

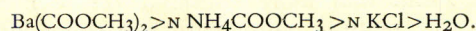
## EXTRACTABLE ALUMINIUM CONTENT IN SOME HAWAIIAN SOILS

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Extractable aluminium in 22 soil samples from a transect on the northern slope of Kawaioloa ridge in the Hawaiian islands was determined with four different extracting solutions such as distilled H<sub>2</sub>O, N KCl, N NH<sub>4</sub>COOCH<sub>3</sub> and Ba(COOCH<sub>3</sub>)<sub>2</sub>. The last two solutions were buffered at pH 4.8. According to the extracting power the solutions may be arranged in decreasing order as follows:



All the solutions extracted higher amount of aluminium from the subsoils than those in the surface soils. In the soils where the pH was low the extractable aluminium content was high with all the extracting solutions except distilled water. Extractable aluminium was low where the pH of the soil was below 6.0. Although N NH<sub>4</sub>COOCH<sub>3</sub> and Ba(COOCH<sub>3</sub>)<sub>2</sub> solutions were buffered at pH 4.8, the extractability of aluminium depended on original pH of the soils. There are positive correlations between extractable aluminium with N KCl and Ba(COOCH<sub>3</sub>)<sub>2</sub> solutions, and also between extractable aluminium with N NH<sub>4</sub>COOCH<sub>3</sub> and Ba(COOCH<sub>3</sub>)<sub>2</sub> solutions. The amount of aluminium in the sugarcane sheaths ranged from 14 to 47 ppm.

Aluminium is thought to be the third most abundant element in the Earth's crust and is found in considerable quantities in all soils. The distribution and abundance of aluminium in soils depend on the climatic conditions in which the soils are located. Under the humid tropical conditions the concentration of aluminium is high near the surface, but in the soils of the colder climates the concentration of this element is higher in the subsoil zones.

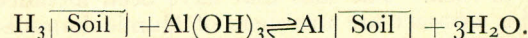
The fate of aluminium in the final decomposition of primary aluminosilicates may be exhibited by adopting the convenient diagram prepared by Goldschmidt,<sup>1</sup> in which the lithophile and atmophile elements of invariant valency are entered as points of which the (*r*) is the ionic radius and (*Z*) the ionic charge. Goldschmidt<sup>1</sup> pointed out that the elements of intermediate potential, such as aluminium, form insoluble oxides and hydroxides on weathering.

In soils, therefore, aluminium occurs as oxides, hydroxides and hydrated oxides. Aluminium also occurs in lattices of different primary and secondary silicates. In Hawaii, where due to intense leaching of soils the bases are removed very easily, the aluminium minerals of wide range of stability develop.<sup>2</sup> The high acidity, in the presence of active aluminium, has caused concern over the possibility that activity of aluminium might become harmful to sugarcane.<sup>3,4</sup>

Recently, considerable attention is being given to soluble aluminium as a factor in the harmful effects of acid soils upon plant growth. It is held by some authors that the soil acid reacts with aluminium compounds present in the soil forming

soluble aluminium salts and that the amount of soluble aluminium salts thus formed, rather than the degree of acidity, determines largely the toxicity to plant growth.<sup>5</sup>

According to Magistad<sup>6</sup> the amount of aluminium present in soil solution depends on at least two factors: firstly, the amount and kind of aluminium compounds present in the soil, and secondly, the reaction of the system. Magistad<sup>6</sup> believed that when a neutral soil is treated with AlCl<sub>3</sub> the chief replacement is one of H<sup>+</sup> for the exchangeable bases of the soil. The H<sup>+</sup> in the soil reacts subsequently with salts to give free acid which dissolves Al(OH)<sub>3</sub> from the soil. McAuliffe *et al.*<sup>7</sup> and Low<sup>8</sup> have emphasized the conclusion of Paver *et al.*<sup>9</sup> that acid clays are in reality H-Al clays. The latter authors proposed a mechanism of reaction as follows:



Ayres *et al.*<sup>3</sup> made an attempt to determine the source of water-soluble aluminium in soils. He inserted some of his own data in the expression of solubility product of gibbsite as follows:

$$\text{pH} - \frac{1}{3}\text{pAl} = 14 - \frac{1}{3}\text{pKSp} \quad (1)$$

in which pH is that of the extract and the activity of aluminium is expressed in moles/l. With the more acid soils the same values for pK were obtained and aluminium values for activities were calculated from the following equation:

$$(\text{Al}^{+++}) = \frac{[\text{Total Al}]}{\frac{1}{f}\text{Al}^{+++} + \frac{K}{(\text{H}^+)}f\text{Al}(\text{OH})^{2+}} \quad (2)$$



which was substituted in equation (1). In equation (2)  $K$  was taken as constant for the simple first stage hydrolysis of aluminium. The activity coefficients for  $Al^{+++}$  and  $Al(OH)^{2+}$  were taken to be unity on the basis that in these highly leached soils ionic strength may be resumed to approach zero.

Mattson<sup>10</sup> carried out some interesting experiments in which soils were extracted with dilute acid, washed and then treated with a neutral salt. The whole sequence of operations was repeated several times successively. He found that more sesquioxides were present in the neutral salt filtrate than in the dilute acid filtrate and that as often as the soils were rendered unsaturated and treated with neutral salt solutions, aluminium was brought into solution. In explaining these results he suggested that the activity of the acid is greatly increased by the presence of neutral salt.

The present study was undertaken for the purpose of throwing light on: (1) the amount of aluminium extracted by different extracting solutions from soils belonging to different great soil groups, (2) the suitability of extracting solutions for determining extractable aluminium in the Hawaiian soils and (3) the relationship between the amount of rainfall and extractable aluminium in soils.

### Materials and Methods

For the collection of soil and plant samples used in this study a suitable transect was chosen on the northern slope of Kawaihoa Ridge of Waialua Sugar Plantation in the Hawaiian islands. The transect runs from north to south and both rainfall and altitude increase towards the south. All the soils in this transect developed on basaltic type of rock. The soils that have been included in this transect are members of Humic Latosols, Low Humic Latosols and Gray Hydromorphic Soils.<sup>11</sup>

All the soils were collected from sugarcane fields. In all, soils were collected from eleven sites, more or less half a mile apart. From each location two samples were collected—one surface soil and the other subsurface soil. The soils were air-dried in laboratory and passed through 10-mesh sieve. All the analyses were done on those samples. Apart from soils, sugarcane sheaths were collected from each location for plant analysis. The plant samples were dried in the oven at 70°C and ground for aluminium determination.

*Methods of Extraction.*—Extraction of aluminium from soils as carried out by four methods, such

as distilled  $H_2O$ ,  $N$   $KCl$ ,  $NH_4COOCH_3$  buffered at pH 4.8 and  $Ba(COOCH_3)_2$  buffered at pH 4.8. To obtain water-soluble aluminium 100 g of air-dried soil was mixed with 100 ml of distilled water. After standing for 24 hr the wet mass was transferred to a Buchner funnel and was subjected to a mild suction for extraction.

For extraction with  $N$   $KCl$  solution the method of Chapman *et al.*<sup>12</sup> was followed in which 10 g of soil was taken in a beaker. 50 ml of  $N$   $KCl$  solution was added and mixed with it. It was immediately filtered on a Buchner funnel and was washed with five 10-ml lots of  $N$   $KCl$  solution.

$Ba(COOCH_3)_2$ -extractable aluminium was determined by the method given by Plucknett *et al.*<sup>4</sup> in which 10 g of soil was taken into a beaker and 50 ml of  $Ba(COOCH_3)_2$  solution was added and allowed to stand for 12 hr. The suspension was filtered through a Buchner funnel and the soil was washed 5 times with 10-ml lots of the extracting solution.

Extraction with  $N$   $NH_4COOCH_3$  solution was carried out in the same way as the  $Ba(COOCH_3)_2$  extraction above. Only  $N$   $NH_4COOCH_3$  solution was used in place of  $Ba(COOCH_3)_2$  solution. In all cases the extracted aluminium was determined colorimetrically by the aluminon method as described by Chapman *et al.*<sup>12</sup>

For the determination of aluminium in plant samples of Chapman *et al.*<sup>12</sup> wet ashing method was followed.

### Results and Discussion

*Aluminium in Soils.*—The results of extractable aluminium obtained by four methods from 22 soil samples have been presented in Table 1. All the soils show acidic reaction. The pH varies from 4.4 to 6.8. It may be noted that as the pH of the soils increases, the amount of extractable aluminium decreases with all the extractants except distilled water. A similar trend was reported by Yuan *et al.*<sup>13</sup> and McLean *et al.*<sup>14</sup> In their study with some Hawaiian soils Rixon *et al.*<sup>15</sup> and Plucknett *et al.*<sup>4</sup> have found that liming in soil reduced the extractable aluminium.

It may be noted that distilled water extracted a negligible amount of aluminium from the soils under study. This kind of aluminium is comparatively higher in subsoils than those in the surface soils. This possibly is due to the fact that the surface soils are highly oxidised and therefore aluminium there is less reactive to water than those underneath. Soil pH does not seem to have



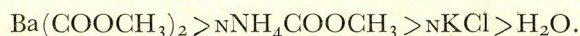
TABLE I.—EXTRACTABLE ALUMINIUM CONTENT IN SOME SOILS OF HAWAII.

Soil No.	pH	Extractable Al in soils				Total Al in plants ppm	
		H <sub>2</sub> O ppm	N KCl ppm	N NH <sub>4</sub> COO- CH <sub>3</sub> ppm	Ba(COO- CH <sub>3</sub> ) ppm		
Rainfall decreases ↓	T	6.6	.00	4	66	72	47
	T	4.5	.00	80	328	362	38
	T	5.0	.10	68	416	412	29
	T	4.5	.04	56	338	350	27
	T	4.4	.10	83	378	406	22
	T	4.9	.00	41	216	200	16
	T	5.1	.00	18	166	141	14
	T	6.7	.05	1	13	31	18
	T	6.8	.10	4	7	22	21
	T <sub>10</sub>	6.8	.09	1	19	45	17
	T <sub>11</sub>	6.7	.07	2	9	17	31
Mean	—	.05	32	178	187	25	
S <sub>1</sub>	4.8	.21	55	272	300		
S <sub>2</sub>	4.7	.11	99	394	470		
S <sub>3</sub>	4.9	.12	95	460	492		
S <sub>4</sub>	4.5	.18	100	372	450		
S <sub>5</sub>	4.7	.14	60	366	381		
S <sub>6</sub>	5.1	.13	30	213	218		
S <sub>7</sub>	5.4	.05	10	166	131		
S <sub>8</sub>	6.8	.22	4	38	59		
S <sub>9</sub>	6.7	.11	1	17	31		
S <sub>10</sub>	6.6	.14	7	21	43		
S <sub>11</sub>	6.8	.19	1	7	31		
Mean	—	.14	42	211	237		

T = Surface Soils. S = Subsurface Soils.

effect on the amount of water-extractable aluminium. Lindsey<sup>16</sup> pointed out that for very different soils, aluminium in soil solution is generally not above 0.1 ppm where soil pH is above 5.5. It is interesting to note here that in few subsoils, such as S<sub>8</sub>, S<sub>9</sub>, S<sub>10</sub>, and S<sub>11</sub> the water-extractable aluminium content has far exceeded the limit of 0.1 ppm although the pH values are above 6.6.

All the extracting solutions except distilled water extract out high content of aluminium from soils. According to the aluminium replacement ability these extractants may be arranged in decreasing order as follows:



In the case of all the extracting solutions except distilled water the aluminium extraction from soils depends on pH of the soils. Usually, all the

above reagents extracted comparatively higher amount of aluminium from subsoils than those from surface soils. This shows that the extractable aluminium is high in the subsoils than those in the surface soils.

N KCl solution-extractable aluminium in the soils under study ranges from 1 to 100 ppm. Since KCl solution was not buffered, the pH of the suspension tended to come to the approximate pH of the soils during the process of extraction. As a result, this solution extracted high amount of aluminium from those soils which have low pH (pH 5), but in those soils which have higher pH value, the extractable aluminium content was low (Table I). This trend holds good both for surface soils and also for subsoils. There is a highly significant correlation between N KCl-soluble and Ba(COOCH<sub>3</sub>)<sub>2</sub>-soluble aluminium in the soils under study (Fig. 1). This finding is in agreement with those of Yuan *et al.*<sup>13</sup>



and Ayres *et al.*<sup>3</sup> Lin *et al.*<sup>17</sup> reported that  $N$  KCl solution displaced definite amount of exchangeable aluminium from soils and clays. In the present study aluminium extraction by  $N$  KCl solution seems to be controlled by the pH of the soils. Another interesting point to note is the fact that the soils of higher rainfall areas have higher content of  $N$  KCl extractable aluminium than those of lower rainfall areas.

$N$   $NH_4COOCH_3$  solution extracted high amount of aluminium from the soils under study. Although  $N$   $NH_4COOCH_3$  solution was buffered at pH 4.8, it extracted higher amount of aluminium from those soils which have lower pH. This indicates that the extraction of aluminium with  $N$   $NH_4COOCH_3$  solution depends on the pH values of the soils.

$Ba(COOCH_3)_2$  solution extracted the highest amount of aluminium from the soils under study.  $N$   $NH_4COOCH_3$  comes in the second position. There is a highly significant correlation between  $N$   $NH_4COOCH_3$  and  $Ba(COOCH_3)_2$  soluble aluminium in the soils (Fig. 2). McLean *et al.*<sup>18</sup> stated that only small amount of soil aluminium is usually extracted by  $Ba(COOCH_3)_2$  at pH 7.0, but when the pH of the solution is adjusted to 4.8 it is capable of extracting soil aluminium which is related to some characteristics of soils. He further noted that at this pH level  $Ba(COOCH_3)_2$  solution extracted enough aluminium from most soils for accurate measurement with little possibility of damage to the clay crystals.

Although  $Ba(COOCH_3)_2$  solution was buffered at pH 4.8, results in Table 1 show that in

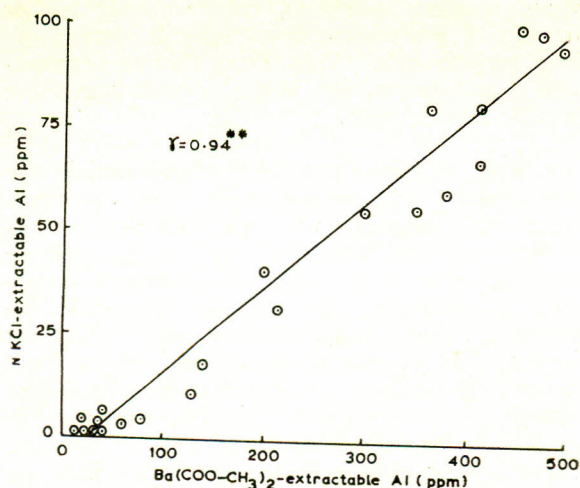


Fig. 1.—Relationship between  $Ba(COOCH_3)_2$  and  $N$  KCl-extractable Al in the soils.

soils which have low pH, the extractable aluminium was high. The ability to extract aluminium by this solution from soils is, therefore, pH dependent. Ayres *et al.*<sup>3</sup> studied the capability of  $Ba(COOCH_3)_2$  solution for extracting aluminium at different pH levels. He reported that extractable aluminium increases with decrease in pH. He further stated that at the same pH level highly weathered soils generally release more aluminium than the less weathered ones. The same pattern is probably true for some soils under the present study. As the rainfall decreases the weathering intensity decreases and the  $Ba(COOCH_3)_2$  extractable aluminium also decreases. The highly weathered soils at the upper levels of the slope (*viz.* site No.  $T_2, T_3, T_4, T_5, T_6, T_7$ ) released higher amount of aluminium.

The speed with which aluminium comes into solution during the time of extraction is very important. Kappen<sup>19</sup> has found the reaction to proceed so quickly that the pH measurements made at various times from the start of the reaction gave no significant difference. He used this fact as a cogent argument against the theory that aluminium appears by a secondary process of solution. Ayres *et al.*, on the other hand, have observed that studies on the extractability of aluminium present in the Hawaiian soils provided evidence that dissolution rather than exchange mechanics accounted for much of aluminium appearing in the extracts.

*Aluminium in Plants.*—Recently Fox *et al.*<sup>20</sup> reported that aluminium content of Sudan grass

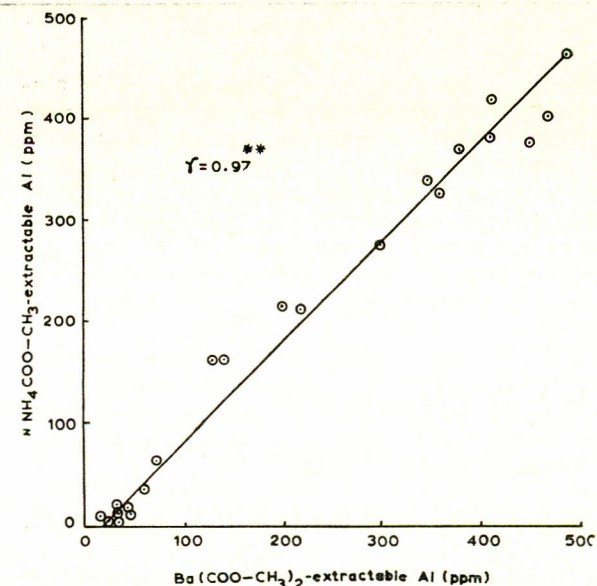


Fig. 2.—Relationship between  $N$   $NH_4COOCH_3$  and  $Ba(COOCH_3)_2$  extractable Al in the soils.



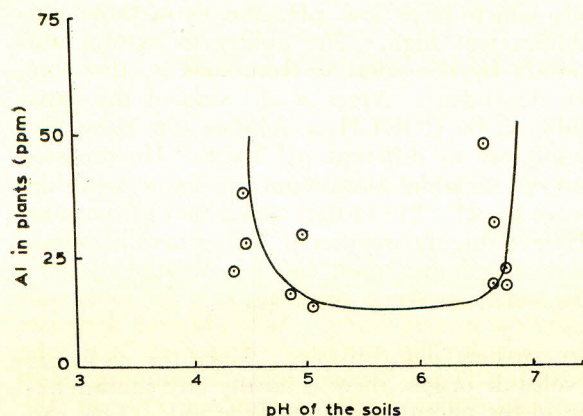


Fig. 3.—Relationship between the pH of the soils and total aluminium in plants.

growing in pots on Humic Latosol soils decreased on addition of limestone. The aluminium content in the sugarcane samples under the present study is maximum around two pH belts—one around pH 4.7 and the other around pH 6.7 (Fig. 3). The high aluminium uptake by sugarcane around pH 4.7 is quite likely because the solubility of this element is high in this pH level. It is not known as to why the aluminium uptake by sugarcane was high when the pH level of the soil was 6.7.

The aluminium content in the sugarcane sheaths under the present study ranges from 14 to 47 ppm, a value quite comparable with those of Burgess *et al.*<sup>21</sup> It is generally believed that aluminium in sugarcane sheath is far less than that in stem or root.<sup>22</sup>

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