The chemistry of aluminum in the environment

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Abstract

There is increased concern over the effects of elevated concentrations of Al in the environment. Unfortunately, studies of the environmental chemistry and toxicity of Al have been limited by our understanding of the processes regulating the aqueous concentration, speciation and bioavailability of this element.

Although Al is the most abundant metallic element in the Earth's crust, it is highly insoluble and generally unavailable to participate in biogeochemical reactions. However, under highly acidic or alkaline conditions, or in the presence of complexing ligands, elevated concentrations may be mobilized to the aquatic environment. Ecologically significant concentrations of Al have been reported in surface waters draining "acid-sensitive" regions that are receiving elevated inputs of acidic deposition. Acid- sensitive watersheds are characterized by limited release of basic cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and/or retention of strong acid anions (SO_4^{2-}, NO_3^-, Cl^-). Under these conditions inputs of strong acids are not completely neutralized, but rather acidic water is exported from the terrestrial environment. It has been hypothesized that acidic deposition to acid-sensitive watersheds mobilizes Al within the mineral soil, causing elevated concentrations in soil solutions and surface waters. As a result of mineral phase solubility constraints, concentrations of aqueous Al increase exponentially with decreases in pH below 6.0.

Monomeric Al occurs as a series of complexes in the aqueous environment, including aquo, OH^-, F^-, SO_4^{2-}, HCO_3^- and organic species. Of these aquo, OH^-, F^- and organic complexes are the most significant in natural waters.

Elevated concentrations of Al are ecologically significant because: 1) Al is an important pH buffer in acidic waters, regulating the lower limit of pH values following acidification by strong acids; 2) through adsorption and coagulation reactions, Al may alter the cycling and availability of important elements like phosphorus, organic carbon and certain trace metals; 3) Al may serve as a coagulant facilitating the removal of light attenuating materials, thereby increasing the clarity and decreasing the thermal stability of lakes; and 4) Al is potentially toxic to organisms. Better understanding of the chemistry and speciation of Al is essential to assess these effects.

Introduction

There is increasing concern over the environmental and biological effects of elevated concentrations of Al in natural waters. Unfortunately, studies of the environmental chemistry and toxicity of Al have long been limited by our understanding of the processes regulating the aqueous concentration, speciation and bioavailability of this element. In this paper we provide an overview of the environmental chemistry of Al, which includes a discussion of the distribution and transformations involving Al, an evaluation of concentrations and speciation of Al in natural waters, as well as an assessment of the environmental consequences of elevated concentrations of aqueous Al. Our analysis of the environmental chemistry of Al utilizes a series of thermodynamic calculations. These calculations were conducted with the chemical equilibrium model ALCHEMI. This model allows for determination of the speciation of aqueous Al in equilibrium with a variety of solution controlling solid phases or adsorbing surfaces. A description of the thermodynamic data (see Appendix 1) and numerical approach used in this program, as well as a detailed uncertainty analysis associated with chemical equilibrium calculations is provided in Schecher and Driscoll (1987, 1988b). A summary of the symbols used in this paper are summarized in Appendix 2.

Distribution and Transport of Aluminum in the Environment

Aluminum constitutes about 8% by weight of the Earth's outer crust and is the most abundant metallic element (Garrels *et al.*, 1975; Hem, 1986). Of sedimentary rocks, shales generally have the highest content of Al (7.8-8.2%) followed by sandstones (2.5-4.2%) and carbonates (0.4-1.3%) (Clarke and Washington, 1924; Green, 1959). Clays and other secondary minerals range from 45% Al for boehmite to 3% Al for glauconite (Hem 1978).

Although quantitatively important, the Al cycle is complicated and poorly understood. Aqueous, particulate and biological transformations of Al may be conceptualized through a schematic representation of the Al cycle (Figure 1). This cycle is a series of pools (*e.g.* aqueous, particulate and living biomass) with many fluxes that regulate pool sizes. Some information is available on Al pools within the natural environment, although this is

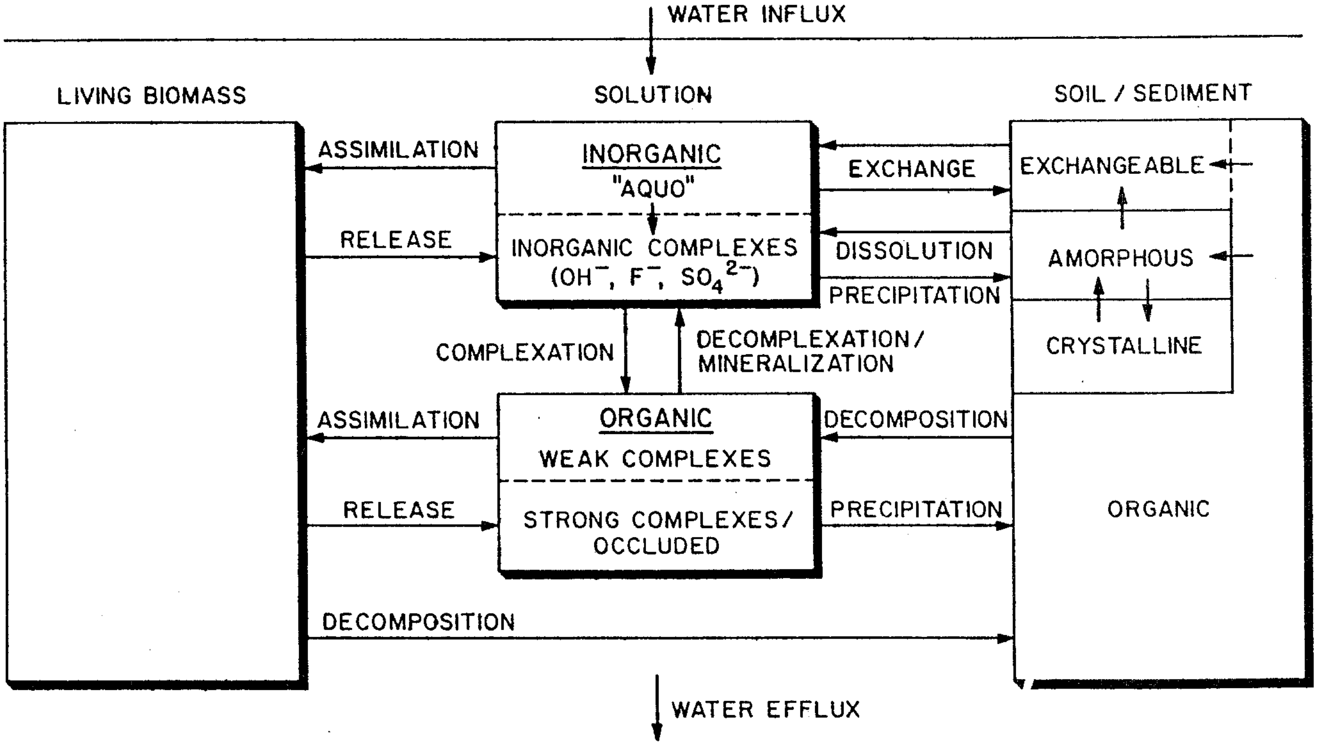

Figure 1 *Schematic representation of the Al cycle. Within the environment, Al can exist in pools of living biomass, solution, or non-living particulate matter. A number of transformations link the individual pools and regulate Al concentrations.*

largely based on operationally defined methods. Unfortunately, there is virtually no information on the relative importance of pathways linking pools or rates of these transformations.

It is not surprising that soil minerals are the primary source of Al to aqueous and biological environments. However, in the lithosphere, Al is largely associated with highly crystalline alumino-silicate minerals. Due to low solubility (May *et al.*, 1979) and slow dissolution kinetics (Bloom, 1983), large pools of soil Al are virtually unavailable for biogeochemical reactions. Through soil development highly crystalline aluminosilicate minerals are decomposed and a small fraction of this Al becomes available to participate in biogeochemical processes.

Soil/sediment available pools of Al are generally characterized by operationally defined extraction techniques and are frequently termed free (nonsilicate bound) soil/sediment Al (McKeague *et al.*, 1971). Many processes contribute to the formation of free soil/sediment pools. For example, weathering of aluminosilicate minerals by H_2CO_3 or organic acid dissolution (Ugolini *et al.*, 1977; Norton and Henriksen, 1983; Reuss and Johnson, 1985) or neutral hydrolysis (Johnson, 1984), followed by reprecipitation of solution Al produces amorphous Al hydroxide (Johnson *et al.*, 1981; Lawrence *et al.*, 1985) or silicate (Farmer *et al.*, 1980; Farmer and Fraser, 1982) mineral forms. Soil Al may also be retained on charged surfaces associated with soil organic matter (Bloom *et al.*, 1979; Cronan *et al.*, 1986) and/or clay minerals (McBride and Bloom, 1983). Finally, free soil/sediment Al may be bound with organic matter through microbial/plant transformations (Messenger, 1975; Messenger *et al.*, 1978) or formed by precipitation with organic solutes within soil solutions (Schnitzer and Skinner, 1963a,b; Ugolini *et al.*, 1977).

All forms of soil/sediment Al may potentially regulate solution concentrations. While mechanisms controlling aqueous and biological concentrations are not clearly established, it is likely that aqueous Al is largely derived from free soil/sediment pools, including exchange from cation exchange sites, dissolution from amorphous mineral phases or decomposition/mineralization of organic forms (Figure 1).

Solution Al is the most chemically and biologically available form, although this pool represents an extremely small fraction of total Al in the environment. Aluminum is a strongly hydrolyzing metal and relatively insoluble in the neutral pH range (6.0 to 8.0) (Stumm and Morgan, 1970; May *et al.*, 1979). Under acidic (pH <6.0) or alkaline (pH >8.0) conditions, and/or in the presence of complexing ligands, the solubility of Al is enhanced, making it more available for biogeochemical transformations. Within the aqueous phase, Al may be associated with a variety of inorganic (*e.g.* OH^-, F^-, $SO_4{}^{2-}$, $PO_3{}^{3-}$, H_4SiO_4, $HCO_3{}^-$) or organic ligands. The extent of complexation depends on the availability of soil/sediment Al, solution pH, concentrations of complexing ligands, ionic strength and temperature. Aqueous Al may be redeposited to free soil/sediment pools, assimilated by living biomass or transported from the system (Figure 1).

Biological cycling of Al is generally assumed to be quantitatively unimportant. Aluminum is not a plant or animal nutrient (Bohn *et al.*, 1985) and therefore generally does not accumulate in living tissue. For example, Hutchinson (1945) found the Al concentration in terrestrial plants and mammals to be very low (0.002% and 0.00005% of the total weight, respectively). Indeed, elevated concentrations of Al are toxic to a wide variety of organisms (Foy, 1974; Driscoll *et al.*, 1980; Pavan *et al.*, 1982; Helliwell *et al.*, 1983; Clark and LaZerte, 1985). Wood (1985) hypothesized that the selection and use of nutrients in the biochemical evolution of organisms was dictated by their abundance in the Earth's crust, as well as solubility under the anaerobic conditions that occurred during that period, 4 x 10^9 years ago. Although Al is abundant in the Earth's crust, it was undoubtedly very insoluble under the conditions which life evolved, and probably relatively unavailable for transport into primitive anaerobic bacteria. As a result, most organisms have not adapted to elevated concentrations of bioavailable Al and cannot survive large intracellular accumulation. Nevertheless, organisms do assimilate limited quantities of Al, with some plants accumulating high concentrations (Chenery, 1948; Foy, 1974). Chenery (1948) found 1821 species of plants which contained more than 0.1% Al by dry weight in their leaves. Given solubility constraints, Hem (1978) suggested that if it is of any nutritional importance it would most likely be found in organisms that either contain or reside under acidic conditions.

Processes Regulating Inputs of Aluminum to Surface Waters

Inputs of Al to surface waters may occur through a variety of processes and exhibit many forms. On the global scale, Al inputs to the aqueous environment appear to be largely associated with particulate matter. For example, Garrels *et al.* (1975) estimate the global stream flux of Al as 760 mol/ha-yr. This Al is virtually all associated with sediment transport, as Al is abundant in particulate minerals and relatively insoluble in most freshwaters. There have been very few studies comparing particulate and dissolved transport of Al in surface waters. However, good information is available from a small watershed study in New Hampshire (Likens *et al.*, 1977). This site exhibits very low erosion and transport of particulate matter (33 ± 13 kg/ha), even though the catchment has a steep slope (12-13°) as well as elevated precipitation inputs (132 ± 7 cm/yr) and runoff (83 ± 7 cm/yr). Moreover, streamwater from the HBEF characteristically has elevated concentrations of dissolved Al, due to acidic conditions which facilitate leaching losses (Johnson *et al.*, 1981; Lawrence *et al.*, 1985). From an eight-year study, Likens *et al.* (1977) concluded that total Al exported from the HBEF was 125 mol/ha-yr, with 41% associated with particulate matter and 59% in a dissolved form. So particulate transport would appear to be a quantitatively important component of total Al inputs to surface waters, even for those areas with minimal sediment loading and elevated concentrations of dissolved Al. However, as mentioned previously, Al associated with mineral matter is relatively unavailable to participate in chemical and biological transformations. Therefore, our review will focus on processes regulating concentrations of relatively labile forms of Al in surface waters.

Regulation of aluminum transport in the absence of strong acid inputs

Mobilization and subsequent deposition of Al is an integral component in the development of well drained soils. A variety of interrelated factors are critical to soil development and associated transport of Al, including climate, watershed elevation and slope, temperature, vegetation, nature of soil minerals as well as the movement of drainage water. In northern temperate regions the process of podzolization strongly influences the transport of Al within a soil profile. Podzolization is traditionally thought to involve the mobilization of Al (and Fe) from upper to lower mineral soil horizons by organic acids leached from foliage and the forest floor (Coulson *et al.*, 1960a,b; Ugolini *et al.*, 1977; Johnson and Siccama, 1979; DeConnick, 1980). As alumino-organic complexes are transported through the mineral soil, processes of complexation and/or microbial oxidation increase the Al to organic carbon ratio of these solutes, thereby reducing their solubility (Schnitzer and Skinner, 1963a,b). In pristine environments Al appears to be largely retained within the lower (B horizon) mineral soil. For example, Ugolini *et al* (1977) reported that there was little transport of Al from soil to surface water associated with soil development at Findley Lake in Washington.

Recently, several researchers have hypothesized that CO_2 may have an important role in the solubilization and transport of Al (Norton and Henriksen, 1983; Reuses and Johnson, 1985, 1986). Under elevated partial pressures of CO_2 that accumulate within soil (up to 10^{-1} atm) (Bohn *et al.*, 1985, the dissociation of H_2CO_3 acidifies the soil solution and may facilite leaching losses of Al.

Within soil, dissolution of Al generally occurs under acidic conditions and/or in the presence of complexing ligands. The dissociation of organic acids and/or H_2CO_3 results in the formation of temporarily mobile (transient) anions, which may allow for the transport of Al by serving as complexing ligands and/or counterions. Concentrations of these transient anions are dependent upon a variety of solution conditions, which may vary over time and between different soil horizons. When a transient anion is removed from solution, its associated Al (and Fe) is deposited within the soil profile. The formation of transient anions in the upper soil, their transport and removal with associated Al (and Fe) in lower soil horizons is central to soil development.

The concept of transient transport of Al is probably most easily illustrated with reactions involving the hydration and dissociation of CO_2 (Figure 2). In the soil environment elevated partial pressures of CO_2 cause the formation and dissociation of H_2CO_3 to H^+ and HCO_3^-. Proton production may solubilize Al, while HCO_3^- serves as a counterion for the transport of cationic Al through the soil. When the solution emerges from the soil to surface water, it equilibrates with atmospheric conditions (CO_2 partial pressure of $10^{-3.5}$ atm), CO_2 degasses, resulting in the removal of HCO_3^- and hydrolysis/precipitation of Al (Figure 2). To illustrate the range of conditions under which the mobilization of Al by CO_2 can occur, some hypothetical calculations were made using ALCHEMI (Figure 3). Over a range of acid neutralizing capacity

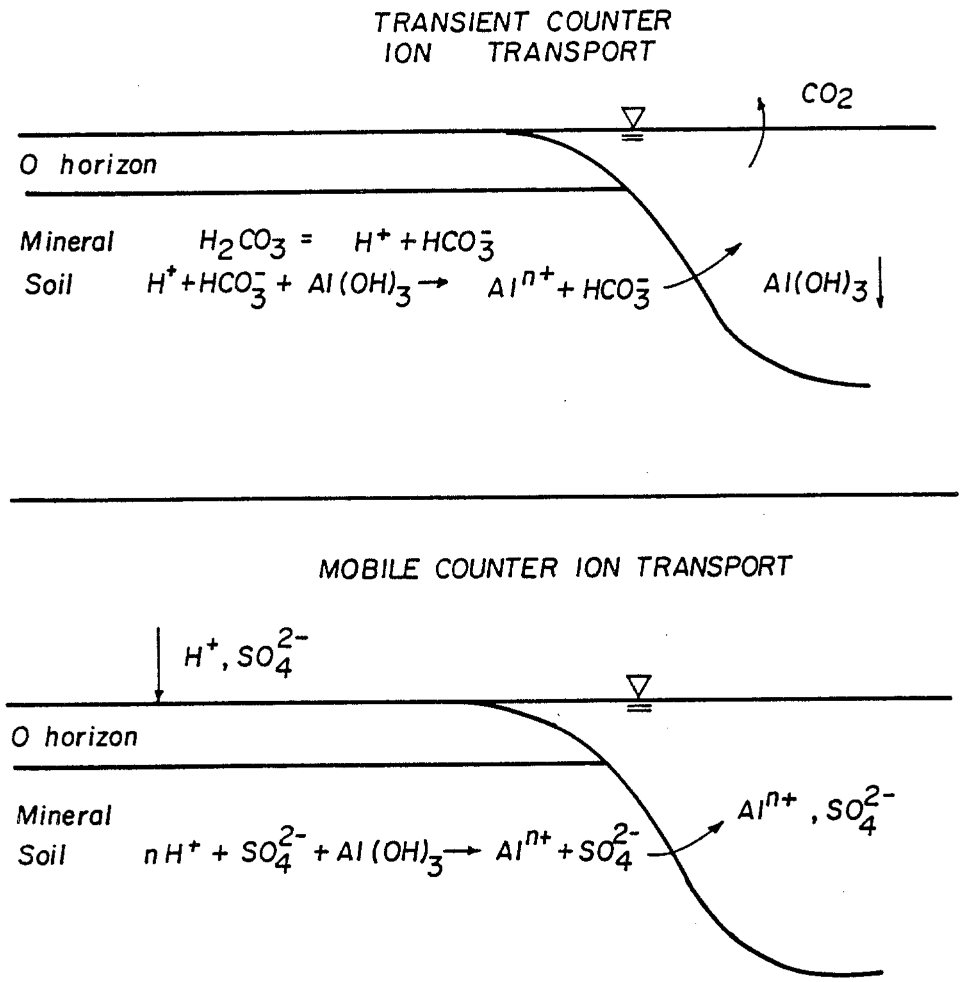

Figure 2 *Conceptual model depicting the transport of Al by a transient anion (a, HCO_3^-) and a mobile anion (b, SO_4^{2-}). Dissociation of H_2CO_3 in soil under elevated partial pressure of CO_2 produces a H^+, solubilizing Al, and HCO_3^-, which can serve as a counterion in Al transport. When the solution equilibrates with atmospheric conditions, for example, upon discharge to a surface water, CO_2 degasses resulting in Al hydrolysis and precipitation. Acid inputs associated with a mobile anion (e.g. SO_4^{2-}) can solubilize and transport Al to surface water.*

(ANC) and partial pressure of CO_2, the amount of Al solubilized by CO_2 was determined. This "CO_2 mobilized Al" is calculated with ALCHEMI by initially allowing the solution to come in equilibrium with $Al(OH)_3$ for a given set of conditions (ANC, partial pressure of CO_2), followed by reequilibrating the sytem with atmospheric CO_2 ($10^{-3.5}$ atm). The difference in aqueous Al concentrations due to precipitation represents the Al solubilized by elevated soil CO_2.

Mobilization of Al by CO_2 is maximum at values of ANC near zero (pH near 5.0) and increases with increasing partial pressure of CO_2 (Figure 3). The extent of this phenomenon is closely coupled to the acid/base characteristics of dissolved inorganic carbon and Al. At low values of ANC and pH significant concentrations of Al are available, due to pH-dependent ($Al(OH)_3$ solubility. However, acidic conditions restrict the dissociation of CO_2 (H_2CO_3) to H^+ and HCO_3^-; thereby limiting H^+ to solubilize Al as well as decreasing concentrations of the counterion HCO_3^-. Conversely, at high ANC and pH values elevated concentrations of HCO_3^- occur, but the solubility of Al is low so dissolution is limited. Because CO_2 is a weak acid, elevated concentrations do not substantially depress pH values. Therefore, the concentrations of Al mobilized under elevated partial pressures of CO_2 are relatively low.

Concentrations of dissolved Al are generally low in most natural waters due to the relatively low solubility of natural Al minerals under circumneutral pH values and low concentrations of complexing ligands. Stumm and Morgan (1970) report a median value of 0.4 µmol/L for terrestrial waters, while Bowen (1966) gives an average concentration of a 9 µmol/L for freshwaters including bogs. Durum and Haffty (1963) give a median concentration of Al in North American rivers of 9 µmol/L, with higher concentrations observed during periods of high discharge.

Role of strong acid inputs in the transport of aluminum to surface waters

The introduction of strong acids (*e.g.* H_2SO_4. HNO_3) from atmospheric deposition is superimposed on the natural process of soil development in parts of eastern North America (Cronan and Schofield, 1979) and Europe (van Breemen *et al.*, 1982). Many regions are "sensitive" to inputs of strong acids. Acid-sensitive watersheds are generally underlain by granitic bedrock and have shallow acid soil with small pools of "readily-available" (*e.g.* exchangeable, easily weatherable) basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+). These systems may also be characterized by an inability to retain inputs of strong acid anions (SO_4^{2-}, NO_3^-, Cl^-) through soil adsorption or biological retention. Therefore, high loadings of strong acids are not attenuated within the terrestrial environment, but rather exported from the watershed with drainage water. Complete neutralization of strong acids is accomplished by dissolution or exchange of basic cations and/or retention of strong acid anions within lake/watershed systems. However, when these processes are limited, neutralization is incomplete and

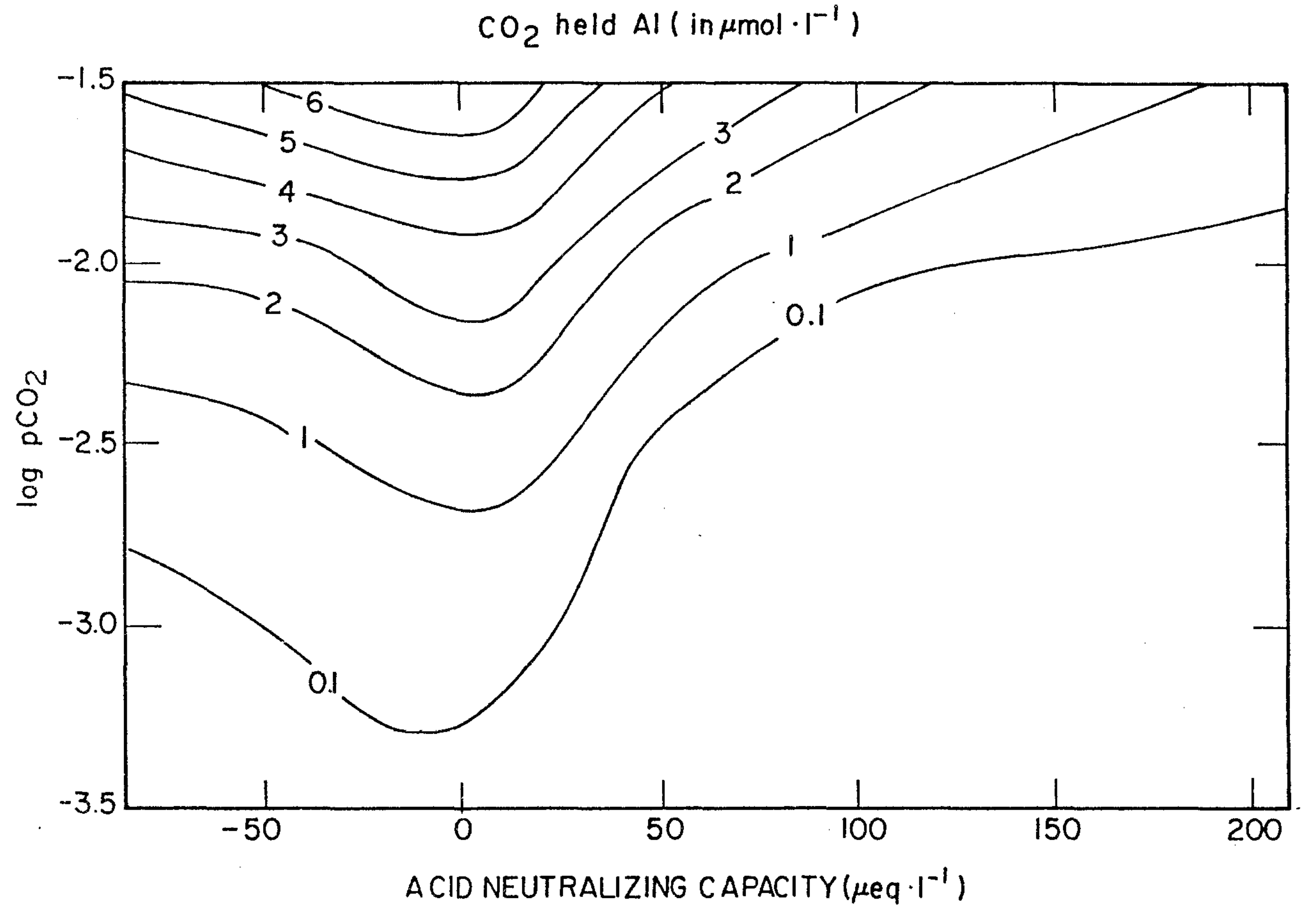

Figure 3 *Diagram indicating Al mobilization by CO_2 (in μmol/L) under different values of acid neutralizing capacity (ANC) and partial pressure of CO_2 (pCO_2) for a system in equilibrium with natural $Al(OH)_3$ (Driscoll and Schecher, 1988).*

acidic cations (H^+, Al^{n+}) are transported from soil to surface water (Figure 2).

Cronan and Schofield (1979) have hypothesized that strong acids from atmospheric deposition have altered the natural process of podzolization in northern temperate soils by facilitating the leaching of Al from soil to surface waters. Evidence to support this contention is available through water chemistry data collected from acid-sensitive regions that are receiving high atmospheric loading of strong acids (Baker, 1982). When concentrations of strong acid anions (*e.g.* $SO_4{}^{2-}$, $NO_3{}^{-}$) approach or exceed concentrations of basic cations on an equivalence basis, high concentrations of acidic cations (H^+, Al^{n+}) are observed in surface waters (Figure 4; Driscoll and Newton, 1985).

In order to better understand the Al cycle and to develop predictive models to assess the effects of acidic deposition, it is critical to identify the source of mobile Al (Figure 1). Researchers have suggested several hypotheses for a solid phase regulating Al concentrations in dilute water systems, including poorly crystallized 1:1 layer clays (Hem *et al.*, 1973), kaolinite ($Al_2Si_2O_5(OH)_4$) (Norton, 1976), $Al(OH)_3$ (Johnson *et al.*, 1981; Driscoll *et al.*, 1984), hydroxy sulfate minerals (*e.g.* basalunite, $Al_4(OH_{10})SO_4$; alunite, $KAl_3OH(SO_4)_2$; or jurbanite, $Al(OH)SO_4{:}H_2O$ (Nilsson and Bergkvist, 1983; Meiwes *et al.*, 1980) and dissociation from soil organic matter (Bloom *et al.*, 1979; Cronan *et al.*, 1986).

Johnson *et al.* (1984) and Driscoll *et al.* (1984) evaluated the chemistry of surface waters in New Hampshire and in the Adirondack region of New York, respectively, and reported that solution Al concentrations were generally close to the theoretical solubility of $Al(OH)_3$ (Figure 5). As a result, Al release is often depicted by $Al(OH)_3$ solubility relationships in computer models developed to simulate Al geochemistry (Gherini *et al.*, 1985; Cosby *et al.*, 1985; Schecher and Driscoll, 1987). Deviations from this pattern of solution control, however, are evident in the literature. For example, solutions draining organic horizons in forest soil (David and Driscoll, 1984; Driscoll *et al.*, 1985) and in peaty soils (Driscoll and Newton, 1985) are often highly undersaturated with respect to $Al(OH)_3$ solubility. Gherini *et al.* (1985) have suggested that under these conditions release of Al is no longer in equilibrium with $Al(OH)_3$, but rather kinetically controlled. Other researchers (Bloom *et al.*, 1979; Cronan *et al.*, 1986), however, contend that in the presence of soil organic matter, solution Al is regulated by cation exchange which is a function of the concentration of Al on exchange surfaces. Finally, in regions of Europe experiencing very high $SO_4{}^{2-}$ loading, a number of investigators have reported that the activity of aquo Al (Al^{3+}) in groundwaters (Erickson, 1981) and soil solutions (Nilsson and Bergkvist, 1983) appears to be regulated by the solubility of jurbanite ($Al(OH)SO_4{:}5H_2O$).

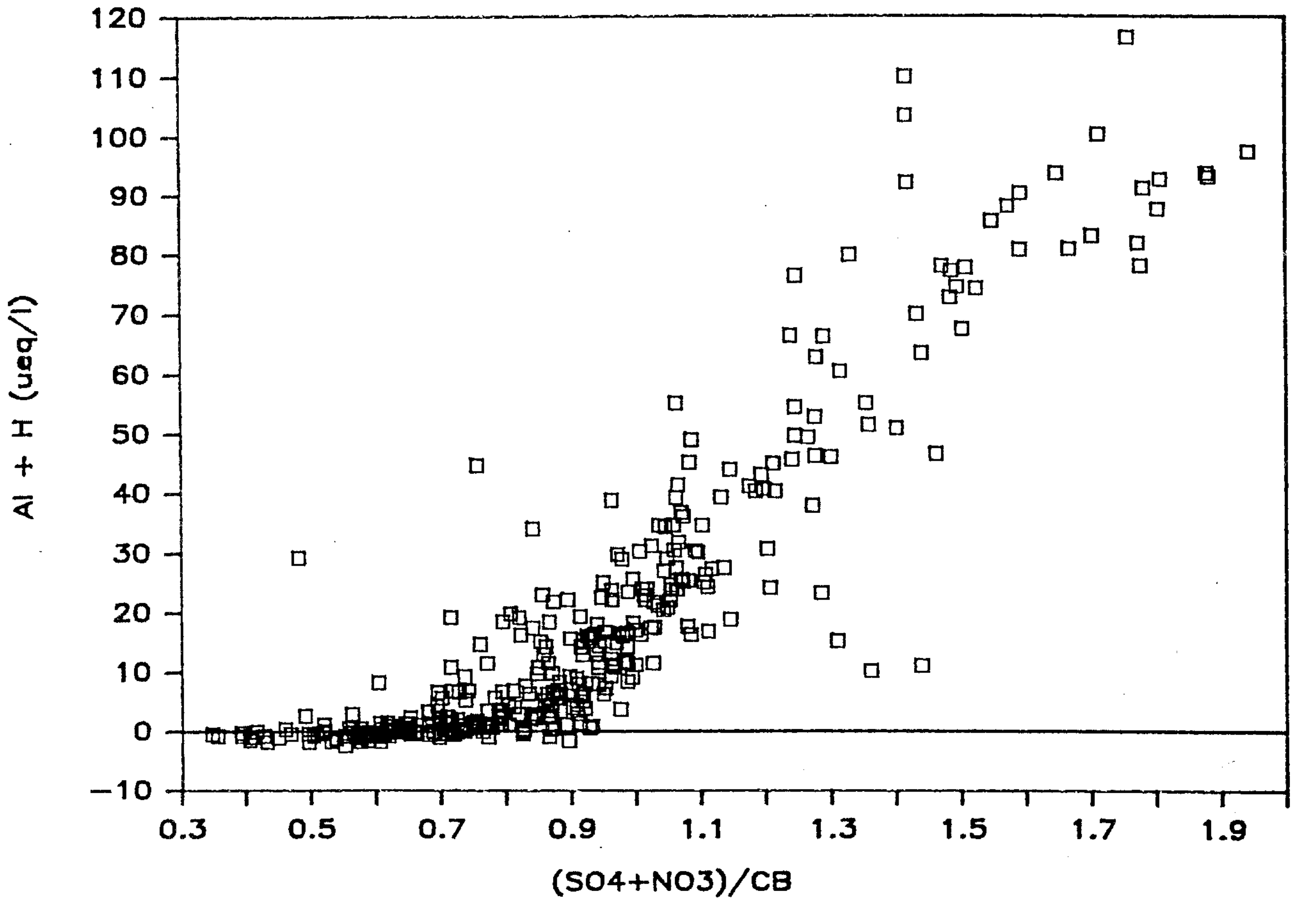

Figure 4 *Concentration of acidic cations (H^+, Al^{n+}) as a function of the ratio of SO_4^{2-} and NO_3^- concentration to basic cation concentration C_B, Ca^{2+}, Mg^{2+}, Na^+, K^+) on an equivalence basis for Adirondack NY surface waters (Driscoll and Newton, 1985). As this ratio approaches one, increases in the concentrations of acidic cations (H^+, Al^{n+}) are observed. The equivalence of Al was computed with ALCHEMI.*

Additional information on processes regulating aqueous concentrations of Al is available through soil solution and soil chemistry data. Studies of soil solution and soil Al from the Adirondack region of New York (David and Driscoll, 1984) and New Hampshire (Driscoll *et al.*, 1985) have yielded comparable results. Solutions draining organic soil horizons contained remarkably high concentrations of Al, which appeared to be largely associated with organic solutes. These solutions were highly undersaturated with respect to the solubility of readily forming mineral phases. In the lower mineral soil (B horizon), inorganic Al concentrations were elevated and solutions approached the solubility of natural $Al(OH)_3$. David and Driscoll (1984) also evaluated differences in Al chemistry between coniferous and deciduous vegetation. Solutions draining coniferous vegetation contained higher Al concentrations than deciduous stands in all soil horizons. This enrichment of Al was attributed to complexation by organic solutes and coincided with elevated dissolved organic carbon (DOC) concentrations.

Results of field studies in the northeastern USA (David and Driscoll, 1984; Driscoll *et al.*, 1985) have led investigators to conclude that the organic horizon is an important source of mobile Al. Aluminum transported from organic horizons is largely in an organic form and probably the by-product of decomposition processes. These observations are to some extent inconsistent with the traditional views of soil development (podzolization theory) and suggest that biocycling (vegetation assimilation and microbial decomposition) may be an important component of the Al cycle in forest ecosystems. Elevated concentrations of inorganic Al were generally observed only in solutions draining from the mineral soil. Therefore, it is likely that organic and inorganic fractions of Al observed in surface waters originate from different processes (organic decomposition and dissolution by strong acids, respectively) and at different locations within the soil profile (organic and mineral horizons, respectively).

It is apparent that there are inconsistencies in the literature on the processes regulating aqueous Al concentrations in drainage waters. These inconsistencies are, to some extent, the result of researchers relying on total Al measurements to interpret processes. Fractionation procedures to evaluate the speciation of Al in solution have only recently been developed and applied to natural waters (Bloom and Erich, 1989). Unfortunately, there is no accepted procedure for the fractionation of aqueous Al. These techniques, for the most part, are operationally defined; results obtained from a study using a given procedure may reflect procedural bias rather than actual environmental trends (Hodges, 1987; Bloom and Erich, 1989).

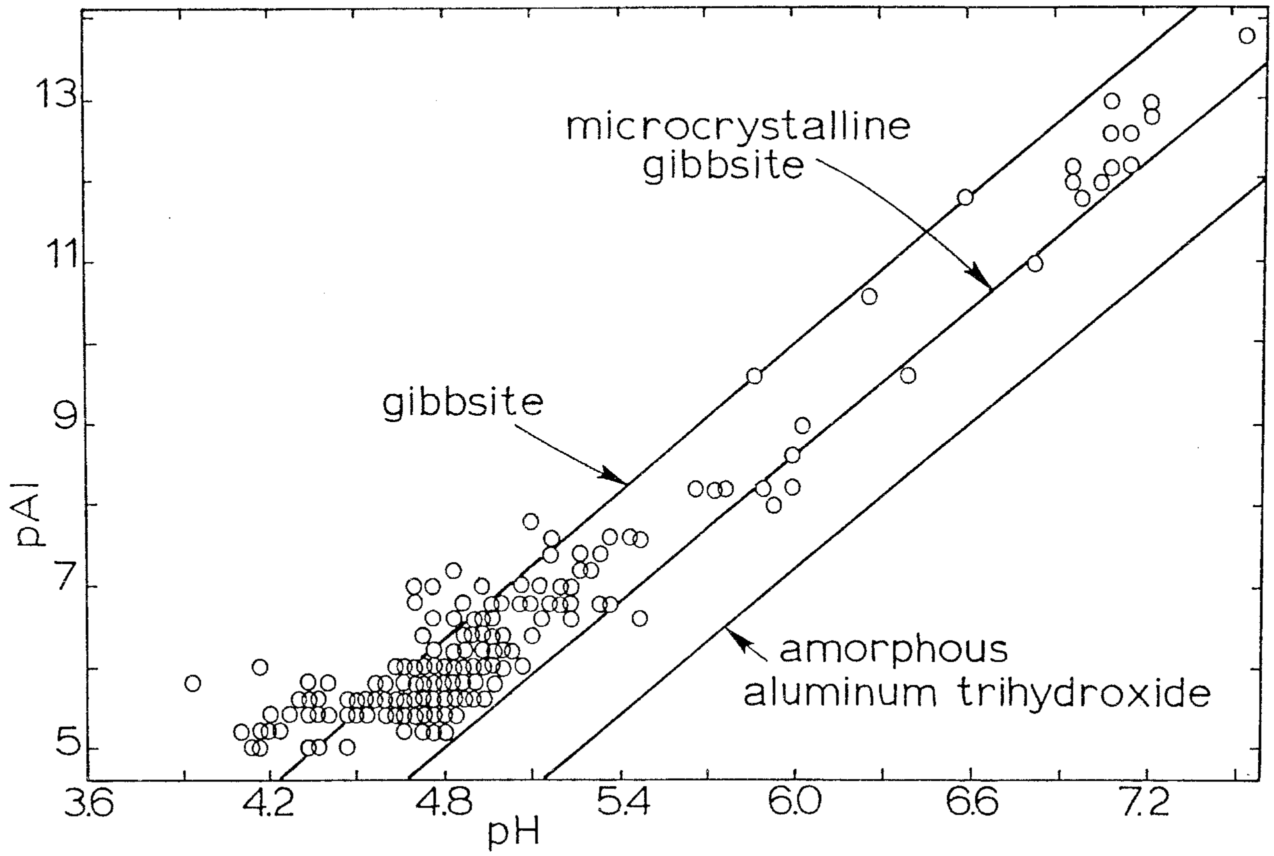

Figure 5 *The logarithm of activity of aquo Al as a function of pH in the Adirondack surface waters (Driscoll et al., 1984). The activity of* Al^{3+} *was calculated from measurements of inorganic monomeric Al, pH,* F^-*, and* SO_4^{2-} *using a chemical equilibrium model.*

Concentration and Speciation of Aluminum in Surface Waters

Researchers often rely on operationally defined procedures to evaluate the concentration and forms of Al in natural waters. Unfortunately, the accuracy of many of these methods is difficult to evaluate and there is considerable uncertainty as to what form(s) of Al are actually represented. The inability to precisely and accurately differentiate between aqueous and particulate Al, as well as between inorganic and organic forms of aqueous Al, have hampered studies of the environmental chemistry of this element.

Determinations of total (unfiltered) Al in natural waters are made using a wide variety of digestion procedures as well as extraction periods, resulting in a range of operational methods and considerable uncertainty in measured values. A number of studies have employed filtration in an effort to distinguish between dissolved and particulate Al forms. However, because particulate materials exhibit a continuous size distribution, no discrete distinction between dissolved and particulate forms can be made, and results show a strong dependence on filter pore size. For instance, in examining the dissolved and particulate fractions in a California stream, Kennedy *et al.* (1974) found that the concentration of Al in the filtrate decreased as filter pore size decreased from 0.45 to 0.1 µm.

In an attempt to eliminate problems and uncertainty associated with filtration, many researchers have relied on the addition of a complexing agent (*e.g.* 8-hydroxyquinoline, pryocatechol violet) followed by either rapid detection or extraction in an organic solvent (*e.g.* methyl isobutyl ketone, butyl acetate) to partition between aqueous and particulate Al (Turner, 1969, 1971; Smith and Hem, 1972; Dugan and Wilson, 1974; Barnes, 1975; James *et al.*, 1983). Rapid extraction techniques, however, are not without problems. For example, results vary with reaction time (Smith and Hem, 1972); the greater the contact time the larger the measured concentrations of Al. Also, it is unclear to what extent the complexing agent desorbs Al from particulate matter or competes with naturally occurring ligands for Al. In view of the wide range and operational nature of collection and procedures, comparisons of studies of Al in natural waters should be made with caution.

Concentrations of aluminum in surface waters

A wide range of Al concentrations have been reported for surface waters. Elevated concentrations of Al have generally been found in acidic waters within regions receiving high inputs of acidic substances, such as Sweden, Norway, Belgium, the Netherlands, West Germany, Canada and the United States (Table 1). Many investigators have observed an exponential increase in Al concentrations with decreasing solution pH (Vangenechten and Vanderborght, 1980; Baker, 1982; Driscoll *et al.*, 1984; Schoen, 1986). This phenomenon is characteristic of the theoretical and experimental solubility of a number of Al minerals. Unfortunately, synoptic surveys have used a

Table 1 *Aluminum concentrations in surface waters.*

Location	*Description*	*pH range*	*Total Al range (μmol/l)*	*Reference*
Lakes				
Europe				
Belgium	Moorland Pools 1975-79	3.5 - 8.5	11 - 300	Vangenechten and Vanderborght, 1980
Norway	Regional Survey 1974-77	4.2 - 7.8	0 - 27	Wright *et al.*, 1977
Sweden	West Coast 1976	4.0 - 7.4	0.4 - 27	Dickson, 1978
Scotland	Southwest Scotland	4.4 - 6.4	1 - 11	Wright *et al.*, 1977
North America				
Canada	Ontario, 1980	4.1 - 6.5	0.2 - 32	Kramer, 1981
Canada	Sudbury, Ontario	4.3 - 7.0	5 - 42	Scheider, 1975
Canada	Quebec	4.7 - 7.0	0.8 - 13	Campbell *et al.*, 1983
USA	Adirondacks 1977-78	3.9 - 7.0	0.1 - 31	Driscoll *et al.*, 1984
USA	New England 1978-81	4.0 - 8.2	0 - 21	Haines and Kielaszeck, 1983
USA	New England	4.2 - 7.0	0 - 16	Norton *et al.*, 1981
Streams				
Europe				
Sweden	Central Sweden 3 brooks	4.6 - 5.2	5.9 - 15	Rosen, 1982
West Germany	Snowmelt	3.7 - 7.5	0 - 740	Schoen, 1986
North America				
USA	Adirondacks 1977-78	4.0 - 7.6	3 - 43	Driscoll *et al.*, 1984
USA	New England 1978-81	4.1 - 7.7	0.5 - 14	Haines and Kielaszeck, 1983

variety of methods to determine solution Al, so only broad patterns should be interpreted.

In a synoptic survey of 1798 lakes in acid-sensitive regions of the eastern United States, Linthurst *et al.* (1986) measured two forms of Al. Total Al was determined on an unfiltered sample which was acid digested (pH <2) and measured by atomic absorption spectrophotometry (AAS). To provide an estimate of concentrations of aqueous Al, extractable Al was determined by filtration (0.4 μm polycarbonate) followed by 8-hydroxyquinoline complexation, extraction using methyl isobutyl ketone and detection by AAS. Lakes sampled as part of the Eastern Lake Survey (ELS) were divided into regions and subregions within the eastern USA to facilitate geographical assessments.

Results of the ELS indicated that lakes in acid-sensitive regions were generally circumneutral (Table 2). Linthurst *et al.* (1986) defined acidic lakes as those systems with pH values below 5.0. A relatively small number of lakes had pH values below 5.0. For example, in the Northeast region only 3.4% of the lakes were acidic. Within the Adirondack subregion, 10% of the lakes were acidic, in southern New England, 5% and all other Northeast subregions had less than 2% acidic lakes. In the Upper Midwest, only 1.5% of the lakes surveyed had pH values below 5.0; with the Upper Peninsula of Michigan having 9% and all other Upper Midwest subregions having 2% or less. In the Southeast region, the Southern Blue Ridge contained no acidic lakes, while the Florida subregion had 12% of the lakes with pH values below 5.0.

As a result of the relatively low number of acidic lakes, very few of the waters sampled contained elevated Al concentrations. Lakes generally exhibited much higher concentrations of total Al than extractable Al (Table 2), suggesting that water column Al was largely in a particulate form. Because extractable Al is thought to be more labile and bioavailable, analysis of these data has focused on this measurement. Aluminum leaching to surface waters may occur by strong acid and/or organic acid inputs, so our evaluation of concentrations from the ELS has included separate analysis of clearwater (dissolved organic carbon, DOC, concentrations below 500 μmol C/L and colored water (DOC above 500 μmol C/L) systems (Table 3).

Estimates of clearwater lakes with elevated concentrations of extractable Al were consistent with pH trends. Generally, concentrations of extractable Al were below 1 μmol/L for clearwaters with pH values above 6 and increased exponentially with decreases in pH below

Table 2 *Summary of aluminum concentrations in lakes from acid-sensitive regions of the eastern USA (Linthurst* et al.*, 1986). Mean value and range are given in mol/L.*

Location	*n*	*pH*	*Total Al*	*Extractable Al*
Northeast				
Adirondack	203	6.3 (4.2 - 9.4)	5.1 (0.3 - 28)	1.6 (0 - 12)
Poconos/Catskills	156	6.7 (4.9 - 9.5)	2.4 (0 - 24)	0.5 (0 - 9.6)
Central New England	213	6.7 (4.4 - 9.5)	3.3 (0.2 - 19)	0.5 (0 - 5.5)
S. New England	127	6.5 (4.5 - 7.8)	2.2 (0.2 - 11)	0.4 (0 - 6.9)
Maine	184	6.9 (4.3 - 8.4)	3 (0.3 - 30)	0.5 (0 - 10)
Upper Midwest				
N.E. Minnesota	159	6.8 (5.6 - 8.3)	2.8 (0.1 - 19)	0.6 (0 - 4.7)
Upper Peninsula	156	6.5 (4.4 - 8.6)	2.2 (0 - 16)	0.7 (0 - 7.9)
N. Cen. Wisconsin	187	6.5 (4.7 - 8.0)	1.4 (0 - 16)	0.3 (0 - 0.6)
Upper Great Lakes	142	6.9 (5.4 - 8.7)	1.4 (0 - 15)	0.3 (0 - 6.7)
Southeast				
S. Blue Ridge	112	6.9 (5.9 - 8.3)	4.3 (0.3 - 40)	0.1 (0 - 1.5)
Florida	159	6.3 (3.8 - 9.0)	3.3 (0.3 - 50)	0.8 (0 - 16)

that value. Significant numbers (>5%) of clearwater lakes with elevated concentrations of extractable Al were only evident in those subregions showing relatively large numbers of low pH lakes, including the Adirondacks, the Poconos/Catskills, the Upper Peninsula of Michigan and Florida (Table 3). The Adirondack region of New York clearly contained the largest number of low DOC lakes with elevated concentrations of extractable Al.

Several of the subregions also showed a significant number of colored (DOC >500 µmol C/L) lakes with elevated concentrations of extractable Al (Table 3). These lakes generally coincided with very high DOC waters and were found in districts with a large percentage of high DOC waters, including northeastern Minnesota, the upper Peninsula of Michigan, North Central Wisconsin and Florida.

Speciation of aluminum in surface waters

In assessments of the environmental chemistry of Al, it is particularly useful to be able to distinguish between species of aqueous Al. It is well established that Al forms strong complexes with OH^-, F^-, $SO_4{}^{2-}$ (Roberson and Hem, 1967) and organic ligands (Lind *et al.*, 1975). Fortunately, thermodynamic data for OH^-, F^-, $SO_4{}^{2-}$ complexation are well established and allow for precise estimates of the speciation of inorganic Al in solution (Schecher and Driscoll, 1987).

The speciation of Al is pH-dependent. At low pH values dissolved Al is almost entirely present as an aquo form (Al^{3+}). As pH values increase Al undergoes hydrolysis, resulting in a series of OH^- complexes ($Al(OH)^{2+}$, $Al(OH)_2{}^+$) and decreases in solubility. The solubility of Al is minimum near pH 6.5 and increases at higher pH values due to the formation of $Al(OH)_4{}^-$ (Figure 6).

Fluoride is similar in size and therefore readily substitutes for OH^- in metallic complexes. Under acidic conditions F^- has a strong affinity for Al (Figure 7a). The stoichiometry of Al-F complexes varies with the total F^- concentration. As F^- concentrations increase, H_2O or OH^- ligands are displaced in a step-wise manner resulting in higher ligand number complexes until all octahedral positions of Al are occupied by F^- (*e.g.* $AlF_6{}^{3-}$ (Roberson and Hem, 1967). Concentrations of F^- in natural waters are typically low (median concentrations of freshwaters 10 µmol/L (Stumm and Morgan, 1970). At pH values below 5.5 molar concentrations of dissolved Al generally exceed concentrations of F^-, and low ligand number complexes predominate (*e.g.* AlF^{2+}, $AlF_2{}^+$). The concentration of Al-F complexes in natural acidic solutions is therefore generally limited by total concentration of F^- available for complexation (Driscoll *et al.*, 1984). At high pH values (>7), OH^- concentrations are elevated and it becomes

Table 3 *Estimates of percent of low DOC (<500 mol C/L), high DOC (>500 mol C/L) and total lakes in the USA. US EPA Eastern Lake Survey with concentrations of extractable Al above values of 2 and 5 mol/L.*

Location	*n*	*Total* *>2 (mol/L)*	*>5 (mol/L)*	*n*	*Low DOC* *>2 (mol/L)*	*>5 (mol/L)*	*n*	*High DOC* *>2 (mol/L)*	*>5 (mol/L)*
Northeast									
Adirondacks	203	21.4	12.4	172	24.6	14.0	31	3.2	3.2
Poconos/Catskills	156	5.2	0.6	132	6.8	0.7	24	0	0
Cen. New England	213	3.8	0.9	166	3.6	0.6	47	4.2	2.1
S. New England	127	3.9	0.8	95	4.2	1.0	32	3.1	0
Maine		184	1.6	1.1	111	0.9	0.9	73	2.7
Upper Midwest									
N.E. Minnesota 159	7.5	1.2	35	2.8	0	124	8.9	1.6	
Upper Pen. Michigan	156	7.0	1.3	78	6.4	1.3	78	7.7	1.3
N. Cen. Wisconsin	187	3.7	0.5	126	0	0	61	11.4	1.6
Upper Great Lakes	142	2.1	0.7	55	0	0	87	3.4	0.7
Southeast									
S. Blue Ridge	112	0	0	108	0	0	4	0	0
Florida	159	8.2	1.9	82	9.7	2.4	77	6.4	1.3

increasingly difficult for F^- to compete with OH^- for aqueous Al. As a result OH^- complexes predominate over F^- complexes under alkaline conditions.

Like F^-, $SO_4{}^{2-}$ forms complexes with Al under acidic conditions and is displaced by OH- complexes under alkaline conditions (Figure 7b). The predominate Al-SO_4 complex is $AlSO_4{}^+$ at low $SO_4{}^{2-}$ concentrations and shifts of $Al(SO_4)^{2-}$ at higher $SO_4{}^{2-}$ concentrations. Sulfate complexes of Al are not as strong as F- complexes. Although $SO_4{}^{2-}$ concentrations are typically higher than F- in freshwaters (median concentration 400 µmol/L; Stumm and Morgan, 1970), Al-SO_4 complexes are significant only at high $SO_4{}^{2-}$ concentrations and low pH values.

There is some qualitative evidence in the literature to suggest the importance of Al-Si species (Luciak and Huang, 1974; Farmer *et al.*, 1980; Farmer and Fraser, 1982). Unfortunately, there are no reliable thermodynamic data or aqueous Al-Si reactions. Given the concentration range of dissolved Si in freshwaters (median concentration 300 µmol/L; Stumm and Morgan, 1970), it might be reasonable to hypothesize the existence of Al-Si complexes, if only as metastable templates for clay formation. Due to the absence of thermochemical data, current studies on the distribution of inorganic Al in natural waters have generally ignored Al-Si complexes. However, if Al-Si complexation proves to be significant it could dramatically alter current views of the speciation of Al in natural solutions.

Other inorganic anions, found in natural waters (*e.g.* $HCO_3{}^-$, Cl^-, $NO_3{}^-$) do not appear to form important complexes with Al. Recently, Hedlund *et al.* (1987) provided thermodynamic for polynuclear complexes of Al with $HCO_3{}^-$; however, these species are not significant under conditions typically found in natural waters.

Naturally occurring organic solutes may have a marked effect on the solubility and speciation of Al. Unfortunately, the chemistry of naturally occurring organic solutes is poorly understood. The complicated and diverse nature of dissolved organic matter leads to special problems in understanding and modeling aqueous Al chemistry. Not only is it an inherently complex ligand mixture which exhibits a distribution of binding sites with varying affinity for Al, but electrostatic interactions between ligand sites on the same molecule, configurational changes and aggregation reactions arise (Lakatos *et al.*, 1977; Sipos *et al.*, 1976; Gosh and Schnitzer, 1981; Ritchie and Posner, 1982), making rigorous thermochemical descriptions difficult.

Due to uncertainty in thermodynamic data, particularly involving naturally occurring organic solutes, it is useful to analytically distinguish between forms of aqueous Al. This information is critical to interpret process-level research on mechanisms controlling the concentration, transport and bioavailability of Al. A number of fractionation procedures have been developed in recent years to attempt to distinguish between aqueous forms of Al. These techniques include rapid reaction with complexing agents (Barnes, 1975; James *et al.*, 1983), dialysis (LaZerte, 1984), batch chelating resin (Campbell *et al.*, 1983), column cation exchange (Driscoll, 1984), F ion selective electrode (Driscoll, 1984) and morin addition followed by fluorimetric detection (Browne *et al.*, 1989a,b). All these procedures are operationally defined and undoubtedly detect somewhat different forms of Al (Hodges, 1987; Bloom and Erich, 1989).

Until recently there have been few studies of the speciation of Al in natural waters. Most of the available data have been obtained from regions with waters that have been acidified by atmospheric deposition and contain

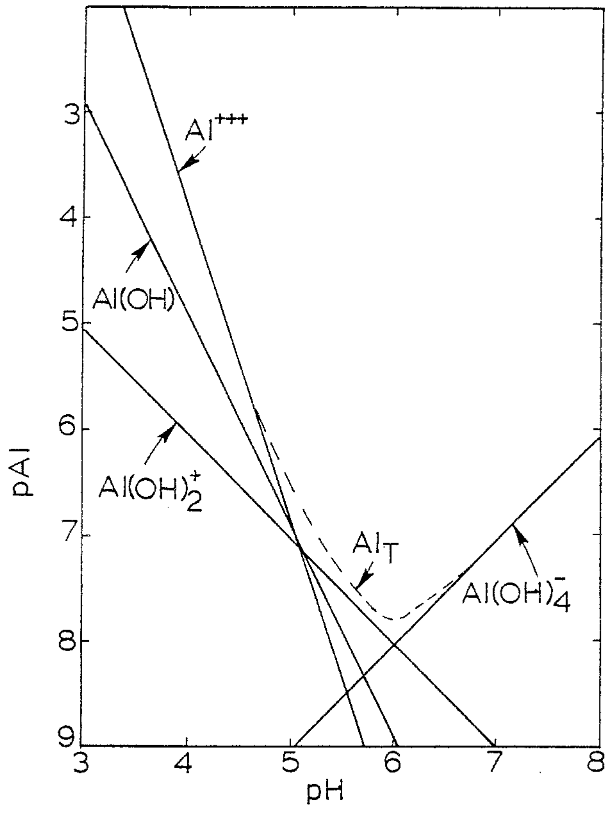

Figure 6 *The solubility of Al in equilibrium with $Al(OH)_3$.*

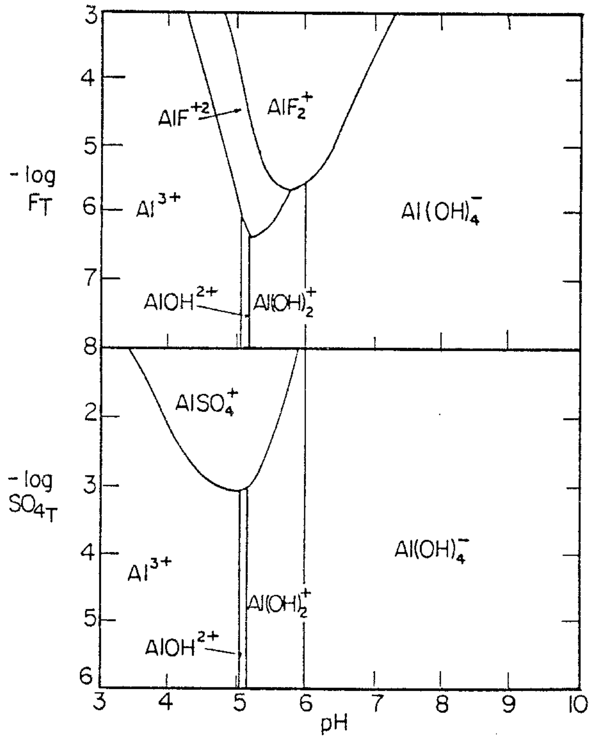

Figure 7 *Predominance area diagram depicting the distribution of aqueous Al controlled by the solubility with various concentrations of F^- (a) and SO_4^{2-} (b) as a function of pH.*

elevated concentrations of Al. Studies of Al chemistry in surface waters of the Adirondack region of New York (Driscoll *et al.*, 1984) and New Hampshire (Johnson *et al.*, 1981), using the cation exchange column fractionation procedure, have yielded similar results. Concentrations of inorganic monomeric Al increased exponentially with decreases in solution pH below 5.5 (Figure 8). Concentrations of organic monomeric Al were strongly correlated with organic carbon concentration in both Adirondack (Al-Org = - 3.36 x 10^{-6} + 0.0204 TOC; where Al-Org is organic monomeric aluminum in µmol/L and TOC is total organic carbon concentration in µmol C/L, $n = 322$, $r^2 = 0.76$, $p < 0.0001$; Figure 9; Driscoll *et al.*, 1984), and New Hampshire (Al-Org = -7.3 x 10^{-7} + 0.0155 DOC; where DOC is in µmol C/L, $n = 69$, $r^2 = 0.85$, $p < 0.0001$; Driscoll, 1984) surface waters.

Recently, Driscoll and coworkers (Driscoll and Newton, 1985; Driscoll *et al.*, 1987; Schecher and Driscoll, 1988b) investigated the speciation of Al in 20 drainage lakes of the Adirondack region of New York as part of the Regionalization of the Integrated Lake Watershed Acidification Study (RILWAS). The lakes studied included a broad range of basin characteristics and water chemistry (*e.g.* pH, DOC). Again, waters exhibited marked variations in Al concentration and speciation, with inorganic monomeric Al concentrations increasing with decreasing pH (Figure 10) and Al-Org concentrations correlated with DOC concentrations (Driscoll and Newton, 1985; Driscoll *et al.*, 1987). In this analysis it was also evident that concentrations of Al-Org also increased with decreases in pH (Figure 10), suggesting that the mobility of Al-Org is enhanced under acidic conditions. Further evidence to support this contention was available through trends in the organic monomeric Al to DOC ratio (Al-Org/DOC) in surface waters (Figure 11). Under circumneutral pH conditions the Al-Org/DOC was low and systematically increased with decreasing pH. As mentioned previously, increases in the Al-Org/DOC generally coincides with decreases in the solubility of organic solutes, facilitating immobilization of organic carbon and Al (Schnitzer and Skinner, 1963a,b; Ugolini *et al.*, 1977). The high values of Org-Al/DOC at low pH are again suggestive that leaching of alumino-organic solutes from soil is enhanced under acidic conditions.

Using ALCHEMI, detailed speciation of Al was investigated for the RILWAS lakes. Marked variations in the relative distribution of Al complexes were evident with lake pH. Under acidic conditions (pH 4.5-6.0) inorganic species of monomeric Al predominated, although organic forms were also important (Figure 12). Under highly acidic conditions (pH <5) concentrations aquo Al (Al^{3+}) were significant, but declined markedly as pH increased above 5.0. In the pH range 5.0 to 6.0 alumino-fluoride (Al-F) complexes were the dominant form of inorganic monomeric Al. As pH values increased above 6.0, alumino-hydroxide (Al-OH) species represented the major form of aqueous Al. Aluminum sulfate ($Al\text{-}SO_4$) complexes were insignificant, representing less than 5% of monomeric Al in the study lakes. Alumino-organic solutes (Al-Org) were a major component of monomeric Al over a broad pH range of 4.3 to 7.0. This trend suggests that Al-Org species are highly stable in natural waters.

LaZerte (1984) and Campbell *et al.* (1983) have studied the speciation of Al in Canadian surface waters, using the dialysis and batch chelating resin techniques, respectively. In these waters pH values were generally

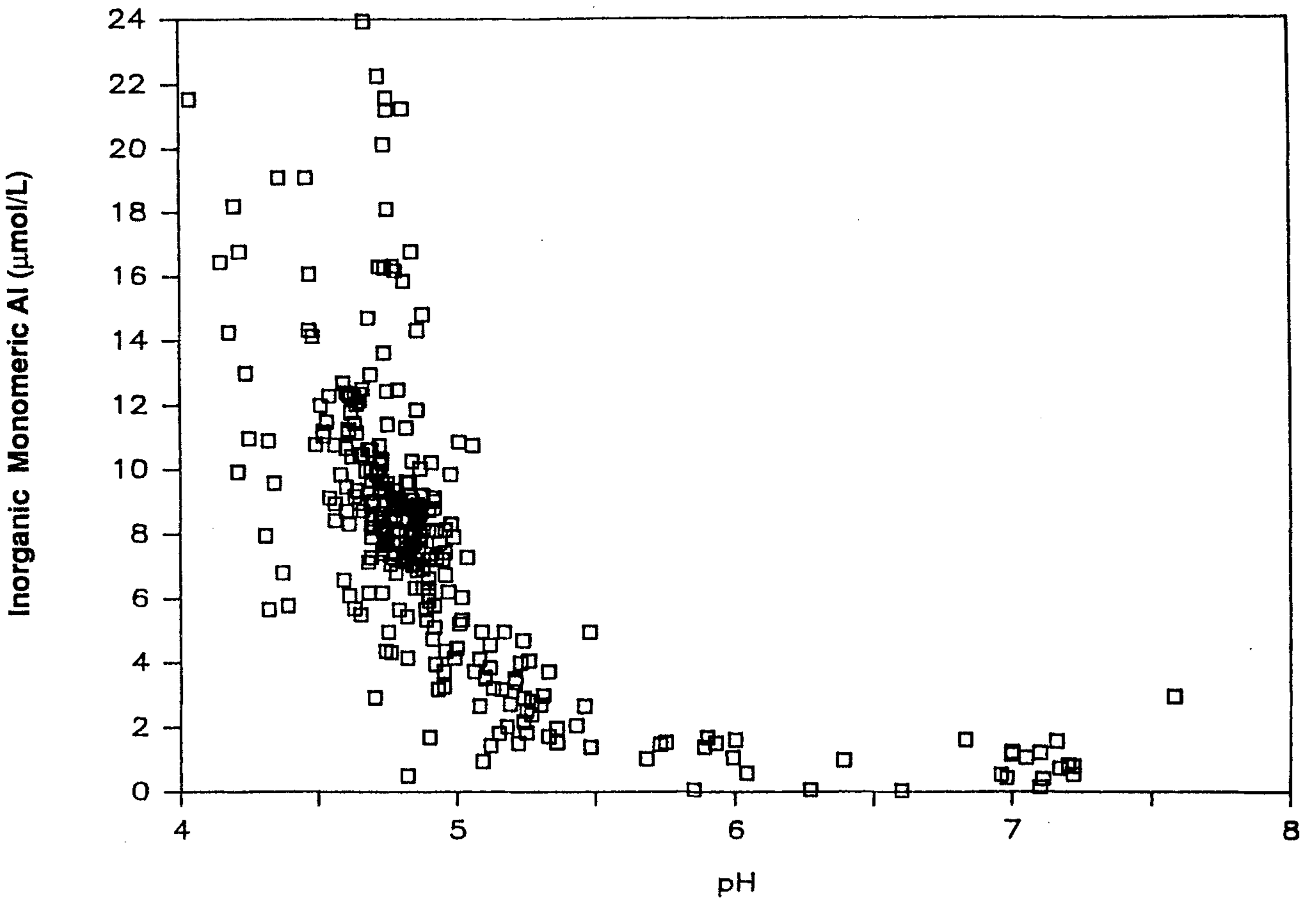

Figure 8 *Concentrations of inorganic monomeric Al as a function of pH in Adirondack surface waters (Driscoll* et al., *1984).*

higher than highly acidic waters in the northeastern USA, so Al concentrations were generally lower and largely in an organic form. However, as surface water pH decreased the distribution of Al shifted, with increasing predominance of inorganic forms. Moreover, LaZerte (1984) reported that in Ontario waters inorganic Al was predominantly complexed with F.

Lee (1985) evaluated the speciation of Al in the Lake Gardsjon catchment of Sweden, using the column cation exchange procedure. At this study site surface waters were highly acidic (pH <4.5) and Al concentrations ranged from 11 to 33 μmol/L. Monomeric Al was predominantly in an inorganic form and largely associated with aquo (30-55%) or F complexes (10-30%). Organic forms ranged from 0 to 43% of monomeric Al.

Models of aluminum speciation in natural waters

The speciation of aqueous Al is not routinely determined in synoptic surveys or monitoring programs of water chemistry. However, this information is critical for water quality assessments, because the effects of aqueous Al are not only due to elevated concentrations, but also its speciation. Researchers often rely on models to calculate the speciation of Al when direct measurements are not available. Calculations of the speciation of inorganic Al are relatively straightforward, because of the availability of good thermodynamic data (Schecher and Driscoll, 1987). However, natural waters contain a complex mixture of organic solutes which are capable of binding with Al. Therefore difficulty arises in estimating Al-Org concentrations. Fortunately, a few models are available in the literature which allow for the calculation of Al species given measurements of pH, total or monomeric Al and ligand concentrations (LaZerte, 1984; Gherini *et al.*, 1985; Backes and Tipping, 1987).

Schecher (1988) has coupled a chemical equilibrium model for the speciation of inorganic Al (ALCHEMI), with a series of proton and Al binding reactions thought to be applicable to acid-sensitive waters. This model was developed using field data collected from the Adirondack region of New York (RILWAS sites), in which Al was fractionated using the cation exchange column method. Thermodynamic data used in this model are summarized in Appendix 1. In ALCHEMI organic solutes are represented as a triprotic acid, while two species of alumino-organic solutes are depicted. Thermodynamic constants were calibrated using field observations and a good fit of the data was obtained ($r^2 = 0.86$, $n = 31$).

Using ALCHEMI hypothetical calculations were made to illustrate the speciation of the model organic acid and Al for conditions that are typical of acid-sensitive waters in the Adirondack region of New York (Driscoll and Newton, 1985). Model calculations were made using F^- concentrations of 5 μmol/L and $SO_4{}^{2-}$ concentrations of 100 μmol/L, and in equilibrium with the solubility of natural ($Al(OH)_3$) (Appendix 1). Two concentrations of dissolved organic carbon (100 and 1,000 μmol C/L) indicative of clear and colored waters, respectively, were

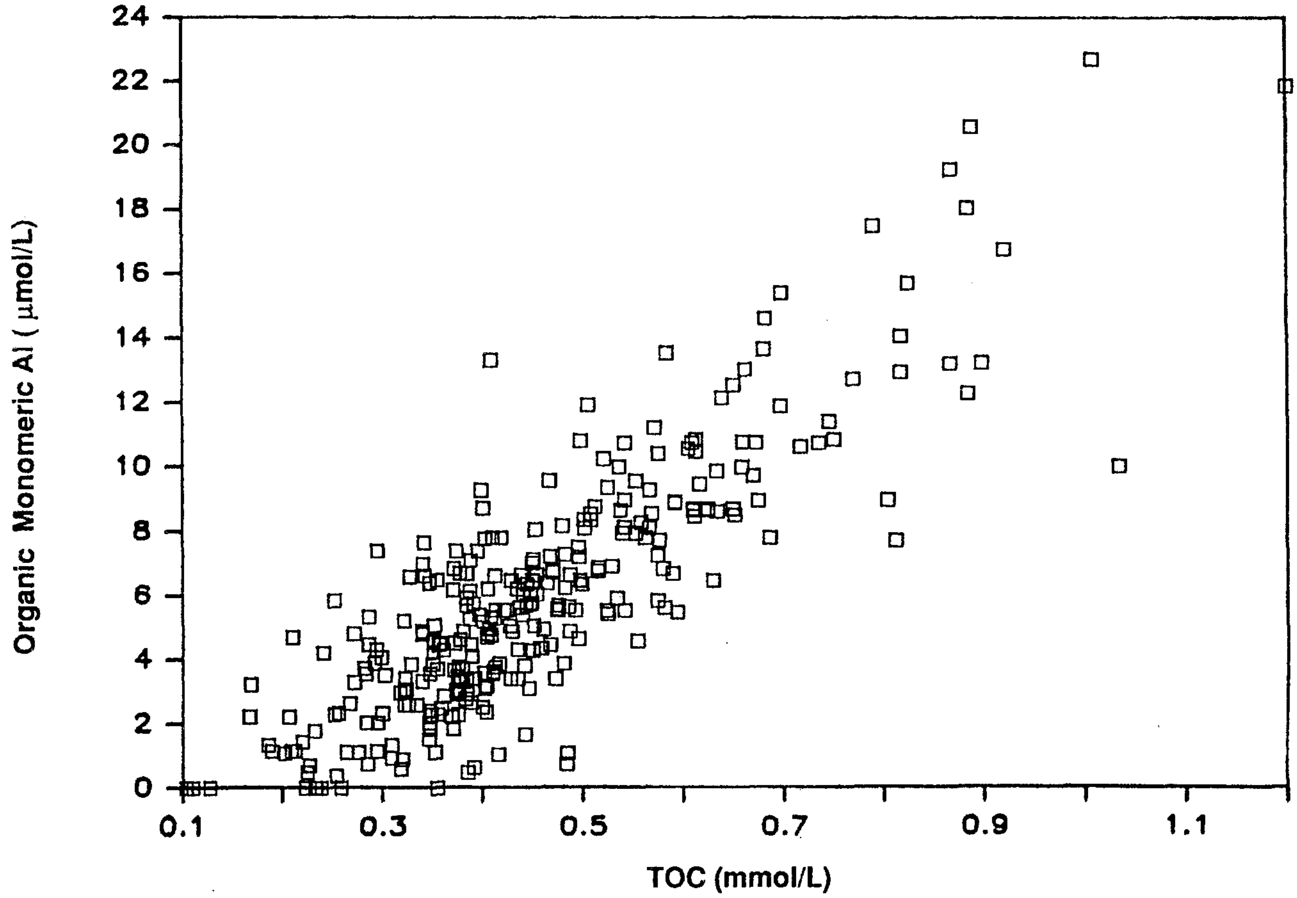

Figure 9 *Concentrations of organic monomeric Al as a function of total organic carbon concentration (μmolC/L) in Adirondack surface waters (Driscoll* et al., *1984).*

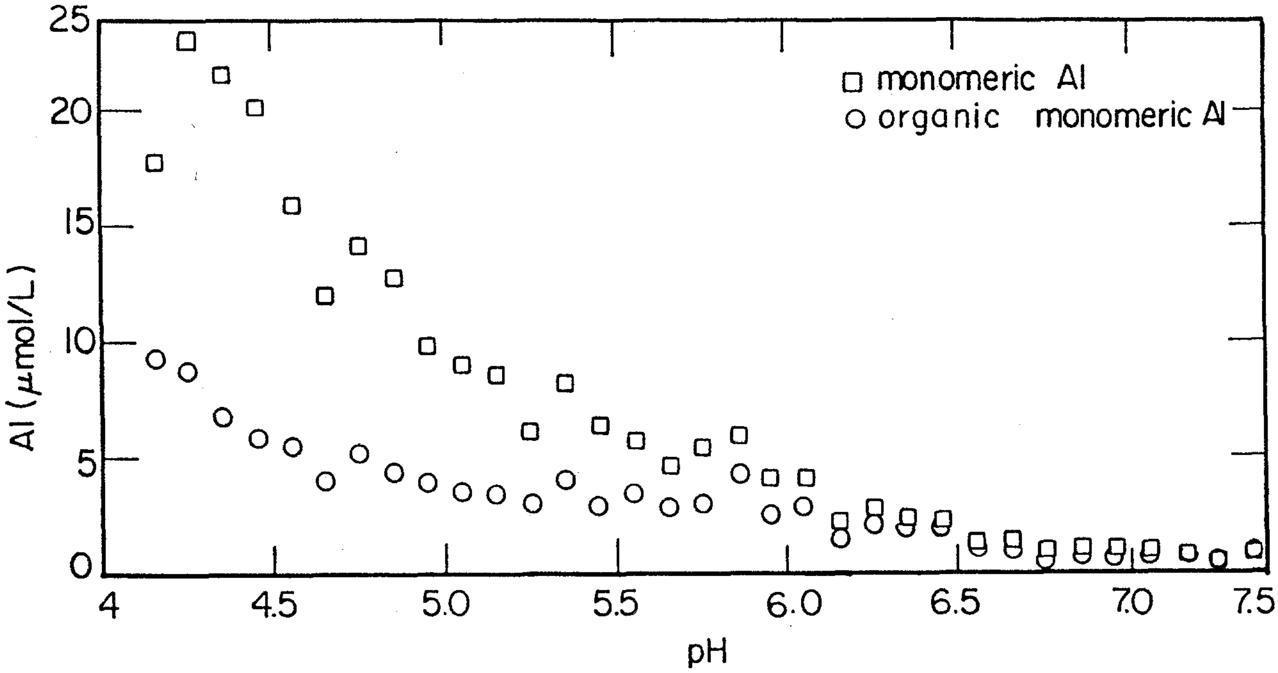

Figure 10 *Concentrations of monomeric Al and organic monomeric Al as a function of pH. The difference between these values is an estimate of inorganic monomeric Al. Values shown represent mean concentration at 0.1 pH unit intervals. This procedure reduces the database while still exposing the central tendency.*

used to demonstrate the role of organic solutes in the speciation of Al.

For both concentrations of DOC calculations show that a shift in the speciation of the model organic acid occurs with changes in pH (Figure 13). In the neutral pH range the triprotic organic solute is essentially fully deprotonated. As pH values decrease below 7, the organic anion protonates producing a series acidic species. At low

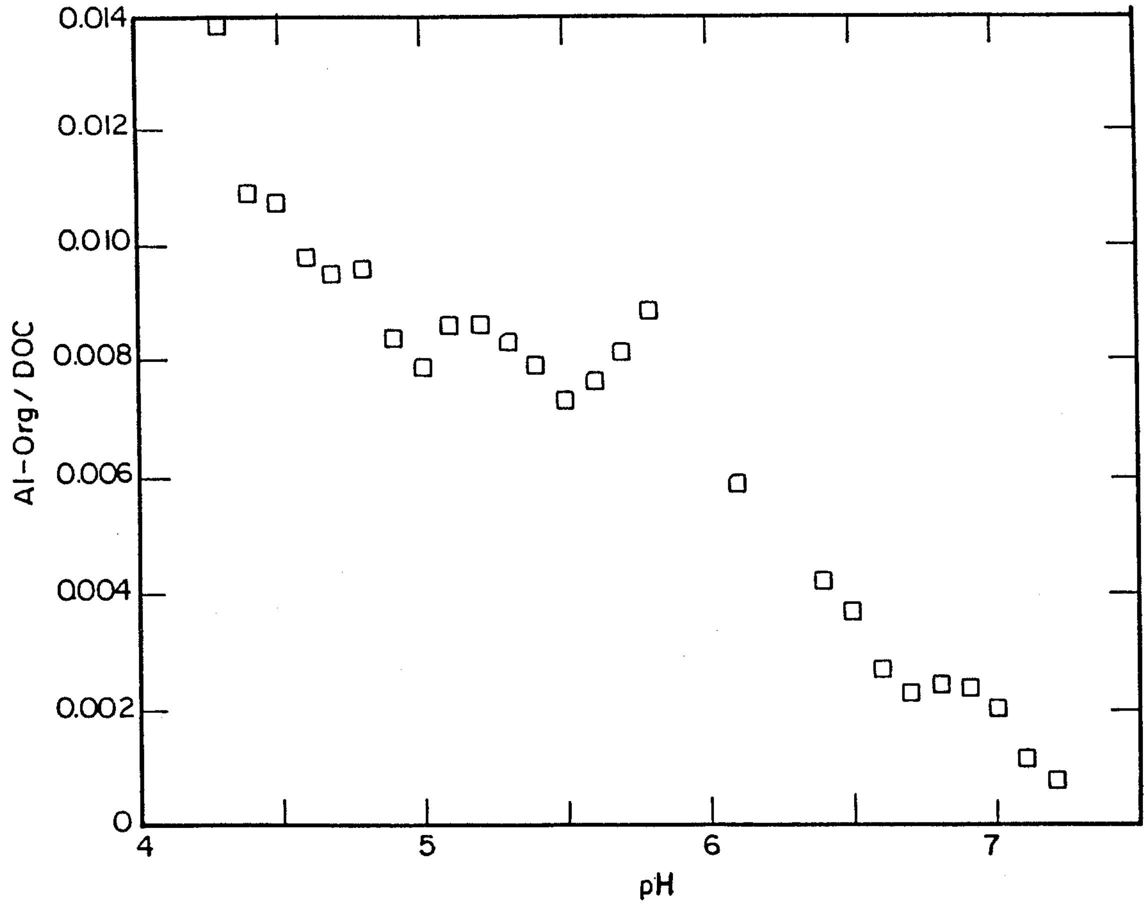

Figure 11 *Ratio of organic monomeric Al (Al-Org) dissolved organic carbon (DOC) as a function of pH for RILWAS study lakes. Values shown represent mean of observations at 0.1 pH unit intervals.*

pH values complexation of the organic anion by Al is evident and below pH 4.5 these species represent the dominant organic form. At very low pH values a cationic alumino-organic complex is evident, suggesting that surface water acidification may enhance the mobility of organic forms of Al, as well as inorganic forms.

Hypothetical calculations of acid-sensitive waters demonstrate that the speciation of Al is highly dependent on pH, as well as total ligand concentrations (Figure 14). In acidic waters aquo Al is generally the dominant form because the pH-dependent solubility of $Al(OH)_3$ results in Al concentrations which greatly exceed concentrations of available ligands. At higher pH values total Al concentrations decrease and the relative importance of complexing ligands increase. In low DOC waters (100 µmol C/L; Figure 14*a*), Al-F represents the dominant fraction of aqueous Al between pH 5.0 and 6.0. Increased concentrations of DOC (1000 µmol C/L; Figure 14*b*) allow additional complexation of Al, greatly increasing the relative significance of these species. At neutral pH values hydrolysis is evident and $Al(OH)_4^-$ is the predominant form of aqueous Al.

Chemical equilibrium models describing the aqueous chemistry of Al have been incorporated as subcomponents into detailed acidification models (Reuss and Johnson, 1985; 1986; Cosby *et al.*, 1985; Gherini *et al.*, 1985). These comprehensive solute transport models have been developed in order to simulate soil and drainage water acidification in forested watersheds. To make assessments of surface water quality, an important output of acidification models is the concentration and speciation of Al (Schecher and Driscoll, 1988*a*). Acidification models are highly variable in their depiction of Al chemistry; ranging from simple $Al(OH)_3$ dissolution and hydrolysis reactions (Reuss and Johnson, 1985; 1986) to detailed representations of soil and drainage water, including kinetically controlled release of solid phase Al and comprehensive aqueous speciation (Gherini *et al.*, 1985). Although the representation of Al chemistry is currently quite sophisticated in some acidification models, it is important that these models are continuously evaluated and modified to reflect ongoing advances in the biogeochemistry of Al.

Environmental Effects of Elevated Concentrations of Aluminum

Chemical and physical consequences of aqueous Al

There are a variety of ecological effects associated with elevated concentrations of aqueous Al. A number of investigators have demonstrated the role of Al in relating the pH buffering of waters under acidic conditions (Dickson, 1978; Johannessen, 1980; Glover and Webb, 1979; Henriksen and Seip, 1980; Driscoll and Bisogni, 1984; Driscoll *et al.*, 1987). This characteristic is effectively depicted through the model of pH buffering developed for dilute waters by Driscoll and Bisogni (1984; Figure 15). Buffering capacity is defined as the quantity of

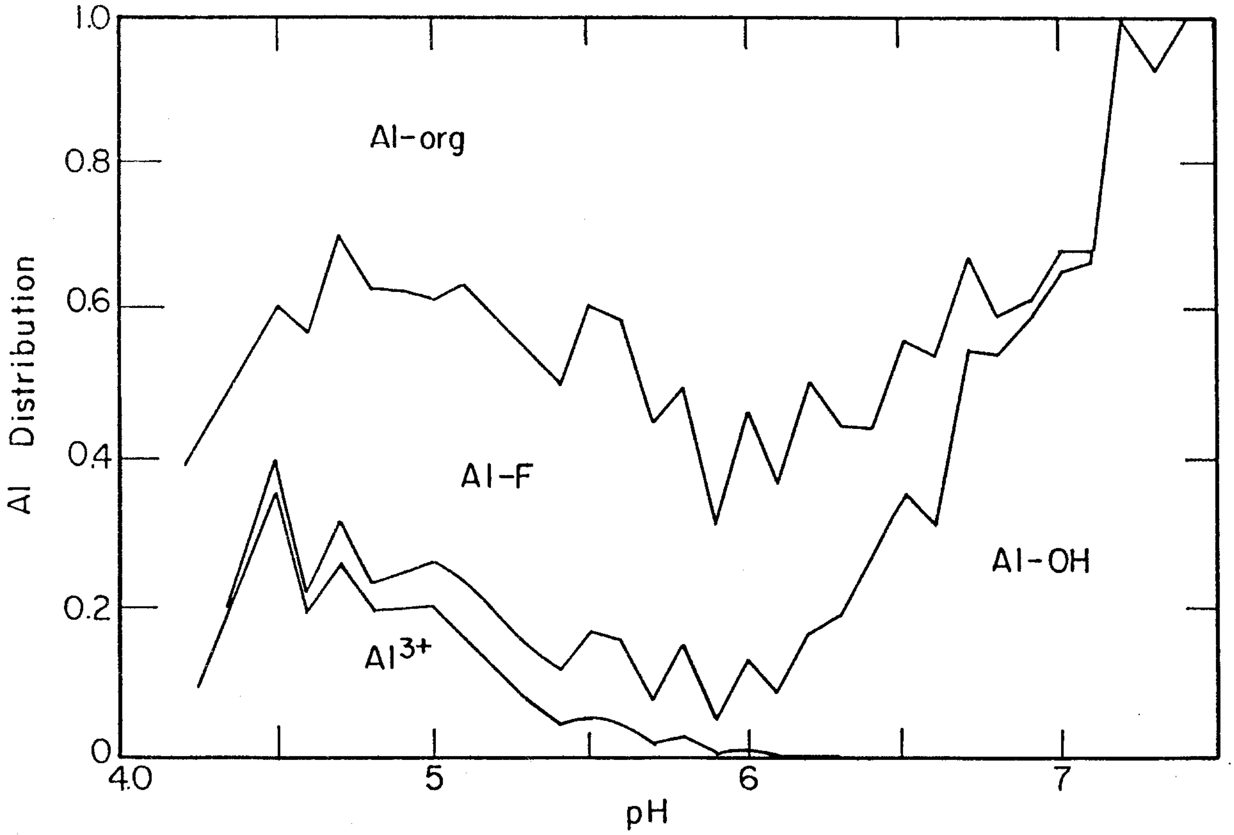

Figure 12 *Distribution of the speciation of Al, including aquo Al (Al^{3+}), alumino-fluoride complexes (Al-F), alumino-hydroxide complexes (Al-OH) and alumino-organic solutes (Al-Org) as a function of pH for RILWAS lakes. All observations were evaluated for Al speciation using ambient water quality data with ALCHEMI. Values shown represent mean of calculated speciation at 0.1 pH unit intervals.*

strong acid or base (mol/L) required to change the pH of a liter of solution by one unit. In this model naturally occurring organic acids were fit to a monoprotic proton dissociation constant (pKa = 4.4) and proton dissociation sites of organic solutes were quantified from potentiometric titrations. Aquo Al activity (Al^{3+}), calculated from field observations, appeared to fit an $Al(OH)_3$ solubility model (Figure 5). Finally, dissolved inorganic carbon concentrations were determined by assuming equilibrium with atmospheric CO_2. Under circumneutral conditions pH buffering of natural waters is regulated by inorganic carbon equilibria. Inorganic carbon buffering decreases with decreases in pH, resulting in a minimum in buffering capacity over the pH range 5- 6. Under acidic conditions (pH <5.0) buffering capacity increases, with Al species dominating the buffering system. This trend suggests that the lower limit of pH observed in acidic waters may be regulated by the dissolution of Al. Moreover, solution Al represents an important component of the acidity of low pH waters. Aluminum acidity would have to be neutralized in order for acidic water to attain neutral pH values through reduction in strong acid inputs or base treatment.

Aqueous Al also has the potential to interact with a variety of other element cycles through complexation, direct precipitation or adsorption reactions. Of these processes, adsorption may be particularly significant. At certain times of year and within certain regions, within a stream or lake, acidic solutions may become oversaturated with respect to the solubility of readily forming Al mineral phases. The processes generally responsible for this condition generally include retention of NO_3^- (Driscoll and Schafran, 1984) or organic anions, and the degassing of CO_2 (Norton and Henriksen, 1983). During conditions of oversaturation, Al will hydrolyze, forming particulate Al oxyhydroxide. These materials would include microcrystalline hydroxide particles and their polymeric hydroxycation precursors. Smith and Hem (1972) observed that during the polymerization process, Al hydroxide units displayed metastable ionic solute behavior until they contained from 100-400 Al atoms. When particles developed to that size their behaviour was characteristic of a suspended colloid. Microcrystalline precipitates have a very high specific surface area and readily sorb both inorganic (Huang, 1975; Hohl and Stumm, 1976) and organic (Davis and Gloor, 1981; Davis, 1982) solutes. Studies have suggested that the cycling of PO_4^{3-} (Dickson, 1978), Pb (White and Driscoll, 1985) and DOC (Dickson, 1978; Driscoll *et al.*, 1982; Effler *et al.*, 1985) may be altered in acidic surface waters through interactions with Al.

Of particular interest is adsorption, coagulation and subsequent removal of DOC that may be facilitated by elevated concentrations of Al. Organic solutes represent an important weak acid/base system that regulates the pH buffering of dilute acidic waters (Johannessen, 1980; Driscoll and Bisogni, 1984). Moreover, in acidified lakes, Al induced changes in DOC may contribute to changes in the attenuation of light and patterns of water column

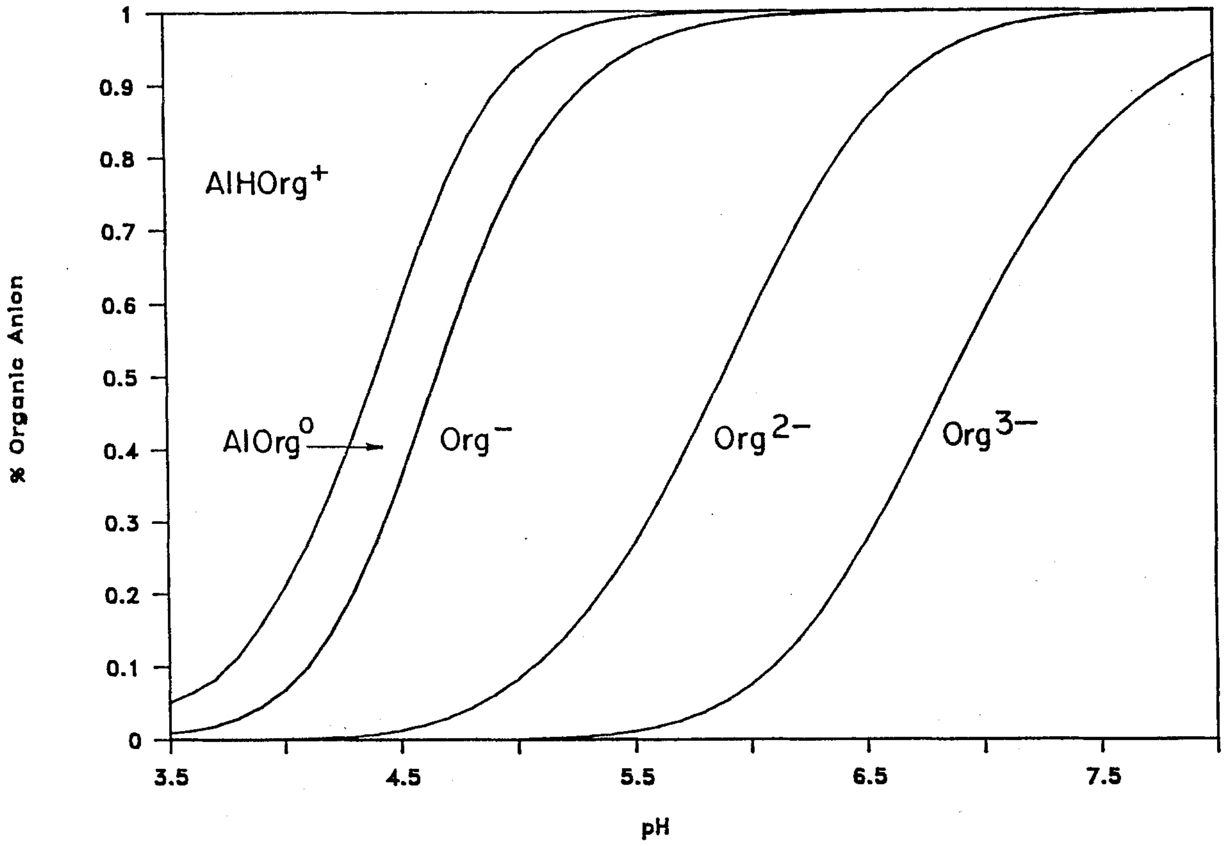

Figure 13 *Distribution of model organic solute as a function of pH for a system in equilibrium with Al(OH)3. Organic acid is represented as a triprotic solute which can complex Al (Appendix 1; after Driscoll and Schecher, 1988).*

heating. Effler *et al.* (1985) reported that temporal variations in the DOC of an acidic Adirondack lake accounted for much of the seasonal change in the attenuation of light. These researchers also observed that variations in DOC within the photic zone were correlated with Al concentrations. They suggested that in-lake hydrolysis/precipitation of Al facilitated the removal of DOC from the photic zone (by adsorption, coprecipitation or coagulation processes) and increased lake clarity through the summer season. Other researchers have reported marked changes in thermal stratification following changes in the acid/base chemistry of dilute lakes (Almer *et al.*, 1974; Malley *et al.*, 1982; Yan, 1983). Decreases in attenuation of light may allow heating of the lower waters thereby decreasing the thermal stability of lakes. Changes in the heating and thermal stratification of lakes may have profound effects on these ecosystems by altering vertical transport of solutes and restricting cold-water fisheries.

Aluminum toxicity

There is considerable evidence to suggest that exposure to elevated concentrations of bioavailable Al results in toxicity to a wide variety of organisms. Although Al may cause deleterious effects, there is considerable uncertainty in the form of bioavailable Al as well as the mechanism of toxicity. Moreover, the biological response to Al appears to be highly variable.

In recent years there has been considerable interest in the toxicity of Al to fish. Adverse effects of aqueous Al may occur at concentrations above 4-8 μmol/L (Schofield and Trojnar, 1980; Muniz and Leivestad, 1980; Baker and Schofield, 1982). Schofield and Trojnar (1980) evaluated the effects of 12 water quality parameters on the survival of brook trout (*Salvelinus fontinalis*) in Adirondack, NY lakes and observed that Al was the primary factor controlling survival. The toxicity of Al varies with the life history stage of fish. In acidic solutions (pH 4.2-4.8) the presence of Al improves egg survival, while reducing survival and growth of white sucker (*Catostamus commersoni*) and brook trout sac fry and fry (Baker and Schofield, 1982).

The extent of toxicity appears to be dependent on the concentration as well as the speciation of aqueous Al. Driscoll *et al.* (1980) and Baker and Schofield (1982) reported that toxicity to fry was greatly reduced when Al was complexed with organic solutes. Moreover, the survival of brook trout and white sucker fry in acidic Adirondack waters were correlated with inorganic monomeric Al concentrations and pH (Driscoll *et al.*, 1980). Henriksen *et al.* (1984) reported that episodic changes in pH and inorganic monomeric Al during high flow, snowmelt conditions were responsible for a fish kill of Atlantic salmon (*Salmo salar*) in southern Norway. Aluminum toxicity also appears to be acute in acidic solutions that are oversaturated with respect to $Al(OH)_3$ solubility (Baker and Schofield, 1982). Moreover, the toxic response of Al is mitigated with increasing Ca^{2+} concentrations (Brown, 1983).

The mechanism of Al toxicity to fish has been attributed to the inability of fish to maintain their osmoregulatory balance and respiratory problems associated with coagulation of mucus on the gills. Muniz

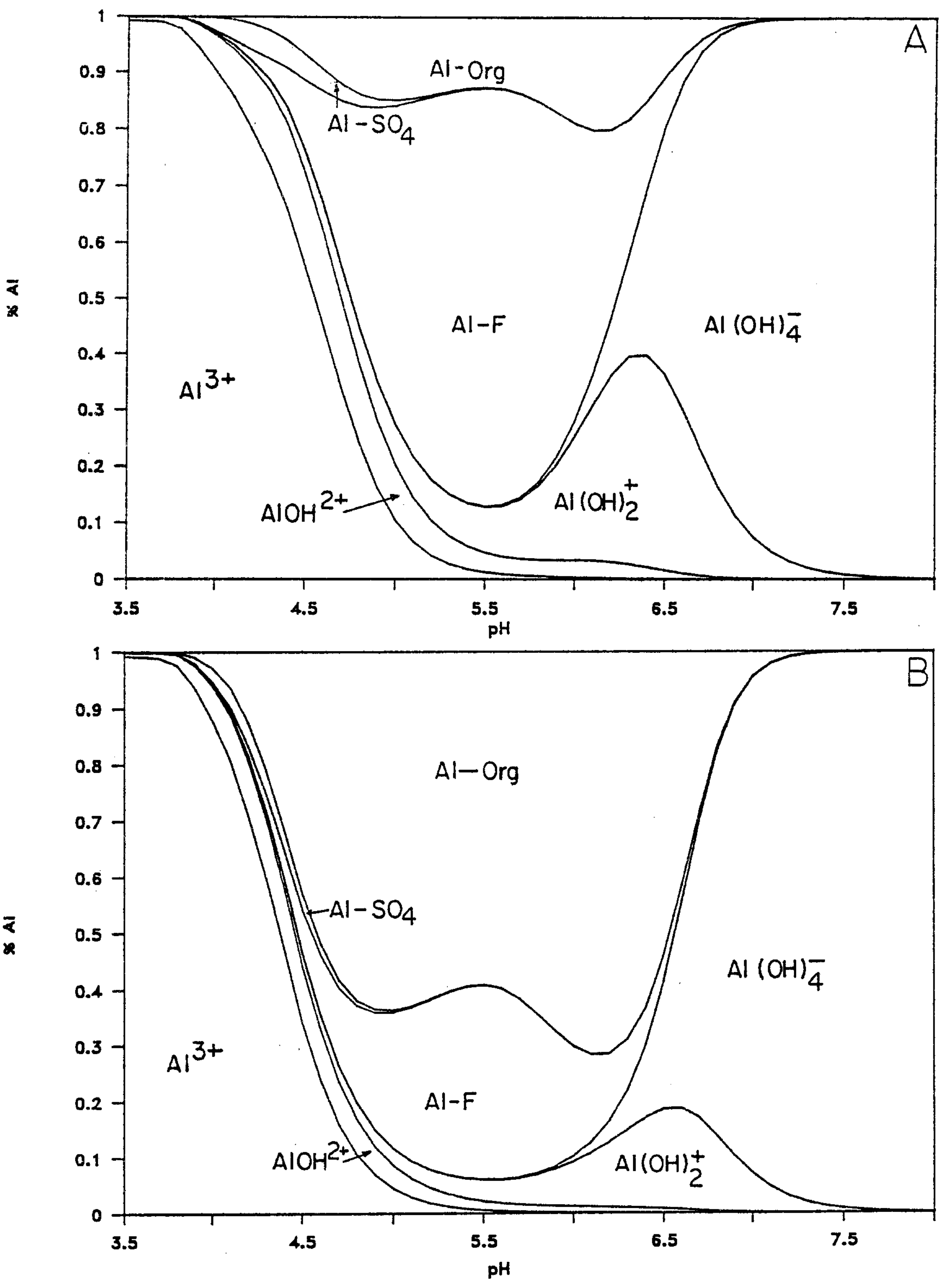

Figure 14 *Distribution of aqueous Al as a function of pH at two concentrations of dissolved organic carbon. The low concentration, 100 µmol C/L (a), is indicative of clear waters, while the higher concentration, 1000 µmol C/L (b), is used to represent colored waters. Calculations were made in equilibrium with* $Al(OH)_3$ *and with 5 µmol/L F and 100 µmol/L* SO_4^{2-}*, which are typical of acid sensitive waters in the Adirondack region of New York (after Driscoll and Schecher, 1988).*

and Leivestad (1980) reported the loss of Na^+ and Cl^- from the blood of brown trout (*Salmo trutta*) in solutions containing 7 µmol/L Al at a pH of 5.0. Schofield and Trojnar (1980) observed gill damage to brook trout at Al concentrations of 18-30 µmol/L in acidic solutions.

There have been a few studies of Al toxicity to aquatic organisms other than fish. Hall *et al.* (1985) reported that increased rates of invertebrate drift followed Al addition to a New Hampshire stream. The drift rate of immature aquatic insects generally increased with increasing concentrations of added inorganic Al, suggesting a stress avoidance response that was a function of Al concentration. Helliwell *et al.* (1983) evaluated the effects of Al on the algae *Chlorella pyrenoidosa* and found that maximum toxicity occurred at pH 5.8-6.2 where as little as 0.18 µmol/L inorganic Al inhibited growth. They implicated $Al(OH)_2{}^+$ as the toxic species of Al.

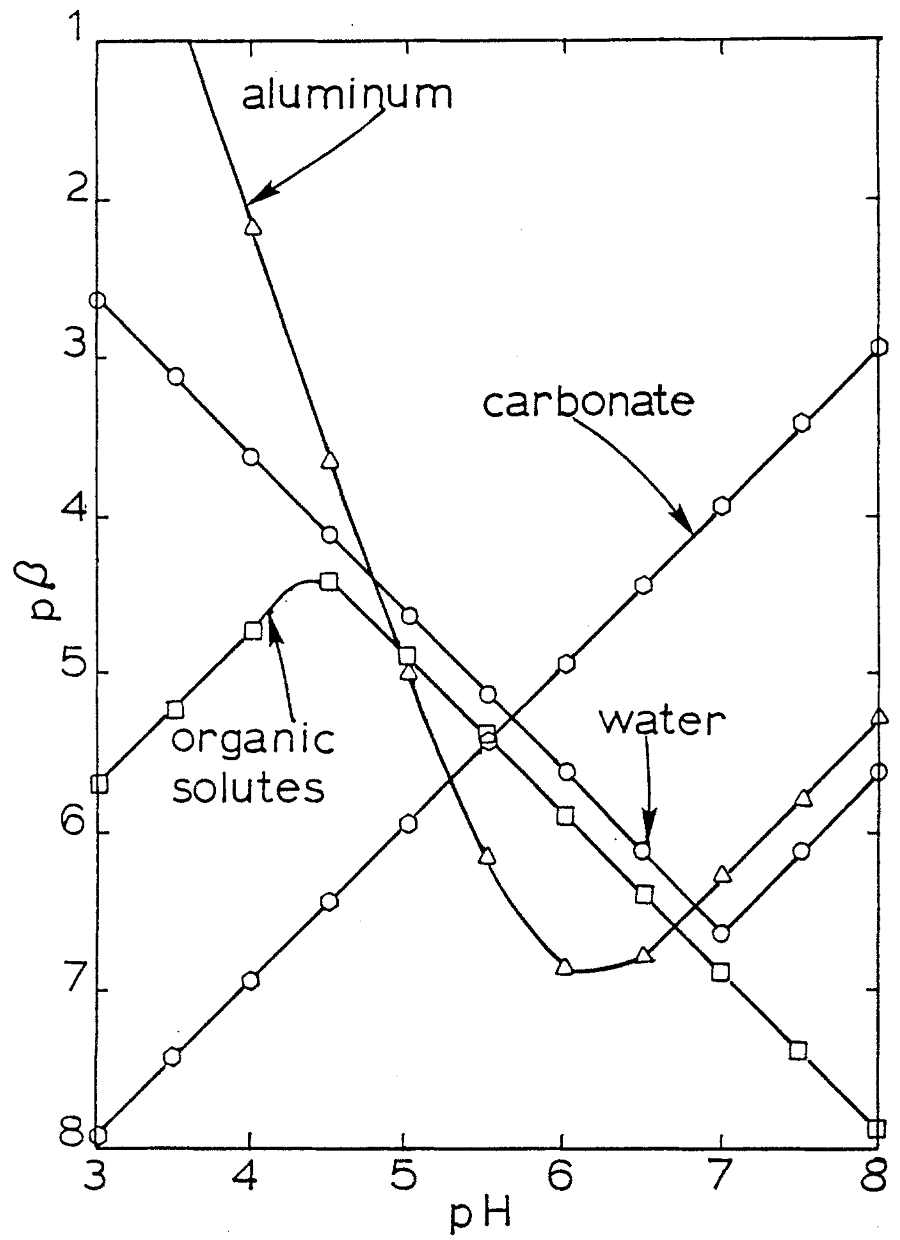

Figure 15 *Buffer intensity diagram for Adirondack surface water system. Equilibrium with* $Al(OH)_3$ *(*p^*K_{so} *= 8.49), organic solutes (*C_T *2 x* 10^{-5} *mol/L;* pK_a *= 4.4) and atmospheric* CO_2 *(*PCO_2 *=* $10^{-3.5}$ *atm) was assumed (after Driscoll and Bisogni, 1984).*

It is well established that soil Al is toxic to many plants and may greatly impair growth and development (Foy, 1974). While many investigations have demonstrated Al toxicity to plants, the work of Pavan *et al.* (1982) is of particular interest because they establish a clear linkage between aquo Al (Al^{3+}) activity and toxicity to coffee (*Coffea arabica*). More recently in carefully controlled experiments Parker *et al.* (1987) demonstrated toxicity of Al^{3+} to wheat (*Triticum aestivum*); while Al associated with complexing ligands (OH^-, F^-, SO_4^{2-}, organic) was not toxic. Interestingly, these investigators also noted that polymeric Al species resulted in a marked reduction in root growth and appeared to be highly toxic. The exact mechanism of Al toxicity to plants is not established. However, the interference of Al with Ca^{2+} metabolism has led investigators to suggest that Al binding alters the function of the Ca^{2+} regulatory protein, calmodulin (Haug, 1984).

Finally, elevated intake of Al has been implicated in a number of human neurological (Alzheimer's disease, dialysis encephalopathy, amyotrophic lateral sclerosis) and osteological (asteoporosis, osteomalacia) dysfunctions. As with other organisms, the exact mechanism of Al toxicity has not been established. Aluminum has been found to bind with phosphate groups associated with DNA (Dryssen *et al.*, 1987) and other organo-phosphate compounds (Karsch *et al.*, 1987). As suggested for plants, Al may also cause alter Ca^{2+} homeostasis due to high binding affinity with the protein calmodulin (Haug, 1984).

Humans are exposed to Al through a wide range of sources, including water, foods, antacids as well as inhalation of dust and fumes. Estimates of the average rates of Al ingestion range over 370-550 µmol/day (Alfrey, 1987). Unfortunately, our understanding of the bioavailability of various forms of Al for human intake is limited. Recently, Slanina and coworkers (Slanina *et al.*, 1984; 1985; 1986) have shown that uptake of Al is greatly enhanced in the presence of citrate. These observations have led to suggestions that low molecular weight, neutral complexes of Al may be absorbed within the gastrointestinal system ultimately leading to toxic effects (Martin, 1986). In view of these findings, better information is needed on concentrations of Al- Org in natural solutions and their bioavailability.

Conclusions

Aluminum may be mobilized in acidic soils by weak or strong acid leaching. Leaching by strong acids results in the transport of ecologically significant concentrations of inorganic Al to waters, while inputs of organic acids may result in high concentrations of alumino-organic solutes. Within soil and aquatic environments Al exhibits a variety of forms which vary greatly in chemical and biological reactivity. The speciation of Al in natural solutions depends on many factors, including solution contact with particulate phases, pH, concentrations of complexing ligands (F^-, SO_4^{2-}, organic solutes), temperature and ionic strength. Elevated concentrations of Al in natural waters may have a wide range of chemical, physical and biological consequences, including: 1) regulating the pH buffering of acidic waters; 2) interactions with critical element cycles (P, organic carbon, trace metals); and 3) toxicity to organisms. An understanding of the speciation of aqueous Al is critical to assessments of the environmental effects of elevated concentrations of Al.

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Appendix 1 *Aqueous thermochemical data.*

Reaction	*log K*[a]	*Reference*	*H_r*[b]	*Reference*
$Al^{3+} + H_2O = Al(OH)^{2+} = H^+$	; -4.99	Ball *et al.*, 1986	11,900	**Ball *et al.*, 1986**
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	;-10.10	Ball *et al.*, 1986		**Ball *et al.*, 1986**
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	;-23.0	Ball *et al.*, 1986	44,060	**Smith and Martell, 1974**
$Al^{3+} + F^- = AlF^{2+}$	; 7.02	Hem, 1968	1,100	**Smith and Martell, 1974**
$Al^{3+} + 2F^- = AlF_2^+$	; 12.76	Hem, 1968	2,000	**Smith and Martell, 1974**
$Al^{3+} + 3F^- = AlF_3$	; 17.03	Hem, 1968	2,500	**Smith and Martell, 1974**
$Al^{3+} + 4F^- = AlF_4^-$	; 19.73	Hem, 1968	2,200	**Smith and Martell, 1974**
$Al^{3+} + 5F^- = AlF_5^{2-}$	; 20.92	Ball *et al.*, 1980	1,800	**Ball *et al.*, 1980**
$Al^{3+} + SO_4^{2-} = AlSO_4^{2-}$	; 3.020	Ball *et al.*, 1980	2,150	**Ball *et al.*, 1980**
$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^-$	; 4.92	Ball *et al.*, 1980	2,840	**Ball *et al.*, 1980**
$H_2CO_3^* = H^+ + HCO_3^-$	; -6.35	Ball *et al.*, 1980	2,247	**Ball *et al.*, 1980**
$HCO_3^- = H^+ + CO_3^{2-}$	; -10.33	Ball *et al.*, 1980	-3,617	**Ball *et al.*, 1980**
$CO_2\ (g) = CO_2(aq)$	; -1.452	Ball *et al.*, 1980	-5,000	**Ball *et al.*, 1980**
$H^+ + F^- = HF$	; 3.169	Schecher, 1988	3,460	
$H_3Org = H^+ + H_2Org^-$	; -1.76	Schecher, 1988		
$H_2Org^- = H^+ + H\ Org^{2-}$	; -5.90	Schecher, 1988		
$HOrg^{2-} = H^+ + Org^{3-}$	; -6.83	Schecher, 1988		
$Al^{3+} + Org^{3-} = AlOrg$	; 8.39	Schecher, 1988		
$Al^{3+} + H^+ + Org^{3-} = AlHOrg^+$	; 13.09	Schecher, 1988		
Solubility:				
$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	;			
Natural Gibbsite	8.77	May *et al.*, 1979		
Microcrystalline Gibbsite	9.35	Hem, 1968	-22,800	**Hem, 1968**

[a] At 25°C

[b] In cal^{-}/mol

Org is naturally occurring organic anion; ALCHEMI uses 0.43 mol Org$^-$/mol DOC.

Appendix 2 *Symbols used in manuscript.*

Parameter	*Symbol*
Aluminum hydroxide complexes	$Al\text{-}OH = [Al(OH)^{2+}] = [Al(OH)_2{}^+] + [Al(OH)_4^-]$
Aluminum fluoride complexes	$Al\text{-}F\ = [AlF^{2+}] + [AlF_2^+] + [AlF_3] + [AlF_4^-] + [AlF_5^{2-}] + [AlF_6^{3-}]$
Aluminum sulfate complexes	$Al\text{-}SO_4^{2-} = [AlSO_4^+] + [Al(SO_4)_2^-]$
Aluminum equivalence	$nAl^{n+} = 3[Al^{3+}] + 2[(Al\text{-}OH)^{2+}] + [Al(OH)^+] + 2[AlF^{2+}] + [AlF_2^+]$ $+ [AlSO_4^+]\ [Al(OH)_4^-] - [AlF_4^-] - 2[AlF_5^{2-}] - 3[AlF_6^{3-}] - [Al(SO_4)_2^-]$
Aluminum organic complexes	$Al\text{-}Org = [AlOrg] + [AlHOrg^+]$
Organic anions	$nOrg^{n-} = [H_2Org^-] + 2[HOrg^{2-}] + 3[Org^{3-}]$
Sum of basic cations	$C_B = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+]$