Aluminum geochemistry in peatland waters

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Abstract. The chemical speciation of aluminum was examined in surface water samples from *Sphagnum* peatlands in north-central Minnesota, from peatlands along the Canadian east coast, and from bogs in the Pennine Mountain area of England. In highly organic ($[DOC] \approx 50\,mg\,L^{-1}$), low pH waters, 80–90% of total dissolved Al was complexed with organic matter (OM), while in waters with low DOC ($[DOC] \approx 5\,mg\,L^{-1}$) 54–86% of total dissolved Al existed as Al^{+3} or other inorganic Al species. Batch titrations of OM with Al revealed a high Al binding capacity, $1.4–2.8\,\mu mol\,(mg\,DOC)^{-1}$, that generally was unsaturated with Al. Titrations of OM with Al in conjunction with a continuous distribution model were used to determine Al-OM conditional stability constants. Binding capacity ($\mu mol\,Al$ $(mg\,DOC)^{-1}$) and strength (formation constant) increased from pH 3 to 5 but decreased above pH 5 due to formation of Al-hydroxy species including $Al(OH)_3(s)$. The high binding capacity of OM in bog waters facilitates metal mobility, especially in low pH (< 5) wetlands where metal solubility is high and OM concentrations are highest. Results showed that the relative degree of organic matter saturation with metal ions was important in modeling Al speciation in bog waters.

Introduction

Peatlands are widely distributed across the northern U.S., Canada, and the Gulf and Atlantic coastal areas of the U.S. (e.g., Kivinen & Pakarinen 1981). Throughout these regions, many streams and lakes are strongly impacted by drainage from peatlands. Bogs (i.e., peatlands that receive no ground water or runoff from mineral soils) typically have acidic, nutrient-poor, highly organic soils. Bog waters and streams receiving bog drainage exhibit low pH (3–5), high concentrations of dissolved organic carbon ($[DOC] = 5$–$55\,mg\,L^{-1}$), and frequently high concentrations of Al (3–74 $\mu mol\,L^{-1}$; Verry 1975; Schurr 1983; Urban et al. 1987a; Clair & Freedman 1986). Understanding the controls on Al in peatland waters is important for evaluating the effects of acidic precipitation on peatlands and surface waters (Gorham et al., 1984), the utility of peatlands for removal of metals derived from industrial and mining effluents or highways (Eger et al. 1981; Coker &

DiLabio 1979; Wieder et al. 1988), the effects of natural organic ligands on metal ion reactivity and dissolution (e.g., Waite et al. 1988), and the autecology of bog plant species (e.g., Sparling 1967).

Aluminum biogeochemistry has received increased attention in recent years because Al mobilized in acidic environments may contribute to declines in fish populations and forest vegetation (Ulrich et al. 1980; Baker & Schofield 1982; Muniz & Leivestad 1980; Dickson 1980). Increases in H^+ and Al concentrations in acid-sensitive lakes and streams often are associated with periods of high flow and shifts in hydrologic flow paths to upper, organic soil horizons where Al-organic matter complexes (Al-OM) are important (Lawrence et al. 1986; Hendershot et al. 1986; Hooper & Shoemaker 1985; Schofield et al. 1985; Edwards et al. 1986; Driscoll et al. 1985). In peatlands, water flows continuously through similar organic horizons, and the low pH and high DCC concentrations in peatland waters enhance the mobility of Al. Sparling (1967) hypothesized that toxic Al concentrations limit the occurrence of *Schoenus nigricans* in British peatlands.

Prediction of Al transport in bogs requires an understanding of equilibrium and kinetic constraints on the competition between inorganic and organic ligands. Because Al forms strong complexes with both inorganic ligands such as hydroxide ($AlOH^{+2}$, $Al(OH)_2^+$, $Al(OH)_4^-$), fluoride (AlF^{+2}, AlF_2^+), sulfate ($AlSO_4^{+2}$), and natural organic ligands (Johnson et al. 1981; LaZerte 1984), its speciation determines its reactivity, transport and biological availability. Polymeric, colloidal or microcrystalline Al hydroxides also may be present in natural waters depending on environmental conditions (Hem & Roberson 1967; Driscoll 1984). Hydroxy Al complexes and Al^{+3} are the most toxic forms to fish (Driscoll et al. 1980), while both organic and inorganic Al complexes may be harmful to trees (Arp & Ouimet 1986; Hutchinson et al. 1986). Precipitation of Al-OM complexes limits mobility of both Al and organic matter in many forests (e.g., Ugolini et al. 1977; Driscoll et al. 1988). The heterogeneity of natural organic matter (OM) complicates modeling Al-OM interactions (Reuter & Perdue 1977; Sposito 1986; Turner et al. 1986; Tipping et al. 1988), and has hindered our understanding of these important reactions.

The objective of this research was to characterize Al geochemistry in peatland waters by
— examining Al speciation in peatland waters,
— demonstrating the effects of solution conditions (pH, [DOC], [Al]) on Al binding, and
— determining conditional stability constants of Al-OM complexes to assess their usefulness for equilibrium modeling.

Speciation of Al was examined in water samples from peatlands exhibiting a wide range of conditions (pH, DOC, Al concentrations). These variables also were experimentally varied in the laboratory, and the quantitative relationships obtained from these experiments were used to predict the speciation in the field samples.

Methodology

Sampling sites

Water samples were collected from seven peatlands: the S-2, S-3, and S-4 peatlands in northern Minnesota, the Gros Morne peatland in Newfoundland, the Fourchu peatland in Nova Scotia, and two sites (Holme Moss, Bleaklow Bog) in England. The sites cover large gradients in three important environmental parameters; viz., pH, DOC and concentration of dissolved Al. Surface water samples were collected on only one occasion at all sites except the S-2 site where extensive sampling was performed.

The Minnesota sites are all located within the Marcell Experimental Forest in northcentral Minnesota (47°32′N, 93°28′W). All three peatlands (S-2, S-3, S-4) occupy small (3–25 ha), kettle-hole depressions and comprise 24–30% of their respective catchments (Verry 1975). Each has a stream outlet and none has a stream inlet. The S-2 and S-4 sites are bogs; i.e., they receive no ground water inputs and runoff from the surrounding uplands does not penetrate far into the peatland but is funneled around the bogs in a lagg or moat. These two sites are similar vegetatively; both support stands of black spruce (*Picea mariana*), an understory of ericaceous shrubs, and ground layers of sedge and *Sphagnum* moss. The S-4 site is a floating-mat bog. Peat depths at the sites range from 4–8 m. Upland soils at both sites are deep, moderately well-drained, gray clay-loam tills supporting mature stands of quaking aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*; Verry & Timmons 1982). The S-3 site is a ground-water fen with much higher pH (6.8–7.7) than in the bogs (3.8–4.5). The site supports a dense stand of alder (*Alnus rugosa*) and a ground layer of *Sphagnum*. Because of continuous groundwater inputs, the water yield from this site is much higher and more constant than from the other two sites (Verry 1975). All three sites have been extensively studied and described previously by the U.S. Forest Service (e.g., Verry 1975, 84; Verry & Timmons 1982; Timmons et al. 1977), and the S-2 site was the focus of a 5-year NSF study (e.g., Urban & Eisenreich 1988; Urban et al. 1989a; Rapaport & Eisenreich 1988).

The Canadian maritime sites were among those surveyed in the NSF

study of North American peatlands (e.g., Gorham et al. 1985; Glaser & Janssens 1986; Urban et al. 1987a, b). The Gros Morne site is a fen complex (pH 5–6) located near Rocky Harbor, Newfoundland (49°49′N, 57°51′W). Samples also were taken from bog and poor-fen areas in a coastal Nova Scotian peatland (45°41′N, 60°15′W) near Fourchu. Vegetation at both sites is described in Santelmann (1988). In contrast to the Minnesota sites, the coastal sites are not forested, have high and stable water tables, and experience high annual precipitation (130 vs. 76 cm; Thomas 1953).

Water samples also were obtained from two bogs in the southern Pennine mountain region of England. As a result of atmospheric pollution in this industrial region, *Sphagnum* has all but disappeared from these peatlands (Tallis 1964; Lee et al. 1987), and microbial activity in peat is reduced (Press et al. 1985). Elevated concentrations of SO_4^-, NO_3^-, and Al in bog waters (Urban et al. 1987b; Gorham & Detenbeck 1986; Lee et al. 1987) and elevated concentrations of nitrogen and trace metals in peat from this area (Lee & Tallis 1973; Livett et al. 1979; Lee et al. 1987) attest to the persistence of regional atmospheric pollution. Twenty years ago, Sparling (1967) postulated that Al toxicity restricted the occurrence of *Schoenus nigricans* in bogs of this region. These facts together with the low DOC concentrations characteristic of these peatlands make a study of Al speciation particularly relevant. The two sites selected were Bleaklow Bog and Holme Moss, both near the border of Derbyshire.

Sample collection

Water samples (1-L) collected from the S-2 site from 1984–1986 included a surface water transect through the lagg to the bog center, samples from the bog outflow, and upland surface (5 cm) and subsurface (9–17 cm) runoff from plots south of the bog (Timmons et al. 1977). In addition, 20-L volumes of bog water were collected for titrations. In 1985 and 1986, surface water samples were collected from the other sites including 1 from the S-4 bog, 3 from the S-3 fen, 5 from coastal peatlands in Nova Scotia and Newfoundland (courtesy of M.V. Santelmann) and 3 samples from each of two English bogs.

Water samples collected at Marcell and English bogs were filtered under N_2 through 0.4 μm polycarbonate (Nuclepore) membrane filters and stored in cleaned linear polyethylene (LPE) bottles. The large-volume samples used for batch titrations were gravity filtered through 0.4 μm Millipore membrane filters. Samples collected in 1984 and 1985 were filtered at the field site and sub-sampled for water chemistry within 24 hours. Samples collected in 1986 from Marcell and the coastal peatlands were mailed refrigerated and

stored for up to six weeks at 4 °C or frozen for up to 12 months prior to analysis. Samples from the English bogs were mailed frozen and analyzed within one week of collection. Studies conducted to evaluate effects on Al speciation of sample storage indicated that organically bound Al was stable at low pH, but small changes ($< 10\%$) occurred at circum-neutral pH and 20 to 40% losses in organic Al were observed if DOC was low (< 5 mg/L; Helmer 1987; see also Rogeberg & Henriksen 1985; Campbell et al. 1986). Of data presented here, however, only one fen sample with high pH was stored for longer than one month. All other samples stored for periods longer than one month had high concentrations of DOC and most Al was organically complexed and stable over the period of storage. All samples were highly undersaturated with respect to Al-silicates at both 25 and 1 °C, and thus precipitation of such phases is not thought to have occurred as a result of freezing. The single exception was the water from Bleaklow bog in England which was close to saturation with respect to kaolinite at 25 °C. Some precipitation of Al in this sample would not alter our interpretation of its speciation.

Sample analysis

Major anions ($SO_4^=$, Cl^-, F^-) were measured on filtered samples by ion chromatography with a Dionex Model 10. Major cations (Ca^{+2}, Mg^{+2}, Na^+, K^+, Fe) were measured by flame atomic absorption spectrophotometry (AAS; Varian Model AA175). Organic carbon on filtered samples (DOC) was measured by infrared detection following persulfate-assisted UV oxidation (Dohrman TOC Analyzer).

The technique used to determine inorganic and organic Al in filtered bog waters was similar to that used by Campbell et al. (1983). The method does not separate "monomeric" Al as is commonly done (e.g., Driscoll 1984), but rather separates positively-charged inorganic Al from all other forms. Samples were mixed with Chelex 100 resin pre-treated with synthetic solutions containing Ca^{+2}, Mg^{+2} and H^+ concentrations equal to those in the bog water such that solution pH would not change while samples were in contact with the resin. In principle, inorganic cationic forms of Al were retained on the resin and Al-OM complexes remained in solution. Thus Al bound by OM (Al_0) was determined (in duplicate) following removal of hexaquo Al^{+3} and positively-charged inorganic Al complexes (e.g., $AlOH^{+2}$; AlF^{+2}) by chelation with the resin and subsequent acidification to 0.75% HNO_3. Inorganic Al (Al_I) was calculated as the difference between total dissolved Al (Al_T) and Al_0, and its speciation was determined by chemical equilibrium modeling. Total dissolved Al (Al_T) was determined on filtered subsamples

acidified to 0.75% with Ultrex HNO_3. Experiments showed that a 30-minute equilibration time was sufficient for positively charged, inorganic Al complexes to be taken up by the resin with minimal uptake or alteration of Al-OM complexes (Helmer 1987; also Campbell et al. 1983; Miller & Andelman 1987).

Aluminum was analyzed with pyrocatechol violet (PCV) as a chromophoric ligand (Dougan & Wilson 1974). In this study, 10 ml of sample acidified to 0.75% HNO_3 were put into 30 ml LPE bottles and 0.25 ml of hydroxylammonium chloride/1,10 phenanthroline solution (14%/0.14%) was added to reduce and complex Fe(III). Next, 0.5 ml of 0.052% PCV solution was added followed by 2.5 ml of 42% hexamethylene tetramine buffer solution to raise pH to 6.0 (the buffer solution contained 2.3% NH_4OH). Samples were mixed for 10 seconds after addition of each reagent. Color was allowed to develop for 18–20 minutes prior to measurement of absorbance at 585 nm with a Beckman Model 26 spectrophotometer. Over the concentration range of 5 to 300 μg/L, precision was 3.4%, and the detection limit was 0.4 μg/L.

Aquatic OM interferes with Al complexation by PCV at high [DOC] (Helmer 1987). Acid digestion at pH 1 does not adequately eliminate this interference. Therefore, a digestion step was added to oxidize OM in both the resin-treated and untreated fractions of all samples. A 3-hr digestion at 90 °C with 1.35% $(NH_4)_2S_2O_8$ was required to fully digest the OM (cf. Seip et al. 1984; Cronan 1985). Only after this extended digestion were concentrations of total dissolved Al equal whether measured by PCV or graphite AA. Prior to addition of the reagents described above, 0.25 ml of a 54% ammonium persulfate solution was added to each 30 ml bottle containing sample or standard, and bottles were placed in a 90 °C oven. Potassium hydroxide (20.6%) was added to the original buffer solution to neutralize H^+ ions produced during persulfate oxidation of organic matter. Precision for this technique was 5%, but the $(NH_4)_2S_2O_8$ and KOH used in the digestion step contributed a high, consistent blank of 45 μg/L. Consequently, graphite furnace atomic absorption (AA) was used to measure those samples with $[Al_T] \leqslant 60 \mu$g/L.

The chemical equilibrium program MINEQL (Westall et al. 1976) was used to calculate the speciation of Al_I at 25 °C (the temperature at which the resin extraction was performed) given values for pH and concentrations of total dissolved Al, F^-, and SO_4^{-2}. Equilibrium constants for metal complexes used in the calculations are listed in Table 1. Preliminary calculations with MINEQL indicated that polymeric forms were insignificant ($\ll 1\%$ Al_I) in all samples except surface runoff. Ion activity coefficients were estimated with the extended Debye-Huckel equation (Stumm & Morgan

Table 1. Equilibrium constants used for calculation of inorganic Al speciation.

Equation	Log K	Reference
Soluble hydroxide, fluoride and sulfate complexes:		
$Al^{+3} + H_2O \Rightarrow Al(OH)^{+2} + H^+$	-4.99	May et al. 1979
$Al^{+3} + 2H_2O \Rightarrow Al(OH)_2^+ + 2H^+$	-10.13	ibid.
$Al^{+3} + 3H_2O \Rightarrow Al(OH)_3^0 + 3H^+$	-16.0	ibid.
$Al^{+3} + 4H_2O \Rightarrow Al(OH)_4^- + 4H^+$	-22.16	ibid.
$Al^{+3} + F^- \Rightarrow AlF^{+2}$	7.01	Roberson & Hem 1969
$Al^{+3} + 2F^- \Rightarrow AlF_2^+$	12.75	ibid.
$Al^{+3} + 3F^- \Rightarrow AlF_3^0$	17.02	ibid.
$Al^{+3} + 4F^- \Rightarrow AlF_4^-$	19.72	ibid.
$Al^{+3} + 5F^- \Rightarrow AlF_5^{-2}$	20.91	ibid.
$Al^{+3} + 6F^- \Rightarrow AlF_6^{-3}$	20.86	ibid.
$Al^{+3} + SO_4^{-2} \Rightarrow Al(SO_4)^+$	3.2	Roberson & Hem 1969
$Al^{+3} + 2SO_4^{-2} \Rightarrow Al(SO_4)_2^-$	5.1	ibid.
Polynuclear species:		
$2Al^{+3} + 2OH^- \Rightarrow Al_2(OH)_2^{+4}$	20.3	Campbell et al. 1983
$3Al^{+3} + 4OH^- \Rightarrow Al_3(OH)_4^{+5}$	42.1	ibid.
$13Al^{+3} + 28OH^- \Rightarrow Al_{13}O_4(OH)_{24}^{+7}$ $+ 4H^+$	293.3	ibid.
$7Al^{+3} + 17H_2O \Rightarrow Al_7(OH)_{17}^{+4} + 17H^+$	-48.29	Kramer 1983
Aluminum trihydroxides:		
$Al^{+3} + 3H_2O \Rightarrow Al(OH)_3 + 3H^+$		
Synthetic Gibbsite	-8.11	May et al. 1979
Natural Gibbsite	-8.77	ibid.
Microcrystalline Gibbsite	-9.35	ibid.
Amorphous aluminum trihydroxide	-10.8	Stumm & Morgan 1981
Aluminosilicate minerals:		
$1/2Al_2Si_2O_5(OH)_4 + 3H^+ \Rightarrow Al^{+3} +$ $H_4SiO_4 + 1/2H_2O$		
Kaolinite	3.3	Stumm & Morgan 1981
Halloysite	5.64	Hem et al. 1973
$K^+ + 2H^+ + Al^{+3} + 3SiO_3^{-2} \Rightarrow$ $KAlSi_3O_8 + H_2O$		
Microcline	63.86	Holm et al. 1987
$K^+ + 3Al^{+3} + 3SiO_2(OH)_2^{2-} \Rightarrow$ $KAl_3Si_3O_{10}(OH)_2 + 4H^+$		
Muscovite	49.11	ibid.
$5Mg^{+2} + 2Al^{+3} + 6H_2O + 3SiO_2$ $(OH)_2^{-2} \Rightarrow Mg_5Al_2Si_3O_{10}(OH)_8 + 4H^+$		
Chlorite	-8.06	ibid.
$Mg^{2+} + 14Al^{+3} + 22SiO_2(OH)_2^{2-} \Rightarrow$ $MgAl_{14}Si_{22}O_{60}(OH)_{12} + 16H_2O$		
Mg-montmorillonite	439.2	ibid.
$Ca^{2+} + 14Al^{+3} + 22SiO_2(OH)_2^{2-} \Rightarrow$ $CaAl_{14}Si_{22}O_{60}(OH)_{12} + 16H_2O$		

Table 1. (Continued)

Equation	Log K	Reference
Ca-montmorillonite $(Al(OH)_3)_{(1-x)}(SiO_2)_x + (3 - 3x)H^+ \Rightarrow$ $(1 - x)Al^{+3} + xH_4SiO_4 + (3 - 3x)$ H_2O^a	440.65	ibid.
Amorphous ideal aluminosilicate	$-5.7 + 1.68pH$	Paces 1978
Reversible nonideal aluminosilicate	$-5.89 + 1.59pH$	ibid.
Aluminum sulfate minerals:		
Basic aluminum sulfate, $Al(OH)SO_4$	-17.23	Van Breeman 1978
Jurbanite, $Al(OH)SO_4 \cdot 5H_2O$	-17.8	Nordstrom 1982
Basaluminite, $Al_4(OH)_{10}SO_4 \cdot 2H_2O$	-117.7	Nordstrom 1982
Alunite, $KAl_3(SO_4)_2(OH)_6$	-85.4	Adams & Rawajfih 1977

[a] $x = 1.24 - 0.135pH$; Paces 1978

1981). Saturation indices (SI) were computed as $SI = \log(IAP)/K_s$ where IAP is the ion activity product, and K_s is the solubility constant for the mineral phase.

Fluoride concentrations were not measured for all samples. However, measured F^- concentrations were low and generally constant (0.05 to 0.1 mg/L). At the Al^{+3}/F^- ratios, pH, and [DOC] of these waters, Al-F complexes were essentially equal regardless of whether the minimum or maximum observed F^- concentration was used. To be conservative, a F^- concentration of 0.1 mg L^{-1} was used for all samples for which no measurement was available.

Binding of Al by OM was examined in batch titrations at constant ionic strength (0.005 M $NaNO_3$). Subsamples of filtered bog water were transferred to clean LPE bottles, and Al added from a standard solution (0.018 M; 1% HNO_3). The pH of each sample was readjusted to a target pH and solutions equilibrated for 24 hours (Pott et al. 1985; Campbell et al. 1986). Speciation of Al at each titration point was determined by the chelation method described above. Titrations were conducted at pH values between 3.0 and 5.5, and at DOC concentrations between 5 and 50 mg L^{-1}.

Mean conditional stability constants describing Al-OM interactions (K_{av}) were calculated for each titration with the Perdue-Lytle distribution model described in the computer code FITGAUSS (Perdue & Lytle 1983). The model assumes that in a heterogeneous mixture of natural organic ligands, relative ligand concentration is normally distributed with respect to the log of the conditional stability constant for each ith class of ligands (K_i). An iterative nonlinear regression is used to determine the mean stability

constant (K_{av}), the spread of the distribution about the mean (σ), and the total ligand concentration or binding capacity of the ligand mixture.

Equilibrium binding constants calculated from the titration data with FITGAUSS were used with MINEQL (Westall et al. 1976) to determine the adequacy with which Al speciation was predicted. Bog water samples from this study and data from Johnson et al. (1981) were selected that had pH values within 0.1 pH unit of the titrations discussed above. Aluminum speciation for these samples was calculated with MINEQL using concentrations of Al_T, total F^-, SO_4^{-2}, H^+ and organic ligand concentrations. When necessary, precipitation of solid phases was suppressed in MINEQL. Organic ligand concentration was calculated as the concentration of DOC times the binding capacity determined for a specific pH value. Conditional K'_{av} values (calculated for $I = 0$) were corrected for Al^{+3} activity using Equation (1):

$$^cK''_{av} = \tau_3 K'_{av} \tag{1}$$

where $^cK''_{av}$ is the conditional stability constant applicable at the ionic strength of natural samples and τ_3 is the Al^{+3} activity coefficient. Falls Brook data were modeled by allowing $Al(OH)_{3(s)}$ precipitation using the solubility products for both natural (N) and microcrystalline (MC) gibbsite (May et al. 1979; Hem and Roberson 1967) for comparison with the measured "acid reactive" fraction (Al_R).

Results and discussion

Aluminum and organic carbon concentrations in bog waters

The water samples showed a wide range in concentrations of organic carbon (OC), H^+, and Al (Table 2). High concentrations of DOC in the S-2 bog (44 to 65 mg L^{-1}) were coupled with high H^+ concentrations (pH 3.4–5.7). The S-3 fen exhibited low concentrations of both DOC (5.5–29 mg L^{-1}) and H^+ (pH 6.9–7.5). Waters from the maritime fens and bog had DOC (17 to 25 mg L^{-1}) and pH values (4.2–5.8) generally between the S-2 and S-3 sites. In contrast, the English bogs had low DOC concentrations (3.9–5.7 mg L^{-1}) but high H^+ concentrations (pH = 3.8–4.3). The upland runoff samples had intermediate DOC (15–28 mg L^{-1}) coupled with low H^+ concentrations (pH 6.3–6.9). This wide range of conditions provided an excellent opportunity to examine the geochemical controls on Al in waters high in OM.

Aluminum concentrations in surface waters of Marcell bog ranged from

Table 2. Ranges of pH, aluminum and organic carbon concentrations in peatland waters.

Location	pH	Al (μmol/L)	DOC (mg/L)	Reference
Marcell S-2, Mn – bog				
surface waters	3.7–5.7	13–20	44–65	this study
stream outflow	3.6	8.1–63	–	Verry 1975
	3.9–5.6	3.6–32	16–72	Urban 1987
pore water	3.1–4.4	13–44	40–80	Schurr 1983
Marcell S-3, Mn – fen				
surface waters	6.9–7.5	0.7–7.4	5.5–29	this study
stream outflow	6.5	5.9	–	Verry 1975
Minnesota bogs	5.6	57		Clausen, Brooks 1983
Minnesota fens	7.0	9.2		ibid.
Northeastern North America – bogs				
surface waters	3.8–4.4	0.5–18	4–49	Urban et al. 1987
Canadian maritime bogs & fens				
surface waters	4.2–5.8	1.6–15	18–25	this study
bogs	4.5–5.5	0–37	–	Sparling 1966
fens	5.2–5.7	0–3.7	–	ibid.
Ontario bog				
surface water	4.0	14		Shotyk 1986
pore water	7.0	4.8		ibid.
Hardwood Swamp, NJ				
surface waters	3.1–4.2	44		Turner et al. 1985
pore waters	3.1–4.2	50		ibid.
Cedar Swamp, NJ				
surface waters	4.5–4.8	2.4		ibid.
pore waters	4.5–4.8	3.2		ibid.
Virginia bogs		37–74	–	Robinson 1930
England & Ireland – bogs and fens				
surface waters	3.8–4.3	2.5–46	3.9–5.7	this study
surface waters	3.9–4.6	1–57	–	Sparling 1966
Swedish bog	7.0	26		Lovgren et al. 1987
Artificial fen	4.2	56–144		Wieder et al. 1988

14.8 to 20.4 μmol L^{-1} in 1984, and 13.0 to 18.1 μmol L^{-1} in 1985. The values are comparable to those observed previously in streamflow from Marcell S2 (Verry 1975; Urban et al. 1987a; Table 2). Seasonally, Al concentrations vary in response to evaporative concentration and rate of water flow through the bog. Porewater concentrations of Al in the Marcell S-2 bog vary from 13.3 to 44.4 μmol L^{-1} (Schurr 1983); the higher values occur in deeper peat where pH is higher and some proportion of the Al may be colloidal.

Aluminum concentrations in the circum-neutral waters of the S3 fen (0.7 to $7.4\,\mu\mathrm{mol\,L^{-1}}$) were lower than in the acidic waters from bog S2. Verry (1975) also reported lower concentrations for S3 ($5.9\,\mu\mathrm{mol\,L^{-1}}$). Carbonate alkalinity from groundwater flowing through the S3 fen neutralizes the organic acids, maintains a circum-neutral pH, and increased water flow dilutes the OM. Verry (1975) attributed lower Al concentrations in fen relative to bog waters to precipitation of excess Al as gibbsite, lower OM concentrations, and higher streamflow (i.e., greater dilution; Table 2). Turner et al. (1985) observed similar differences in Al concentrations and pH between a hardwood and cedar swamp in the New Jersey Pine Barrens. Pore and surface waters of the hardwood swamp had Al concentrations averaging 44.4 and $50.0\,\mu\mathrm{mol\,L^{-1}}$, respectively, and pH of 3.1 to 4.2. In the higher pH waters of the cedar swamp (≈ 4.6), surface and pore water Al values were lower (2.4 and $3.2\,\mu\mathrm{mol\,L^{-1}}$, respectively). Turner et al. hypothesized that H^+ competition with Al for soil exchange sites in the cedar swamp was less than in the hardwood swamp, permitting greater Al sorption and lower aqueous concentrations in the higher pH environment. Other investigators also have reported higher Al concentrations in bogs than in fens (Sparling 1966; Clausen & Brooks 1983; Shotyk 1986).

Aluminum concentrations in coastal bogs and poor fens of Canada's maritime provinces (1.5 to $15.6\,\mu\mathrm{mol\,L^{-1}}$) were generally lower than at Marcell S2. Lower [Al] was attributed to diminished supply of Al from atmospheric dust input away from the prairies of the mid-continent (Urban et al. 1987a).

Aluminum – organic matter interactions

The Al present in the bog waters was bound primarily to organic matter. The relationship of organic (Al_0) and inorganic (Al_i) Al concentrations to total dissolved Al concentrations in bogs and fen waters is shown in Fig. 1. (Throughout this paper, total dissolved Al (Al_T) refers to the sum of inorganic and organic Al measured in filtered ($0.4\,\mu\mathrm{m}$) water.) Over the entire range of pH (3.7–7.5) and DOC concentration (5.5–$65\,\mathrm{mg\,L^{-1}}$) a nearly constant fraction ($88 \pm 0.06\%$) of the total dissolved Al was measured as organically bound Al in North American peatland waters including samples from the S-2 site, the S-4 bog, S-3 fen, and the coastal peatlands. Because the analytical scheme employed does not distinguish organic Al from inorganic colloidal Al, in the high-pH samples from fens and upland runoff in which such species might have existed, the fraction of Al that was organically bound may have been overestimated. The high, constant fraction of Al bound by OM suggests that OM was present in excess relative to Al at least
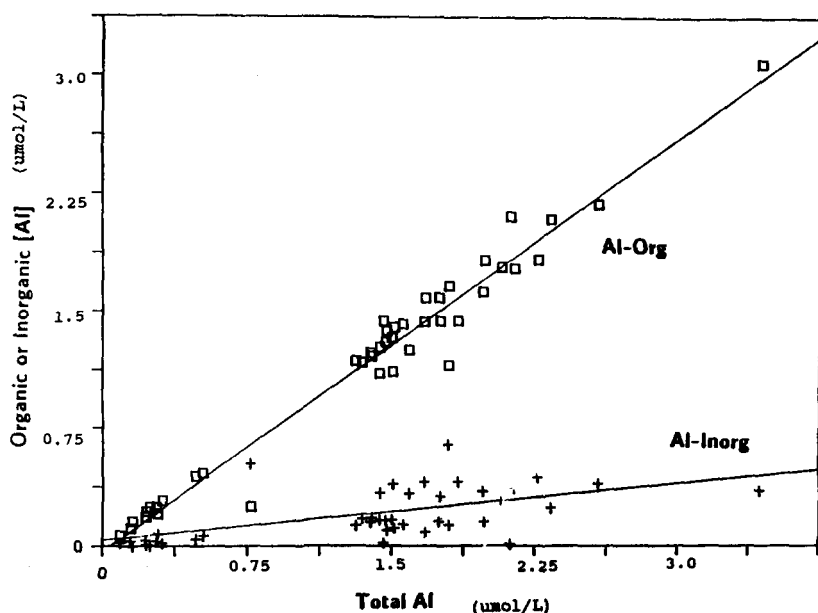
Marcell Bog, Upland, Fen and Coastal

Fig. 1. In all North American samples analyzed, organic Al was the dominant fraction accounting for $\approx 88\%$ of total dissolved Al as indicated by the regression lines shown $(Al_0 = 0.88 \pm 0.06 \, Al_T - 0.3; \, r^2 = 0.97, \, n = 43, \, p < 0.01; \, \square - Al_0, \, + - Al_1)$.

in all low-pH samples, and indicates that rates of Al supply to bogs may limit Al concentrations in bog waters (Urban et al. 1987a).

The binding of Al by OM caused interference in Al measurements with pyrocatechol violet (PCV). Total-dissolved and organic Al fractions of a subset of samples were used to compare measurements of Al by graphite furnace AAS and the PCV procedure without persulfate digestion. The furnace AAS technique gives an accurate measure of total dissolved Al present due to thermal degradation of the residual OM. At the high [DOC] of test samples, $54 \pm 3.4 \, mg \, L^{-1}$, Al concentrations determined with PCV following only acid digestion averaged 48% of those measured by furnace AAS. It is unlikely that any amorphous or crystalline Al-oxides were present in these test samples after acid digestion at pH 1 (Driscoll 1984). Thus interference observed using PCV was attributed to competition with the OM present.

To determine the DOC concentration at which interference became significant, all Marcell bog samples collected in 1986 and six dilutions of one sample were acidified to pH 1 and analyzed for Al_T and Al_0 using the PCV technique with and without digestion. The Al_T concentrations in 1986
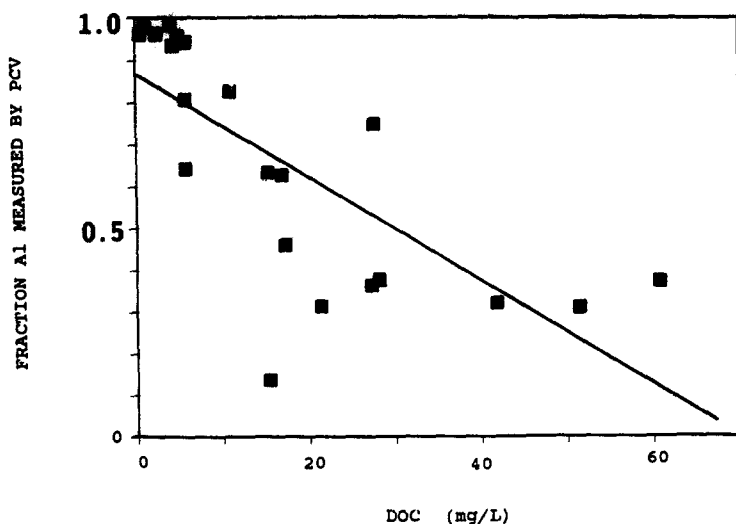
Fig. 2. Comparison of Al measurements by graphite furnace atomic absorption spectrophotometry and pyrocatechol violet with acid digestion but without digestion of OM with persulfate indicate that PCV seriously underestimates total dissolved Al. The regression line (Fraction Al measured $= 1.04 - 0.023 \cdot DOC$; $n = 22$; $r^2 = 0.55$, $p < 0.05$) indicates that at DOC $> 6 \, mg \, L^{-1}$ the error will exceed 10%.

samples averaged $15.9 \, \mu mol \, L^{-1}$. Al was added to the serially-diluted sample to maintain a concentration of $11.1 \, \mu mol \, L^{-1}$. The data indicate that DOC concentrations in excess of a few $mg \, L^{-1}$ interfere with the determination of Al (Fig. 2). Only at DOC concentrations less than $2 \, mg \, L^{-1}$ was no interference observed. At DOC concentrations greater than $10 \, mg \, L^{-1}$ Al concentrations were underestimated by more than 10%.

There are two implications of this interference. First, "monomeric" Al measured with PCV (without acid or persulfate digestion) will include an unknown and variable fraction of the organically bound Al. The fraction of organically bound Al measured as "monomeric" will vary as a function of DOC. Clearly, to model interactions between Al and OM, the total quantity of organically bound Al must be measured (cf. Tipping et al. 1988). Second, use of PCV as a chelating agent for the determination of total dissolved Al requires thorough sample digestion prior to analysis to minimize interference by natural OM. Whereas complete digestions of organic matter have not been conducted in most previous studies, concentrations of Al_0 may have been underestimated in cases when DOC exceeded $2 \, mg \, L^{-1}$ (cf. Cronan 1985; Seip et al. 1984; Driscoll et al. 1985). The "acid-reactive" fraction measured in low-pH waters that are undersaturated with respect to gibbsite may be composed largely of organic Al complexes when DOC exceeds

$10 \, mg \, L^{-1}$ (Johnson et al. 1981; Miller & Andelman 1987). Current methods fail to distinguish organic Al complexes from polymeric, microcrystalline and colloidal alumino-hydroxy species (Lalande & Hendershot 1985; Miller & Andelman 1987).

Effects of pH on Al geochemistry

Numerous studies have shown that concentrations of Al at pH $>$ 5–5.5 are regulated primarily by the pH-dependent solubility of Al-trihydroxide phases (Stumm & Morgan 1981; Campbell et al. 1983, 84, 86; Driscoll et al. 1984; David & Driscoll 1984; Lawrence et al. 1986; Hooper & Shoemaker 1985; Johnson et al. 1981; Nordstrom & Ball 1986; Seip et al. 1984; Schafran & Driscoll 1988). This generalization appears to hold for peatland waters as well. In fen samples with pH $>$ 5.5, concentrations of Al^{+3} are close to saturation with one of the Al-trihydroxide phases (Fig. 3).

Below pH 5, natural waters typically are undersaturated with respect to gibbsite (e.g., Nordstrom & Ball 1986; Hooper & Shoemaker 1985; Schafran & Driscoll 1988; Cronan et al. 1986). This undersaturation may result from precipitation of Al sulfate minerals (jurbanite, basaluminite, alunite; e.g., van Breemen 1973; Nordstrom 1982; Karathanasis et al. 1988), short water residence times relative to the kinetics of dissolution and precipitation (Nordstrom & Ball 1986), precipitation of Al-humates (Urban et al. 1989b), or equilibrium with exchangeable Al in organic soils (Cronan et al. 1986). This phenomenon of undersaturation with respect to gibbsite at pH $<$ 5 is observed in the peatland waters of this study as well (Fig. 3). Organically bound Al is the major form of Al in peat (Wieder et al. 1986), and it seems likely that aqueous concentrations of Al are controlled by partitioning between the solid-phase organically-bound Al and solution (Cronan et al. 1986; Clair & Freedman 1986; Turner et al. 1985; Dawson et al. 1978; Ugolini et al. 1977). The model of Cronan et al. (1986) assumes that aqueous Al^{+3} concentrations are in equilibrium with Al on organic ion exchange sites. While quantitative data are lacking to explicitly test the model of Cronan et al., a simplistic evaluation shows discrepancies between our data and the model predictions. The model of Cronan predicts a dependence of Al^{+3} concentration on pH, but no such relation is observed for the bog data (Fig. 3). Also the concentrations of Al^{+3} predicted by this model in the pH range 3.8–4.5 are much higher (pAl = 5.4–3.2) than any observed in the North American peatlands (pAl = 5.6–10). When values of Al^{+3} and pH from this study are used in this empirical model to predict the bound Al fraction, negative values are obtained. Without refinement, this model does not explain our peatland data. In so far as Al concentrations in peat are
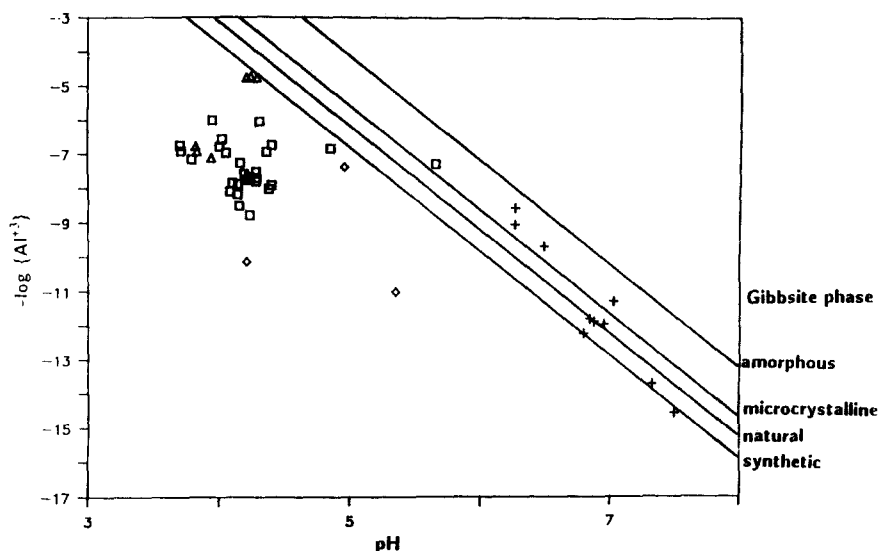
Fig. 3. Comparison of pH and Al concentrations of all samples with the theoretical solubility of gibbsite indicates that all samples with pH $\geqslant$ 5.5 are saturated with respect to gibbsite. In these samples the total dissolved Al in solution is limited by the solubility of gibbsite and the amount of DOC present. In samples with pH < 5.5, gibbsite phases are undersaturated, and the total dissolved Al concentration is limited only by the available supply of Al from atmospheric deposition and that organically bound in the peat. Although this diagram was constructed for the samples at 25 °C, the conclusions are valid at the field temperatures of the samples. At lower temperatures, sample points would be lower on this diagram relative to the gibbsite phase lines. Thus all samples at pH < 5.5 are even further undersaturated at lower temperature while samples at higher pH are less supersaturated. At 1 °C all but three samples (pH > 5.5) would be supersaturated with respect to synthetic gibbsite, and at 10 °C all but two would be supersaturated. ($\square$ – S-2; + – fen & upland; $\diamond$ – Coastal bogs & fens; $\triangle$ – English bogs).

controlled by rates of atmospheric deposition of Al (e.g., Gorham & Tilton 1978; Furr et al. 1979), rates of atmospheric supply indirectly control Al concentrations in peatland waters (Urban et al. 1987a).

The average distribution of organic and inorganic Al species in bog waters, upland surface and interflow water at Marcell S2, fen waters at Marcell S3, and in coastal bogs and poor fens in Nova Scotia and New-foundland was influenced by pH (Fig. 4). In all locations, Al_0 was the dominant aqueous form representing from 88% of Al_T in bog waters at pH 4.1 to 67% in fen waters at pH 7.1. In acidic bog waters below pH 5, Al_i was dominated by AlF_x^+ complexes ($[F^-] \approx 0.1$ mg/L). At circum-neutral pH, the dominant aqueous form of Al_i was anionic $Al(OH)_4^-$. Even though concentrations of F^- were similar in upland runoff and bog waters, OH^- outcompeted F^- for Al_i at the higher pH of the upland runoff. Other field
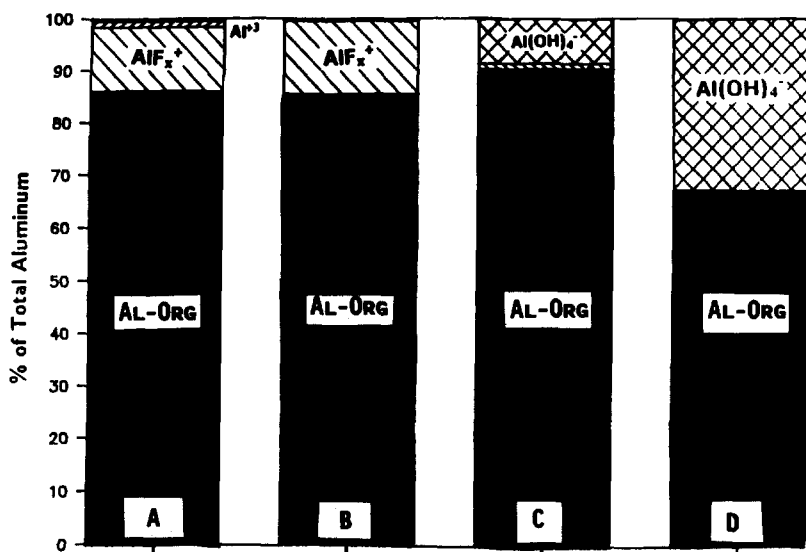
Fig. 4. A comparison of Al speciation in peatland waters of varying pH reveals that Al_o is the dominant species in all cases, but at high pH (> 5.5) OH^- outcompetes F^- for Al and the solubility of $Al(OH)_3$ in conjunction with the [DOC] limit the total dissolved Al concentration. (*A*) Marcell S-2, pH = 4.1, [DOC] = 25 mg L^{-1}, Al_T = 17.5 μM. (*B*) Coastal Bogs – pH = 4.6, [DOC] = 25 mg L^{-1}, Al_T = 7.1 μM. (*C*) Upland Runoff – pH = 6.5, [DOC] = 17 mg L^{-1}, Al_T = 11.4 μM (*D*) S-3 Fen – pH = 7.1, [DOC] = 11 mg L^{-1}, Al_T = 3.0 μM.

studies also have demonstrated the reduced influence of F^- at pH values above 5.5 (e.g., Schofield et al., 1985). Polymeric species were calculated to be important (50% Al_1) only in upland surface runoff samples.

The speciation of Al in bog waters is strongly dependent on DOC concentrations and Al supply as well as pH. Speciation of Al differs significantly in Marcell bog which has high DOC concentrations and abundant Al supply, and the English bogs that have low DOC concentrations and variable Al_T (Fig. 5). At high DOC concentrations, the dominant Al species is Al_o. However, at low DOC concentrations and low Al supply dominant Al forms are AlF_x^+ and Al_o (Holme Moss site). If Al supply is abundant and DOC concentrations are low, Al_o is a minor species and inorganic forms, especially Al^{+3}, dominate (Bleaklow site). In this case, the natural OM is saturated with Al (see next section) and is no longer the primary determinant of Al speciation. Concentrations of Al are sufficiently high at Bleaklow to bind all F^- as Al-F complexes. Increased supply of Al to the Holme Moss bog probably would result in Al speciation similar to that at Bleaklow bog, which implies that dilute peatland waters (low in pH and organic and inorganic complexing anions), may be highly sensitive to increases in supply
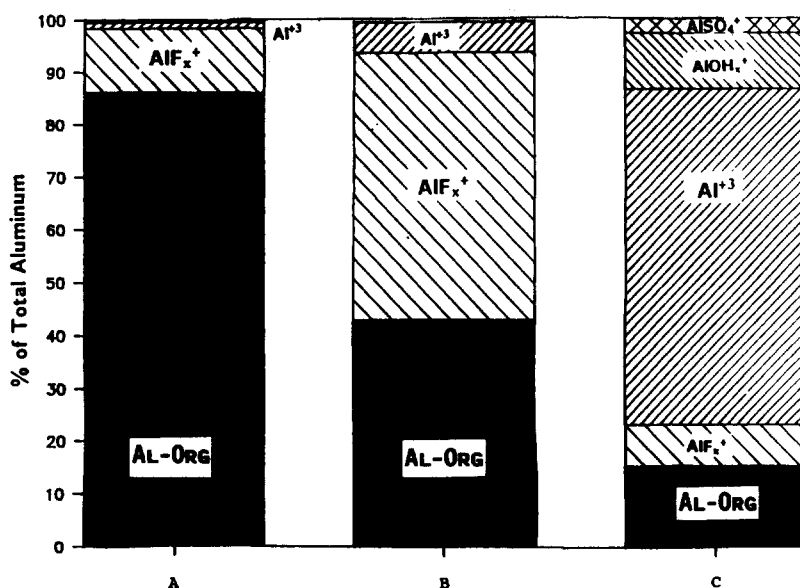
Fig. 5. Comparison of Al speciation in low-pH samples with varying DOC: (*A*) At high [DOC] even large concentrations of Al are organically bound (Marcell S-2: $Al_T = 17.5\,\mu M$, pH = 4.1, [DOC] = 52 mg L^{-1}). (*B*) At low [DOC] and low Al_T, F$^-$ and OM are important ligands (Holm Moss: $Al_T = 2.8\,\mu M$, pH = 3.8, [DOC] = 5.6 mg L^{-1}). (*C*) At low [DOC] and high Al supply the F$^-$ and OM become saturated with Al (Al:OC = 1.19) and free Al^{+3} is the dominant species (Bleaklow Bog: $Al_T = 42\,\mu M$, pH = 4.2, [DOC] = 4.5 mg L^{-1}).

of dissolved metals due to greater toxicity of free metal cations to organisms (cf. Press et al. 1985).

Al binding capacity of organic matter

As has been noted previously (e.g., Fish et al. 1986; Turner et al. 1986), procedural limitations often render it infeasible to conduct titrations of OM with Al up to or beyond the binding capacity. Only by extrapolating the titration curve with one of several models can the theoretical binding capacity by calculated. Four limitations were encountered in using batch titrations with the resin speciation method. Two are associated with solution chemistry of Al and Al-OM complexes; viz., precipitation of Al(OH)$_3$ at pH ≥ 5.5 and precipitation of Al-destabilized organic colloids at pH < 4.4. The other two limitations are associated with the resin. These include: inconstant solution pH due to H$^+$ displacement from the resin by Al (pH ≤ 4); and slow kinetics of Al uptake by the resin at pH 3. As a result of these limitations, the maximum Al$_0$:OC ratio observed in the titrations (Fig. 6), generally underestimates the total binding capacity.
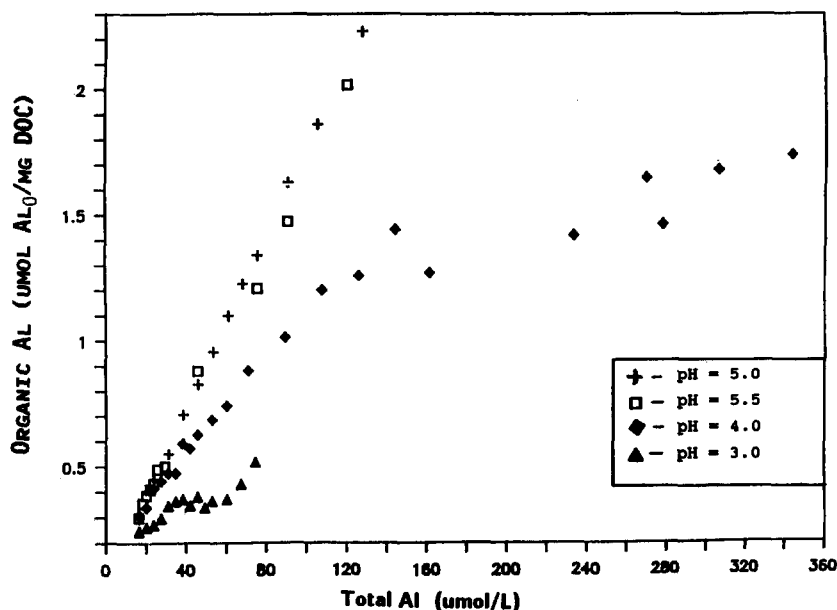
Fig. 6. Titrations of bog water ([DOC] = 51 mg L^{-1}) with Al reveal the operationally-defined binding capacities. At pH 5.5 this was limited by precipitation of Al(OH)$_3$, and at pH 4 and 3 by precipitation of Al-OM complexes.

The first two of these limitations occur in the field as well, however, and prevent OM from every being saturated with Al. Thus the maximum observed Al$_0$:OC ratios observed in the titrations are effective binding capacities under many field situations and indeed are similar to Al$_0$:OC ratios in field samples where OM is likely to be saturated with Al (Table 3). The Al$_0$:OC ratios in Marcell bog samples (avg = 0.28 μmol mg^{-1}), those in coastal samples (0.20 μmol mg^{-1}), samples from Holme Moss (0.21 μg mg^{-1}), and samples in upper (O) horizon soil solutions (0.15 to 0.83 μmol mg^{-1}; David & Driscoll 1984; Driscoll et al. 1985) are much lower than the binding capacities measured by titration and indicate undersaturation of organic binding capacity. In contrast, organic matter at Bleaklow bog was much more saturated with Al (Al$_0$:OC = 1.43 μmol mg^{-1}), as also indicated by the abundance of Al^{+3} and AlF complexes. Similarly high Al$_0$:OC ratios have been observed in terrestrial watersheds (Al$_0$:OC = 0.92 μmole mg^{-1}; Lawrence et al. 1986), Adirondack lakes (Al$_0$:OC = 1.70; Driscoll et al. 1984), and in soil solutions of illuvial soil horizons (Al$_0$:OC = 1.39–3.79; David & Driscoll 1984; Driscoll et al. 1985), where alumino-organic complexes precipitate (DeConnink 1980; McDowell & Wood 1984). The similarity in maximum Al$_0$:OC ratios for peatland and

other samples suggests that OM from bogs has a binding capacity for Al similar to that of OM from other sources.

Aluminum-organic matter conditional stability constants

The equilibrium constants, binding capacities and statistical parameters obtained from modeling the titration curves with the FITGAUSS model are listed in Table 4. Mean binding constants and binding capacities were calculated using the Gaussian distribution model in two ways:
— by fixing C_L, the binding capacity, as the highest point on a given titration curve (i.e., the maximum observed binding; Fish et al. 1986), and
— by allowing C_L, $\log K'_{av}$ and σ to vary.

Allowing all three parameters to vary resulted in a slightly better fit of titration data (lower residual sum of squares, RSS), an estimated total binding capacity greater than the maximum observed binding, and a lower $\log K'_{av}$ (Table 4). Titration curves predicted by the model frequently underestimated Al_0 at low Al_T concentrations. As noted previously, at low metal:ligand ratios, metal binding is stronger than predicted by the normal ligand distribution (Fish et al. 1986; Fig. 7). The actual distribution of Al binding strengths may be skewed in the direction of larger $\log K$ values associated with strongly-binding ligands and/or formation of complexes having 2 or more organic ligands per Al (Lovgren et al. 1987).

Organic binding of Al increases from pH 3 to 5, but decreases above pH 5 (Fig. 8). The constants shown for the pH 3.0 titration are those for which C_L was allowed to vary. The Al concentration that induced flocculation at pH 3 was greater than at pH 4, and lower organic Al concentrations at equivalent total-dissolved-Al and DOC concentrations (Fig. 6) indicate that organic binding of Al is less at pH 3.0 than at pH 4.0. Increasing competition with H^+ causes a decreased binding capacity (and concomitant decreased binding constant) as pH decreases below 5. Above pH 5, the decrease in binding capacity and binding constants reflects the limitation on organic binding of Al imposed by the solubility of $Al(OH)_3$.

Alumino-organic stability constants determined in this study lie within the range of values determined in other studies. The range of $\log K'_{av}$, 3.7 to 6.2, is smaller than the range determined by Young and Bache (1985) who performed potentiometric titrations at pH 4.0 using an intrinsic binding site model and determined a range of apparent stability constants of 2.0 to 14.5. Pott et al. (1985) determined conditional stability constants for binding of Al by Aldrich (TM) humic acid at a DOC concentration of $2\,mg\,L^{-1}$ using a one-component Scatchard model. The constants determined by Pott et al.

Table 3. Comparison of pH, DOC, Total dissolved Al, and Al$_0$:DOC ratios in various systems.

Location	pH	DOC mg/L	Total Al μmol/L	Al$_0$:DOC μmol/mg	Reference
Marcell S2, MN	4.1	52	17	0.28	This study
Upland Surface	6.9	22	3.4	0.14	
Upland Interflow	6.3	16	19	1.04	
Coastal N.E. Canada	4.6	22	5.1	0.20	
Holme Moss, England	3.9	5.6	2.8	0.21	
Bleaklow, England	4.2	4.5	42	1.43	
Can. Shield Lakes	4.5–7.7	4	4	0.42	Campbell et al. 1984
Nova Scotian streams	4.6–5.6	5.6–14	2.6–7	0.46–0.71	Clair & Freedman 1986
Fe + Al				0.67–1.3	ibid.
HBEF[5] streams					
WS5 and WS6	4–5	5	19	0.92	Lawrence et al. 1986
Falls Brook, Apr	4.7–5.4	2–3	4–21	1.68	Johnson et al. 1981
Falls Brook, May	4.8–5.3	3–4	8–21	0.46	ibid.
Falls Brook, Oct	5.3–6.3	3–4	4–6	0.80	ibid.
Satilla River, GA	3.8–6.8	25–72	1–30	0.65	Perdue et al. 1976
Al + Fe				0.94	Beck et al. 1974
Adirondack Lakes	3.9–7.6	2–12	6–36	1.70	Driscoll et al. 1984
Lake Inlets: (Winter pH and Al$_M$')					Schofield et al. 1985
Panther Lake	6.9	3.1	–	0.04	Cronan 1985
Woods Lake	4.6	4.2	17	0.79	
Sagamore Lake	5.1	5.8	4.7	0.25	
HBEF Soil Solns – Site III					
O Horizon	4.5	29	7	0.15	Driscoll et al. 1985
E	5.0	12	13	0.83	ibid.
B	5.2	6	10	1.56	ibid.

Adirondack Soil Solns. – Connifer Site				
Throughfall	4.4	9.6	4.1[1]	0.42	David & Driscoll 1984
O Horizon	4.0	52	27	0.47	ibid.
E	4.2	42	41	0.81	ibid.
B	4.6	6	30	3.79	ibid.
Al-Organic Titrations – Binding Capacities[2]				
UTR Creek, SC	3.0	3.4	60[3]	0.99	Pott et al. 1985
Sept	4.0	2.4	60	1.84	ibid.
Aug	4.0	1.1	10	2.86	ibid.
Marcell S2	3.0[3]	51	75	1.13	This study
	4.0	51	343	1.74[4]	
	4.0	5	76	1.49	
	4.4	28	136	1.51[4]	
	4.4	14	133	2.75[4]	
	5.0	51	120	2.02	

[1] Al_M, monomeric Al, measured colorimetrically without sample digestion, is given rather than total dissolved Al.
[2] Al_0:DOC ratios at highest point in titration (maximum observed binding).
[3] Total Al listed at pH 3.0 was the highest point in that titration; the binding capacity given was obtained from the normal distribution model.
[4] Al-OM flocculation occurred at and prior to this titration point.
[5] HBEF – Hubbard Brook Experimental Forest, New Hampshire.

Table 4. Equilibrium constants and binding capacities calculated from Aluminum-organic matter titrations.

pH	DOC (mg/L)	μ[1] (I = 0)	σ^2 (μmol Al/L)	C_L[3]	Al$_0$:DOC[4] (μmol/mg)	RSS[5] ($\times 10^6$)
(1) C_L not fixed						
3.0	51.4	3.69	2.82	57.9	1.13	2.1
4.0	51.4	3.68	1.76	186	3.62	29.1
5.0	51.4	5.00	2.24	176	3.42	44.2
5.5	51.4	3.62	1.80	980	19.1	13.4
4.4	27.5	4.51	1.50	53.3	1.94	23.7
4.4	13.8	4.22	0.00	87.5	6.34	3.9
4.0	5.0	5.33	1.29	6.8	1.36	1.2
(2) C_L fixed as maximum observed binding						
3.0	51.4	5.82	1.34	26.7	0.42	2.6
4.0	51.4	5.08	0.94	89.3	1.74	44.0
5.0	51.4	6.24	1.78	104	2.02	48.8
5.5	51.4	3.60	10.6	95.7	1.86	82.4
4.4	27.5	4.97	1.14	41.7	1.51	25.7
4.4	13.8	4.80	0.00	37.9	2.75	6.2
4.0	5.0	5.34	1.44	7.4	1.49	1.2

[1] $\mu = \log K'_{av}$ corrected $= \log (^cK'_{av}/\tau_{3,I=0.005})$
[2] σ = Standard deviation of $\log K$ for the ligand distribution.
[3] C_L = Total ligand concentration (binding capacity).
[4] Al$_0$:DOC $= C_L$/DOC = Binding capacity for Al per mg organic carbon.
[5] RSS = Residual sum of squares $= \Sigma(v_{av,calc} - v_{av,exp})^2/v_{av,exp}$

(1985) range from 6.9–7.1 (pH 3.0 to 5.0) and are larger than the mean log-K values of this study. Hargrove and Thomas (1982) determined binding constants based on sorption of Al to soil organic matter at pH 3.0 to 4.25. Except for the pH 3.0 titration, the range of constants, 2.0–3.9, were lower than those measured for bog water at 5–50 mg/L DOC. Lovgren et al. (1987) examined OM concentrated from bog water and successfully modeled Al binding with a finite-ligand model and binding constants in the range of 4.2–4.4. To adequately describe binding at low metal:ligand ratios a secondary complex (Al·L$_2^-$) was invoked as well as binding of Al(OH)$^{2+}$. Similarly, Tipping et al. (1988) modeled titrations of organic matter from lakes with a 2-ligand model for which the binding constants were both similar (3.4–3.8) and also found evidence of Al(OH)$^{2+}$ binding to OM. The range of binding constants reported in these studies reflects experimental conditions employed (e.g., [Al$_T$], [OM], source and form of OM), and methods of measurement and calculation. However, the fact that binding constants measured for OM from bog waters fall within the range reported for OM from widely varying sources indicates that OM in water draining peatlands does not differ greatly from OM from other surface waters and soils.
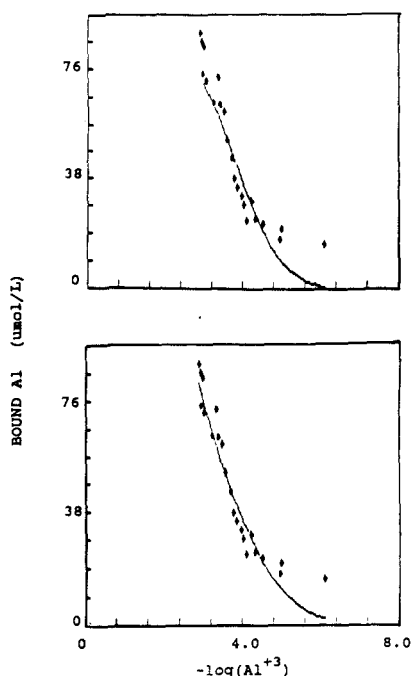
Fig. 7. Al-OM titration curves at pH 4.0 and 50 mg L^{-1} DOC: points represent experimental data; lines represent prediction by normal distribution model. In (*A*) C$_L$ was fixed at the maximum ratio observed in the titration. In (*B*) C$_L$ was allowed to vary to improve the model fit.

Prediction of organic and inorganic Al speciation in natural waters

Binding capacities and equilibrium constants determined with the FIT-GAUSS model and used with the equilibrium speciation model MINEQL did not adequately predict Al speciation across a wide range of pH and DOC concentration. Modeling results were accurate when Al$_0$:OC ratios were high, but underestimated organic Al when the organic matter was undersaturated with Al (Fig. 9). Predicted Al$_0$ was within 3% of that measured for the Bleaklow sample with an Al$_0$:OC ratio of 1.2 and within 4–6% for the Falls Brook samples with Al$_0$:OC ratios averaging 1.33 $\pm$ 0.65 μmol (mg)$^{-1}$. However, predictions underestimated organic Al by 7–27% for bog water samples with Al$_0$:OC ratios between 0.21 and 0.28. Underestimation of organic Al likely results from use of a mean equilibrium constant for Al-organic matter complexes rather than the range of binding strengths actually exhibited by natural organic matter. In waters with low Al$_0$:OC ratios, only the strongest ligands (i.e., ligands with the highest values of K$_i$L$_i$; Fish et al. 1986) would bind with Al. In such a case the effective
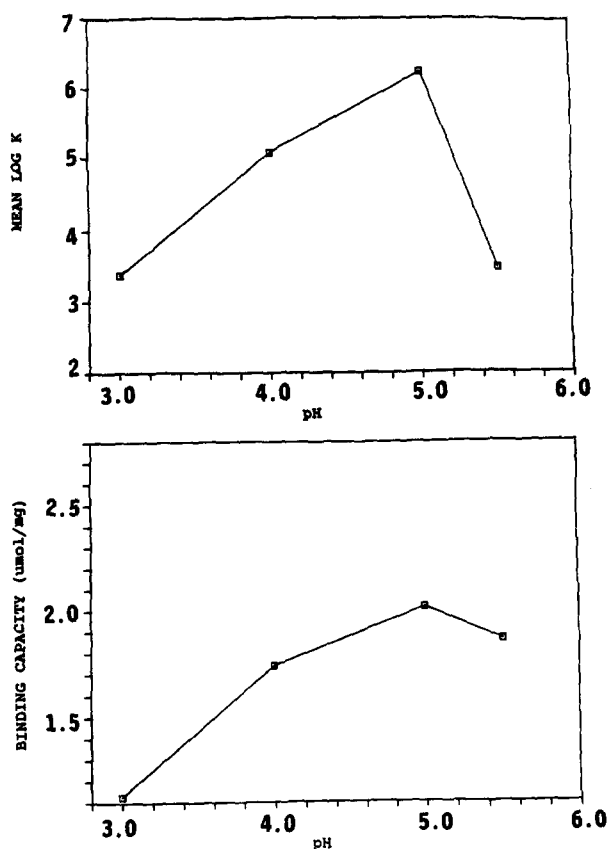
Fig. 8. Both binding capacity (*A*) and formation constant (*B*) show an increase from pH 3 to 5 and a subsequent decrease at pH > 5. The decrease in the operationally defined binding capacity above pH 5 results from precipitation of $Al(OH)_3$. Precipitation of organic colloids destabilized by bound Al may cause underestimation of binding capacities and constants at pH 3 & 4.

Al-organic equilibrium constant would be greater than the mean equilibrium constant measured in titrations, and modeling efforts would underestimate organic Al. The above error might be obviated by interfacing MINEQL with a gaussian distribution model (Perdue et al. 1984), but organically bound Al might still be underestimated if, as discussed above, the natural distribution is skewed.

Conclusions

In low-pH waters rich in organic matter draining from peatlands 80–90% of dissolved Al is complexed by OM. In fens, the total concentration of
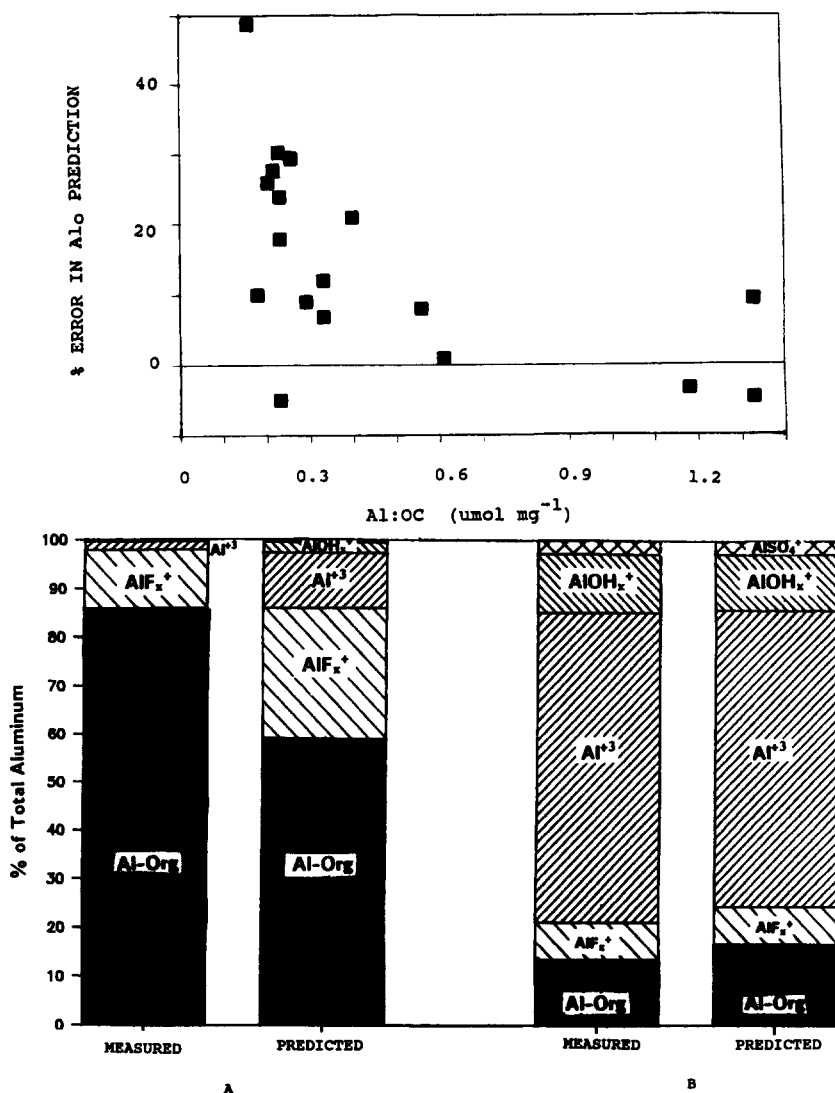
% ERROR IN Al₀ PREDICTION — $\%$ ERROR IN Al$_o$ PREDICTION

40

20

0

Al:OC (umol mg^{-1})

0   0.3   0.6   0.9   1.2

% of Total Aluminum

100
90
80
70
60
50
40
30
20
10
0

Al^{-3} AlF$_x^+$ AlOH$_x^+$ AlSO$_4^+$

AlF$_x^+$ Al^{+3} AlOH$_x^+$ Al^{+3} AlF$_x^+$ Al-Org

Al-Org   Al-Org   Al-Org   Al-Org

MEASURED   PREDICTED   MEASURED   PREDICTED

A   B

Fig. 9a. Prediction of Al speciation in natural water samples is accurate when the OM is nearly saturated with Al (i.e., high Al:OC ratios). At low Al:OC ratios, however, the predicted concentration of Al$_0$ greatly underestimates that measured (*A, B*) because only the strongest ligands (binding constants > Kav) are complexed with Al. Predictions were obtained by using the mean binding constant for a given pH from FIT-GAUSS in MINEQL.
Fig. 9b. Legend missing.

dissolved Al is regulated both by the solubility of gibbsite and the hydrologic conditions that determine concentrations of DOC. In all North American bogs examined, the large binding capacity of OM for Al (1.1–2.8 μmol mg^{-1}) was highly undersaturated as evidenced by a low ratio of

organic Al to OM. Therefore, Al concentrations likely were limited by availability of Al. Binding constants ($\log K = 3.7$–6.2) determined for Al-OM complexes were similar to those reported for OM from other sources. The strong binding of Al by OM causes interference with colorimetric measurement of Al with pyrocatechol violet when concentrations of DOC exceed $2\,mg\,L^{-1}$. Our titration results indicate the distribution may be skewed. Successful modeling of Al speciation in the presence of organic matter will require interfacing the appropriate distribution, or a finite number of constants, with chemical equilibrium programs such as MINEQL to account for the relative degree of organic matter saturation.

Acknowledgements

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