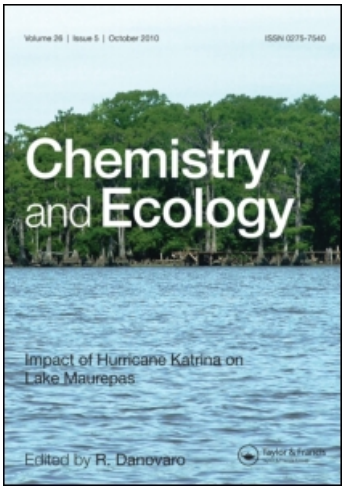

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EIFAC† WATER QUALITY CRITERIA FOR EUROPEAN FRESHWATER FISH: REPORT ON ALUMINIUM

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1. INTRODUCTION

1.1 *Sources and Uses of Aluminium*

Aluminium (Al) is a silver-white metallic element with a relative atomic mass of 26.98 and a relative density of 2.58. It is the world's most common metal, making up 7–8% of the earth's crust and the third most abundant element. The free metal is not found in nature; it is extremely reactive with a high oxidation potential. Aluminium compounds are found in almost all rocks, in surface waters, and in living organisms (although it is not considered to be an essential element). The primary minerals in which it is present include feldspars and micas in igneous rocks and, less commonly, cryolite and crystalline alumina.

As a result of prolonged weathering of the primary minerals, aluminium occurs in the sedimentary clay minerals kaolinite and montmorillonite. When the silica is dissolved by weathering, hydrate aluminium oxides such as gibbsite and boehmite may be formed. Bauxite (the principal ore, containing about 55% aluminium oxide) and laterite contain these secondary minerals. Weathering may also lead to the formation of sulphates such as alum, aluminite or alunite.

The utilisation of aluminium reflects its properties. The pure metal is ductile, but soft and weak. Its low density is therefore used to advantage in alloys with other elements (copper, silicon) to give products with high tensile strengths. Aluminium has good thermal and electrical conductance. All these properties explain its wide use in structural engineering, in the motor and electrical industries and in the manufacture of cooking utensils.

† EIFAC: European Inland Fisheries Advisory Commission of the FAO (UN).
The authors were specially appointed members of an EIFAC Sub Commission III Working Party on Water Quality Criteria for European Freshwater Fish.

Chemical forms of aluminium of particular note are aluminium chloride and aluminium sulphate (alum), although the latter is strictly a generic name for a large number of isomorphous compounds which are made up of a univalent metal or radical, a tervalent metal, two or four sulphate radicals and 12 or 24 molecules of water of crystallisation. Aluminium chloride is used as a pigment and in the petroleum and organic chemical industries as a catalyst. Aluminium sulphate is used in the pulp and paper industries and in treatment of potable water supplies where it acts as a coagulant.

1.2 *Chemistry of Aluminium in Fresh Water*

Although aluminium is such a common element, its concentrations in most fresh waters are usually very low, generally <1 mg/l (ppm).† This is partly a consequence of the relationship between pH and the solubility of aluminium minerals. In the pH range 5 to 8, aluminium has a very low solubility but outside this range, solubility increases markedly.

Thus the possibility exists for two types of problem arising from aluminium in surface waters—(i) the action of dissolved material in acid or alkaline water outside the range pH 5.5 to 8 and (ii) the action of insoluble aluminium compounds in the form of suspended material between these pH values.

In waters of low pH (~5.5) and low ionic strength, dissolved aluminium can reach concentrations which are toxic to aquatic organisms. Such waters can arise from mine drainage, acid sulphate soil waters, geothermal waters and, of particular current concern, poorly buffered lakes and streams receiving acid runoff. The susceptibility of such waters will depend to a large extent on the bedrock geology, on the buffering capacity (base reserve) of the soils in the catchment and on the land use of the catchment. Soil chemistry and the effects of aluminium on freshwater fisheries are therefore intimately linked.

Since one of the inputs of acidic water to catchments is *via* rain, arising from the solution of the gaseous forms of nitrogen, chloride, sulphur and carbon in the atmosphere, it is necessary to understand the atmospheric processes that result in the deposition of acid i.e. of hydrogen ions and accompanying anions and cations. These include atmospheric "loading" (i.e. deposition) not only of acid generating materials such as oxides of sulphur and nitrogen, but also of neutralising agents such as ammonium and alkaline "dusts."

Furthermore, land-form in relation to prevailing winds, and enhanced atmospheric scouring by tall vegetation, particularly coniferous trees (Ormerod *et al.*, 1989), increase deposition on both a localised and a regional scale. Trees accumulate acid-forming materials from the atmosphere by dry deposition between rain events and by scavenging aerosols and droplets in mist and fog. During rain events, these substances, together with any exudates from the tree canopies, are washed on to the soil beneath. The trees, in addition, have selectively sequestered chemicals from the soil which could otherwise have neutralised the acid deposition; as a consequence the acidity of soil water below the trees may be enhanced. Whether aluminium dissolved by acid conditions then

† Since the speciation and valency of Al compounds in natural waters are uncertain, depending on water quality, concentrations in this review will be given usually as mass (e.g. mg) values per unit volume (e.g. litre), unless otherwise specified.

leaves the soil and enters drainage channels will depend on local microscale conditions. Incautious exposure and draining of poorly buffered soils resulting in oxidising and acidic conditions may be one reason why high concentrations of dissolved aluminium are found in surface waters of certain streams.

A quite different problem may arise from the use of aluminium compounds in industrial processes and particularly in the treatment of potable waters. Where aluminium sulphate is used as a coagulant, sludge and water from the filter back-wash may be discharged to watercourses, or the coagulant may be released inadvertently to the water supply mains, in turn released by subsequent flushing operations to watercourses. The concentrated solutions released on these occasions have resulted in a considerable decline in pH (Bielby, 1988; Hunter *et al.*, 1980). Aquatic life may therefore be subject to relatively brief exposures to high aluminium concentrations at low pH, and/or large quantities of aluminium-containing floc.

The mode of toxic action of aluminium on aquatic life depends on its physical and chemical state in the ambient conditions prevailing. The identification or separation of the various species of aluminium may be important since, as is generally evident, not all species have the same toxicity. In arriving at tentative water quality standards for aluminium, it has been necessary to define the species of the element present in test vessels and environmental samples and to define a standard only in terms of the toxic (inorganic or labile) species. The standards proposed for ammonia (Alabaster and Lloyd, 1982) are an analogous early example, the toxic species being ammonia (NH_3) and not ammonium (NH_4^+).

Aluminium in solution is amphoteric and can form both organic and inorganic complexes, tending to polymerize (e.g. Driscoll and Schecher, 1988). These properties encourage the formation of various molecular species, depending largely on pH, but also on the presence of other dissolved substances, and to a lesser extent, on temperature and the period of exposure (i.e. ageing) of the water (Burrows, 1977; Driscoll and Schecher, 1988; Leivestad, 1989). It is a Group III element found in solution only in the trivalent state, and although metallic, it exhibits marked covalent tendencies thus forming relatively stable complexes with a variety of inorganic and organic materials.

It is important to differentiate between aluminium fractions and aluminium species. "Fractions" are operationally defined (see below) e.g. as "total," "inorganic monomeric," "polymeric complexes" (Driscoll, 1984) and these will be described in Section 1.3. "Species" are distinct chemical entities, several of which may occur together in a particular fraction (Driscoll and Schecher, 1988). Thus, considering the sequence from the trivalent species Al^{3+} to the dominant hydroxide species at $pH > 5$ to 6, at least four species exist, all included in the fraction "inorganic monomers" (Driscoll and Schecher, 1988): Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, (Figure 1.1).

A further species, $Al(OH)_3^\circ$ is hypothesised (Baes and Mesmer, 1976) but its presence awaits chemical confirmation.

Aluminium salts of non-complexing acids (such as aluminium perchlorate) dissociate in water and probably form the aluminium ion: $Al(H_2O)_6^{3+}$. As this is hydrolysed, an acidic solution results: $Al(H_2O)_6^{3+} + H_2O = Al(H_2O)_5OH^{2+} + H_3O^+$.

If the original solution contained 10^{-3} M (i.e. ppm levels) aluminium perchlorate, the initial pH in pure water would be about 4. Since this pH would, in any

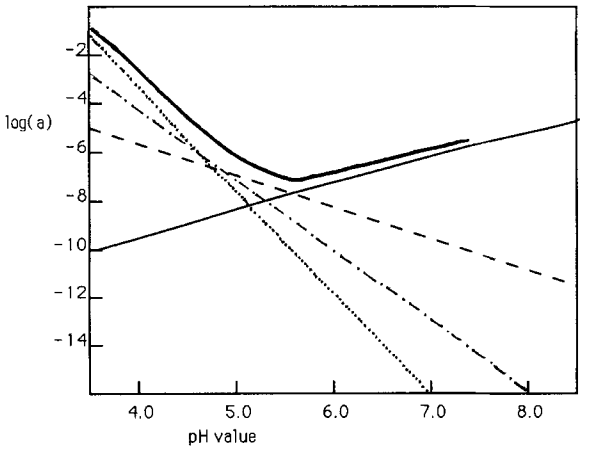

Figure 1.1 Activities calculated for inorganic Al species in equilibrium with gibbsite, as a function of pH. Al^s is the sum of all other inorganic species in solution (after Seip *et al.*, 1984). $Al(OH)_4^-$— $Al(OH)_2^+$ -·-·- Al^{3+} ····· Al^s—$Al(OH)^{2+}$----.

event, be toxic to many aquatic organisms, the toxicity in this case might be more reasonably, but paradoxically, be attributed to acidity than to the effects of Al^{3+}. A realistic toxicity experiment would, however, employ a much lower concentration, say 10^{-5} M (i.e. ppb), and hydrolysis of aluminium would contribute little to the acidity of the test medium.

In attempting to define which forms of aluminium may be present in a natural water it is important to know, not only the forms and valencies of the aluminium species, but also the amounts of the various possible ligands present which can combine with the aluminium (Birchall and Espie, 1986; Birchall *et al.*, 1989), the rates of formation of the resulting complexes, the ultimate balance between the species and any effects of other factors in the environment. Given the composition of the mixture in total, an appreciation of the possible precipitation of each species is needed in order to predict equilibrium conditions (Lydersen, pers. comm.), but it must be appreciated that in many situations in which fish are exposed to aluminium, equilibrium may not have been reached; although solution equilibrium is attained rapidly, in-stream conditions are highly variable.

1.3 *Analytical Methods*

It is not the aim of this review to provide details or procedures for the analysis of aluminium (and its fractions or species) in environmental samples (see Table 1.1). The complex speciation of aluminium, however, requires some comment on the methods of analysis in current use, their comparability with one another, and their relation to the expected forms of aluminium (Driscoll and Schecher, 1988). As the section above has indicated, aluminium may occur in a variety of forms, depending on pH, the presence of other dissolved substances (organics, silicate, fluoride) and, to some degree, on the temperature (Lydersen, pers. comm.) and "ageing" during the period of exposure. The principal species of aluminium in a water sample are inorganic monomeric forms, organic monomeric forms,

Table 1.1 Standard methods for aluminium detection and levels of detection.

	Detection limit mg/l	*Ref.*
8-hydroxyquinoline ("Oxine")	0.01–0.05	LaZerte, 1984
Graphite furnace AAS (GFAAS)	0.01–0.02	Barnes, 1975; Burrows, 1977; LaZerte, 1984
Catechol violet	0.003	Dougan and Wilson, 1974
	0.02 (routine)	LaZerte *et al.*, 1987
	0.005 (field)	Sadler and Lynam, 1986
Inductively coupled plasma spectroscopy	0.02	Winge *et al.*, 1977

polymeric complexes, aluminium hydroxide colloids, and precipitates and clays. An attempt is made in Figure 1.2 to link these known chemical forms with the operationally defined fractions commonly in use.

Analytical methods can be distinguished as those which measure "total" aluminium in water and those which measure some fraction of the total ("speciation"). However, even those methods which purport to measure "total" aluminium may do so in varying degrees. Inorganic and exchangeable aluminium fractions are usually derived from the difference between a measured "total," and what is not retained by a chelating resin (Driscoll, 1984). "Adsorbed" monomeric aluminium can also sometimes be significant (Goenaga and Williams, 1988) but is usually not included.

1.3.1 *"Total" aluminium*

A common procedure is to subject samples to acid digestion to dissolve the aluminium (as Al^{3+}) before complexation by an organic colour reagent and

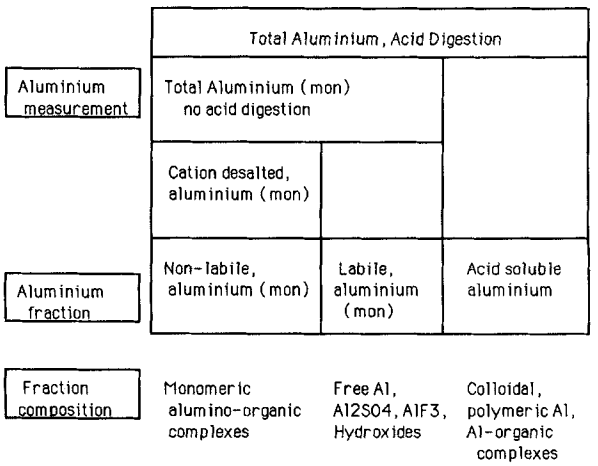

Figure 1.2 Schematic representation of the Driscoll aluminium fractionation procedure (after Sadler and Lynam, 1986).

subsequent analysis. Although the details of acid digestion vary in different procedures, dissolution is assumed to be complete with respect to particulate and colloidal aluminium hydroxides; aluminium from clays, however, would not usually be dissolved. In waters with a high refractory organic matter content, an ultraviolet digestion may also be required (Campbell *et al.*, 1983).

1.3.2 *Aluminium fractionation*

A separation of particulate from non-particulate (or filterable) aluminium requires filtration (usually with a 0.45 μm polycarbonate filter) and analysis of the filtrate by any of the "total" methods described above (Driscoll, 1984). Salbu (1987) has made a plea for "*in situ*" hollow fibre separations to improve the consistency of analytical preparation in advances of charge fractionation methods (complexing agents, cation exchange resins) for chemical speciation, but this technique has not been adopted widely.

Many of the "total" methods using an organic complexing reagent after acid/UV digestion have also been used without any prior digestion or filtration and so may include fine particulate material. The results are inevitably quite variable and dependent upon reagent concentrations, temperature, duration of the reaction, and pH. For example, LaZerte (1984) used a rapid (15 s) oxine extraction to estimate "fast reactive Al" and a slow (3 to 6 h) extraction to estimate a "total reactive Al"; the difference between the two is thought to be polymeric aluminium, the "fast reactive aluminium" roughly corresponding to inorganic monomeric plus organic aluminium.

In general these methods provide an aluminium fraction which can be interpreted as the inorganic monomeric fraction plus (most of) the organic aluminium, and excluding (most of) the polymeric, colloidal and solid fraction (Figure 1.2). This fraction is usually termed "reactive," "labile" or "total monomeric" aluminium. The "total monomeric" terminology of Driscoll (1984) has gained the widest acceptance. It has been shown by Seip *et al.* (1984) that this "total monomeric" fraction estimated by the catechol violet method is equivalent to that estimated by the oxine extraction method. The difference between "total monomeric" and an acid digested "total" is usually referred to as the "acid soluble" fraction, which should include polymeric, colloidal and particulate (if unfiltered) aluminium hydroxides.

Once "total monomeric" aluminium is separated, most schemes distinguish organic or inorganic forms by dialysis or cation exchange. The ion exchange (Driscoll, 1984) method gives a slightly lower organic aluminium fraction than equilibrium dialysis (Backes and Tipping, 1987), a discrepancy which increases with the ratio of aluminium bound per gram of humic material. In contrast, LaZerte (1984) found agreement within 5% between the two techniques. Cation exchange, moreover, is the more practical procedure in the field, although the contact time (LaZerte, 1984) and resin preparation and flow (Sadler and Lynam, 1986) can influence the degree of aluminium retention. The inorganic monomeric (potentially toxic) aluminium fraction is calculated by subtracting the organic monomeric fraction (not retained on resin) from total monomeric aluminium (filtered sample). This procedure lacks precision in those cases where the concentrations of the toxic fraction of interest is derived from the difference between the other, larger, measured components. This method is only applicable

at pH values less than about 6.5 where the inorganic fraction is dominated by positively charged monomers. When neutral or negatively charged monomers (at pH values greater than 6.5) or positively charged polymers exist (neutralising conditions) the method will be in error and the dialysis method may be preferred.

Although these fractionation methods are strictly operational, there is evidence that they do distinguish meaningful components.

1.3.3 *Field procedures*

Application of one or other of the procedures described briefly above should be adequate to separate aluminium components in environmental samples and to provide insight into the forms of aluminium present. Inorganic aluminium includes inorganic monomeric aluminium plus acid-soluble aluminium fractions, but excludes the organic monomeric and clay fraction. If it is known that a water sample contains a negligible amount of suspended clays, as for most acid upland waters, then a GFAAS or ICP "total" measurement minus the organic monomeric fraction will provide a reasonable estimate of inorganic aluminium. However, if suspended clays are present, filtration (0.45 μm or less) should be employed and perhaps a less destructive "total" method (Dougan and Wilson, 1974) might be more appropriate. The same considerations apply to "total" aluminium as used in Section 1.3.1, except that the estimation and subtraction of organic monomeric aluminium is not required.

It should be noted that samples collected in the field are not stable. An increase in temperature can induce over-saturation and precipitation of aluminium species in those samples where they were close to saturation (Seip *et al.*, 1984); similarly, CO_2 degassing of ground waters (Stumm and Morgan, 1981) may occasionally induce sufficient pH elevation on exposure to atmosphere for over-saturation and precipitation. Photosynthetic activity in a stored sample can similarly remove CO_2 and raise the pH. Samples collected for aluminium speciation should be analysed immediately if possible, and refrigerated until analysis if not.

1.4 *Occurrence in Water, Soils and Sediments*

1.4.1 *Surface water: aluminium concentrations*

Concentrations vary quite substantially in different regions, reflecting geology and hydrology and the degree of weathering (Stumm and Morgan, 1981), as well as land use. Surface waters of pH <5.5 have higher concentrations of aluminium, as well as of manganese, iron and other heavy metals, compared with circumneutral waters (see, for example, Almer *et al.*, 1978; Dickson, 1980). Table 1.2 summarises some reported values for several locations with oligotrophic and acid waters.

Aluminium concentrations in the United Kingdom are generally ~100 μg/l even in poorly buffered soft waters (e.g. Loch Lomond and Gryfe Water, Hunter *et al.*, 1980) but are reported to be higher in afforested areas (Harriman and Morrison, 1982; Stoner *et al.*, 1984; Stoner and Gee, 1985) and during high flows. In Scandinavia, concentrations in lakes are 100 to 800 μg/l (Dickson, 1978; Overrein, 1980), sometimes even higher during acid episodes (Grahn, 1980). A

Table 1.2 Range of reported aluminium concentrations at selected sites.

Sites, times	*pH Range*	*Aluminium fraction (μg/l):*			*Reference*
		Total	*Acid sol.*	*Non-labile*	*Labile*	
Global fresh waters	6.0 to 9.0	240 to 11				1
Groundwaters	~7.0					2
Norway sites:						
Birkenes (stream)	5.3 to 4.2				160–590	3
Tovdal (river)	4.7 to 4.2				390–480	4
Selura (lake)	4.9 to 4.0				220–250	5
Southern lakes	6.0 to 4.0	to 350				6
Sweden sites:						
Lofssjon (streams)	6.8 to 4.0	50–200 or				7
Hallsjon (lake)	7.4 to 4.7	more	200–400			8
Gardsjon (lake)	4.9 to 4.2		400			9
UK sites:						
C & N Wales	7.7 to 4.8	12–139	8–76	0–65	0–94	10
England, Peak	7.2 to 3.3	29–1113	3–226	4–420	0–644	10
England, Lake District	6.2 to 4.3				500	11
Scotland, Galloway	6.6 to 4.4	25–395				12
N. America:						
Ontario lakes	9.0 to 4.5	0–300				13
Nova Scotia rivers	<4.5 to 5.9	160–328			11–27	14
Adirondack, Big Moose	7.1 to 5.0				300–1200	15
Hubbard Brook (stream)	5.4 to 5				162–405	16

References:
1. Bowen, 1966
2. Stumm and Morgan, 1981
3. Christophersen *et al.*, 1982
4. Muniz *et al.*, 1987
5. Muniz *et al.*, 1987
6. Henriksen *et al.*, 1988
7. Anderssen and Nyberg, 1984
8. Hasselrot *et al.*, 1987
9. Hasselrot *et al.*, 1987
10. Sadler and Lynam, 1986
11. Tipping *et al.*, 1989
12. Wright and Henriksen, 1980
13. Neville, 1987
14. Lacroix and Kan, 1986
15. Driscoll *et al.*, 1981
16. Hooper and Shoemaker, 1985

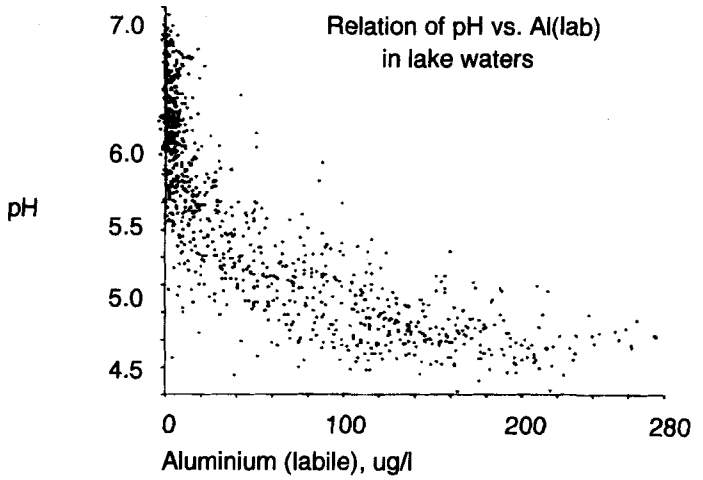

Figure 1.3 Relationship of pH vs aluminium in more than 1000 lakes in Norway (after Henriksen *et al.*, 1988).

recent 1000-lake survey in Norway (Henriksen *et al.*, 1988) shows that below pH 5.5, labile aluminium concentrations are as high as 280 μg/l (Fig. 1.3). In north-eastern America, extensive regional surveys also show that lakes of lower pH have higher aluminium; in the Adirondacks, 90% of those lakes with pH ≤5 have aluminium concentrations of >150 μg/l (Linthurst *et al.*, 1986a). In eastern Canada, close to the Sudbury smelter, Ontario, concentrations of 150 to 1150 μg/l were reported before emission control (Scheider *et al.*, 1979); subsequent improvements, however, are neither consistent with distance from the source (Hutchinson and Havas, 1986) nor with the difference in pH. In 234 Nova Scotian lakes (Canada), total aluminium is 310 μg/l ± 280 (Underwood *et al.*, 1986). In 5 rivers in the same area, dissolved total aluminium is reported to be 160 to 328 μg/l, of which only 11 to 27 μg/l is "labile" inorganic aluminium, and thus about 90% is considered to be the organic "non-labile" fraction (Lacroix and Kan, 1986).

In Belgium, values as high as 8 mg/l (at this concentration no doubt some is as fine particulate material) have been reported for acid humic moorland pools (Vangenechten and Vanderborght, 1980). In New Zealand, high total aluminium concentrations were found in acid streams (123 to 363 μg/l) but never exceeded 84 μg/l in alkaline streams (Collier and Winterbourne, 1987). In these humic acid waters, toxic inorganic aluminium was <50 μg/l.

A global value of 240 μg/l was given by Bowen (1966) for fresh waters, including bogs, but such early values must be in doubt because of inadequate techniques. Some of the quoted values for "total" aluminium are greater than predicted by mineral equilibria, and suspended micro-crystals were probably present (Altshuller and Linthurst, 1984).

In areas where soils are podsolised (commonly high altitude, cool, moist temperate areas with unimproved soils), aluminium is mobilised in the soil profile by percolation of organic and inorganic acids through the upper soil horizons, precipitating in the lower soil horizons where pH is raised (Bache, 1984). Where runoff to surface waters is principally via surface soils in areas with unimproved, "natural," soils, aluminium mobilisation is likely to be significantly greater than from managed agricultural soils.

Several mechanisms have been proposed for the solid-phase control of aluminium concentrations in soil solutions and more dilute water systems (e.g. see Altshuller and Linthurst, 1984). Calculated values of aluminium in interstitial soil water from Swedish sites (Eriksson, 1981) are consistent with those predicted for basic aluminium sulphates, $Al(OH)SO_4$ (van Breemen, 1973), supporting the claim that atmospheric sulphate deposition has acidified and transformed aluminium oxides to the hydroxysulphates (Eriksson, 1981). This hypothesis, however, fails to take account of fluoride, silicate, sulphate and organic complexation reactions, and it is now doubted whether aluminium sulphate minerals (jurbanite, alunite, basaluminite) control aluminium levels in acidified waters; furthermore, analysis of soils and sediments by X-ray diffraction has failed to confirm the presence of these solution controlling minerals (Baes and Mesmer, 1974; Driscoll *et al.*, 1984). Moreover, H^+ concentrations are sufficient to explain aluminium reactions in soil solution, in the absence of organic complexing materials (Glover, 1987). The consequent release of aluminium from soil sources appears to be determined by the presence of "mobile anions" in the soil solution (sulphate, nitrate, and chloride; Johnson and Cole, 1980).

1.4.2 *Surface water; short-term changes*

Acidic episodes in upland waters are associated with high concentrations of total aluminium (e.g. Muniz and Leivestad, 1980a; Schofield and Trojnar, 1980; Hendershot *et al.*, 1986, Sullivan *et al.*, 1986). Related changes in stream flow, pH, dissolved organic carbon (DOC) and aluminium fractions reflect changes in hydrological pathways, especially during heavy rain or after drought. These conditions determine the residence time of drainage water in soils, as well as the possible mobilisation of aluminium from soils or stream sediments.

High flows in streams at snow melt or following storms, and even the epilimnion of lakes in these conditions, have been associated with increased anions and sometimes with lowered calcium and raised aluminium concentrations. "Episodes" of this kind have been observed in the field in Scandinavia and North America (Baird *et al.*, 1987; Campbell *et al.*, 1986; Driscoll *et al.*, 1980; Harvey and McArdle, 1986; Hendershot *et al.*, 1986; Schofield and Trojnar, 1980; Skogheim *et al.*, 1984), and more recently in the United Kingdom (Harriman *et al.*, 1987; Potts *et al.*, 1989; Stoner *et al.*, 1984; Tranter *et al.*, 1988). Some attempts have also been made to simulate events of this kind in the field by addition of acid and aluminium in solution directly to small streams or lakes (Hall *et al.*, 1980; 1985; 1987; Henriksen *et al.*, 1988; Ormerod *et al.*, 1987a; Playle, 1987).

Rain events may also result in stream acid pulses when precipitation rich in sea salt, but low in acidity, is deposited. In this case salts (especially of marine sodium and magnesium) exchange for other cations and hydrogen ions in the soil. This phenomenon is reported in the field (e.g. Harriman *et al.*, 1987; Langan, 1987), in laboratory and plot experiments (Johnson *et al.*, 1986; Christopherson *et al.*, 1982), and in a field experiment (Wright *et al.*, 1988). In these events, high chloride concentrations in runoff are associated with increases in basic cation (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and the acid ions (H^+ and Al^{n+}); the pH of runoff

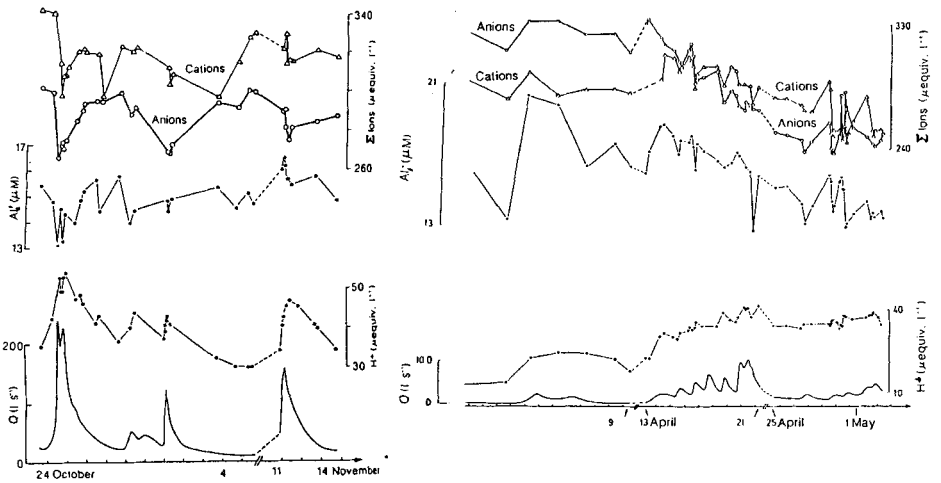

Figure 1.4 Stream flow (Q) and concentrations of major cations and anions, Al_i and H^+, at Birkenes in southern Norway; (a) during runoff following a protracted dry spell in autumn, 1984, and (b) during snowmelt in spring, 1985 (after Sullivan *et al.*, 1986).

water is substantially less than that of incoming rain, and may fall by 1 pH unit or more. Aluminium (labile) was increased 8-fold in the simulated field experiment.

Recent studies have recognised the need to "capture" short-term episodes by frequent or continuous sampling and for coincident aluminium analysis. Some examples of such events are shown in Figure 1.4. Recent investigations (e.g. Harriman *et al.*, 1987; Henriksen *et al.*, 1988; Jacks *et al.*, 1986; Sullivan *et al.*, 1986) show consistently that when acid episodes are observed with sufficiently detailed time resolution, labile aluminium concentration and acidity increase and as flow increases, calcium concentration is diluted. These observations have led to speculation that (a) the initial response to heavy rainfall or snow melt is to displace soil water that has been in contact with soil through the winter; or (b) the initial acid pulse mobilises aluminium previously deposited on inert or biological materials within a lake or stream; or (c) the rapid runoff washes accumulated sediments or flocculated materials from the catchments into streams and lakes, where its aluminium is mobilised or exchanged for hydrogen ions.

At present it is not possible to select one of these as most probable—indeed it seems possible that any one or a sequence of these mechanisms may operate, according to conditions at the observation site. The time-scale of such events is rapid, with a significant variation even within a few hours (Reader and Dempsey, 1989) so that earlier records based on weekly or longer sampling frequencies are difficult to interpret and indeed may be misleading as a guide to fish exposure.

The observations of Sullivan *et al.* (1986) suggest that initial high aluminium concentrations observed at the start of a thaw, before a significant pH drop and increased flow, result from displacement of soil waters with a high aluminium content; for example, concentrations >40 mg/l have been reported for soil waters (Hultberg and Wenblad, 1980). The form of aluminium in these episodes is strongly influenced by prevailing water and soil conditions, particularly the content of organic materials, but also of silica, fluoride and other ions (Campbell *et al.*, 1986; Gunn and Keller, 1986; Hendershot *et al.*, 1986; Sullivan *et al.*, 1986). These observations are supported by studies of flow pathways during episodes (Bishop and Richards, 1988 pers. comm.). However, others (Jacks *et al.*, 1986; Baird *et al.*, 1987) found increases in aluminium in association with the thawing of ice and snow. Some of the enhanced levels of aluminium, however, are attributable to mobilisation of deposited aluminium on stream bed material or on submerged vegetation during acid events within the stream (Henriksen *et al.*, 1988; Tipping and Hopwood, 1988).

Drainage water quality thus reflects the pathways of flow, and equilibria are probably never established; furthermore, the gibbsite equilibrium cannot explain the resulting stream water aluminium chemistry (French, 1985; Nordstrom, 1982; Sullivan *et al.*, 1986) and factors other than pH apparently influence the fraction of potentially toxic inorganic aluminium. During natural episodes, total aluminium concentration may double, but total organic carbon (TOC) may also increase so that labile monomeric (inorganic) aluminium does not always increase proportionately. Sullivan *et al.* (1986) distinguish the temporal course of events with inorganic aluminium and hydrogen ion concentrations both increasing with flow in the early phase of snow melt, but with inorganic aluminium decreasing during autumn (high flow) events and in the later phase of snow melt (Figure 1.4).

Shallow, inshore, lake waters have been shown to be more affected during melt

conditions than the main body of lake water, where soil drainage is more diluted (Gunn and Keller, 1986). Similarly, spatial variations are observed in streams as soluble forms precipitate out and acidity is neutralised (Johnson, 1979).

1.4.3 *Aluminium in soils and sediments*

In soils, aqueous phase composition varies widely, depending on the nature of the controlling species and leaching conditions. At a given soil CO_2 pressure, the possible H^+ and HCO_3^- concentrations can vary by 5 to 100-fold, calcium up to 50-fold and aluminium 1000-fold or more. In conditions of low calcium and bicarbonate, and high aluminium and acidity, control could indeed be via stable aluminosilicates e.g. kaolinite or aluminium sulphates such as alunite, while the metastable $Al(OH)_3$ minerals produce conditions with concentrations above or below the ranges given above. The former circumstances may be expected when a fresh input of water to a soil system comes into equilibrium with the stable minerals already in the soil. These conditions of high total aluminium could arise when groundwater, saturated with aluminium under elevated CO_2 pressures in the soil, degasses at atmospheric conditions and precipitates out more soluble $Al(OH)_3$ minerals. The conditions in which basic aluminium sulphate minerals might form in soils have been discussed by Reuss and Johnson (1985, 1986). However, the kinetic and thermodynamic properties of basic aluminium sulphates suggest that their occurrence under natural conditions is unlikely (Glover, 1987). It should be noted in defence of the hypothesis of aluminium sulphate accumulation in soils that thermodynamic parameters are subject to considerable uncertainty, and that the long residence times in soil may allow some species such as alunite to be formed over an extended time period. A systematic feature of the solution behaviour of aluminium minerals is the persistence of metastable conditions for several years or more. This makes the indirect evidence from groundwater composition unreliable as proof of the presence within soils of specific aluminium minerals.

Drainage waters from forestry areas have aluminium concentrations surpassing those of drainage from adjacent moorland (Harriman and Morrison, 1982; Reynolds *et al.*, 1986; Stoner and Gee, 1985); these and other changes are coincident with canopy closure in forests (Krug and Frink, 1983; Miller, 1984; Reynolds *et al.*, 1986) when anion deposition is increased.

Lake sediments also influence the aluminium concentrations of overlying waters since ion exchange and sulphate reduction there provide major mechanisms for neutralisation of acidity, and hence the precipitation or solubilisation via humic acids which will form complexes with aluminium, maintaining its solubility above that predicted by equilibrium with solid-phase minerals (Baker *et al.*, 1985). These reactions result in direct precipitation or coprecipitation which may explain the reported decrease in concentrations of aluminium downstream or through lake systems (Johnson, 1979; Kullberg and Petersen, 1987; Wieder *et al.*, 1980). A significant fraction may be adsorbed to sediments (Goenaga and Williams, 1988). Field experiments, where aluminium has been dosed into small streams (e.g. Hall *et al.*, 1987) or lakes (Playle, 1987) also confirm this finding.

In summary, the dynamic situation in the aquatic environment is to be contrasted with that in soils, where metastable conditions may exist over periods of several years or more. It might be expected that when soil water is displaced in

association with that from snow melt or heavy rainfall events, equilibrium or steady-state conditions in water are replaced by disequilibrium and the rapid metamorphosis of aluminium species. The disequilibrium conditions may be likely to have different effects on target biota than those that pertain in sustained or equilibrium conditions.

1.4.4 *Aluminium in natural waters*

In surface waters, fast reacting aluminium appears to consist of Al^{3+}, soluble complexes with OH^-, F^-, SO_4^{2-} and organic ligands, while slow reacting, "inaccessible" species such as aluminium oxyhydroxides and aluminium silicates are also present. Organic complexed aluminium is often the predominant form; in acid natural waters at Lake Gardsjon, Sweden, Lee (1985) found 10–40% in this form, 3–30% as AlF^{2+} and 3–10% as $AlSO_4^+$. At pH 6 the organic aluminium fraction predominates, and at pH 5 AlF^{2+}, leaving the aluminium hydroxy complexes as the principal components in the more natural pH 5 to 6 range. Strong organic complexes in natural surface waters further reduce the proportion of inorganic forms (Figure 1.5). As more aluminium is bound to organic material, total aluminium may increase, but these stable complexes do not easily release aluminium and toxicity may decrease (Kramer *et al.*, 1989). Similar conditions appear to prevail in acid Nova Scotian lakes and rivers where about 90% of total aluminium is associated with organic components; dissolved organic materials there are commonly in excess of 10 mg/l (Lacroix and Kan, 1986).

The degree of binding appears to be dependent on the humic substances (HS) present, as well as on pH and the amount of dissolved aluminium. An empirical relationship can be demonstrated for natural waters between the levels of organic aluminium, acidity and HS; this relationship is consistent for a wide range of natural samples as well as for laboratory data (Tipping *et al.*, 1988) and is supported by modelling Al-HS reactions involving the carboxyl and phenolic groups of HS (Backes and Tipping, 1987). The model provides a reasonable prediction of the inorganic components of dissolved monomeric aluminium and supports the assumption that chemical speciation in natural waters involves

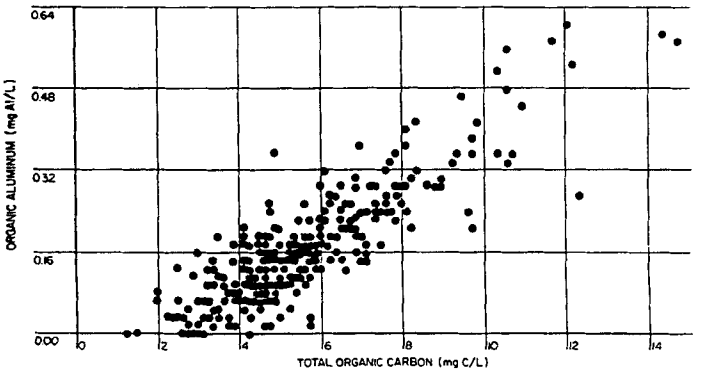

Figure 1.5 Organic monomeric aluminium concentrations in Adirondack surface waters in relation to TOC in solution (after Driscoll *et al.*, 1982).

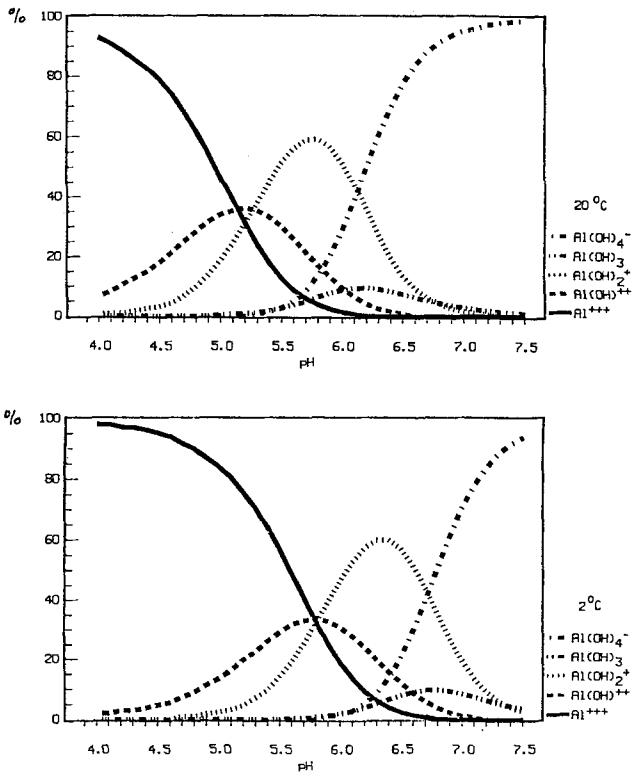

Figure 1.6 Calculated shift of aluminium species distribution with temperature, 2° and 20° (after Lydersen, in press).

rapidly established equilibria among Al^{3+} and its complexes (Tipping *et al.*, 1988).

Tipping (1989) compares data from Duddon streams in 1973 and 1986 to deduce the effect of change in the sulphate and acid deposition. Soil chemistry, cation weathering, evapotranspiration, N uptake by plants, aluminium dissolution from soil minerals, and precipitation in base rock zone and/or streambed, Al^{3+} hydrolysis, and carbonate equilibria are all considered pertinent to the mobilisation of aluminium from soils to surface waters.

A shift of aluminium species distribution is calculated within a realistic range of temperature, possibly increasing toxic components ($Al(OH)^{2+}$ and $Al(OH)_2^+$) to a higher pH as temperature falls (Fig. 1.6).

Considerable attention has been given to distinguishing the component species of aluminium in natural waters, both to elucidate chemical equilibria in the field, and to explain the variable effects observed in fish and other freshwater organisms especially where organic substances are present. It is clear that reported values of "total" aluminium in natural soft waters are misleading as a guide either to aluminium chemistry or to the potential toxicity to aquatic organisms and rather little is published with regard to the assumed or demonstrated toxic species in these natural waters.

2. LABORATORY STUDIES ON TOXICITY TO AQUATIC ORGANISMS

There is some evidence from laboratory studies that $Al(OH)^{2+}$ is the most toxic component of the labile monomeric aluminium fraction for trout and salmon (Fivelstad and Lievestad, 1984; Sadler and Lynam, 1987b) whereas $Al(OH)_2^+$ appears to be the species most highly correlated with toxicity to algae (Helliwell *et al.*, 1983). In contrast to field conditions, where the species of aluminium is often not known, in experimental exposures (both laboratory and field) aluminium is added to experimental media as soluble inorganic aluminium although speciation will change as equilibria are developed. In earlier studies of toxicity and physiological effects of "low pH," results were seen which may not have been wholly attributable to increased hydrogen ion concentration. Many of these investigations did not specify the exposure conditions sufficiently and it is possible that effects reported were due to other components of the experimental media present at low pH rather than the effects of low pH *per se*; this may also be true in the case of aluminium toxicity. In instances where, for example, naturally acidified stream water was used, it is possible that effects attributed to aluminium may have been due to other agents.

2.1 *Mode of Action in Fish*

The physiological mechanisms of aluminium toxicity have been investigated mostly for fish (especially salmonid species) and there are fewer investigations on other organisms. Disruption of respiratory (gas) exchange across the gills, and impairment of ion regulation have been observed. Other sub-lethal indications of aluminium toxicity stress have also been reported, for instance, reduced growth, histopathology, aberrations in behaviour and changes in skin coloration. This review will focus on evidence of aluminium toxicity to European fish species, with confirmatory data of relevance drawn from publications on non-European fish species (see Annex 1).

2.1.1 *Respiratory effects*

Rosseland (1980) measured metabolism in terms of oxygen consumption, and gill ventilation in terms of respiratory rate (but not respiratory volume) in brown trout (*Salmo trutta*) and brook trout (*Salvelinus fontinalis*) at pH 5.0 with a total aluminium concentration of 450 $\mu g\,l^{-1}$—a combination of pH and aluminium reported for the Tovdal River during "acid episodes." Brown trout showed significantly more "stress" symptoms than brook trout. Metabolic rate increased immediately on exposure and remained elevated until ceasing at death after 48 hours. Respiratory rate was also increased to a level of permanent hyperventilation. At death the fish had reduced plasma chloride levels and the gills were clogged with mucus. Although the initial hyperventilatory response of brook trout was similar to that of brown trout, metabolic rate of the former returned to normal/subnormal levels after 12 hours exposure. After 42 hours, the plasma chloride level was normal (130 mmol/l) as was venous pO_2, although the gills

Annex 1 Summary list of literature on aluminium effects on freshwater fish species relevant to European waters.

Literature sources listed in full in bibliography, here sorted by species; not all of these sources are discussed in the text, but for the reader's convenience, are listed in the references. Note that "fry" as used here includes larvae (yolk sac fry) as well as later stages; "juv" are juveniles.

1. *Salmo trutta* (brown trout)

Field, survival	adults	trace metals	Andersson, Nyberg, 1984
Lab, Cl fluxes	juveniles	pH, Al	Battram, 1988
Lab, survival	eggs, fry	pH, cations	Brown, 1981
Lab, survival	eggs, fry	pH, Ca, Al	Brown, 1983
Lab, survival	fry, juv.	pH, Ca, Al	Dalziel, Brown, 1984
Lab, survival	fry	pH, Ca, Al	Dalziel *et al.*, 1986
Lab, Na fluxes	fry	pH, Ca, Al	Dalziel *et al.*, 1987
Lab, survival	fry	pH pulse	Dempsey, 1987
Lab, ion fluxes	fry, 2+ yr	pH, Al	Fivelstad, Leivestad, 1984
Lab, survival	fry	pH, Ca, Al	Howells *et al.*, 1983
Field, survival	adults	pH, misc.	Hunter *et al.*, 1980
Field, gill acc.	adults	pH, Al	Karlsson-Norrgren *et al.*, 1986
Field, density	adults	pH, Al	Linlokken, 1988
Field, survival	adults, fry	pH, misc.	McCahon *et al.*, 1987
Field, physiol.	adults	pH, Al	Muniz *et al.*, 1987
Field, survival	juveniles	pH, Al	Muniz, Leivestad, 1980a
Field, survival	adults	pH pulse	Muniz, Leivestad, 1980b
Field, survival	juveniles	pH pulse	Muniz *et al.*, 1979
Field, survival	adults	pH, Al	Ormerod *et al.*, 1987a
Field, expt.	adults	pH, Al	Ormerod *et al.*, 1987b
Field, distrib.	adults	pH	Prigg, 1983
Lab, physiol.	fry	pH, Mn, Al	Reader *et al.*, 1988
Lab, physiol.	fry	trace metals	Reader *et al.*, 1989
Lab, ion fluxes	fry	pH, Cd, Mn, Al	Reader, Morris, 1988
Lab, metab.	juveniles	pH	Rosseland, 1980
Field, survival	adults	pH, Ca	Rosseland, Skogheim, 1987
Field, physiol.	1–2 yr	pH, Al	Rosseland *et al.*, 1986
Lab, growth	2+ yr	pH, Ca, Al	Sadler, Lynam, 1987
Lab, devel.	fry	pH, Al	Sadler, Lynam, 1989
Lab, gills	fry	pH, Al	Segner *et al.*, 1988
Lab, survival	eggs, fry	pH, Al	Skogheim, Rosseland, 1984
Field, survival	adults	pH, Al	Skogheim *et al.*, 1984
Field, distrib.	adults	pH, Ca, Al	Stoner, Gee, 1985
Field, distrib.	all	pH, Ca, Al	Turnpenny *et al.*, 1987a
Field, distrib.	all	pH, misc.	Turnpenny *et al.*, 1987b
Field, survival	eggs, fry	pH, Ca, Al	Weatherley *et al.*, 1989
Field, distrib.	adults	pH	Wright, Snekvik, 1979

2: *Salmo salar* (Atlantic salmon)

Lab, survival	fry	pH, Si, Al	Birchall *et al.*, 1989
Lab, ion fluxes	fry, 2+ yr	pH, Al	Fivelstad, Leivestad, 1984
Field, survival	adults	pH, Ca, Al	Henriksen *et al.*, 1984
Lab, gills	eggs, fry	pH, Al	Jagoe *et al.*, 1987
Field, status	all	pH, misc,	Haines, 1987
Field, plasma	adults	pH, misc.	Lacroix, 1985a
Field, survival	eggs, fry	pH, misc.	Lacroix, 1985b
Field, physiol.	eggs, 2+ yr	pH, misc.	Lacroix, 1989
Field, survival	fry	pH, misc.	Lacroix *et al.*, 1985
Field, ion fluxes	1+ yr	pH, misc.	Lacroix *et al.*, 1989
Field, physiol.	parr	pH, misc.	Lacroix, Townsend, 1987
Field, survival	fry	pH, Al	Leivestad *et al.*, 1987

Annex 1 (continued)

Field, survival	fry	pH, Al, misc.	McCahon *et al.*, 1987
Field, survival	fry	pH, Al, DOC	Peterson *et al.*, 1989
Lab, Na fluxes	spawners	pH, Al	Potts *et al.*, 1989
Lab, physiol.	eggs, fry	pH, Al	Rosseland, Skogheim, 1982
Lab, physiol.	1–2+ yr	pH, Al	Rosseland, Skogheim, 1984
Lab, physiol.	eggs, fry	pH, Ca, Al	Rosseland, Skogheim, 1986
Field, survival	all	pH, Ca	Rosseland *et al.*, 1986
Field, physiol.	1–2+ yr	pH, Al	Rosseland *et al.*, 1986
Lab, survival	eggs, fry	pH, Al	Skogheim, Rosseland, 1984
Field, survival	smolts	pH, Al	Skogheim, Rosseland, 1986
Field, survival	adults	pH	Skogheim *et al.*, 1984
Lab, survival	smolts	pH, bases	Skogheim *et al.*, 1986a
Lab, survival	smolts	pH, humic subs.	Skogheim *et al.*, 1986b
Field, survival	smolts	pH pulse	Skogheim *et al.*, 1987
Field, survival	smolts	pH, lime	Skogheim *et al.*, 1987
Field, survival	spawners	pH, Al	Skogheim *et al.*, 1984
Lab, gills	1–2+ yr	pH, Al	Stuarnes *et al.*, 1984
3. *Salmo gairdneri* = *Oncorhynchus mykiss* (rainbow trout)			
Lab, field, gills	juveniles	pH, Al	Evans *et al.*, 1988
Lab. physiol.	2+ yr	pH, Al	Freeman, 1973
Lab, survival	1+ yr	pH, Al	Freeman, Everhart, 1971
Lab, plasma	2+ yr	pH, Al	Goss, Wood, 1988
Field, physiol.	adults	pH, Al	Harvey, McArdle, 1986
Lab, plasma	juveniles	pH	Heming, Blumhagen, 1988
Lab, survival	adults	pH, Al	Hunter *et al.*, 1980
Lab, survival	adults	pH, Al	Jones *et al.*, 1983
Lab, plasma	adults	pH, Al	Malte, 1986
Lab, respir.	adults	pH, Al, NaCl	Malte, Weber, 1988
Lab, physiol.	juveniles	pH, Al	Neville, 1985
Lab, toxicity	fry to 2+	pH, Ca, Al	Neville, Campbell, 1989
Lab, respir.	adults	pH, Al	Ogilvie, Stechey, 1983
Lab, physiol.	adults	pH, Ca, Al	Playle *et al.*, 1989
Field, mortality	1–2+yr	pH, Al	Rosseland, Skogheim, 1984
Lab, physiol.	eggs, fry	pH, Ac, Al	Thomsen *et al.*, 1988
Lab, plasma	1+ yr	pH, Ca, Al	Witters, 1986
Lab, haematol.	1+ yr	pH, Al	Witters *et al.*, 1987a
Lab, physiol.	1+ yr	pH, Al	Witters *et al.*, 1987b
Lab, tissues	adults	pH, Al	Youson, Neville, 1987
4. *Salvelinus fontinalis* (American brook trout)			
Lab, survival	eggs, fry	pH, Al	Baker, Schofield, 1980
Lab, ion fluxes	adults	pH, Al	Booth *et al.*, 1988
Lab, ion fluxes	juveniles	pH, Al	Chevalier *et al.*, 1987
Lab, toxicity	eggs, fry	pH, Al	Cleveland *et al.*, 1986
Lab, survival	?	pH, Al, Fe	Decker, Menendez, 1974
Field, survival	adults	pH pulse	Gagen, Sharpe, 1987
Field, tissues	adults	pH, trace metals	Haines *et al.*, 1987
Field, survival	eggs, fry	pH, Al	Hunn *et al.*, 1987
Lab, ion fluxes	eggs, fry	pH, Ca, Al	Ingersoll *et al.*, 1985
Field, ion fluxes	1–2+ yr	pH, Al, misc.	Lacroix *et al.*, 1989
Field, Na flux	adults	pH, Al	McDonald, Milligan, 1988
Lab, metab.	juveniles	pH	Rosseland, 1980
Lab, physiol.	1–2+ yr	pH, Al	Rosseland, Skogheim, 1984
Lab, survival	all	pH, Al	Schofield, Trojnar, 1980
Lab, survival	juveniles	pH, Al	Siddens *et al.*, 1986
Lab, survival	eggs, fry	pH, Al	Skogheim, Rosseland, 1984

Annex 1 (continued)

Field, survival	adults	pH	Skogheim *et al.*, 1984
Lab, respir.	2+ yr	pH, Al	Walker *et al.*, 1988
Lab, physiol.	adults	pH, Al	Wood *et al.*, 1988b
Lab, ion fluxes	fry	pH, Ca, Al	Wood *et al.*, 1989
Lab, plasma	adults	pH, Al	Wood *et al.*, 1988a
Lab, physiol.	adults	pH, Al	Wood *et al.*, 1988c
Lab, survival	eggs, fry	pH, Al	Hutchinson *et al.*, 1987
Lab, survival	eggs, fry	pH, Al	Hutchinson *et al.*, 1989
5. Other species, considered relevant in European waters			
5.1 *Salvelinus namaycush* (American lake trout)			
Field, survival	sac fry	pH pulse	Gunn, Noakes, 1987
Lab, survival	eggs, fry	pH, Al	Hutchinson *et al.*, 1987
Lab, survival	eggs, fry	pH, Al	Hutchinson *et al.*, 1989
5.2 *Coregonus albula* (Cisco, whitefish)			
Field, survival	adults	pH, Al	Grahn, 1980
5.3 *Catastomus commersoni* (common sucker)			
Lab, survival	eggs, fry	pH, Al	Baker, Schofield, 1980
Field, plasma	adults	pH, misc.	Lacroix, 1985
5.4 *Anguilla anguilla* (Atlantic eel)			
Lab, survival	elvers	pH, Al	Fjellheim *et al.*, 1985
5.5 *Gasterosteus aculeatus* (stickleback)			
Lab, survival	adults	pH, metals	Jones, 1939
5.6 *Perca fluviatilis* (European perch)			
Field, survival	adults	pH, Al	Linlokken, 1988
Field, survival	adults	pH, Al	Grahn, 1980
Field, survival	adults	pH	Rask, Virtanen, 1986
Field, fecundity	embryos	pH, Ca, Mg	Valtonen, Laitinin, 1988
Perca flavescens (yellow perch)			
Field, population	adults	pH	Sun, Harvey, 1986
Field, histology	adults	pH, Cl cells	Leino *et al.*, 1987
5.7 *Tinca tinca* (tench)			
Lab, physiol.	adults	pH	Jensen, Weber, 1987
5.8 *Alosa pseudoharengus* (alewife)			
Field, plasma	adults	pH, misc.	Lacroix, 1985
5.9 *Brachydanio rerio* (zebra fish)			
Lab, survival	eggs, fry	pH, Cd, Fe, Al	Dave, 1985
5.10 *Micropterus dolomieui* (small-mouth bass)			
Lab, survival	fry	pH, Al	Kane, Rabeni, 1987
5.11 *Pimephales notatus* (fathead minnow)			
Field, histology	adults	pH, Cl cells	Leino *et al.*, 1987
Field, survival	adults, fry	pH, Al	McCormack *et al.*, 1989
5.12 *Lepomis gibbosus* (pumpkinsed)			
Field, population	adults	pH	Sun, Harvey, 1986
5.13 *Cyprinus carpio* (common carp)			
Lab, survival	adults	pH, Al	Muramoto, 1981
5.14 Mixed species			
Lab, survival	eggs, fry	pH, Al	Holtze, Hutchinson, 1989
Field, diversity	adults	pH, misc	Baker *et al.*, 1984
Field, diversity	adults	pH, Ca, Al	Wales, Beggs, 1986

were apparently still clogged with mucus. Histopathological changes and increased mucus production in the gills of fish may inhibit gaseous exchanges across the gill membrane; thus at low pH and high aluminium, death may be due to respiratory failure rather than impaired ion regulation (Malte, 1986; Rosseland *et al.*, 1988; Wood and McDonald, 1987). Neville (1985) found that in a slightly acidic water mortality was due to respiratory failure, but as acidity was increased (to pH <5.0) ion regulatory failure was the prime cause of death. Hyperventilation is a specific response to labile aluminium exposure; it is reversed by citrate additions (Rosseland *et al.*, 1988). Muniz and Leivestad (1980a, 1980b) reported that venous blood samples from brown trout exposed to low pH and raised aluminium concentrations showed lowered oxygen tension, but blood P_{CO2} and pH were unaffected. Coughing, and clogging of the interlamellar spaces in the gills, was observed at pH and aluminium combinations which caused other physiological stress symptoms.

Similar results with *S. fontinalis* are reported by Wood *et al.*, (1988). Playle *et al.*, (1989) found respiratory effects at pH 5.2 only when aluminium (105 μg/l) was present, but this response was moderate with higher calcium (20 mg/l).

2.1.2 *Ion regulatory effects: haematocrit and blood composition changes*

Muniz and Leivestad (1980a and b) analysed venous blood plasma of brown trout exposed to elevated aluminium concentrations at low pH for osmolality and the ions Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-; plasma Na^+ and Cl^- declined rapidly at toxic aluminium levels. A greater response, in terms of plasma ion disturbance, was found with 900 μg total Al/l added as aluminium sulphate at around pH 5.0, while at pH 4.3 and 4.5 the response was less, and at pH 6.0 plasma ion levels remained normal. This concentration of total aluminium is unrealistically high compared with most field observations but further experiments in the field at pH 5.0 showed that 190 μg total Al/l added as sulphate reduced plasma chloride. In contrast, at pH 4.4, the addition of 380 μg Al/l moderated the effect of acid exposure compared with the effect on plasma ion levels at this pH when no aluminium was added.

Similar plasma ion disturbance in Atlantic salmon (*Salmo salar*) was observed by Rosseland and Skogheim (1982). Haematocrit and plasma chloride levels were measured in pre-smolt stage fish after exposure to total aluminium concentrations of 186–531 μg/l at pH 4.9–5.0. Haematocrit increased and plasma chloride dropped after exposure to all aluminium concentrations tested, the highest concentrations producing the most dramatic changes. The increase in haematocrit was attributed to a reduction in blood volume, rather than to cellular swelling, but no measurements were made to confirm this. The rate at which the plasma chloride level in salmon dropped (0.88 mmol Cl/h) was considerably more rapid than for brown trout (0.33 mmol Cl/h) exposed to similar conditions of aluminium and pH, although there was a higher water conductivity in the salmon experiment (Muniz and Leivestad, 1980a). Wood *et al.* (1988a), using brook trout, found that addition of 333 μg total Al/l at pH 4.4 and 4.8 caused a marked decrease in plasma Na and Cl concentration and a moderate disturbance to blood gas partial pressures before death.

Flux studies (Dalziel *et al.*, 1986, 1987), using brown trout, showed that total aluminium additions (as chloride) above about 40 μg/l at pH 4.5 and 4.0 severely

inhibited Na uptake but had no effect on Na efflux. Inhibition of Na uptake was not observed with the addition of aluminium at pH 5.4. Booth *et al.* (1987) also found inhibition of Na uptake in brook trout and rainbow trout (*Salmo gairdneri* = *Oncorhynchus mykiss*), but in contrast, they found efflux stimulated, although it returned to control levels over 24–48 hours of exposure. Influx inhibition persisted indefinitely and was responsible for net Na loss over the long term. Inhibition of active Na uptake is consistent with decreased Na-K-ATPase and carbonic anhydrase activity found in Atlantic salmon and rainbow trout exposed to 200 μg total Al/l at pH 5 (Reite and Stuarnes, 1987; Stuarnes *et al.*, 1984). In contrast, McDonald and Milligan (1988) found an increase in Na-transport in brook trout at pH 5.2 with 150 μg Al/l.

Exposure of juvenile rainbow trout to pH 4.0–4.5 with 76 μg inorganic Al/l resulted in mortality due to electrolyte loss (Neville, 1985), although survival time at pH 4.0 with aluminium present was greater than at pH 4.0 alone. Similar results were found by Playle *et al.* (1989).

A comparative study of the effects of elevated aluminium and low pH on salmon, sea and brown trout, and brook trout by Rosseland and Skogheim (1984) further confirmed a decrease in plasma Cl concentration and an increase in haematocrit (except for brook trout). This study also demonstrated the difference in sensitivity to high aluminium/low pH combinations seen in different fish species. Salmon (particularly the pre-smolt stage) were most sensitive, followed by sea trout and brown trout, with brook trout being the most resistant. Other plasma chloride concentration measurements have been made by Leivestad and Muniz (1976) at fishkill sites following acid episodes in the River Tovdal (brown trout) and by Skogheim *et al.*, (1984) during a salmon kill in the River Ogna. In both cases, plasma Cl levels of fish from the area of fishkill were about 15% lower than normal; the Tovdal brown trout returned to the normal levels after 10 days.

The clogging of the gills by mucus already reported (Muniz and Leivestad, 1980a; Rosseland, 1980) was also observed in the experiments of Rosseland and Skogheim (1982, 1984) on pre-smolt salmon, when the aluminium concentration of the water was increased to the supersaturated concentrations used in earlier studies, suggesting that it is associated with oversaturation of aluminium with respect to the insoluble phase, $Al(OH)_3$. A similar supersaturation of aluminium (at about 200 μg total Al/l at pH 5.4) was invoked to explain an increase in aluminium in the gills of salmon found dead in the River Ogna (Skogheim *et al.*, 1984).

Precipitated aluminium on the gill surfaces is possibly due to increased ammonium (NH_4^+) excretion at the gill, causing irritation and oedema, lamellar fusion and increased mucus and chloride cell production (Jagoe *et al.*, 1987; Karlsson-Norrgren *et al.*, 1986; Schofield, 1977; Schofield and Trojnar 1980; Youson and Neville, 1987), but this response is not universal and mucus production may be irrelevant in natural conditions (Rosseland *et al.*, 1989).

Increased aluminium concentrations in blood plasma have not been found, although some has been detected in gill tissues (Lacroix *et al.*, 1989; Rosseland *et al.*, 1989) (see paragraph 3.1).

2.1.3 *Sublethal effects: development and growth*

Adverse effects of aluminium on development and growth of larval fish have been documented. Baker and Schofield (1982) found that development of brook trout

larvae was very slow when they hatched in media with over-saturated aluminium concentrations (pH 5.2 and 5.5 with 300 and 500 μg Al/l added as chloride). Stressed larvae were small, and had large quantities of yolk sac still remaining at a time when control larvae had begun feeding and swim-up; the same observation was made by Reader *et al.* (1988) for brown trout larvae exposed over 30 days to sublethal levels of aluminium at pH 5.4 and 4.5. In addition to grossly impaired development, delayed skeletal calcification was also reported along with reduced uptake of calcium, sodium and potassium. In contrast, Wood *et al.* (1989) found that the effect of total aluminium (12 to 1000 μg/l on the net uptake of these ions in brook trout larvae and fry was parabolic, with intermediate concentrations having a slight positive influence. Depressed growth and development of brook trout larvae with aluminium exposure at pH 5.4 and 4.5 was found by Cleveland *et al.* (1986) who noted that although inactive most of the time, exposed larvae tended to scrape their abdomens or sides along the bottom of the exposure vessel instead of assuming the normal posture. Skogheim and Rosseland (1984) found that the period of development from fertilisation to the initiation of feeding for Atlantic salmon, sea trout, brown trout and brook trout in terms of degree-days, was significantly longer in acid streams (pH 5.6–4.8, 93–183 μg labile Al/l) than in lake water at pH 6.4–6.8 containing 10 μg labile Al/l.

Retarded growth of yearling brown trout was recorded by Sadler and Lynam (1987) with concentrations of inorganic aluminium greater than 27 μg/l at pH <5.5; increasing the ambient calcium concentration ameliorated the effect of aluminium (see Section 2.4.1).

There is little reported information for non-salmonid species physiology (see Annex Table). Fjellheim *et al.* (1985) observed lower activity and increased secretion of mucus from the gills and the body of European eel (*Anguilla anguilla*) elvers before death at pH 5.1 with 230 μg total Al/l.

Histopathological changes and increased mucus production in the gills of fish may inhibit gaseous exchanges across the gill membrane; at low acidity and high aluminium, death has been attributed to respiratory failure rather than to impaired ion regulation (Malte, 1986; Rosseland *et al.*, 1989; Wood and McDonald, 1987).

2.1.4 *Effects at pH ≥ 7.0*

There is little concern for concentrations of aluminium <1 mg/l in waters of pH >6.5, and this is reflected in the paucity of work to investigate effects at circumneutral or alkaline pH. In these conditions it is not possible to distinguish organic or inorganic forms by simple procedures, nor are non-toxic organic forms established. As a consequence, aluminium has to be considered as "total," excluding the clay fraction (which would be included in an acidified sample). There appears to be no direct relationship between pH and aluminium toxicity at pH >6.5 to 7.8, and there are insufficient data to show whether there is such a relationship at pH 7.8 to 9.0.

Discharge of aluminium compounds from industrial plant or water treatment works justifies interest in toxicity of aluminium at pH >7.0 (Hunter *et al.*, 1980). In these conditions, dissolved aluminium is largely in the form of $Al(OH)_4^-$. There is some evidence that concentrations <1 mg Al/l may be toxic. Effects reported include death in rainbow trout at 400–500 μg Al/l (Birge *et al.*, 1980), in

goldfish (*Carassius auratus*) embryos and fry at 150 μg/l (Birge, 1978), and in largemouth bass (*Micropterus salmoides,* a North American species) at 170 μg/l (Birge, 1978). Other sublethal symptoms of aluminium stress are reported; Freeman and Everhart (1971) found that rainbow trout fingerlings exposed to >500 μg Al/l showed reduced activity, cessation of feeding, equilibrium problems, gill hyperplasia and darkening of skin colour in the pH range 7 to 9. Rainbow trout juveniles exposed to 52 μg Al/l over 45 days at pH 7 to 9 showed no effects (Freeman and Everhart, 1971).

2.2 *Physiological Effects on Other Aquatic Organisms*

It is speculated that algae sensitive to acid and aluminium lack a protective plasmalemma, so that aluminium penetrates the cell and becomes localised near the nucleus (Stokes *et al.* cited by Havas and Jaworski, 1986). One effect is an inhibition of algal motility (Tease and Coler, 1984) related to plasmolysis and membrane function. Chronic exposure of desmids (1 mg total Al/l) leads to loss of spines, suggesting that aluminium complexation leads to phosphorus limitation (Butcher, 1987). Reduced phosphate uptake (by 50%) is reported (Paul, 1984) at total aluminium concentrations of 200 μg/l and 100 μg/l in two lakes, pH 6.1 to 6.6 and 5.2 to 6.2. Algal communities respond to aluminium exposure over the long term by increase in phosphatase production to maintain the enzymatic recycling of organic phosphates (Jansson, 1981); algal phosphatase activity in an acid lake with total aluminium 300 μg/l was ten times higher than expected.

Aquatic macrophytes appear to be unaffected (Rosseland *et al.,* 1989) and are relatively tolerant of aluminium in water (Butcher, 1987); however, as in sensitive terrestrial species, aluminium appears to affect both calcium and phosphorus levels, and symptoms of toxicity may resemble those of phosphate or calcium deficiency. An inhibition of root growth is reported for *Myriophyllum spicatum* (water milfoil), as with sensitive terrestrial plants (Stanley, 1974). Liverwort (*Nardia compressa*) has been shown to contain large residues of aluminium, up to 40 mg/g dry wt (Tipping and Hopwood, 1988).

In invertebrates, as in fish, aluminium toxicity often impairs ion regulation; for example, the sodium and chloride levels of the blood and tissues are reduced in the water flea (*Daphnia catawba*) and sodium uptake is inhibited and efflux increased (Havas, Hutchinson and Likens, 1984). Acute aluminium toxicity over 47 hr occurs at >300 μg/l at pH 5 to 6.5 in soft water (2.5 mg Ca/l) (Havas, 1985). A toxicity threshold for crustacean zooplankton in general is thought to be >100 μg/l over the pH range 5 to 8.5 (Butcher, 1987).

Aluminium seems to attach to the chloride cells of sensitive species, but not in tolerant species such as *Holopedium sp., Chaoborus sp.* or *Chironomus arthrocinus.* A significant decrease in the body calcium of *D. catawba* (Havas and Likens, 1985), and of the crayfish (*Orconectes virilis*) (Malley and Chang, 1985) is also associated with aluminium exposure. A further effect of aluminium exposure in invertebrates is an increased respiration rate, observed in mayfly nymphs (*Ephemera danica, Heptagenia sulphurea*) at levels of 500 μg/l and 2 mg total Al/l (Hermann and Andersson, 1985). This could be the result of poor oxygen transport linked with greater osmoregulatory and ion transport stress, or of the physical impact of aluminium deposition at the gill surface.

2.3 *Toxicity to Fish*

2.3.1 *Eggs*

Most studies of the toxicity of aluminium to fish eggs have been made in acid conditions, and for a number of species a protective effect of aluminium, counteracting the toxic effect of increased hydrogen ion concentration (pH ≤5), has been demonstrated. It should be emphasised that this general effect of aluminium at low pH is applicable to egg survival and hatch; during and immediately after hatching, aluminium can have an opposite, deleterious, effect on the survival of the emergent larvae (see below) at low pH. The presence of aluminium has also been shown to be deleterious to embryo development and egg hatching.

The most studied species is the American brook trout. Using a medium of dechlorinated, softened tap water (2.2 mg Ca/l) Baker and Schofield (1982) found that at pH 4.2 addition of 200 μg Al/l increased egg hatch from 0 to 52%, compared with the hatch when aluminium was absent, and at pH 4.4 addition of 100 μg Al/l increased hatch from 58% to 83%. With 300 μg total Al/l and pH 4.5, mortality was significantly reduced and the hatch of brook trout eggs increased from 6% in the absence of aluminium to 45.9% (Hunn *et al.*, 1987); a similar beneficial effect of aluminium was also demonstrated by Ingersoll *et al.* (1985) at low pH (4.4–5.2). Complete survival of eggs of Atlantic salmon was obtained at pH 5.0 within a range of 186 to 531 μg Al/l (Rosseland and Skogheim, 1982). Eggs of brook trout, Atlantic salmon, sea trout and brown trout, all reared in acid brook water containing 20–130 μg labile Al/l at pH 4.8–5.6, suffered little mortality until time of hatch (Skogheim and Rosseland, 1984). In contrast, Cleveland *et al.* (1986) found that egg mortality and hatch of brook trout in a soft water medium were not significantly affected with 300 μg Al/l (nominal concentration) at pH 4.5, 5.5 or pH 7.2. Baker and Schofield (1982), found that, at higher pH, addition of aluminium reduced hatch; 500 μg Al/l at pH 5.2 reduced hatch from 98% to 88%, and 300 μg Al/l at pH 5.5 reduced hatch from 93% to 80%.

Aluminium chloride added to water (≥200 μg Al/l) at pH <5.0 protected eggs of white sucker (*Catostomus commersoni*) by increasing survival through to the eyed stage, but not through to hatching. At pH 5.2 and above, aluminium resulted in embryo deformities and a successful hatch of only 1% (Baker and Schofield, 1982). Little effect of aluminium up to 10 mg/l and a pH range of 4 to 7 was found on the egg hatch of zebra fish (*Brachydanio rerio*), although aluminium tended to counteract the deleterious effects of the lower pH exposures (Dave, 1985). However, this author employed organic buffers for pH control, and most aluminium would be complexed.

2.3.2 *Larvae*

(The term larvae will be restricted to the yolk-sac stage from hatching to the point at which feeding begins, i.e. the swim-up stage. The term fry will encompass the stages of development from swim-up until juvenile i.e. until 1+ year-old).

Baker and Schofield (1982) found 300 μg total aluminium/l at pH 4.2 and at "oversaturated" levels at pH 5.2 and 5.5 to be toxic to brook trout larvae. Hunn

et al. (1987) also found that 300 μg Al/l at pH 4.5 and 5.5 was highly toxic to brook trout larvae, particularly at pH 5.5 where 100% mortality occurred within 15 days. However, in water of a higher calcium concentration, 300 μg Al/l at pH 4.5 did not result in significantly greater mortalities than with no aluminium, but at pH 5.5 there was, once again, significantly greater mortality when aluminium was present (Cleveland *et al.* 1986) (see para 2.4.1). Ingersoll *et al.* (1985) also found reduced survival of brook trout larvae with low pH (4.4) and aluminium concentrations over the range 12–1000 μg total Al/l.

In contrast to these findings, Brown (1983) found nominal additions of 250 and 500 μg Al/l (added as $AlCl_3$) at pH 5.4 to 4.5 deleterious to the survival of brown trout larvae over 16 days; Skogheim and Rosseland (1984) found that over a three-week hatching period the cumulative mortalities for larvae of salmon, sea trout, brown trout and brook trout, were 38.9%, 99.1%, 61.0% and 12.4% respectively in natural acid water (pH 5.6 to 4.8) with 93 to 183 μg labile Al/l. Mortality continued after hatching, with cumulative mortality increasing to >99% for sea trout, >93% for salmon, 87% for brown trout and about 13% for brook trout. White suckers in the presence of 100 μg Al/l at pH 5.0–5.5 showed substantially reduced survival; at lower pH there was 100% mortality over 13 days even in the absence of aluminium (Baker and Schofield, 1982).

2.3.3 *Fry and juveniles*

(Fry and juveniles are taken to include the swim-up stage until sexual maturity.)

It is generally believed that sensitivity to aluminium increases with age (e.g. Baker and Schofield, 1980; Brown, 1983), although there are rather few studies where the same exposure conditions have been used with a range of life stages. Some studies using different life stages suggest, in contrast, that this may not always be true (Dalziel and Brown, 1984; Fivelstad and Leivestad, 1984).

Brook trout fry and juveniles are the most investigated species, as for eggs and larvae. Fry which had been held for 37 days since hatching in a soft water medium at pH 7.2 without aluminium and were then exposed to pH 5.5 and 4.5 with either 0 or 300 μg Al/l (as chloride) showed significantly greater mortality in the presence of aluminium (Cleveland *et al.*, 1986). Schofield and Trojnar (1980), using brook trout fry over a pH range from 4.0 and 5.2 and aluminium (as chloride) up to 1000 μg/l, found no effect additional to the toxicity of hydrogen ion at pH 4.0, but above pH 4.4 concentrations greater than 100 μg Al/l caused significantly greater mortality. With 100 μg Al/l or less, mortality was reduced at pH 4.4 and was minimal at pH 4.9 and 5.2. Baker and Schofield (1982) found that aluminium chloride additions of 200 μg Al/l or greater at pH 4.2–5.5 adversely affected brook trout fry survival. The effects of these conditions on this life stage were more severe compared with those on larvae, but a trend to greater susceptibility in older fish was not found in white suckers in the same study.

For brown trout, Brown (1983) found that the median period of survival was significantly shorter after the swim-up stage than for yolk sac fry of brown trout exposed to pH 5.4 with 500 μg Al/l, while Fivelstad and Leivestad (1984) found Atlantic salmon swim-up fry were more sensitive to 110–300 μg Al/l at pH 5.5 than were larvae 2 weeks younger. Dalziel and Brown (1984), however, found an inconsistent pattern of susceptibility of brown trout from larvae though to post swim-up stage over the range 25–200 μg Al/l (added as $AlCl_3$). The presence of

250 and 500 μg total Al/l prolonged survival times of one-year-old brown trout at pH 4.0 and 3.5 in deionised river water to which dilute sodium chloride had been added to restore total ionic strength (Brown, 1981).

Unpigmented elvers of the European eel suffered only few mortalities in water at pH 6.6 and 5.1 with less than 170 μg Al/l but with 230 μg Al/l at pH 5.1 mortality increased significantly (Fjellheim *et al.*, 1985).

2.3.4 *Adults*

(Adults are here considered as sexually mature fish). Fewer toxicity studies have been performed on fish 2+ years and older, than with egg, larval and fry stages, possibly because of difficulties involved in keeping and handling adult fish. Rosseland and Skogheim (1984) found 100% mortality within 48 hours at pH 4.9–5.0 of Atlantic salmon pre-smolts (age 2+) with a mean concentration of 245 μg labile Al/l. At higher concentrations of labile aluminium (313 and 463 μg/l), 100% mortality was reached in about 30 hours. Two-year-old salmon were thus more sensitive than one-year-olds which suffered 100% mortality within 64 hours with a mean concentration of 463 μg labile Al/l. A similar marked difference in sensitivity between 1+ and 2+ fish was not recorded for brown trout in the same study. Potts *et al.* (1989) found physiological changes (impaired ion regulation) and mortality in prespawning (migrating) adult Atlantic salmon, exposed over 48 h to >500 μg Al/l (as the chloride) and pH 5, and transferred directly from sea to fresh water. The normal rate of sodium loss during upstream migration was enhanced and sodium uptake rate was reduced, so that plasma sodium dropped. However, such ion imbalance is characteristic of salmon during the initial passage from sea to fresh water.

Booth *et al.* (1988) exposed adult brook trout for 11 days to a matrix of acidity, calcium and aluminium concentrations (pH's 4.4, 4.8 and 5.2, Al 111, 333 and 1000 μg/l; Ca 25 and 400 ueq/l). Sodium fluxes following the lower aluminium exposures returned to normal levels after about 72 h, even at pH 4.8. Wood *et al.* (1988) also showed that adult brook trout were able to acclimate to adverse pH, Ca, and Al conditions over a 100 week exposure period. No respiratory symptoms were observed with sub-lethal acid exposure (pH 5.2), nor with sublethal acid with 333 μg Al/l, but significant differences in blood acid-base balance were found at low calcium (25 ueq/l). It was also concluded that prior exposure to sublethal conditions of pH, Al, and Ca generates an acclimatory response to more severe acid and aluminium exposure both in respect to ion regulation and respiratory response. Thus fish in natural conditions will have a greater resistance to short term peaks of aluminium in association with episodes of acidity.

2.3.5 *Toxicity at pH ≥ 7.0*

Little information is reported of the effects of aluminium exposure at pH levels in the circumneutral to alkaline range, pH 7.0 to 9.0.

Zebra fish exposed at pH 7.0–7.5 and pH 7.9–9.0 with >500 μg Al/l showed reduced hatch (Dave, 1985). Freeman and Everhart (1971) used dechlorinated tap water to which aluminium and NaOH were added to investigate the toxicity of aluminium over 45 days to rainbow trout fingerlings in the alkaline pH range,

Table 2.1 Summary of effects of exposure of aquatic species to aluminium in the pH range >6.5 to 9.0

Class/species	*pH*	*Al*	*Time*	*Effects reported*	*Reference*
Diatom: *Cyclotella meneghiniana*	7.9	0.81	8 d	Growth inhibition	Rao, Subramian
Algae: *Selenastrum capricornatum*	7.6–7.5	0.57–<0.2	4 d	Biomass reduced; EC_{50} at 96 hr exposure	Call *et al.*
Selenastrum capricornatum	8.2–7.5	0.46–<0.2	4 d	As above	Call *et al.*
Crustacea: *Daphnia magna*	7.7	0.32	21 d	Reduced reproduction	Biesinger, Christiansen
Insecta: *Tanytarsus dissimilis*	6.8	0.83	55 d	37% mortality	Lamb and Bailey
Pisces: *Salmo gairdneri*					
—eggs	7.2	0.50	8 d	56% mortality	Holtze,
—fingerlings	7.3–6.6	0.51	44 d	<50% mortality	Freeman and Everhart
—embryos, fry	7.4	0.56–0.37	28 d	Death and deformity EC_{50}	Birge *et al.*
—fingerlings	8.0–	50.0	10 d	40% mortality, 96 hr	Hunter *et al*
—fingerlings	8.5	50.0	10 d	100% mortality, 42 hr	Hunter *et al*
—fingerlings	7.0	50.0	10 d	No effects	Hunter *et al*
—fingerlings	7–9	0.05	45 d	No effects	Freeman, Everhart
Salmo trutta	6.9	0.14	10 mo	Gill deformity, skin dark, incr. respir	Karlsson-Norrgren

pH 7.0–9.0. Mortalities and behavioural aberrations were observed with a concentration of 5.4 mg Al/l throughout the range of pH, being most pronounced at pH 9.0. Over a period of 10 days, Hunter *et al.* (1980) found no mortality of rainbow trout fingerlings at 50 mg Al/l at pH 6.0 and 7.0; increasing the aluminium concentration to 200 mg/l at pH 7.0 failed to produce any mortality. However, Hunter *et al.* (1980) reported rainbow trout mortalities with 50 mg Al/l at pH 8.0, 8.5 and 9.0.

Effects of aluminium at pH >6.5 are summarised in Table 2.1; diatom growth is inhibited at 0.8 mg/l, and algal biomass reduced at 0.6 mg/l; a daphniid showed reduced reproduction at 0.3 mg/l. It should be noted that these single reports need support from further investigations.

2.4 *Toxicity to Other Aquatic Organisms*

Although most aluminium toxicity studies have concentrated on fish, some studies have used other aquatic organisms possibly significant in the food chain.

2.4.1 *Invertebrate fauna*

2.4.1.1 *Introduction.* In comparison with fish, there are fewer data available on the toxicity of aluminium, or its fractions, to invertebrates. While there are some studies of invertebrate occurrences at field sites where aluminium has been

analysed, this begs the question of whether the absence of a particular biological species is attributable to an excessive concentration of this putative toxic agent, or to another cause. There is now, however, a growing literature reporting on laboratory exposures of selected invertebrate species to aluminium, but these tests have often not been carefully designed, nor adequately monitored, so that the exposure conditions are sometimes in doubt. Furthermore, the invertebrates present a greater diversity of physiology where a common response to a toxic agent is unlikely; those groups which have ion-regulatory systems analogous to those of fish seem to be those most probably affected by aluminium. Only a limited variety of species have been tested, and only some life stages, so that the body of information is much less than for fish. Almost nothing is known about sublethal effects on invertebrate species and only very few papers try to analyse the mechanisms of toxic action. The potential for field exposure trials has scarcely been recognised, although one or two such experiments are now reported (Ormerod *et al.*, 1987; Hall *et al.*, 1985).

In this review, help has been sought from recent Canadian reviews (Brett, 1989; Butcher, 1987; Neville, 1987) with selection of those species or genera which are common or analogous with Europe. Recent literature (to end 1989) reporting on European species has also been assessed and summarised. It has often been assumed that invetebrates must be as sensitive to aluminium as fish, and that toxic mechanisms are also similar. The evidence for this assumption will be assessed in the light of the information available.

2.4.1.2 *Protozoa:* There appears to be wide variation in tolerance of protozoan species; *Peranema trichophorum* and *Euglena gracilis* exposed to unrealistically high concentrations, 560 and 1000 mg Al/l, for 3 h at pH 5.5 to 6.5 and 6 to 7, respectively, showed no mortality (Ruthven and Cairns, 1973) but some sensitive species, *Tetrahymena pyriformis* and *Chilomonas paramecium,* could tolerate exposure to only 1 mg/l at pH 5.5 to 7.4 (Ruthven and Cairns, 1973). The high exposure concentrations may have been less than stated, due to precipitation during exposure.

2.4.1.3 *Crustacea:* The most studied species is *Daphnia magna,* commonly used to define acceptable water quality criteria, largely because of its near universal availability and ease of handling. *Daphnia magna* exposed to 1.4 mg/l for 48 hr at pH 7.5 to 8.2 was immobilized and a 48 hr LC50 of 3.9 mg/l at pH 7.7 was derived (Anderson, 1944). This species exposed for 24 hr to $\geqslant$300 μg/l Al (total) in soft water of 2.5 mg calcium/l at both pH 5 and 6.5 showed mortality but aluminium was more toxic than acidity at pH 5.5. Aluminium decreased survival by 10% at 54 μg/l with 4 mg Ca/l and 20 mg Ca/l and by 50–60% with lower calcium, 0.4 mg Ca/l and 0.04 mg/l (Havas, 1985 and pers. comm. in Neville, 1987). *Daphnia magna* exposed to 320 μg total Al/l at pH 7.7 for 21 d showed reduced (16%) reproduction; the LC50 was 1.4 mg Al/l (Biesinger and Christensen, 1972). Mortality is reduced if organic content of the water is high (Burton and Allen, 1986). Vangenechten *et al.* (1989) reviewed laboratory studies on invertebrate survival and physiology, mostly work on daphniids, insect larvae, and gammarids. Aluminium protected against pH 5.0 exposure in *Daphnia magna*; other daphniid species appear to be less sensitive, and insect larvae are less sensitive than crustaceans. *Gammarus fossarum* is highly sensitive to pH <6.0 with low buffering; Na improves survival, but not K, Mg or Ca.

Other crustacean species in the zooplankton, e.g. *Daphnia* sp. and *Cyclops* sp., exposed to 100 μg total Al/l for 72 hr exhibited acute mortality: 80 to 100% at pH 5; 25 to 30% at pH 6 to 7.2; and 50 to 65% at pH 8.5. In the same conditions, *Diaptomus* sp. showed 70% mortality at pH 5, zero at pH 6 and 7.2, and 90% at pH 8.5 (Minzoni, 1984), and is apparently a more resistant species, at least in these conditions. Two north American species, *Daphnia catawba* and *Holopedium gibberum,* were judged to tolerate concentrations up to 1 mg/l at pH 6.5 (Havas *et al.*, 1984).

Brett (1989) has reviewed published work on the effects of acidification (including exposure to aluminium) on zooplankton communities, confirming the relative sensitivity of daphniids and copepods. A variety of sub-lethal responses are identified—reduced filtering, ecdysis mortality and impaired reproduction, as well as physiological effects which parallel those found for fish. He notes that studies of acute exposure on single species may not represent what is seen in the field. Surveys have been useful to elucidate trends in community structure, but many studies are not statistically significant and their ecological relevance is not well understood. The reduced species occurrence in acid waters is thought to reflect the relative fitness of a species to biotic stress rather than to chemical factors, or direct toxicity of pH or aluminium, which seldom "explain" the community variations observed.

Planktonic crustaceans (Cladocera, Cyclopids, Diaptomids and Rotifera) exposed in lake enclosures dosed with $Al_2(SO_4)_3$ to concentrations from about 120 to about 200 μg Al/l over a period of 22 days showed a mean decrease in numbers (57%), but concentrations of aluminium declined during exposure due to flocculation; the authors concluded that the aluminium concentration was "probably too low to be toxic to planktonic organisms" (Zarini *et al.*, 1983). Hornstrom *et al.* (1984) argued that the impoverished plankton communities of acid lakes is not attributable to low pH as such but to a raised level of aluminium which produces oligotrophic conditions by precipitation of phosphorus. There is also evidence of a direct toxic effect on some species where, at concentrations $\geq$100 μg Al/l, reduced growth was observed in 13 of 19 species tested, including desmids and diatoms. In contrast, most zooplankton species, while not very sensitive to low pH, reflect the oligotrophic conditions. In lakes with Al >180 μg/l, 10 of 30 species originally present were lost, possibly due to Al toxicity, and demonstrated at 150–300 μg/l for the daphnids, *Daphnia magna* and *Acroperus harpae.*

Larger crustaceans show a greater degree of tolerance: no mortality of crayfish is reported as due to aluminium (Berrill *et al.*, 1988). The crayfish, *Orconectes virilis,* exposed to 200 μg total Al/l at pH 5.5 showed reduced (by 20%) calcium uptake but this effect was not evident at lower pH (<5) or at higher pH (6 to 6.7) (Malley and Chang, 1985). The water louse, *Asellus intermedius,* exposed to 250 μg Al/l in natural stream water at pH 5 showed no increased mortality but addition of 500 μg Al/l at pH 4 did cause significant additional mortality (Burton and Allan, 1986) in cold (2°C) but not warm (15°C) water. McMahon and Stuart (1989) review physiological problems of crayfish in acid waters; several studied species (*Orconectes rusticus, Procambaris clarki, O. virilis*) are rather tolerant to pH exposure (pH <3.0), while *O. propinquus* shows 30% mortality at pH 4.0 (5 days). Physiological effects include Na flux changes, haemolymph acid-base status. *P. fallax* is a species which occurs naturally in acid waters.

2.4.1.4 *Insect larvae:* Aquatic insect larvae, especially of mayfly species, are thought to be limited in upland streams by water quality, particularly pH and aluminium (Sutcliffe, 1983) but tolerance to aluminium exposure has rarely been tested directly and presence of other ions (sodium and chloride) is also important (Sutcliffe and Hildrew, 1989). The stonefly, *Nemoura* sp., exposed to 250 μg Al/l in natural stream water at pH 5 showed no mortatlity, but 500 μg Al/l and pH 4 caused additional mortality; it was again increased significantly in cold (2°C) compared with warm (15°C) water (Burton and Allan, 1986). Dipterans, *Chaoborus punctipennis* and *Chironomus anthrocinus,* exposed to levels of 20 μg/l to 1.02 mg Al/l at pH 4, 4.5, 5 and 6.5 for 8 days were unaffected and *Chironomus riparius,* exposed in the field to levels greater than 20 mg/l were abundant (Havas and Hutchinson, 1983). Another dipteran, *Tanytarsus dissimilis* (second and third instars), exposed to 832 μg total Al/l for 55 days at pH 6.8 showed 38% mortality; exposure at 6.5 and 78 mg/l for 96 hr showed no effects, but exposure to the same concentrations for 14 to 38 d resulted in complete mortality (Lamb and Bailey, 1981). *Heptagenia sulphurea* and *Ephemera danica* exposed to 500 μg Al/l at pH 4 and 4.8 for 10 d showed increased respiration but no mortality (Butcher, 1987; Herrmann and Anderson, 1986).

Ion regulation, as in fish, is affected in *D. magna,* crayfish, mayflies and corixids, with inhibited sodium influx reflected in lower plasma concentrations (Appelberg, 1985; Havas and Likens, 1985; Herrmann, 1987; Otto and Svenson, 1983; Witters *et al.,* 1984). At very low pH, aluminium can ameliorate acid toxicity, as in fish (Havas, 1985; Havas and Likens, 1985; Herrman, 1987; Rosseland *et al.,* 1989).

2.4.1.5 *Mollusca:* Mollusca are generally absent or rare in acid, low-calcium waters, so that aluminium toxicity is somewhat irrelevant; a few investigations have been reported. No mortality due to aluminium as much as 100-fold greater than the natural range of concentrations (>100 μg/l) found in Ontario lakes has been demonstrated for bivalves or gastropods (Herrmann, 1987; Mackie, 1986; Rosseland *et al.,* 1989). However an extensive kill of *Limnea peregra* was seen during an acid episode in a limed Swedish lake (Hultberg and Andersson, 1982), possibly due to high aluminium. The snail, *Physella heterostropha,* exposed to 250 μg Al/l in natural stream water at pH 5 showed no mortality and further addition of 500 μg Al/l at pH 4 did not increase mortality (Burton and Allan, 1986). The freshwater mussel, *Anodonta grandis,* exposed in a field experiment to 2.24 mg total Al/l at pH 4.5 (reduced from 5.9) showed changes in blood composition (Na and Cl decline, Ca increase) but no mortality after 26 d (Malley *et al.,* 1987).

2.4.1.6 *Macroinvertebrate communities:* Macroinvertebrate assemblages in upland streams are recognisably poorer in acid waters (Sutcliffe and Hildrew, 1989) possibly in association with higher aluminium concentrations. Thus, acid streams (New Zealand) with pH 4.3 to 5.7 and 123 to 363 μg total Al/l had 47 taxa compared with 64 in more alkaline streams with lower aluminium (84 μg/l) (Collier and Winterbourne, 1987). Ormerod and Edwards (1987) analysed communities in relation to environmental factors at 45 upland sites in Wales but did not include aluminium although concentrations are reported elsewhere (Ormerod *et al.* 1987a) to be high. Several recent reports (Hall *et al.,* 1987;

Kullberg and Petersen, 1987; Ormerod *et al.*, 1987c) provide evidence of an increase in invertebrate drift when streams are subjected to pulsed additions of aluminium (as Al^{3+}). Altitude is also a significant and confounding influence, along with physical conditions of the stream bed and macrophyte abundance (Sutcliffe, 1986).

2.4.1.7 *Summary:* In summary, it can be seen that invertebrate groups have a wide diversity of response to aluminium, no doubt reflecting different modes of respiration and ion regulation. Protozoa appear to be highly tolerant, although the reported response of a few cultured species to high exposures may be unrepresentative. Crustaceans are sensitive in soft acid water, but to concentrations typically at about an order of magnitude higher than those that affect fish; in the field, species diversity is related to a number of water quality variables, many of them (like pH, Ca, Al) inter-related, so that the influence of aluminium alone is difficult to judge unless other water quality characteristics are documented and their contributory effects known. Insect larvae are diverse; they can be sensitive (e.g. mayfly species) or tolerant (e.g. chironomids). This reflects their distribution in upland acid waters where again other water quality and stream characteristics, as well as altitude, are known to be influential. Molluscs seem to be insensitive to aluminium at realistic (i.e. about 100 μg/l) concentrations; other associated conditions in acid waters, such as low calcium and presence of other toxic ions, are more limiting. Ecological considerations are also important; herbivorous taxa are scarce in acid upland streams and "shredders," "collectors" and predators are the dominant feeding guilds (Townsend *et al.*, 1983). Insect communities of lakes or streams are also profoundly influenced by fish predation (Zaret, 1980) and introduction of fish to acid lakes (or vice versa) has changed the character of invertebrate communities (Eriksson *et al.*, 1980).

2.4.2 *Plants*

2.4.2.1 *Diatoms:* Growth of *Cyclotella meneghiniana* exposed to 810 μg total Al/l for 8 d at pH 7.9 was inhibited and mortality occurred after exposure to 6.5 mg/l for 8 d at pH 7.9 (Rao and Subramian, 1982).

2.4.2.2 *Algae:* The algal species, *Selenastrum capricornutum,* exposed to a 150-fold range of concentrations (200 to 570 μg total Al/l) for 96 hr at pH 7.6–7.5 showed (50%) reduced biomass after 4 d; exposure to >200 to 460 μg total Al/l for 0–96 hr at pH 8.2–7.5 showed the same effect (Call *et al.*, 1984). The same organism exposed to 990 μg Al/l for 14 d at pH 7 showed reduced cell counts and increased mortality (Peterson *et al.*, 1960). *Chlorella pyrenoidosa* exposed to 30 μg total Al/l for 48 hr at pH 5.2 in synthetic hard water showed 50% growth reduction (Campbell and Stokes, 1985); toxicity was strongly reduced in the presence of organic ligands (Helliwell *et al.*, 1983). The same species exposed to high aluminium concentrations has a tolerance of 24 mg/l, and some strains have even higher tolerance, according to Foy and Gerloff (1972). Another species, *Chlorella vulgaris,* exposed to 4 mg Al/l for 3 to 4 mo at pH 7 showed growth inhibition (De Jong, 1965 in Butcher, 1987). The colonial form, *Spirogyra varians,* exposed to 135 μg Al/l (form not specified) at unknown pH resulted in 100% mortality (Bohm-Tuchy, 1960).

Phytoplankton communities in Canadian Shield lakes exposed to added aluminium (50 μg Al/l) concentrations showed significant decreases in phosphate uptake and photosynthesis at pH 5.2 to 6.9 (Nalewajko and Paul, 1985).

In contrast, it is reported elsewhere that "Many algal species have high aluminium tolerance; *Spirogyra sp.* from a peat bog needed a minimum exposure to 27 mg Al/l (form not specified) to cause mortality after 96 hr" (Butcher, 1987, quoting Bohm-Tuchy, 1960). Butcher suggests that species with poorly developed plasmalemmas are easily penetrated by the aluminium ion. These contradictory findings also probably reflect inadequate characterisation of aluminium species in the presence of organic ligands and uncertainty concerning concentrations of dissolved species.

2.4.2.3 *Macrophytes:* Aquatic macrophytes are relatively tolerant to aluminium (Butcher, 1987). Duckweed, *Lemna minor,* was exposed to aluminium concentrations of 300 μg/l to 46 mg/l (i.e. a range of 1500–fold) at pH values of 7.6 and 8.2 for 96 hr without significant effect (Call *et al.*, 1984, cited in Butcher, 1987).

The observation that macrophytes are less diverse in acid, high aluminium waters, may reflect also the influence of altitude which has a dominating influence for this group (Stokoe, 1983). A study of upland streams in Wales, U.K., (Ormerod, Wade and Gee, 1987) showed that floral assemblages were related statistically, most strongly to pH and aluminium concentrations, among other water quality variables. In turn, the macroinvertebrate fauna is less diverse at acidic sites with sparse flora. In contrast, the high tolerance of certain plant species to these conditions leads to dominance of some such as the liverworts, *Scapania undulata* and *Nardia compressa* (even at pH <4 and aluminium >2 mg/l), which are able to take up and release aluminium from and to the ambient medium as pH changes, without harm (Caines *et al.*, 1985; Tipping and Hopwood, 1988).

In summary, it appears that algae and diatoms are often insensitive to aluminium at environmental concentrations but a few sensitive tested species show sublethal response (reduced growth, decreased phosphate utilisation) at 30 to 130 μg Al/l. Some species colonising acid environments, on the other hand, seem to have a tolerance to "total" levels much higher (i.e. mg/l) but in reality may have been exposed to lower (dissolved) concentrations. Macrophytes are also tolerant of high concentrations, although species are limited in acid, upland waters with high aluminium concentrations, possibly because of other, associated, chemical and physical conditions.

2.4.3 *Amphibia*

Bufo bufo exposed to 2.5 and 5 mg total Al/l at pH 4.0, 4.5 and 5.0 showed slight increase in mortality at pH 4.5, about 50% mortality at pH 4.0, and 100% mortality at pH 3.5. Similar results were found for 3 species of *Rana.* Effects are seen mostly in egg hatch; the larvae become progressively less sensitive and adults of these species are found in waters of a wide range of pH (down to pH 3). Some *Triturus* species and *R. arvalis* are able to exploit waters of pH 4 to 4.5, presumably with high aluminium concentrations, which more sensitive species cannot tolerate (Leuven *et al.*, 1986).

Bufo americanus exposed to aluminium showed reduced hatch as concentration was increased from 35 μg labile Al/l to 46 μg/l (total Al 69 μg/l to 75 μg/l) and transferred from pH 6.0–6.5 to pH 4.3 for 4 d; no mortality of tadpoles was seen (Clark and Hall, 1985). The authors concluded that pH differences are associated with other chemical variables, "making it impossible to distinguish the effects of any one."

Rana sylvatica exposed to the same conditions also showed reduced hatching at pH 4.3 but not at pH 4.8, but no mortality of tadpoles at pH 4.3 (and inconsistent results at pH 4.8 and 4.75) (Clark and Hall, 1985); acute threshold concentrations for these species was judged to be 69 μg total Al/l at pH 4.3 (Butcher, 1987).

Data for *Rana arvalis, R. temporaria*, and *R. esculentus* exposed to high aluminium and pH 3 to 5 are included in Leuvens *et al.* (1986) (see *Bufo bufo* above); lethal pH levels are <3.5, and critical pH levels are <4.0, for all three species, but *R temporaria* mortality is increased to 60% at pH 5 and to 95% at pH 4.5 by exposure to 2.5 mg total Al/l.

Ambystoma maculatus exposed to 37 μg labile Al/l (63 μg total Al/l) at pH 4.8 for 23 d showed reduced hatching (23%, according to Butcher, 1987), but the authors (Clark and Hall, 1985) say "At the pH levels tested . . . there can be no conclusive statements . . . for this species."

Cummins (1986) exposed tadpoles of the common frog (*Rana temporaria*) to 800 and 1600 μg Al/l. With 1600 μg Al/l, 50% mortality occurred before metamorphosis was reached. With 800 μg Al/l, 42% mortality occurred at metamorphic climax (foreleg emergence). Those tadpoles which survived through metamorphosis were very small and it is likely that their fitness would have been severely affected. A comparison of *R. temporaria* eggs taken from lowland and upland sites showed that the embryos were not affected by low pH in the absence of aluminium. Increasing aluminium concentrations reduced survival of lowland embryos from lowland waters even in circumneutral water, while upland embryos were unaffected. In acid waters, survival of embryos hatched from eggs of both areas was reduced with increasing aluminium concentrations, or growth abnormalities or reduced growth were observed (Tyler-Jones *et al.*, 1989). In contrast, Gascon *et al.* (1987) found that hatching of *R. sylvatica* eggs was not affected by exposure to 200 μg total Al/l at pH 4.5. Aluminium complexed with fluoride is reported to be toxic to amphibian eggs, in contrast to fish eggs (Clark and Hall, 1985; Clark and Lazerte, 1985).

In summary, it is evident that amphibia, except at egg hatch, are tolerant to aluminium exposure at environmental levels characteristic of acid waters. Chronic toxicity of aluminium appears to be pH dependent for amphibia—as pH drops, aluminium sensitivity increases (Butcher, 1987) in contrast to fish eggs where aluminium is reported to mitigate the effects of low pH <5.2.

The reported lack of amphibian "success" in colonising acid, upland waters might thus be explained by other chemical or physical variables rather than by aluminium at environmental concentrations.

2.5 *Factors Modifying Toxicity*

While pH is shown to be important in modifying aluminium toxicity, other components in water can also be critical. For instance, it is known that temperature can influence the relative proportions of aluminium species (Figure

1.6 (p. 130)). The presence of elevated levels of other potentially toxic metals in addition to aluminium could, of course, produce more severe responses compared with aluminium alone, but other water quality factors which mitigate the toxicity by protecting physiological sites of action or by interacting directly with aluminium to produce complexes which render it less harmful than if present in an uncomplexed form.

2.5.1 *Calcium concentration*

The protective role of calcium in countering the toxic effects of elevated hydrogen ion concentrations in fish is well documented (Booth *et al.*, 1988; Howells *et al.*, 1983; Howells, 1984; Muniz and Leivestad, 1980; Playle *et al.*, 1989; Rosseland *et al.*, 1989; Wood *et al.*, 1989). Increased calcium concentration has also been reported to mitigate the toxicity of aluminium in a number of laboratory and field studies.

As already noted above, with a Ca concentration of >3 mg/l compared with <0.5 mg/l, Cleveland *et al.* (1986) found lower mortalities of brook trout at pH 4.5 with 300 μg Al/l. Ingersoll *et al.* (1985) also found that increasing calcium concentration over the range 0.5–8.0 mg/l, improved survival of brook trout larvae and fry exposed to pH 4.0 to 6.5 and aluminium to 1.0 mg/l. Survival of brown trout larvae was also improved in exposures of 0.25 or 0.50 mg total Al/l at pH 5.4–4.5 if the calcium concentration was raised from 0.5 to 1.0 mg/l or greater (Brown, 1983).

Gascon *et al.* (1987) found 100% mortality of *Rana sylvatica* tadpoles if only 0.5 mg Ca/l was present with 200 μg total Al/l at pH 4.5. Mortality was reduced to about 20% if calcium was increased to 100 mg/l and the pH raised.

In a study of aluminium toxicity (100 μg/l at pH 5.35) to rainbow trout, Dietrich (1988) tested the ameliorating effect of added sodium chloride, but only concentrations of 4 meq/l (i.e. 92 mg/l) or more were effective.

2.5.2 *Inorganic and organic complexes*

The most commonly occurring inorganic complexes of aluminium are those with fluoride; aluminium hydroxides, sulphates and silicates and simple organic aluminium complexes also occur naturally. It has become evident (see Sections 1.2, 1.4.4 and Figure 1.2) that organic complexed aluminium, although often the predominant soluble form of aluminium, is relatively non-toxic to most aquatic biota. Thus acid waters of high DOC (>10 mg/l) or humic content are usually non-toxic even though of high aluminium content (Lacroix and Townsend, 1987). However, since conditions in natural waters are rarely in equilibrium, a potential for toxicity will remain if speciation changes in response to water quality fluctuations.

In non-calcareous soils in temperate climates, weathering products include mobile hydrous aluminium silicates (imogolite) from which aluminium can be leached to surface waters (Farmer, 1986). Independent studies of human physiology (Birchall & Espie, 1986) suggest that interaction between silicic acid and aluminium hydroxides in bone tissue protect against the toxic effect of aluminium on enzyme activity. In the natural environment the levels of silicon in soil solutions and streams (above 3 mg Si/l) favours the formation of imogolite,

and silicon will always be in excess of that needed to complex the aluminium present (Farmer, 1986); this is possibly a reason why aluminium is not a toxic agent in many fresh waters. Birchall *et al.* (1989) found that the acute toxicity of soluble inorganic aluminium was entirely eliminated by concentrations of silicic acid $(SiOH)_4$ which provide a 13:1 ratio of Si:Al. They argue that this is present in many natural waters, thus explaining some fish presence even when aluminium concentrations are high.

Citrate has been demonstrated to detoxify dissolved aluminium; citrate and other similar anions from plant decomposition may be important in field conditions. Brook trout larval survival after 14 days exposure at pH 5.2 and pH 4.4 with 0.5 mg Al/l was significantly improved when 0.5 mg F/l was added (Baker and Schofield, 1982; Driscoll *et al.*, 1980) but addition of 30 mg citrate/l at pH 5.2 and 4.4 with 0.5 mg Al/l resulted in survival which was not significantly different from control conditions without aluminium at the same pH levels.

A test using the commercial "Beckman microtox" system with marine bacteria (*Photobacterium phosphoreum*) (Gunn *et al.*, 1986) also demonstrated the lack of toxicity of the aluminium citrate complex up to concentrations of 27 mg total Al/l, compared with an EC50 in the absence of citrate of 300 μg Al/l. Aluminium fluoride did exhibit some toxicity, although significantly less than that of "free" aluminium. Additions of 10 mg/l and 40 mg/l fulvic acid also reduced the toxicity of aluminium (200 μg Al/l) by 24% and 61% respectively. A natural water sample of high humic acid content, with low pH and calcium, had an EC50 of 2100 μg Al/l (Gunn *et al.*, 1986). Addition of 0.2 mg F/l, however, did not mitigate the effect of aluminium additions at pH 4.32 and 4.14 on hatching of eggs of *Rana sylvatica* and *Bufo americanus* (Clark and LaZerte, 1985).

In humic natural waters, there is a strong tendency for dissolved aluminium to form polymeric species e.g. with carboxylic and phenolic groups (Backes and Tipping, 1987), and thus to be detoxified. Where there are three or more hydroxide molecules for every Al^{3+}, the tendency to form polymeric species is enhanced (Smith and Hem, 1972). Many polymeric forms are unstable and convert to a solid precipitate upon aging. The increasing size of polymeric forms in unstable solutions is often associated with decreased concentrations of toxic monomeric aluminium and decreased pH. Some polymeric solutions are, however, quite stable; $Al_{13}O_4(OH)_{24}^{7+}$, for example, may be an important chemical form even at low aluminium concentrations around pH 6 (Baes and Mesmer, 1976). Supporting observations in laboratory, and field tests using Nova Scotian stream waters with high humic acid content (DOC >10 mg/l) (Lacroix and Kan, 1986; Lacroix and Townsend, 1987; Stewart *et al.*, 1990) indicate that acidity rather than aluminium is the toxic agent responsible for salmon loss in these waters.

A positive statistical relationship between rates of Alzheimer's disease in man and drinking water aluminium concentrations has been shown (Martyn *et al.*, 1989). It has been suggested that since water intake of aluminium is only <1% of the total daily intake, its bioavailability in drinking water is greater than in foodstuffs. However, other variables may play some role.

2.5.3 *Summary*

The chemical speciation of aluminium and thus its toxicity is explained primarily by pH and secondarily by the availability of fluoride, citrate, and organic ligands.

As pH and available ligands vary from one body of water to another (even within the same catchment), aluminium species distributions will also differ. Therefore, the characterisation and estimation of aluminium toxicity in aquatic environments will be dependent on chemical species identification and quantification so as to permit the development of reliable relationships.

3. ACCUMULATION IN AQUATIC ORGANSIMS

3.1 *Accumulation in Fish*

Data for accumulation of aluminium in fish or other aquatic organisms are rather few, and are difficult to interpret. First, it is not always clear from the reports of analytical studies that the accumulated aluminium is truly lodged within the tissues, or whether it is deposited as a surface precipitate or adsorbed floc; this is particularly uncertain when whole animals are analysed. Secondly, it is assumed, in deriving a "bioconcentration factor" (i.e. a ratio between ambient water or sediment concentrations and that of the organism), that exposure conditions have been relatively constant; it is evident that in the field this condition is exceptional and that even in the laboratory the stability of aluminium species in test media is in question.

The gills of fish are recognised as a major uptake site for aluminium from the ambient water and a number of reports provide evidence of gill mucus production on aluminium exposure; this response, as well as the sharp gradient of pH and other chemical conditions across the gill membrane is known to cause precipitation and flocculation. The degree to which aluminium is transferred across the gill membrane is thus uncertain, particularly as contamination in preparing gill material is virtually impossible to control. Nonetheless, some values given in the literature are as follows:

The whitefish, *Coregonus albus*, 47 μg Al/g† was found in gills of exposed fish compared with 6 μg/g for fish from non-acid waters (Grahn, 1980).

Rainbow trout had gill concentrations 100 times greater than those of muscle, visceral tissues, gonads (Buergel and Soltero, 1983). In this species, Neville (1985) was unable to demonstrate uptake following 75 $\mu g\,l^{-1}$ exposure over 6 to 11 days in viscera or gonads, but there was evidence that some aluminium was present in gill epithelial cells (Youson and Neville, 1987).

Brown trout fry tissues contained 0.4 to 3.5 mg Al/g (dry) in streams with 180 to 154 μg Al/l (Stoner *et al.*, 1984).

The carp, *Cyprinus carpio*, accumulated aluminium in 48 hr exposure in gill > viscera > other tissues with almost ten times greater accumulation in the gills (Muramoto, 1981).

There is no evidence of biomagnification through the food chain; char are reported to have the same level of aluminium as their prey (Wren *et al.*, 1983), and although levels of aluminium in plankton in an alum treated lake were high, trout tissues had only 1/10th of plankton concentrations (Buergel and Soltero, 1983).

Buergel and Soltero (1983) and Berg and Burns (1985) also report that aluminium in trout tissues can be higher in lakes with no measurable aluminium

† Concentrations in this section refer to Al/unit wet weight, unless stated.

than in lakes with 100 to 320 μg/l, possibly indicating uptake via benthic food items exposed to aluminium in the sediments, or to changed lake water quality.

3.2 *Accumulation in other Organisms*

Phytoplankton and algae have geen shown to accumulate aluminium with levels of 180 μg/g (*Euglena gracilis*) to 4500 μg/g (*Rhizoclonium*) and 720 mg/g in filamentous algae; at least part of this material is likely to be due to surface adsorption. In the presence of organic complexing materials (e.g. humic/fulvic acids) some aluminium concentrated by *Mougeotia* spp. could be removed (Stokes, pers. comm. cited in Butcher 1987). These high concentrations are not transferred to zooplankters feeding on phytoplankton or algae.

High concentrations accumulated by macrophytes (e.g. *Nymphaea* sp., 180 to 1730 μg/g, Butcher 1987) are similar to those of terrestrial plants, suggesting that root uptake is from sediments rather than from the water column.

Crustacea, although apparently not accumulating aluminium via the food chain, can take it up from the ambient water; Havas (1985) found that in *Daphnia* (whole body) concentrations rose from a pre-exposure level of 320 μg/g to 3000 μg/g after 24 hours in 20 μg Al/l at 6.5, and even to 11,000 μg/g in >1000 μg Al/l. The aluminium was partly superficial and some was in the gut, but some was found in "chloride" cells. Others (e.g. Cowgill and Burns, 1975) found lower levels of whole body accumulation in this and other daphnid species (115 μg/g and 120 μg/g).

The crayfish is reported not to accumulate aluminium by exposure to 500 μg/g for 14 days (Malley and Chang, 1985) and indeed lost aluminium when starved, suggesting that any aluminium residues are derived from food, especially benthic organisms which can have high concentrations in association with high sediment levels (Butcher, 1987).

Benthic invertebrates, overall, contained up to 8.4 mg Al/g (dry) in streams with 180 to 150 μg Al/l, according to Hall and Likens (1981).

No information is available for Amphibia.

Although aluminium accumulates on arthropod bodies, most of this is shed with the exuviae on ecdysis, and so is associated only with the aquatic life stages (Otto and Svenson, 1983); there is also some evidence that total body residues decline with increasing maturity.

There seems little good evidence for aluminium accumulation through the food chain and high levels are not universally found in insects living in acid waters (Herrmann, 1987). It is not known how these residue concentrations in invertebrate taxa are related to toxic response in predatory fish since most toxicity studies refer to exposure via the ambient medium, and not via food or tissue concentrations.

It has been hypothesised that reproductive failure in some riparian birds is due to a high aluminium content of their diet (Nyholm, 1981); however, aluminium levels in the diet were not reported in this study. A later report (Herrmann, 1987) gives a value of 1.3 mg/g (dry) for the stoneflies in Nyholm's study. A detailed study of the dipper (*Cinclus cinclus*) (Ormerod *et al.*, 1986) shows that in upland acid streams draining spruce forests (where aluminium concentrations are high) fewer invertebrate prey items are present, leading to an extension of dipper territories and thus to a lower density/mile of breeding pairs. Multiple dis-

criminant analysis indicated that aluminium, along with broad-leaved trees along stream banks, and pH, are highly significant factors. Dippers were found to be absent from sites with >100 μg/l filterable aluminium; however, the causal explanation of these observations has still to be elucidated. Another riparian species, the grey wagtail (*Montacilla cinerea*), not feeding directly on aquatic insect larvae, showed no differences between acid and less acid streams (Ormerod and Tyler, 1987).

In conclusion, it has to be said that the effects of aluminium on freshwater invertebrates are rather contradictory. While field observations hint at a possible indirect effect, mortality effects reported are usually at concentrations higher than encountered in the field, and certainly less significant than those that might be anticipated from experience with fish. There is growing evidence that aluminium affects respiration and ion regulation of some invertebrates, as in fish, but the diversity of mechanisms for both these processes in the wide variety of invertebrates suggest that only some classes will be susceptible.

4. FIELD STUDIES

4.1 *Field Studies with Fish*

4.1.1 *Studies in acid water*

In a field experiment to simulate episodic events in stream water quality, Ormerod *et al.* (1987a) added acid (H_2SO_4) to a stream followed by aluminium ($Al_2(SO_4)_3$) to a further section downstream. Acidity was increased (pH 6.6 to 4.28 and 5.02) in these treated sections and aluminium was raised in the lower section from 52 to 347 μg/l. Effects on fish and some invertebrates were mostly evident in the lower stream section; only 8–10% of fish (brown trout) were affected in the "acid-only" reach. Recent detailed investigations of snow melt events also suggest that aluminium stress alone might be sufficient to cause mortality. Further, the concentration of calcium, an important "cofactor" influencing the toxicity of both acidity and aluminium, was relatively constant in this field trial.

A similar experiment was carried out at Vikedal, Norway, in a natural stream (Henriksen *et al.* 1988); dosed sulphuric acid was observed to mobilise aluminium when the pH was reduced from 5–6, to 4.0; an estimated 150 mg total Al/m^2 was released from the bed surface of the brook. As a consequence, fish plasma chloride was reduced, and 100% mortality of fish occurred within 72 hours.

In a stream within the Hubbard Brook catchment (northeast USA) transient changes in water quality were induced by HCl and $AlCl_3$ additions (Hall *et al.*, 1987); both rapid, and gradual and progressive, additions were made to reduce pH from >6.0 to 4.0, and to increase aluminium from 0.28 mg/l to 4 mg/l. Acid additions resulted in increased Ca^{2+}, Mg^{2+} and Al^{3+} concentrations due to cation exchange and Al^{3+} dissolution; even greater mobilisation of Ca^{2+} and Mg^{2+} was seen with $AlCl_3$ addition. Production of surface foam with $AlCl_3$ addition was interpreted as due to reduced surface tension of the stream associated with the complexation reactions between aluminium and DOC at low pH (4.5). This effect was associated by the authors with an increased drift of mayfly nymphs, blackfly and chironomid larvae.

Liming of Lake Gardsjon, an acidified lake in SW Sweden, led to reduced concentrations (by about 50%) of aluminium and iron (Broberg, 1988); similar observations were made in the limed Loch Fleet, SW Scotland, where reintroduced fish thrived after treatment (Howells and Dalziel, 1988). Following limestone applications to forest, moorland and a headwater *Sphagnum* bog at Loch Fleet, aluminium concentrations in stream water were reduced, mostly attributable to a lower proportion of inorganic, labile monomeric aluminium (Brown *et al.*, 1987); the concentrations of the labile Al fraction dropped from about 30 μg/l (range 43 to 78) to about 10 μg/l. Over the same pre- to post-liming period TOC concentrations were typically 2 to 8 mg/l and showed no significant change with limestone treatments (Howells and Dalziel, 1988). In an acid humic stream in Sweden dosed directly with $CaCO_3$ (Kullberg and Peterson, 1987), liming similarily had little significant effect on DOC, although organic particulate matter was reduced immediately downstream (1 km) of the lime dosing silo. It can be assumed that monomeric aluminium concentrations were reduced, but concentrations were not reported (or measured). Similarly, alum additions to a small lake did not affect levels of phosphorus or organic carbon (Playle, 1987).

4.1.2 *Water treatment procedures*

Rivers are occasionally subject to high aluminium discharges from water treatment plant. If alkalinity is high, this is generally not considered to be a hazard to fish (Hunter *et al.*, 1980). The usual alum dose for water treatment is 1–3 mg/l but it is the sludge which is released, not the water in the treatment tanks. It is likely that the toxic labile (monomeric) fraction of aluminium will tend to be low in the circumneutral conditions of most downstream waters, perhaps explaining why healthy trout fisheries coexist with discharge levels possibly hazardous (Freeman and Everhart, 1971). The short residence time of particulate aluminium in the water column in eutrophic waters, with relatively high alkalinity, make toxicity to fish a "remote possibility" (Welsh, 1980). There are, however, reports of fish deaths below discharges to streams with low buffering ability. In these circumstances, the discharge causes a fall in pH (Bielby, 1988; Hunter *et al.*, 1980) and high concentrations of the toxic dissolved aluminium species. Sedimentary accumulation of discharged sludge provides a potential reserve of dissolved aluminium and benthic communities may be affected. It has been proposed (Neville, 1987) that the stream concentration after treatment should not exceed 50 μg dissolved aluminium/l which is the level tolerated by trout over the short term, but it should be noted that toxic concentrations vary with alkalinity and potential organic ligands present in the ambient water.

4.1.3 *Field studies in neutral to alkaline waters*

Studies on waters of pH >7 show that aluminium is toxic at quite low concentration levels with increasing pH in alkaline conditions, including the effect of suspended (particulate) aluminium (Freeman and Everhart, 1971). These authors reported that exposure of trout over 45 d at pH 7.0 and 8.0 with 5.2 mg Al/l resulted in 30% mortality; at pH 8.5, 50% mortality was seen at 8

days and at pH 9.0, 50% mortality was seen at 2 days. Other reported data are summarised earlier in Table 2.2.

Hunter *et al.* (1980) observed fish mortalities when the discharge from a backwash filter of a water treatment plant (pH 6.3 to 7.3) was mixed with river water (at pH about 8.5); total aluminium concentrations in the river rose to 530 mg/l, but soluble (i.e. filterable) aluminium to only 0.36 mg/l. More than 43,000 salmonids and other fish were estimated to have been killed in 1988 in the Rivers Camel and Allen (Cornwall, UK) within a few hours of accidental releases to the watercourses of aluminium sulphate at high concentrations during mains flushing operations. No river samples were taken during the incident, but it is estimated that the pH fell to 5.0–5.2 and that total aluminium concentration was >0.63 mg/l in these low conductivity waters (Bielby, 1988). Welsh (1980) argues that alum treatment to lakes may produce a sedimenting floc, giving a maximum alum dose of 15 mg Al/l for an alkalinity of about 100 ppm $CaCO_3$.

4.2 *Studies with Other Organisms*

Few observations have been made in the field on the response of invertebrate species to changes of water quality.

Ormerod *et al.* (1987a) dosed a sensitive stream with acid and aluminium to create episodes of increased acidity, and acidity and aluminium. Control (i.e. upstream) pH was 7.0 and total Al 52 μg/l; calcium was 2.3–3.7 mg/l throughout. The next lower stream section was acidified with H_2SO_4 to pH 4.28. The third stream section received aluminium sulphate to reach a pH of 5.02 and 347 μg Al/l. Three invertebrates were found to be unaffected—*Chironomus riparius, Hydropsyche augustipennis* and *Dinocras cephalotes*—while others—*Ecdyonurus venosus, Baetis rhodani,* and *Gammarus pulex*—showed up to 25% mortality in both the acid and the acid + aluminium zones during the expsoures, and over the following 72 hr. Drift of Simuliidae and other groups also increased; the most affected organism was *Baetis rhodani* (×8.4) and this species also showed decreased benthic density.

Hall *et al.* (1985) reported an increase in downstream drift of benthic invertebrates in a stream dosed with 280 μg/l total Al, suggesting that this might have been the result of a 20% decrease in surface tension. Bernhard (1985; cited in Butcher, 1987) also observed a tripling of drift density with aluminium levels increased from 50 to 75 μg/l to >225 μg/l. Playle (1985) added alum to an oligotrophic lake, raising aluminium from <50 μg/l to 100 μg/l, and changing pH from 5.1 to 4.7; no effects were seen on the benthos (mostly chironomids) with the exception of *Procladius* which decreased near the site of alum addition.

5. DERIVATION OF CRITERIA FOR ALUMINIUM IN NATURAL WATERS

5.1 There is considerable range of sensitivity to aluminium among fish species; it is generally accepted that salmonid fish are the most sensitive group, and that other groups of fish are less so. However, there are non-systematic differences. The common most sensitive European species (including two introduced species),

on the basis of literature reports are:

Salmo gairdneri > *S. salar* > *S. trutta* > *Salvelinus fontinalis*
⟨Most sensitive ..... Least sensivite⟩

Among other species, the minnow (*Phoxinus phoxinus*) appears to be sensitive, although there are few laboratory studies. Two North American species reported in the literature to be of similar sensitivity are *Notropis cornutus* (common shiner) and *Catostomus commersoni* (white sucker); they do not appear to have been established in European waters.

It should be recognised that only a handful of species has been investigated in rigorous conditions, and although there are reports of fish population declines or of fish kills which have been attributed to acid/aluminium exposure, these claims cannot yet be substantiated. In particular, loss of roach and perch populations from acidified waters have been reported even though there is little direct evidence that these species are sensitive to aluminium.

A further problem is that species from different strains, and possibly with different histories of exposure may exhibit a range of response.

Notwithstanding these problems, in the conditions found in acidified waters, it is judged that criteria to protect the common salmonid species should protect other fish species.

5.2 There is ample evidence, at least for the common species identified above, that the various life stages of any species show different levels of sensitivity. While the egg, at fertilisation, is highly sensitive to the ionic composition of the ambient medium, the developing egg is protected by the chorion and thus is less sensitive. At this stage, aluminium confers some protection against acid exposure. The emerging sac fry are far more sensitive, but following yolk sac adsorption, sensitivity increases further, at least for salmonids. In addition, migrating juvenile salmonids (smolts) are highly sensitive. However, there is some evidence that aluminium toxicity, in the strict sense, is more critical for larger fish than for fry. Criteria to protect early life stages, however, will generally serve for older fish.

Acid/aluminium criteria for protection should reflect the species of concern as well as the development stage at the location to be protected. A "put-and-take" fishery may need less rigorous control than that required for spawning and hatching, or for a self-sustaining population. A special case may need to be made for migratory fish.

5.3 Water quality considerations must be extended to more than acidity (pH) or aluminium fractions (of which only some of the inorganic monomeric species are toxic). Thus, it is well established that calcium concentrations are critical when low— <1–2 mg/l— and where reasonable levels of calcium are found, toxicity of acidity or aluminium (or both) is greatly reduced.

In addition, levels of dissolved organic materials, typically >10 mg/l, may ameliorate or even eliminate aluminium toxicity because of the formation of complexed organic forms of aluminium. Similar, but less convincing, claims are also made for inorganic complexes with sulphate, silicate and fluoride. In some studies, there is insufficient information about some of these ions to quantify relationships clearly or to specify protective conditions.

Other water constituents, including trace metals often mobilised in acid soils and waters, are also recognised as toxic. These include zinc, lead, iron,

manganese, cadmium and copper, although the latter two are more indicative of mineralised geology. Their possible effects makes attribution to aluminium toxicity per se difficult or impossible. There is little evidence, however, that toxicity of mixtures of these elements is more than additive (Alabaster *et al.*, 1988).

Criteria must thus be specified in the context of total water quality conditions, not on aluminium concentrations alone.

5.4 A further complexity in assessing toxic potential of dissolved aluminium is that of temperature; thermodynamic reaction rate calculations show that a shift of temperature of about 18°C (from 20°C to a more realistic 2°C) will shift the aluminium species distribution significantly in relation to pH. Aluminium solubility varies inversely with temperature and the solubility of the toxic aluminium hydroxides ($Al(OH)^{2+}$; $Al(OH)_2^+$) fraction shifts to a higher pH as temperature falls (Lydersen, pers. comm.).

5.5 Biological (between species) interactions may appear to be influenced by different sensitivity between competing species, for example the replacement of minnows by a species (*Notropis*) previously rare in the recovering Lake 223 (Mills and Schindler, 1986). However, in the absence of toxicity tests to establish such sensitivity, especially of sublethal response, this cannot be accommodated in criteria.

5.6 While a variety of invertebrate species have been shown to be sensitive to acid/aluminium exposure, especially those that employ respiratory membrane mechanisms for ion regulation, the evidence reported suggests that invertebrates exhibit similar symptons to aluminium toxicity as do fish, but are much less sensitive. It follows that criteria to protect fish will be more than adequate to safeguard invertebrate populations, at least in respect of their role as fish food items.

5.7 There is little evidence that aluminium is transferred to, or stored, significantly in body tissues; thus neither accumulation in fish used for human food, nor in insects comprising fish food, are important and criteria for tissue concentrations are not required.

5.8 The pattern of exposure of fish to acid/aluminium conditions is important. Short-term episodes of acidity in surface waters are often accompanied by peaks of inorganic aluminium concentration, and acute effects follow, in particular ion regulatory impairment or respiratory symptoms, leading to mortality. More sustained exposure over time is likely to lead to sublethal responses, including reduced growth, poor calcification, and reduced reproductive potential; criteria need to address short-term conditions and sustained conditions separately.

5.9 Aluminium toxicity in circumneutral and alkaline waters is attributed to different mechanisms, specifically to gill deposits as aluminium comes out of soluble phases, so affecting respiratory gas exchange. In these conditions, different cirteria are needed. Attention is drawn to the EIFAC criteria developed for suspended particulates (Alabaster and Lloyd, 1982).

5.10 The criteria developed in this review relate to the combined effects of acidity and aluminium, together with moderating constituents in surface waters. For acidity alone EIFAC criteria are to be found in Alabaster and Lloyd (1982).

6. RECOMMENDED CRITERIA

For low conductivity, acid waters with [Ca^{2+}] <2 mg/l, DOC <10 mg/l: Based on findings for fry or 1+ fish:

1. For pH 4.5 to 5.0, aluminium speciation does not favour the most toxic hydroxy species, being predominantly in the form of Al^{3+}; the guideline concentration for the soluble inorganic aluminium fraction should not exceed 30 μg/l.

2. For pH 5.0 to 6.0, aluminium speciation favours the most toxic species, and the soluble inorganic aluminium fraction should not exceed 15 μg/l. This is particularly critical for low ionic strength waters, where [Ca^{2+}] is low.

3. For pH >6.0, conditions unlikely in oligotrophic waters, the aluminium is progressively in the form of $Al(OH)_4^-$, and is less toxic; the soluble inorganic aluminium fraction should not exceed 75 μg/l for any life stage for these waters. For other higher ionic strength and less soft waters, a number of ameliorating factors in addition to calcium may be important. They include silicate, fluoride, and humic substances.

4. Where waters contain >5 mg/l Ca, or a Si : Al ratio >13 or DOC >10 mg/l, these criteria may be increased by up to 2-fold. There is little quantitative information for other possible ameliorating factors, although total ionic strength or NaCl may also be effective.

5. For circumneutral and alkaline waters (expected of higher ionic strength), soluble inorganic aluminium can exceed 100 μg/l. EIFAC criteria for particulates may be more relevant here.

Summary of Quality Criteria; all concentrations refer to the soluble inorganic fraction of aluminium, except for high ionic strength waters of pH >6.5:

[Ca] <2 mg/l; pH >4.5 – <5.0; Al <30 μg/l

[Ca] <2 mg/l; pH >5 – <6.0; Al <15 μg/l

[Ca] <2 mg/l; pH >6.0; Al <75 μg/l

[Ca] >5 mg/l; pH >4.5 – <5.0; Al <60 μg/l

(or where DOC >10 μg/l; or Si : Al >13)

[Ca] >5 mg/l; pH 5.0 – 6.0; Al <30 μg/l

[Ca] >5 mg/l; pH >6.0; Al <100 μg/l

[Ca] >10 mg/l; pH >6.5 – 8; Al (tot) <1 mg/l

7. SUMMARY AND CONCLUSIONS

7.1 Aluminium in some forms is highly toxic to fish and other aquatic organisms. It assumes greatest importance below pH 6.5–6.0 to 5.0 when the hydroxy forms $Al(OH)_2^+$ and $Al(OH)^{2+}$ predominate. The primary mechanism of toxicity is the impairment of the ion regulatory system in the gill membrane. However, its toxicity is independent of pH effects per se. The independent

effects of pH have been the subject of an earlier EIFAC assessment. At pH 6.5 where $Al(OH_4)^-$ is significant and concentrations are supersaturated, effects are thought to be due to flocculation of material at the gill surface where respiratory gas exchange may be affected, resulting in asphyxia. The dose-response relationship is poorly reported, and the mechanism of toxicity is scarcely investigated.

7.2 A variety of other ameliorating factors are known to influence the toxicity of aluminium. They include ambient concentrations of calcium, silicate, fluoride, and humic substances. The criteria values proposed in Section 6.2 are minimal concentrations of soluble aluminium which can be safely increased if the ambient waters contain sufficient levels of these components. Where these substances are absent or very low, the criteria should not be exceeded. Further investigation of the extent to which toxicity is moderated, and of the mechanisms, is needed.

7.3 In some instances, for example for eggs and possibly for juveniles, the presence of aluminium confers some protection against toxic levels of acid exposure. Further studies throughout all life stages are needed.

7.4 Aluminium appears to be more toxic at 2°C than at 20°C, due to a shift in the peak of the hydroxy species to a somewhat higher pH. Confirmation of this change in species distribution in natural waters is needed, as well as further studies of the relative toxicity of the various aluminium species.

7.5 Development of chemical methods of analysis in relevant water quality and concentrations is still required, so that more appropriate data on exposure conditions in the field and dose-response relationships can be generated.

7.6 Much of the work on dose-response in the literature, even that of only 5 years ago, is flawed by insufficient attention to, and reporting of, associated water quality (see para 7.2 above). Investigators should note the need for adequate chemical characterisation of the test medium, and for monitoring the aluminium concentrations to which fish are exposed. "Nominal" concentrations (based on aluminium salt additions) are seldom maintained for long during the course of a bioassay.

7.7 There is a lack of information about the effects of very high concentrations of dissolved aluminium, or large quantities of particulate aluminium compounds, on fish exposed for very short periods (<6 h). These conditions may occur during stream pollution as a result of water treatment at supply works and industrial plant.

7.8 The response of fish, at various life stages, to transient and/or repeated exposures, is poorly studied. There are some indications that previous exposure may confer some reduction of sensitivity.

7.9 The responses of fish vary substantially between species, or even between strains of the same species. They also vary between different life stages; the young fry and the migrating smolts of salmonids appear to be the most sensitive stages. Most work has focussed on salmonid species; more studies need to be made on other common freshwater fish such as minnows, roach and perch, often reported to be affected by acid waters in which soluble, inorganic aluminium concentrations are relatively high.

7.10 Aquatic invertebrate fauna is also affected by soluble inorganic aluminium, but they are much less sensitive than fish. Planktonic crustaceans are the most sensitive, with daphniids more sensitive than copepods, in turn less sensitive than insect larvae. The primary mechanism of toxicity (impaired ion regulation) appears to be the same as that affecting fish. Only a relatively few species have been investigated. The effect on fish diets seems to be unimportant.

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