Chapter (non-refereed)

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Aluminium fractionation in fresh waters

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1 Introduction

Aluminium is the most abundant metal and the third most abundant element in the earth's crust. Aluminosilicate minerals are common in igneous and metamorphic rocks, and as clay minerals in well-weathered soils.

Although the original source of aluminium to fresh waters is, most likely, the underlying bedrock, weathering processes are slow, so most available aluminium is present in soils. Even here, aluminium is usually complexed in the lower profiles of soil, and is fairly immobile (Jacks *et al.*1984).The process by which mobilization into fresh waters takes place is complex, and not fully understood, but van Breemen *et al.* (1984) have explained the process in terms of the internal and external proton sources in soils. In acid soils, soil acidification is relatively slow; in consequence, external proton sources of anthropogenic origin may exceed internally generated protons, leading to a release of inorganic aluminium into soil solution, from where it may be flushed into streams and lakes. Here, at low pH levels, when Ca concentrations are very low, the dissolved aluminium may even replace the usual calcium/bicarbonate buffering system.

The importance of this release of aluminium is not just as an indicator of external proton sources, or the creation of an aluminium buffering system in the acid water draining the soil; the importance lies in the toxicity of inorganic aluminium to freshwater organisms, in particular fish.

Aluminium toxicity has been the subject of many investigations, and the results are as complex as the chemistry of aluminium itself. The toxic effects are dependent upon the species and the life stage of the fish, the concentration of calcium in the water, and the pH. The pH may not only affect how a fish responds to dissolved aluminium, but can have a pronounced effect upon the chemistry of aluminium itself. Driscoll *et al.* (1980) have shown that complexation of aluminium can have a marked ameliorating effect on its toxicity. It is important, therefore, to understand something of the chemistry of aluminium, in order to measure the relevant complexes in solution and so predict the consequences of these solutions in streams and lakes.

2 Aluminium chemistry

The complexity of aluminium chemistry lies not only in its ability to form a variety of soluble complexes in aqueous solution, but also in its ability to create hydroxide polymers which may grow until, ultimately, microcrystalline minerals result.

At low and high pHs, there is general agreement on the chemical species of aluminium predominating in solution. At pH>7.5, the aluminate anion complex $Al(OH)_4^-$ is the major ion in solution, whilst at pH<4 the hexa-aquo-Al(III) ion $Al(H_20)_6^{3+}$ dominates (Smith 1972). Between these 2 pHs, there is likely to be little agreement on the exact concentrations of chemical species present for any given set of chemical conditions, because there is disagreement on the exact values of the relevant equilibrium constants. Assuming values for equilibrium constants between the different chemical species enables their concentrations to be predicted. Smith (1972) has done the calculation for the Al/hydroxide system over the pH range 3.5—7.0 (Figure 1). It is clear that at pH 5 several species have similar concentrations. Therefore, any uncertainty in the equilibrium constant values may have a marked effect on the relative concentrations of aluminium species. Calculations are further complicated when fluoride and organic chelates, which are found in fresh waters and effectively compete with hydroxide, are included.

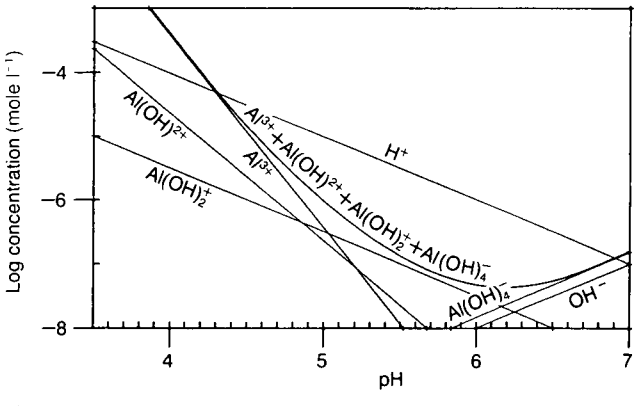

Figure 1. Aluminium concentration against pH (Smith 1972)

Although we may not be able to define the composition of an aluminium solution in precise terms, this definition may not be necessary. If our aim is to evaluate the biological impact of a given solution, a much more simplified approach may be used.

Driscoll (1980) has defined 3 'types' of aluminium species in solution (Figure 2). These types have

been shown to have biological significance, as well as being defined fairly clearly in chemical terms. *Inorganic monomeric aluminium* is the chemically labile form of aluminium which has been correlated with toxic effects on fish (Driscoll 1980). It does, however, include fluoride complexes which are less toxic. *Organic monomeric aluminium*, the non-labile monomeric aluminium, is far less toxic than the inorganic species. It is complexed, fairly strongly, to organic molecules, often of large molecular weight. *Acid soluble aluminium* is a mixture of polymeric species and strongly bound organic complexes. It is considered non-toxic. The 3 fractions together represent the total (reactive) aluminium in solution.

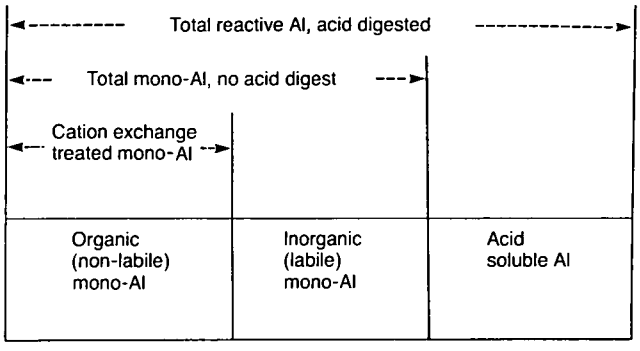

Figure 2. Summary of an aluminium fractionation procedure (Driscoll 1984)

3 Total reactive aluminium analysis

There are 2 major requirements for an analytical method suitable for total aluminium, indeed suitable as an analytical method for any aluminium species in fresh water. First, the method must be sensitive: aluminium is generally found in concentrations of <1 mg l^{-1} in fresh waters. Second, the method must be free from interferences. Unfortunately, conventional atomic absorption spectrometry (AAS) is not very sensitive, and many colorimetric methods are prone to interference.

Driscoll's early work on aluminium speciation (Driscoll 1980) was done using the ferron-orthophenanthroline colorimetric method (Rainwater & Thatcher 1960). By acidifying samples to 0.1 N with HCl, a 'cold acid digest', the total reactive aluminium is changed to monomeric form. This form reacts readily with the ferron reagent. The method is not very sensitive, so large cuvettes are needed. The method also suffers from interferences, particularly from dissolved iron and colour. Corrections are, therefore, needed, adding to errors and increasing analysis time.

Improved sensitivity and reduced interference problems are obtained with a method using catechol violet as the complexing agent (Dougan & Wilson 1974). Sensitivity is almost an order of magnitude greater, and iron interference is suppressed with hydroxyl-ammonium chloride and 1,10 phenanthroline. Colour correction is usually minimal as the catechol complex absorbs at 585 nm compared with 270 nm for ferron. The method is applied to acidified samples as above. Its main practical disadvantage is the increase of optical absorption that occurs with the catechol violet complex with time. An initial rapid absorption is complete within the first few minutes, but a further slow increase continues for many hours. The rate of increase is sufficiently slow and predictable, however, so that consistent results are obtained by waiting for a fixed time interval before absorption is measured. Times ranging from 4 to 40 minutes have been used by different workers.

The ferron and catechol methods have been compared by Seip *et al.* (1984), using some Norwegian freshwater samples. The agreement is very good, but they recommend the catechol method because of its sensitivity and lack of interferences. These findings are confirmed by work in our own laboratory.

Flameless atomic absorption spectrometry (FAAS) and inductively coupled plasma (ICP) spectrometry both give greatly improved sensitivity over conventional AAS. ICP equipment is, however, expensive and is still not available to many laboratories. FAAS does offer a reasonable alternative to colorimetry; under suitable graphite furnace conditions, the method is almost as sensitive as the catechol method and is relatively free from matrix effects (Campbell *et al.* 1983; ITE Merlewood, pers. comm.).

It may be expected that not all polymeric aluminium detected by ICP or FAAS would be measured using the 'cold acid digest' of the colorimetric methods. However, Bull and Hall (1986) have found that FAAS and catechol give very similar results for the same samples. Furthermore, Seip *et al.* (1984) observed only a 6% increase in aluminium concentration when acidified solutions were boiled with $K_2S_2O_8$ prior to catechol violet analysis.

Recently, Driscoll (1984) and LaZerte (1984) have used an extraction procedure developed by Barnes (1975), which effectively concentrates the aluminium in solution and may be used to prevent interferences. The aluminium is first coupled with oxine (8-hydroxyquinoline), the pH of the solution is next adjusted to 8.5, and then the oxine complex is extracted with methyl isobutyl ketone. To ensure polymeric aluminium is extracted, a reaction time of 3—6 hours is used (Turner 1969). Alternatively, water samples are acidified to pH 1 for one hour before analysis (Driscoll 1984). The oxine extract may be stored in a freezer until required for analysis. The extract may be analysed colorimetrically (at 390 nm) or, to avoid interferences, FAAS may be used.

4 Monomeric aluminium analysis

We have already described above the 2 types of monomeric aluminium — inorganic and organic, but it is also important to know the concentrations of each, as the toxicity of the organic fraction is much lower (Driscoll 1980). Most laboratories use a 2-step analysis procedure. First, the total monomeric aluminium concentration is measured. Next, either the inorganic or organic fraction is measured and the third fraction found by difference. A different method, used by Campbell *et al.* (1983), is described later.

Total monomeric aluminium analyses make use of the reactive nature of these species in unacidified solutions. The methods rely upon the speed with which these compounds react with a chelating agent. The ferron analysis (Driscoll 1980) is applied directly to unacidified samples, and the absorption measured soon after adding the agents. If the reaction time is short, polymeric aluminium has no chance to react. Seip *et al.* (1984) compared the ferron method with a similar approach (unacidified samples and short reaction time), using the catechol violet method. The results were comparable, though again the catechol violet method was recommended because of its sensitivity and lack of interferences. However, using a short reaction time presents some problems because the colour development time usually recommended is 10—30 minutes (Dougan & Wilson 1974). Seip *et al.* found that a reaction time of 4 minutes was sufficient for colour development but avoided reactions with aluminium polymers. Bull and Hall (1986) have used a reaction time of 10 minutes, which Seip *et al.* suggest gives an over-estimation of 2—3% in the monomeric aluminium due to depolymerization.

The oxine extraction procedure (Barnes 1975) may also be applied to measuring total monomeric aluminium. Now, however, a rapid extraction is substituted for a short colour development time. Driscoll (1984) has used this technique, whilst LaZerte (1984) has modified the method to give an extraction time of about 15 seconds.

Organic monomeric aluminium concentrations may be measured by remeasuring monomeric aluminium in solutions from which the inorganic fraction has been removed. Driscoll (1980) has shown that the inorganic, labile, fraction binds rapidly to a suitable ion exchange resin, leaving the non-labile, organic, fraction in solution. Passing a freshwater sample containing aluminium through a column of ion exchange resin effectively removes the inorganic monomeric species, leaving only organic monomeric aluminium in the eluate. Driscoll used 9.5 ml of Amberlite IR-120 resin in a 1 cm^2 cross-section column. A flow rate of at least 35 ml min^{-1} was needed. The resin, in the hydrogen form, was pre-treated with dilute NaCl solution so that eluted samples retained their original pH value. The same procedure has been used by other laboratories (Seip *et al.* 1984; Bull & Hall 1986). The organic monomeric aluminium may be measured using one of the methods described above for total monomeric aluminium, while inorganic monomeric aluminium is calculated by difference. Seip *et al.* report that direct colorimetric measurements using either ferron or catechol give comparable results. Driscoll originally used the ferron method (Driscoll 1980), but more recently has used the Barnes extraction on eluted samples (Driscoll 1984). Organic monomeric aluminium was measured in a different way by Campbell *et al.* (1983). They used fractionally loaded Chelex-100 resin in a batch technique (Laxen & Harrison 1981) to remove inorganic monomeric aluminium from solution. However, under the conditions used, low molecular weight polymers are also retained by the resin. This technique has the advantage that the organic fraction can be measured using a method for total aluminium. Campbell *et al.* have used FAAS. However, without knowing the concentration of total monomeric aluminium, the inorganic, toxic, fraction cannot be estimated. Campbell *et al.* did not make such measurements directly but used equilibrium calculations (see below).

Inorganic monomeric aluminium may be separated and measured directly using dialysis (LaZerte 1984). The small, mobile, inorganic ions pass readily through a dialysis membrane, whilst the larger, less mobile, organically bound aluminium is retained. Again, any convenient method for total aluminium may be used on the dialyte.

Individual aluminium species have been calculated by several workers using thermodynamic data. Early work by Hem and Roberson (1967) and Smith (1972) on hydroxide complexes in synthetic solutions has been extended by other workers to include other complexes in natural fresh waters.

Equilibrium calculations show that only Al^{3+}, hydroxide and fluoride complexes are present in most natural waters in significant concentrations (Hem 1968). Sulphate complexes are often included in the calculations but are usually of little importance (Seip *et al.* 1984). Concentrations of fluoride complexes may be found by calculation using fluoride levels measured with a fluoride selective electrode, and the appropriate equilibrium constants (Seip *et al.* 1984; LaZerte 1984; Driscoll 1984). Fluoride measurements also provide the means of calculating inorganic monomeric aluminium concentrations, as long as AlF^{3-} species dominate the total fluoride (LaZerte 1984; Driscoll 1984). Drummond (1984) reports on the work of Turner who has compared literature values of equilibrium constants. Turner notes that

fluoride constants are better characterized than those for hydroxide. Whilst hydroxide complexes predominate at high pHs, fluoride complexes are more important at low pHs. Although there is no direct evidence, on statistical grounds mixed fluoride/hydroxide complexes should be possible. The limitations of thermodynamic calculations are illustrated by an example by Hunt, also reported by Drummond (1984). Using 2 'alternative' sets of equilibrium constants, Hunt shows that the 2 sets of ion ratios resulting from his calculations give 2 different interpretations to a series of toxicity tests on algae. Further information on aluminium complexes has been obtained by the work of Tipping (Drummond 1984), who has used kinetic studies to look at aluminium species. He has identified a less labile fluoride complex at pH 4—4.3, which he suggests is AlF_2^+.

Individual organic monomeric aluminium species are even more difficult to characterize because of the vast range of humic substances present in fresh waters (Gjessing 1967). Drummond (1984) reports work by Lee who concludes that most complexation in Lake Gardsjon is caused by low molecular weight fulvic acids. Other work (Water Research Centre, pers. comm.) has shown that aluminium complexation with organics extracted from natural waters is very different from that complexed to commercially available humic and fulvic acids. It is perhaps sufficient to conclude that we know organic monomeric aluminium has a much reduced toxicity and is non-labile, and that the best approach for measuring its concentration at present is to use a purely practical means, such as that suggested by Driscoll.

5 Sample collection and pre-treatment

There are risks that concentrations of ions in solution may change between collection of a sample and its analysis, giving a false picture of what was present in the original sample. This is particularly true for aluminium species which are sensitive to pH changes.

One of the first decisions to be made is whether to filter water samples. Some workers have avoided filtration where possible, because many acid waters are low in suspended solids and direct measurements are made of monomeric species (Driscoll 1984; Bull & Hall 1986). Avoidance is not always possible with natural samples. Drummond (1984) reports that Wells has used glass fibre filters which he has tested satisfactorily with spiked samples. He also summarizes work by Salbu, who found it necessary to filter samples through a 0.45 μm filter in order to obtain reproducible results using neutron activation analysis, which presumably measures both dissolved and solid aluminium together. Campbell *et al.* (1983) have tested 0.4 μm filters in a polycarbonate apparatus and found no contamination or loss of analyte. Nevertheless, if pH changes are caused by filtration, some shift of species may occur.

Samples for total aluminium analysis samples can be 'fixed' soon after sampling by acidifying them to 0.1 N. These solutions remain stable for many weeks.

Monomeric aluminium is not so easily 'fixed' in aqueous solution. If solutions are being stored for analysis, they should be kept tightly stoppered with minimal air space, at, or near, the temperature when sampled. Solutions should be analysed as soon as possible, though we have found some samples are stable for 2—3 weeks or longer. The rapid extraction of oxine into MIBK offers a method for on-site extraction of monomeric aluminium (LaZerte 1984; Drummond 1984). The organic solution is stable for several months, if stored at low temperature.

Organic monomeric aluminium may also be separated in the field using Driscoll's ion exchange column. If followed by the oxine/MIBK extraction, concentrations can be fixed for future analysis. Otherwise, care is needed to prevent equilibria shifts whilst samples are transported to the laboratory and stored. We have found unacidified samples transported by car from Cumbria to Huntingdon and then passed through the ion exchange column show only small increases in organic complexation, compared with samples columned on-site. Such increases, which are not found with all samples, may be due to pH changes or to equilibrium of a non-equilibrated aluminium/organic mixture collected in the field.

6 Aluminium concentrations in the Rivers Esk and Duddon

In our studies of the Esk and Duddon and their tributaries, we have measured total, and inorganic and organic monomeric aluminium concentrations. We have not done any detailed calculations on fluoride species, though the total fluoride concentrations measured are low.

In the River Esk (Table 1), we find that lower pHs and higher aluminium concentrations are found in the upper reaches of the river. Downstream, pH values are higher and aluminium levels fall. The concentrations of organic monomeric aluminium have generally been low throughout the Esk under all the conditions sampled. Where the total aluminium levels are high, usually the proportion of inorganic monomeric aluminium is also high and the pH low. At higher pHs, the inorganic monomeric aluminium levels are, not surprisingly, lower. The acid soluble aluminium levels also fall, but not as quickly. Some of the aluminium losses may be explained by dilution of the river water by non-acid tributaries with low aluminium levels.

Most of the losses, however, must be due to polymerization of inorganic monomeric aluminium to acid soluble polymers, followed by further polymerization to 'insoluble' aluminium. Absorption, too, is likely to occur during the polymerization process.

Table 1. Al (μg l^{-1}) in River Esk — moderate flow

Distance upstream (km)	pH	'Total' Al	Mono-Al Organic	Mono-Al Inorganic	(%)
0	6.2	70	—	10	(14)
5.6	5.5	220	—	110	(50)
7.4	5.2	260	5	225	(86)
8.6	5.1	310	20	260	(84)
13.7	4.8	370	—	250	(68)

The tributaries of the Esk and Duddon vary considerably in their chemistry, both geographically and with time. Thus, in the Duddon (Table 2), we find that the upper reaches are less acid than the middle reaches of the river. Some tributaries in the upper Duddon are unexpectedly less acid because of the geology of the catchment bedrock (Sutcliffe & Carrick 1973). In contrast, other tributaries, further down the valley, some of which drain afforested catchments, are much more acid and contain higher aluminium concentrations (Bull & Hall 1986), as reflected in the chemistry of the main river.

Table 2. Al (μg l^{-1}) in River Duddon — moderate flow

Distance upstream (km)	pH	'Total' Al	Mono-Al Organic	Mono-Al Inorganic	(%)
0	6.7	80	—	—	—
3.5	6.0	150	—	20	(13)
7.9	5.0	360	20	170	(47)
12.0	5.3	190	30	100	(53)
13.8	5.6	90	10	40	(44)

Some tributaries show dramatic changes in their chemistry over quite short distances. Dodknott Gill, in the middle reaches of the Esk, drains from Harter and Birker Fells. Under most conditions, the water running from the fell-side (Figure 3, site A) is fairly acid, pH 4.5–5.2. Between the fell and the confluence with the Esk (Figure 3, site D), the tributary flows through several hundred metres of improved pasture land. It receives water from land drainage and from springs along this stretch; both sources are more alkaline than the gill itself. As a result, pH, calcium levels and alkalinity increase with distance downstream, whilst aluminium concentrations fall (Figure 3). An important consequence of these changes is likely to be a condition of super-saturation of aluminium along some stretches of the gill. Baker and Schofield (1982) have suggested that such conditions are highly toxic to fish. It may be that similar conditions occur in other parts of the Rivers Esk and Duddon on occasions, with important biological consequences.

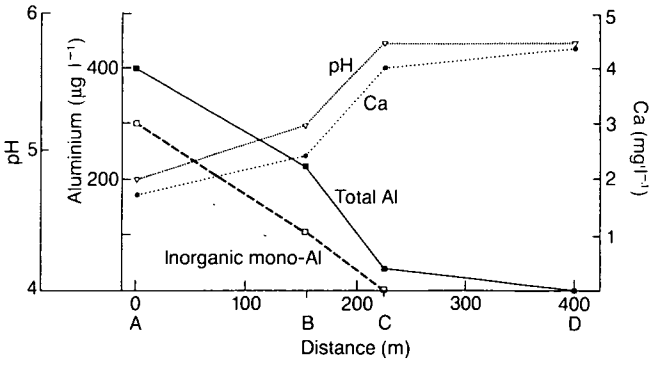

Figure 3. Aluminium, calcium and pH levels in water collected from 4 points (A, B, C, D) along Dodknott Gill, Cumbria

7 Summary

Aluminium chemistry in fresh waters is complex; the metal may exist in a variety of different species, largely dependent upon the pH of the solution and dissolved anions present. Because different aluminium species have different toxicities to biota, it is important that some estimation of the species present is made. We have discussed some of the procedures used by various workers to determine aluminium concentrations, together with findings of our own. Some results for the Rivers Esk and Duddon, Cumbria, are used to illustrate the concentrations of aluminium which may be found in running waters.

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