

5-1-1982

TB105: The Composition of Equilibrium Soil Solutions from Forest Soil B Horizons

Ivan J. Fernandez

Roland A. Struchtemeyer

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Recommended Citation

Fernandez, I.J., and R.A. Struchtemeyer. 1982. The composition of soil solutions from forest soil B horizons. Life Sciences and Agriculture Experiment Station Technical Bulletin 105.

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THE COMPOSITION OF EQUILIBRIUM SOIL SOLUTIONS FROM FOREST SOIL B HORIZONS

by

Ivan J. Fernandez and Roland A. Struchtemeyer

**LIFE SCIENCES AND AGRICULTURE EXPERIMENT STATION
UNIVERSITY OF MAINE AT ORONO**

May 1982

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Life Sciences and Agriculture Experiment Station
University of Maine at Orono

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INTRODUCTION

The composition of soil solutions provides valuable information on properties of the soil ecosystem. Soil solution composition is a very different chemical entity when compared to data obtained through conventional soil analyses. In many cases it has been demonstrated that the equilibrium soil solution provides a better indication of the availability of critical nutrients for plant uptake (33).

Interest in characterizing the soil solution began early in this century and provided the foundation for many of today's concepts in soil science. Information on the importance of aluminum and organic compounds in acid soil chemistry was among the earlier contributions from soil solution research (26, 34). The chemical activity of an ion in solution and its relationship to the activities of the other ions present, provide valuable information on its "availability" to plant roots (39, 40, 43). Not only is this a critical relationship for the nutrient elements, but in acid soil environments the activity of hydrogen and aluminum ions can be factors limiting vigorous plant growth (1, 11, 18).

Soil solution investigations have likewise been valuable in providing an understanding of pedogenetic processes. Water percolating through soil in temperate, northeast climates provides the major mechanism for soil development. The movement and composition of the soil solution reflect the rate and stage of soil weathering (22, 28). A great deal of attention has also been focused on theoretical models which predict the formation, stability, and weathering of soil minerals from thermodynamic data (based on soil solution composition) (24, 25, 32, 35).

Watershed research aimed at evaluating element budgets often

¹Research Assistant and Professor of Forest Soils, respectively,
University of Maine, Orono, Maine 04469.

depends on data from streamwater composition analyses to estimate soil weathering rates and nutrient losses (20, 23). One of the current critical environmental concerns is the effect of acid deposition on the soil resource. It has been shown that increased inputs of acidic components in the soil environment can cause a greater activity of aluminum in soil solutions and ultimately in freshwater ecosystems by way of subsurface flow (10, 45). These additions of aluminum are potentially toxic at high levels to natural fish populations in streams and lakes (12).

The objective of the present study was to evaluate the composition of B horizon equilibrium soil solutions from selected Maine forest soils. The B horizon was chosen for evaluation because it 1) best expressed the weathering processes active in the soil, 2) occupied the greatest volume of the solum, 3) had the most complex chemistry of the major horizons, and 4) provided the major corridor in forested ecosystems for subsurface flow and chemical alteration of ground waters.

MATERIALS AND METHODS

The study area was located in eastern Maine within Aroostook, Hancock, Penobscot, and Washington counties. Twenty-two sample plots were chosen adjacent to growth sites in even-aged spruce-fir stands previously established by Schiltz (37). The soils were classified as Typic Haplorthods having formed in loamy glacial till.

Sample plots were established within 12 meters of the original growth sites with uniform slope, aspect, and elevation. Soil pits were excavated to a depth of one meter and samples of the B2 horizon were collected for analyses. Soil samples were transported in plastic bags and air dried in the greenhouse.

Air dried but unsieved 1 kg soil samples were equilibrated at field capacity by weight. Field capacity had been previously estimated by gravimetric procedures using 100 g soil samples. After 10 days of equilibration at room temperature, soil solutions were obtained by suction filtration of the samples under a 20 psi vacuum. Soil solutions were passed successively through Whatman #3 and 0.22 μ Millipore filters.

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Solutions were stored in acid washed polyethylene bottles under refrigeration and all analyses were completed within 24 hours.

Soil solutions were analyzed for calcium and magnesium by atomic absorption spectrophotometry using a 1 percent strontium chloride solution to suppress anionic interferences. Flame emission was used to determine potassium, sodium, and manganese. Determinations of aluminum, iron, and phosphorus were accomplished colorimetrically by the aluminon, orthophenanthroline, and phosphomolybdate blue methods, respectively (6, 30). Soil solution pH by glass electrode and electrical conductivity by platinized electrode were determined on samples kept at 25°C in a constant temperature water bath (6).

Air dried soil samples of the B horizons were sieved through a 2 mm mesh sieve and subjected to chemical analysis. Soil pH was determined by glass electrode in distilled water and 0.01 M CaCl_2 using a 1:1 dilution. Soils were extracted using 1 N NH_4OAc of pH 4.8 (6) for determination of extractable Al, Fe, and Mn and exchangeable Ca, Mg, K, and Na. Exchangeable Al was determined using 1 N KCl (6). Exchange acidity, available phosphorus (by dilute acid fluoride), and readily oxidizable organic matter by Walkley-Black methodology were also determined (6). Total organic matter content was calculated by weight loss following ignition at 700°C for 2 hours. Analyses for Al, Fe, Mn, Ca, Mg, K, Na, and P were conducted as previously indicated for analyses of the soil solution.

Soil solution ionic strength was estimated according to $\text{IS}=0.013 (\text{EC})$ where IS ionic strength in moles/liter and EC electrical conductivity in millimhos/cm at 25°C. Activity coefficients were subsequently calculated using the full Debye-Hückel model (16).

All thermodynamic constants were taken from Lindsay (24). Descriptive statistics and simple correlation coefficients were calculated by the SAS program on an IBM 3031 computer system available at the University of Maine. In all cases $n=22$.

RESULTS AND DISCUSSION

Composition of Equilibrium B Horizon Soil Solutions

Results from the analyses of equilibrium B horizon soil solutions are presented in Table 1. Soil solution composition was in good agreement with other analyses for groundwaters draining granitic materials (41, p. 408). Soil solution pH was somewhat lower than would be expected for granitic solutions, which may be attributable to organic acids and a relatively high Al activity in the solution. Although mean soil solution

Table 1. Descriptive statistics for the composition of B horizon equilibrium soil solution extracts (n=22).

Variable	Units	Mean	Range		Coefficient of Variation
pH	moles/liter*	5.61	4.59	6.31	8
pAl	moles/liter	4.89	4.15	6.23	9
pFe	moles/liter	4.29	3.50	5.14	11
pMn	moles/liter	4.82	3.74	6.32	14
pCa	moles/liter	4.50	3.68	5.05	9
pMg	moles/liter	4.48	4.09	4.72	3
pK	moles/liter	4.41	4.13	4.66	3
pNa	moles/liter	4.12	3.76	4.34	3
pH ₂ PO ₄	moles/liter	5.95	5.36	6.51	5
pIS	moles/liter	3.00	2.82	3.26	29

* All values presented as logarithm of ionic activities calculated or measured as described in the Methods section.

Al activity was equivalent to 0.35 mg/l, the range in values encountered was between 0.016 to 1.9 mg/l. This could be biologically significant because it has been shown that 1 to 2 mg/l Al in soil solution and

greater than 0.2 mg/l in aqueous solutions can be toxic to trees and freshwater fish, respectively (10, 45). Of the elements examined, P had the lowest activity, indicating potential deficiencies in relation to tree nutrition on these sites. Soil solutions were approximately one order of magnitude more dilute than agricultural soil solutions which typically average 0.01 molar in ionic strength.

Simple correlation coefficients between ionic activities and total ionic strength in solution provide some insight into interactions between elements in soil solution. It is evident that the activity of Ca and Mg is positively and significantly correlated; however, only Mg was significantly correlated with ionic strength. This could reflect a greater bonding strength for Ca by soil exchange sites, which buffered Ca activity against changes in the activity of the soil solution. Evidence of greater soil selectivity for Ca can be seen in the low Mg/Ca selectivity coefficient in Table 2.

Ionic strength was positively correlated with most cations, showing significant positive correlations with Fe and Mg. The strong positive correlation between ionic strength and Fe may result from lower leaching losses and a more highly reduced environment for more poorly drained sites, which increased Fe activity.

Correlations for the Na cation showed that a positive relationship with Al and K existed in soil solution. This relationship may indicate that a balance exists in the soil solutions between these cations and the divalent bases. Positive correlations between K and H_2PO_4 activities may reflect a charge balance relationship between these ionic species in the soil solution. Research has shown that uptake of P by tree roots can be a process dependent on K availability (42). Correlations for soil solution pH with other soil solution variables are difficult to interpret in this instance but suggest that higher pH values were associated with lower activities of all species, with Fe and Al hydrolysis having the greatest impact on pH.

Table 2. Simple correlation coefficients (r) between the activities of ions in the equilibrium soil solution extracts.

	Al	Fe	Mn	Ca	Mg	K	Na	H ₂ PO ₄	Ionic Strength
pH	-0.26	-0.55**	-0.33	-0.19	-0.35	-0.27	-0.33	-0.40	-0.46*
Al		+0.10	-0.32	+0.12	+0.11	+0.15	+0.59**	+0.18	-0.12
Fe			-0.05	+0.26	+0.59**	+0.10	-0.14	+0.27	+0.72***
Mn				-0.19	-0.05	+0.34	-0.24	+0.35	+0.29
Ca					+0.89***	-0.29	+0.05	+0.14	+0.23
Mg						-0.10	-0.07	+0.30	+0.48*
K							+0.50*	+0.58**	+0.30
Na								+0.27	-0.02
H ₂ PO ₄									+0.24

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels respectively.

Theoretical Equilibrium Diagrams For Soil Minerals

Theoretical equilibrium diagrams are useful in evaluating potential dissolution and precipitation reactions which can occur in soils. One of the critical elements in acid soils is Al (1, 11, 18, 26). The role of Al in northeast forest ecosystems has recently received greater attention due to the increased activity of Al in soil solutions and freshwaters associated with the acid deposition phenomenon (10, 19). Figure 1 illustrates the relationship between the composition of equilibrium soil solutions from this study and Al solid phases which can control Al solubility in soils. It is evident that these solutions were supersaturated with respect to gibbsite or amorphous $\text{Al}(\text{OH})_3$. The mean value for $-\log \text{Al}(\text{OH})_3$ was 29.91 in these soil solutions, which indicated more Al was present than would occur if gibbsite ($\text{pK}=34.03$) or amorphous $\text{Al}(\text{OH})_3$ ($\text{pK}=32.33$) were controlling Al solubility. Under these circumstances, if true equilibrium was achieved, a more soluble Al phase must be controlling the level of labile Al in soil solution (27).

Figure 2 represents various Al, Fe, and Ca solid phases with P that commonly control the solubility of these elements in soil systems. Data points representing experimental soil solution compositions show these solutions to be undersaturated with respect to the Ca-P or Fe-P compounds but within the range of saturation for the precipitation of variscite. Since freshly precipitated $\text{Al}(\text{OH})_3$ would be amorphous and slowly change with time to a more crystalline, gibbsite-like phase (29), the exact nature of the $\text{Al}(\text{OH})_3$ possibly present in these soils falls between the gibbsite and amorphous $\text{Al}(\text{OH})_3$ boundaries of this diagram. Therefore, it is impossible to determine if equilibrium exists with a particular variscite- $\text{Al}(\text{OH})_3$ system.

Bache (2, 3) presented evidence that strict thermodynamic solubility constants would probably not be in control of solubility equilibria for soil solutions such as these. Indeed, evidence presented elsewhere showed that the formation of a complex between organic matter, Al, and P controlled the activity of Al and P in these B horizon soil samples (13). Other research also supports the concept that under field

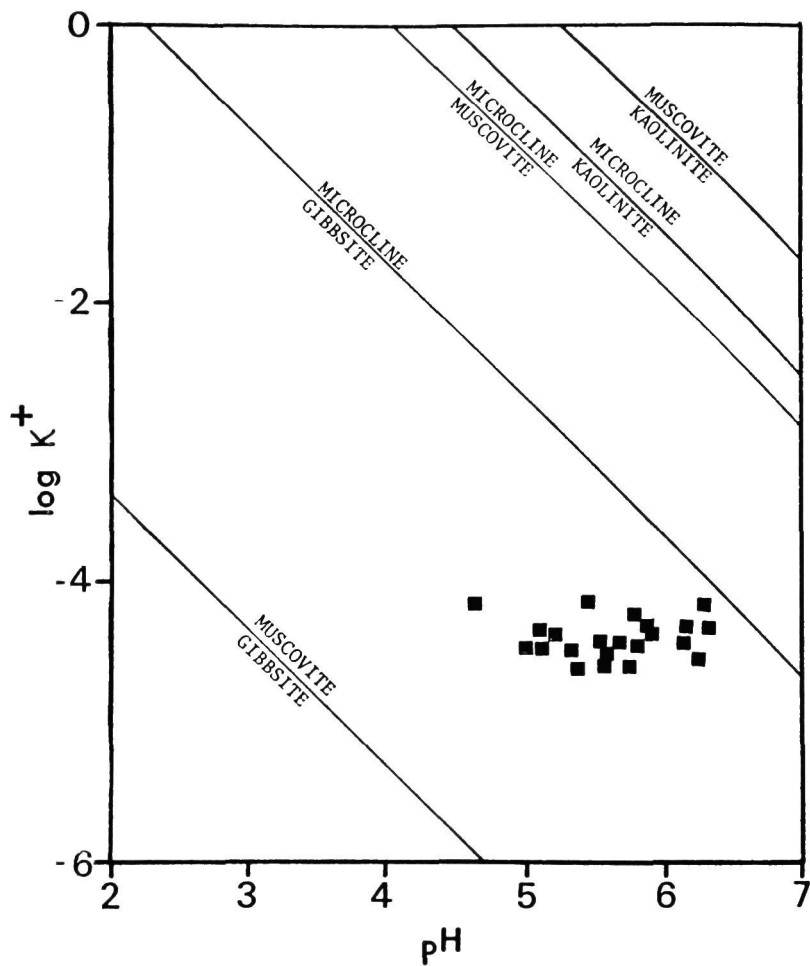


Figure 1 The solubility of aluminum hydroxides at 25°C.

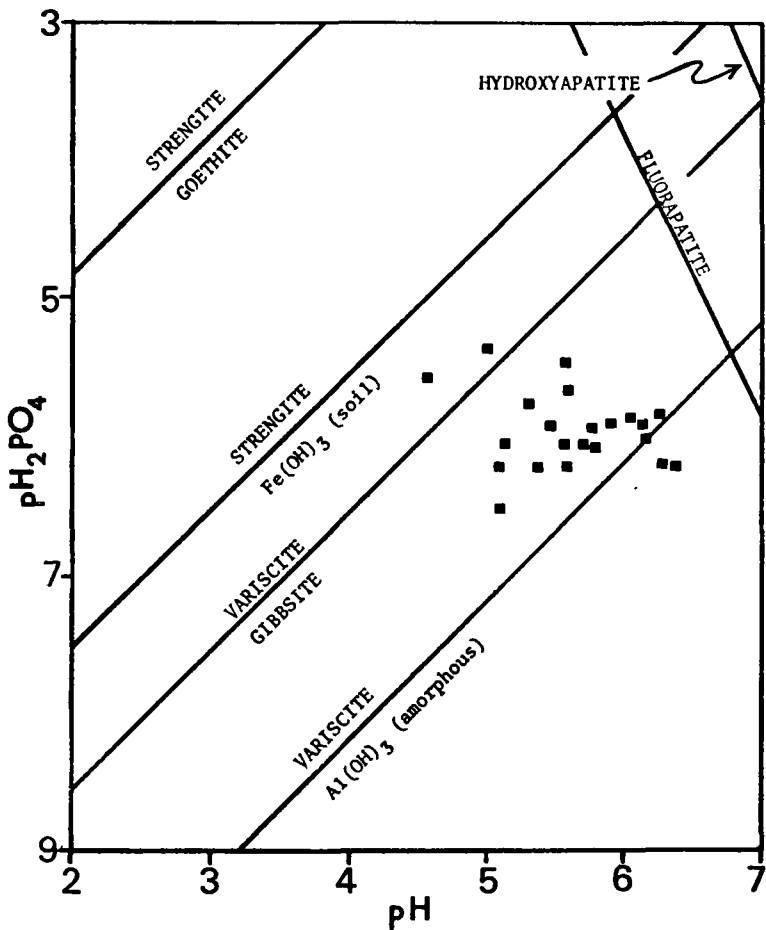


Figure 2 Sojubility diagram for phosphate compounds in soils at 25°C, modified from Lindsay and Moreno (25) for $\text{pCa}=4.50$ and at equilibrium with goethite, gibbsite, $\text{Fe}(\text{OH})_3$ -soil and $\text{Al}(\text{OH})_3$ -amorphous phases as described in Lindsay (24).

conditions, the chemistry of soil Al and P is dominated by interactions with organic compounds (4, 7).

Figure 3 shows that the composition of soil solutions was nearly in equilibrium with the feldspar minerals. Since these are relatively young soils, they would be described as being in an "early stage" of weathering dominated by unweathered primary minerals with a clay fraction containing amorphous phases, chlorite, and 2:1 clays like vermiculite and illite (8). The soil solution analysis suggests that rapid weathering of chlorite would be occurring in these soils. If true equilibrium were not attained or the silica activity were less for these solutions, then an even greater potential for congruent dissolution of the minerals in this diagram existed.

It has been shown that under podzol weathering conditions, K is retained in pedogenic clays after release from primary silicate minerals (20). Figure 4 illustrates stability boundaries for some common soil minerals with respect to K and pH while conserving Al. The data clearly indicate the potential weathering of muscovite and microcline to kaolinite or gibbsite. The probable end product of pedogenesis in these soils would be kaolinite, as is often seen in the weathering of granitic materials (17). Considering the low pH and silica activity required for gibbsite precipitation (15), all but the microcline-kaolinite boundary in this diagram would be metastable.

The Effect of Soil Solution Ionic Strength on Ionic Activity Coefficients.

Thermodynamic interpretations of equilibrium soil solution data rely on theoretical relationships which exist between the activities of ions in solution and in solid phases. It is important to understand that the activity of any species is a product of its absolute concentration and activity coefficient. Due to the effect of valence on the activity coefficient calculated by the Debye-Hückel model, changes in ionic strength have significantly greater consequence for an ion with a larger valence (31). This reveals two important aspects of soil solution data

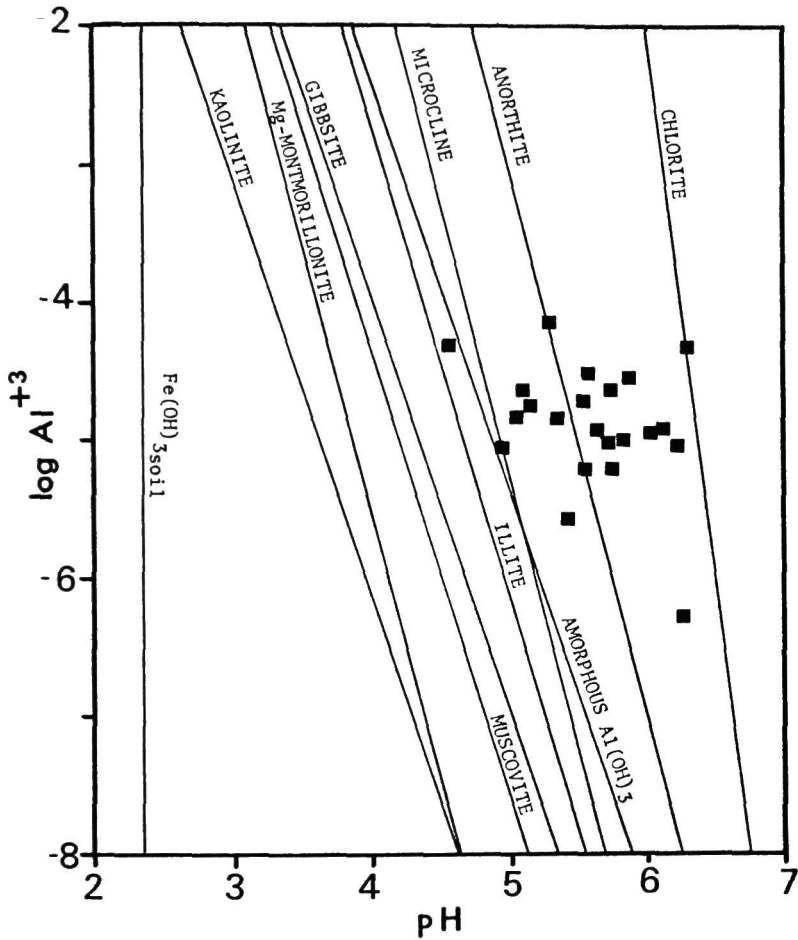


Figure 3 The solubility of some common soil minerals at 25°C using mean soil solution values from the equilibrium soil solution extracts ($pCa=4.50$, $pMg=4.48$, $pK=4.41$, $pFe=4.29$), assuming $pH_4SiO_4=3.1$, and taking equilibrium constants from Lindsay (24).

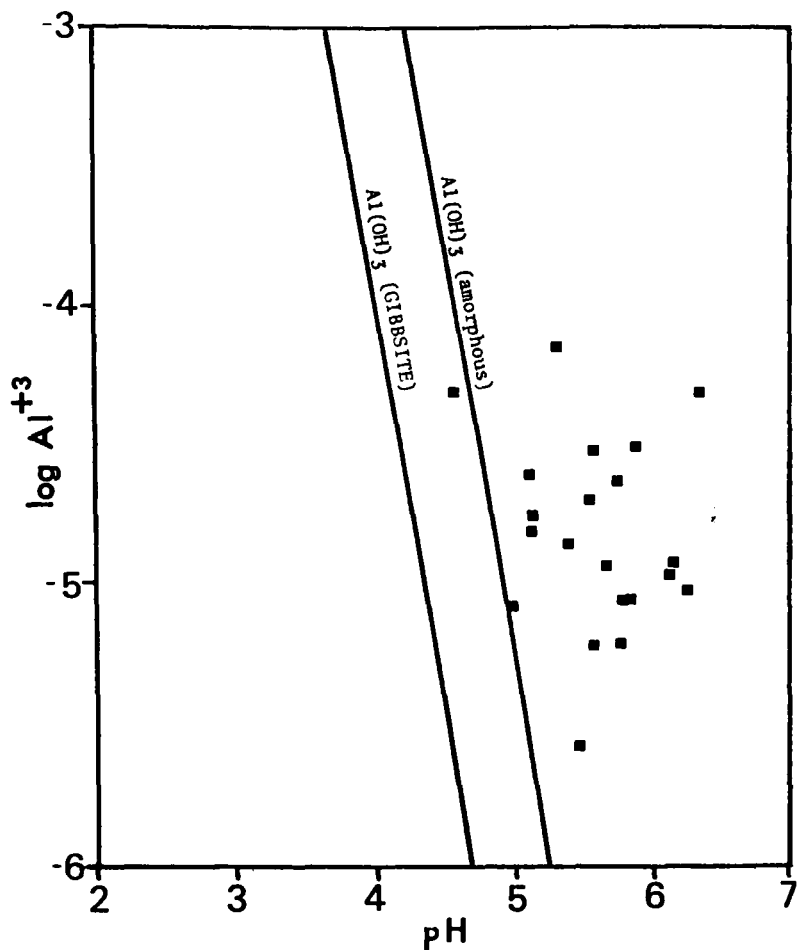


Figure 4 Predominance diagram illustrating the stability of some mineral phases at 25°C assuming $pH_4SiO_4=3.1$, and taking equilibrium constants from Lindsay (24).

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interpretation: 1) increased ionic strength will reduce ion activities due to a lower activity coefficient if concentration remains constant, and 2) increased ionic strength will reduce the activity of an ion more, the higher its valence state in solution.

For example, Table 3 shows simple regression models for the effect of ionic strength on the soil solution activity coefficients of the mono-, di-, and trivalent cations K, Ca, and Al. Judging by the slopes of these

Table 3. Simple linear regression analysis and ranges for the activity coefficients of selected ions as influenced by ionic strength.

Y*	a	b	X	R ²	Signifi- cance Level	Activity Coefficient Range	
						-moles/liter-	
aluminum	0.845	-104.34	IS	0.988	0.0001	0.693	0.794
calcium	0.930	58.11	IS	0.989	0.0001	0.845	0.900
potassium	0.982	16.95	IS	0.993	0.0001	0.957	0.974

* Simple linear regression analysis in the form of (activity coefficient) $a + b$ (ionic strength) for the measured ionic strength range of 0.00055 to 0.00151 moles/liter.

equations, Al activity coefficients decreased 6.15 times faster than those of Ca, and Ca activity coefficients decreased 3.43 times as fast as those of K with increasing ionic strength in these solutions. The range in activity coefficients encountered for these soil solutions was lower, overall, as ionic valence increased.

As a result of spring leaching and late summer desiccation of field soils, it is expected that a wide range of ionic strengths must exist for soil solutions of a given site. The correlation between a theoretical evaluation of soil solution data and its applicability to natural soil environments may be significantly altered by the relationship between ionic strength and ion activity variations.

Relative Affinity of Solution Cations For The Soil Exchange Complex

The "exchange constants" used in ion exchange equations are truly "selectivity coefficients" which can be used to determine the affinity of cations for clays over a range of cation ratios (14, 39). Gapon coefficients were therefore calculated using soil and soil solution data from this study to provide insight into the selectivity of B horizon exchange sites for cations in soil solution. Table 4 shows these $K_{A/B}^G$ values where coefficients >1 or <1 indicate a greater or lesser selectivity by exchange sites for cation A, as compared to cation B, respectively (44).

Table 4. Matrix of mean values for Gapon coefficients (K_G) of selected cations.

	Ca/	Mg/	Mn/	K/	Na/	H/
/Al	1.52	0.31	0.42	136.61	31.71	647306
/Ca		0.23	0.25	140.06	38.02	608811
/Mg			0.49	413.88	108.39	1857118
/Mn				613.70	176.76	2360447
/K					0.25	4934
/Na						16388

The coefficients indicate that selectivity for cations by B horizon exchange sites increased in the order $Mn < Mg < Al < Ca < Na < K < H$. The stronger retention of K and Ca within alkali and alkaline earth cations is in agreement with the typical lyotropic series (5, 36). Overall, the monovalent cations were more tenaciously adsorbed than the divalent cations, which is contrary to what is typically expected. The position of Al in this series may result from monovalent and divalent Al ionic phases being dominant in these soil solutions which ranged in pH between 4.59 and 6.31.

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If assumptions of equilibrium and the dominance of exchange reactions for hydrogen are made, then it appears that this cation is strongly adsorbed by exchange surfaces. The position of H in a replaceability series can be extremely variable depending on the exchange material. The exchange complex in these B horizon forest soils was extremely diverse and includes a variety of clay and organic colloids. In the case of hydrogen, both covalent bonding and strong electrostatic bonding of this extremely small cation may have produced a high energy of retention. With averages of 7.41 percent total organic matter and 9.57 percent clay, by weight, in these soils, the dissociation of hydrogen from organic functional groups likely dominated the chemistry of exchangeable hydrogen in these materials.

Relationships Between Soil Solution Composition and Soil Analysis

Simple correlation coefficients were calculated to examine the relationship between soil solution chemistry and results from standard chemical analysis of B horizon soils (Table 5). Soil solution pH was best correlated with soil pH measured in dilute salt solution. Possibly 0.001 M CaCl_2 should be studied for forest soil pH determinations, because this concentration better approximates soil solution ionic strength at field capacity. Higher soil solution pH was associated with lower exchangeable cations in the soil. This may have resulted from 1) lower cation exchange capacity due to a decreased contribution from the dissociation of organic functional groups which supply protons and produce exchange sites or 2) less Al hydrolysis due to lower exchangeable Al, which had a significant influence on solution pH. The correlation between solution pH and Walkley-Black readily oxidizable organic matter would support the first hypothesis.

The activity of soil solution Al was best estimated by soil extractions using 1 N KCl and increased overall as exchangeable cations increased, probably reflecting cation exchange capacity differences. The use of 1 N NH_4OAc of pH 4.8 in soil analysis produced the best correlation between soil and soil solution levels for the Mn and

Table 5. Significant simple correlation coefficients (r) between soil solution and soil variables for forest soil B horizons.

Soil Variables	Soil Solution Variables								
	pH	Al	Fe	Mn	Ca	Mg	K	Na	H ₂ PO ₄
pH(H ₂ O)	+43*	-	-	-	+59**	+46*	-	-	-
pH(CaCl ₂)	+56**	-	-	-	-	-	-47*	-63**	-
ex. acidity	-47*	-	+49*	-	-	-	-	-	-
Al(KCl)	-61**	+41*	-	-	-	-	+49*	+58**	+50*
Al	-	-	-	-	-49*	-	-	-	-
Mn	-	-	-	+79**	-	-	-	-	-
Fe	-	-	-	-	-	-	-	-	-
Ca	-45*	+44*	-	-	-	-	-	-	-
Mg	-50*	+47*	+61**	-	+74***	+80***	-	-	-
K	-	-	-	-	+42*	-	-	+47*	-
Na	-62**	+47*	-	-	+45*	+52**	-	+47*	-
P(Bray#1)	-	+56**	-	-	-	-	+53**	+86***	-
Total O.M.	-	-	+42*	-	-	-	-	-	-
Walkley-Black O.M.	-49*	-	+55**	-	-	-	-	-	-

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels respectively.

Mg cations. This extractant did not measure Al, Fe, Ca, and K phases which were significantly correlated with soil solution activities of these cations.

Greater soil organic matter content was positively correlated with Fe activity in solution. Reducing conditions induced by organic matter decomposition might explain this relationship due to Fe mobility being much greater in the reduced form.

The correlations between soil solution Al activity, H_2PO_4 activity, exchangeable Al, and extractable P indicated a simultaneous increase and decrease in the activity of Al and P in these soil-soil solution systems. Since basic inorganic chemistry dictates the precipitation of an Al-P compound with increased activity once the solubility product is attained, it is probable that the previously discussed organic matter-Al-P complex must have controlled Al and P activity. Under such conditions, lower organic matter content permits a simultaneously greater Al and P activity due to less complexation. This appears possible within a limited pH range for these soils (7, 13).

There was a greater activity of K and Na in soil solution with lower soil pH ($CaCl_2$), which corresponded to greater exchangeable Al, extractable P, and soil solution Al (Table 2). This suggests a dominance of the K, Na, and Al cations over the alkaline earth cations in more acid soil environments. Correlations also lend support to the idea of a charge balance relationship between H_2PO_4 and monovalent cations (Tables 2 and 5).

SUMMARY AND CONCLUSIONS

The analyses of equilibrium B horizon forest soil solutions indicated that solution compositions were characteristic for the weathering of granitic parent materials. Solution Al activity was high and may pose potential toxicity problems in relation to the biological components of these ecosystems. Variation in soil solution ionic strength best correlated with solution Fe activity. Organic matter decomposition and drainage may play the dominant role in controlling Fe mobility due to this element's sensitivity to solution redox potential.

Equilibrium soil solution models suggested that these were young soils actively undergoing dissolution of primary minerals. The end product of secondary clay formation in these materials would probably be kaolinite. Input of sulfur from acid deposition is a significant factor in modern soil chemical considerations, particularly in the northeast (9, 20, 21, 45). Future soil solution work utilizing solubility and stability diagrams should include this element for a more applicable interpretation of soil chemical dynamics. Research should also address the influence ionic strength variation in soil solutions has on ion activities and equilibria under typical field conditions.

The affinity of the various cations in solution for soil exchange sites increased in the order $Mn < Mg < Al < Ca < Na < K < H$. Hydrogen was tenaciously adsorbed by exchange surfaces which reflected the probable dominance of organic matter functional groups in the overall B horizon exchange complex.

Correlations between soil and soil solution analyses showed solution Al was significantly correlated with 1 N KCl extractable Al. The extraction of soils using 1 N NH_4OAc of pH 4.8 best reflected the activity of Mg and Mn, and to a lesser extent Na, in soil solution. The NH_4OAc extractant provided results which were not significantly correlated with soil solution activity for Al, Fe, Ca, and K. There is some evidence to suggest that a lower contribution of organic functional groups to the cation exchange capacity resulted in higher solution pH levels. Organic matter may be critical to Al and P chemistry in these soils although neither fraction of organic matter measured in this study was significantly correlated with solution Al or H_2PO_4 .

The activity of any ion in equilibrium soil solutions is ultimately determined by an equilibrium governed by mineral solubility, ion exchange, ion pairing, and chelation in solution. This study provides some insight into the nature of these forest soil solutions and possible chemical phenomena which are found in the B horizon.

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