Studies on the Influence of Different Algerian Rock Phosphates when Reinforced with Leguminous Plant Material Like Cow-Pea (*Vigna-Sinensis*) on Carbon Transformations, Exchangeable Calcium and pH of the Alkali Soil

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The importance of phosphates is due to the reason that phosphorous is an essential constituent of plant and animal life; the quantity in the average soil is relatively small, particularly in alkali soil, and there is no atmospheric supply of this element on which plants can grow. It is seldom that crop fails to respond with increased yields when soluble phosphates are applied to soils that have been under cultivation for 25 years or more. Collings¹⁾ has stated as follows:-

“Low crop yields are more often due to the lack of phosphoric acid than due to the lack of any other nutrient. Phosphoric acid has often been called the ‘master key’ to agriculture. Phosphoric acid appears to be concerned in the production of nucleo-proteids, and it appears that phosphoric acid influences the production of seeds or grain more particularly than does nitrogen or potash”.

It is well known that when water-soluble phosphates are added to the soil, a major part is rapidly converted into insoluble form, i.e., fixed by the soils and only a small portion of the added phosphate is taken up by the plants. Soils vary greatly in their capacity to fix phosphates. The organic matter, the pH, the amount of soluble calcium and magnesium, the amount and chemical nature of the clay colloids and the amount of iron and alumi-

nium present in the soils are all important factors affecting the phosphate fixing power of the soils and the nature of the compound formed. According to Russel²⁾, in neutral and alkaline soils, the dicalcium phosphate appears to react with more calcium, giving perhaps first a compound of the octa-phosphate type $\text{Ca}_4\text{H}(\text{PO}_4)_3$ before reverting to an apatite CaX_2 , $\text{Ca}_3(\text{PO}_4)_2$ where $\text{X}=\text{OH}$ or F .

The present studies were undertaken by us to see the effect of decomposing organic matter on the increased availability of phosphates added and the beneficial effect of the solubilized phosphates on the pH value of the alkali soil together with an increase in the availability of phosphate and exchangeability of calcium.

METHODS AND MATERIALS

Total carbon was estimated by the Robinson, McLeans and Williams³⁾ method. Exchangeable calcium was determined by the NaCl method of Hissinik⁴⁾. Available phosphate was determined by the 2% citric acid method of Dyer⁵⁾; the pH was determined by a Beckman pH-meter.

The soil used in the experiments was collected from “Community Project Area”, Phulpur Allahabad (India) and from Soraon, Allahabad, (India). Five samples of Algerian rock phosphates were obtained

1) G.H. Collings, Commercial Fertilizers, p. 393-94 (1954); McGraw Hill Book Company.

2) E.J. Russell, Soil Conditions and Plant Growth, p. 457, 1950 Edition, Longmans.

3) G.W., Robinson, W. McLeans, and R. Williams, The Determinations of Organic Carbon in Soils: *J. Agri. Sci.*, **29**, 315 (1929).

4) D.J. Hissinik, Method for Estimating Adsorbed Bases in Soils and the Importance of these Bases in Soils: *Soil Sci.*, **15**, 269-76 (1923).

5) B. Dyer, On the Analytical Determination of Probably Available ‘Mineral’ Plant Food in Soils: *Trans. Chem. Soc.*, **65**, 115-167 (1894).

from France. The leguminous plants (cow-pea) were brought from the Agricultural Institute, Naini, Allahabad (India).

Two hundred grams of well-powdered alkali soil, after being passed through a 80 mesh sieve, were taken in shallow enamelled dishes. To these soils 1.0% carbon in one set of Phulpur soil and Soraon soil and 0.5% carbon only in Phulpur soil in another set were added in the form of cow-pea (*Vigna-sinensis*). To these sets 0.25% P_2O_5 in the form of the five Algerian rock phosphates, named, respectively A, B, C, D₁ and D₂ were added. The contents of the dishes were taken in a pestle and mortar and mixed thoroughly to make a homogeneous mixture. About 20% of distilled water was added to each dish. These dishes were exposed to the light of 500 Watt electric bulb hung at a distance of nearly two feet. The contents of the dishes were stirred on alternate days to facilitate aeration and about 20% of water was added on alternate days. Composite samples were taken and analysed for total carbon, exchangeable calcium, available phosphate and pH, respectively.

RESULTS

TABLE I

ANALYSIS OF ALGERIAN ROCK PHOSPHATES
FOR TOTAL P_2O_5 AND AVAILABLE P_2O_5

Algerian Rock Phosphate	Total P_2O_5 %	Available P_2O_5 %
A	29.62	7.57
B	26.45	5.62
C	33.37	6.64
D ₁	39.58	3.01
D ₂	39.78	3.09

TABLE II

PERCENTAGE CHEMICAL COMPOSITION
OF THE SOILS USED

	Phulpur soil	Soraon soil
1. Moisture	1.3	1.7
2. Loss on ignition	3.2	1.9
3. HCl insoluble	84.19	82.10
4. Sesquioxide	7.05	9.85
5. Fe_2O_3	4.03	1.68
6. CaO	1.20	1.12
7. MgO	1.30	1.73
8. P_2O_5 (total)	0.11	0.13
9. Available P_2O_5	0.017	0.016
10. Total carbon	0.23	0.11
11. Total nitrogen	0.04	0.03
12. Exchangeable Ca	4.5 m.e.%	3.8 m.e.%

Experiments with Soraon alkali soil

Average temperature—30°C

TABLE III

200 g soil + 1% C as Cow-pea + 0.25% P_2O_5
as Algerian Rock Phosphate (A).

Period of exposure in days	Total Carbon %	Carbon oxidized %	Available P_2O_5 %	Ex. Ca. in m.e. %	pH
0	1.11	—	0.036	3.9	10.3
80	0.72	0.40	0.049	5.3	9.4
160	0.63	0.49	0.070	6.2	8.5
270	0.48	0.63	0.076	6.7	7.4

TABLE IV

200 g soil + 1% C as Cow-pea + 0.25% P_2O_5
as Algerian Rock Phosphate (B)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Available P_2O_5 %	Ex. Ca. in m.e. %	pH
0	1.11	—	0.028	3.8	10.3
80	0.73	0.38	0.039	5.1	9.6
160	0.65	0.47	0.064	6.0	8.6
270	0.49	0.62	0.07	6.6	7.6

TABLE V

200 g soil + 1% C as Cow-pea + 0.25% P_2O_5
as Algerian Rock Phosphate (C)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Available P_2O_5 %	Ex. Ca. in m.e. %	pH
0	1.11	—	0.003	3.8	10.3
80	0.73	0.39	0.042	5.2	9.4
160	0.64	0.48	0.067	5.8	8.6
270	0.49	0.62	0.072	6.6	7.5

TABLE VI

200 g soil + 1% C as Cow-pea + 0.25% P_2O_5
as Algerian Rock Phosphate (D₁)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Available P_2O_5 %	Ex. Ca. in m.e. %	pH
0	1.11	—	0.024	3.8	10.3
80	0.74	0.37	0.033	5.0	9.6
160	0.65	0.46	0.059	5.9	8.6
270	0.50	0.62	0.064	6.6	7.6

TABLE VII

200 g soil + 1% C as Cow-pea + 0.25% P_2O_5
as Algerian Rock Phosphate (D₂)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Available P_2O_5 %	Ex. Ca. in m.e. %	pH
0	1.11	—	0.025	3.8	10.3
80	0.74	0.38	0.038	5.2	9.5
160	0.65	0.46	0.062	5.9	8.7
270	0.50	0.61	0.064	6.5	7.7

Experiments with Phulpur Alkali soil

Average temperature—30°C

TABLE VIII

200 g soil+1% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (A)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	1.23	—	0.038	4.6	9.6
60	0.78	0.45	0.051	6.2	8.8
120	0.68	0.55	0.069	6.9	7.7

TABLE IX

200 g soil+1% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (B)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	1.23	—	0.028	4.6	9.7
60	0.78	0.46	0.040	5.4	9.1
120	0.72	0.51	0.060	6.0	7.9

TABLE X

200 g soil+1% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (C)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	1.23	—	0.034	4.6	9.7
60	0.79	0.44	0.043	5.7	8.6
120	0.71	0.52	0.067	6.5	7.8

TABLE XI

200 g soil+1% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (D₁)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	1.23	—	0.025	4.6	9.6
60	0.87	0.37	0.030	5.6	8.8
120	0.73	0.50	0.060	6.2	7.9

TABLE XII

200 g soil+1% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (D₂)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	1.23	—	0.026	4.6	9.6
60	0.83	0.40	0.038	5.5	8.8
120	0.71	0.52	0.063	6.2	7.7

TABLE XIII

200 g soil+0.5% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (A)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	0.83	—	0.036	4.6	9.6
60	0.56	0.27	0.048	5.3	8.6
120	0.45	0.38	0.070	6.0	7.8

TABLE XIV

200 g soil+0.5% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (B)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	0.83	—	0.028	4.6	9.6
60	0.51	0.32	0.041	5.4	8.8
120	0.45	0.38	0.058	6.0	7.9

TABLE XV

200 g soil+0.5% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (C)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	0.83	—	0.034	4.6	9.6
60	0.53	0.30	0.040	5.5	8.8
120	0.47	0.36	0.060	6.1	7.8

TABLE XVI

200 g soil+0.5% C as Cow-pea+0.25% P₂O₅
as Algerian Rock Phosphate (D₂)

Period of exposure in days	Total Carbon %	Carbon oxidized %	Availa-ble P ₂ O ₅ %	Ex. Ca. in m.e. %	pH
0	0.83	—	0.026	4.6	9.6
60	0.53	0.30	0.039	5.2	8.9
120	0.46	0.37	0.058	5.8	7.6

DISCUSSION

A close study of the foregoing results clearly shows that carbonaceous material in the form of cow-pea is oxidised more quickly when added to the alkali soil in conjunction with phosphate, such as Algerian Rock Phosphates. In some blank experiments without the addition of cow-pea, it was observed that no change in pH, available phosphate or exchangeable calcium took place even after the lapse of one year.

The oxidation of organic matter like cow-pea greatly enhances the availability of insoluble Algerian Rock Phosphates when these phosphates are added in combination with organic materials to the alkali soil. This is due to the reason that tricalcium phosphate, which is present in these Algerian rock phosphates, is converted into more soluble form of phosphates, such as dicalcium phosphate and monocalcium phosphates by the action of carbonic acid produced during the decomposition, ammonification and nitrification of added organic matter. This is clear from the following equations:-

The following observations of Dhar⁶⁾ are of great interest in this connection:-

"The third dissociation constant of phosphoric acid is smaller than the first and second dissociations constants of carbonic acid and hence, carbonic acid converted tricalcium phosphate into dicalcium phosphate, which is more soluble than tricalcium phosphate. Thus, the availability of phosphate is increased in the soil richer in carbonic acid obtained from the oxidation of organic materials. Similarly, nitrous and nitric acids formed in the soil from ammonification and nitrification of proteins make phosphates more readily available. Thus, phosphates are more useful in the presence of organic matter like farmyard manure, straw etc. undergoing slow oxidation".

The above experimental results are also supported by a number of workers. Jensen⁷⁾ found that the addition of organic matter to a soil increases the solubility of both lime and phosphoric acid from 30-100%. Hester and Shelton⁸⁾ have also shown that the ap-

plication of suitable organic matter to the sandy truck soils of the coastal plains of U.S.A. may reduce the fixation of phosphates to an available form so that optimum yields of crop may be produced with much less superphosphate than is commonly used. Copeland and Markle⁹⁾ and Gerretsen¹⁰⁾ have also made similar observations.

The results recorded by us also clearly indicate that the exchangeable calcium of the system is greatly increased when Algerian rock phosphates are added in conjunction with cow-pea. This increase in exchangeable calcium may be ascribed to the dissolving action of carbonic acid and other weak acids, liberated by the oxidation of organic matter, on CaCO_3 of the alkali soil or CaCO_3 or CaO present in rock phosphates. In this way soluble Ca-ions replace the Na-ions from the exchange complex of the soil, thus, increasing the exchangeable calcium of the system. The carbon dioxide produced may also react with $\text{Ca}_3(\text{PO}_4)_2$ present in rock phosphate or calcium phosphate present in alkali soil, forming more soluble dicalcium phosphate which introduces more Ca-ions in the system.

In all the cases, the introduction of insoluble phosphates with organic matter greatly helps in lowering the pH of the alkali soil. This is due to the fact that the dicalcium phosphate, formed by the decomposition of organic matter on tricalcium phosphates, when comes in contact with water, partially behaves as a dilute solution of monocalcium phosphate and can reclaim alkali soils slowly.

SUMMARY

The beneficial effect of various sparingly soluble phosphates such as Algerian rock phosphates, when mixed with organic matter

6) N.R. Dhar, The Value of Calcium Phosphate in Atmospheric Nitrogen Fixation in Soils: *Kung. Lantbruks Annaler*, **21**, 49-78 (1954).

7) C.A. Jensen, Effect of Decomposing Organic Matter on the Solubility of Certain Inorganic Constituents of the Soil: *J. Agri. Research*, **9**, 253-268 (1917).

8) J.B. Hester, and F.A. Shelton, Soil Organic Matter Investigations upon Coastal Plain Soils: *Virginia Truck Expt. Sta. Bull.*, **94**, 1397-1428 (1937).

9) O.L. Copeland, and F.G. Merkle, The Influence of Certain Soil Treatments upon the Fixation and Availability of Applied Phosphates: *Soil Sci. Soc. Amer. Proc.*, **6**, 321-327 (1942).

10) F.C. Gerretsen, The Influence of Micro-organisms on Phosphate Intake by Plants: *Plant and Soil*, **1**, 51-81 (1948).

like cow-pea and added to the alkali soils, is clear from the fall in pH of these alkali soils. Not only the pH is lowered but also the exchangeable calcium, and, the availa-

bility of phosphates increases markedly. Hence, these alkali soils ultimately become fertile and cultivable.