

Aluminum Soil Chemistry: Influence on Soil Health and Forest Ecosystem Productivity

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How to cite this paper: Aide, M. (2022) Aluminum Soil Chemistry: Influence on Soil Health and Forest Ecosystem Productivity. *Agricultural Sciences*, 13, 917-935. <https://doi.org/10.4236/as.2022.138057>

Received: July 3, 2022

Accepted: August 7, 2022

Published: August 10, 2022

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Abstract

Soil aluminum phytotoxicity has been a major research area since the inception of modern soil science. Acid soils, which typically manifest plant aluminum toxicity, are frequently dedicated to food production, thus yield and quality reductions influence food security. This manuscript reviews our modern understanding of 1) soil aluminum hydrolysis and polymerization, 2) aluminum complexation with inorganic and organic anions, 3) aluminum interference with vital plant physiological processes, 4) aluminum and forest ecosystem productivity, and 5) demonstrates the software simulation of aluminum reactivity and its role in predicting soil behavior. The manuscript also provides a perspective for future soil-aluminum research critical to maintaining food security and food quality.

Keywords

Aluminum, Soil Acidity, Hydrolysis, Rhizosphere, Soil Health

1. Introduction

The objectives of this soil aluminum chemistry review and simulation manuscript are: 1) to document the soil chemistry of aluminum, and 2) to detail the influence of aluminum toxicity on soil health and forest ecosystem productivity. The manuscript will explore aluminum hydrolysis, complexation with organic and inorganic ligands, adsorption/desorption reactions, and mineral weathering. The manuscript will also explore soil chemistry simulations for provide further insight into the influence of aluminum on plant development, soil genesis, and forest ecosystem productivity.

2. Aluminum Soil Chemistry

Aluminum (Al) having an electronic configuration of $\{[\text{Ne}] 3s^2 3p^2\}$ resides as a group III element with a small and highly polarizing ionic radius (trivalent) of 0.0535 nm. Aluminum bearing minerals include: 1) boehmite ($\gamma\text{-AlOOH}$), 2) diaspore ($\alpha\text{-AlOOH}$), 3) corundum ($\alpha\text{-AlOOH}$), and 4) gibbsite ($\alpha\text{-Al(OH)}_3$) [1] [2]. In addition to aluminum oxides and oxyhydroxides, aluminum exists as a lattice constituent in tetrahedral and octahedral coordination in numerous silicates, including phyllosilicates [3] [4]. Aluminum may also reside in isomorphic substitution with Fe^{3+} in iron oxides and oxyhydroxides [5].

Aluminum will form stable sequences of aluminum octahedra in the interlayer regions of phyllosilicates, most notably smectites and vermiculites. The degree of hydroxy-aluminum interlayer may vary from incidental to pillaring to complete polymeric aluminum placement. Inclusion of hydroxy-Al interlayers stabilize smectite and vermiculite from the loss of H_4SiO_4 and limit the conversion of these 2:1-layer phyllosilicates to kaolinite [6]. With the presence of hydroxy-Al interlayers the shrink-swell capability is appreciably reduced. The cation exchange capacity expression is similarly reduced [6].

Active or available acidity is the titratable soil solution acidity [4]. The hydronium (H^+ or more accurately H_3O^+) and aluminum species in the soil's aqueous phase are perceived as labile or eminently available for plant uptake. Exchangeable acidity is the amount of acidity associated with the cation exchange complex and is experimentally estimated by salt displacement. The value of the exchangeable acidity is frequently method sensitive, that is differences in the experimental values may be attributed to: 1) the displacing species and its valence (Ca^{2+} , Mg^{2+} , Ba^{2+} , K^+ , Na^+ , etc.), 2) the displacing salt concentrations, 3) the solution to soil ratio, and 4) reaction time [4]. Non-exchangeable or residual acidity involves hydronium or aluminum species that are adsorbed by soil organic matter, variably charged mineral surfaces or as components of mineral lattices [4]. In the residual acidity category, the hydronium and aluminum are not displaced, or are only very slowly displaced, by salt solutions. Reserve acidity is total titratable acidity associated with the solid phase. Exchangeable acidity will buffer changes in active acidity and residual acidity will buffer changes in exchangeable and active acidity.

2.1. Aluminum Hydrolysis and Polymerization

Hydrolysis is a chemical reaction (substitution, elimination, and solvation), where a water molecule, usually in a hydration shell, acts as a nucleophile, resulting in deprotonation. Aluminum, which is highly polarized atom with a comparatively small ionic radius and a valence of three, readily supports hydrolysis. Determination of the proton dissociation of hydration water has been an active research area [7]-[12]. Baes and Mesmer [13] list typical aluminum hydrolysis values (Table 1). Other hydrolysis values for $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ are provided by Baes and Mesmer [13].

Table 1. Aluminum hydrolysis reactions.

Hydrolysis Reaction	pH
$\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})^{2+} + \text{H}^+$	5.5
$2\text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$	7.7
$6\text{Al}^{3+} + 15\text{H}_2\text{O} \leftrightarrow \text{Al}_6(\text{OH})_{15}^{3+} + 15\text{H}^+$	47.0
$\text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_2^{1+} + 2\text{H}^+$	9.9
$\text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$	15.6
$\text{Al}^{3+} + 4\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_4^- + 4\text{H}^+$	23.0

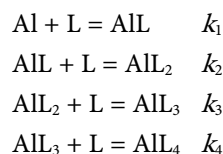
Source: Baes and Mesmer [13].

2.2. Aluminum Inorganic Complexes

Estimation of inorganic and low molecular weight organic aluminum complexes may be characterized as:

$$\text{Al}_T = \text{Al} + \text{AlL} + \text{AlL}_2 + \dots + \text{AlL}_n,$$

where L is the inorganic or organic coordinating molecule (ligand), Al is the Al^{3+} species concentration (activity), and Al_T is the total analytical aluminum concentration. If aluminum undergoes hydrolysis, then the $\text{Al}(\text{OH})$, $\text{Al}(\text{OH})_2$, ..., $\text{Al}(\text{OH})_n$ and their appropriate L complexes would be incorporated. The Al-L complex reactions may be represented as:



Then:

$$\text{Al}_T = [\text{Al}] \left\{ 1 + k_1[\text{L}] + k_1k_2[\text{L}]^2 + k_1k_2k_3[\text{L}]^3 + k_1k_2k_3k_4[\text{L}]^4 \right\}$$

with knowledge of the k_1 to k_4 constants, coupled with experimentally determined Al_T and [L] values, the $[\text{Al}^{3+}]$ may be calculated and subsequently the individual AlL_x species may be computed.

Collignon *et al.* [14] compiled aluminum thermodynamic data for hydrolysis, fluorine, phosphate, and silicic acid complexation/reactions. Bergera *et al.* [15] demonstrated that fluoride-Al complexes were an important Al complex that dominate boreal river chemistry and support aluminum transport. Fluoride as a ligand will form a series of stable Al complexes (AlF to AlF_4) [16].

2.3. Aluminum Organic Complexes

Soil organic matter is approximately 60% of the global terrestrial carbon pool [17]. The conversion of forest soil to cultivated land may release up to 75% of the stored soil organic carbon as CO_2 . Stable soil organic matter may be envisioned as being in equilibrium with soluble soil organic matter (dissolved organic carbon). Carbon turnover is highly influenced by water regimes, tempera-

ture, and modified by carbon additions from litter (residue) or root exudates [17]. High molecular weight compounds include humic and fulvic acids [4]. Humic and fulvic acids may be metabolized into aliphatic and aromatic low molecular weight compounds.

Soil organic matter stability, which is an active research area, is influenced by: 1) selective enrichment of organic compounds, 2) chemical stabilization with primarily iron and aluminum complexation reactions, and 3) soil organic matter residing in the interiors of soil aggregates typically because of reduced microbial activity [18] [19]. Fe-oxides in subsoils may be the most efficient sorbents for organo-mineral associations [20]. Kogel-Knabner *et al.* [21] demonstrated that chemical protection may be predictable from assessment of soil clay mineralogy, and chemical Al- and Fe-extractions. Boudot *et al.* [22] showed a protective influence of non-crystalline aluminum species on selected organic compounds.

Soil organic matter is frequently partitioned into high and low molecular weight organic compounds, with the division between low and high molecular weight organic compounds not definitively specified. Low molecular weight organic acids may be formed from forest floor litter and crop residue mineralization. Additionally, low molecular weight organic acids may be exuded from plant roots, especially into the rhizosphere [23]-[34]. Forest species tend to promote acetic, aconitic, and oxalic acid, whereas cereal and legumes frequently demonstrate preferential soil accumulation of citric, malic, and oxalic acids. Metabolic activities and mineralization, supported by free-living fungi and mycorrhizal associations, result in enhanced concentrations of oxalic acid, whereas bacteria tend to support enhancement of acetic and formic acids. Low molecular weight organic acids are ubiquitous in soil and water environments, especially in the root rhizosphere [23]-[34]. Low molecular weight organic acids, such as oxalic acid and citric acid, and high molecular weight acids, such as fulvic acids, bind approximately 80% of the aluminum species not associated with phyllosilicates and primary minerals [26] [34].

Low molecular weight organic acids preferentially complex aluminum, potentially reducing their phytotoxicity. Commonly observed low molecular weight organic acids include acetic, aconitic, benzoic, caffeic, cinnamic, citric, ferulic, formic, fumaric, gallic, gentisic, lactic, maleic, malonic, malic, oxalic, p-coumaric, phthalic, protocatechuic, p-hydroxybenzoic, salicylic, sinopic, succinic, syringic, tartaric, and vanillic [30] [35] [36]. Siecinska and Nosalewicz [37] observed that plant-aluminum soil interactions were dependent on 1) soil pH, 2) soil mineral nutrient availability, 3) presence of heavy metals, 4) soil organic matter content, 5) oxidative stress, and 6) water availability. Siecinska and Nosalewicz further documented that aluminum influenced root growth, reduction of nutrient uptake because of inhibition of transport processes through ion channels, and gene silencing. Drabek *et al.* [38] showed that the most abundant species of exchangeable aluminum included Al^{3+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{SO}_4)^+$, AlF_2^+ , $\text{Al}(\text{oxalate})^+$, $\text{Al}(\text{H-citrate})^+$ and other Al organic acid species.

3. The Influence of Aluminum on Plant Physiology

Approximately 40% of all arable land possesses some degree of aluminum toxicity [39]. When soils become acidic, greater aluminum concentrations are typically present, which frequently become phytotoxic. Woody plant species generally are Al accumulators, whereas cereals typically have smaller aluminum accumulation rates [40]. For example, the leaves of *Oryza sativa*, *Glycine max* and *Zea mays* generally have aluminum concentrations less than 200 mg Al kg⁻¹. Rahman *et al.* [40] ranked important food crops for 1) high aluminum sensitivity (*Hordeum vulgare*, *Triticum aestivum*, *Glycine max*, *Phaseolus vulgare*), 2) moderate aluminum sensitivity (*Sorghum bicolor*, *Avena sativa*, *Medicago sativa*, *Secale cereale*), and 3) low aluminum sensitivity (*Oryza sativa* and *Zea mays*).

Aluminum adversely influences plant physiology, both in foliar and root organs, with root disturbances perceived as particularly troublesome. Krstic *et al.* [39] observed aluminum toxicity in the humid northern temperate and humid tropic zones. Examined soils exhibited acidic parent materials that were marginal in calcium, magnesium, potassium, and sodium contents or were extensively leached of these cations. Aluminum toxicity was more pronounced in the root apex, exhibiting reduced cell division and cell elongation. Root morphology changes with increasing aluminum toxicity include: 1) stunting, lateral root inhibition, 2) induction of β -1-3-glucan, and 3) restricted water and ion uptake. Trivalent aluminum (Al³⁺) and Al₁₃ [AlO₄ - Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺ were considered toxic [39] [41]. Rahman *et al.* [40] also indicated the phytotoxicity of both Al³⁺ and Al₁₃.

Phytotoxic Al primarily affects root growth, whereas shoot growth is a secondary effect [42] [43] [44]. Yang *et al.* [42] reviewed the interaction of soil available aluminum and drought stress on root growth and crop yield, with a special emphasis on acid soils. Plant responses to combined influences of Al phytotoxicity and drought are not simply the sum of the individual stressors. Phytotoxic Al modifies the cell wall and the plasma membrane, effectively reducing cell wall porosity. Aluminum accumulates in the root tip at the basal portion of the zone of cell division (meristem), effectively altering the cell wall plasticity and inhibiting cell enlargement in the adjacent zone of cell elongation. In the root apoplast aluminum binds with the pectin matrix, contributing to the cell wall's limited elasticity, ultimately limiting root hydraulic conductivity. Aluminum will also limit basipetal auxin signaling, associated with abscisic acid and cytokinin flux into the foliar components, which is manifested in stomatal closure and reduced leaf expansion. Aluminum phytotoxicity extends to the photosynthetic process with plant injury associated with 1) chloroplast alterations, 2) damage to photosystem II, 3) alterations in the photosynthetic electron chain. Rahman *et al.* [40] noted that phytotoxic aluminum levels influenced: 1) phosphorus (P) increased root respiration, chlorophyll content, and dry matter accumulation, 2) magnesium (Mg) prevented Al migration through cytosolic plasma

membrane in root tips, and 3) sulfur (S) protects plant functions from elevated concentrations of many metals. Merino-Gergichevich *et al.* [45] reported that Al^{3+} -toxicity promotes an increase in reactive oxygen species, causing damage to roots and chloroplasts by impairing membrane functionality. Aluminum toxicity encourages 1) leaf necrosis and chlorosis, 2) reductions in chlorophyll content, 3) reduced photosynthesis rates, and 4) abnormal chloroplast structure. Aluminum uptake may reduce calcium uptake, permitting calcium plant deficiency.

Calcium may form Al-Ca interactions which improve physiological and biochemical plant processes. Calcium plant uptake may reduce aluminum toxicity by 1) displacement of Al^{3+} on the cell surface by blocking plasma membrane channels, 2) restoration of Ca^{2+} on the membrane surface, and 3) other Al-Ca interactions. Although cultivar dependent, Vasconcelos *et al.* [46] used *Phaseolus vulgaris* to demonstrate that calcium reduced the deleterious effects of aluminum on growth and mineral nutrition; however, Ca did not reduce the deleterious effects of aluminum on leaf anatomy. Perry and Amacher [47] assessed the distribution of Ca:Al molar ratios across the conterminous United States. The study inferred that smaller Ca:Al ratios were associated with calcium leaching and mineral weathering or where free calcium carbonates exist (Western USA). The authors also noted that white/red and jack pine (*Pinus strobus*, *Pinus resinosa*, *Pinus banksiana*) are more tolerant of low Ca/Al ratios. In Vermont, Borer *et al.* [48] performed selective, sequential extractions involving red spruce (*Picea rubens*) plant tissues. The extractions included water, acetic acid, and hydrochloric acid. Calcium recovery from plant tissue perceived as deficient or sufficient was primarily associated with the water and acetic acid extractions. Plant tissue having calcium concentrations perceived as surplus exhibited calcium concentrations in the HCl extractions. Aluminum immobilization was related to the calcium extraction ratio of HCl to water and acetic acid, suggesting calcium sequestration, as Ca oxalate, was associated with aluminum tolerance.

Rao *et al.* [43] reviewed aluminum toxicity in soils having reduced availabilities of nitrogen and phosphorus. In their review, Rao *et al.* noted that high soil aluminum is associated with 1) inhibited root elongation with swollen and malformed root tips, 2) the rhizosphere presence is correlated with Al root hair tolerance, 3) inhibition of lateral roots, 4) inhibition of cell expansion and cell division, 5) disruption of the cell membrane, and 6) increased carboxylate production.

Eldhuset *et al.* [24] performed a solution culture experiment involving Norway spruce (*Picea abies*) and using glass beads as a soil substitute, with equilibrating solutions having a range aluminum activity. Norway spruce roots further cultured with and without mycorrhiza. Mycorrhiza increased oxalic acid exudation to the rhizosphere, which was associated with aluminum resistance. Jaiswal *et al.* [41] reviewed the influence of aluminum on legume microsymbionts. The noted reduced rhizobia populations, suppression of nitrogen metabolism, reduced nitrogenase activity, suppression of nodulation genes in symbiotic rhizo-

bia. They concluded that there appears to be a synergistic relationship between aluminum tolerance and ammonium nutrition. Zhang *et al.* [49] investigated aluminum toxicity upon earthworm (*Eisenia fetida*) populations. These authors showed that aluminum toxicity thresholds for earthworms were equal to or greater than 100 mg Al kg⁻¹. York *et al.* [50] demonstrated that root phenes may predict root characteristics. characterize root total root length or root length density is a function of axial root length, the number of axial roots, and the extent of lateral branching.

4. Aluminum and Forest Ecosystem Productivity

Soils in humid climates tend to become acidic. Rainfall in equilibrium with atmospheric CO₂ concentrations produce carbonic acid (H₂CO₃). Carbonic acid is a Bronsted acid that will buffer rainwater to a pH of approximately 5.6 [4] [10]. Thus, rainfall is naturally acidic and will slowly cause soil acidification. Rainfall also supports additional plant growth and development, encouraging more robust organic acid product and release to the soil. Rainfall with hydronium will cause calcium, magnesium, potassium, sodium and other cations to leach, providing exchange capacity for the retention of hydronium and aluminum [4] [10].

In agricultural systems, aluminum toxicity is alleviated using calcic or dolomitic limestone. The three-step process involves 1) finely divided limestone dissolution, 2) cation exchange of H₃O⁺ and Al³⁺ displacement involving cation exchange reactions with Ca²⁺ and Mg²⁺, and 3) H₃O⁺ neutralization with HCO₃⁻ and Al³⁺ neutralization with hydrolysis [4] [10].

It is well demonstrated that aluminum will adversely effect plant physiology; however, it is also very apparent that phytotoxic aluminum will influence ecosystem functioning, soil genesis and land management. Concentrating on temperate forest ecosystems, Aide *et al.* [51] investigated soil genesis of Ultisols and Alfisols in rhyolite residuum, detailing elemental loss and relative elemental gain, noting that aluminum interlayered vermiculite and kaolinite were substantially present in the eluvial horizons, thus limiting soil profile aluminum losses. Aide *et al.* [52] observed weathering of acidic bisequal Alfisols formed on loess over limestone residuum, noting the importance of soil profile aluminum retention and the loss of silicic acid upon the conversion of smectite to kaolinite. Aide and Aide [53] observed Wisconsin soils having spodic over alfic horizons, demonstrating the role of aluminum in Spodosol genesis.

Investigating Spodosols in the Adirondacks of New York, David and Driscoll [54] remarked that throughfall and leachates from the O, E and B soil horizons predominately contained aluminum complexes of organic acids and fluoride, with smaller quantities of sulfate and hydroxy-Al complexes. Biocycling of aluminum was considered a major aluminum transport pathway. Scheel *et al.* [55] showed that dissolved organic matter was precipitated by aluminum and subsequently stabilized against microbial decay. In the interior Pacific Northwest, Brown *et al.* [56] evaluated lime amendments in their efficiency in correcting 1) soil acidity, 2)

altering the aluminum soil chemistry, and 3) improving crop response. Modeling indicated the aluminum complexes with fulvic acid [FA_2Al^+ , $\text{FA}_2\text{Al}(\text{OH})$] substantially reduced the aqueous Al^{3+} activity. The solid and solution aluminum complexes control the Al^{3+} activity at pH levels less than 5.5. In the interior Pacific Northwest, the high levels of soil organic matter reduced the Al phytotoxicity, a feature attributed to reduced Al^{3+} activity [56].

Lundstrom *et al.* [57] reviewed the major mechanisms of the genesis of Spodosols including 1) the production and role of organic acids and their soluble complexes with aluminum/iron, 2) illuviation and subsequent precipitation and/or adsorption at greater soil profile depths. Precipitation of soluble complexes of organic-aluminum and organic-iron involves reduced solubility with additional Al or Fe complexation or because of microbial degradation of the organic complexes. April *et al.* [58] discussed Spodosol genesis in the Adirondack Mountains of New York, noting the importance of aluminum sesquioxide's in the formation and functioning of spodic horizons.

Dahlgren *et al.* [34] observed the soil chemistry influence on root activities in a subalpine Spodosol in Washington. Pacific silver fir (*Abies amabilis*) accumulated aluminum, particularly in fine roots. The aluminum root concentrations were not closely related to the total aqueous aluminum concentration; however, aluminum speciation was shown to be influential on plant uptake. Soil solution compositions demonstrated that 1) the highest concentrations of aluminum were in the E horizon and declined on progression from the Bh_s to B_s to C horizons, 2) organic anion concentrations paralleled the aluminum solution concentrations, suggesting the organic-Al complexes reduced Al-toxicity, and 3) calculated Al^{3+} activities were associated with root aluminum concentrations. Organic-Al complexes were presumed to have been more intensely adsorbed on the Bh_s and B_s horizons. Fulvic acids was the prevailing organic anion.

Collignon *et al.* [14] investigated aluminum toxicity in Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) forest stands in France, with an emphasis on seasonal sampling to discern seasonal variations in the soil chemistry. Aluminum toxicity was generally more intense under Norway spruce than beech. Trivalent aluminum and exchangeable aluminum increased significantly in February under the Norway spruce stand. Mineralization of soil organic matter and subsequent nitrification supported acidification, increasing the seasonal exchangeable aluminum concentration. The soil in the rhizosphere exhibited reduced aluminum phytotoxicity, a feature presumably attributed to a greater abundance of aluminum-soil organic matter complexes. Conversely, Gottlein *et al.* [32] documented that oak (*Quercus*) roots had a limited capacity to detoxify rhizosphere aluminum.

Turpault *et al.* [59] observed seasonal soil chemistry variations in the bulk soil and rhizosphere in Douglas fir (*Pseudotsuga menziesii* (Mirb) Franco) in the Beujolais Mounts of France. These authors demonstrated the pH, organic carbon, the cation exchange capacity, and base saturation increased on transition

from the bulk soil to the rhizosphere. Given the greater soil biological activity, the seasonal differences were more pronounced in June than March. The seasonal differences were attributed to nitrification and the uptake of nitrate by the roots, with the root response being the release of OH^- and HCO_3^- to preserve electrical neutrality. In France, Calvaruse *et al.* [60] compared soil physical and chemical properties of bulk soil with soil from the rhizosphere. They documented that the rhizosphere from a variety of forest species was typically enriched in carbon, nitrogen, calcium, magnesium, and potassium. The intensity of the enrichment of the rhizosphere was forest species dependent. Dieffenbach and Matzner E (2000) [61] demonstrated the influence of Norway spruce (*Picea abies*) on the rhizosphere, with significant increases of rhizosphere K^+ concentrations and smaller concentrations of Al^{3+} , H^+ and NH_4^+ .

In the northeastern United States, Lawrence *et al.* [62] investigated aluminum mobilization and calcium depletion in the forest floor of a red spruce (*Picea rubens*). They documented that acid-extractable calcium levels in the Oa horizons have appreciably declined. Correspondingly, extractable, and acid-extractable aluminum concentrations have increased. Recently, also in the northeastern United States, Hazlett *et al.* [63] showed that soil acidification has abated because of atmospheric sulfate reductions. Site factors important to documenting soil recovery from acidic rainfall included: 1) the duration of the recovery period, 2) sulfate history and deposition rates, 3) exchangeable levels for calcium and aluminum, and forest floor and soil pH levels.

In the Jizera Mountains (Czech Republic) Mladkova *et al.* [64] reported that Al_{13} , an aluminum polynuclear composed of one aluminum tetrahedron and 12 aluminum octahedrons, and trivalent aluminum (Al^{3+}) were the most toxic aluminum forms. The extraction of O and B horizons demonstrated that exchangeable Al was inversely related to exchangeable calcium and organic complexation of aluminum dominated the extractability of aluminum. Bradova *et al.* [23] observed aluminum variations in soils under spruce (*Picea abies*) and beech (*Fagus sylvatica*) in the Jizera Mountains in the Czech Republic. The organic horizons (F and H) exhibited greater concentrations of extractable aluminum than the eluvial inorganic horizons. The maximum concentrations of water extractable aluminum were determined in summer and the least in spring.

In northwestern Connecticut, Dijkstra and Fitzhugh [25] compared Al solubility and mobility in surface soil horizons having stands of sugar maple (*Acer saccharum*), white ash (*Fraxinus americana*), red maple (*Acer rubrum*), American beech (*Fagus grandifolia*), red oak (*Quercus rubra*) and hemlock (*Tsuga canadensis*). They examined the forest floor and soil under each tree stand for routine soil characterization, pyrophosphate extractable Al for assessment of organically bound Al, total carbon, and soil water chemistry. The forest floors in stands of red maple, beech, and red oak exhibited greater exchangeable and extractable aluminum. Greater exchangeable calcium concentrations in the sugar maple stand and elevated exchangeable hydronium in the Hemlock stand suppressed

exchangeable aluminum. Percolating dissolved organic carbon under hemlock appeared to have accumulated aluminum; however, the influence of tree species did not statistically influence the soil profile aluminum distribution.

The best plant species to cultivate are typically native plants. In agricultural settings nonlegumes are better able to grow and develop than legumes if the pH is between 5.5 and 6.0 [4].

5. Simulations of Aluminum Soil Chemistry

Minteq is software designed to determine solution equilibria with consideration of precipitation and dissolution, interactions with atmosphere species, inorganic and organic complex and ion-pair associations, oxidation-reduction reactions, and adsorption-desorption reactions [65]. In simulations in this manuscript, the ionic strength was established with 0.01 M NaNO₃, whereas activities were established using the Debye-Huckel equation at 25°C [66]. The aluminum total analytical concentration was set at 10⁻⁵ mol·L⁻¹ and all organic concentrations were set at 10⁻³ mol·L⁻¹.

The simulation of soil organic matter with aluminum utilized concepts associated with the NICA-Donnan [67]. Fulvic (FA) and humic (HA) acids and dissolved fulvic acids had two aluminum adsorption sites. Given the imposition of 0.01 g·l⁻¹ for the solid FA and HA and 0.02 g·l⁻¹. The site#1 and site#2 concentrations in units of mmol·L⁻¹ were FA (Site #1 of 0.059 and Site #2 of 0.019), HA (0.039 and 0.026), and FA dissolved (0.118, 0.037) [67].

The first simulation concerns assessment of the total aluminum concentrations in an aqueous system composed of Al³⁺ in equilibrium with freshly precipitated Al(OH)₃ across various pH intervals from 4 to 8 (Figure 1). The minimum aluminum solubility is near pH 6.5, with a rather gradual aluminum concentration increase upon transition into alkaline media. Upon transition to acidic media, aluminum solubility increases dramatically, especially on transition to pH levels less than pH 5.

The second simulation involves aluminum hydrolysis over the range of pH 4 to pH 8 (Table 2). Table 2 only presents data for Al³⁺, Al(OH)₂⁺, Al(OH)₂²⁺, Al(OH)₃, and Al(OH)₄⁻. Aluminum dimers and aluminum trimers are present at trace amounts given the Al solubility is presumed in equilibrium with non-crystalline Al(OH)₃. The simulation shows 94% of the aluminum is the trivalent species (Al³⁺) at pH 4, whereas 98% of the aluminum is Al(OH)₄⁻ at pH 8.

The Minteq simulation shows that aluminum-fluoride complexation is slightly pH dependent with AlF₃ and AlF₄ as the dominant Al-F species across the pH interval pH 4 to pH 7 (Table 3). The sum of the aluminum fluoride species is approximately 99% of the analytical aluminum concentration.

At pH levels of 4, 5 and 6 the simulation of Al with oxalate (Ox) shows that Al-(Ox)₃³⁻ is the dominant species, whereas at pH 7 the species Al(OH)₂-(Ox)⁻, Al-(Ox)₃³⁻ and Al(OH)-(Ox)₂²⁻ are the dominant species (Table 4). At pH 8,

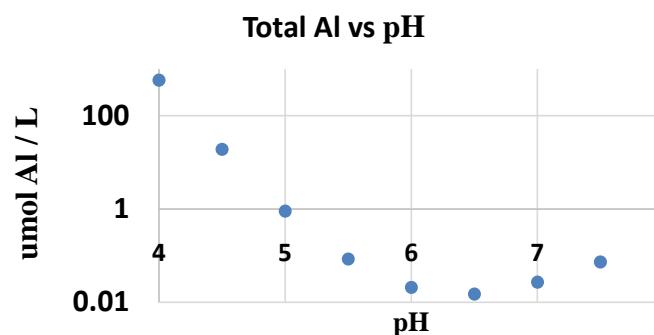


Figure 1. Total aluminum is equilibrium solution with respect to pH and equilibria with $\text{Al}(\text{OH})_3$.

Table 2. Aluminum hydrolysis species with respect to pH.

pH	Al^{3+}	$\text{Al}(\text{OH})$	$\text{Al}(\text{OH})_2$	$\text{Al}(\text{OH})_3$	$\text{Al}(\text{OH})_4$
	%	%	%	%	%
4	94	5.4	0.2	0	0
5	55	33	12.1	0.4	0.02
6	2.4	14	53.4	19.7	10.5
7	0	0.1	4.1	14.8	80.9
8	0	0	0.05	1.8	98.2

$\text{Al}_3(\text{OH})_4$ was less than 0.01 across all pH levels; $\text{Al}_2(\text{OH})_2$ was 0.8% at pH 4 and 0 elsewhere; $\text{Al}(\text{OH})_3$ was present as an infinite solid.

Table 3. Simulation of aluminum and fluoride across pH intervals.

pH	4	5	6	7
	%	%	%	%
AlF	0.04	0.03	0.03	0.03
AlF_2	8.2	7.1	7	7
AlF_3	64.4	62.9	62.7	62.5
AlF_4	27.4	29.4	30.2	30.2

$\text{Al}(\text{OH})_2\text{-(Ox)}^-$ is the dominant species (91%), showing the extensive pH-dependency of the aluminum oxalate species. The sum of the oxalate species is approximately 99% of the analytical aluminum concentration.

Simulations using Minteq for aluminum complexation with oxalate, acetate, citrate, DTPA (Diethylenetriamine pentaacetate), EDTA (Ethylenediaminetetraacetic acid), glutamate, malate, and catechol were performed (Table 5). The organic acids oxalate (oxalic), citrate (citric), DTPA, EDTA, and to a lesser extent catechol were very effective in forming Al complexes, whereas glutamate and malate were ineffective in forming aluminum complexes. Acetate did demonstrate a pH dependency, with pH 5 showing 91% of the aluminum showing complexation, whereas pH 7 demonstrating only 5% complexation. Drabek *et al.*

Table 4. Important aluminum oxalate species across pH intervals.

pH	4	5	6	7	8
	%	%	%	%	%
Al(OH) ₂ (Ox)	trace	trace	0.6	29.3	91.1
Al(Ox) ₂	24.9	14	12.1	5.9	0.2
Al(Ox) ₃	74.8	85.4	82.5	41.3	1.3
Al(OH)(Ox) ₂	0.1	0.5	4.5	22.3	7
Al(OH)(Ox)	trace	trace	0.3	1.3	0.4
Al(Ox)	0.2	trace	trace	trace	trace

(OX) is oxalic acid (oxalate).

Table 5. Aluminum complexation with several substrates.

Organic	pH 5	%Al complexed	pH 7	% Al complexed
Oxalate	Al-3(Oxalate) (85%)	99	Al-3(Oxalate) (85%)	99
	Al-2(Oxalate) (14%)		Al(OH)-Oxalate (29%) Al(OH) ₂ -Oxalate (22%)	
Acetate	Al(OH)-acetate (98.8%)	91	Al(OH)-acetate (99.9%)	5
Citrate	Al-2(Citrate) (76%)	99	Al-2(Citrate) (98%)	99
	Al-Citrate (24%)		Al-Citrate (2%)	
DTPA	Al-DTPA (72%)	99	Al-DTPA (48%)	99
	AlH-DTPA (27%)		Al(OH)-DTPA (52%)	
EDTA	Al-EDTA (93%)	99	Al-EDTA (13%)	99
	Al(OH)-EDTA (6%)		Al(OH)-EDTA (87%)	
Glutamate	Al-Glutamate (37%)	2	Al-Glutamate (0.6%)	1
	Al(OH)-Glutamate (62%)		Al(OH)-Glutamate (99%)	
Malate	No Malate-Al complexes	0	No Malate-Al complexes	0
Catechol	Al-catechol (94%)	85	Al-2(catechol) (83%)	99
	AlH-catechol (6%)		AlH-2(catechol) (14%)	

Numbers in parenthesis indicate percentage of Al complexed by that species relative to the total Al content that is complexed by all Al-organic anion species.

[68] used ion-exchange chromatography and high-performance liquid chromatography to demonstrate that oxalic acid and fulvic acid were much more efficient than citric or malic acid on influencing aluminum speciation.

Minteq simulated the influence of humic acids (HA), fulvic acids (FA) and dissolved FA on aluminum complexation (Table 6). As expected, the deprotonated mole fractions of FA, HA, and dissolved FA increased with increasing pH, supporting soil organic matters contribution to the cation exchange capacity. Aluminum complexation with FA was greatest for site#1 at pH 6 and greatest for

Table 6. Fulvic/humic acid complexation of aluminum across pH levels (Percent).

Organic species	Protonated	Deprotonated	Al-Complexed
pH 4			
Fulvic Acid-Site#1	61.4	38.3	0.23
Fulvic Acid-Site#2	96.9	1.8	1.2
Humic Acid-Site#1	72.1	26.9	0.97
Humic Acid-Site#2	93.6	4.7	1.8
Fulvic Acid Dissolved-Site#1	51.2	48.7	0.12
Fulvic Acid-Dissolved-Site#2	97	1.8	1.2
pH 5			
Fulvic Acid-Site#1	46.1	53.4	0.47
Fulvic Acid-Site#2	90.9	5.4	3.7
Humic Acid-Site#1	52.2	45.4	2.4
Humic Acid-Site#2	87.1	8.7	4.2
Fulvic Acid Dissolved-Site#1	33.4	66.3	0.18
Fulvic Acid-Dissolved-Site#2	91.4	5.1	3.4
pH 6			
Fulvic Acid-Site#1	30.6	68.7	0.6
Fulvic Acid-Site#2	78.9	12.6	8.6
Humic Acid-Site#1	29.8	66.7	3.5
Humic Acid-Site#2	77.4	14.7	7.9
Fulvic Acid Dissolved-Site#1	18.4	81.4	0.16
Fulvic Acid-Dissolved-Site#2	81.0	11.4	7.6
pH 7			
Fulvic Acid-Site#1	17.0	82.7	0.3
Fulvic Acid-Site#2	71.4	17.1	11.5
Humic Acid-Site#1	14.3	83.7	2.0
Humic Acid-Site#2	72.0	19.2	8.8
Fulvic Acid Dissolved-Site#1	8.8	91.1	0.06
Fulvic Acid-Dissolved-Site#2	74.3	15.6	10.1

site#2 at pH 7, whereas aluminum complexation with HA was greatest for site#1 at pH 5 and greatest for site#2 at pH 7. The humic acid fraction exhibited the greatest aluminum complex activity at pH 4 to 6, whereas the FA dissolved site#2 fraction at pH 7 had the greatest aluminum complexation activity.

6. Perspective and Potential Areas for Investigation

In many regions, agricultural limestone has been soil applied to 1) reduce soil acidity and aluminum phytotoxicity, 2) improve soil structure, 3) support a

more robust microbial community and 4) supply calcium and possibly magnesium. However, calcite and dolomite also release CO₂ during the reaction interval, an important greenhouse gas. Thus, alternatives to the widespread usage of agricultural limestone are desired. One attractive option is breeding for aluminum plant tolerance. Molecular investigation in the biochemical pathways influenced by aluminum may provide additional information for cultivar selection and breeding. Similarly, new technologies for ammoniacal nitrogen applications are desired to minimize nitrification and its amplification of soil acidity.

Aluminum has been associated with soil organic matter complexation/precipitation and promoting soil organic matter stability against further microbial decay. Thus, new technologies for supporting soil carbon sequestration deserve greater scrutiny. Additionally, agriculture systems that support soil organic matter buildup likely have the benefit of reducing aluminum phytotoxicity.

Acidic rainfall is defined as rainfall having a pH less than 5.6, which is the theoretical value for rainfall influence by nominal carbon dioxide partial pressures. Pollution controls associated with coal combustion and similar industries has reduced the influence of acidic rainfall. However, this beneficial activity needs to be more universally supported. The influence of aluminum on soil biology remains largely unexplored.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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