

Ecological Soil Screening Level for Aluminum

Interim Final

OSWER Directive 9285.7-60



U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

November 2003

This page intentionally left blank

TABLE OF CONTENTS

SUMMARY ECO-SSLs FOR ALUMINUM

1.0	INTRODUCTION	<u>1-1</u>
2.0	ALUMINUM CHEMISTRY	<u>2-1</u>
3.0	EFFECTS OF ALUMINUM ON PLANTS	<u>3-1</u>
	3.1 General Effects	<u>3-1</u>
	3.2 Essentiality	<u>3-3</u>
	3.3 Effect on Phosphorus and Calcium	<u>3-3</u>
	3.4 Differential Tolerance of Plants to Aluminum Toxicity	<u>3-4</u>
4.0	UPTAKE AND ACCUMULATION OF ALUMINUM BY PLANTS	<u>4-1</u>
	4.1 Plant Uptake of Aluminum	<u>4-1</u>
	4.2 Accumulation of Aluminum in Plant Tissue	<u>4-2</u>
5.0	EFFECTS OF ALUMINUM ON SOIL INVERTEBRATES	<u>5-1</u>
6.0	UPTAKE AND ACCUMULATION OF ALUMINUM IN SOIL INVERTEBRATES	<u>6-1</u>
7.0	MEASURING ALUMINUM IN SOILS	<u>7-1</u>
	7.1 Total Aluminum	<u>7-1</u>
	7.2 Exchangeable and Extractable Aluminum	<u>7-1</u>
	7.3 Soluble Aluminum	<u>7-3</u>
8.0	CONCLUSIONS ON SCREENING SOILS FOR ALUMINUM TOXICITY	<u>8-1</u>
9.0	LITERATURE CITED	<u>9-1</u>

This Page Intentionally Left Blank

SUMMARY OF ECO-SSLs FOR ALUMINUM

Aluminum (Al) is the most commonly occurring metallic element, comprising eight percent of the earth's crust (Press and Siever, 1974). It is a major component of almost all common inorganic soil particles, with the exceptions of quartz sand, chert fragments, and ferromanganiferous concretions. The typical range of aluminum in soils is from 1 percent to 30 percent (10,000 to 300,000 mg Al kg⁻¹) (Lindsay, 1979 and Dragun, 1988), with naturally occurring concentrations varying over several orders of magnitude.

EPA recognizes that due to the ubiquitous nature of aluminum, the natural variability of aluminum soil concentrations and the availability of conservative soil screening benchmarks (Efroymson, 1997a; 1997b), aluminum is often identified as a COPC for ecological risk assessments. The commonly used soil screening benchmarks (Efroymson, 1997a; 1997b) are based on laboratory toxicity testing using an aluminum solution that is added to test soils. Comparisons of total aluminum concentrations in soil samples to soluble aluminum-based screening values are deemed by EPA to be inappropriate.

The standard analytical measurement of aluminum in soils under CERCLA contract laboratory procedures (CLP) is total recoverable metal. The available data on the environmental chemistry and toxicity of aluminum in soil to plants, soil invertebrates, mammals and birds as summarized in this document support the following conclusions:

- Total aluminum in soil is not correlated with toxicity to the tested plants and soil invertebrates.
- Aluminum toxicity is associated with soluble aluminum.
- Soluble aluminum and not total aluminum is associated with the uptake and bioaccumulation of aluminum from soils into plants.
- The oral toxicity of aluminum compounds in soil is dependant upon the chemical form (Storer and Nelson, 1968). Insoluble aluminum compounds such as aluminum oxides are considerably less toxic compared to the soluble forms (aluminum chloride, nitrate, acetate, and sulfate). For example, Storer and Nelson (1968) observed no toxicity to the chick at up to 1.6% of the diet as aluminum oxide compared to 80 to 100% mortality in chicks fed soluble forms at 0.5% of the diet.

Because the measurement of total aluminum in soils is not considered suitable or reliable for the prediction of potential toxicity and bioaccumulation, an alternative procedure is recommended for screening aluminum in soils. The procedure is intended as a practical approach for determining if aluminum in site soils could pose a potential risk to ecological receptors. This alternative procedure replaces the derivation of numeric Eco-SSL values for aluminum. Potential ecological risks associated with aluminum are identified based on the measured soil pH. Aluminum is identified as a COPC only at sites where the soil pH is less than 5.5.

This Page Intentionally Left Blank

1.0 INTRODUCTION

Aluminum (Al) is the most commonly occurring metallic element, comprising eight percent of the earth's crust. Only oxygen and silicon are more abundant (Press and Siever, 1974). It is a major component of almost all common inorganic soil particles with the exceptions of quartz sand, chert fragments, and ferromanganiferous concretions. The typical range of aluminum in soils is from 1% to 30% (10,000 to 300,000 mg Al kg⁻¹) [compiled by Lindsay (1979) and Dragun (1988)]. In his text book on *Chemical Equilibria in Soils*, Lindsay (1979) used an arbitrary aluminum reference concentration for all soils as averaging 7.1% (71,000 mg Al kg⁻¹).

Aluminosilicates, including the feldspars, micas, and clay minerals, are the most common primary and secondary minerals in soils (McLean, 1965). Aluminum oxide, Al₂O₃, occurs as corundum and emery. The hydroxide, Al(OH)₃, occurs as gibbsite. Diaspore (AlOOH) and cryolite are other sources of soil aluminum (Hesse, 1972). Aluminum also occurs in interlayer positions in clays, often forming complete layers to which the term chlorite is sometimes applied.

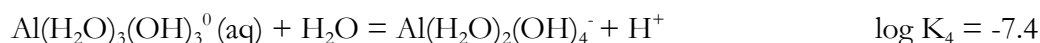
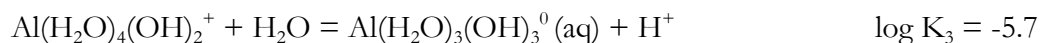
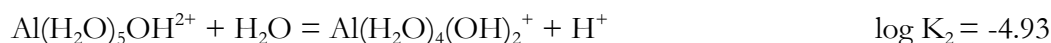
This Page Intentionally Left Blank

2.0 ALUMINUM CHEMISTRY

The aluminum ion bonds through oxygen to form a wide variety of functional groups. In igneous rocks, aluminum is largely bonded to oxygen ions in tetrahedral coordination. As the rocks weather, aluminum progressively acquires more octahedral bonding. The weathering release of aluminum from 2:1 layer silicates in soils is enhanced by inputs of acids from the natural decomposition of organic matter and minerals and from pollution (McBride, 1994). Acids as weak as dilute H_2CO_3 have been shown to decompose the silicate and montmorillonite layers facilitating the release of aluminum (Jackson, 1963).

The hydrated aluminum ion (Al hexahydronium ion) is an acid in the general sense that it contains protons (hydrogen ions) removable from the six water molecules ($-\text{OH}_2$) surrounding the aluminum in an octahedral coordination. For simplicity these hydrolysis species are generally written without the hydrated water even though the water is present. This trivalent cation complex occurs in acid solutions of pH 5.0 or 5.2 and below (Jackson, 1963; McLean et al., 1965; Tisdale and Nelson, 1975). As the pH of the soil solution increases, first one and then two of the ($-\text{OH}_2$) groups lose a hydrogen ion to form an ($-\text{OH}$) ion, resulting in di- or mono-valent hydroxyaluminum cations. All three of these cation species are adsorbed by negatively charged (cation) exchange sites in the soil. The di- and monovalent forms are adsorbed more strongly than $\text{Al}(-\text{OH}_2)_6^{3+}$ (McLean et al., 1965; Jackson, 1963). This ion is octahedrally hydrated and therefore less strongly held electrostatically and by hydrogen bonding than are the di- or mono-valent hydroxy-aluminum cations (Jenny, 1961). It is readily displaced from the clay with a neutral salt such as potassium chloride (Jenny, 1961; Jackson, 1963; McLean et al., 1965; Tisdale and Nelson, 1975).

As the pH increases still further, the third ($-\text{OH}_2$) group loses a hydrogen ion, and aluminum hydroxide, $\text{Al}(\text{OH})_3 \bullet 3\text{H}_2\text{O}$, is formed. The steps in the dissociation of protons from the hydrated aluminum ion in dilute solution may be represented by the following equations (Jackson, 1963; Black, 1968; Lindsay, 1979; McBride, 1994; Tisdale and Nelson, 1975):



The concentrations of these species as a function of pH are shown in Figure 2.1.

Once soil pH is lowered much below 5.5, aluminosilicate clays and aluminum hydroxide minerals begin to dissolve, releasing aluminum-hydroxy cations and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ that then exchange with other cations from soil colloids. The fraction of exchange sites occupied by $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and its hydrolysis products can become large once the soil pH falls below 5.0.

Furthermore, as the pH is lowered, the concentration of soluble aluminum, which is toxic, increases (McBride, 1994).

The chemistry of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (normally written without the water molecules as Al^{3+}) in soil solution is complicated by the fact that soluble inorganic and organic ligands form complexes with Al^{3+} . Whether a ligand increases or decrease aluminum solubility depends on the particular aluminum-ligand complex and its tendency to remain in solution or precipitate. Ligands that increase the overall solubility of aluminum include F^- , oxalate²⁻, citrate³⁻, fulvic acid, and monomeric silicate. Those that decrease the overall solubility of aluminum include phosphate, sulfate, polymeric silicate, and hydroxyl. It is usually the case that a large fraction of the soluble aluminum is found in the form of organic and fluoride complexes. Some of the aluminum may also be complexed with soluble silicate. There is evidence that these various complexed forms of aluminum are much less phytotoxic than soluble Al^{3+} or Al-hydroxy cations. In fact, the Al^{3+} activity in soil solution is better correlated to diminished root growth in acid soils than is total soluble aluminum or exchangeable aluminum as a fraction of cation exchange sites (McBride, 1994).

There is some evidence to suggest that the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ polymeric cation is highly phytotoxic. This is a metastable species, however, that may not exist in soil solutions. It may be formed by localized and transitory high pH conditions created during the titration of aluminum salt solutions with strong base (McBride, 1994).

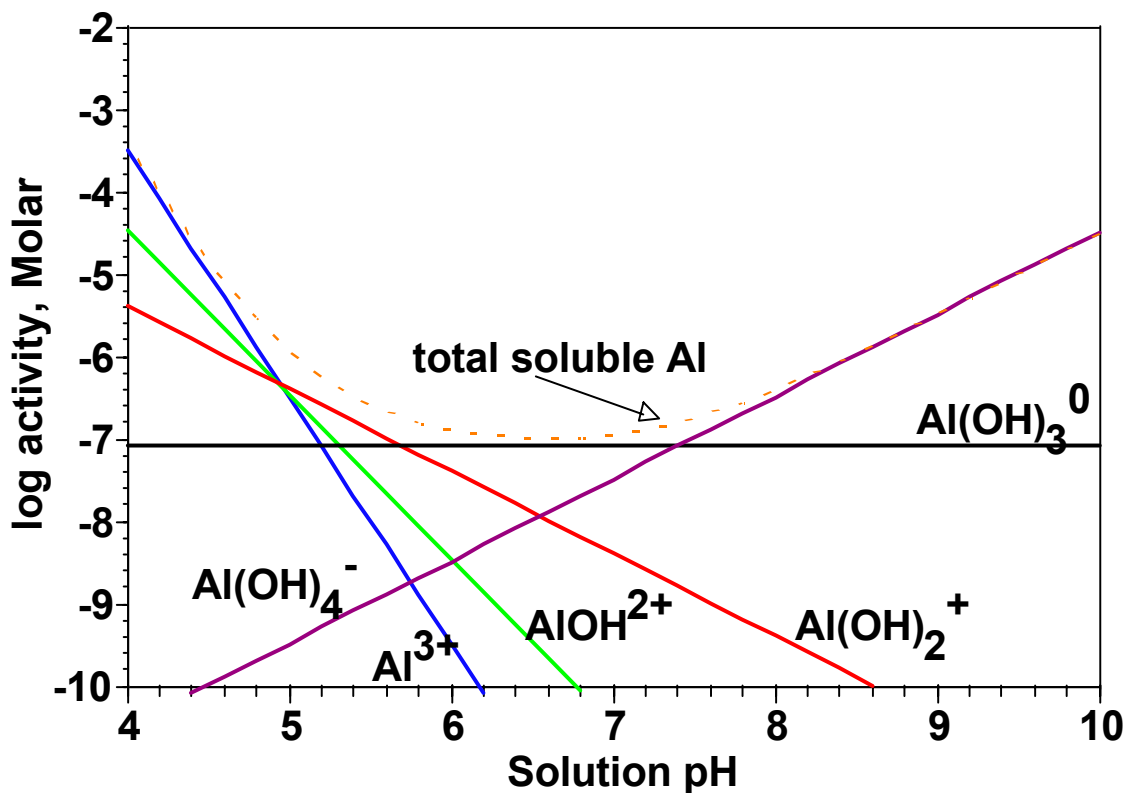


Figure 2.1. Solubility diagram of the most significant species of aluminum in an aqueous solution of AlCl_3 . Gibbsite (Al(OH)_3) is present as the solid phase at all pH values. The broken line depicts total soluble aluminum (sum of all species concentrations). Polymetric aluminum- hydroxy cations are not significant species under the conditions of this system (from McBride, 1994).

This Page Intentionally Left Blank

3.0 EFFECTS OF ALUMINUM ON PLANTS

The extensive research literature in the agricultural sciences on the effects of aluminum on plants dates back nearly a century. There is an ongoing need to identify not only the essential plant nutrients but also factors that limit optimal plant growth and productivity. Once aluminum was found to limit plant growth, efforts were made to discover the modes of action for aluminum toxicity, the ways to predict which soils were aluminum toxic, the methods to amend these problem soils to ameliorate aluminum toxicity, and breeding programs to produce aluminum tolerant plants.

3.1 General Effects

The toxic effects of aluminum on plants has been noted by many workers. Toxic levels of aluminum decrease the height and both the fresh and dry weight yields of plants (Rees and Sidrak, 1961; Munns, 1965; Hortenstine and Fiskell, 1961). The effects on roots occur long before any noticeable effects to the tops (McLean and Gilbert, 1927). The first evidence of injury in the roots is a discolored appearance. Then lateral roots become stunted, or fail to develop, and the whole root system fails to elongate (McLean and Gilbert, 1927; and Rhue and Grogan, 1977). This effect on root elongation has also been reported by Clarkson (1965), Matsumoto et al. (1976), Keser et al. (1975), Lafever et al. (1977), Rees and Sidrak (1961), and Fleming and Foy (1968). Injury to roots is characterized by a disorganization of the root cap, root apex, and vascular elements (Fleming and Foy, 1968). According to a study by McLean and Gilbert (1927), it appeared as if aluminum decreased the permeability of the roots to water and nutrients

The toxic effects of aluminum to plants are observed in association with soluble aluminum (Al^{3+}). For example, Mulder et al. (1989) observed a dose response relationship between 'Tyler' wheat root length versus the concentration of Al^{3+} (see Figure 3.1).

In addition, several studies of conifers grown in Al-enriched solutions at a pH lower than 5.5 resulted in reduced root growth rates (Hutchinson et al. 1986), shorter roots, less root mass, and lower root:shoot ratios than controls (Nosko et al. 1988), and reduced root elongation (Eldhuset et al. 1987). When beech trees were exposed to Al-enriched solutions at a pH range of 4.2 to 5.4, their leaves, roots and stems were 21% to 44% lower than controls (Bengtsson et al. 1988) (Sparling and Lowe, 1996).

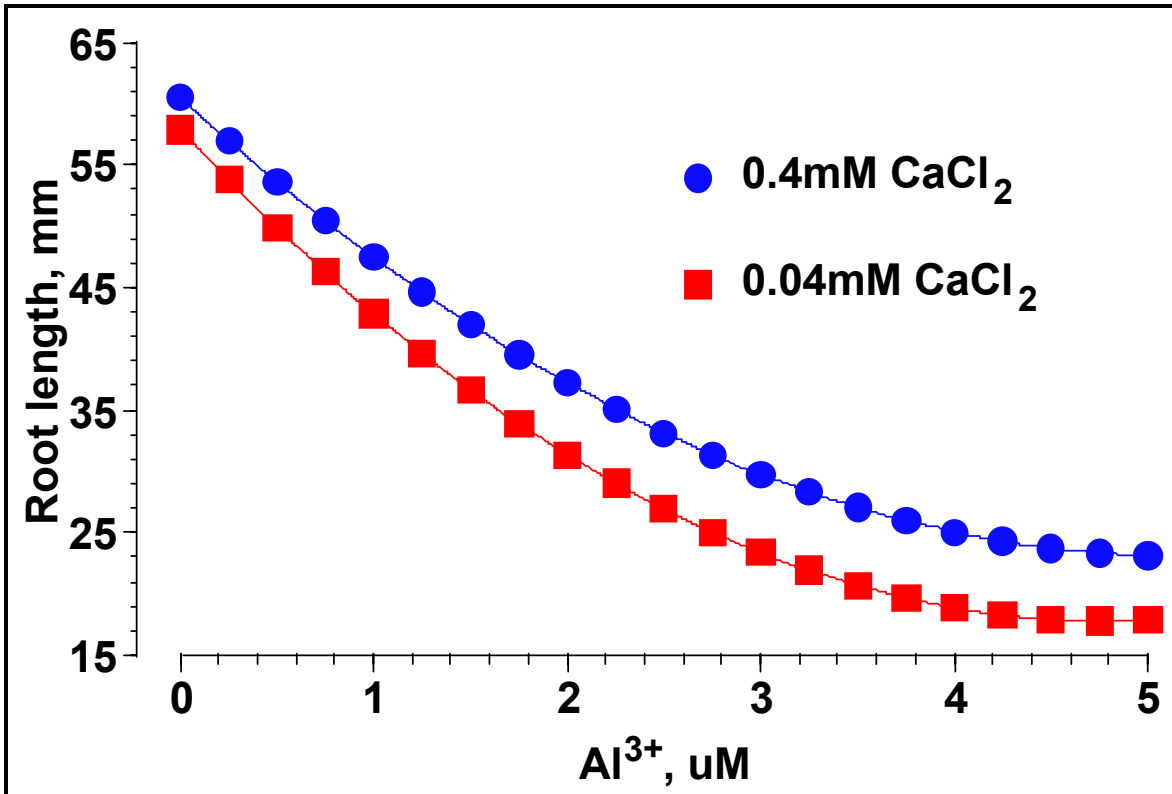


Figure 3.1. 'Tyler' wheat root length versus concentration of Al³⁺ (from Parker et al., 1989).

3.2 Essentiality

Although there is no convincing evidence of its essentiality in plants, aluminum has long been known to be a constituent of a blue pigment in *Hydrangea* (Chenery, 1948). There also have been many examples reported over the past 50 years in which plant growth has been stimulated by subtoxic concentrations of aluminum (Matsumoto et al., 1976; Bertrand and de Wolf, 1968). The beneficial effects of aluminum may relate to reduction by the aluminum of the uptake of a second element present in the root environment at potentially toxic concentrations (Liebig et al., 1942; Suthipradit, 1988). In most cases in which positive effects of aluminum on plant growth have been reported, there has been insufficient supporting information to establish whether or not they were indirect effects mediated through alleviation of toxicity of another element. Most positive responses to aluminum have been observed at nominal aluminum concentrations of ≤ 37 mmM. However, because of the ease with which free aluminum ions are lost from solution by complexation, polymerization, and precipitation reactions, the actual aluminum concentrations in solution have probably been much lower (Asher, 1991)

3.3 Effect on Phosphorus and Calcium

In addition to root growth inhibition, a decrease in the uptake and utilization of phosphorus is the primary symptom of aluminum toxicity in some susceptible plant species (MacLean and Chiasson, 1966; Naidoo et al., 1978). Aluminum inactivates phosphorus, primarily within the roots of plants, and thus interferes with the normal phosphate metabolism of plants (Wright, 1943; Wright, 1945; Wright and Donahue, 1953). Naidoo et al. (1978) found that aluminum and phosphorus were mainly concentrated on or in the outer cells of the root caps. Utilizing a scanning electron microscope focused at one point, Naidoo et al. (1978) found that "spot" analysis of the outer cell of snapbean and cotton root caps at high magnification showed that aluminum and phosphorus formed a precipitate at the cell surface when aluminum was present in nutrient solution. Data from Clarkson (1966) indicated that 85 to 95% of the aluminum in the roots was located in the cell wall fraction. This aluminum seemed to fix the phosphorus by an absorption-precipitation reaction, an extension of the reaction found in soils. According to McCormick and Borden (1972 and 1974), the Al-PO₄ precipitate occurred as scattered globules rather than as a continuous layer. The absorption-precipitation phenomenon occurred in the extracellular and intercellular material of the root cap. McCormick and Borden (1972) also concluded that aluminum may not only reduce phosphate availability by preventing the uptake of external sources, but also may be able to "extract" the phosphate from the root tissue and disrupt important metabolic activities.

In addition to the nonmetabolic interaction between aluminum and phosphate at the cell surface or in the free space, a small proportion of the total aluminum found in the root appears to be inside the cell. Internal precipitation of phosphorus cannot explain the rapid cessation of cell division in terms of phosphorus starvation. Any interaction between aluminum and phosphorus must be at a metabolic level rather than a phosphorus deficiency through precipitation in order for cell division to stop suddenly. The results of Clarkson (1965) showing reduction and cessation of root growth might be explained by an effect of aluminum on the turn-over of certain key phosphorylated compounds such as adenosine triphosphate (ATP). Observations suggested

aluminum may either inhibit hexokinase or combine with the substrate to make it unavailable (Clarkson, 1966).

Aluminum within root cells probably accumulates by ion exchange onto enteric phosphorus in the nucleic acids and membrane lipids. aluminum in the nuclei may act directly to reduce or inhibit cell division by interference with nucleic acid replication (Clarkson, 1965; Matsumoto et al., 1976; Naidoo et al., 1978). Ragland and Coleman (1962) and Rees and Sidrak (1961) postulated that aluminum may cause a rearrangement of cell constituents and the protoplasm to coagulate.

Researchers have observed that aluminum causes a calcium deficiency in plants (Long and Foy, 1970; Armiger et al., 1968; Vlamis, 1953; Evans and Kamprath, 1970; MacLean and Chiasson, 1966) which was due not to a deficiency of calcium in the growth medium, but to the detrimental effect of aluminum on adsorption and translocation of calcium.

3.4 Differential Tolerance of Plants to Aluminum Toxicity

Species of plants show a considerable difference in the amount of aluminum they are able to tolerate. Susceptible plants can tolerate no more than one or two parts per million (ppm) in nutrient solutions while other plants can tolerate over 100 ppm with little damage (McLean and Gilbert, 1927; Ligon and Pierre, 1932; Peiffer, 1976; Chapman, 1966). Rhue and Grogan (1977) and Reid et al. (1969) theorized that aluminum tolerance is genetically controlled. Vose and Randall (1962) cite the cation exchange capacity of the roots as a possible factor in aluminum resistance. Tolerance to both aluminum and manganese toxicities was associated with a low cation exchange capacity of the plant root, which favors mono- to di-valent uptake in accordance with the Donnan theory. Naidoo et al. (1978), Keser et al. (1975), and Foy et al. (1978) postulated that tolerant plants have a mechanism for preventing aluminum uptake. Foy et al. (1978) found that certain aluminum-tolerant cultivars of wheat, barley, rice, peas, and corn had the ability to increase the pH of the small quantities of nutrient solutions in which they were grown. The increase in pH decreased the solubility and toxicity of aluminum. The exact physiological mechanism of aluminum- tolerance or toxicity, however, was unresolved (Foy et al., 1978).

4.0 UPTAKE AND ACCUMULATION OF ALUMINUM BY PLANTS

4.1 Plant Uptake of Aluminum

According to Rasmussen (1968), the epidermal cells appear to effectively exclude the aluminum from entering the root at the root cap. The mode of aluminum entry begins with the growth of a lateral root from the pericycle. As the lateral root enlarges, the cells of the endodermis divide, and, as the root forces its way through the cortex of the parent root, the lateral root is encased in an endodermal layer. Once the root breaks through the surface, however, the endodermal layer dies and sloughs-off, creating a path by which aluminum and other elements can penetrate into the cortical and vascular tissue of both the lateral and parent roots.

Bioavailability of aluminum for plant uptake and toxicity is associated with pH, since aluminum is soluble and biologically available in acidic (pH <5.5) soils and waters, but is biologically inactive in circumneutral to alkaline (pH 5.5-8.0) conditions. In alkaline soils and solutions (pH >8.0), the solubility of aluminum increases, but its bioavailability is poorly known (Sparling and Lowe, 1996).

Weathering or acidification to pH below 5.5 increases the dissolution kinetics of Al and places some of the metal into solution, where it is readily bioavailable to living organisms (although dissolved organic carbons, such as F, PO_3^{3-} and SO_4^{2-} can ameliorate toxicity by reducing bioavailability) (Sparling and Lowe, 1996). Once in solution, Al may combine with several organic complexes, especially oxalic, humic, and fulvic acids. Aluminum may also combine with inorganic molecules, including sulfate (SO_4^{2-}), fluoride (F⁻), phosphate (PO_3^{3-}), bicarbonates (HCO_3^-), or hydroxides (OH⁻), depending on the relative concentrations of these anions. Biological activity and toxicity vary with composition. For example, Al sulfates are generally considered less toxic than hydroxide or organically bound Al (Driscoll and Schecher 1988). Aqueous Al (Al^{3+}), however, is more chemically and biologically active than that bound to soil or sediments (Sparling and Lowe, 1996).

Monomeric and hydrolyzed forms of Al [Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$] are typically the most toxic, whereas, polymeric and organically bound forms have slight to no phytotoxicity (Fageria et al. 1988; Taylor, 1988). Often, the sum of the concentrations of monomeric Al is used to estimate the phytotoxicity to a growing medium. Although Parker et al. (1989) contended that polymeric Al can be as toxic as Al^{3+} in nutrient solutions, polymeric Al is generally not soluble in soil and therefore, should not be as toxic. In soil, the concentration of Al^{3+} may suffice to predict toxicity (Sparling and Lowe, 1996).

4.2 Accumulation of Aluminum in Plant Tissue

Root staining techniques have shown that aluminum accumulates principally in the root tips of the main root and lateral root tissue, with small quantities in the cortex and epidermal cells (McLean and Gilbert, 1927; Fleming and Foy, 1968; Matsumoto et al., 1976). Aluminum has a high affinity for pectin so that cell wall surfaces of the Donnan Free Space are the most obvious areas for aluminum to concentrate upon entering the root (Rorison, 1965; Clarkson, 1967).

Data on aluminum uptake by roots suggest that, in the initial stages, most of the aluminum incorporated becomes bound to the adsorption sites in the cell wall, most likely to free carboxyl groups. Aluminum may also be precipitated on the root or cell surfaces as $\text{Al}(\text{OH})_3$ by the hydrolysis of $\text{Al}(\text{OH})_2$ and $\text{Al}(\text{OH})$ by free carboxyl groups (Clarkson, 1967). The positively charged amorphous aluminum hydroxides are known to adsorb and precipitate phosphorus from solution, forming $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$. This same thing can happen on cell surfaces effectively reducing the concentration of phosphorus available for metabolic uptake (Clarkson, 1967).

5.0 EFFECTS OF ALUMINUM ON SOIL INVERTEBRATES

A preliminary review of the literature revealed only one study on the toxicity of aluminum to earthworms or other soil invertebrates. Van Gestel and Hoogerwerf (unpublished), as reported by Van Gestel (1992), determined the influence of soil pH on the sublethal toxicity of aluminum for *Eisenia andrei* in artificial soil. Effects on growth and reproduction were studied in worms exposed for 6 weeks (Table 5.1). Results were expressed in terms of a No-Observed-Effect-Concentrations (NOEC). They concluded that low soil pH significantly increased aluminum toxicity. At the highest pH tested (7.3), earthworm growth was significantly increased at high aluminum concentrations in soil. This increased growth was not related, however, to the aluminum dose. The effect of aluminum on cocoon production did not seem to be influenced by soil pH. At pH 3.4 (lowest pH reported), all worms died at 1000 mg Al kg⁻¹ dry soil. At this pH level cocoon production was almost completely inhibited at 320 mg Al kg⁻¹, whereas at pH 4.3 and 7.3 it was only halved at this concentration. Cocoon production in control groups was significantly reduced at pH 3.4 compared to the two higher pH soils. Aluminum extracted with 1N calcium chloride appeared to decrease with increasing soil pH. The effects on growth and cocoon production could, however, only partially be related to the amount of free aluminum in the soil. They concluded that other factors apparently also played a role.

Table 5.1. Influence of soil pH on the effect of aluminum on <i>Eisenia andrei</i> in artificial soil (6 weeks exposure).			
Parameter	NOEC (mg Al/kg dry soil) at pH		
	3.4	4.3	7.3
Survival	320	1000 ^a	1000 ^a
Growth	100	1000 ^a	32 ^b
Cocoon production	100	100	100
Cocoon fertility	100	1000 ^a	1000 ^a
Juveniles/fertile cocoons	100 ^a	1000 ^a	1000 ^a

^a Reliability of this value is low due to a low number of cocoons
^b Growth was significantly increased at higher concentrations of aluminum

This Page Intentionally Left Blank

6.0 UPTAKE AND ACCUMULATION OF ALUMINUM IN SOIL INVERTEBRATES

Data on the uptake and accumulation of aluminum from soil pore water into soil invertebrates could not be located for review.

This Page Intentionally Left Blank

7.0 MEASURING ALUMINUM IN SOILS

When researchers, using nutrient solutions, displaced soil solutions, and soils at various pH levels, discovered that conditions toxic to plants in acid soils were due, in many cases, to toxic levels of aluminum, it was apparent that a way of determining the plant available aluminum could be useful for the evaluation of the potential toxicity of a particular soil. Many different methods of measuring aluminum in soils have been used. Displacement of the soil solution, the use of acid solutions, and buffered and unbuffered salt solutions are reported as methods for extracting aluminum.

7.1 Total Aluminum

Total aluminum is often measured in soils because it provides useful information on the characterization of soils with respect to the origin of parent materials and weathering. It also serves as a basis for calculating the mineralogical composition of the sample (Bertsch and Bloom, 1996). Total soil aluminum as a direct measure of aluminum toxicity, however, appears to have little or no value based on the previously presented information. It is not possible to correlate the soil solution concentration of aluminum to the total soil aluminum measurement. Mulder et al. (1989) measured total soil aluminum (%) and soil solution aluminum in samples collected below plant rooting zones and found no relationship between the two concentrations (Figure 7.1).

7.2 Exchangeable and Extractable Aluminum

Exchangeable and extractable aluminum, displaced most commonly with an unbuffered salt solution such as 1M KCl, 0.5M CaCl₂, or 0.5M BaCl₂, traditionally have had two primary uses. The first is the formulation of lime requirements for acid soils (Kamprath, 1970; Reeve and Sumner, 1970; Amedee and Peech, 1976; Farina et al., 1980; Juo and Kamprath, 1979; Oates and Kamprath, 1983a,b). Second, because of its importance as a predominant cation in acid soils, exchangeable aluminum is a critical variable in establishing effective cation exchange capacity (ECEC) values, which are utilized for soil management and classification purposes, and in evaluating changes in forested soils influenced by acidic deposition and land-use practices (Juo et al., 1976; Pavan et al., 1984; Evans and Zelazny, 1987; Mulder et al., 1987; Lillieholm and Feagley, 1988; Adams et al., 1990; Reuss et al., 1990; Rasmussen et al., 1991). For these applications, investigators are interested in arriving at a reproducible measure of exchangeable Al³⁺ that reflects aluminum exchange equilibria as accurately as possible (Bertsch and Bloom, 1996).

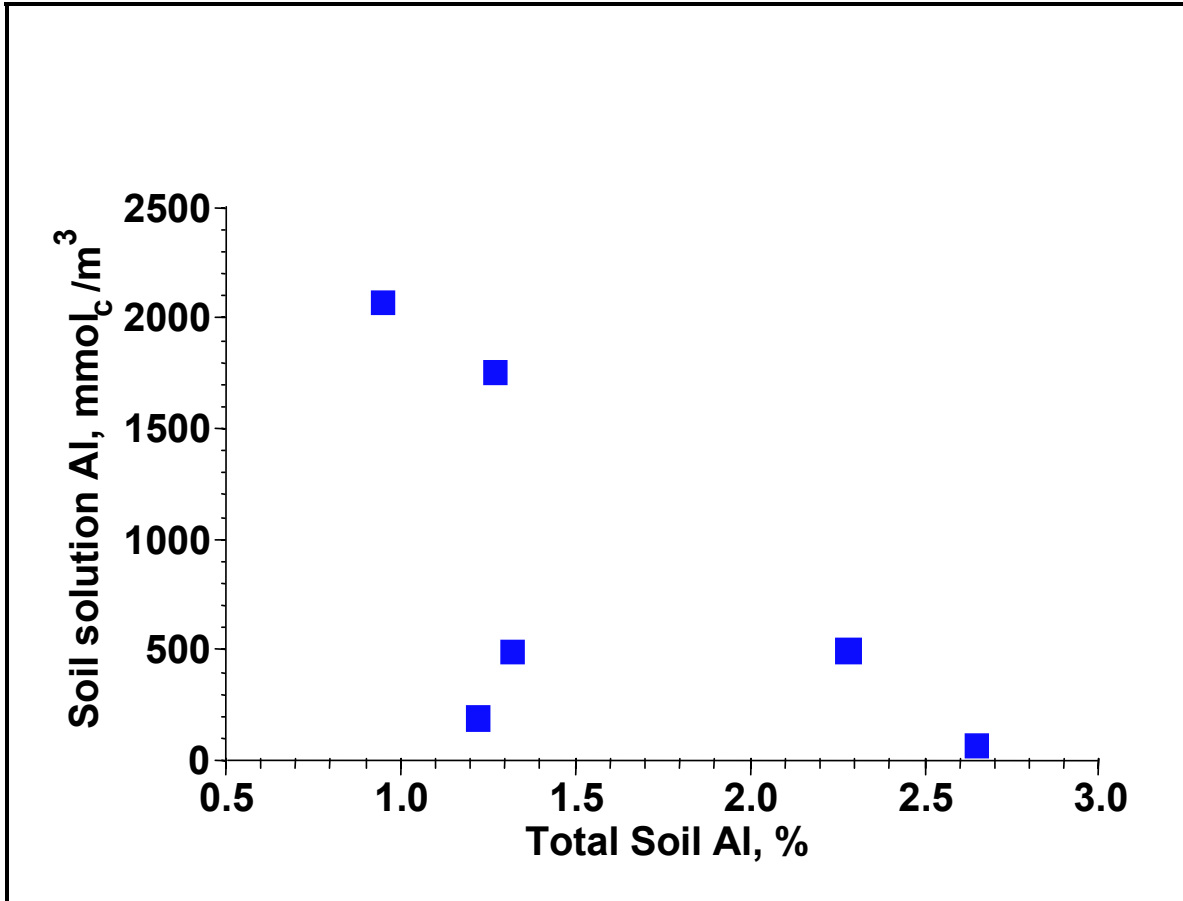


Figure 7.1. Soil solution aluminum collected below plant rooting zones (from Mulder et al., 1989).

7.3 Soluble Aluminum

Soluble aluminum in soil solutions can be an important parameter to study the impact of acidification on forest soils and watershed, the formation (or dissolution) of secondary soil minerals, and to assess aluminum toxicity to plants in acid soils and aquatic organisms in acidified watersheds. Most techniques used to obtain soil solutions for chemical analysis of the typical predominant soil cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) also can be used for aluminum. More care is needed, however, since aluminum is typically present in soil solution at much lower concentrations and at much higher concentrations in the whole soil than the other soil cations. Also, the solubility of aluminum is pH dependent and factors that result in change of pH to a value near neutrality can result in loss by precipitation. Many commonly utilized sampling devices can result in either the removal of aluminum through sorption, or contamination of aluminum through dissolution reactions. Collection of samples with low aluminum concentrations require great care to minimize contamination from background sources. Methods of collecting soil solutions in which to measure soluble aluminum include *in situ* sampling with lysimeters, miscible displacement of soils in packed columns, centrifugation with or without a heavy liquid immiscible with water, and filtrations of soil solution samples through a nonreactive membrane filter with pore sizes of 0.45- μm or less (Bertsch and Bloom, 1996).

Mulder et al. (1989) demonstrated that the relationship between soil solution pH and soluble aluminum concentrations and demonstrated that above a pH of 5.0 soluble aluminum is not measured (Figure 7.2). This data supports the conclusion that at a soil pH of 5.0 and higher, soluble aluminum does not occur and toxicity associated with aluminum in soils is not expected.

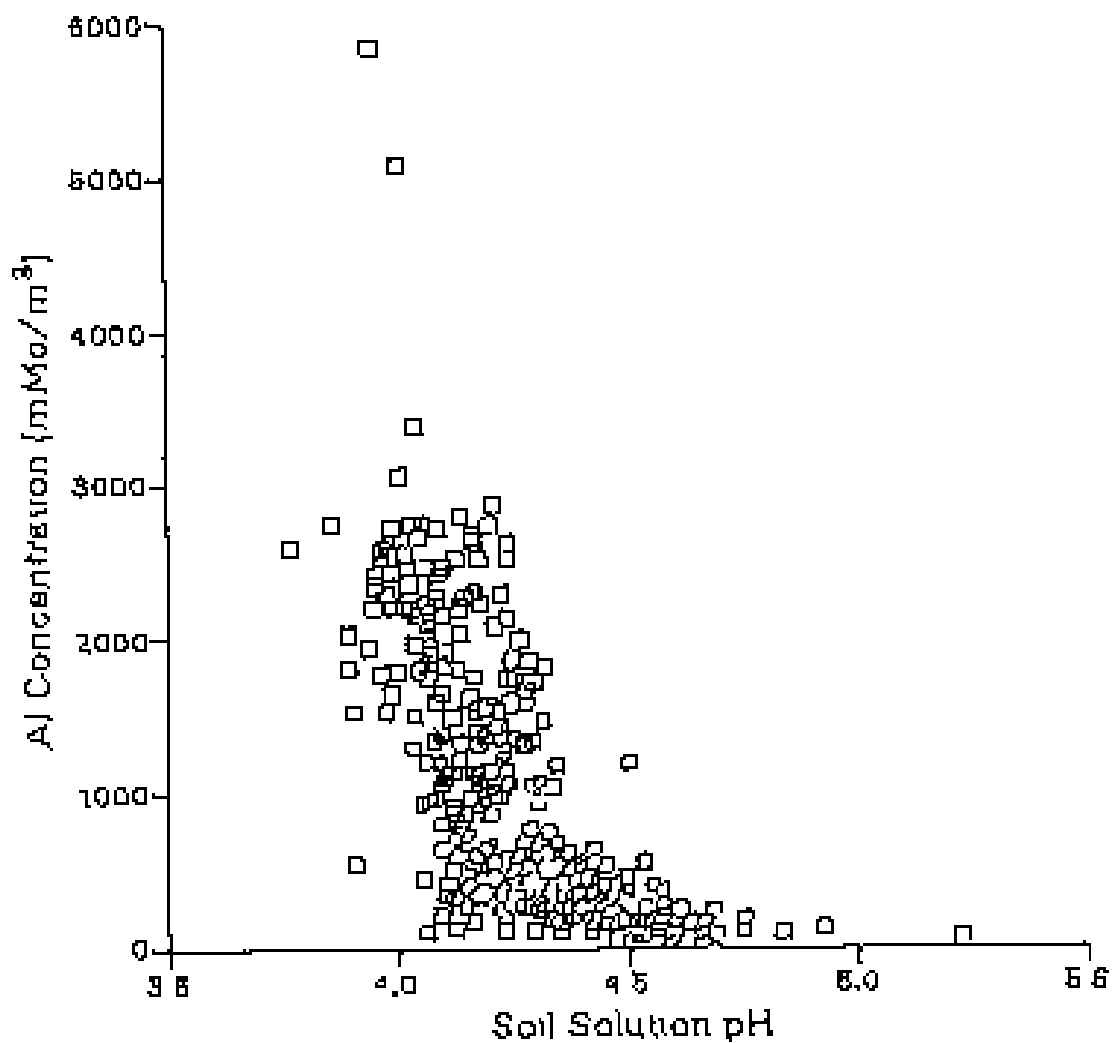


Figure 7.2. Aluminum soil solution concentrations versus soil solution pH in sub-soil solutions (below 50 cm depth) at six study sites (from Mulder et al., 1989).

8.0 CONCLUSIONS ON SCREENING SOILS FOR ALUMINUM TOXICITY

Aluminum (Al) is the most commonly occurring metallic element comprising eight percent of the earth's crust (Press and Siever, 1974). It is a major component of almost all common inorganic soil particles with the exceptions of quartz sand, chert fragments, and ferromanganiferous concretions. The typical range of aluminum in soils is from 1% to 30% (10,000 to 300,000 mg Al kg⁻¹) (Lindsay, 1979 and Dragun, 1988) with naturally occurring concentrations variable over several orders of magnitude.

EPA recognizes that due to the ubiquitous nature of aluminum, the natural variability of aluminum soil concentrations and the availability of conservative soil screening benchmarks (Efroymson, 1997b), aluminum is often identified as a contaminant of potential concern (COPC) for ecological risk assessments. The commonly used soil screening benchmarks (Efroymson, 1997b) are based on laboratory toxicity testing using aluminum solution amendments to test soils. Comparisons of total aluminum soil concentrations to solution based screening values are deemed by EPA to be inappropriate.

The standard analytical measurement of aluminum in soils under CERCLA contract laboratory procedures (CLP) is total recoverable metal. The available data on the environmental chemistry and toxicity of aluminum in soil to plants and soil invertebrates as discussed in the preceding chapters supports the following conclusions:

- Total aluminum in soil is not correlated with toxicity to the tested plants and soil invertebrates.
- Aluminum toxicity is associated with soluble aluminum.
- Soluble aluminum and not total aluminum is associated with the uptake and bioaccumulation of aluminum from soils into plants.

Measurement of Soluble Aluminum in Soils

Chemical and toxicological information suggests that aluminum must be in a soluble form in order to be toxic to biota. It is, however, difficult to measure accurately or with precision the concentration of soluble aluminum in pore water or in soil extracts. The difficulties associated with the measurement of soluble aluminum are discussed in detail in the previous chapters and include the following:

- Contamination problems. Aluminum is ubiquitous and the possibility of contamination of pore water or soil extract samples with aluminum from other sources is high. Sampling requires special handling to minimize background contamination.
- Forms of soluble aluminum which may be toxic are poorly understood

- Techniques for measurement of soluble aluminum are not well developed and would require refinement in order to consistently provide reproducible results that could be used with confidence.

Based on the available information, it is not possible at this time to recommend the direct measurement of soluble aluminum as the method for prediction of toxicity of aluminum in soils. It is possible to recommend as an alternative the measurement of soil pH. The presence of soluble aluminum forms is pH dependent. Thus, the measurement of soil pH provides an indirect but reliable approach for assessing if soluble aluminum could be present. The use of a pH screening level of 5.5 is considered environmentally protective .

Alternative Screening Procedure for Aluminum

Potential ecological risks associated with aluminum in soils is identified based on the measured soil pH. **Aluminum is identified as a COPC only for those soils with a soil pH less than 5.5.** The technical basis for this procedure is that the soluble and toxic forms of aluminum are only present in soil under soil pH values of less than 5.5. Site-specific considerations could, however warrant inclusion of aluminum as a COPC.

9.0 LITERATURE CITED

- Adams, W.A., A.Y. Ali, and P.J. Lewis. 1990. Release of cationic aluminum from acidic soils into drainage water and relationships with land use. *J. Soil. Sci.* 41:255-268.
- Amedee, G., and M. Peech. 1976. The significance of KCl extractable Al(III) as an index to lime requirement of soils of the humid tropics. *Soil Sci.* 121:227-233.
- Al-Khafaji, A.A., and M.A. Tabatabai. 1979. Effects of trace elements on arylsulfatase activity in soils. *Soil Sci.* 127(3):129-133.
- Armiger, W. H., C. D. Foy, A. L. Fleming, and B. E. Caldwell. 1968. Differential tolerance of soybean varieties to an acid soil high in exchangeable aluminum. *Agron. J.* 60:67-70.
- Asher, C.J. 1991. Chapt. 18: Beneficial elements, functional nutrients, and possible new essential elements. pg. 703-723. In J.J. Mortvedt (ed.) *Micronutrients in Agriculture*, 2nd Ed. No. 4, Soil Sci. Soc. Amer. Book Series, Madison, WI USA.
- Bengtsson, B. H. Asp, P. Jensen, D. Berggren. 1988. Influence of aluminum on phosphate and calcium uptake in beech (*Fagus sylvatic*) grown in nutrient solution and soil solution. *Physiol. Plant* 74:299-305.
- Bertrand, D., and A. de Wolf. 1968. Physiologie vegetale. L'aluminium, oligo-element necessaire au maïs. *C.R. Acad.Sci. Ser. 2* 267:2325-2326.
- Bertsch, P.M., and P.R. Bloom. 1996. Chapter 18: Aluminum. In D.L. Sparks (ed.) *Methods of Soil Analysis, Part 3; Chemical Methods*. No. 5. Soil Sci. Soc. Amer, Inc. pg. 517-550.
- Black, C. A. 1968. Soil-plant relationships. 2nd Ed. John Wiley and Sons, Inc., New York.
- Chapman, H.D. 1966. Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences.
- Chenery, E.M. 1948. Aluminum in plants and its relation to plant pigments. *Ann.Bot.* 12:121-136.
- Clarkson, D. T. 1967. Interaction between aluminum and phosphorus on root surfaces and cell wall material. *Plant Soil* 27:347-356.
- Clarkson, D. T. 1966. Effect of aluminum on the uptake and metabolism of phosphorus by barley seedlings. *Plant Physiol.* 41: 165-172.

Clarkson, D. T. 1965. The effect of aluminum and some other trivalent cations on cell division in the root apices of *Allium cepa*. *Ann. Bot. N.S.* 29:311-315.

Dragun, J. 1988. *The Soil Chemistry of Hazardous Materials*. Hazardous Materials Control Research Institute. Silver Spring, MD USA.

Driscoll, C.T. and W.D. Schecher. 1988. Aluminum in the environment. In: Sigel, H., and A. Sigel (eds). *Metal Ions in Biological Systems*, Vol. 24. Aluminum and its role in Biology. Marcel Dekker, New York. pp 59-122.

Efroymson, R.A., M.E. Will, and G.W. Suter II, 1997a, *Toxicological Benchmarks for Potential Contaminants of Concern for Effects on Soil and Litter Invertebrates and Heterotrophic Process*, ES/ER/TM-126/R2, Oak Ridge National Laboratory, Oak Ridge, TN.

Efroymson, R.A., M.E. Will, G.W. Suter II, and A.C. Wooten, 1997b, *Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision*, ES/ER/TM-85/R3, Oak Ridge National Laboratory, Oak Ridge, TN.

Eldhuset, T., A. Goransson, and T. Ingestad. 1987. Aluminum toxicity in forest tree seedlings. In: Hutchinson, T.C., K.M. Meems (eds). *Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems*. Vol. G16, NATO ASI Series. Springer-Verlag, Berlin. pp 401-409.

Evans, A., Jr., and L.W. Zelazny. 1987. Effects of sulfate additions on the status of exchangeable aluminum in a Cecil soil. *Soil Sci.* 143:410-417.

Evan, C. E. and E. J. Kamprath. 1970. Lime responses as related to percent aluminum saturation, solution aluminum, and organic content. *Soil Sci. Soc. Am. Proc.* 34:893-896.

Fageria, N.K., V.C. Baligar, and R.J. Wright. 1988. Aluminum toxicity in crop plants. *J. Plant Nutr.* 11:303-319.

Farina, M.P.W., M.E. Sumner, C.O. Plank and W.S. Letsch. 1980. Exchangeable aluminum and pH as indicators of lime requirement for corn. *Soil. Sci. Soc. Am. J.* 44: 1036-1041.

Fleming, A. L. and C. D. Foy. 1968. Root structure reflects differential aluminum tolerance in wheat varieties. *Agron. J.* 60:172-176.

Foy, C. D., R. L. Chaney, and M. C. White. 1978. The physiology of metal toxicity in plants. *Ann. Rev. Plant Physiol.* 29:511-566.

Hesse, P. R. 1972. *A Textbook of Soil Chemical Analysis*. Chemical Publishing Co., New York.

Hortenstine, C. C. and J. G. Fiskell. 1961. Effects of aluminum on sunflower growth and uptake of boron and calcium from nutrient solutions. *Soil Sci. Soc. Am. Proc.* 25:304-307.

Hutchinson, T.C., L. Bozic, and G. Munoz-Vega. 1986. Responses of five species of conifer seedlings to aluminum stress. *Water Air Soil Pollut.* 31:283-294.

Jackson, M. L. 1963. Aluminum bonding in soils: A unifying principle in soil science. *Soil Sci. Soc. Am. Proc.* 27:1-10.

Jenny, H. 1961. Reflections on the soil acidity merry-go-round. *Soil Sci. Soc. Am. Proc.* 25:428-432.

Juma, N.G., and M.A. Tabatabai. 1977. Effects of trace elements on phosphatase activity in soils. *Soil Sci. Soc. Am. J.* 41:343-346.

Juo, A.S.R., S.A. Ayanlaja, and J.A. Ogunwale. 1976. An evaluation of cation exchange capacity measurements for soils in the tropics. *Commun. Soil Sci. Plant Anal.* 7:751-761.

Juo, A.S.R. and E.J. Kamprath. 1979. Copper chloride as an extractant for estimating the potentially reactive aluminum pool in acid soils. *Soil Sci. Soc. Am. J.* 43:35-38.

Kamprath, E. J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. *Soil Sci. Soc. Am. Proc.* 34:252-254.

Keser, M., B. Neubauer, and F. Hutchenson. 1975. Influence of Al^{+3} on developmental morphology of sugar beet roots. *Agron. J.* 67:84-88.

Lafever, H. N., L. G. Campbell, and C. D. Foy. 1977. Differential response of wheat cultivars to aluminum. *Agron. J.* 69:563-568.

Liebig, G.F., Jr., A.P. Vanselow, and H.D. Chapman. 1942. Effects of aluminum on copper toxicity, as revealed by solution-culture and spectrographic studies of citrus. *Soil Sci.* 53:341-351.

Ligon, W. S. and W. H. Pierre. 1932. Soluble aluminum studies. II. Minimum concentrations of aluminum found to be toxic to corn, sorghum and barley in culture solutions. *Soil Sci.* 34: 307-321.

Liliehalm, B.C., and S.E. Feagley. 1988. Effects of simulated acid rain on soil and leachate acidification of a Lexington silt loam. *Soil Sci.* 146:44-50.

Lindsay, W.L. 1979. *Chemical Equilibria in Soils.* John Wiley & Sons, New York.

Long, F. L. and C. D. Foy. 1970. Plant varieties as indicators of aluminum toxicity in the A₂ horizon of a Norfolk soil. *Agron. J.* 62:679-681.

- Matsumoto, H., F. Hirasawa, H. Torikai, and E. Takakaski. 1976. Localization of absorbed aluminum in pea roots and its binding to nucleic acid. *Plant and Cell Physiol.* 17:127-137.
- MacLean, A. A. and T. C. Chiasson. 1966. Differential performance of two barley varieties to varying aluminum concentration. *Can. J. Soil Sci.* 46:147-154.
- McBride, M.B. 1994. *Environmental Chemistry of Soils*. Oxford University Press. New York.
- McCormick, L. H. and F. Y. Borden. 1974. The occurrence of aluminum phosphate precipitate in plant roots. *Soil Sci. Soc. Am. Proc.* 38:931-934.
- McCormick, L. H. and F. Y. Borden. 1972. Phosphate fixation by aluminum in plant roots. *Soil Sci. Soc. Am. Proc.* 36:799-802.
- McLean, E. O. 1965. Aluminum. p. 978-998. In C.A. Black (ed.) *Methods of Soil Analysis*, Part II: Chemical and microbiological properties of soils. Am. Soc. of Agron., Inc. Madison, Wis.
- McLean, E. O., D. C. Reicosky, and C. Lakshmanan. 1965. Aluminum in soils: VII. Interrelationships of organic matter, liming, and extractable aluminum with "permanent charge" (KCl) and pH dependent CEC of surface samples. *Soil Sci. Soc. Am. Proc.* 29:374-378.
- McLean, F. T. and B. E. Gilbert. 1927. The relative aluminum tolerance of crop plant. *Soil Sci.* 24:163-176.
- Mulder, J., J.J.M. van Grinsven, and N. van Breemen. 1987. Impacts of acid atmospheric deposition on woodland soils in The Netherlands: III. Aluminum chemistry. *Soil Sci. Soc. Am. J.* 1640-1646.
- Mulder J, N. Van Breemen, L. Rasmussen, and C.T. Driscoll. 1989. Chapter 10: Aluminum Chemistry of Acidic Sandy Soils with various inputs of Acidic deposition in the Netherlands and Denmark. In T.E. Lewis (Ed) *Environmental Chemistry and Toxicology of Aluminum*. Lewis Publishers, pg171-194.
- Munns, D. N. 1965. Soil acidity and the growth of a legume: II. Reaction of aluminum and phosphorus in solution and effects of aluminum, phosphorus, calcium, and pH on *Medicago sativa* L. in solution culture. *Australian J. Agric. Res.* 16:743-755.
- Naidoo, G. J., McD. Stewart, and R. J. Lewis. 1978. Accumulation sites of aluminum in snapbean and cotton roots. *Agron. J.* 70:489-492.
- Nosko, P., P. Brassard, J.R. Kramer, K.A. Kershaw. 1988. The effect of aluminum on seed germination and early seedling establishment, growth, and respiration of white spruce (*Picea glauca*). *Can. J. Bot.* 66:2305-2310.
- Oates, K.M., and E.J. Kamprath. 1983a. Soil acidity and liming: I. Effect of the extracting

solution cation and pH on the removal of aluminum from acid soils. *Soil Sci. Soc. Am. J.* 47:686-689.

Oates, K.M., and E.J. Kamprath. 1983b. Soil acidity and liming: II. Evaluation of using aluminum extracted by various chloride salts for determining lime requirements. *Soil Sci. Soc. Am. J.* 47:690-692.

Parker, D.R. L.W. Zelazny, and T.B. Kinraide. 1989. Chemical Speciation and plant toxicity of aqueous aluminum. In: Lewis, T.E. (ed) *Environmental Chemistry and Toxicology of Aluminum*. Lewis Publishers, Chelsea, MI. pp. 117-145.

Pavan, M.A., F.T. Bingham, and P.F. Pratt. 1984. Redistribution of exchangeable calcium, magnesium, and aluminum following lime or gypsum applications to a Brazilian oxisol. *Soil Sci. Soc. Am. J.* 48:33-38.

Peiffer, R. A. 1976. *Inter- and Intra-Specific Plant Differences in Tolerance to Aluminum*. Ph.D. Thesis. The Pennsylvania State Univ., University Park, Pa.

Press, F. and R. Siever. 1974. *Earth*. W. H. Freeman and Co., San Francisco.

Ragland, J. L. and N. T. Coleman. 1962. Influence of aluminum on phosphorus uptake by snapbean roots. *Soil Sci. Soc. Am. Proc.* 26:88-90.

Rasmussen, H.P. 1968. Entry and distribution of aluminum in *Zea mays*. *Planta* 81: 28-37.

Rasmussen, P.E., S.L. Schiff, and H.W. Nesbitt. 1991. The determination of exchangeable cations in acid soils: Errors caused by weathering reactions during neutral salt extraction. *Can. J. Soil Sci.* 71:155-163.

Rees, W. J. and G. H. Sidrak. 1961. Inter-relationships of aluminum and manganese toxicities toward plants. *Plant and Soils* 14:101-117.

Reeve, N.G. and M.E. Sumner. 1970. Effects of aluminum toxicity and phosphorus fixation on crop growth on Oxisols in Natal. *Soil Sci. Soc. Am. Proc.* 34: 263-267.

Reid, D. A., G. A. Jones, W. H. Armiger, C. D. Foy, E. J. Koch, and T. M. Starling. 1969. Differential aluminum tolerance of winter barley varieties and selections in associated greenhouse and field experiments. *Agron. J.* 61:218-222.

Reuss, J.O., P.M. Walthall, E.C. Roswall, and R.W.E. Hopper. 1990. Aluminum solubility, calcium-aluminum exchange, and pH in acid forest soils. *Soil Sci. Soc. Am. J.* 54:374-390.

Rhue, R. D. and C. O. Grogan. 1977. Screening corn for aluminum tolerance using different calcium and magnesium concentrations. *Agron. J.* 69:755-760.

Rorison, I. H. 1965. The effect of aluminum on the uptake and incorporation of phosphate by excised sanifoin roots. *New Phytol.* 64:23-27.

Sparling, D.W. and T.P. Lowe. 1996. Environmental Hazards of Aluminum to Plants, Invertebrates, Fish and Wildlife. Reviews of Environmental Contamination and Toxicology, Vol. 145. Springer-Verlag New York, Inc.

Suthipradit, S. 1988. *Effects of Aluminum on Growth and Nodulation of Some Tropical Crop Legumes*. Ph.D. thesis. University of Queensland, Australia.

Taylor, G.J. 1988. The physiology of aluminum phytotoxicity. In: Sigel, H., Sigel, A. (eds) Metal Ions in Biological Systems, Vol. 24. Aluminum and Its Role in Biology. Marcel Dekker, New York. p. 123-164.

Tisdale, S. L. and W. L. Nelson. 1975. *Soil Fertility and Fertilizers*. 3rd ed. Macmillan Publishing Co., Inc., New York.

Wright, K. E. 1943. Internal precipitation of phosphorus in relation to aluminum toxicity. *Plant Physiol.* 18:708-712.

Wright, K. E. 1945. Internal precipitation of phosphorus in relation to aluminum toxicity. *Plant Physiol.* 18:708-712.

Wright, K. E. and B. A. Donahue. 1953. Aluminum toxicity studies with radioactive phosphorus. *Plant Physiol.* 28:674-680.

Van Gestel, C.A.M. 1992. The influence of soil characteristics on the toxicity of chemicals for earthworms: a review. In P.W. Greig-Smith, H. Becker, P.J. Edwards, and F. Heimbach (eds.) *Ecotoxicity of Earthworms*. Intercept Ltd, Andover, UK. pg. 44-54.

Vlams, J. 1953. Acid soil infertility as related to soil solution solid-phase effects. *Soil Sci.* 75:383-394.

Vose, P. B. and P. J. Randall. 1962. Resistance to aluminum and manganese toxicities in plants related to variety and CEC. *Nature* 196:85-86.