fish populations. Cumulative effects of numerous or persistent pollutions may eliminate entire fish stocks, though, as in the loss of the salmon runs from the Thames and Trent following the industrialisation and urban development of their catchments.

* Throughout the report, references are given as numbers enclosed in square brackets [99]. Correspondingly numbered publications are listed alphabetically in Section 7.

During the last 20 years a different form of pollution has been recognised and studied. Emissions of pollutants into the atmosphere have been found to contaminate the rain, the primary source of all freshwaters, bringing about acid precipitation and the acidification of surface waters. It is not only rain that carries pollutants, snow melt, mist droplets and dry deposition of pollutants are also important. The mechanisms of its occurrence make it a threat unrestrained by local or national boundaries. Its severity and current extent give it global importance to freshwater ecology, especially to the salmonid and other fisheries in affected areas. The potential for damage to aquatic resources is enormous.

This report describes important elements of the acidification problem, outlines its history and details mitigation techniques available to protect fishery resources with particular emphasis on Atlantic salmon. The information presented was gathered principally during the tenure of the 1989/90 Bensinger-Liddell Memorial Fellowship which permitted visits to be made to Scotland, Norway, Canada and the United States (Appendix 1). Additional information has been drawn from a short study tour of the Göteborg area of Sweden made in 1988, together with material from the work of the National Rivers Authority Severn-Trent Region Fisheries Department (formerly Severn Trent Water Authority) and published sources.

2 ACIDIFICATION: THE PROBLEM

2.1 Essential Concepts

The acidification of freshwaters is a dynamic complex of chemical processes which in turn influences the ecology of affected waters. Much of the chemistry involved is complicated but relatively few basic concepts are required to appreciate the main aspects of the situation.

One of the most important properties of water is its ability to contain other substances in solution. The identity and concentration of the various chemicals dissolved in a water body will determine ecological richness and diversity. Many substances that dissolve in water are present not as entire molecules or atoms but as ions, particles which may be composed of one or more chemical elements but have the common feature of possessing an electrical charge. Water itself may exist in the form of ions and serves as a good example. Water molecules consist of two atoms of hydrogen (H) linked to one of oxygen (O), represented by the conventional formula H_2O. Each molecule of water can split, or dissociate, to give one hydrogen ion, which carries a single positive charge and one hydroxyl ion carrying a single negative charge. This may be represented by:

$$\begin{array}{ccccc} H_2O & ==> & H^+ & + & OH^- \\ \text{water} & ==> & \text{hydrogen ion} & + & \text{hydroxyl ion} \end{array}$$

In absolutely pure water H^+ and OH^- ions will always be present in equal numbers but when certain substances dissolve they produce an imbalance in this relationship. A solution with excess H^+ ions is recognised as acidic and indeed an acid may be defined as a substance which produces H^+ ions when it dissolves in water [69]. A solution with excess OH^- ions is alkaline.

An example of an acidic dissociation is that of sulphuric acid, which proceeds as shown below:

H_2SO_4 ==> $2H^+$ + SO_4^{--}
sulphuric acid ==> hydrogen ions + sulphate ion

Each molecule of sulphuric acid yields two hydrogen ions and whilst these are in electrical balance with the double-negative charge of the sulphate ion they upset the hydrogen/hydroxyl ion balance of the water in favour of H^+, producing an acidic solution.

The greater the excess of H^+ ions in a solution the more acidic it is and acidity is commonly measured in terms of the concentration of H^+ ions and expressed in pH units. The pH scale runs from 0 to 14; pH 7.0 indicates neutrality and at this point the H^+ and OH^- ions are in balance. Values lower than 7.0 are increasingly acidic and values above 7.0 are increasingly alkaline. A crucial aspect of the pH scale is that it is logarithmic (base 10) meaning that a change of one pH unit represents a tenfold increase in H^+ concentration. If the pH of a solution changes from 6.0 to 4.0 it has, therefore, become 100 times more acidic.

Acidity may be neutralised by restoring the balance between the H^+ and OH^- ions. Neutralisation can be achieved in two ways; alkalis, for example sodium hydroxide (NaOH), directly contribute OH^- ions to a solution when they dissolve and consequently raise the pH. Alternatively, acidity may be reduced by compounds which combine with free H^+ ions, removing them from the H^+/OH^- balance. In freshwaters, this second method of neutralisation frequently results from the reaction between H^+ and $HCO3^-$ (bicarbonate) ions, as below:

H^+ + HCO_3^- ==> CO_2 + H_2O
hydrogen ion + bicarbonate ion ==> carbon dioxide + water

The concentration of bicarbonate and carbonate in lakes and streams depends on the weathering rates of rocks and soils in the catchment area. The sum of the weathering sources is measured as alkalinity and was traditionally quoted as mgl^{-1} $CaCO_3$. Waters with a high positive alkalinity have an adequate capacity to neutralise any acidifying inputs whereas those with a low alkalinity (low neutralising capacity) are susceptible to acidic inputs, which may remove all the available alkalinity leaving free acidity in the water. Since, however, bicarbonate ions can exist in solution down to pH 5.5, a water is still classed as alkaline between pH 5.5 and 7.0.

2.2 Origins and Mechanisms

Acidification of freshwaters occurs when a lake or stream catchment area receives acid input at levels such that the natural buffering capacity is exceeded and the chemistry of the surface waters is altered as a result. The sources of this excess acidity, the pathways by which it enters surface waters and its effects on their ecology are discussed below.

2.2.1 Historical perspective

The effects of acidification of surface waters have entered public awareness only relatively recently but the processes responsible have been in operation for some considerable time. Evidence for this has been provided by studies of lake sediments, with changes in water quality over great time periods inferred from plant remains.

Diatoms are a large group of microscopic plants characterised by a cell structure consisting largely of silica. These "skeletons" remain identifiable to species in lake sediments almost indefinitely. Individual species of diatoms vary in their tolerance of pH and a change in the species composition of the diatom assemblage in a lake is assumed to reflect changes in mean pH [26]. By identifying the species of diatom remains present at different depths in lake sediments it is possible to chart the inferred historical pH of the water, assuming that modern representatives of a particular species have the same pH tolerance as their forebears. A realistic timescale can be attached to the diatom record by means of ageing techniques based on the amount of radioactive lead isotopes present at varying depths in the sediments [30].

Studies of the type described above have shown that whilst some lakes appear to have a tendency to acidify very slowly over extensive time periods, there has been a widespread and rapid acceleration of acidification over recent decades. In Sweden, Lake Gårdsjön showed a decline in pH from approximately 6.8 to 5.8 between 10,000 BC and the early 1950's. Between 1950 and 1979 the lake underwent a further rapid pH drop to approximately 4.5 [87]. Similar results have been observed in Welsh [30] and Scottish [26] lakes although in these cases the onset of acidification began between 100 and 150 years ago.

The beginning of the recent increase in the acidification process coincided with the massive upsurge in fossil fuel consumption that accompanied the industrial revolution and the development of heavy industry in the latter part of the nineteenth century. The link between fossil fuel consumption and acidification is strengthened by the appearance of carbon particles (soot) in lake sediments in the same time period as the apparent pH decline.

2.2.2 Sources of acidifying compounds

The burning of fossil fuels, mainly coal and oil, results in emissions to the atmosphere of large amounts of waste products, including the oxides of sulphur and nitrogen, compounds that are the first link in a chain of events culminating in acidification of surface waters. These oxides are often referred to by their chemical formulae, SO_2 (sulphur dioxide) and NO_x, representing a mixture of nitrogen/oxygen compounds. Major point sources of acidifying emissions are electricity generating stations, smelting plants and other heavy industrial processes. Domestic consumption of fossil fuels and vehicle engines also contribute to the atmospheric pollutant load. The quantities involved are staggering; in 1987 European sulphur emissions were approximately 21.5 million tonnes [02A].

2.2.3 Acid deposition

Atmospheric pollutants may be transported by winds over great distances before returning to earth. It is widely accepted, for instance, that a considerable proportion of the acidifying pollutants present in precipitation over Sweden and Norway originate in other European countries, including the UK, West Germany and France [21]. Similarly, acidification of surface waters in Canada has been linked to emissions in the USA [05].

Whilst in the atmosphere, the oxides of sulphur and nitrogen dissolve in the water droplets of clouds to form sulphuric and nitric acids, respectively, creating the "acid rain" of the popular press. Both of these acids are "strong" in the chemical sense, meaning that they dissociate completely, supplying the extra sulphate, nitrate and hydrogen ions that drive the acidification process when they enter the terrestrial water cycle. Acid precipitation may actually take the form of rain but can also occur as fog or mist, particularly on high ground, and this latter process is termed occult deposition. In addition to these two forms of wet deposition, there may also be dry deposition of acidifying compounds as gases directly on to soils, vegetation, water surfaces and buildings.

The pH of rain that is uncontaminated by atmospheric pollutants is usually between 5.0-6.0 and is slightly acidic as a result of the presence of carbonic acid, produced when carbon dioxide dissolves in water. "Acid rain" has a much lower pH, with values of 4.0-4.5 frequently recorded [108]. In addition to increased concentrations of acid-forming compounds, polluted precipitation carries a much heavier load of other dissolved substances including lead, zinc, and carbon [107].

The degree of contamination of precipitation varies with geographical location and is influenced by emission sources and prevailing wind patterns. Proximity to the sea also affects the chemical composition of precipitation and the marine effect can be significant and extend some distance inland [eg 78, 121]. Because of these influences there are often gradients in pollutant loads in precipitation across individual countries or continents. In the UK, for example, rainfall in the East Midlands of England is the most acid in the country with a mean pH of 4.2 [109] compared to a mean pH of 4.5-4.7 over much of Wales [15]. This difference in mean pH does not mean, though, that there is less of an acidification threat in Wales as the volume of precipitation there is much greater than in the East Midlands. Consequently the absolute amount of acidity deposited, measured as H^+ ions, sulphur or nitrogen is similar in both areas [15].

3 THE EFFECTS OF ACIDIFICATION

3.1 Extent of the Problem

Acid deposition and its effects on the chemistry, ecology and fisheries of freshwaters have been observed and extensively studied over the last decade. Scandinavia, particularly Sweden and Norway, the United States, Canada and the United Kingdom have invested considerable effort in assessing the degree and extent of the problem both individually and in cooperation. Coordination and funding of applied research have been seen as national or federal responsibilities over and above the regular level of academic research. In several countries governmental bodies have controlled acidification investigations partly or in whole. For example the USA in 1980, by means of an act of congress (Energy Security Act), instigated the National Acid Precipitation Assessment Program (NAPAP) and undertook to provide resources for 10 years of research into the processes of acid deposition.

Some of the larger-scale water chemistry and biological monitoring programmes carried out in recent years are presented in Appendix 2.

3.2 Chemical Effects of Acid Precipitation

All water bodies, flowing or still, are in a constant state of flux, receiving input of precipitation and dissolved and suspended materials via surface or underground drainage and losing them through flow, seepage or evaporation. The chemical composition of any water body is therefore a product of the quality of the initial precipitation and any changes which may occur as it passes through the drainage system of the catchment area. The nature and degree of changes induced by the vegetation, soils and bedrock of a catchment will determine whether or not acid deposition will lead to acidification of the surface waters.

Vegetation of one sort or another is an almost universal feature of non-polar land areas with significant amounts of rainfall. The species composition, abundance and life-cycle stage of the vegetation in a catchment will all exert some influence upon the chemistry of incoming precipitation as it filters through the plant canopy. Vegetation brings about chemical changes in precipitation in several ways. By the purely physical process of evaporation from the often extensive surface area of leaves, plants concentrate dissolved substances present in the precipitation; as much as 20% of the original volume may be lost [52]. There is a similar process, evapotranspiration, by which plants remove water from the soil by means of the root system and lose it to the atmosphere through the leaves, thus concentrating solutes in the soil waters and this effect may also be considerable, especially where the vegetation is forest.

Like all living organisms, plants need certain chemical nutrients to maintain their metabolic processes and are able to absorb some of these through the leaves. Of particular importance in this respect are calcium and potassium which have been found in lower concentrations after passage through vegetation than in the precipitation [52]. Conversely, there may also be leaching of ions including organic compounds from the plants into the water. Uptake of nutrients occurs principally through the root systems of plants and the concentrating effect of evapotranspiration may be offset to some degree by the selective acquisition of some ions by plants in this way.

Vegetation of all types acts as a passive collector of atmospheric pollutants which may take place as dry or occult deposition. Subsequent rainfall dissolves the accumulated deposits and the concentrations of many solutes are elevated, including those responsible for acidification. The nature of the vegetation is important in determining the extent of this effect and generally, the larger the plants, the greater the effect, with forest acting as a more effective scavenger than grassland [28]. (The role of commercial forestry in the acidification process is discussed separately, Section 4.)

Within any one group of vegetation, species may vary in their effect on precipitation chemistry. Coniferous trees, for example, have been found to cause greater changes than decidous species and some species of conifer such as larch exert more influence than spruce under similar conditions [52]. There are also seasonal variations in the effects of vegetation and these may be the result of changes either in the plants' level of activity or in the temporal pattern of dry/occult deposition.

As a generalisation, vegetation in a catchment subject to acid deposition has the effect of increasing the concentration of acid anions (sulphate, nitrate and, to a minor degree where precipitation includes a marine component, chloride). This increase is important to the processes which occur in the soil waters. Acidity as H^+ concentration is not always increased by vegetation and in some circumstances may be reduced.

Within soils, important chemical events involve H^+ and the acid anions derived from acid deposition and their interactions with various compounds present in the soil structure. In non marine-influenced catchments, the predominant acid anion is sulphate. Nitrates, also present in water entering the soils, tend to decrease as they are selectively removed by the root systems of plants. Acid anions are mobile, in the sense that they pass through the soils with the water flow and because ionised solutions must always be in electrical balance, acid anions leaving the soil are accompanied by an appropriate number of cations. These need not be the H^+ ions which entered the soil waters as the anions' "partners", however, as by the process of ion exchange other cations from the soils may replace the H^+ ions, which are retained. In this way the acidity (as pH) of the drainage waters is reduced but conversely the acidity of the soils increases.

The buffering capacity of soils is determined by their chemical composition and variations in soil type can be used to predict the sensitivity of an area to acidification [51, 39]. Calcareous soils have almost infinite buffering capacity, with incoming hydrogen ions exchanged for calcium ions and catchments on this soil type are very rarely acidified. Soils sensitive to acidification are often naturally acid, like blanket peats, or can become acidified over time through leaching of base cations. Sensitive soil types have very low buffering capacity and acid deposition is likely to result in acidification of water draining from them, with incoming H^+ ions passing through the soils and into the surface waters of the catchment.

Aluminium is an element present in abundance in soils and can provide an alternative source of the cations exchanged for H^+, thus acting as a buffer, especially in calcium-poor or acidified soils. The consequent leaching of aluminium to surface waters is of particular relevance to the acidification process because of its potential toxicity to fish and invertebrates (Section 3.4). Aluminium may be present in solution as the metal, in one or more combinations with hydroxyl ions or as complexes with fluoride or organic compounds, the proportions of each species controlled by pH, temperature and total aluminium concentration [75, 18]. Studies have shown that the most severe toxic effects of aluminium are associated with the group of species termed "labile monomeric", "inorganic monomeric", or "exchangeable Al" [55]. Amongst these, aluminium hydroxides are thought to be the most important [17, 90]. Toxicity of aluminium to fish is greatest between pH 5.0 and 5.5 [07].

Because of the complexity of aluminium chemistry and the unwieldy nature of some of the analytical techniques, mathematical models to predict the speciation of aluminium from more easily measured parameters have been developed, including ALCHEMI [93] and SPECIAL [33].

The bedrock geology of a catchment also exerts influence on the quality of the surface waters, either by determining the soil quality or by directly affecting the chemistry of groundwater which enters lakes and streams. Most often, soils and bedrock are similar in a given area and calcareous soils tend to overly rock types rick in calcium. Acid soils, too, tend to be associated with particular rock types, including granites and some shales. There can be significant differences in general rock and soil type where, for instance, glacially-derived soils are deposited at great distance from their origin and soils with high buffering capacity may overly acid rock types.

If water comes into contact directly with the rock of a catchment, either as a result of very thin or absent soils or as a consequence of deep-flowing groundwater, there may be buffering of acid deposition by the bedrock. As with soils, rock types have been classified according to their buffering capacity and used to predict the sensitivity of catchments to acidification [eg 51]. Rock types with high buffering capacity include limestones, chalks, some marls and some mudstones, all of which are characterised by significant content of calcium or magnesium carbonates and/or weatherable silicates. Common low-buffering capacity rock types are granites, gneisses, quartz sandstones and some shales and slates.

The degree to which acid deposition is modified by the vegetation, soils and geology of a catchment is dependent upon the length of time that the water is in contact with the various catchment features and the ambient temperature. In periods of heavy rainfall, snowmelt, or during storm events, a large proportion of the incident precipitation can enter watercourses by flowing over the surface of the ground or in the upper layers of the soil. Such rapid flow allows only minimum soil/water contact time and the buffering action of the soils may be negligible, giving rise to "pulses" of acidity in streams. During acid episodes of this nature pH can decrease extremely rapidly over short time periods (Fig. 1). Lowered pH can be accompanied by elevated levels of aluminium which may originate from the stream bed as well as from the catchment [77, 46], creating potentially toxic conditions for fish and invertebrates. Duration of acid episodes is often relatively short, from the onset of pH decline to the return to "normal" conditions taking from 18 to 72 h (STWA data).

3.3 Response of Lakes and Streams

Because of the different hydrological conditions that exist in still and flowing surface waters lakes and streams tend to respond differently to acidifying input. Lakes respond more slowly than streams because of their greater water mass. The volume of water within a lake at the onset of acidification will contain a certain amount of buffering capacity and this will delay the first ecological effects of acid input. Large lowland lakes, which may have a water turnover period of several years, will respond more slowly than small, mountain tarns where turnover may be measured in weeks.

Fig 1 pH fluctuations during an acid episode on the Afon Twrch, Powys, UK

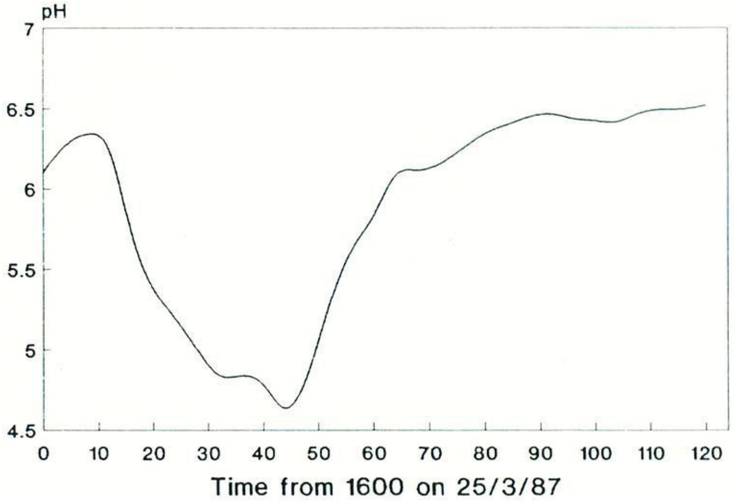
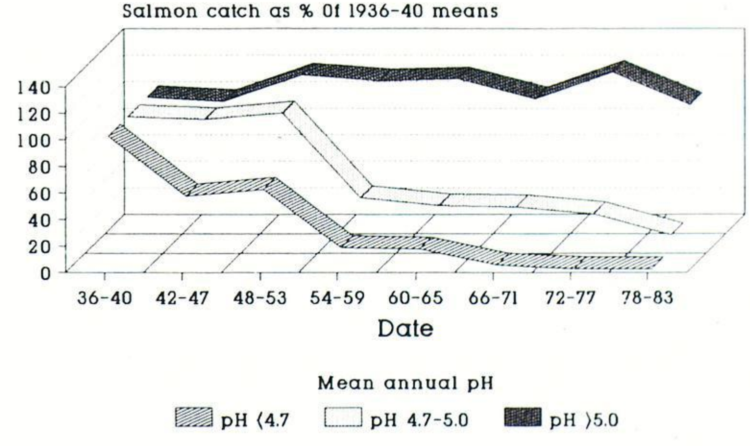


Fig 2 Salmon rod-catches from 22 Nova Scotia rivers from 1942-83, as affected by pH changes since early 1950's.



Drawn from data presented in (54)

Flowing waters respond more quickly than lakes as they have virtually no water retention time. For streams and rivers, important aspects are catchment-oriented and relate to the time that precipitation is in contact with the geology, soils and vegetation of the catchment before entering the watercourse and the sensitivity of the catchments soils and geology. In small, steep catchments with thin soils, water is in contact with potentially neutralising materials for only a very brief time and runoff tends to be more acidic than in large catchments where contact time is greater.

3.4 Biological Consequences of Acidification

The changes in water chemistry associated with acidification affect impacted aquatic ecosystems and it is generally accepted that the first signs of biological response begin to appear when pH reaches 5.5 or below, either permanently as a result of progressive acidification, or intermittently as acid episodes. Biological effects are caused mainly through the influence of three ions, hydrogen, aluminium and calcium. Hydrogen and aluminium act through direct toxicity whilst calcium is important in an ameliorative sense as it can be involved in the buffering of acidity and also reduce the toxicity of aluminium to some animals.

Although the disappearance of fish stocks from a freshwater is perhaps the most dramatic effect of acidification and the most readily perceived by the public, all trophic levels of the aquatic ecosystem are affected to some degree. Algae, the simplest form of plant life, are vitally important to the entire ecosystem harvesting the energy of sunlight and making it available to higher levels. In circumneutral or alkaline waters there may be over 50 different species of algae present; in acidified waters there are frequently less than 10 species. Reduced species diversity is typical of extreme environmental conditions but is not always accompanied by impoverished abundance. Some comparisons of algal standing crop have shown that in naturally or experimentally acidified waters, biomass was equivalent to or higher than in non-acidified conditions [73, 25]. Abundance of algae is often reduced, however, and a common feature of acidified lakes and streams is great water clarity.

Higher plants are affected in a similar way to algae and acidifying waters are characterised by decreasing species diversity of macrophytes [34]. Species that are tolerant of acid conditions can be prolific, benefiting from reduced competition from other species and in lakes from the increased light penetration resulting from decreased phytoplankton abundance. *Sphagnum* mosses and the rush, *Juncus bulbosus* are plants which typically dominate aquatic vegetation in acidified waters.

Animals in acidified waters may be affected directly by water quality, in an indirect way as a consequence of changes in the phytoplankton or macrophyte communities or as a result of changes occurring amongst other animal species. Direct effects on invertebrates are caused by the toxic effects of pH rather than aluminium [13, 45]. Zooplankton and macroinvertebrates show a similar response to that of plants in acidified waters, exhibiting poor species diversity in waters of low pH and elevated aluminium [82, 31] but again the species that are acid tolerant can be relatively abundant, providing standing crops similar to those in non-acidified waters [eg 42].

In lakes, acid-tolerant invertebrates include water boatmen (Corixids), alderflies (*Sialis* sp) and dragonflies (Odonata). For the larger invertebrates, part of the reason for increased abundance in acidified lakes is likely to be a reduced level of predation where fish have declined [09]. In flowing waters, several species of mayfly (Ephemeroptera) and some species of caddis fly (Trichoptera) are acid sensitive whilst stoneflies (Plecoptera) are tolerant and can be abundant [102, 117]. Crustaceans such as the freshwater shrimp (Gammarus) and molluscs are particularly acid-sensitive with mortalities of >90% recorded at pH 6.0 [40] but their absence from acid waters may be caused as much by a lack of calcium as by H^+ or aluminium toxicity.

Directly toxic effects of acidified water to fish result from the action of hydrogen or aluminium upon the physiological processes of blood chemistry control and respiration. For all species of fish in freshwater there is a continual tendency for the blood to become more dilute through osmosis. Because the blood is more concentrated than the surrounding water, solutes, predominantly sodium (Na^+) and chloride (Cl^-) ions, move passively outwards across the fish/water interface and water moves into the fish. The main site of this activity is the gills, where the primary function of gas exchange demands that blood and water are in very close proximity, a situation which also maximises osmosis.

To keep the blood at its correct concentration, fish actively excrete water via the kidneys (although this also results in the loss of some blood salts) and minimise ion loss at the gill surface by active uptake of Na^+ and Cl^- through the chloride cells. Chloride cells are one of the components of the gill membrane and are thought to be the site of active ion transport between water and blood [Evans, 1987]. Enzymatic processes which remove carbon dioxide and ammonia from the blood to the water are involved in the uptake of Cl^- and Na^+ respectively [23].

In acidified water hydrogen ions and aluminium reduce the efficiency of the blood regulatory processes occurring at the gill/water interface and can cause physiological distress or mortality in fish. If pH is acting in isolation from the influence of aluminium pH 5.0 appears to be the threshold for physiological response [118]. Below this point, passive ion loss increases through increased permeability of the gill membranes to Na^+ and Cl^- [68]. In addition, the active uptake of Na^+ may be inhibited by H^+ [118].

The speciation and solubility of aluminium and hence its toxicity are variable (see Section 3.2), with the most toxic forms occurring in the range pH 5.0-6.0 [07, 29]. The mode of aluminium toxicity is similar to that of H^+, with increased passive loss of ions from the blood. Enzyme activity involved in ion uptake may also be inhibited [101]. Aluminium affects respiration more severely than H^+, with reduced levels of oxygen and elevated carbon dioxide in the blood [71], probably as a result of decreased gas permeability of the gill membranes.

If the net loss of Na^+ and Cl^- from the blood is sufficiently great (>30%) then mortality will result following failure of the circulatory system [118]. Mortalities are likely to occur during periods of rapid water quality change such as those experienced during acid episodes in streams. Long-term but sub-lethal increases in H^+ or aluminium may reduce the respiratory efficiency of the gills through thickening and fusion of the lamella and promote an increase in the number of chloride cells [56] which may be a compensatory mechanism to counter increased passive ion loss.

The toxicity to fish of both H^+ and aluminium is mediated at least partially through the displacement of calcium from the gill membranes [70]. If there are sufficiently high concentrations of calcium in the environment, the toxic effects may be lessened to some degree by a reduction in this displacement and consequently in the amount of passive ion loss from the gills [62]. Calcium may also decrease the toxicity to fish of other metals which may be present in elevated concentrations in acidified water [92]. The amount of calcium required to cause a beneficial effect is small in an absolute sense, in the region of 1-2 parts per million (mg/l) but even this amount may be many times what is naturally available in acidified waters. Cations other than calcium, such as magnesium and sodium, may also ameliorate the toxicity of H^+ and aluminium, but their effects are usually less pronounced [71].

The presence of organic carbon in acidified waters can ameliorate aluminium toxicity by chelation of the toxic species [17]. Various workers have suggested 5 mg/l of dissolved organic carbon as a threshold value, above which aluminium toxicity is reduced [eg 62, 63]. Acidified waters draining peat soils often contain enough carbon to obviate the danger to fish from aluminium and in such catchments (eg in Nova Scotian rivers) observed fish mortalities are attributable to H^+ toxicity alone and occur at lower pH values than in other areas where H^+ and aluminium toxicity operate together.

Fish species vary in their susceptibility to the effects of acidification. Among the salmonids, Atlantic salmon and brown trout (*Salmo trutta*) are relatively sensitive, compared to some char (*Salvelinus* sp). There is a similar variation in non-salmonid species, with roach (*Rutilus rutilus*) at the sensitive end of the scale, perch (*Perca fluviatilis*) and pike (*Esox lucius*) more tolerant and eels (*Anguilla anguilla*) probably the most resistant.

A great deal of research has been carried out on the responses of the various stages of the salmonid life cycle to acidified conditions and variations in sensitivity have been observed. Atlantic salmon ova are relatively resistant as the shell of the egg protects the embryo within but it has been found that the proportion of eggs successfully hatching is inversely related to pH of the incubation site with 50% failure to hatch recorded at pH 4.7 and total failure expected at pH 4.1 [62]. At higher pH levels hatching may be successful but delayed [84] and this effect can reduce subsequent survival through reduced opportunity for growth in the first year. Newly hatched salmon and trout alevins are resident in the stream gravels for some time and during this phase show similar sensitivity to that of the ova, with mortalities observed at pH values of less than 5.0 [85].

When salmonid fry emerge from the gravel of the stream bed and begin to feed, mortality is much higher than during the pre-emergence phase. In acidified waters this is exacerbated, with lower than average survival of salmon due to a failure to begin feeding successfully recorded at pH 5.2 and possible total mortality at pH 4.7 [63]. Fish that reach the parr stage successfully are comparatively tolerant of low pH and aluminium [90] but at smoltification the physiological changes taking place again render the fish more sensitive [58].

Adult salmon and migratory trout (sea trout) returning to freshwater to spawn undergo similar, but opposite, changes to those of smoltification but the adults do not appear to be as sensitive as the smolts, although some effects have been observed. In adult Atlantic salmon, depressed levels of some steroid hormones were found in males and in females reduced egg viability in fish from acidified rivers of Nova Scotia [114]. Mortalities of adult fish on their spawning migration in freshwater have also been recorded during acid episodes in rivers in England, Wales and Scandinavia [41, 72, 47].

Vertebrates other than fish are also affected by acidification. Damaging effects have been observed in amphibians, some species of riverine birds and otters [eg 94, 82].

3.5 Effects of Acidification on Fisheries

Cumulative effects of acidification upon individual fish can be manifested in changes in fish populations and the commercial or recreation fisheries that they support. Fishery loss does not often result from a single catastrophic event but is more likely to be a consequence of progressive decline of fish stocks following successive years of poor recruitment or year-class loss [eg 48]. Populations of fish in lakes may persist in decline for longer than those in rivers as a result of longer life expectancy of adults. During the period of decline lake fisheries are often characterised by catches of fewer but significantly larger than average individuals, as the decreased number of fish temporarily benefit from increased food availability. Sub-lethal effects of acidification may cause fish to emigrate from a particular section of stream either temporarily or permanently and thus reduce their availability to fishermen.

Because of their sensitivity to water quality, combined with the coincidence of their geographical range with acid-sensitive catchments, Atlantic salmon and brown trout fisheries are susceptible to damage or loss through acidification, with economic as well as ecological consequences. In Wales, for example, where the total fishery resource is predominantly dependent upon salmonids, the gross annual revenue from fisheries is estimated to be in the region of £15 million [72].

In Norway, Atlantic salmon fisheries have been lost completely from 19 river systems in the south of the country with a mean pH of 4.90 to 5.82, representing over 2000 ha of freshwater habitat and an annual adult production of 90,000-300,000 fish [55]. Loss of salmon production in Swedish west-coast rivers due to acidification has been estimated at between 14,000 and 23,000 adult fish.

The proportion of Canadian salmon fisheries affected by acidification is a relatively small part of the whole resource but there is real concern in the Southern Uplands region of Nova Scotia where, since the mid 1930's there has been clear degradation of salmon fisheries associated with declining water quality (Fig. 2). Of the 60 rivers in the region offering physically suitable habitat for Atlantic salmon, 13 are completely devoid of the species; these rivers have a recent mean pH of <4.7. In a further 18 rivers, with mean pH of 4.7-5.0, there are only remnant populations of salmon in certain tributaries. Only in the 16 rivers with mean pH >5.4 are salmon stocks considered to be normal [114].

Loss of production of adult fish in the Nova Scotian Southern Uplands has been estimated by comparing theoretical production, based on available habitat and known survival rates, with observed and deduced yields and escapement. Between 15,000 and 22,500 adult salmon per year are thought to have been lost to acidification [114].

In the UK there has, as yet, been no catastrophic loss of Atlantic salmon fisheries but there is some evidence of declines in catches for certain river systems in Wales and Scotland. Falling catches in some rivers in south-west Scotland over the last 30 years or so have occurred and a possible causal link with the development of forestry in the catchments of spawning and nursery streams has been suggested [20]. Elsewhere in Scotland, acidic streams have been found to contain lower densities of salmon parr than circumneutral streams but overall smolt production is not thought to be constrained by acidification at present [55].

Analysis of salmon rod-catches from major Welsh rivers showed a decline from the decade 1966-75 to 1976-85 which was most pronounced in those where >20% of the catchment had been classed as acidic [107]. Preliminary estimates of the economic loss from the Welsh fisheries are in the order of £5-25 million [72]. The Afon Tywi, second only to the Wye in terms of salmon catches, was one of the rivers showing a declining yield and there is circumstantial evidence of decreased smolt production in the form of failed stockings of parr in the upper reaches of this river [72]. More definite evidence of acidification as a cause of the decline of Welsh salmon fisheries has been observed, with mortalities amongst adult salmon and sea trout occurring during acid episodes on the Afon Glaslyn [72].

Decline of fisheries exploiting anadromous fish other than salmon have also been observed and at least partially attributed to the effects of acidification. On the east coast of the United States the striped bass fishery virtually disappeared from the mid to late 1970's, with commercial catches decreasing at a rate of 22% per year. Although overfishing and other factors were involved in the decline, low pH/high aluminium episodes in some of the spawning rivers were associated with greatly reduced larval survival [86]. Also in Chesapeake Bay, egg and larval mortalities in blueback herring (*Alosa aestevalis*) were being associated with acid episodes [61].

Destruction of lake fisheries for salmonid and non-salmonid species has been extensively reported, with the number of lakes affected measured in thousands in Scandinavia, Canada and the north-eastern USA. Similar losses but on a much smaller scale, have occurred in Wales and Scotland with the disappearance of several noted brown trout fisheries.

4 THE ROLE OF FORESTRY IN ACIDIFICATION

In the UK in particular, those parts of the country which are susceptible to the effects of acid deposition are also favoured for the development of silviculture. The same geological and soil features that lead to a catchment being acid-sensitive result in the land being generally poor in agricultural terms and hence of low enough value to make forestry profitable. Unfortunately, these are also the catchments which often provide spawning or residential habitat for Atlantic salmon and brown trout.

Problems associated with forestry change as the production cycle progresses. At the beginning of the cycle, land disturbance is maximal and physical effects are most severe. In many cases, a pre-requisite of forestry development is drainage of the land and this activity can have profound effects upon the hydrology of streams flowing from drained catchments. During spates, higher peak flows are reached much faster than in undrained catchments and annual water yield from the catchment may increase. Concentrations of suspended sediments also increase following draining, a condition which may persist for several years [88] and this, together with the increased flashiness of streams resulting from drainage operations can lead to ecological degradation.

Pre-planting land preparation is another activity at the beginning of the forestry cycle and whilst it is often an extension of drainage work can include the application of nitrate and phosphate fertilisers, part of which may enter the water system of the forested catchment.

The main chemical effects of afforestation occur when the plantations have reached the "closed canopy" stage of growth, normally between 12 and 20 years after planting. The dense planting patterns of the conifer species cultured and the great surface area of their foilage leads to efficient scouring of atmospheric pollutants and subsequent effects on the quality of deposition and soil and stream water chemistry (see Section 3.2).

Comparative studies of streams draining forested and unafforested catchments of otherwise similar nature in England, Scotland and Wales have repeatedly shown that afforestation is associated with higher levels of aluminium and sulphate and lower mean pH values [eg: 42, 43, 99, 100]. Forest streams have also been shown to react in a more extreme way than moorland streams during storm events, particularly in winter [10]. This is not to say that unafforested catchments do not suffer from acidification because they clearly do, but the presence of coniferous forest does appear to accelerate and exacerbate the chemical and ecological effects.

At the end of the production cycle, 40-60 years after planting, tree harvesting exerts further physical effects upon the aquatic environment. The activity of cutting and removing timber involves the use of large mobile plant and leads to similar land disturbance to that of the pre-planting land preparation phase. Short term increases in sedimentation of streams result and can cause fish and invertebrate mortalities [eg 95].

Clear felling of forest in acid sensitive areas has been associated with increased mobilisation of nitrates from the soils into forest streams, driving the acidification processes in the same way as sulphate and leading to elevated aluminium concentrations and depressed pH [eg 65, 64]. In contrast, in areas of non-sensitive geology and soils, clear felling of natural forest may have an insignificant [11] or possibly beneficial [74] effect upon stream invertebrates and fish.

Because of the growing awareness of the involvement of forestry in surface water acidification and other ecological issues there is an increasing pressure from planning authorities and those agencies commenting on grant aid applications upon the forestry industry to restrict new plantings in sensitive areas or at least to revise their techniques so as to minimise environmental damage. In response to this pressure the Forestry Commission has recently produced a technical publication [78] which reviews the published literature and questions the validity of some of the conclusions drawn regarding the existence of a forest effect in acidification. The widely held opinion amongst scientists outside the Forestry Commission is still, however, that the great weight of evidence is firmly behind a positive association between forestry and an intensification of the acidification process.

In a more positive vein, the Forestry Commission have also produced a set of guidelines [27], providing recommendations to forestry managers on issues concerning conservation of watercourses through sound management practices aimed at minimising the physical impact of forestry. If these guidelines are followed it may also bring about some reduction in the effects of forestry on water chemistry.

5 AMELIORATION OF SURFACE WATER ACIDIFICATION

The acidification of surface waters is a potentially disastrous threat to freshwater ecosystems in many parts of the world and to the fisheries they support. As these problems have been created exclusively by human activities it is to be hoped that at least some of them may be solved in the same manner. Over the past decade or so, much academic and applied research has been carried out in this field and there are now at least some techniques available to combat the processes of acidification.

5.1 Reduction of Acidifying Emissions

Removing the cause of any problem is the only sure way to eliminate its effects but the burning of fossil fuels is essential to the continuation of modern, industrialised society. Whilst the cessation of fuel consumption is not a viable proposition, it is possible to reduce the amounts of polluting waste produced, but the additional costs involved has made industries and governments reluctant to implement the necessary regulations.

A recent legislative change may change this situation in Europe at least, where the Large Combustion Installation Directive (LCID) is an agreement binding upon governments to achieve a specified schedule of reduced SO_2 emissions from existing oil and coal-fired generating stations over a 15 year period from 1988. In the UK, the targets compared to the SO_2 emission level in 1980 are for overall reductions of 20% by 1993, 40% by 1998 and 60% by 2003.

The two main generating concerns in the UK, Powergen and the National Power Company, both propose to comply with LCID by a combination of methods. At the largest stations (>4 gigawatts) including Drax, Ferryside and Ratcliffe on Soar, Flue-Gas Desulphurisation (FGD) technology will be implemented at a probable cost of around £350 million per station. FGD will reduce station emissions by over 90% and is likely to reduce total UK emissions from generating stations by over 30% [Powerglen and National Power Press Offices, pers. comm.].

For smaller, existing stations, other avenues are open, including burning of low-sulphur coal which is available from some sources or by bioreduction of the sulphur content of "ordinary" coal or oil through genetically engineered microorganisms. New generating stations will be less polluting than their predecessors as they are likely to consume alternative fuels. Combustion of natural gas is foreseen as a possible energy source which will produce no SO_2 and significantly less CO_2 and NO_x than current fuels. Nuclear energy is another possible alternative for the power industry which carries no penalty in the form of acidifying pollutants but, of course, has its own particular problems in the arena of environmental safety.

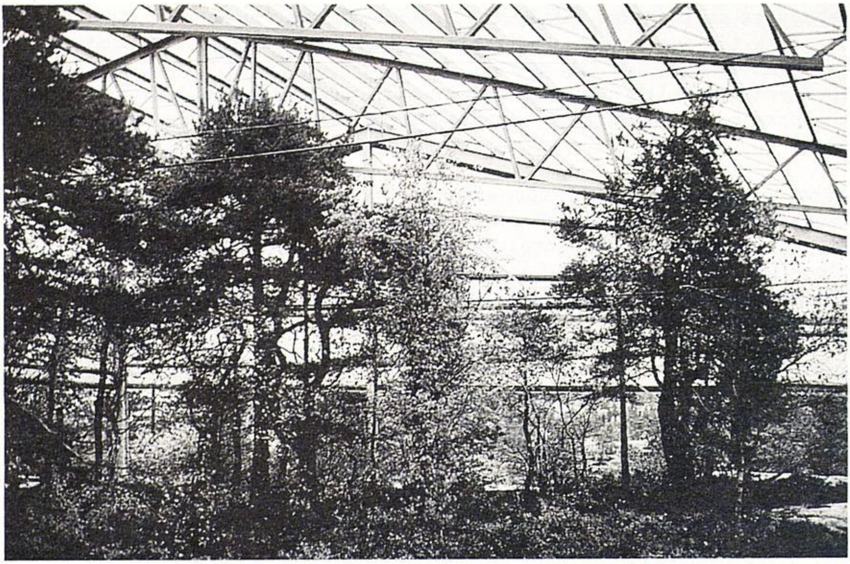
A practical assessment of the effects of eliminating acid deposition is currently in progress in Norway, where the RAIN project (Reversal of Acidification In Norway) involves the manipulation of deposition quality coupled with the monitoring of run-off water chemistry. At Sogndal, in Western Norway, where natural precipitation is relatively unacidified, the effects of experimental addition of sulphuric acid or a mixture of sulphuric and nitric acids to the incident deposition are being assessed. Risdalsheia, in Southern Norway, receives severely acidified deposition (pH 4.2) and here experiments are carried out in large (1200 m^2) open-sided shelters (Plate 3). Incoming precipitation is collected from the roofs and chemically filtered to restore it to "pristine" condition before it is re-applied to the catchment by sprinkler. In winter, artificial snow is applied to the catchments.

The RAIN project is a continuing piece of research but early results suggest that a shift in precipitation chemistry is quite rapidly reflected in runoff chemistry [120]. At Sogndal, acidifying the deposition caused increased levels of sulphate, decreased alkalinity and slightly elevated nitrates (where nitric acid was added) in runoff. Loss of base cations from the soils (predominantly calcium and magnesium) also increased following acidification of the deposition. At Risdalsheia, the cleaning-up of the precipitation led to decreased sulphate, increased alkalinity and decreased nitrate in runoff, together with reduced loss of base cations from the soils.

At both of the RAIN project sites, the soils are extremely thin and poor, with up to 50% of the experimental catchments' areas consisting of exposed bedrock. In catchments with different soil characteristics, a reduction in acid deposition could have considerably less effect upon surface water quality. Where soils are relatively thick and have become exhausted in terms of base cations due to acidification, it could be decades, rather than years, before water quality returned to pre-acidification levels.

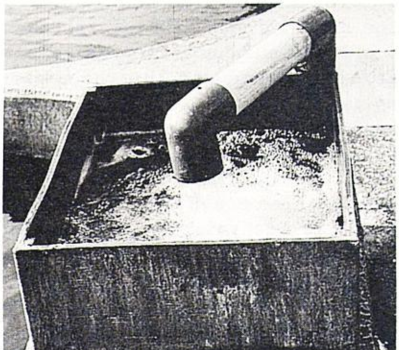
Prediction of the effects of reduced emissions have been made using various mathematical models. A commonly used model is MAGIC (Model of Acidification of Groundwater In Catchments) which describes known chemical processes occurring in deposition, soils and surface waters in terms of sets of equilibrium and mass balance equations. Changes in any of the input parameters can be fed into these equations and resultant changes in the processes can be estimated.

MAGIC may be extended to include locally important factors which were not present in the original model. For catchments in Wales, adjustments were made to incorporate the effects of forestry and allow the prediction of fish density and invertebrate diversity [116, 83] under different emission reduction scenarios. For Welsh streams, even assuming that reductions of 50% in emissions could be made over the next 20 years, the predictions of MAGIC are for a lessened degree of deterioration rather than a return to pre-acidification conditions over the next century. The situation in Wales is typical of other



Inside the RAIN project at Risdalsheia, Norway, where acid precipitation is purified before being reapplied to the vegetation within the roofed area.

A basket-doser in the Mosquito Creek watershed, Pennsylvania, U.S.A. Limestone powder can be seen as it is washed out of the doser loaded with limestone briquettes.



Treatment of acidified water by passage through limestone chippings at Mersey Fish Culture Station, Nova Scotia, Canada. The supply to each hatchery pond is treated individually.

parts of the UK where extensive forestry has taken place. For this reason it is essential to develop operational techniques for the long-term protection of aquatic ecosystems and fisheries for those catchments where recovery following emission reduction is likely either not to take place at all or to be very delayed.

5.2 Operational Techniques to Mitigate Acidification

5.2.1 Available options

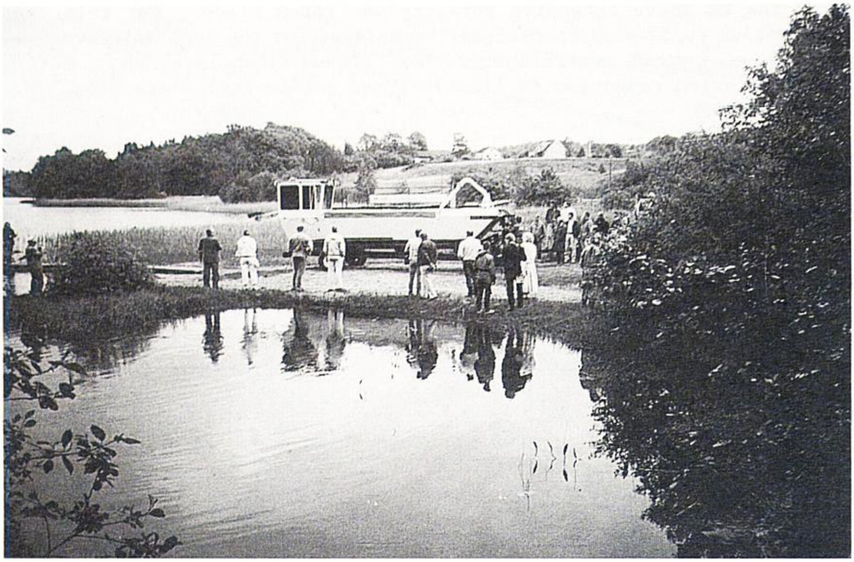
The objective of ameliorative techniques is to prevent the occurrence of toxic conditions in acidified freshwaters. In simple terms, this requires the provision of the buffering capacity that may have been lost from or may never have been present in the soils and waters of a catchment. Various means exist to achieve this result but the one which has received most research effort and is employed widely in practical mitigation projects is the use of limestone which consists largely of calcium carbonate ($CaCO_3$). In solution, calcium carbonate dissociates and promotes the elevation of pH by reaction between H^+ and CO_3--, to produce bicarbonate ions (HCO_3-). In addition to this, calcium has a beneficial effect in reducing the toxicity of aluminium to fish (see Section 3.4). A further benefit of calcium carbonate is that it is virtually non-toxic to fish and accidental overdosing is not a real threat. (In fish-culture though, very high calcium concentrations have been shown experimentally to be detrimental to salmonid hatching success [60].)

It would be possible to use other bases as acid neutralisers but generally they do not confer the same overall advantages as limestone. Sodium hydroxide (caustic soda, NaOH) is a strong alkali which is effective in neutralising acidity by contributing OH^- direct to the solution but has no additional benefits. Indeed, NaOH is potentially hazardous to users and to the environment and there are real practical problems in its application.

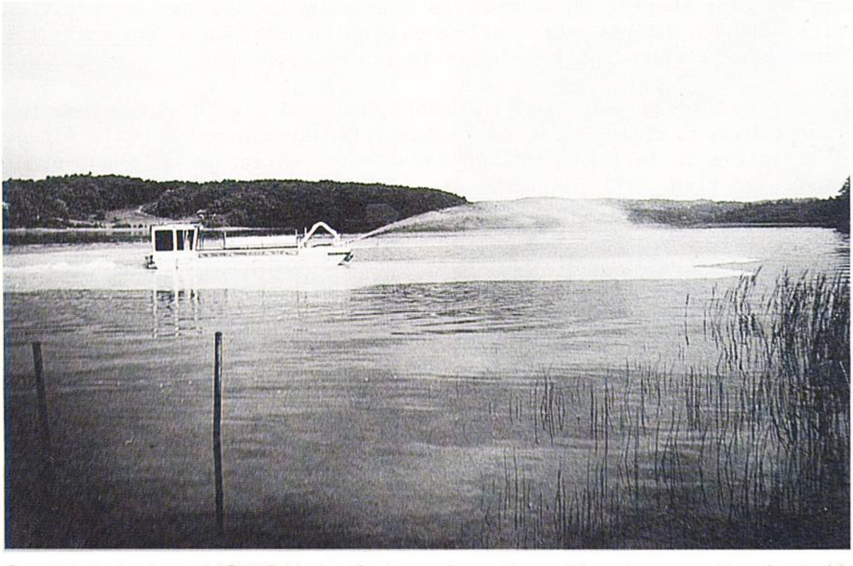
Soda ash (Na_2CO_3) has been used to neutralise acid mine drainage and in an experimental way to treat acidified streams in Pennsylvania, USA [04]. Although it is effective in raising pH it is relatively costly and also potentially dangerous to fish [97]. There are, however, negligible effects upon invertebrates in treated streams [04].

One possible alternative to limestone as a mitigating agent is seawater, which has been used successfully in Norway, where the addition of 2-3% by volume of seawater improved survival of salmonids [91]. This method has obvious geographical limitations but has been used to advantage in shore-based smolt production units [McWilliams, pers. comm.]. There are also possible risks of disease transmission with this technique and although this can be obviated in the fish culture situation by the use of ultra-violet sterilisation such treatment would not be feasible for the larger volumes of water necessary to mitigate acidification in a river or lake, even if this were practicable.

Whether or not limestone is selected as a neutralising agent for mitigation, the major problem is in ensuring that the right amount of chemical is available at the right time and in the right place. There are two fundamental approaches, each of which has merits and weaknesses. Attempts can be made to neutralise acid deposition before it enters surface waters, by treatment of the land



Swedish liming boat (MOVAB Liming Co.) being manoeuvred into a lake near Goteborg on its motorised trailer.



Swedish liming boat (MOVAB Liming Co.) spraying a slurry of limestone powder mixed with lake-water on to the surface of a lake near Goteborg.

surface of the catchment; this approach influences the quality of surface waters indirectly. Alternatively, the water bodies themselves may be treated directly by the addition of neutralising material.

5.2.2 Indirect mitigation strategies

Indirect mitigation strategies aim to neutralise acid deposition as it passes over and through the soils of the catchment. Available techniques involve the application of limestone in one form or another to all or part of the catchment to be treated. The effectiveness of indirect liming is determined by many factors and field trials in recent years have led to the development of predictably successful methods.

Chemical composition of the limestone used is important in determining the success of catchment treatments. Dolomitic limestone, which contains significant amounts of magnesium carbonate is less soluble than the high-calcium limestones and is therefore not so effective. Although it may appear that the lower solubility of magnesium limestone could be advantageous by prolonging the effective treatment time this is not usually the case.

The physical form of the limestone applied to catchments is one of the most important determinants of mitigation efficiency. Because dissolution of limestone is proportional to the surface area of the particles in contact with soil water, very finely ground limestone gives the best results. Products with 50% < 10 microns* and 95% < 50 microns have been found to be effective and to give prolonged treatment [111]. One of the negative aspects of using very finely ground limestone is its higher cost compared to coarser material.

Practical considerations also come into play as the very fine powder is difficult to apply on a large scale, especially in remote catchments. Where access is restricted, helicopters have been used to distribute limestone powder (eg Welsh Water Authority) but this method is limited by a lack of precision in delivering the payload accurately, especially in high winds. Problems have also been experienced with the limestone failing to penetrate forest canopies successfully [50]. Methods of improving the aerial distribution of powdered limestone have been explored, including mixing the powder with water and spraying the resulting slurry on to land or within forest plantations [12]. Forming limestone powder together with binding agents into pellets that are intended to break down on contact with water has allowed much greater penetration of forest canopy and accuracy of application from the air [105].

Dose rates of limestone applied in entire or partial-catchment treatments have varied from 3 to 50 tonnes/hectare [81, 89, 53] with the highest rates used when very specific parts of the catchment are treated. For partial-catchment treatments, selection of the area to receive the limestone is critical to the success of the operation. Flushes or wetlands, where water

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* 1000 microns = 1 millimetre

seeps from the soils either directly into the streams or collects in small, boggy areas are suitable liming sites and successful treatments using high dosage rates have been carried out in Sweden, Scotland and Wales. In contrast, some partial catchment treatments have been almost completely unsuccessful, with the limed area apparently exerting little influence on the overall hydrology or chemistry of the whole catchment [50].

Efficiency of catchment liming, measured as the proportion of calcium applied that enters surface waters, has been found to vary considerably, ranging from 1-3% up to a maximum of 13% in Norway [89]. The effects of catchment liming are principally to bring about significant increases in pH and calcium concentrations and decreases in the concentrations of aluminium in surface waters, although this latter effect may be seen as a suppression of seasonal peaks of aluminium rather than an overall decline. In this way, environmental conditions enabling the reinstatement of lost fish populations or the prevention of degradation of existing resources can be produced. A summary of the results of various treatment trials is shown in Figure 3.

Because the objective of catchment liming is to change the chemical processes occurring on the land surface and within the soils, there are potentially negative side-effects of this technique. As many of the catchments vulnerable to acidification are composed of soils which were originally acidic to some degree, the application of large quantities of neutralising agents can damage the plant and animal communities that have evolved to prefer acid conditions [119]. Some species of *Sphagnum* mosses, liverworts and lichens may be destroyed by liming [eg 105].

The way in which the possibly negative effects of catchment liming is viewed varies from country to country. In Sweden, for example, the damage to relatively insignificant areas of acid communities is regarded as an acceptable trade-off for the benefit to aquatic ecosystems, fisheries and, ultimately, people [Sverdrup, pers. comm.]. In the UK, a different view is held, with great conservation value attached to individual sites of ecological interest. This leads to possible conflict amongst different conservation agencies' efforts to protect the resource they are particularly concerned with and scope for the application of catchment liming techniques may therefore be somewhat limited, especially as the amount of acidic, upland environments still remaining in their original state is continually diminishing.

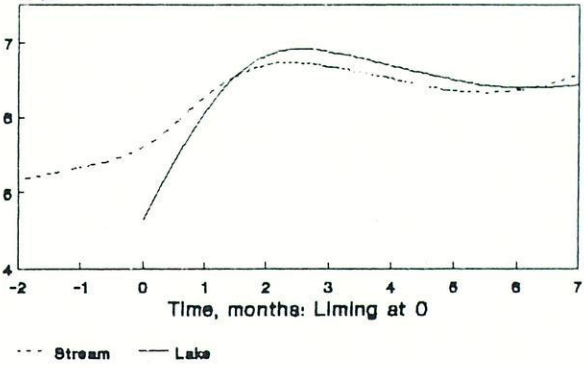
5.2.3 Direct mitigation strategies

The introduction of neutralising materials direct to the acidified water body bypasses the environmental disadvantages of catchment liming techniques and is also generally more efficient in terms of the proportion of applied material dissolving in the target water. Treatment of lakes is by now a well developed operational technique, especially in Norway and Sweden where commercial operators carry out this work on a routine basis. Treatment of flowing waters is a more technically difficult proposition but again reasonably successful strategies have been developed.

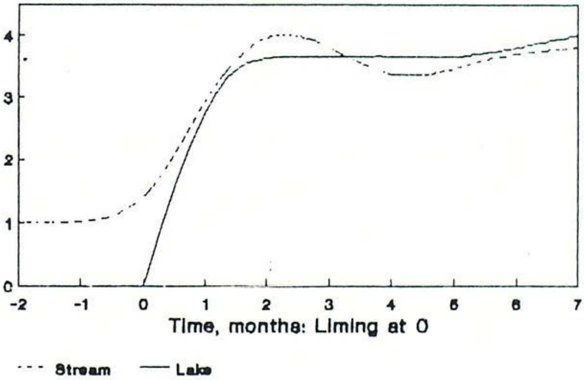
For lakes, liming methods are influenced by the volume and turnover time of the lake but otherwise the operation is relatively straightforward. The most commonly used neutralising agent is crushed limestone and a "lake-liming powder" consisting of particles from 1-200 microns has been found to give

Fig 3 Effects of catchment liming on water chemistry in streams and lakes

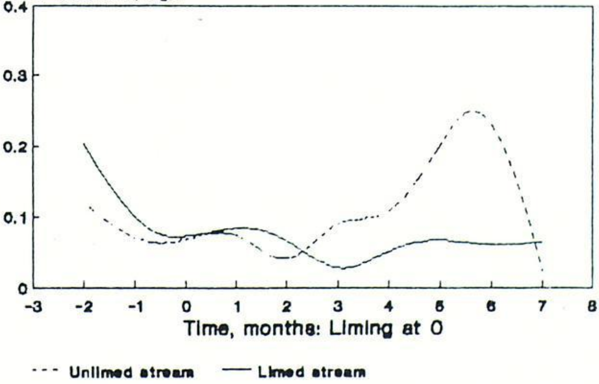
a) pH



b) Calcium, mg/l



c) Aluminium, mg/l



Drawn from data presented in [06,50]

good results [113]. The use of coarser grades of limestone leads to a greater proportion of the applied material sinking to the lake bed where it becomes relatively unavailable to the water body, although dissolution of limestone from the lake sediments may be of significance over longer time periods [103]. Dosage rates may be calculated from knowledge of existing and target water quality parameters and vary not only from lake to lake but may also differ between shallow and deep zones of the same lake. Rates between 2 and 30 t/hectare at the point of application have been used in Sweden [14].

Methods of applying limestone to lakes are numerous. Direct application to the water surface from boats, by hand or more often by some sort of mechanical delivery system is the most frequent and has been developed to a fine art in Scandinavia with the construction of special vessels. Plates 1 and 2 show a typical liming boat being demounted from its transport trailer and distributing lime slurry to the lake surface. Mixing the dry powder with water before distribution has been shown to increase dissolution by as much as double compared to dry application [113]. Efficiency of this liming technique, in terms of utilisation of applied limestone is very good, with 80-90% dissolving over 2.5 years [57].

Similar results to those achieved by spraying from boats have been obtained by spreading limestone on frozen lakes during the winter period. This method has the advantage that relatively cheap, agricultural machinery can be used but there are obvious geographical limitations as to where it is practical. In inaccessible areas helicopters have been used to apply lime to lakes.

Spreading limestone on the shore zone of lakes has given successful treatment in Norway (eg Hovvatn) but this approach tends to produce changes in water quality more slowly than direct application. Efficiency is also lower than direct application to the water surface, with dissolutions over 2.5 years post-treatment in the order of 50% [57].

In Rhode Island, USA, an alternative approach to lake liming is used whereby a reservoir managed as a pike-rearing facility is drained annually to harvest the fish and the lake bed is limed before refilling to counter acidity from the inflowing stream (Lapin, pers. comm.).

Because liming of lakes has no effect upon the inflowing water from the catchment, limed lakes will reacidify over a period of time as the original volume of treated water is replaced. The rate of reacidification is determined largely by the turnover period of the lake but is also influenced by the quality of tributary streams and the amount of limestone remaining on the lake bed after the initial treatment period. Models of reacidification have been produced which allow the prediction of effective treatment duration for lakes of different turnover times [103, 104].

Direct manipulation of water quality in streams is a much more complicated task than in lakes. The volume of water which needs to be treated and its quality can change significantly and rapidly, leading to problems in ensuring adequate dosing of the stream under varying flow conditions. A considerable range of methods for introducing neutralising materials to streams has evolved, from simple, manual operations to sophisticated, high-technology systems costing many thousands of pounds.

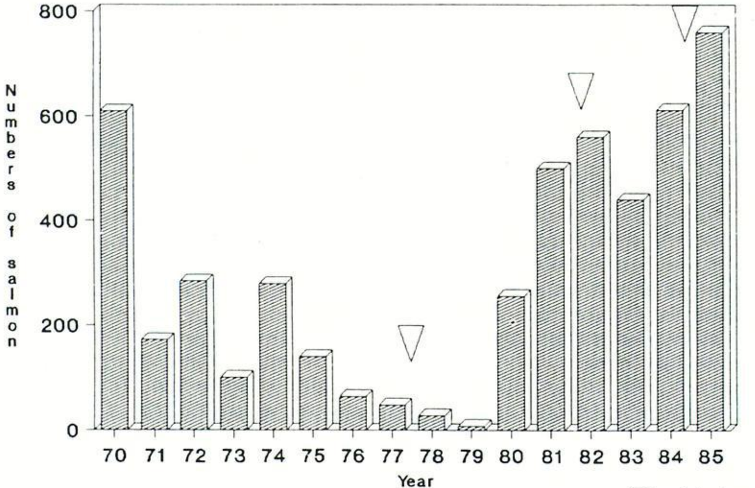
Certain river systems lend themselves to perhaps the simplest stream-liming technique which is that of treating lakes that lie on the river course, thus benefiting from established lake-liming methods. In Norway and Sweden river courses often include numerous lakes and this approach has been used successfully in these countries to protect or reinstate salmon fisheries (eg River Hogsvaden, Fig. 4). The most elementary direct stream-dosing method is the introduction of shell sand or crushed limestone to streams by hand, as practised in some parts of Norway. Dosage is determined by experience and flow response is provided by the personnel responsible undertaking liming during periods of heavy rainfall prior to river levels rising. Any undissolved material remaining in the stream bed after the initial high flow period acts as a low-level treatment during low flow conditions. In the stream, water turbulence keeps the particles of limestone in suspension, causing abrasion and producing very fine particles, thus maximising dissolution. Although this method is limited by the availability of suitable manpower it has proved effective in preserving salmonid populations in small acidified streams.

On a larger scale too, the introduction of crushed limestone direct to the stream bed has been tried as a mitigation measure. The theory of the operation is identical to the manual method described above but flow response comes from a heavy initial dose rather than repeated small introductions at times of anticipated flow increase. Tipping relatively large quantities of crushed limestone of a reasonably coarse grade ("lime sand", particle size <2.5 mm), at a single point in the stream leads to an initially limited dispersal downstream with much of the lime sand settling in areas of low water velocity or on the stream bank. When flow increases, velocity patterns change and settled particles are resuspended with rising water levels "washing-in" additional material from the banks. Turbulence and agitation during high flows prolong contact time and ensure good dissolution. Preliminary results of experiments of this type in Virginia, USA are encouraging and work to quantify chemical effects, sedimentation and downstream transport of introduced limestone are currently under way [Kauffman, pers. comm.].

Introductions of lime sand appear to be successful in streams with steep gradients and high water velocity/turbulence. Flatter gradient streams do not respond so well to this treatment as the sedimented lime sand fails to resuspend in response to increased flows. Application of this method is therefore not universal but if initial results are reliable then it may provide a reasonably economical way of treating small affected streams in the UK, especially in the Welsh uplands and Scotland.

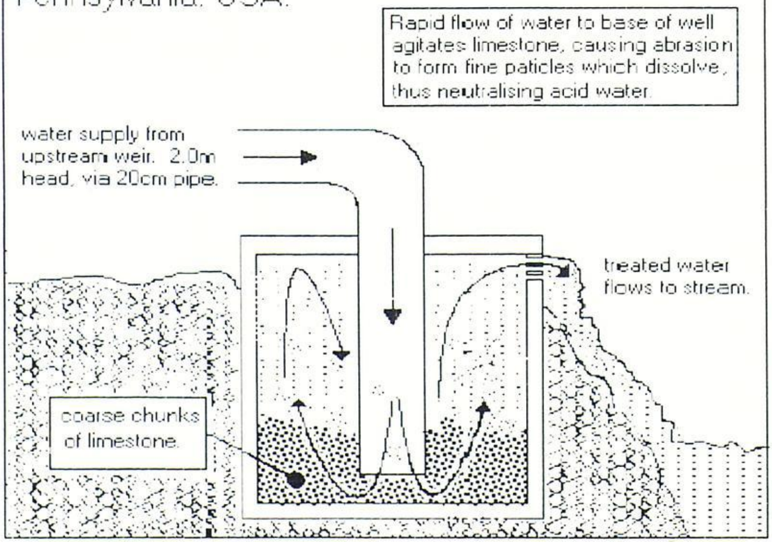
Earlier trials of depositing limestone in stream beds were less effective. Creation of artificial riffles made from limestone gravel was tried in Canada [114] but although some beneficial effects were observed at low flows there was a general failure to respond to increases in flow, mainly because of reduced contact time between the water and limestone and the reduced limestone/water volume ratio. Such failures are all the more serious as they provide little or no protection from high aluminium and low pH conditions which pertain during acid episodes occurring in flood events. Some benefit, in the form of increased survival of salmonid ova and alevins may be derived from the incorporation of limestone gravel into stream beds, as has been reported for rainbow trout and brook trout [35, 36].

Fig 4 Salmon catches from R Hogsvadsan, Sweden, before and after liming.



Drawn from data presented in [54]

Fig 5. Design of diversion well on Stony Creek, Pennsylvania, USA.


Rapid flow of water to base of well agitates limestone, causing abrasion to form fine paticles which dissolve, thus neutralising acid water.

Construction of permeable weirs or barriers from neutralising materials has been tested as a way of providing flow response, the theory being that given a barrier of sufficient height which allows the stream to flow through rather than over it, increases in water level are catered for simply by more of the barrier becoming submerged as the water rises. In Gifford Run, a headwater stream of the Mosquito Creek catchment in Pennsylvania, USA, barriers consisting of gabions filled with dolomitic limestone were installed but resulted only in a minimal and short lived effect upon water chemistry [04] with an elevation in pH from 5.3 to 5.5 for a period of only two weeks. Blocking of the barriers with leaves and coating of the limestone gravel with what was thought to be a bacterial film reduced permeability of the barrier and effective water contact. This installation may also have functioned better with the use of a different type of limestone containing a higher proportion of calcium and less magnesium.

Using a similar flow-through methodology, the Pennsylvania basket doser (Plate 4) was developed originally for use with soda-ash "briquettes" in 1985 [04]. The soda-ash was contained in a vertical basket of expanded metal mesh and gravity-fed from a hopper, the whole unit being small and easily portable with an overall height of approximately 1.5 m and a hopper capacity of 90 kg. This type of doser was designed for use in very small streams and trials in tributaries of the Mosquito Creek watershed proved successful, raising pH from 5.20 to 6.83 in the most successful trial. Unfortunately, the soda-ash briquettes dissolved too quickly to allow realistic maintenance schedules but this could be overcome by the use of larger capacity hoppers.

In 1989 further trials of the basket dosers were begun, with the substitution of limestone for soda-ash as the active ingredient in the briquettes. The limestone briquettes are composed of finely powdered limestone mixed with clay binders and compressed into pellets approximately 50 mm long by 25 mm diameter and were designed to release the limestone at a constant rate. Early results are encouraging but difficulties are being experienced with premature disintegration of the briquettes, which coalesce into a solid mass within the hopper, preventing continued dosing of the stream [Arnold, pers. comm.]. If these practical problems can be solved the basket-dosers may have a real application in the treatment of small salmonid spawning and nursery streams.

The principle of "filtering" flowing water through a neutralising substrate has also been successfully used in fish hatcheries affected by acidified supplies. As early as the 1920's acid water in Norwegian salmon hatcheries was neutralised by passing it through limestone filters [13A]. In Nova Scotia, Canada, the Mersey Atlantic salmon hatchery suffered unacceptably high mortalities amongst early-feeding fry in the late 1970's. At this time, the pH of the water supply to the hatchery facility was 4.9-5.0 and in an attempt to improve survival the manager instigated a simple water treatment programme [24]. The water supply to individual hatchery ponds was passed through a perforated box containing marble limestone chips from 6 to 10 mm in size (Plate 5). This elementary process raised the pH to 5.5-5.6, bringing it back above the threshold for high salmon mortality and fry losses were reduced from over 30% to less than 3%. The limestone boxes have been successfully used since their introduction in 1979 and are still adequate to protect the salmon fry. Their treatment capacity is limited, however, and if the water supply deteriorates further in quality then the system may fail.

Alternative methods of treating acidified flowing waters have developed along lines of varying technical complexity. Presently available options can be divided into passive and active dosing systems. Passive systems rely on water as the sole motivational force and contain no moving parts. Diversion- or lime-wells are simple treatment units of this type that have been found to function reliably in Scandinavia and the USA. Whilst there are several slightly different designs the basic principle of operation is the same (Fig. 5) and relies upon water velocity within the structure to agitate, abrade and dissolve a reservoir of neutralising material. Crushed limestone is the most commonly used material in these devices but in Norway, for example, marl (shell sand) has also been employed [06]. Individual lime wells have a degree of flow response as the volume of water passing through them is proportional to the hydrostatic head and as flow rises this will increase but where this limited flexibility is inadequate to cover the whole range of stream flows it is possible to design a system of several wells such that second and subsequent units come into operation at increasing river levels.

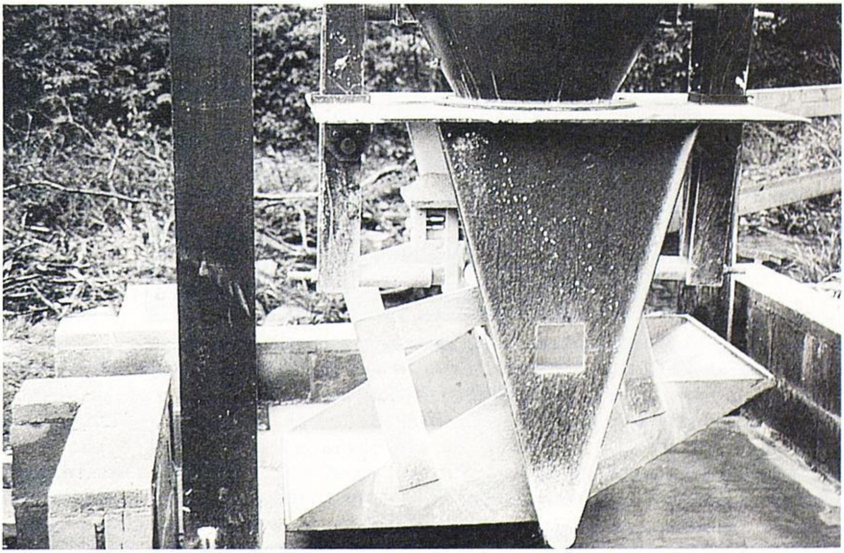
A successful example of a diversion well is in operation in Stony Creek, a tributary of the Susquehanna River, Pennyslvania (Plate 6). At this location, a combination of acid mine drainage and acid deposition had led to the extinction of local populations of brook trout but following the installation of the well in 1987, it was possible to restock with fish in 1988, when the mean pH had risen from 4.3 to 5.5 [Arnold, pers. comm.]. The Stony Creek diversion well has been found to consume approximately 1.5 tonnes of limestone per month. An interesting feature of this particular installation is that it is the result of cooperation between several federal, state and university agencies together with an input of labour and materials from the local fishing organisation, who actually maintain the well in operative order.

Active stream dosers have been constructed in several countries but most follow an original Swedish design consisting of a cylindrical hopper containing up to 25 tonnes of very finely powdered limestone which feeds through a mechanical or electrical dispensing system to the stream (Plate 7). In catchments remote from electricity supply, water power from a small weir is used to drive the lime dispensing devices, usually by means of an oscillating or tipping bucket mechanism which also mixes the lime powder with water before it enters the stream (Plate 8). As flow in the stream varies, the speed with which lime is dispensed changes accordingly and in theory the dose remains proportional to stream flow.

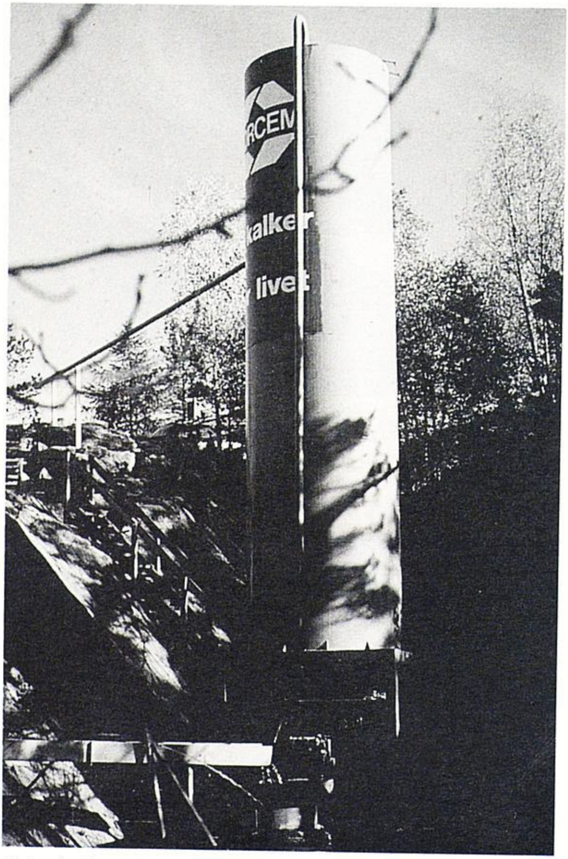
Where electricity is available there is the option of more refined systems that allow streams to be dosed only when water quality exceeds preset conditions, with sensors in the stream detecting changes in flow or pH and triggering the dosing mechanism when necessary. With these dosers it is possible to mix the limestone powder with the stream water into a slurry before delivery to the stream. This is a great aid to dissolution, especially in streams of relatively low water velocity and turbulence.

Stream dosers have been shown to be effective in improving water quality in acidified streams. In Norway, trials of various dosers demonstrated that it is possible to elevate pH by a considerable amount and to raise calcium concentrations from 0.5-1.2 mg/l to 2.0-2.5 mg/l [06], creating conditions suitable for fish to exist where they had previously become extinct. In the stream zone immediately downstream of the doser, where mixing of the treated

The Stony Creek diversion well, Pennsylvania, U.S.A.



Tipping bucket mechanism used to dispense limestone at a rate proportional to stream flow and mix it with stream water (Wolf Run, Pennsylvania, U.S.A.).



A typical stream-dosing machine which dispenses finely-powdered limestone from the cylindrical hopper via a water-powered mechanical device.

and untreated water takes place, there may be strong fluctuations in aluminium concentrations, with significant rises in labile aluminium [57]. Whilst these increases in aluminium concentration are potentially dangerous to fish they are often negated by the accompanying increased levels of calcium.

Several severe problems have attended the development of stream dosers and not all of them have yet been satisfactorily solved. The most frequent difficulty encountered is the cavitation or bridging of limestone powder within the hopper, leading to a supply failure even when many tonnes of lime remain. This is exacerbated in the damp conditions found adjacent to streams, especially during periods of sub-zero temperatures. It is not possible to by-pass this problem by using a coarser grade of limestone as the very fine particle size is essential to obtain satisfactory dissolution in the stream, but at least one Swedish manufacturer (Boxholm) has developed a mechanical agitator which keeps the lime powder mobile by striking a flexible panel in the tapered section at the base of the hopper every time the tipping bucket operates. This particular brand of doser is in this respect probably the most reliable of those presently available.

For mechanical dosers that operate continually there can be some degree of overdosing, especially in times of low flow or when water quality is better than average. Under these conditions undissolved limestone powder tends to accumulate in the stream adjacent to the doser. There are no physiological or chemical problems associated with overdosing, though, and any disadvantage is purely aesthetic. Accumulated lime may even be advantageous as it may act as an "insurance" against either doser failure or extremely sudden increases in flow by providing a reservoir of lime available for dissolution within the stream [122, 123]. There is inevitably some price to pay for any amelioration operation and if the presence of a doser can be tolerated in a scenic location, the additional visual cost of a small area of lime sediment is no great additional burden.

Climatic factors may influence the operating efficiency of powder or slurry dosing equipment during winter, a period when their successful functioning is essential to protect salmonid eggs or fry resident in the stream gravels. Water powered dosers are prone to freezing and there may also be difficulties where the stream itself freezes for prolonged periods. Electrically powered dosers are subject to the vagaries of the power supply and tend to rely more heavily on chemical sensors and supporting computer control systems which can fail unexpectedly.

One type of doser which overcomes many of the problems of reliability associated with the powder/slurry equipment has been developed and is in operation in West Virginia, USA. On Dogway Fork, a tributary of the Cranberry river, a treatment station was installed in 1983 and has since been refined and increased in efficiency. The operating principle of this station is different from that of other dosers in that it uses low-cost, crushed limestone chunks that are ground into a slurry inside rotating, water powered steel drums to produce fines with a mean particle size of <11 um at a rate of up to 15 g/sec [123, 32]. The drums are automatically fed with limestone by a storage hopper holding up to 9 tons and require servicing at approximately weekly intervals. Flow response in this system is provided by variation in drum rotation speed and grinding efficiency as a result of changes in water velocity and on a larger scale by the cutting in of a second and potentially a third drum at flows above a certain level, ensuring that a consistent proportion of the stream flow is treated.

The treatment efficiency of the Dogway Fork drum installation is high, with pH of the stream raised from 4.4-5.5 to 7.0-8.9 a short distance below the installation with satisfactory treatment extending over a stream length of 13 km and a flow range of 0.14 to 1.2 cumecs. The unit operates successfully in periods of low temperature and has performed satisfactorily down to -33°C [123]. Brook trout populations previously lost from this stretch of stream have been re-established over the operating period of the drum dosing installation and the fishery is to be opened for angling in the near future.

Because of its relatively high degree of mechanical sophistication the Dogway Fork drum doser was expensive to build and install, costing slightly in excess of $300,000 at 1988 prices but annual operating costs are low, in the region of $5,500 for limestone plus manpower costs. The high capital investment required for an installation of this type is therefore offset by low recurrent costs and over an extended period of 20 years or so a drum doser system may well be the most cost-effective option for river treatment.

Reinstatement of valued sport fisheries lost through acidification can be used as a source of revenue to support mitigation programmes. In the case of the Dogway Fork treatment station, for example, it is estimated that in excess of 20,000 angler-days per year will become available on the treated stretch of river and that they will generate a major part of the operating costs of the installation [Zurbuch, pers. comm.].

Recovering costs from the ultimate beneficiaries is not always practicable, however, as the parts of the river system that are afflicted by acidification are not necessarily the stretches where exploitation of the resource takes place. On the River Severn, UK, the commercial and sport fisheries for Atlantic salmon are located in the estuary and in the main river and larger tributaries, respectively, whilst they are maintained by spawning and nursery areas in unfished headwaters and upland tributaries, some of which appear to be at risk from acidification. It would be very difficult, given the fishery ownership and licensing system of England and Wales, to impose an additional charge upon those fishermen who may ultimately derive benefit from any liming carried out to protect the salmon resource.

5.2.4 Alternatives to mitigation by liming

In some instances the mitigation of acidification by a liming strategy cannot be justified on ecological, political or economic grounds. Reinstatement of lost and declining salmon fisheries in the Southern Uplands of Nova Scotia, for example, by means of a comprehensive liming programme had an estimated cost of approximately $400 per fish landed, compared to an actual value of less than $100 per fish [114]. Where such conditions pertain there are some options available which may allow the effects of acidification to be limited without recourse to water quality manipulation.

The commercial and sport fisheries for Atlantic salmon in the River Severn (UK) are supported by natural spawning in the upper reaches of the main river and its tributaries. Whilst some of the more important spawning and nursery streams are currently considered to be under threat from acidification, many others are not endangered in this way but are simply inaccessible to migrating adults. Somewhere in the region of 40% of potentially suitable spawning habitat in the Severn catchment is unavailable to salmon because of man-made physical obstructions to migration. Smolt production lost through acidification of sensitive streams could feasibly be compensated for or even exceeded by opening up these unacidified but inaccessible areas by the installation of fish pass facilities.

A similar compensatory approach is to improve existing spawning and nursery habitat physically, rather than chemically, to allow increased recruitment to the dependent fishery and the techniques for this type of work are well established [eg 98]. Maximum benefit from habitat improvement would be derived in non-acidified catchments but could counter production loss in other parts of the catchment which were affected.

In lakes where fisheries are in decline through failure of recruitment due to acidification of inflowing spawning streams, stocking with takeable fish can prolong the fishery's life. However, once the fishery has become dependent upon stocking it has become artificial to a large degree and may have lost much of its original value, as well as having become a temporary resource. Where recreational fisheries are locally important, though, maintenance by stocking is likely to be more economically viable than catchment or stream liming.

Introductions of different species may also prolong the useful life of lake or stream fisheries in some cases. Amongst the salmonids commonly providing sport fisheries there is a range of acid-tolerance, with some species of char, eg the brook trout (*Salvelinus fontinalis*) being significantly better able to withstand acid conditions than the brown trout. Replacement of sensitive with resistant species may allow a self-sustaining fishery to continue for longer than would otherwise be the case.

Variations in acid tolerance are also found within single species of fish, although these are not so great as between-species differences, and relocation of naturally occurring resistant strains may be feasible. Similarly, the production of resistant fish by selective breeding of hatchery stock may be possible in the future as to some extent acid tolerance may be genetically controlled and therefore heritable [eg 66].

The various alternatives to chemical manipulation of water quality are in some cases feasible ways to protect individual fisheries but cannot be considered as general solutions to the problems of acidification. Rather, they are a form of compensation and are limited in scope and applicability. They are unlikely to make a major impact upon the overall situation.

6 FUTURE PROSPECTS FOR FISHERIES IN ACIDIFIED CATCHMENTS

The recent years of intensive study of the causes and mechanisms of and possible solutions to the problem of surface water acidification mean that the future for freshwater ecosystems in areas receiving acid precipitation may be an optimistic one. Whilst the various mitigation strategies available are to varying degrees effective, it cannot be overemphasised that they are no more than temporary devices which may protect and maintain threatened resources until the real solution is realised. Nevertheless, mitigation has a vital role to play in the short and medium term future and this has been recognised by a few countries which have implemented coordinated schemes of operational lake and river liming, financed partly or entirely by government funds eg Sweden [67] and Norway [89].

Continuation of the academic and applied research into the nature of acidification and possible ways of countering its effects is essential to the future of the ecology and fisheries in acidified waters but may not be assured in the current political and financial atmosphere. As in any other field of activity which does not produce a saleable commodity, research relies upon external funding which is influenced by many factors. In the USA, 1990 marks the end of the 10 year programme of investigation (NAPAP) of acid precipitation, with official funding ceasing as from 1991. Although much progress has been made during the life of NAPAP the puzzle is by no means solved but workers in the field are of the opinion that the new and very high profile research area of global warming/ozone depletion may well divert vital funding away from the acidification arena. Elsewhere, the situation is similar with acid rain suffering from being an increasingly "old" problem and hence less likely to attract research investment than previously.

Perhaps the most encouraging recent development has been the growing international accord to tackle the problem at its roots by making realistic attempts to drastically reduce emissions of contaminants into the atmosphere. Progress along this avenue has already been made but even greater achievements are the only way to eliminate the ecological desecration that results from the acidification of freshwaters.

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APPENDIX 1 ITINERARY FOR 1989/90 BENSINGER-LIDDELL TRAVELLING FELLOWSHIP

Dates	Facility to be Visited	Contact	Study Topic
8/10/89	Fly London/Oslo		
9-10/10/89	NEVA, Oslo and area	B O Rosseland and colleagues	Stream and lake liming techniques
11-12/10/89	NINA, Trondheim	L Hansen and colleagues	Liming techniques and admin
13/10/89	Bergen University	P MacWilliams	Mitigation in salmon hatcheries
15/10/89	Fly Oslo/London		
17/10/89	Fly London/New York		
18/10/89	Orientation and confirmation of US itinerary		
19-20/10/89	Rhode Island Division of Fish and Wildlife	W J Lapin	Marsh/lake liming for pike production
21-22/10/89	Travel to New York State		
23/10/89	New York State Dept Environmental Conservation	H A Simonin	Adirondak lakes/stream liming
24/10/89	Syracuse University, New York State	C T Driscoll	Aluminium speciation and modelling
24-25/10/89	Adirondak Lakes Survey Commission, NY	W A Kretser and colleagues	Headwater stream monitoring programme
26/10/89	Travel to Orono, Maine		
27/10/89	US Fish and Wildlife Zoological Dept, University of Maine	Dr T A Haines and colleagues	Acidification research in New England States

APPENDIX 1 (Contd)

Dates	Facility to be Visited	Contact	Study Topic
28-29/10/89	Rest day and travel to St Andrews, New Brunswick		
30-31/10/89	St Andrews Biol Station, New Brunswick	Dr G Lacroix	Stream acidification/liming strategies
1-2/11/89	Fisheries and Oceans, Halifax, Nova Scotia	Dr Farmer, W J White	Acidification/salmon physiology, experimental liming of streams
3/11/89	Mersey Fish Culture Station, Nova Scotia, also McGowan Lake Hatchery	T Goff	Hatchery water treatment
4-5/11/89	Rest day and travel to Pennsylvania		
6-8/11/89	Cooperative Fisheries Unit, Penn State University	Dr D Arnold and colleagues	Field trials of lime dosers admin and economics
9/11/89	Travel to Virginia		
10/11/89	Dept Game and Inland Fisheries, Charlottesville, VA	J Kauffman	Little Stoney Creek liming project
11-12/11/89	Rest day, travel to W Virginia also visit National Fisheries Research Centre, Kearneysville	K Schreiber	General discussions re national approach to acidification
13-14/11/89	State Dept Natural Resources, Elkins, WV	P E Zurbuch	Stream neutralisation projects
15/11/89	Pittsburgh, Pennsylvania	P E Zurbuch, R Menendez	Attend conference on acid deposition in mid Atlantic states, USEPA
15-16/11/89	Return Pittsburgh/Washington		
16-17/11/89	Fly Washington/New York Fly New York/London		

APPENDIX 2

SOME OF THE MAJOR RESEARCH PROJECTS CARRIED OUT IN RECENT YEARS TO DETERMINE THE EXTENT AND EFFECTS OF SURFACE WATER ACIDIFICATION

Date	Country	Outline of Work	Major Findings	References
1979	USA (Pennyslvania)	Survey of chemical and fisheries status of streams in the state.	60% of streams surveyed showed decline in species diversity which was associated with chemical degradation typifying acidification effects. 15% of watersheds devoid of fish life. Estimates of loss of fishing valued at 50-125 million dollars per annum.	[03]
1983	USA (New England)	Survey of streams and lakes in six New England states.	8% waters found to have pH <5.0, 29% with pH <6.0. Lakes contained high sulphate concentrations. Over half of waters considered to have become acidified.	[37]

APPENDIX 2 (Contd)

Date	Country	Outline of Work	Major Findings	References
1984	USA (New England)	Assessment of water quality in salmon rivers in the six New England states.	Water quality not yet critical in high order streams but approaching critical in first order streams comprising 20-40% available habitat.	[38]
1983-1986	USA	National Surface Water Survey; a chemical survey of waters thought to be at risk from acidification covering lakes and streams. Stratified sampling programmes allowed extrapolation to target populations of water bodies.	Acid waters concentrated in six areas, mostly in NE USA; 4.2% of lake target population acidic and 2.7% of streams; relationship found between SO_4 in deposition and surface waters, causative link suggested; in affected areas, up to 80% of lakes and 50% of streams considered at risk.	[08]

APPENDIX 2 (Contd)

Date	Country	Outline of Work	Major Findings	References
1984-1986	USA (NY State)	Adirondack Lakes Survey Corporation surveyed chemical status of 1250 lakes in Adirondack mountains.	Over 200 lakes had become acidic over a relatively short timespan. Survey now extended to include streams as well as lakes.	[01]
1986	Norway	Norwegian State Pollution Control Authority carry out a chemical survey of 1000 lakes throughout the country.	70% of lakes surveyed found to be acidic, 40% with pH <5.0. Location of acid lakes coincided with areas receiving acidic deposition, SO_4 concentrations decreased over preceding decade in southern part of country.	[79]

APPENDIX 2 (Contd)

Date	Country	Outline of Work	Major Findings	References
1988	Norway	Survey of fish population status in the same 1000 lakes covered in chemical survey above.	In worst areas (south and west of country) 70% of fish populations extinct. Fish losses correlated to pH and aluminium in water. Overall 52% of lakes contained damaged or threatened fish stocks.	[80]
1984	Sweden	Chemical and biological sampling of 4000 lakes and streams across the country.	Results of survey extrapolated to whole water resource suggest 90,000 km of streams and 20,000 lakes have become acidified. Most severe damage found in southwestern part of country.	[02]

APPENDIX 2 (Contd)

Date	Country	Outline of Work	Major Findings	References
1983-1985 and to present	UK (Wales)	Survey of deposition and surface water quality and biological status of 120 streams. Intensive work on selected catchments continues, especially with regard to the involvement of forestry in the acidification complex.	Relationships between precipitation geology and land use identified. Role of emissions elucidated and models developed to predict effects of changing emission scenarios. Forestry recognised as accelerator of acidification.	[19]
1983	UK	Survey of deposition chemistry at 38 sites across England, Scotland and Wales.	Acidity of rainfall found to increase from west to east, most acidic precipitation in east Midlands.	[108]

APPENDIX 2 (Contd)

Date	Country	Outline of Work	Major Findings	References
1986	Finland	Prediction of sensitive areas from geological information and comparison with water quality in 8900 lakes.	Acidified lakes found mainly in sensitive areas. Extent of acidification in Finland not great at present.	[59]
1988	Canada	Chemical survey of aboriginal Atlantic salmon rivers in Canada representing 950 km^2 of riverine habitat.	107 km^2 of habitat considered vulnerable to acidification, 6.0 km^2 no longer suitable for salmon (all in Nova Scotia).	summarised i [54]
1985-89	UK Norway Sweden	Surface water acidification programme (SWAP) funded by GECB and British Coal		Final report now available

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