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THE ENVIRONMENTAL IMPACT OF ACID MINE DRAINAGE

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EXECUTIVE SUMMARY

Acid mine drainage (AMD) is a multi-factor pollutant. It affects aquatic ecosystems via a number of direct and indirect pathways. Major impact areas are coastal waters, rivers, lakes, and estuaries, although AMD affects different aquatic ecosystems in different ways. Due to its complexity, the impact of AMD is particularly difficult to quantify and predict in lotic systems. Acid mine drainage pollution can be split into a number of major impact categories. These are (a) metal toxicity, (b) sedimentation processes, (c) acidity, and (d) salinization.

The impact of AMD is very difficult to predict due to the variability of the rate of discharge from adits, seasonal variation in adit strength and composition, the effect of surface runoff from exposed areas of the mines during heavy rainfall, and the effect of the catchment discharge characteristics which affects both dilution and the concentration of organic matter in the water. Assessment is difficult due to the complexity of the impacts, although diversity and abundance are key variables for biotic evaluation. Fish movement and migration are also useful indicators.

Acid mine drainage systems may be so complex that no useful information can be obtained from attempting to model them. A simpler approach, concentrating on the major interactions (e.g. toxicity of key metals or the degree of substrate modification caused by iron precipitation which is directly linked to pH), may prove to be more useful in understanding AMD impacts and predicting effects.

CONTENTS

1. ACID MINE DRAINAGE

Over the past two decades there has been an increase in public awareness of the potential hazards that exist from the contamination of the mining industry. Although any mineral deposit which contains sulphide is a potential source of acid mine drainage, certain types of mining are more prone than others. There are records of acid drainage where coal, pyritic sulphur, copper, zinc, silver and lead amongst others have been mined (Barton, 1978). Coals and shales of marine origin tend to contain higher concentrations of sulphide than strata from freshwater palaeoenvironments (Eddlemon and Tolbert 1983). Some of the more important sulphide minerals are listed below, with those that occur in the Avoca region in bold print.

Mineral	Composition
Arsenopyrite	$FeS_2.FeAs$
Bornite	$CuFeS_4$
Chalcocite	Cu_2S
Chalcopyrite	**$CuFeS_2$**
Covellite	CuS
Galena	**PbS**
Millerite	NiS
Mobybdenite	MoS_2
Pyrite	**FeS_2**
Pyrrhdite	$Fe_{11}S_{12}$
Sphalerite	**ZnS**

Chemically pyrite, the most important mineral, is iron disulphide (FeS_2). Its breakdown is affected by variations in its morphology such as crystallinity and particle size, as well as its reactivity. Crystalline forms in particular are less subject to weathering and oxidation than amorphic forms (Riley, 1960; Barnes and Romberger, 1968). The reactions involved in the breakdown of pyrite in the presence of water and oxygen to yield sulphuric acid are well known (Singer and Strumm, 1970).

$FeS_2 + {}^7/_2O_2 + H_2O$	---->	$Fe^{2+} + 2SO_4{}^{2+} + 2H^+$	(1)
$Fe^{2+} + {}^1/_4\ O_2 + H^+$	---->	$Fe^{3+} + {}^1/_2\ H_2O$	(2)
$Fe^{3+} + 3H_2O$	---->	$Fe(OH)_2 + 3H^+$	(3)
$FeS_2 + 14Fe^{3+} + H_2O$	---->	$12Fe^{2+} + 2SO_4{}^{2+} + 16H^+$	(4)

Whilst there are a few cases of naturally occurring acid streams, most occur as a result of mining activities. Pyrites can remain in their reduced state in undisturbed strata so long as they are anaerobic.

The rate limiting step is the oxidation of the ferrous iron (Singer and Strumm, 1970) . There is a propagation cycle between reactions (2) and (4) where Fe^{3+}, one of the products of reaction (2), acts as an oxidant of the pyrite in reaction (4) and Fe^{2+} produced by this reaction can be used as a reductant in reaction (2). As the process is limited by the oxidation of pyrite, the surface area available for oxidation determines the rate of the reaction (Gottschlich *et al.,* 1986).

2. ENVIRONMENTAL IMPACT OF ACID MINE DRAINAGE

Acid mine drainage affects lotic systems via a number of direct and indirect routes. The overall effect on community structure is the elimination of species, simplification of the food chain, resulting in a significant reduction of ecological stability. Effects can be loosely categorized as chemical, physical, biological or ecological (Fig. 1).

AMD

Chemical	Physical	Biological	Ecological
Increased acidity	Substrate modification	Behavioural	Habitat modification
Reduction in pH	Increase in stream velocity	Respiratory	Niche loss
Destruction of bicarbonate buffering system	Turbidity	Reproduction	Bioaccumulation within food chain
Increase in soluble metal concentrations	Sedimentation	Osmoregulation	Loss of food source or prey
Increase in particulate metals	Adsorption of metals onto sediment	Acute and chronic toxicity	Elimination of sensitive species
	Reduction in turbulance due to sedimentation increasing laminar flow	Death of sensitive species	Reduction in primary productivity
	Decrease in light penetration	Acid-base balance failure in organisms	Food chain modification
		Migration or avoidance	

Fig. 1. Summary of the major effects of AMD on a lotic system

Acid mine drainage is recognised as a multi-factor pollutant and the importance of each factor varies within and between affected systems. The main factors are the acidity itself, salinisation, metal toxicity and sedimentation processes. These are dealt with in Section 3, while the biological and ecological inputs are examined in Section 4.

3. PHYSICO-CHEMICAL IMPACT

Acidity

The pH is an intensity factor measuring the log of hydrogen ion concentration. In acid mine drainage situations both the concentration and the availability of hydrogen ions to neutralise bases up to pH 8.3 are significant i.e. the excess of H^+ over other ions. This quantity is referred to as total acidity and appears to be the key to understanding the differences between acid mine drainage and other acid ecosystems. A broad indication of the nature of different acid waters is given in Table 1.

Extreme acid mine drainage characteristically has high total acidity and high conductivity. When this is diluted by streams in the catchment the water quality can come to resemble soft, low-acidity waters affected by acid precipitation. Once destroyed, the alkalinity of a water body may take some time to recover even if no further acid is added to the system. In once instance a stream took three and a half months to recover its bicarbonate buffering system following a pulse of acidity from a mine (Parsons, 1977). The rate of recovery was dependent upon the rate at which sources of alkalinity from the catchment could replenish the stream.

Flocculation of silt and clay is increased at low pH which may result in an increase in their rate of precipitation, resulting in water of low turbidity (Dills and Rogers, 1974). This may be offset by the iron (III) precipitate formed when the iron (II) salts in solution are neutralised.

Table 1. Comparison of waters receiving acid mine drainage, acid rain and peat drainage. Acidity is given in mg/l $CaCO_3$ conductivity in μScm/1 (Kelly, 1988).

Type of Water	Acid mine Drainage	Acid Precipitation	Peat Drainage
Source of acid	Oxidation of pyrites	Atmospheric sulphurous and nitrous oxides	Polyuronic acids in cell wall of *Sphagnum*
Main acids present	H_2SO_4	H_2SO_4 and HNO_3	COOH groups in polysaccharides
pH	1.5 - 3.0	4.0 - 5.7	3.2 - 6.0
Acidity	110-64,000	2.00-4.21	0.56 - 0.82
Conductivity	600-30,000	<50	<100

A more general geochemical effect is an increased rate of decomposition of clay minerals, feldspars and carbonates. Elements released by this process include toxic metals. As the acidity from acid mine drainage tends to dissolve minerals as it runs over them, it is usually associated with hard water. The mean values of calcium from different studies includes 416 mg/l (Barton, 1978) and 269 mg/l (Hargreaves *et al.,* 1975). Some deleterious effects on the biota may occur because of the hardness of the water but such effects are very difficult to separate from the other problems associated with acid mine drainage.

The effects of acid on the biota result in a general malaise, termed 'acidaemia' by Warner (1971), which can completely kill organisms. Specific physiological effects include an upset of the ionic balance across organism membranes and hydrolysing or denaturing of cellular components, especially where these are exposed to the environment (Carlson-Gunoe *et al.,* 1983). There may be a general loss of plants, in particular macrophytes, that use bicarbonate as their inorganic source resulting in a reduction in primary productivity. Calcium carbonate in the shells of molluscs and some crustaceans is likely to be dissolved. The reduction in habitats and species diversity cause a simplification of the food chain (Fig. 2).

The influence of external pH has been examined closely as part of the study of the effects of acid rain (Vangenechten *et al.* 1989). Acid-base effects on fish are both direct and indirect. Direct effects result from the actual H^+ permeability of the external surfaces, especially the gills, and the relationship between internal and external [HCO_3]. At pH values much below pH 6.0, there is virtually no HCO_3 present, and at pH 4.0, the H^+ gradient between blood and water is more than 1000:1 (Cameron, 1989). Indirect effects may result in increased permeability to various other strong ions and internal imbalances of these ions will often result in changes in the acid-base status. Extreme imbalance in acid-base status can lead to death of species, thereby modifying the food chain.

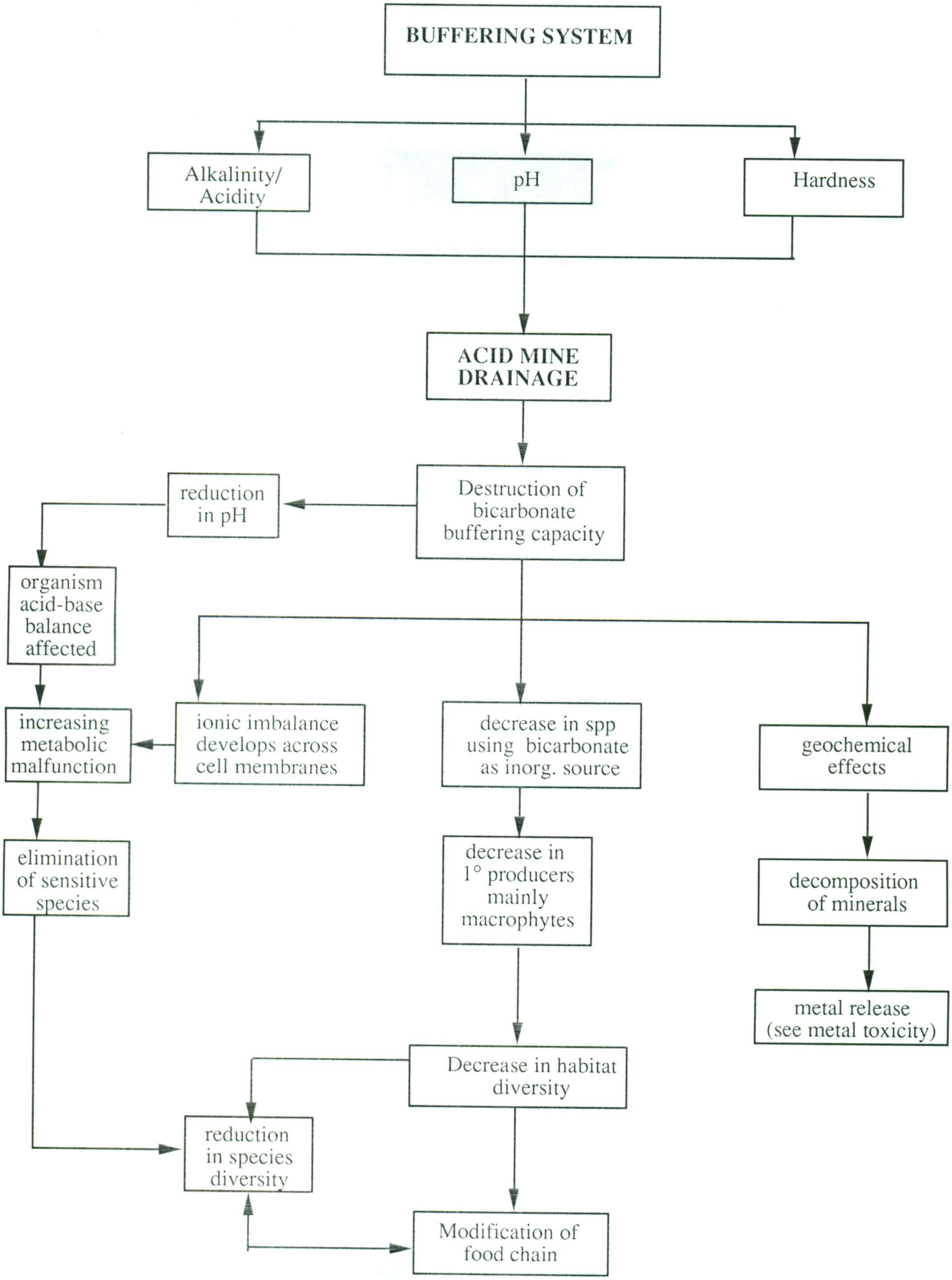

Fig. 2. Impact of acidity arising from AMD on lotic systems.

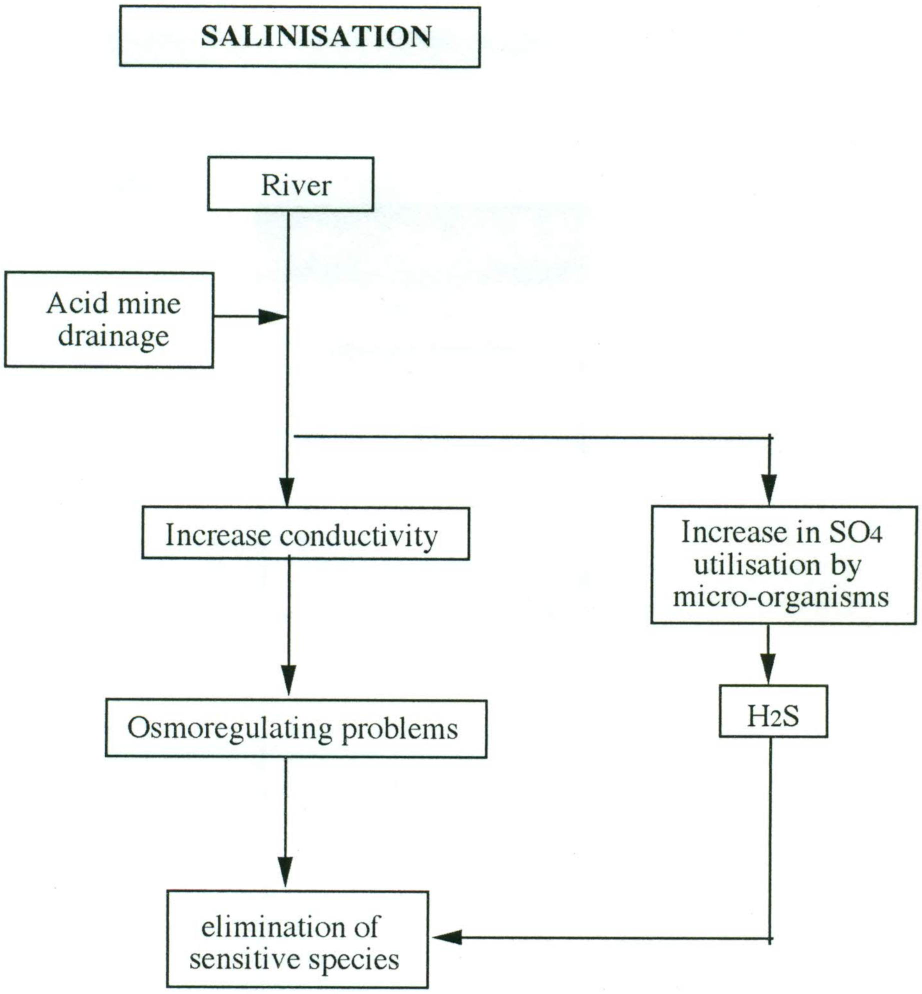

Fig. 3. Impact of salinization arising from AMD on lotic systems.

Salinisation

The high conductivity characteristic of acid mine drainage is due to the presence of high concentrations of metal salts and sulphate (Kelly, 1988; Gray, 1995). These extreme concentrations and resultant high conductivity values can cause osmoregulatory complications in organisms, eliminating sensitive species (Fig. 3). The interest in sulphide arises because of its toxicity and also the odour problem associated with the presence of the undissociated hydrogen sulphide (H_2S) produced by anaerobic reduction of the sulphate. There is an equilibrium between the dissociated and undissociated H_2S forms which are dependent on pH. Hydrogen sulphide has a significant affect on aquatic life and a concentration not exceeding 2μg/l is recommended for the protection of fish and aquatic life in freshwater (USEPA, 1979).

Metal toxicity

The major types of toxic pollutants have been divided into two Categories under the EU Dangerous Substances Directive. List I (or black list) contains the most dangerous toxic compounds such as organohalogens, mercury, cadmium, while List II (or grey list) contain the less dangerous substances such as. copper, zinc, lead (Mason, 1991).

Some metal ions have low toxicity while others are toxic to a wide range of organisms at very low concentrations. Metals have been arranged in descending order of toxicity based on the ease with which they pass into solution as positively charged ions or the ease with which metal ions in solution give up their charge to combine with other ions or compounds. In general the most important metals from the point of view of water pollution may be listed in order of decreasing toxicity as follows: Hg, Cd, Cu, Zn, Ni, Pb, Cr, Al and Co (Abel, 1989).

Metals occur naturally, but large-scale release to the aquatic environment requires human intervention. Industrial processes, particularly those concerned with mining, are the main source of heavy metal pollution in aquatic ecosystems (Abel, 1989). Heavy metals which have been found at high concentrations in acid waters include copper, zinc and lead (Hargreaves *et al.,* 1975; Barton 1978). Some of these metals (e.g. copper, zinc, thallium, selenium, etc.) are essential trace elements to living organisms, but become toxic at higher concentrations.

Table 2 List I and II substances specified in the EU Dangerous Substances Directive (76/464/EEC). Highlighted metals are found at elevated concentrations in the Avoca district. Those underlined are also problematic at Avoca, but secondary.

List I (black) substances

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment
2. Organophosphorus compounds
3. Organotin compounds
4. Substances, the carcinogenic activity of which is exhibited in or by the aquatic environment (substances in the Grey List which are carcinogenic are included here)
5. Mercury and its compounds
6. Cadmium and its compounds
7. Persistent mineral oils and hydrocarbons of petroleum
8. Persistent synthetic substances

List II (grey) substances

1. The following metalloids/metals and their compounds

1. **Zinc**	2. **Copper**	3. Nickel	4. Chromium
5. **Lead**	6. Selenium	7. Arsenic	8. Antimony
9. Molybdenum	10. Titanium	11. Tin	12. Barium
13. Beryllium	14. Boron	15. Uranium	16. Vanadium
17. Cobalt	18. Thallium	19. Tellurium	20. Silver

2. Biocides and their derivatives not appearing in the Black List
3. Substances which have a deleterious effect on the taste and/or smell of products for human consumption derived from the aquatic environment and compounds liable to give rise to such substances in water.
4. Toxic or persistent organic compounds of silicon and substances which may give rise to such compounds in water, excluding those which are biologically harmless or are rapidly converted in water to harmless substances.
5. Inorganic compounds of phosphorus and elemental phosphorus
6. Non-persistent mineral oils and hydrocarbons of petroleum origin.
7. Cyanides, fluorides.
8. Certain substances which may have adverse effect on the oxygen balance, particularly **ammonia** and nitrites.

A decline in pH is normally accompanied by an increase in the solubility of metals, giving rise to very high aqueous concentrations. It also results in changes in metal partitioning with less adsorbed onto suspended particulate material and sediment.

Heavy metals affect aquatic ecosystems via a number of direct or indirect pathways (Fig. 4). Direct toxic effects occur at different trophic levels: sensitive heterotrophs, periphyton, plant species, invertebrates and fish.

This gives rise to a decline in primary producers resulting in diminished numbers of herbivores and grazers. The overall reduction in species diversity results in modification of the food chain particularly at the higher trophic levels.

Indirect effects occur as a result of biomagnification or bioaccumulation. With biomagnification there are progressively greater amounts of heavy metals along the food chain, carnivores containing greater concentrations than herbivores, which contain more than plants. Bioaccumulation results from the uptake of elements from the water and is independent of trophic level. The rate of accumulation depends on factors both external and internal to the organism. Many species develop a certain level of tolerance. Some species may exhibit modified behaviour or reproduction problems. Sensitive species may be lost with consumers and predators eliminated. Indirect effects also cause a reduction in species diversity and a modification of the food chain (Fig. 4).

Analysis of water for heavy metals is complicated by the often low concentrations of elements involved and the consequent sophistication of the techniques required. Additional complications are caused by the variable composition of water (e.g. water hardness and pH) and the form of the metal measured. Speciation of a metal at its simplest distinguishes between filterable and particulate fractions. The speciation rather than the total concentration of the metal is the key to understanding its effect on the biota. A number of studies of the aquatic chemistry of metals have considered the detailed chemical speciation of metals in water, but in practice such techniques are not transferable to routine monitoring at present. Therefore the normal operational separation of metal distinguishes between that which will or will not pass through a 0.45 μm filter. These are equated with dissolved and particulate metal respectively.

Sedimentation processes

Virtually all effluents contain suspended matter, particularly those associated with mining (Abel, 1989). Suspended matter may be organic or inert and some forms are chemically reactive, such as ferric hydroxide precipitate. The orange flocs of iron (III) (ferric) precipitate (ochre)

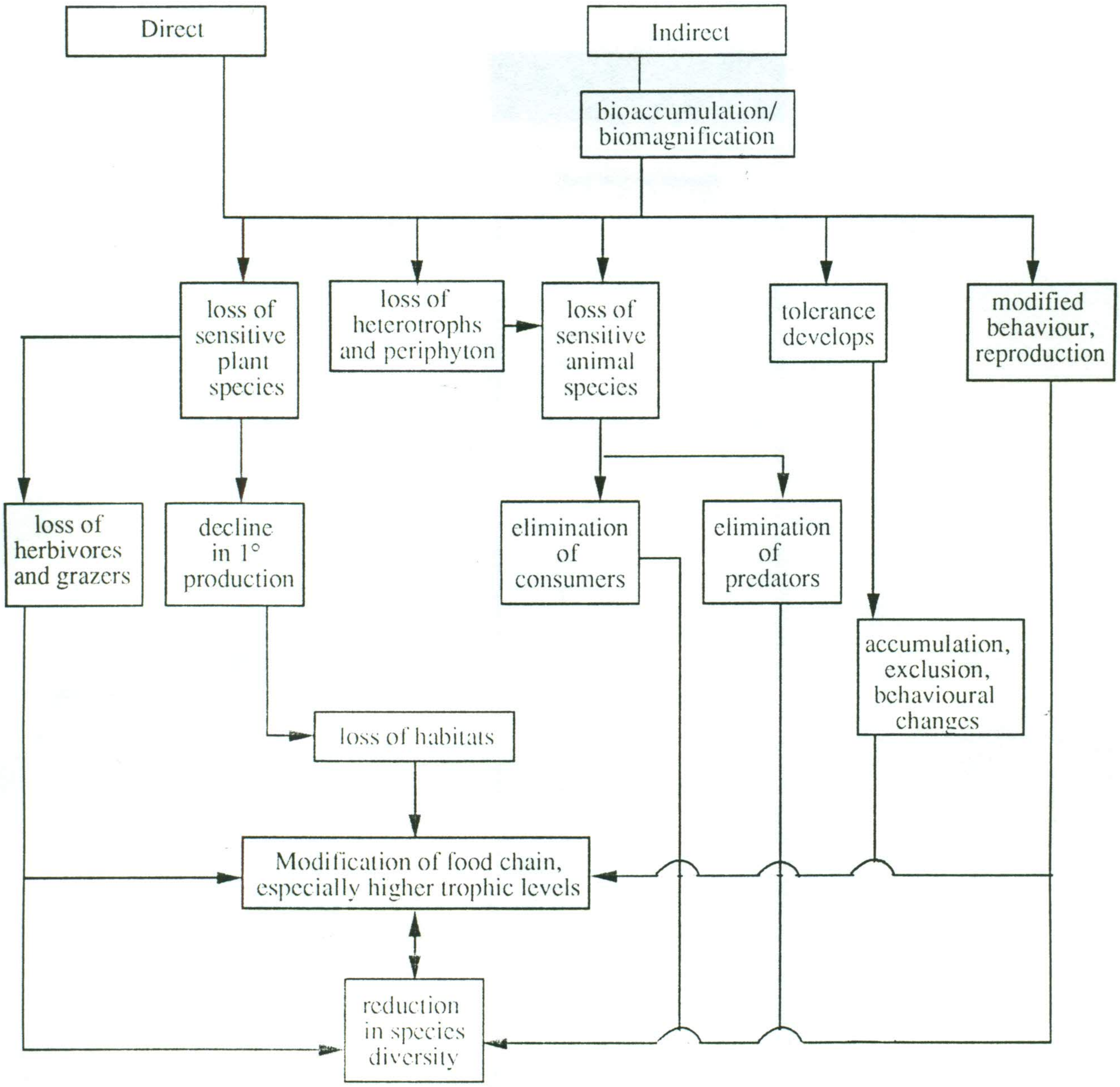

Fig. 4. Impact of heavy metals arising from AMD on lotic systems.

associated with acid mine drainage are composed predominantly of iron (III) hydroxide ($Fe(OH)_3$) resulting from the oxidation of pyrite. The flocs are complex and can contain a number of iron (III) oxyhydroxide hydrates such as $Fe(OH)_3(H_2O)_3$, partially hydrolysed forms (Clarke and Cranshaw, 1979), and iron (III) hydroxysulphate complexes - $Fe(OH)(SO)_4$ (Dugan, 1975). To precipitate metal ions as hydroxides a great deal of neutralisation is often necessary (Table 3).

Table 3. Minimum pH values for complete precipitation of metal ions as hydroxides or other salts (Eyres and Pugh-Thomas, 1978).

Metal	Minimum pH - hydroxides	Minimum pH - other salts
Fe(III)	4.3	
Al	5.2	
Pb (II)	6.3	6.0
Cu (II)	7.2	5.3
Zn	8.4	7.0
Fe (II)	9.5	
Mn (II)	10.6	

Precipitation or adsorption causes the loss of metal ions from solution, especially when the iron (III) flocs are present. The extent of adsorption is dependent upon pH. This was observed in a Cornish river receiving acid mine drainage where the ratio of bound-to-free copper and zinc increased as the pH rose (Johnson and Thornton, 1987). Such relationships can lead to increased concentrations of metals in the sediments as the pH rises (Lampkin and Sommerfield, 1986; Herr and Gray, 1995). A subsequent drop in pH can lead to the release of metals from the oxides (Tipping *et al.,* 1986). This can occur when a pulse of more acid water flows down a stream releasing metals which are bound in sediments with potentially deleterious effects on the biota (Eyres and Pugh-Thomas, 1978). Some soft rivers in mountainous peaty soils are subject to quite wide natural variations in pH.

Flocs form as the acid mine drainage becomes neutralised. At very low pHs the metal ions are soluble but as the pH rises some begin to precipitate out. A pH of about 4.3 is critical for iron (III). Flocs have been noted at low pH values but these were probably formed when the pH was higher (Koryak *et al.,* 1972).

If conditions are favourable for the oxidation of pyrites and neutralisation of the AMD, deposition of floc may take place close to the outflow from the mine. In other cases it may not occur until much further downstream or where the acid stream joins a less acid river which can dilute the acidity and trigger the deposition of the floc. For example, in Japan no iron (III) precipitate was found in the River Aka 3 km below a mine discharging severe acid mine drainage (Noike *et al,* 1983).

When the pH rises, the iron (III) salts come out of solution to form colloids suspended in the water, fine suspended precipitates or heavier amorphous flocs. All of these can have severe direct or indirect effects on the biota. Direct effects result in an overall loss of habitat and species diversity and in modification of the food chain. They include physical abrasion of body surfaces (Eddlemon and Tolbert, 1983), particularly delicate structures such as gills. Physical damage of this kind interferes with respiration and renders the animals susceptible to infections (Abel, 1989). High levels of precipitates may interfere with the filter-feeding mechanism of invertebrates, and possibly with the feeding of fish by impairing their vision. Many species deliberately avoid, or are eliminated from, areas contaminated with high precipitates or suspended solids. Salmonid fishes require aerated gravel beds for egg-laying sites, and the silting of gravel beds can eliminate salmonid populations by depriving the fish of suitable nest sites. Alabaster and Lloyd (1980) suggest waters containing more than 80 mg/l suspended solids are unlikely to support good fisheries.

Indirect effects are mainly due to increased turbidity and the blanketing effect of particulates when they eventually settle. In suspension the flocs reduce or prevent light penetration and so interfere with photosynthesis. This can result in a reduction in primary productivity or the complete elimination of plants with a resultant loss of herbivores and grazers. When the ferric precipitate settles out it can encrust rocks and stones cementing them together, smothering all the benthic biota, filling the interstices between stones and settling to give a deep layer of enveloping deposit (Lackey 1938; Hynes, 1960). The modification of the habitat and the direct or indirect toxicity of the sediment cause a reduction in species diversity resulting in further modification in the food chain (Fig 5).

4. BIOLOGICAL AND ECOLOGICAL IMPACT

Bacteria

Specialised communities of acidophilic micro-organisms, algae and bacteria, thrive in many of the hostile, low pH effluent environments, which are otherwise devoid of life. Bacteria which are able to utilise pyrites as an energy source act as catalysts, and can increase the rate of oxidation by up to one million times (Singer & Strumm, 1970). The most numerous bacteria in acid mine waters are the chemo-autotrophs, those which oxidise sulphur (*Thiobacillus thio-oxidans*) and iron (*Thiobacillus ferro-oxidans*), with densities as high as 10^9 mg/l in acid mine drainage. Walsh (1978) reported that iron-oxidising *Metallogenium* are active in mine waters of between pH 3.5 and 4.5 and create the lower acidic conditions (below 3.5) suitable for the functioning of *Thiobacillus ferro-oxidans*. At a pH greater than 5.0 iron oxidation proceeds rapidly without the need for biological catalysis.

Bacteria use three basic methods to dissolve metals into solution: indirect, direct, and galvanic conversion (Burbank *et al.,* 1990). The indirect method involves the formation of ferric sulphate and sulphuric acid. The direct method occurs by adhesion of bacterial cells to sulphides, which allows bacterial enzymes to catalyse sulphide oxidation resulting in metal dissolution. Bacteria enhance galvanic conversion methods by continuously oxidising the elemental sulphur layer which otherwise forms a physical barrier to galvanic action. Galvanic cells are formed by two dissimilar minerals immersed in sulphuric acid. Irrespective of mechanism, the bacteria cause acidification and metal dissolution.

As the acid mine drainage enters the river and becomes more dilute, much of the substrate becomes smothered with amorphous ferric hydroxide. This is the product of a chemical reaction, but additional deposits on stones and boulders can also result from the activity of enormous growths of the sheath bacterium *Leptothrix ochracea*.

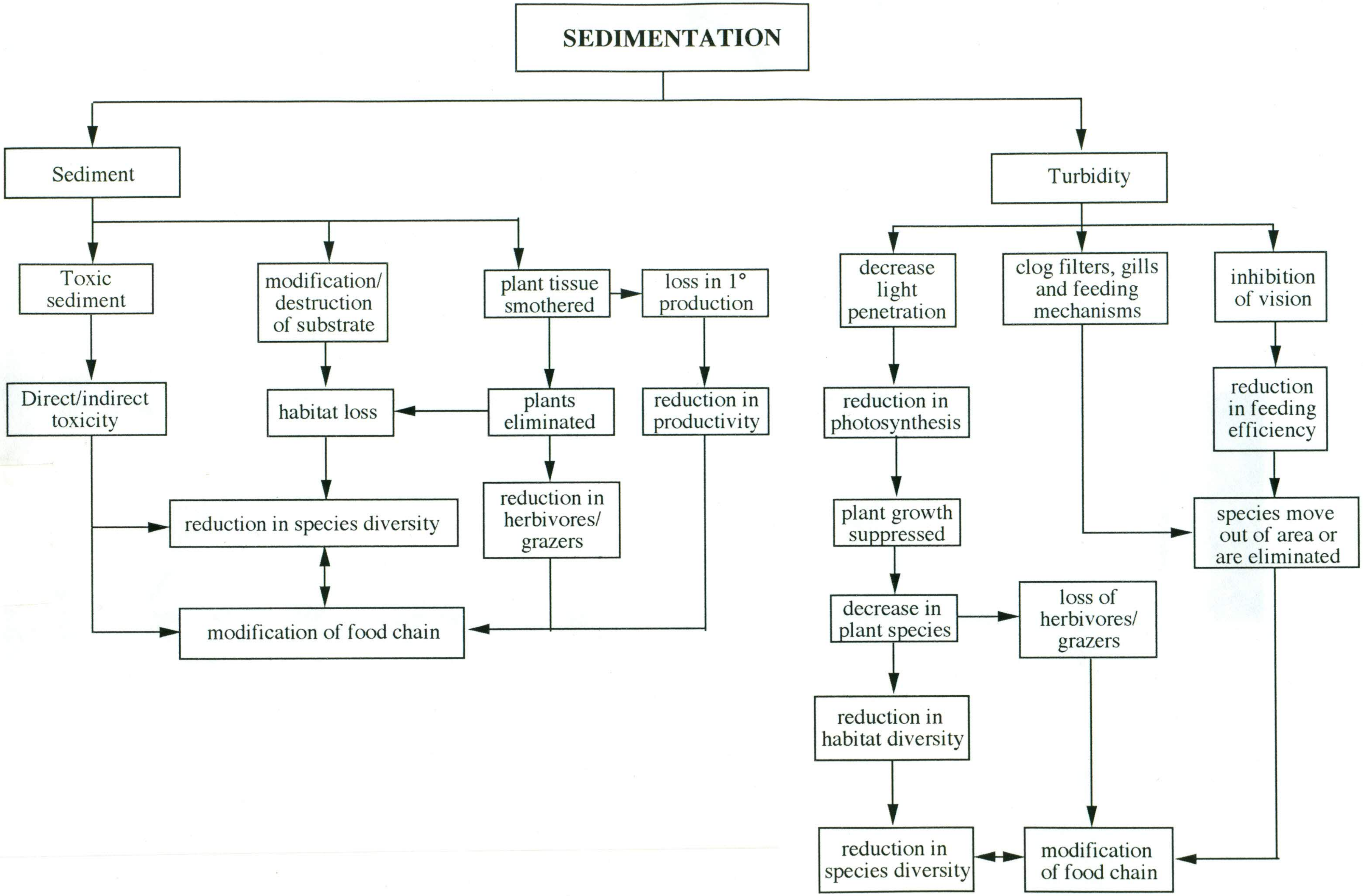

Fig. 5. Impact of sedimentation processes arising from AMD on lotic systems.

Algae

Periphyton comprise a community of a wide range of organisms ranging in size from a few microns to several centimetres (Table 4). Algal periphyton has an intermediate position between the heterotrophic smaller bacteria and fungi on the one hand, and the larger macro-zoobenthos on the other. In the long-term, periphyton communities respond to environmental stress primarily by changes in species composition. The response of organisms in this community can therefore be seen as a temporal integration of contamination in the water during their life span. Long-living species of algae are therefore effective indicators of water quality, particularly for monitoring concentrations of micro-nutrients and micro-contaminants (Whitton, 1984). The position of periphyton in relation to other biota in a river can be characterised by specific features. Periphyton algae, as light-dependent autotrophs, are restricted to the sediment surface and thus frequently hold a fixed position on it, whereas heterotrophic organisms can settle down to interstitial waters.

There are a variety of difficulties facing any autotrophic organism growing in highly acidic environments. Concentrations of bicarbonate are either very low or non-existent so there are difficulties in maintaining a constant internal pH, and there are often high concentrations of metals. However, organisms which overcome these problems generally have little competition for resources. Acidophilic organisms have been the subject of much study both in the field and the laboratory.

Some of the earliest studies on the effects of acid mine drainage on biota were carried out in coal-mining areas of the Appalachians in the eastern USA where coal has been mined continuously since the 18th century (Bennett, 1969). In a survey carried out at over a hundred stream sites in Indiana and West Virginia, no species of blue-green algae were found at a pH of less than 3.7 and only one below pH 7.0 (Lackey, 1938). The most acid tolerant species were *Ulothrix zonata* and an unnamed species of *Chlamydomonas* (both Chlorophyceae); the diatom *Navicula* sp. (Bacillariophyceae); *Chromulina* sp. (Chrysophyceae); and *Euglena mutabilis* (Euglenophyceae). A later study on lakes formed at the sites of strip mines in Ohio showed generally low concentrations of phytoplankton despite the lake pH never being recorded below pH 4.0 (Riley, 1960).

VARIABLE	BACTERIA & FUNGI	PHYTO-PLANKTON	PERIPHYTON ALGAE		MACROPHYTE PLANTS	ZOOBENTHOS		FISH
			microalgae	macroalgae		micro	macro	
SIZE RANGE	1μm-1cm	1μm-10mm	10μm-10mm	10mm-1m	5cm-2m	1μm-5mm	5mm-5cm	1cm-1
LIFE SPAN	1hr-10days	1d-50days	1d-100days	10d-500days	100d-500days	10hr-50d	100d-500d	years
MICRO HABITAT	all substrata	water	solid substrata	sand	sand	all substrata	surface interstitial	water
RESOURCES	organic substrates	light nutrients	light nutrients	light nutrients	organic food	organic food	organic food	plants animals
MOBILITY	high	little	variable	none	none	high	high	high

Table 4. Size, generation time and other variables for characterization of the individual components of biota in a river.

Bennett (1969) looked at a wide variety of aquatic habitats in the coal mining district of West Virginia. Few details of precise pH and acidity ranges in which different organisms were found are given but he recorded a few species as being consistently abundant in the mine entrance. These included *Ulothrix subtilis,* two diatoms (*Pinnularia braunii, Eutonia tenella)* and *Euglena mutabilis,* the latter species being the only alga of any significance at the two most acidic stations.

Euglena mutabilis was abundant at the most acid reaches of another site in West Virginia, Roaring Creek (Warner, 1971). A high diversity (over thirty-three species) of periphyton was found where there was little or no acid pollution and the pH was greater than 4.9. Where the pH was less than 3.8 fewer than twenty species were recorded. This was partly attributed to the smothering effects of iron hydroxides but it was also observed to occur at the point where the stream lost all of its bicarbonate buffering capacity. Of the twenty species found in the more acid reaches ten (five *Chlorophyceae,* four diatoms and *E. mutabilis)* were particularly tolerant and of those *E. mutabilis* plus *Ulothrix tenerrima, Pinnularia termitina* and *Eunotia exigina* were present in large numbers only in the most acid reaches. Droop (1974) suggested that the intolerance shown by many algae to low pH is sometimes due to heavy metal toxicity. Besch *et al.* (1972) found from field studies on diatom communities in acidic and non-acidic zinc and copper polluted waters, that acid tolerant species were also tolerant to high heavy metal concentrations, but that the converse was not true. Other studies, which although less detailed or directly relevant, confirm that algal species diversity is low in acidic streams and rivers, are those of Harrison (1965) in South Africa and Steinback (1966) in Ohio. Parsons (1968) also reported a similar situation of limited biota inhabiting acid mine waters.

In all of these early studies the same general effect was observed, namely a decrease in the number of species as the acidity increased, with only a few highly specialised organisms able to survive in the most highly acidic environments. *Euglena mutabilis* is the species most often recorded as abundant in AMD. It appears to have adapted to the extreme acidity encountered in some acid mine drainages. Early experiments on *E. mutabilis* in the laboratory (Dach, 1943) indicated no growth at pH 0.9 but slight growth at pH 1.4. Maximum growth was observed between pH 4.0 and 4.8 and it subsequently declined, with only slight growth at pH

7.9 and none at pH 8.2. The figures at the lower end agree quite well with Hargreaves and Whitton (1976) who detected growth in the laboratory at pH 1.3 although maximum growth of their strain occurred at pH 2.0, close to the pH of the stream from which it was isolated. In a survey of acid mine drainage sites in England with a pH of 3.0 or less *E. mutabilis* was found to be the most widespread species and the most abundant, sometimes forming eighty percent cover (Hargreaves *et al.,* 1975). The effect of external pH on the internal pH of *Euglena mutabilis* was tested by Lane and Burris (1981). If the interior pH is as low as the external pH, chlorophyll would normally be degraded to phaeophytin, unless there are special physiological adaptations. However maintenance of a near-normal pH would require energy-consuming ion pumps. The internal pH of *Euglena mutabilis* showed some degree of regulation, with an internal pH of approximately 6.0 at an external pH of 3.0, rising to an internal pH of 8.0 at an external pH of 9.0. The rate of photosynthesis appeared to be independent of pH in this species (Lane and Burris, 1981).

Other abundant species recorded by Hargreaves *et al.* (1975) included four diatoms (*Pinnularia acoricola, Nitzschia subcapitellata, N. elliptica* var. *alexandrina, Eutonia exigua)* and the Chrysophyte *Gloeochrysis turfosa* followed by two green algae; *Chlamydomonas applanata* var. *acidophilia* (cf. *C. acidophilia*) and *Hormidium rivulare Kutz.* The latter has been examined to determine its tolerance to zinc concentrations (Say *et al.* 1977). It was found to be widespread in waters free of zinc pollution and also in waters with zinc pollution emanating primarily from mining activities. At sites with zinc concentrations greater than 30.2 mg/l Zn, populations showed increased resistance, being largely, if not entirely, the result of genetic adaptation.

The high concentrations of heavy metals often associated with acid mine drainage may themselves exert an influence on species composition. However it is often difficult to separate out the effects of the heavy metals from the effects of the acidity *per se.* Analysis of records of *Pinnularia acoricola* and *Eunotia exigua* in the field showed the former to be more tolerant of low pH with several records below pH 2.0. *Eunotia exigua* was more likely to be found where copper and zinc concentrations were increased (Whitton and Diaz, 1981). For these two species at least, some distinction between the effects of pH and heavy metals on their distributions can be made.

Macroflora

Ormerod *et al.* (1987) studied the macroflora of acid streams in Wales and believed that the presence or absence of indicator species could be used in the bankside assessment of stream acidity. The presence of liverworts *Scapnia undulata* and/or *Nardia compressa,* and the absence of the large alga *Lemanea* indicate waters in the pH range 4.9-5.2. In waters with the moss *Fontinalis squammosa* present, but *Lemanea* absent, the pH range is 5.6-5.8, and with both of these present the pH is likely to be in the range of 5.8-6.2. Stream water is likely to be above pH 6.2 where *Lemanea* is present but *F. squammosa* is absent.

Even if a plant can overcome acidity itself, it still has to be able to grow in the absence of bicarbonate and probably in the presence of iron oxide precipitate where acid mine drainage conditions prevail. Bryophytes, which use carbon dioxide rather than bicarbonate as their inorganic carbon source, and emergent angiosperms which are not totally dependent upon the inorganic carbon supply in the water, are the two most abundant groups of macrophytes in acid mine drainage (Hargreaves *et al.,* 1975).

Invertebrates

Several studies have been carried out on the effects of acid mine drainage on invertebrate communities in streams (Koryak *et al,* 1972; Scullion and Edwards, 1980; Wickham *et al.,* 1987). The toxicity of heavy metals to organisms in the aquatic system can vary according to concentration, pH, temperature, organic matter content, hardness and other properties of the water (Wickham *et al.,* 1987). Under conditions of high acidity there is a drastic reduction in the number of species of invertebrates which are found. However, those species which are capable of tolerating acidity tend to thrive in the absence of competition and predation. In an acid pool with a pH of 3.2, and contaminated with metals (copper 0.23 mg/l, zinc 4.9 mg/l), from a mining complex in Quebec, Chironomidae comprised 99.5% of the fauna (Wickham *et al.,* 1987). Although this family are clearly tolerant to acidity itself, it is often the zone where the iron (III) hydroxides are deposited that the largest densities are observed (Koryak *et al.,* 1972). This domination of acid mine water by chironomids appears characteristic (Lettermann and Mitsch, 1978; Scullion and Edwards, 1980). Cranefly larvae (Tipulidae) also appear to be common (Koryak *et al.,* 1972) and alder fly larvae (Megaloptera), especially *Sialis* spp. are also common (Dills and Rogers, 1974; Warner, 1971).

Warner recorded an abrupt decrease in the number of invertebrate taxa recorded in Roaring Creek, West Virginia, at about pH 4.2, the pH at which all the natural bicarbonate buffering of a stream is lost. This indicates that below pH 4.2 regulation of the organism's pH becomes much more difficult, and consequently only adapted species can survive. It has been estimated that millions of populations of acid-sensitive organisms in lakes have been eliminated by acidification (Minns *et al.,* 1990). In experimentally acidified lakes, the total number of species declined by one-third between natural pH values of <6.5 and pH 5.0-5.1 (Schindler, 1991). It has been suggested that shredder species have evolved an ability to tolerate local acidity within patches of decaying organic matter enabling them to colonise acidic habitats on a larger scale (Mackay and Kersey, 1985).

Iron (III) hydroxide tends to remain in solution at very low pH values. However, as the pH rises to approximately 4.3 it is precipitated out and creates a very different set of conditions for the benthos. Many streams affected by the deposition of ferric hydroxide also are acidic (Koryak *et al.,* 1972), giving rise to some difficulties in determination of the cause of faunal change. Scullion and Edwards, (1980) however, found no such interpretative problems in the Nant Caeach River near neutral pH (6.3-7.9) and low concentrations of ferric hydroxide (0.5-3.3 mg/l Fe). The reduction in abundance (88%) and density was almost certainly due to direct effects of deposited ferric hydroxide on invertebrates through ingestion, interference with respiratory attachment and feeding mechanisms, or the indirect effects on plant growth. A reduction in faunal abundance and diversity under similar pH conditions (6.0-8.0) has been reported in other streams receiving ferric hydroxide deposits (Greenfield and Ireland, 1978; Lettermann and Mitsch, 1978). In these streams there was a reduction or elimination of the Ephemeroptera, Plecoptera, Trichoptera and Coleoptera and a community dominated by Oligochaetes and chironomids became established. The pH, together with the concentrations of various metals in surface waters, has a profound effect on the distribution of many invertebrates (Vangenechten *et al.*, 1989).

Scullion and Edwards (1980) conclude that for macroinvertebrates there do not appear to be any particular species or taxa indicative of acid pollution. However some separation between the effects of acid *per se* and associated factors such as suspended solids and iron (III) hydroxide is possible. The toxic effects of metals cannot be interpreted solely in terms of the response of the larvae. Three main hypotheses have been developed for the distinct change in faunal composition in acid mine drainage. Firstly, the chemical conditions in acidified waters are intolerable for some taxa or have sublethal physiological effects. Some animals may actively avoid these waters. Secondly, the chemical conditions affect invertebrates indirectly via their food supply. Thirdly the absence of fish from many acidified waters removes predation pressure and produces ramifying community effects (Sutcliffe and Hildrew 1989).

Fish

Fish are very severely affected by acid mine drainage and low pH (Mason, 1991; Sullivan and Gray, 1992). Frequently no fish are recorded in the reaches of rivers contaminated by acid mine drainage. The response of fish to acid conditions is determined by a number of other factors such as related increases in toxic metal levels or indirect effects upon food organisms (Alabaster and Lloyd, 1982; Howells, 1983). Turnpenny (1989) examined the occurrence of fish species in streams of various pH ranges in Great Britain. Brown trout were found in only 28% of streams with pH less than 5.0, but in 95% of streams with pH greater than 6.5. No streams with pH less than 5.5 contained salmon. Warner (1971) found fish only where the pH was greater than 4.9. Fish kills are sometimes observed during high discharge low pH episodes (Reader and Dempsey, 1989). The deaths appear to be the result of metal toxicity accompanying increased concentrations and speciation changes associated with a fall in pH. Failure of ion regulation is also a possible cause of death. Thomas (1989) declares that well-regulated intracellular pH of fish depends absolutely on a constant extracellular pH.

The extensive reviews of the toxicity of copper to fish agree that increasing water hardness reduces the toxicity as measured by acute toxicity tests (Alabaster and Lloyd, 1980; USEPA, 1980a, Mance *et al.,* 1984a). Chronic exposure of fish to lead produces characteristic responses of blackfinning and spinal curvature (loroscoliosis), the latter being neural in origin rather than actual physical deformity (Hodson *et al.,* 1982). Both effects are initially reversible but severe blackfinning develops into irreversible rotting of the fins. These effects have been recognised in several reviews of the toxicity of lead to freshwater fish (USEPA, 1980b; Mance *et al.,* 1984b), which have led to the conclusion that water hardness has an ameliorating effect on lead toxicity.

Reviews and research on the toxicity of zinc to freshwater fish conclude that salmonid species are more sensitive than non-salmonid species (Alabaster and Lloyd, 1980; USEPA, 1980c). High concentrations of suspended solids frequently associated with acid mine drainage cause significant effects on fish including production of excess mucus and the formation of deposits on the gills (Greenfield and Ireland, 1978). Increased yawning and coughing have been suggested as behavioural responses to hypoxia in fish subjected to concentrations of heavy metals (Kelly, 1988). Toxic effects may be exacerbated at early life stages and there may be effects which reduce reproductive fitness (Cochran, 1987).

Overall, it appears that characteristic biota of stream receiving acid mine drainage depends largely upon the extent of oxidation of pyrites with the flora and fauna both being very restricted where the pH is below pH 3.0.

5. CONCLUSIONS

Acid mine drainage affects lotic systems in numerous and interactive ways. This results in multiple pressures, direct and indirect, on the organisms in the ecosystem. The effects are chemical, physical, biological and ecological. The overall impact on the community structure is the elimination of species resulting in simplification of the food chain and thus reduced ecological stability. Ecological stability increases with food chain complexity, and this complexity allows lotic communities to cope with pollutants (e.g. organic matter, solids deposition and degradation, temperature etc.). It also enables recovery once the toxic input has ceased, been biologically degraded, or been removed by physico-chemical processes. The effects of AMD are so varied that community structure collapses rapidly and totally. Few other pollutants on their own can cause such an impact. Recovery is suppressed due to habitat elimination, niche reduction, substrate modification, the toxic nature of sediments, and bioaccumulation of metals in the flora, particularly perhiphyton, and fauna. The overall impact is largely controlled by the buffering capacity of the receiving water and available dilution. Therefore soft, poorly buffered rivers are more severely affected than hard well buffered systems, where the impact may be more restricted with sedimentation being the major effect.

The impact of AMD is very difficult to predict due to the variability of the rate of discharge from adits, seasonal variation in adit strength and composition, the effect of surface runoff from exposed areas of the mines during heavy rainfall, and the effect of the catchment discharge characteristics which affects dilution and the concentration of organic matter in the water. Assessment is difficult due to the complexity of the impacts, although diversity and abundance are key variables for biotic evaluation. There are no indicator species for affected rivers although oligochaetes and dipterans, and chironomids in particular, are generally the dominant macroinvertebrate groups found downstream of AMD discharges. Ephemeropterans are particularly sensitive to AMD and are amongst the last group to recolonize rivers after contamination. Fish movement and migration is also a useful indicator. There has to be a compromise between simplicity and actual interactions. Actual systems may be so complex that no useful information can be obtained from attempting to model them. While a simpler approach, concentrating on the major interactions (e.g. toxicity of key metals or the degree of substrate modification caused by iron precipitation which is directly linked to pH), may prove to be more useful in understanding AMD impacts and predicting them. The interactions of the key pollutants in AMD are summarized in Fig. 6.

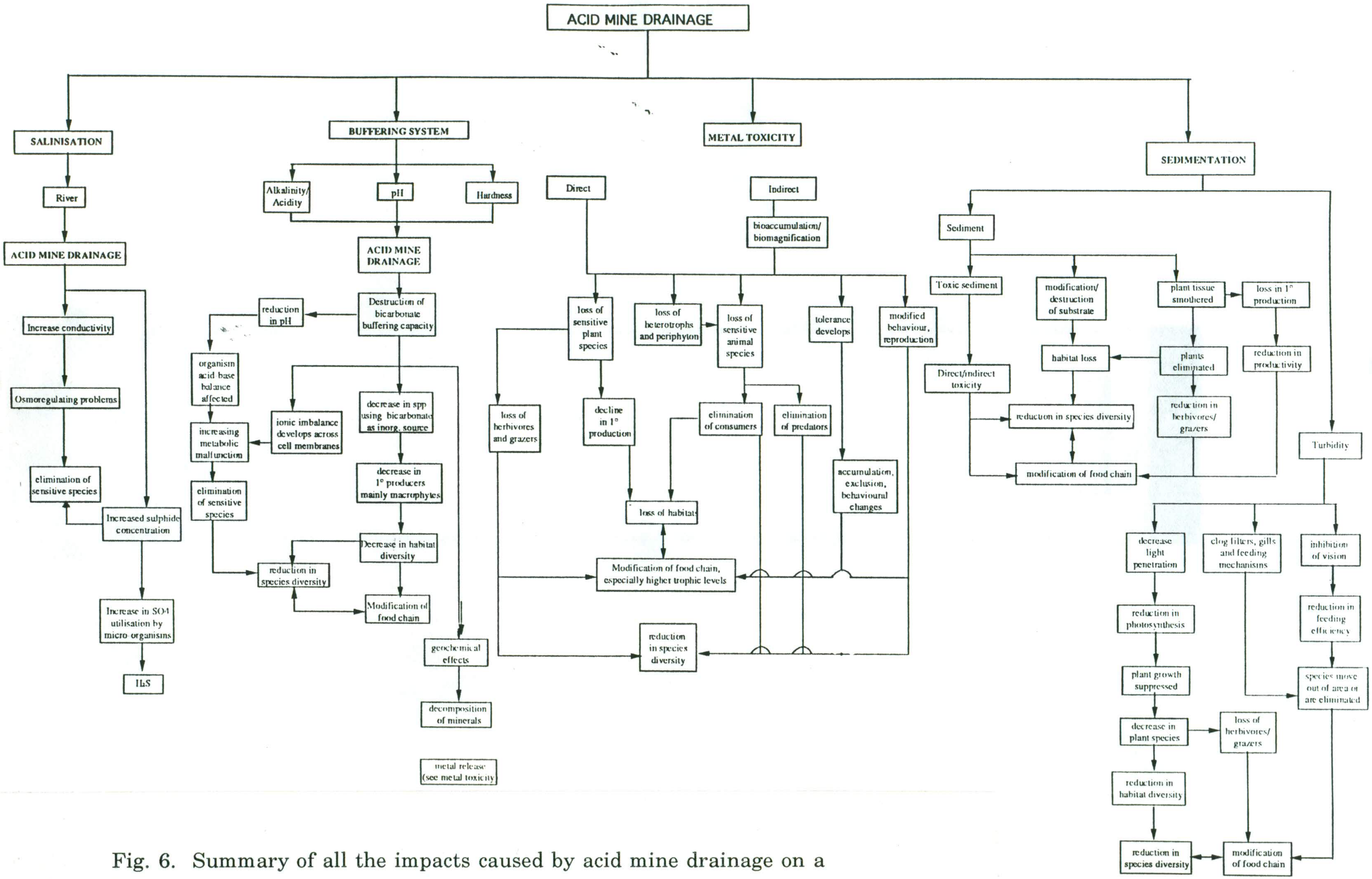

Fig. 6. Summary of all the impacts caused by acid mine drainage on a lotic system.

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