Aluminum in Some Hawaiian Plants[1]

J. C. MOOMAW, MARTHA T. NAKAMURA,
and G. DONALD SHERMAN[2]

THE RECENT INTEREST in Hawaiian gibbsitic soils (Sherman, 1957; Tamura, Jackson, and Sherman, 1955) as a potential commercial source of aluminum has stimulated concurrent interest in the plants of these latosols.

The major and closely related questions that arise concern (1) the role of plant species or plant communities as indicators of aluminum, (2) the ecological significance of plant accumulators of aluminum, and (3) the role of aluminum in plant metabolism and its relation to plant tolerance and toxicity. It is the purpose of this paper to discuss data on a selection of Hawaiian plants with emphasis on the latter two questions. The floristics and ecology of study sites on gibbsitic soils will be considered later.

REVIEW OF LITERATURE

Much of the early development of information concerning aluminum in plants was stimulated by the interest in plant materials as mordants for the dye industry. Aluminum is one of the most abundant elements in the soil and is almost universally present in plants but varies widely in amount. Robinson and Edington (1945) define an "accumulator" plant as one which takes up "the particular element in quantities very far above, sometimes many thousands of times above, the average for 'normal' plants." If the mean Al^{+++} content of herbaceous vegetation is taken to be about 0.02 per cent of the dry matter (Hutchinson, 1943) or 200 p.p.m., the criterion of 1000 p.p.m. or 0.1 per cent used by Webb (1954) in a semiquantitative test would seem to be adequate to qualify a plant as an aluminum accumulator. Many workers have reported aluminum contents of non-accumulator plants, corn for example (Meyer and Anderson, 1952), that equal this level. Several studies have attested to the variability of aluminum content within individual plants, usually with higher concentrations in roots and stems than in leaves and variability within a species when grown on different substrates (Webb, 1954). The extensive work of Webb and of Chenery (1948, 1948*a*, 1951) on local and world-wide floras has resulted in compilation of lists of aluminum accumulators. The highest content of aluminum found in plant tissue is reported for *Symplocos spicata* (Webb, 1954), 7.1 per cent, and for a *Carpinus* species, 8.5 per cent (Howard and Proctor, 1957). Massive deposits of almost pure aluminum succinate have been found in the heartwood cavity of *Cardwellia sublimis* (Webb, 1953) and *Orites excelsa*. Costin (1954) stated *Poa caespitosa* to have an aluminum content of 7.8–10.4 per cent and showed that it produced a material richer in sesquioxides than the parent rock from which the soils of the region were derived.

Chenery (1951) challenges the emphasis of some Russian workers on the role of aluminum accumulators in podzolization and offers other explanation for the observed soil aluminum distribution. Howard and Proctor (1957) studied the floristics of the bauxitic soils of Jamaica and found few of the families of accumulator species in Jamaica and fewer still on the bauxitic soils. They used neither tissue nor soil analyses but reported no species they could call indicators of aluminum and, on the contrary, concluded that factors other than the aluminum content of the soil controlled the success or failure of plants on Jamaican bauxite.

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[1] Published with the approval of the Director of the Hawaii Agricultural Experiment Station, University of Hawaii, as Technical Paper No. 431. Manuscript received September 4, 1958.

[2] Assistant Agronomist, Junior Soil Scientist, and Head of Agronomy and Soil Science, Hawaii Agricultural Experiment Station, respectively.

Aluminum is thought to function in plant maturation and seed setting (Hutchinson, 1943) and in water uptake. The work relating aluminum to the blue pigments in plants (Chenery, 1948), especially in *Hydrangea*, is well known. The element has been thought to exercise a strong influence in plant competition in pastures (Shorland, 1934). Aluminum accumulation is thought to be a primitive phytogenetic character in plants (Webb, 1954) because it is generally confined to the Archichlamydeae and the primitive sections of Metachlamydeae. High aluminum concentrations are rarely found in monocotyledons (Chenery, 1949) and Webb records no positive Gramineae of 16 species tested. In the pteridophytes, accumulators are again confined to more primitive families and *Lycopodium* has been extensively studied to relate aluminum content and alkaloid molecular weight. Hutchinson (1943) considered the evidence in *Lycopodium* to suggest "that the capacity to accumulate the element has been developed more than once in the genus."

Although some workers have reported a requirement for the element in trace amounts (Hutchinson, 1945) by some plants, and stimulation from aluminum, especially of the ferns (Yoshii, 1939), it is not usually considered to be one of the essential nutrients. The more frequently reported condition is that of aluminum toxicity (Gilbert and Pember, 1935; McLean and Gilbert, 1926; Rees and Sidrak, 1956). This effect is usually related to soils below pH 5.5 (Chenery, 1951; Nagata, 1954) and is frequently correlated with high concentrations of manganese and free oxides or soluble aluminum compounds in leached podzolic and latosolic soils (Ellis and Truog, 1955; Perkins *et al.*, 1955). Magistad (1925) reported toxicity on an alkaline soil from a soluble aluminate and demonstrated the insolubility of aluminum in circumneutral soils, nutrient solutions, and water.

The free hydrated oxides of iron and aluminum have been shown to be more effective in fixing phosphorus added to Hawaiian soils than are the crystal lattice clays of either the 2:1 or 1:1 types (Chu and Sherman, 1952). Free aluminum oxides do occur in montmorillonite clays (Ellis and Truog, 1955) however, and do account for most of the phosphorus fixation in soils of this type. Nagata (1954) has shown this effect to be more pronounced on calcicolous plants and Saeki and Okamoto (1954), studying the pure aluminum-phosphorus system, showed complete fixation to occur only when the P/Al ratio was less than unity and that iron and aluminum systems showed an almost identical trend. Perkins *et al.* (1955) attributed phosphate-fixing soluble aluminum to decomposition products of clay minerals.

Wright and Donahue (1953) definitely show aluminum to interfere with the phosphorus metabolism by precipitation on the root surfaces although Wallihan (1948) concludes that aluminum does not interfere with the activity of phosphorus in the tops of ladino clover plants. Rees and Sidrak (1956) found aluminum induced phosphorus deficiency in barley but not in spinach or *Atriplex*.

Hou and Merkle (1950) reported little correlation between pH and aluminum content even though accumulator plants are usually calcifugous and have a greater content of either aluminum or manganese than "acid-indifferent" plants.

METHODS

Collection Procedure

Samples of a selection of plants from three of the Hawaiian Islands were collected during the winter of 1957–58 (October–March). The principal areas of collection were those soil series currently under investigation as potential sources of alumina (gibbsite). About 500 grams of fresh plant material were collected of mature leaf, frond, or shoot unless otherwise specified. Special attention was given to some of the species known to be accumulators of aluminum and in many cases the same species were collected in areas of nonaluminous soils.

The species sampled were about equally divided among Pteridophyta, Dicotyledoneae, and Gramineae, the emphasis on grasses resulting from the present use of these areas mainly for grazing. The plants were identified by J. C. Moomaw and E. Y. Hosaka.

Analytical Procedure

Chenery's colorimetric analysis of aluminum using thioglycollic acid as inhibitor for iron (Chenery, 1948*b*) was followed with a few modifications.

The plant samples were prepared for analysis of aluminum according to the method described by Piper (1944). Two grams of oven-dried plant material were dry-ashed in a Vycor crucible. The ash was put into solution with dilute hydrochloric acid and the silica was separated and destroyed with hydrofluoric acid.

A suitable aliquot of the plant digest was first pipetted into a 100 ml. beaker and diluted to about a 20 ml. volume. To prevent the interference of Fe^{+++}, 2 ml. of 1:100 thioglycollic acid was added to the diluted solution to reduce the Fe^{+++} to Fe^{++}. Next, 10 ml. of the aluminon mixed reagent was added. The pH of this entire mixture was adjusted to 4.2 with NH_4OH using the Beckman pH meter. Although Chenery's mixed reagent is buffered at pH 4.0, the extreme acidity of the plant digest overcomes the buffering capacity and makes this pH adjustment necessary. The intensity of the color of the aluminum lake is highly sensitive to pH changes; therefore, in order to have reproducible results, it was necessary to have the pH of the plant sample and the standards equal.

The adjusted solution was transferred to 50 ml. volumetric flasks and heated in a boiling water bath for 12.5 minutes. The flasks were removed and allowed to stand for 10 minutes, then they were immersed in a cold water bath to be cooled to room temperature. The cooled solution was diluted to mark and mixed. The transmittancy of the solution was read on the Klett-Summerson photoelectric colorimeter using a green filter.

RESULTS AND DISCUSSION

Of the 45 determinations reported in Table 1, 18 exceed the Chenery criterion of 1000 p.p.m., thus designating 13 of the 23 species as aluminum accumulators for one or more of the determinations. Three of the 13 are well known from the literature as accumulators: *Lycodium cernuum*, the club moss or wawae'iole; the staghorn fern, *Gleichenia linearis;* and *Melastoma malabathricum*. The magnitude of the aluminum content of *Lycopodium* species is in good agreement with the 0.71 per cent found in the extensive review of Hutchinson (1943) and others. Staghorn is considered by some to be a fair indicator plant for bauxitic soils and was given special attention in being collected from seven different stations. It shows a high aluminum content from all collections falling in the relatively narrow range of from 3500 to 6300 p.p.m. High aluminum contents from nonaluminous soil areas, such as the Naalehu pahoehoe lava and the Honokaa soil (Table 2), are taken as evidence that it may be an obligate accumulator. *Melastoma* shows a very high content of aluminum, especially in the older tissue; this is a condition frequently mentioned in the literature, although Webb indicates some variability in *M. polyanthum* in New Zealand.

The highest aluminum content was found in *Polypodium phymatodes* on the Haiku series site considered most highly gibbsitic. Webb (1945) found all species in *Polypodium* examined by him to be negative but it is not known whether *P. phymatodes* was one of these. *Stenoloma chinensis*, another of the Polypodiaceae, shows evidence of a strong accumulation tendency, although it becomes a rather low-level accumulator on the Kukaiau soil series.

Pitryogramma and *Nephrolepis* (Boston fern), also in the Polypodiaceae, have a mixed record and indicate a facultative accumulation tendency. Two tree ferns, *Sadleria cyatheoides*

TABLE 1

ALUMINUM (Al^{+++}) CONTENT OF SOME HAWAIIAN PLANT MATERIALS IN PARTS PER MILLION OF DRY MATTER

(All determinations are means of duplicates unless agreement was not closer than 10 per cent, when additional samples were run.)

	MAUI				KAUAI		HAWAII			
Soil Series	Haiku				Kapaa		Pahoehoe lava	Kukaiau	Honokaa	Lithosol
SPECIES	Camp Maui	Halehaku	Haiku	Haiku (beyond gulch)	Bauxite Reclamation Site	Wailua Game Reserve	Naalehu	Hamakua	Kukaiau	Keaau
Pteridophyta										
Cibotium chamissoi									210	
Gleichenia linearis		3490	5670	6300		5875	4650	5725	4825	
Lycopodium cernuum			8950							
Nephrolepis exaltata		350	6660			3850		570		
Pityrogramma calomelanos		204	3525	150						
Polypodium phymatoides				16,000						
Sadleria cyatheodes					210					
Stenoloma chinensis		1795	6100	1550	1200			1200		
Spermatophyta										
Monocotyledons—Gramineae										
Digitaria decumbens	64		780							
Paspalum conjugatum									115	
Paspalum orbiculare			1400		2525 (young shoots)	5970				
Setaria geniculata			1540							
Sporobolus capensis			5475							
Monocotyledons—Orchidaceae										
Spathoglottis plicata			3550							
Dicotyledons										
Cassia leschanaultiana			660			1600				
Macadamia ternifolia (var. 246)										59
Macadamia ternifolia (var. 333)										60
Melastoma malabathricum					5500 (terminal shoots)	10,300				
Metrosideros collina subsp. *polymorpha*					70 (terminal shoots)					
Psidium guajava			247			250			250	
Rhodomyrtus tomentosa									110	
Solanum nodiflorum		3850								
Stachytarpheta cayannensis			680							
Styphelia tameiameiae				880						

in the Polypodiaceae and *Cibotium chamissoi*, contained very low levels of aluminum where they were encountered.

Among the monocotyledons, the common, naturalized, wild orchid, *Spathoglottis plicata* was found to have a sufficiently high aluminum content in the leaves (3550 p.p.m.) to be classed as an accumulator but the single determination is considered insufficient for a firm decision. This is the first known positive report for orchids.

The three positive finds for the grasses are thought to be especially interesting because of their involvement in the phosphorus metabolism of herbivores and because of negative reports for 16 species by Webb (1945), and for the family in general by Hutchinson (1943). Costin (1954) is the only known source of a positive graminaceous determination. All three of the species of grasses with high aluminum are common in the native pastures on the acid soils of the high rainfall areas in Hawaii. Yellow foxtail (*Setaria geniculata*) was relatively low (1540 p.p.m.) for a single determination, but rattail grass (*Sporobolus capensis*) contained more than 5000 p.p.m. in the Haiku area. Rice grass (*Paspalum orbiculare*) qualified as an accumulator in all three of the collection locations and shows a tendency toward increased aluminum content with age as well as a wide range (1400–5970 p.p.m.). It should be pointed out that the accumulation of aluminum in a forage grass may account in part for the observed phosphate deficiency symptoms of cattle grazing in these areas since it has been shown (Hutchinson, 1943) that ingestion of aluminum lowers phosphorus levels in blood, bone, and urine of several other animals. Hilo grass (*Paspalum conjugatum*) and fountain grass (*Pennisetum ruppelii*) were low in aluminum where they were collected and the introduced pangola grass (*Digitaria decumbens*) was very low.

TABLE 2
ALUMINUM CONTENT, DOMINANT SOIL MINERAL, AND CLASSIFICATION OF HAWAIIAN SOILS FROM WHICH PLANT SAMPLES WERE TAKEN

SOIL SERIES	GREAT SOIL GROUP	DOMINANT SOIL MINERAL	ALUMINUM CONTENT (% Al_2O_3)
Haiku	Humic ferruginous latosol	Free oxides	25–40
Kapaa	Aluminous ferruginous latosol	Free oxides	40–60
Kukaiau	Humic latosol	Free oxides, amorphous minerals	20–35
Honokaa	Hydrol humic latosol	Free oxides, amorphous minerals	15–30

The dicotyledons of interest, other than *Melastoma*, are the dark-blue-fruited nightshade, or popolo, *Solanum nodiflorum*, which was high (3850 p.p.m.) in aluminum, and Japanese tea (*Cassia leschenaultiana*), which was positive on Maui but not on Kauai. The widespread and remarkably adaptable ohia lehua (*Metrosideros collina* subsp. *polymorpha*) was very low, as was the closely related Macadamia nut (a member of the Proteaceae). These two plants and pangola grass show such low levels of aluminum that a metabolic device for excluding aluminum seems probable. *Rhodomyrtus* contains a slightly low level but guava (*Psidium guajava*) maintains a consistently "average" value even on soils varying widely in aluminum content (Table 2). Although a more intensive sampling program may reveal more members of these categories as well as more samples of an intermediate nature, it seems reasonable to classify the plants sampled—all calcifugous species growing on soils of low pH, and highly leached root zones—into the following categories:

1. Plants that exclude aluminum to some degree
2. Plants that take up aluminum
   Facultative accumulators
   Obligate accumulators
3. Plants indifferent to aluminum in the substrate

Supporting physiological evidence is needed but it can be inferred from reports in the literature that the exclusion or accumulation of aluminum is closely related to the phosphorus metabolism of a particular species, and that presumably the phosphorus balance in the plant can be maintained either by restricting the intake of aluminum which precipitates phosphorus, or by precipitating aluminum in the leaf or other tissue in a form that will not interfere with the phosphorus metabolism.

SUMMARY

The aluminum content of selected Hawaiian plants was determined using the "aluminon" method. The plants were obtained largely from highly leached latosol soils of low pH known to have a high aluminum content. Aluminum content of some species classed as accumulators of aluminum agree closely with literature sources. High levels of aluminum are reported for the first time from some common grasses (*Sporobolus capensis* and *Paspalum orbiculare*) and from an orchid (*Spathoglottis plicata*). Thirteen of 23 species qualified as accumulators (>1000 p.p.m.) and others had unusually low aluminum levels. A classification scheme to include "aluminum-excluders" is proposed and the relationship to phosphorus metabolism is discussed, including the possible influence of plant aluminum on phosphorus levels of grazing herbivores.

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