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INFLUENCE OF ALUMINIUM ON pH AND RECOVERY OF EXCHANGEABLE ALUMINIUM FROM PEAT

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Incubation experiment was conducted to obtain information on the extent of acidity developed due to added $AlCl_3$ (0, 25, 50 and 100 μg g^{-1}) at different pH levels and changes in exchangeable Al in peat. Results showed that Al at high pH is hydrolysed causing an increased acidity by releasing H^+ from hydroxy aluminium compounds. Concentration of exchangeable Al is tremendously reduced with increasing pH possibly due to formation of mono-aluminium compounds or polynuclear complexes of hydroxy aluminium. Extractable Al in 1M KCl was very low because of the presence of organic binding sites in peat. Thus, the recovery of exchangeable Al from Fison peat (I) containing more humified material was extremely low (1.0-2.1%) in comparison to Red Moss peat (47.6-52.8%).

Key words: Exchangeable Al, Hydroxy Al compounds, Peat.

INTRODUCTION

Exchangeable Al plays a dominant role in acid soils. In extremely acid conditions, Al generally remains in solution mostly as hydrated exchangeable Al maintaining an equilibrium with Al ions in solution. While in strongly acid to moderately acid condition, Al in solution frequently undergoes hydrolysis and releases hydrogen ions causing an increase in soil acidity (Carson and Dixon [1]).

This laboratory experiment was designed to obtain information on the extent of acidity developed due to added Al at different pH levels and a subsequent measure of exchangeable Al. The choice of medium for this type of experiment presents problems because of the inherently high contents of Fe and Al in mineral soils as opposed to their unavailability, due to organic complex formation in organic soils. Acid peat was chosen as the suitable medium of study because of its low metal content but the very high organic content produced further problems through complex formation with the metal.

MATERIALS AND METHODS

Two peats namely commercial sample, Fisons peat (I) and Red Moss peat were incubated separately. Four levels of Al (O, 25, 50 and 100 μg g^{-1} peat) at three different pH levels were applied. Each treatment was replicated twice and arranged in a completely randomized block design. Al was added as aqueous solution of $AlCl_3$ and that of lime as solid powder of $Ca(OH)_2$. Amounts of lime required to raise the pH to 5.55 and 6.80 for Fisons peat (I) and 4.34 and 5.30 for Red Moss peat was calculated from calcium hydroxide/pH titration curves.

Portions of air-dry (2mm) sample (50 g) were weighed out into a series of clean-dry 500 ml conical flasks. Taking quantity of the added solution into account, and extra calculated amount of water was added to bring the peats to 50% WHC and thoroughly mixed. The flasks with light even packing sample were laid out in the constant room temperature at 25° with clingfilm covering. A constant moisture content was maintained throughout the entire experimental period by making up the loss of moisture and aerated every day by removing the clingfilm cover for 5 min.

Replinishing the loss of water, sampling was done after every 5 days over 10 days from Fisons peat (I) and 4 days over 12 days from Red Moss peat of incubation. pH (peat solution ratio being 1:2.5) and exchangeable Al were estimated.

pH was measured from a saturation paste with a combined glass/calomel electrode using a model 7020 pH meter. The procedures outlined by Tinsley [2] were employed for the determination of organic carbon by wet oxidation, total N by Kjeldahl digestion, CEC by 1M NH_4OAc (pH 7.0) and metallic cations by 1M KCl solution. 2M KCl extractable NH_4-N and (NO_2+NO_3) N were determined colorimetrically using a Technicon Auto-Analyzer by forming an emerald-green colour and reddish-purple azo dye complex respectively. Exchangeable cations were determined spectrophotometrically and flame photometrically by using a atomic absorption spectrophotometer (Shandon southern model A 3400). Al was estimated colorimetrically by using the same autoanalyzer using xylenol orange as a colour developing reagent.

RESULTS AND DISCUSSION

Changes in pH. Incubated Fisons peat (I) showed a significant decrease in pH with time irrespective of the treatment combination (Table 2). In Red Moss peat, addi-

Table 1. General characteristics of the peats examined.

Peat	pH	WHC (%)	Org. C	Total N	CEC	NH$_4$ OAo, exchange cations Ca	Mg	K	Na
								meq kg^{-1} peat	
Fisons (I)	4.38	259	41.41	1.53	902.2	554.83	128.30	3.87	14.00
Red Moss	3.40	219	44.56	1.22	816.2	44.92	121.39	3.78	17.40

Peat	Total exchange basis	Base saturation (%)	Available N NH$_4$-N	(NO$_2$+NO$_3$)-N	1M KCl exch. cations Al	Mn	Fe
			(μg g^{-1} peat)			(μg g^{-1} peat)	
Fisons (I)	701.00	77.70	17.00	186.50	2.90	17.20	2.42
Red Moss	187.49	22.97	105.60	6.95	85.05	6.75	19.00

Table 2. Changes in pH due to added AlCl$_3$ during acrobic incubation of peat at 25°.

Peat	Days of incubation	pH	Al (μg g^{-1} peat) 0	25	50	100	LSD at 1% level
		4.38	4.38	4.30	4.25	4.08	
	0	5.55	5.55	4.45	5.33	5.20	0.061
		6.80	6.80	6.75	6.75	6.48	
		4.38	4.37	4.27	4.15	4.03	
Fisons (I)	5	5.55	5.30	5.20	5.14	5.02	0.035
		6.80	6.43	6.37	6.30	6.13	
		4.38	4.25	4.20	4.10	4.00	
	10	5.55	5.15	5.13	5.00	4.93	0.026
		6.80	6.20	6.15	6.10	5.98	
		3.40	3.29	3.40	3.43	3.38	
	0	4.34	4.34	4.32	4.19	3.95	0.081
		5.30	5.30	5.05	4.93	4.87	
		3.40	3.45	3.51	3.45	3.45	
	4	4.34	4.38	4.28	4.23	3.90	0.067
		5.30	5.34	5.17	5.13	4.93	
Red Moss		3.40	3.64	3.45	3.48	3.33	
	8	4.34	4.37	4.28	4.20	3.67	0.285
		5.30	5.18	5.01	5.01	4.80	
		3.40	3.50	3.55	3.45	3.28	
	12	4.34	4.33	4.23	4.19	4.09	0.079
		5.30	5.22	5.12	5.05	4.97	

tion of Al at pH 4.34 and 5.30 reacted in a different manner resulting in a different trend in pH change (Table 2).

It has been found that addition of AlCl$_3$ did not change the pH appreciably at the pH of the peat. However, at higher pH levels, added Al reduced the pH significantly and the situation was made worse as the pH was raised towards neutrality. Maximum depression occurred at the highest level of Al over all ranges of pH used. At high pH, hydrolysis of Al possibly resulted in an increased acidity. Carson and Dixon [1] suggested that increase in pH promoted the formation of monoaluminium compounds or polynuclear complexes of hydroxy Al. Under very acid conditions (pH 4.5) Al^{+3} will be dominant species. At higher pH (4.5 to 6.5) the most prevalent component will be hydroxy compounds. The extent of acidity that would develop depend on the degree of hydrolysis of Al.

$$Al^{+3} + 2H_2O \rightarrow Al(OH)^{+2} + H_3O^{+} \quad [1]$$

$$Al(OH)^{+2} + 2H_2O \rightarrow Al(OH_2^{++} + H_3O^{+} \quad [2]$$

$$Al(OH)_2^{+} + 2H_2O \rightarrow Al(OH)_3 + H_3O^{+} \quad [3]$$

In this study the formation of hydroxy complexes almost certainly occurred as the pH range was from 4.3 to 6.8

Any increase or decrease in pH during incubation may probably be associated with the equilibrium state of hydroxy Al with exchangeable Al in solution. Coleman and Thomas [3] suggested that hydrolysis of Al on organic matter exchange sites is the most important means of buffering pH in acid soils. Bloom *et. al.* [4] also proposed that Al exchange by H^{+} and hydrolysis of Al on organic matter exchange sites are the important sources of pH buffering in acid soils.

Changes in exchangeable Al. Recovery of exchangeable Al increased significantly with added Al (Table 3). The range of recoveries varied from 4.5 to 6.9 and 108.4 to 163.8/μg g^{-1} dry peat in Fisons peat (I) and Red Moss peat respectively at O day incubation. The recovery was very low in Fisons peat (I) as compared to Red Moss peat ranging from 1.0 to 2.1 and 47.6 to 52.8% respectively. Increase in pH reduced the recovery of exchangeable Al as would be expected. In Fisons peat (I), raising the pH from 4.38 to 5.55 lowered the yield of exchangeable Al from 52 to 16%. A further suppression of 32 to 3% in recovery was ob-

Table 3. Changes in exchangeable Al during aerobic incubation of peat at 25°.

Peat	Days of incubation	pH	Al (μg g^{-1} peat) 0	25	50	100	LSD 1% level
		4.38	4.52	4.81	5.13	6.90	
	0	5.55	3.00	3.51	3.28	3.29	0.51
		6.80	2.59	2.40	2.59	2.52	
		4.38	3.60	4.13	4.80	4.88	
Fisons (I)	5	5.55	3.00	3.00	2.51	2.84	0.65
		6.80	2.41	2.41	2.99	2.90	
		4.38	4.00	4.11	4.17	4.30	
	10	5.55	2.61	2.77	2.45	3.00	0.36
		6.80	2.79	3.10	2.38	2.59	
		3.40	108.36	121.69	137.90	163.81	
	0	4.34	9.04	9.67	11.04	13.08	3.02
		5.30	4.32	3.89	3.33	3.82	
		3.40	92.36	98.94	108.69	120.46	
	4	4.34	8.66	10.15	10.23	11.88	1.89
		5.30	5.76	5.00	5.57	4.37	
Red Moss		3.40	99.29	106.44	114.70	130.38	
	8	4.34	10.05	10.67	10.48	12.29	2.07
		5.30	6.22	5.52	6.32	5.93	
		3.40	96.29	112.87	113.74	124.38	
	12	4.34	9.27	10.06	10.96	12.67	3.62
		5.30	6.05	6.80	6.74	5.63	

served in most of the treatments following the rise in pH from 5.55 to 6.80.

A similar trend was found in Red Moss peat with increasing pH level (Table 3). About 90% exchangeable Al became non-exchangeable at pH 4.34. A further increase to pH 5.3 caused about 50% more reduction in most of the treatments irrespective of the time of incubation and dose of Al. Concentration of exchangeable Al changed with addition of lime but values were very low.

Per cent recovery of exchangeable Al in unlimited treatments was due to formation of organo-aluminium complexes between polyanionic polymers and soluble Al through chelation. However, limited hydrolysis of Al might occur at pH 3.40 and 4.38. On the contrary, low yield of Al from lime amended peats might be attributed partly to fixation by peat and formation of insoluble compounds. Bloom *et al.* [4] found that Al was preferentially absorbed by organic matter. Similar results were reported by other investigators (Pionke and Corey [5], Evans and Kamprath [6], Thomas, [7]. As a practical problem, Bloom *et. al.* [4] added that accurate determination of Al at pH above 4.9 is difficult because of variation in pH caused by microbially produced CO_2.

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