

# Influence of acidic atmospheric deposition on soil solution composition in the Daniel Boone National Forest, Kentucky, USA

C.D. Barton · A.D. Karathanasis · G. Chalfant

**Abstract** Acid atmospheric deposition may enter an environmental ecosystem in a variety of forms and pathways, but the most common components include sulfuric and nitric acids formed when rain water interacts with sulfur ( $\text{SO}_2$ ) and nitrogen ( $\text{NO}_x$ ) emissions. For many soils and watersheds sensitive to acid deposition, the predominant chronic effect appears to be a low pH, loss of base cations, and a shift in the mineral phase controlling the activity of  $\text{Al}^{3+}$  and/or  $\text{SO}_4^{2-}$  in solution. Soil solutions from lysimeters at various depths were taken at two sites in the Daniel Boone National Forest, Kentucky, USA, to evaluate potential impacts caused by acid deposition. The sites chosen were in close proximity to coal-burning power plants near Wolfe and McCreary counties and contained soils from the Rayne and Wernock series, respectively. Physicochemical characteristics of the soils revealed that both sites contained appreciable amounts of exchangeable acidity in the surface horizons, and that their base saturation levels were sufficiently low to be impacted adversely by acidic inputs. Soil solution data indicated that the sites were periodically subjected to

relatively high  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  inputs, which may have influenced spatial and temporal variation in Al and pH. As a consequence, the formation of Al-hydroxy-sulfate minerals such as jurbanite, alunite and basaluminite were thermodynamically favored over gibbsite. Given these conditions, long-term changes in soil solution chemistry from acid deposition are acknowledged.

**Keywords** Acid deposition · Aluminum · Solubility control · Soil solution chemistry · Sulfate

## Introduction

Soil solution chemistry provides insight into element cycling, nutrient uptake and availability, mineral transformation, and pollution transport processes within the subsurface environment. Therefore, chemical analysis of the extractable soil water fraction has been utilized in several studies to assess the condition of ecological resources and to identify stresses, and levels thereof, which may be contributing to ecosystem deterioration (Karathanasis 1989; Lawrence and David 1996; Kaiser and Kaupenjohann 1998). The composition of the soil solution as an index of potential Al toxicity and soil acidification from anthropogenic processes has been used extensively and has been instrumental in the development of models for simulating the effects of acidic deposition on soil and water systems (Cosby and others 1985; Reuss and Johnson 1986; Johnson 1995). However, the mechanisms dictating solubility control of different species within the solution phase and how they influence soil acidification are site-specific and remain a topic of debate.

The acidification of water in the atmosphere is typically controlled by carbon dioxide equilibrium in the presence of naturally derived nitric and sulfuric acids. These natural background constituents, however, rarely result in rainwater pH levels below 5.0 and are generally contained in the area of their formation (Spiro and Stigliani 1996). The combustion of fossil fuels, primarily coal and oil, may increase the levels of  $\text{SO}_2$  and  $\text{NO}_x$  in the atmosphere and contribute to significant lowering of rainwater pH levels (National Acid Precipitation Assessment Program 1987). In addition, the area of impact from these emissions can

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be widespread because of tall smokestacks, which loft gases high into the air so as to lessen localized acidic depositional effects. As a result, parts of Scandinavia, northeastern United States and southeastern Canada have been adversely impacted by acid rain, and dry deposition of aerosols, derived from downwind industrial processes (Ulrich 1989).

Anthropogenic acidic deposition is a serious contributor to biotic stress in forest ecosystems through the depletion of soil nutrients, mobilization of ionic Al, and increases in the concentration of acid anions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) in the soil solution (Reuss 1983). The decline of red spruce (*Picea rubens* Sarg.) in the eastern US is often attributed to such changes in the soil solution chemistry (Joslin and others 1992). Atmospheric inputs of  $\text{H}^+$  and acid anions contribute to the dissolution of clay minerals and to the formation of Al-saturated soils (Thomas 1996). Reuss and Johnson (1986) noted that the depletion of exchangeable base cations by acidification and leaching processes results in an abrupt Al increase in the soil solution. Subsequently, Ca and Mg are replaced by Al on the soil exchange sites and Ca/Al or Mg/Al molar ratios decrease. As the concentration of base cations is lowered, the buffering capacity of the soil is similarly reduced and the susceptibility for further acidification is enhanced. Unfortunately, the extent of soil base replenishment from natural weathering and atmospheric deposition is currently too low in much of the eastern US to offset losses that occur through anthropogenically-induced soil exchange process (Johnson and others 1988; Knoepf and Swank 1994). As a result, diminishing long-term forest productivity has been projected for affected areas (Huntington 1996).

The biogeochemistry of aluminum is an important environmental parameter in assessing acidic deposition impacts and is significant because Al, in its bioavailable form, exhibits considerable phytotoxicity as well as aquatic ecotoxicity (Wolt 1994). Soil is composed of 1 to 30% Al, primarily as a component of a variety of aluminosilicates, oxyhydroxides, and nonsilicate minerals (Barnhisel and Bertsch 1982). In well-drained soils where percolating soil water makes prolonged contact with the soil mineral phase, soil solution Al activity is commonly controlled by dissolution-precipitation of discrete mineral phases.

Models applied to soil systems and watersheds mildly affected by acidic deposition often assume that crystalline forms of gibbsite [ $\text{Al}(\text{OH})_3$ ] or kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] control soil solution  $\text{Al}^{3+}$  (Christophersen and Seip 1982; Cosby and others 1985). In many of these watersheds, gibbsite or kaolinite solubility adequately explains soluble  $\text{Al}^{3+}$  concentration and speciation (Budd and others 1981; Johnson and others 1981). However, in many others,  $\text{Al}^{3+}$  levels are too high to be accounted for by these associations (David and Driscoll 1984). Therefore, soluble Al-hydroxy-sulfate compounds have been suggested as alternative controls for solution pH and  $\text{Al}^{3+}$  activity, particularly in acid soils (Wolt 1994). Nordstrom (1982) identified basaluminite [ $\text{Al}_2\text{SO}_4(\text{OH})_{10}$ ], alunite [ $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ], and jurbanite [ $\text{AlSO}_4\text{OH} \cdot 5\text{H}_2\text{O}$ ] as Al-hydroxy-sulfate minerals capable of supporting elevated

levels of Al in the solution of acid soils. Control of solution Al by Al-hydroxy-sulfate minerals is possible in environments where appreciable quantities of sulfuric acid exist, such as those observed in pyritic mine-spoils, drained marine floodplains, and soils that have received anthropogenic acid inputs (Wolt 1981; Nordstrom 1982). Hence, detection of a shift in the mineral phase controlling  $\text{Al}^{3+}$

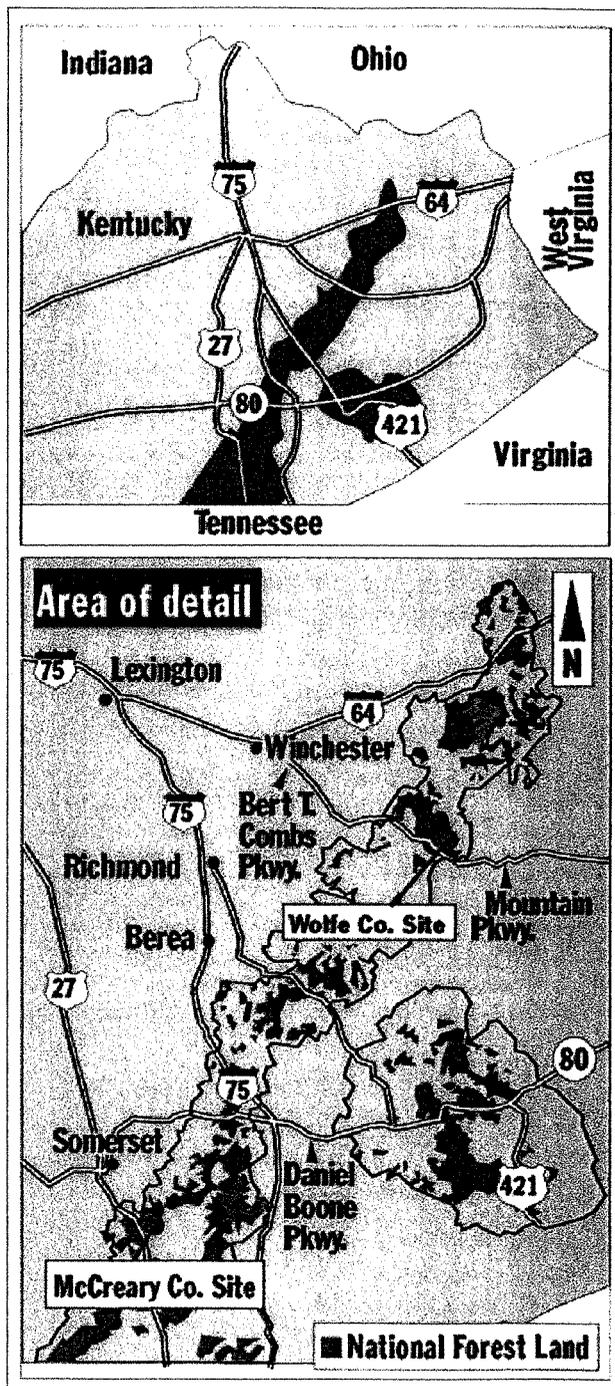


Fig. 1 Site locations in the Daniel Boone National Forest, Kentucky

activity in solution may be useful in predicting and sizing the impact of acidic deposition on soil systems.

A large body of work currently exists on the influence of acid deposition and associated Al chemistry on plant and soil systems, particularly in the northeastern regions of Europe and the United States. Very few studies, however, have been undertaken to examine potential impacts of acid rain on soils in the forests of the southeast US. Therefore, this study was undertaken to examine the soil solution chemistry of two sites in the Daniel Boone National Forest, Kentucky, USA, to assess potential acidification of forest soils from anthropogenic inputs, and to elucidate Al mineral solubility control changes in these systems.

## Materials and methods

### Site description and sampling design

The sites investigated are within the Daniel Boone National Forest in Wolfe and McCreary counties, Kentucky, USA (Fig. 1). They occupy ridge-top positions and are nestled among mature mixed pine-hardwood forest stands. Both sites are in close proximity to coal-burning power plants in Wolfe and McCreary counties, respectively. The Wolfe Co. site contains soils representative of the Rayne silt loam (fine, silty, mixed, mesic Typic Argudolls) series. The McCreary Co. site contains soils representative of the Wernock silt loam (fine, silty, mixed mesic Typic Hapludults) series. Both soils are deep, well drained and formed in material weathered from shale, siltstone, and sandstone. Soil pits were excavated at each site to aid in profile description development, soil sampling, and lysimeter installation. Soils were sampled by horizon from each pit for laboratory characterization. Zero-tension (pan) lysimeters were installed at 30- and 60-cm depths at each site. The pan lysimeters were constructed by removing soil below a desired level using hand tools, thereby creating a "cavity" in which a shallow (50×50×10 cm) pan, filled with pea gravel, could be inserted. A male hose fitting lined with a geofabric material was screwed into a threaded nut that was welded into the bottom of the pan. A polyethylene hose was attached to each pan and the "cavity" was backfilled with soil to aid in support of the overlying undisturbed soil. From each pan, the hoses extended into 20-l polyethylene carboys situated at the bottom of the soil pits. Each carboy was equipped with a

5-cm-diameter PVC pipe that extended 25 cm above the forest floor. The pit was carefully backfilled with soil and PVC caps were placed over the pipes. Water was collected quarterly from the carboys using a diaphragm hand pump. Suction (tension) lysimeters at 15-, 30- and 60-cm depths were also installed at each site (Fig. 2). Lysimeter placement involved coring of a 5-cm-diameter hole to the desired depth using a bucket auger. A portion of the excavated soil was mixed with water to form a slurry. The slurry was poured into the hole and the lysimeter was pushed into the slurry, so that the porous ceramic cup was completely surrounded by the mixture. The remaining area above the slurry was backfilled with the original soil and firmly tamped to prevent short circuiting. A plug of bentonite clay was placed around the lysimeter, at the surface, to further prevent preferential flow of water in the backfilled area. Once installed, a vacuum of 60 centibars was applied to the lysimeter using a hand vacuum pump. A stopper assembly equipped with a neoprene tube and pinch clamp was utilized to contain the applied vacuum. Water samples were extracted from the lysimeters by disconnecting the stopper assembly, installing a hand-crank peristaltic pump, and pumping the collected water into polyethylene bottles. All water samples were packed in ice and transported to laboratory refrigerators where they remained at 4 °C until analyzed.

Additional soil solution extracts were generated from soil samples collected at points adjacent to the lysimeter plots during each sampling event. Duplicate samples from 0–15-, 15–30- and 30–60-cm depths were removed using a bucket auger, then sealed in polyethylene bags. Upon return to the laboratory, the samples were immediately centrifuged for 1 h at  $\times 2,750$  g (3,500 rpm) using a double-bottomed canister consisting of an upper soil chamber with a perforated base, and a lower solution cup. A number 2 glass filter was fitted above the perforations in the soil chamber to prevent particle movement into the solution cup. After centrifugation, soil solutions were filtered through 0.2- $\mu$ m filters, analyzed for pH and electrical conductivity, and transferred to polyethylene bottles for refrigeration and further analysis.

### Soil characterization and solution analysis

Physicochemical properties of individual soil horizon samples collected from each site were determined through the methods of the Natural Resources Conservation Service (NRCS 1996). Extractable bases and CEC were

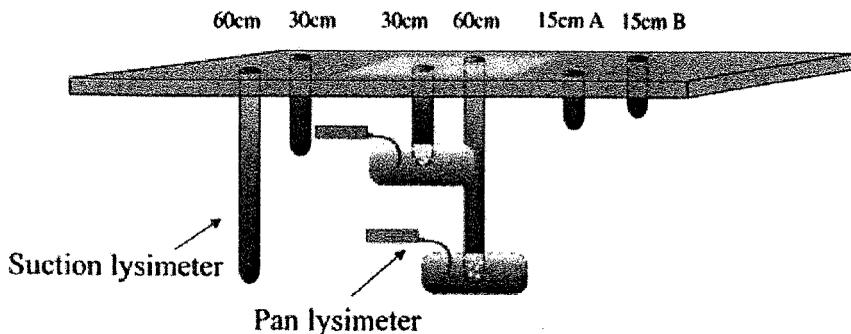


Fig. 2 Schematic depicting zero-tension (gravity) and suction lysimeter placement

analyzed using the 1 M ammonium acetate (NH<sub>4</sub>Oac), pH 7.0 (Buchner funnel) (5B1) (5A1b) methods, respectively (NRCS 1996). Analysis of Ca, Mg, Na, and K was performed by atomic absorption spectroscopy using an Instrumentation Laboratory model S11 AA/AE spectrophotometer. Ammonium (NH<sub>4</sub><sup>+</sup>) was measured using a Technicon Auto-Analyzer II. Organic Carbon (OC) was determined using a Leco Carbon Analyzer, Model CR-12. Particle size analysis was determined using the pipette method (NRCS 1996). Soil pH was measured in a 1:1 soil-water suspension with an Orion pH meter. Extractable acidity was measured by titration, using the BaCl<sub>2</sub>-triethanolamine method (NRCS 1996). The soil mineralogical composition was determined using a Phillips PW 1840 diffractometer interfaced with a PW 1729 X-ray generator. The diffractometer was equipped with a cobalt X-ray tube, operated at 40 kV and 30 mA, and a Bragg-Bretano goniometer. A scanning rate of 2° per 2θ min<sup>-1</sup> from 2–60° per 2θ was used for Mg-saturated clay slides, and from 2–30° per 2θ for all other slides.

Soil solution samples were filtered through 0.2-μm filters before analysis. All sampling handling and solution characterization procedures followed those outlined in the Standard methods for the examination of water and wastewater (APHA 1989). Aluminum was determined colorimetrically by the eriochrome cyanine-R method and measured with a Bio-Tek Instruments spectrophotometer microplate autoreader. Sulfate was determined turbidimetrically using the barium chloride method. Nitrate (NO<sub>3</sub><sup>-</sup>) was measured by ion chromatography using a Technicon Auto-Analyzer II. Geochemical modeling of aqueous-phase chemical equilibria was performed with the MINTEQA2 computer program (Allison and others 1990).

## Results and discussion

### Soil physicochemical and mineralogical characteristics

Physicochemical properties of the soils studied are presented in Table 1. The Rayne soil exhibited a silt loam

texture from the surface to the 60-cm depth, while the Wernock soil exhibited a sandy loam texture at the surface, with a slight increase in clay distribution with depth. Both soils showed acidic (pH <4.0) surface horizons that were underlain by moderately acidic (pH 4.62–4.75) subsoil to the 60-cm depth. The acidic nature of the surface horizon in both soils is probably induced by the organic acids associated with the forest floor litter and the elevated organic matter contents of the A horizons (Rayne 8.69%; Wernock 5.25%, respectively). The Wernock soil exhibited concentrations of total exchangeable bases and percent base saturation that were more than twice the levels observed in the Rayne. However, the Rayne soil exhibited a higher cation exchange capacity over that of the Wernock soil from the surface to the 40-cm depth. The higher base saturation in the Wernock is likely attributed to an enhanced calcium concentration, which may indicate differences in parent material between the two sites. Low base saturation in the Rayne soil may also be reflective of enhanced weathering and leaching of base cations. The high exchangeable acidity and elevated CEC in the Rayne soil is attributed to a greater abundance of dissociable protons (H<sup>+</sup>) from the higher levels of soil humus, which supports more pH-dependent charges.

Mineralogical compositions of the <2-μm clay fraction are reported in Table 2. Both soils exhibited a mixed mineralogy. Kaolinite was the dominant aluminosilicate mineral in the clay fraction of the Wernock soil, whereas the Rayne contained appreciable amounts of hydroxy-interlayered vermiculite near the surface (0–18 cm) and kaolinite at lower depths (18–60 cm). The Rayne soil contained some vermiculite at the 18–60 cm depth and consistently displayed higher mica content than the Wernock soil. Both soils contained low levels of feldspars and quartz. The presence of gibbsite was also detected at low levels in both soils, with the Wernock exhibiting a slightly higher concentration than the Rayne. Diffuse X-ray diffraction peaks for aluminum sulfate minerals were detected in both samples, but the levels were too small to be accurately quantified. The weak diffraction peaks may also indicate the presence of poorly crystalline phases of these minerals. Supporting evidence for the presence of aluminum sulfate

**Table 1**  
Physicochemical properties of the soils included in the study

Depth (cm)	Textural class	pH (1:1)	Ca <sup>a</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	TEB <sup>b</sup>	CEC <sup>c</sup>	EA <sup>d</sup>	Base saturation (%)	Organic matter (%)
Rayne silt loam								
0–5	Silt	3.99	0.06	0.42	13.28	17.32	3	8.69
5–18	Silt	4.68	0.06	0.35	6.59	8.83	5	3.41
18–40	Silt	4.65	0.04	0.29	4.74	6.49	6	1.26
40–60	Loam/silt	4.75	0.07	0.47	6.37	7.31	7	0.57
Wernock sandy loam								
0–5	Sandy loam	3.85	1.28	1.42	7.36	12.31	19	5.25
5–28	Sandy loam/loam	4.62	0.63	0.72	3.72	6.19	19	2.21
28–43	Loam	4.65	0.53	0.65	5.35	7.21	12	0.99
43–60	Sandy clay oam/sandy loam	4.66	0.51	0.65	4.94	6.76	15	0.81

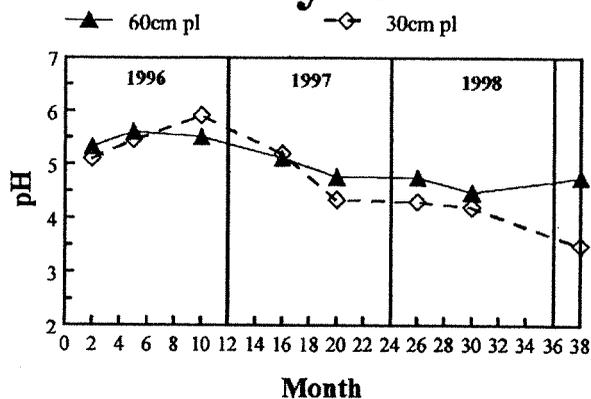
<sup>a</sup>Exchangeable calcium

<sup>b</sup>Total exchangeable bases

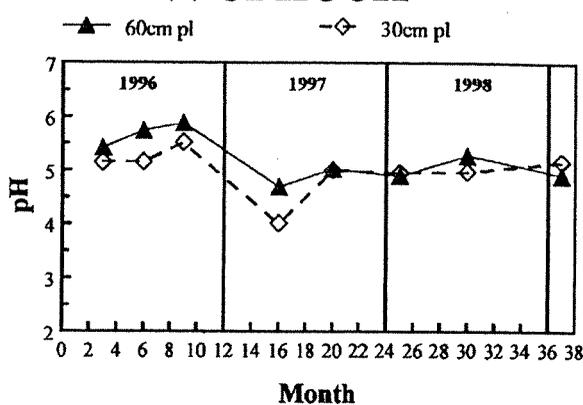
<sup>c</sup>Cation exchange capacity

<sup>d</sup>Exchangeable acidity

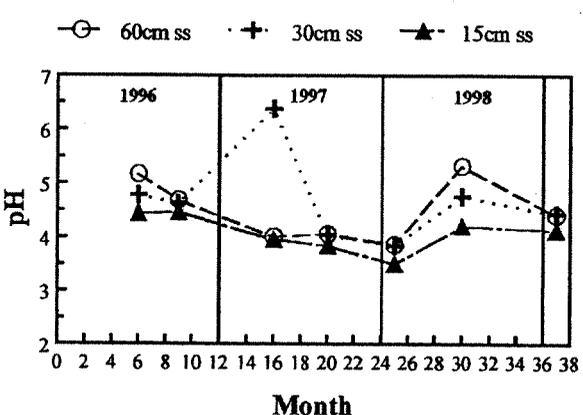
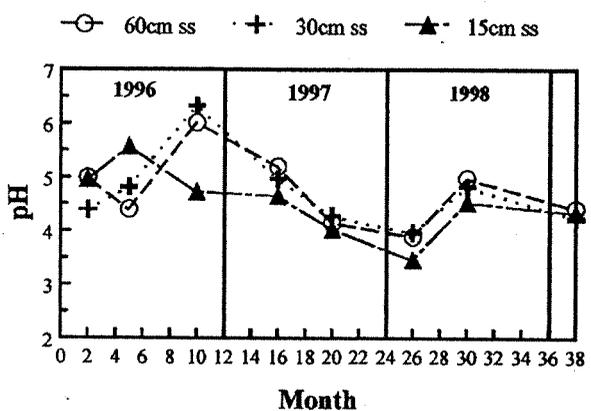
# Rayne



# Wernock



Pan Lysimeter



Suction Lysimeter

Fig. 3

Soil solution pH values for samples collected in tension lysimeters (ss) at 15-, 30-, and 60-cm depths, and in gravity lysimeters (pl) at 30- and 60-cm depths

minerals in these soils was sought through solution composition analysis.

### Soil solution composition

Both tension and zero-tension (gravity) lysimeters were used to collect soil solution samples. Zero-tension lysimeters collect solution that moves downward through the soil by the force of gravity, often through macropores, whereas tension lysimeters use vacuum pressure to collect

both freely draining solution and some that is held by capillary force. Because tension lysimeters are capable of removing water that is held by the micropore fraction of the soil, equilibrium between the soil solution and the soil matrix is more attainable over that observed in the gravity lysimeters. Therefore, some differences in the solution chemistry of the different sample types are anticipated. Soil solution extracts from centrifuged samples were often utilized to replace those from dry tension lysimeters, or when sample volume was inadequate for analysis. Solution pH measurements from the pan lysimeters of the Rayne soil exhibited an acidifying trend through the duration of the study (Fig. 3). Both soils showed gravity

Table 2

Mineralogical composition of the <2- $\mu$ m clay fraction. V Vermiculite; V-HIV hydroxy-interlayered vermiculite; CL chlorite; INT interstratified; K kaolinite; MI mica; Q quartz; GI gibbsite; GO goethite; F feldspars

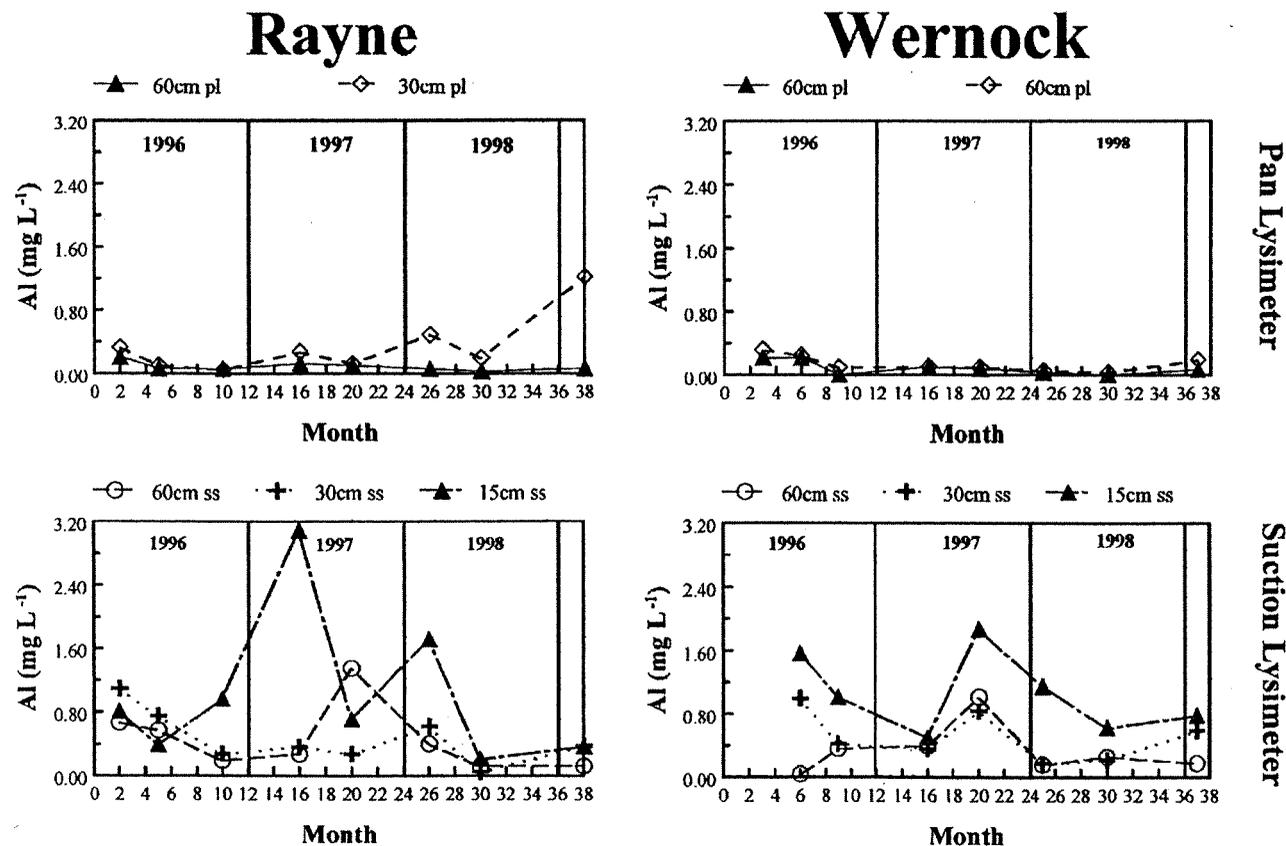
Depth (cm)	V (est. %)	V-HIV	CL	INT	K	MI	Q	GI	GO	F
Rayne silt loam										
0-5		41		6	28	5	17	4		5
5-18		32		4	30	10	16	5		3
18-40	5	30		5	42	10	6	4		3
40-60	6	10			60	15	6			3
Wernock sandy loam										
0-5		38			40	3	12	5		2
5-28		32		6	42	7	8	6		2
28-43		30		5	45	5	6	6		3
43-60		26			57	3	6	6		2

solution pH values that were near 5.5 for the winter of 1996. However, subsequent sampling events revealed that the pH in the Rayne solutions gradually dropped to levels below 4.5, whereas the pH in the Wernock solution remained relatively stable (Fig. 3). The higher base saturation of the Wernock soil likely contributed to better buffering this system against acidic inputs, whereas the Rayne soil was lacking and needed base cations to combat acidification. In most sampling events, the 30-cm gravity lysimeter exhibited elevated acidic conditions over that of the 60-cm lysimeter in both soils. This trend is probably the result of the abundant organic acids associated with the upper horizons of each soil. Solution from the tension lysimeters showed a similar trend, with the lowest pH values occurring near the surface at each site. The trend toward acidification in the Rayne solutions and toward buffering in the Wernock solutions is well-reflected in the tension lysimeter samples. However, the pH variability between sampling events is greater in the tension lysimeter samples over that observed in the gravity solutions. Similar results have been observed by Lawrence and David (1996), and Berggren (1999), and have been attributed to the elevated contact time between the soil solution and the matrix in the tension samples, suggesting that the samples are more representative of equilibrium conditions.

Changes in soil pH over time have been attributed to alterations in cation pools because acidic inputs alter the chemical species composition of a soil matrix (Nilsson and Bergkvist 1983). The net amount of acidification that occurs in response to acidic deposition depends upon the buffering capacity of the ecosystem in question and the potential for base cation replacement via deposition or weathering. Wilklander (1980) hypothesized that soils in the mid-range of typical forest soil, with pH values 4.5–6.0, would be the most sensitive to pH change because more acidic soils are buffered against further acidification by relatively high levels of Al, whereas circum-neutral soils are buffered by a high degree of base saturation. Given these conditions, it is evident that the Wernock soil has a better buffering potential against acidification because of its higher base saturation, but its buffer capacity is not sufficiently high to sustain these conditions.

The introduction of strong mobile acid anions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) into these soil systems may enhance soil acidification via leaching of base cations from the exchange complex and/or through Al mobilization. Examination of the Al solution data from the gravity lysimeters reveals low concentrations ( $<0.4 \text{ mg l}^{-1}$ ) at the 60-cm depth for both soils (Fig. 4). The 30-cm pan lysimeter in the Rayne soil, however, shows a slight elevation in Al concentrations for the duration of the study, with peaks occurring in the spring of 1997 and winter of 1998 and 1999. Considering that the availability of base cations for exchange is limited in the Rayne soil, the response to acid anion or proton input would be through Al mobilization. Soils that are

**Fig. 4**  
Soil solution Al concentrations for samples collected in tension lysimeters (ss) at 15-, 30-, and 60-cm depths, and in gravity lysimeters (pl) at 30- and 60-cm depths



buffered by cation exchange, such as the Wernock, are not as susceptible to increased Al solubility until control of soil pH is shifted further downward into the region of Al buffering (Reuss 1983; van Breeman and others 1984; Ulrich 1989).

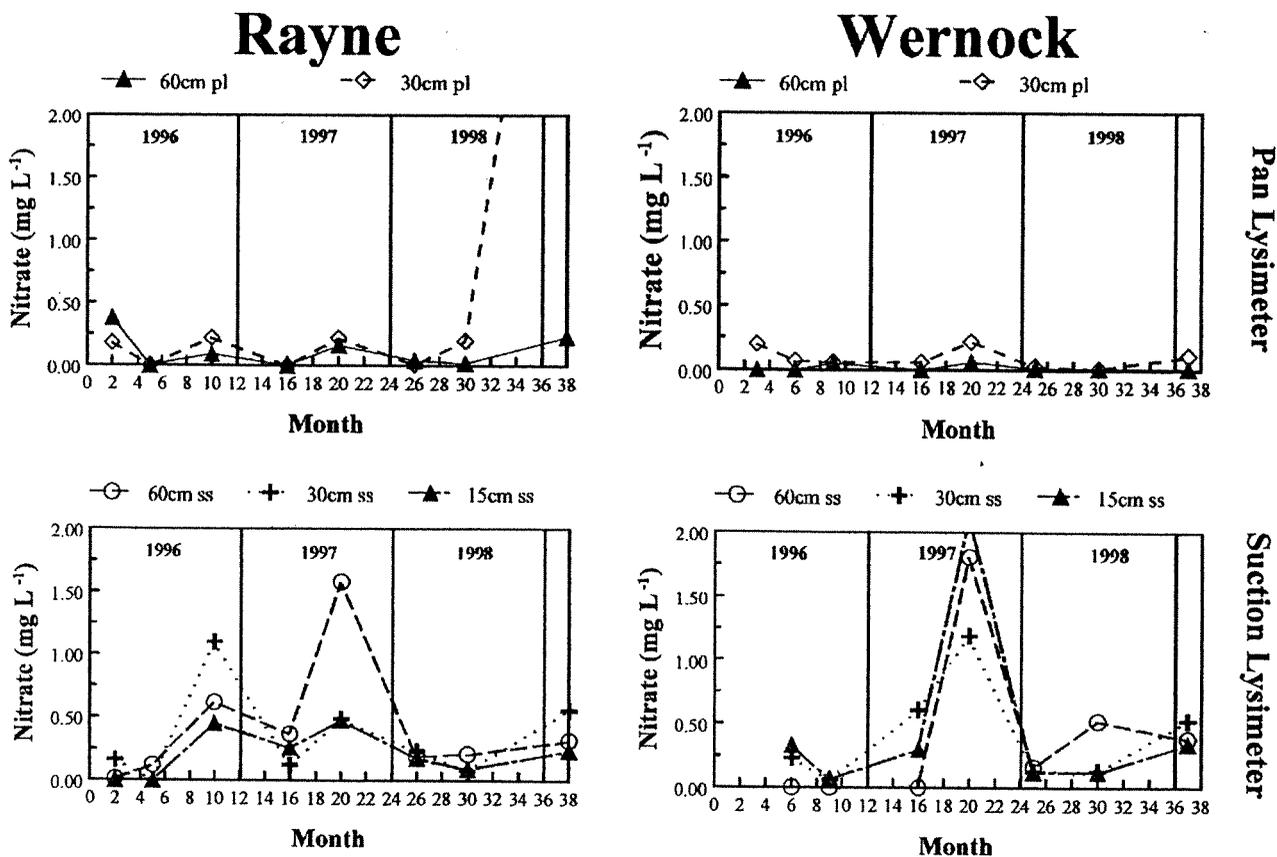
Tension lysimetry data revealed that the Al concentrations in the deeper (>30 cm) zones remained below 1.0 mg l<sup>-1</sup> for the duration of the study in both soils. However, the samples obtained from 15-cm depth displayed a much higher Al concentration and exhibited a wide variability. The Rayne tension lysimeter showed peak concentrations of 3.1 and 1.8 mg l<sup>-1</sup> in the spring of 1997 and winter 1998, respectively. These trends are consistent with those of the gravity lysimeters. The Wernock 15-cm tension lysimeter showed peak Al concentrations of 1.6 and 1.8 mg l<sup>-1</sup> in the summer of 1996 and 1997, respectively, which were not reflected in the gravity lysimetry data. Because the 0–15-cm depth represents areas of high biological activity, Al mobilization in these samples could be a response to the generation and movement of humic and fulvic acids from the microbial breakdown of organic matter (Nilsson and Bergkvist 1983). Conversely, ionic inputs may also have given rise to the mobilization.

Nitrate concentrations in solutions from the gravity lysimeters were low (<0.5 mg l<sup>-1</sup>) throughout the study

period with the exception of the 30-cm sample from the Rayne soil, which had a concentration of 5.34 mg l<sup>-1</sup> in the winter of 1999 (Fig. 5). This elevated concentration corresponds to the Al peak observed at the same time, but other nitrate peaks did not coincide with corresponding rises in Al concentration. Tension lysimeter data from the Rayne soil also exhibited nitrate peaks during the fall of 1996 and the summer of 1997, but with the exception of the summer 1997 data at the 30-cm tension lysimeter, Al and NO<sub>3</sub><sup>-</sup> did not correspond well. The influence of nitrate on aluminum mobilization is difficult to ascertain from the above data because the observed nitrate concentrations are not outside the ordinary variation expected in forest soils in the eastern US. Similar pulses of nitrate concentration in soil solutions have been observed in the southern Appalachians by Johnson (1995), and were attributed to a combination of disturbance (fire), natural biochemical processes, and unusual weather conditions.

The contribution of sulfate to forest floors is primarily of anthropogenic origin (Johnson and others 1988). Because N is often a limiting nutrient in most eastern forests and has shown to exhibit high variability, sulfate is often considered to be the dominant anion with respect to Al mobilization and cation leaching. Relatively high soil solution sulfate inputs were detected at both sites; however, the levels fluctuated widely and an associated impact on Al mobilization was generally not clearly evident (Fig. 6). Peak sulfate levels in the Wernock solution samples from the gravity and tension lysimeters were observed in the spring and summer of 1997. Aluminum concentrations

**Fig. 5**  
Soil solution nitrate concentrations for samples collected in tension lysimeters (ss) at 15-, 30-, and 60-cm depths, and in gravity lysimeters (pl) at 30- and 60-cm depths



also peaked in the summer of this year, possibly indicating a delayed Al mobilization effect triggered by high  $\text{SO}_4^{2-}$  input depositions. Sulfate concentrations in the Rayne solutions did not correspond well with peak Al events either, but a fairly good relationship ( $r^2=0.83$ ) was observed between tension lysimeter  $\text{SO}_4^{2-}$  and Al molar concentrations at the 60-cm depth. The improved association of these components at this depth may suggest that acid anion and Al equilibrium interactions were inhibited in the surface horizons by a macroporous and freely draining matrix, or were masked by more favored Al organic ligand associations. The low anion adsorption capacity of the organically enriched surface soil may have also contributed to the observed phenomenon.

Although the relationship between Al and sulfate appears to be somewhat inconsistent or vague, it is likely that shifts in ionic strength and pH brought on by the acid anion inputs may have influenced solubility controls and placed Al solubility control in a state of flux (transition) from a less soluble to a more soluble mineral. Examination of soil solution electrical conductivity (EC) measurements, which is often utilized as an index for ionic strength, revealed that ionic strength, mainly as a result of  $\text{SO}_4$  inputs, was considerably affected both spatially and temporally (Fig. 7). These changes are conducive to the development

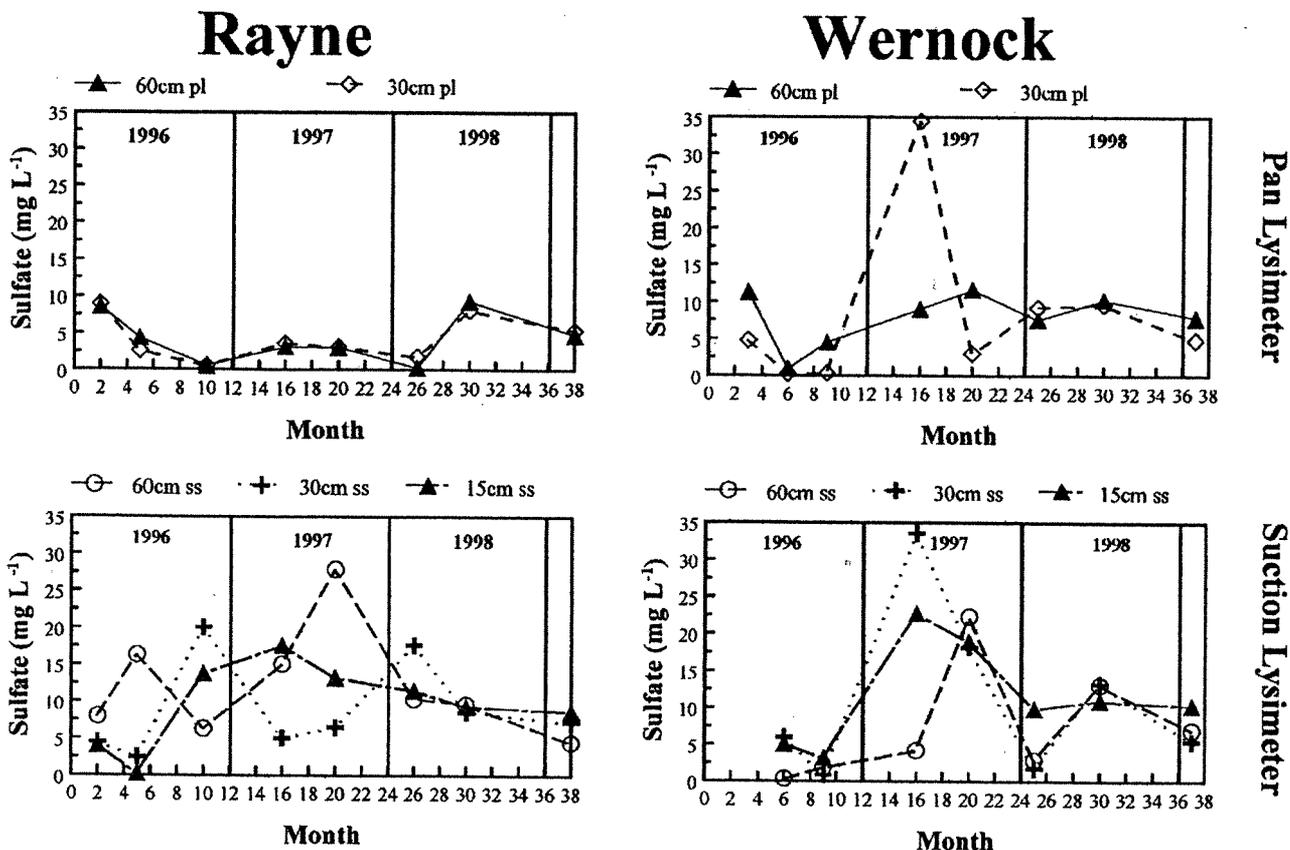
of temporary or permanent alterations to the mineral solubility control patterns impacting these systems.

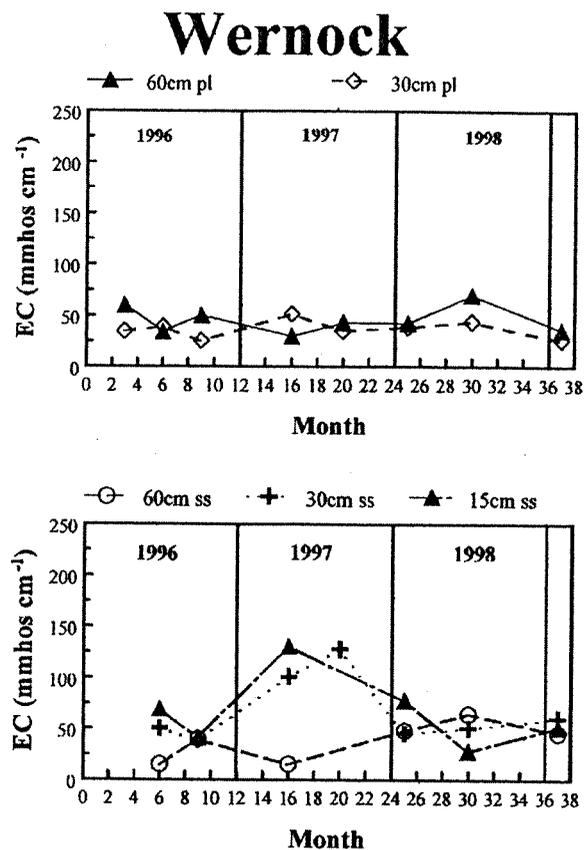
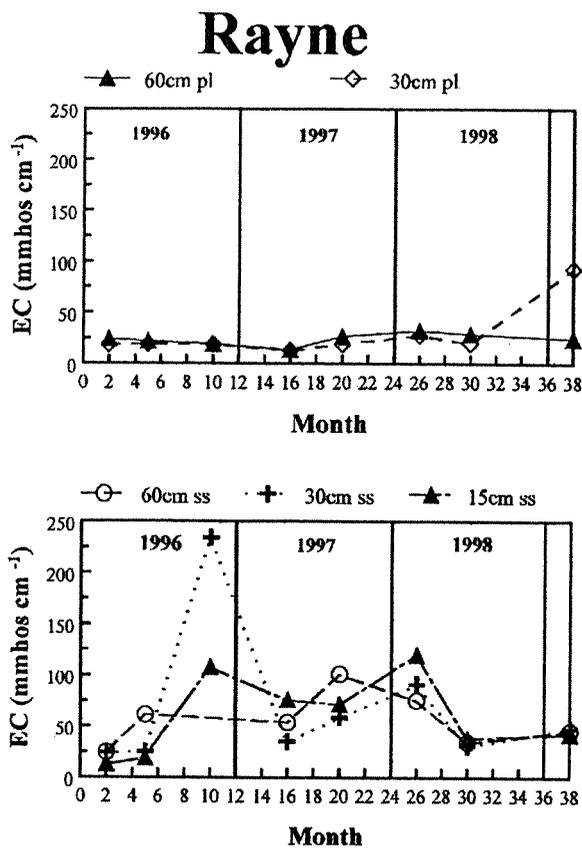
### Mineral solubility control sequences

Ionic activities were utilized to assess potential Al solubility control minerals in soil solution samples using the MINTEQA2 program. Mineral phases examined included gibbsite, alunite, jurbanite, and basaluminite with associated log K values of -33.95, -85.4, -17.2, and -117.5, respectively (Reuss and Johnson 1986). Stability diagrams were constructed from corresponding dissolution reactions and composition points representative of the solution chemistry of the study sites superimposed on the graphs. In these diagrams, points lying above a solubility line indicate supersaturation with respect to the mineral, whereas those below the line indicate undersaturation. Soil solution chemistry data points from the lysimeters at both sites are generally positioned between the stability lines for alunite and jurbanite (Figs. 8 and 9). Nearly all of the data points are in equilibrium or supersaturated with respect to alunite, and undersaturated with respect to jurbanite. The stability line for basaluminite appears to cut the data points in half, with half of the points supersaturated with respect to the mineral and the other half undersaturated. The Wernock soil has a clustering of data points near equilibrium with basaluminite, whereas the solution points of the Rayne soil tend to be more evenly distributed across the diagram. Most importantly, the regression line slope of the solution data points in the Rayne soil is parallel to that of jurbanite (Fig. 8) whereas the Wernock soil is parallel to

Fig. 6

Soil solution sulfate concentrations for samples collected in tension lysimeters (ss) at 15-, 30-, and 60-cm depths, and in gravity lysimeters (pl) at 30- and 60-cm depths





Pan Lysimeter

Suction Lysimeter

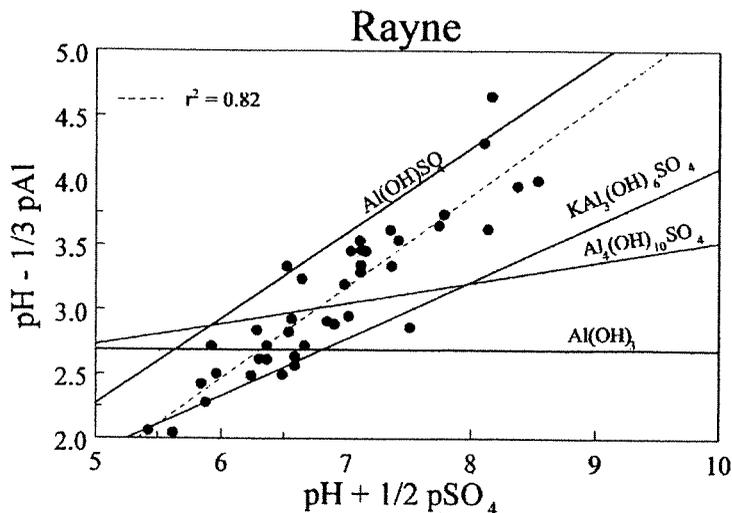
**Fig. 7**

Soil solution EC concentrations for samples collected in tension lysimeters (ss) at 15-, 30-, and 60-cm depths, and in gravity lysimeters (pl) at 30- and 60-cm depths

that of alunite (Fig. 9). This suggests that the stoichiometry of the Al-controlling mineral phase is similar, but of a different solubility, to the above sulfate minerals, and definitely different than that of gibbsite.

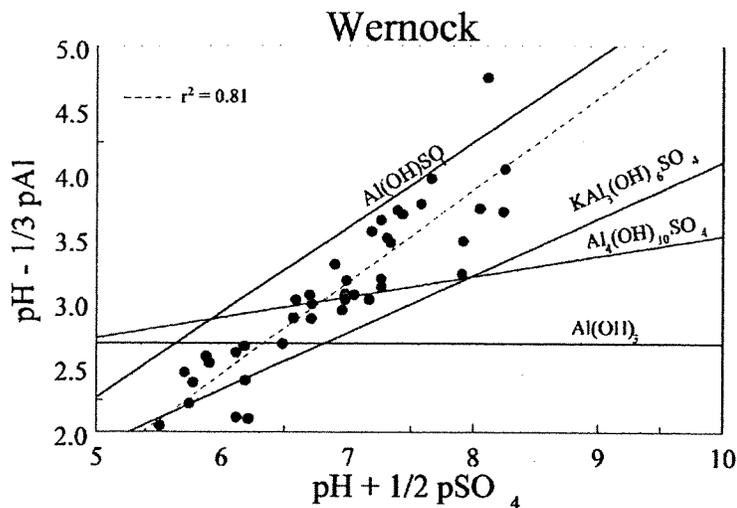
Similar trends have been observed by Nilsson and Bengkvist (1983) and van Breeman and others (1984) in

ecosystems affected by acidic deposition. The control of  $Al^{3+}$  by alunite or basaluminite in soils affected by acidic deposition has been postulated (Reuss and Johnson 1986), but the existing evidence suggests that these minerals may be more likely to serve as  $SO_4^{2-}$  controls. The lysimeter data of this study indicate that jurbanite may serve as the upper solubility limit for both  $Al^{3+}$  and  $SO_4^{2-}$ , with other Al-hydroxy-sulfate minerals, particularly alunite or basaluminite, providing a lower solubility control preferably over that of gibbsite. Given these circumstances, it is likely that continued acid inputs in these areas of the



**Fig. 8**

Rayne soil solution composition points in reference to a mineral stability diagram depicting solubility lines of jurbanite [ $Al(OH)SO_4$ ], alunite [ $KAl_3(OH)_6SO_4$ ], basaluminite [ $Al_4(OH)_{10}SO_4$ ], and gibbsite [ $Al(OH)_3$ ]



**Fig. 9**  
Wernock soil solution composition points in reference to a mineral stability diagram depicting solubility lines of jurbanite  $[\text{Al}(\text{OH})\text{SO}_4]$ , alunite  $[\text{KAl}_3(\text{OH})_6\text{SO}_4]$ , basaluminite  $[\text{Al}_4(\text{OH})_{10}\text{SO}_4]$ , and gibbsite  $[\text{Al}(\text{OH})_3]$

Daniel Boone Forest will continue to shift the soil solution equilibrium towards the precipitation of more thermodynamically favored Al-hydroxy-sulfate minerals.

## Conclusions

For many soils and watersheds considered to be sensitive to acidic deposition, the predominant chronic effect appears to be a shift in mineral solubility phase sequences controlling  $\text{Al}^{3+}$  activity in the soil solution. For soils with considerable sulfur retention, acid deposition may provide the necessary inputs that, in terms of high acidity and high  $\text{SO}_4^{2-}$ , will form conditions favoring control of soil solution  $\text{Al}^{3+}$  and/or  $\text{SO}_4^{2-}$  levels by Al-hydroxy-sulfate minerals. The two sites studied in the Daniel Boone National Forest, Kentucky appeared to fit well into this case scenario. Soil solution quality data taken from lysimeters at various depths in Wernock and Rayne soils suggested that sizeable acidic anion inputs into these systems occur periodically. As a result, the systems appear to be favoring transfers of Al solubility control from gibbsite or kaolinite to jurbanite and/or alunite. In addition, the input of acid anions and proton acidity from anthropogenic sources may be accelerating the depletion of base cations, and, thus, limiting even further the inherently weak pH buffering capacity of these ecosystems.

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