# CLAY MINERALS AND PHOSPHATE AVAILABILITY: II. THE UTILIZATION OF ADSORBED PHOSPHATE BY PLANTS\*

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In Part I it was shown that clay minerals retain phosphate when they come in contact with a solution containing phosphate ions. It was shown that kaolinite had a higher capacity to retain phosphate than montmorillonite and that a difference in solubility evidently existed between the phosphate retained by the two different clay complexes. In order to gain more knowledge on this point two different experiments were set up involving the use of plants as absorbing systems.

Experiment I. Samples of the various adsorbed clay phosphates manufactured in Part I were used as sources of phosphorus in some pure sand and solution cultures. These were compared with an equivalent amount of phosphorus supplied as superphosphate (20 per cent  $P_iO_s$ ). The setup consisted of quart Mason jars each containing 1500 grams of pure Ottawa white sand. The respective phosphate carriers were mixed throughout the sand. Two hundred cc. of Hoagland's solution minus phosphate were added to each jar. The small amount of iron needed was supplied as iron citrate. Minor elements were included. Tomato seed were planted in the jars and one plant was allowed to grow per jar. Distilled water was added daily to keep the moisture content near optimum for growth. All treatments were in duplicate or triplicate. The results are shown in Table 1 and in Figure 1 ABC.

## DISCUSSION OF KAOLINITE RESULTS

The results are significant in showing the effect of the degree of phosphate saturation of the kaolinite and the availability of the absorbed phosphate. From a practical viewpoint, these data support the following recommendations for kaolinitic soils: (1) Where a soluble phosphate like superphosphate is used it is necessary to apply a heavy rate per acre in order to get the desired results; (2) Since the rate of broadcast application necessary to raise the degree of phosphate saturation of this clay is high, it is much better to use a local application in the hill or row. The soluble phosphate applied in this manner would be of greater immediate availability because (a) it is closer to the immediate root system of the plant and (b) although it may be adsorbed by the kaolinitic clay the degree of phosphate saturation of the surrounding clay will be high, and as this experiment indicates the higher the degree of saturation of the kaolinitic clay the greater the availability of the absorbed phosphate; and, (3) The use of a granular or pellet form of phosphate carrier on soils of this character has advantages<sup>2</sup>. The higher the clay content the more important are the above recommendations.

Before discussing the montmorillonite results the second experiment will be recorded.

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TABLE :
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Availability of phosphate adsorbed by different clays at varying degrees of saturation.

Series and No.	Treatment				Saturation Degree of the clay	Average Oven-Dry Weight of Plants	Percent of PO, in plants (oven-dry basis)
Series	A				mg. PO <sub>4</sub> /g.	<b>g</b> .	%
1	66.9	mg.	PO4	as super	phosphate	3.160	0.525
2	"	••	" _	- Kaolin	50.80	1.727	0.277
3	,,	"	,,	,,	37.70	1.868	0.252
4	,,	,,	••	"	29.50	0.990	0.223
5	••	,,	,,	"	24.30	0.280	0.310
6	,,	"	,,	"	16.70	0.155	0.248
Series	в						
7	183.8	mg.	PO,	— Kaolir	n <b>50</b> .80	2.430	0.297
8	**		••	"	37.70	1.875	0.297
9	•,	"	**	,,	29.50	1.440	0.256
10	••	**	••	••	24.30	0.680	0.300
11	••	••	••	••	16.70	Samples los	t (See Fig. 1B)
Series	С						
12	66.9	mg.	PO4	— Volcia	y 23.12	2.785	0.326
18	••	••	••	,,	20.59	2.710	0.303
14	•,	,,	••	,,	14.67	2.886	0.296
15	••	••	••	**	10.18	2.574	0.249
16	••	••	,,	••	7.23	0.745	0.215

Experiment II. Instead of exposing the clay minerals to  $KH_sPO_4$  solutions and using the clay-adsorbed phosphate as source of phosphorus, jars containing 1500 grams of pure Ottawa white sand mixed with 1% of the respective clay were prepared. In each of these jars, various amounts of superphosphate  $(20\% P_sO_5)$  were thoroughly mixed. Other nutrients were supplied as in the first experiment. Tomatoes were grown in the jars. All treatments were in triplicate. Jars containing no clay were used as checks. The results are given in Table 2.

TABLE 2

Influence	of	different	clays	on	superphosphate	efficiency.

Superphosphate added	No clay present	1% Kaolin present	1% Volclay present	
(20% P <sub>s</sub> O <sub>R</sub> )	Yield*	Yield*	Yield•	
g.	g.	g.	g.	
0.50	1.202	0.47	1.122	
0.40	1.135	nil	1.250	
0.25	1.155	39	1.422	
0.15	1.035	**	1.200	

\* Yields are expressed on an oven-dry basis and are the average of the respective triplicated treatments.

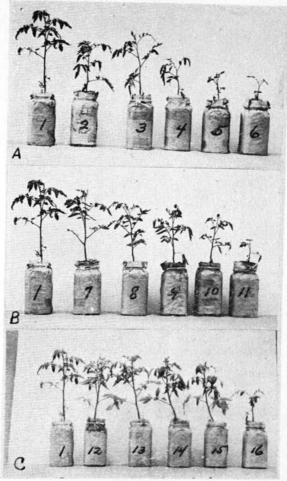


FIGURE 1

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These data indicate that montmorillonite (Volclay) is not decreasing the availability of the applied superphosphate for the tomato. Kaolin, on the other hand, depresses the yield very greatly which is in accord with the fixation data recorded in Part I and the plant use data of experiment I of this paper.

#### DISCUSSION OF MONTMORILLONITE RESULTS

Montmorillonite has an expanding lattice 1. When it is placed in water, water enters between the units and considerable swelling occurs. The suspension becomes quite viscous and gelatinous. The degree of expansion depends on the exchangeable cation present 1 and hence it is considered that the water is retained by cation hydration. In this swelling process it is believed likely that the soluble phosphate ion as well as water may become involved by entering between the units. Whether the phosphate ion is retained by any charge or linkage in this case is not known, but if it is the binding must be very weak because as the experiments indicate it is largely leached out with distilled water (though the leaching process is long and tedious because of the colloidal nature of montmorillonite). Furthermore, the plant usage data indicate a high availability for the retained phosphate.

However, it appears that there may be some small amount of phosphate fixed which is less soluble and available than the rest (See No. 16, Table 1). A possible explanation of this is that the montmorillonite sample was not pure and that it contained perhaps small impurities of a kaolinitic nature. This is entirely possible since it is extremely difficult to secure absolutely pure samples of the various clay minerals. Indeed, it is hard to detect the presence of limited amounts of other clay minerals in a given sample of a nearly pure specimen, and particularly so quantitatively.

Another explanation involves the structure of the clay 1. Direct and indirect methods indicate an anion replacement in which OH groups are involved. In kaolinite there is an exposed OH layer to account for the exchange. Also, some interior OH groups are present. It is considered most likely that the exposed OH layer in general accounts for the fixation of the phosphate ions by the kaolinite because, while the length of time of grinding increases the phosphate fixed, increased grinding-time eventually comes to have little influence. The small increase which occurs with each successive excess-grinding period may be attributed to the exposure of more and more of the interior OH groups on the edges of the frag-With montmorillonite there is no exposed OH layer such as we menta find in the kaolinite group of clay minerals. The OH groups are in the interior of the lattice and hence replacement of them by phosphate ions would be limited to those exposed on the edges of the fragments of the finely divided material. This greatly limits the fixation of the phosphate ions by montmorillonite even though it is highly dispersed.

#### SUMMARY

The results clearly indicate the low availability of the phosphorus held by the kaolin-phosphate complex. The exact nature of this complex is not known at the present time but work is in progress from which it is hoped that more knowledge will be had on this particular combination.

Since the mortmorillonite-phosphate complex is so highly colloidal and gelatinous in character when it is in a moistened condition, there is quite a likelihood of occlusion of soluble phosphate in it. It is very hard to leach out all of the soluble phosphate from this complex. It is, therefore, possible that some occluded soluble phosphate has accounted for the greater crop response, when this complex was used as the source of phosphorus, even though the material was subdivided into small 25 gram (on a dry basis) portions and leached with a large number of aliquots of distilled water over a period of one week.

Possible explanations are offered for some of the fixation phenomena observed.

#### REFERENCES

1 Grim, Ralph E.: Properties of clay, Ill. State Geol. Survey Circular 49, pp. 466-495, 1939.

2 Murphy, H. F.: The role of kaolinite in phosphate fixation, Hilgardia 12, pp. 341-382, 1939.