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Soil physico-chemical properties, productivity and accumulation of heavy metals in fenugreek (*Trigonella foenum-graceum* L.), and their availability in soil as affected by Mussoorie rock phosphate

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Abstract
Two sets of field experiment on fenugreek (*Trigonella foenum-graceum*) with *cultivar* pusa early bunching, was conducted during winter (*rabi*) seasons of 2009-10 and 2010-11 at the Crop Research Form, Department of soil science, Sam Higginbottom University of Agriculture, Technology and Sciences, Allahabad to evaluate the effect of Mussoorie rock phosphate, on soil physico-chemical properties (bulk density, particle density, pH, EC, organic carbon, CEC, available N, P, K, exchangeable Ca, Mg), productivity and accumulation of heavy metals (Cd, Pb, Cr & Zn) in fenugreek and their availability in soil. The experiment was laid out in randomized block design with four levels of MRP (0, 100, 150 and 200 kg ha^{-1}) and replicated five times. The results revealed that green foliage and dry matter yield of fenugreek significantly increased by application of MRP. Highest green foliage (92.56 q ha^{-1}) and dry matter (19.11 q ha^{-1}) yields were noticed in the treatment receiving 200 kg ha^{-1} MRP, whereas plant content of heavy metals were reduced from 0.13 to 0.12 ppm Cd, 0.20 to 0.17 ppm Pb, 0.24 to 0.24 ppm Cr, and 0.37 to 0.34 ppm Zn with every enhancing levels of MRP from 0-200 kg ha^{-1}. Higher reduction of these toxic metals content in fenugreek plant were recorded in treatment receiving 200 $kgha^{-1}$ MRP which were lower than control & below the critical levels of toxicity. The bulk density, particle density, pH, EC & organic carbon content of the post harvest soil were not affected but CEC increased significantly from 15.57 to 15.68 cmol kg^{-1} with increasing levels of MRP. Soil amended with MRP resulted in significant increased in available N, P, K, and exchangeable Ca & Mg in post harvest soil. The maximum value of available N (197.79 kg ha^{-1}), P (30.10 kg ha^{-1}), K (246.95 kg ha^{-1}), exchangeable Ca (4.87 meq 100^{-1}g) and Mg (3.59 meq 100^{-1}g soil) were recorded with treatment where 200 kg ha^{-1} MRP was applied which were over the control. There was a reduction of soil content of DTPA-extractable micronutrients & heavy metals content of soil in comparison to control with the application of MRP and lower value of DTPA-Fe (3.37 ppm), Zn (0.84 ppm), Cd (0.57 ppm), Pb (0.65 ppm) and Cr (0.90 ppm) were recorded with 200 kg ha^{-1} MRP which were lower than control.

Keywords: Mussoorie rock phosphate, soil physico-chemical properties, heavy metals, fenugreek yield, accumulation

1. Introduction

Fenugreek (*Trigonella foenum-graceum L.*) is a most important, self pollinating, condiment and legume crop which is widely cultivated in India and other part of the world [1]. Fenugreek plant is used in foods as a green vegetable & fodder too; seed is used as a spice, in artificial flavoring of syrups as condiments and for the production of steroid and other hormones for the pharmaceutical industry. In addition to its importance as food for human and livestock, fenugreek plays an important role in some agricultural systems due to the ability of the nitrogen-fixing bacteria, it harbors to fix the atmospheric nitrogen under a broad spectrum of environmental conditions in both time (via crop rotation) and in space (via intercrop), which also may indirectly enhance associated diversity of wild flora, as well as soil fauna, which may in turn impact the sustainability of agricultural system. Agronomic studies conducted in different agro-climatic zones of India suggest that productivity of fenugreek can be enhanced by the proper application of phosphorus. Phosphorus is the back bone of any nutrient management programme for intensive cropping system. It is well known that the phosphorus is one of the major nutrients which is required in large quantities particularly for pulse crops for nodulation, N-fixation, optimal growth and yield of growing crops [2-3], but it is a major constraints as 98% soils of India have inadequate supply of P. Hence there is an imminent need for application of P to achieve higher yields of crops in the soil having low P availability.

Large amount of low grade rock phosphate have been found in some parts of India, of which an economically viable deposits occurs in Musoorie, is known as Mussoorie rock phosphate. In nature rock phosphate occurs as deposits of apatite (P-bearing minerals) such as carbonate apatite $[3Ca_3(PO_4)_2.CaCO_3]$, fluoro apatite $[3Ca_3(PO_4)_2.CaF]$, hydroxy apatite $[3Ca_3(PO_4)_2.Ca(OH)_2]$, sulpho apatite $[3Ca_3(PO_4)_2.CaSO_4]$, and oxyapatite $[3Ca_3(PO_4)_2.CaO]$, along with other necessary minerals such as crondallite $[CaO.2Al_2O_3.P_2O_5.5H_2O]$ wavelite $[4AlPO_4.2Al(OH)_3.9H_2O]$, Millisite $[2CaO.Na_2O.6Al_2O_3.4P_2O_5]$ Strengite $[FePO_4.2H_2O]$, Variscite $(AlPO_4.2H_2O)$ etc. In most of the commercial grade rock phosphate the P_2O_5 content is around 32% (w/w). Considerable research has been conducted in the past years on the characteristics and agronomic effectiveness of phosphate rock for direct application in the soil for crop production, the use of phosphate rock is an attractive alternative in comparison to the use of more expensive water soluble P fertilizers such as super phosphate because of the low cost involved. Major factor's which affect the dissolution & agronomic effectiveness of rock phosphate are source (reactivity), particle size [4], soil properties [5] and plant species [6]. Therefore the present study was planned to assess the soil physico-chemical properties, productivity and accumulation of heavy metals in fenugreek (*Trigonella foenum-graceum L.*) and their availability in soil as affected by Mussoorie rock phosphate.

2. Materials and Methods

The field experiment was conducted during *rabi* season of 2009-11 at the Crop Research Form, Department of soil science, Sam Higginbottom University of Agriculture, Technology and Sciences, Allahabad ($25^0$18' N latitude and $81^0$50' E longitude at an altitude of 98 meter above the mean sea level). The treatment consisted of four levels of mussoori rock phosphate i.e. 0, 100, 150, 200 kg ha^{-1}. The experiment was laid out in randomized block design with five replications. The effect of MRP was studied with Fenugreek (*Trigonella foenum-graceum L.*) *var.*Pusa early bunching, was sown in the first week of December during both the years of experiment. The recommended dose of N, P and K (50kg N+ 130kg P_2O_5 + 80kg K_2O ha^{-1}) was applied through urea, di-ammonium phosphate and muriate of potash, respectively. MRP was applied three weeks before sowing. Irrigation was given as and when required, the crop was harvested after 40 days of sowing. Fresh weight and dry weight of the crop were recorded at harvest. The harvested plants were washed with double distilled water, dried at 70^0C, weighed, crushed in a stainless steel grinder and stored in glass vials for chemical analysis. Soil sample were also collected before sowing and at after harvest of the crop. These soil, plant and MRP samples were analyzed for characterization of some properties, nutrients and heavy metals by adopting standard procedures. Soil, plant and MRP samples were digested in a di-acid mixture of conc. HNO_3:$HClO_4$ (3:1). Soil samples were extracted with DTPA-TEA [7] and the contents of Cd, Pb, Cr, Zn & Fe in digest/filtrate of these samples were determined by using atomic absorption spectrophotometer. The mechanical analysis of soil- such as sand, silt, clay% & textural class done by hydrometer method, bulk density & particle density [8]. The pH, EC, organic carbon, available N, P, K, exchangeable, Ca, Mg & CEC of soil samples were determined by adopting standard procedure [9]. The trends of results was similar during both the experimental year's hence, data were subjected to pooled analysis for results and discussion.

3. Result and Discussion

3.1 The Soil

Data given in Table-1 revealed that the soil of the experimental field was slightly alkaline (pH 7.71) in nature, sandy loam textural class, having bulk density 1.49 g cm^{-3}, particle density 2.53 g cm^{-3} and soluble salt concentration was 0.37 dSm^{-1}. The status of soil organic carbon content (0.53%) was medium, low in available nitrogen (182.10 kg ha^{-1}), available phosphorus (16.34 kg ha^{-1}), and medium in available potassium (239.45 kg ha^{-1}). The value of exchangeable calcium & magnesium was 2.04 and 1.42 meq100^{-1}g respectively, cation exchange capacity 15.49 coml kg^{-1}. The DTPA-extractable micronutrients and heavy metals content was i.e., Iron (Fe) 3.32, Cadmium (Cd) 0.61, Lead (Pb) 0.56, Chromium (Cr) 0.96 and zinc (Zn) 0.82ppm.

Table 1: General Characteristic of experimental soil & mussoori rock phosphate used in the experiment

S. No.	Experimental soil	Value	Mussoorie rock phosphate		
	Parameter's		S.No.	Parameters	Value
1.	Bulk density (g cm^{-3})	1.49	1.	Phosphorus as P_2O_5 (%)	19.28
2.	Particle density (g cm^{-3})	2.53	2.	Calcium as CaO (%)	39.43
3.	pH (Soil water suspension (1:2 W/v)	7.71	3.	Magnesium as MgO (%)	6.44
4.	EC (Soil water suspension, 1:2 w/v) dSm^{-1}	0.37	4.	Potassium as K_2O (%)	0.33
5.	Organic carbon %	0.53	5.	Organic carbon (%)	1.17
6.	Available nitrogen (kg ha^{-1})	182.10	6.	Iron as $Fe2O_3$ (%)	5.05
7.	Available phosphorus (kg ha^{-1})	16.34	7.	Cadmium as Cd (ppm)	171.87
8.	Available potassium	239.45	8.	Lead as Pb (ppm)	315.73
9.	Exchangeable calcium (meq 100^{-1}g)	2.04	9.	Chromium as Cr (ppm)	1.05
10.	Exchangeable magnesium (meq 100^{-1}g)	1.42	10.	Zinc as Zn (ppm)	173.13
11.	Cation exchange capacity (cmol kg^{-1})	15.49	_	_	_
12.	Iron (ppm)	3.32	_	_	_
13.	Cadmium (ppm)	0.61	_	_	_
14.	Lead (ppm)	0.56	_	_	_
15.	Chromium (ppm)	0.97	_	_	_
16.	Zinc (ppm)	0.82	_	_	_

3.2 Quality of Mussoorie rock phosphate

Data revealed (Table-1) that MRP used in this experiment contained Phosphorus 19.28%, Calcium 39.43%, Magnesium 6.44%, Potassium 0.33%. Organic carbon content 1.17%, Iron 5.05ppm, Cadmium 171.87ppm, Lead 315.73ppm, Chromium 1.05 and Zn 173.13ppm. Rock phosphate is applied as a fine powdered farm that is thoroughly mixed with soil. This enhances the geometric surface area with continued dissolution of applied rock phosphate. Plant roots are more likely to intercept the phosphorus dissolved from rock phosphate particles that are dispersed widely through the soil.

3.3 Physico-chemical properties of soil as affected by Mussoorie rock phosphate

Bulk density of the soil after harvest the crops was very slightly depleted from the initial bulk density of the soil with enhancing levels of MRP (Table-2). Average of the two year's experimental data shows that among the different levels of MRP, lowest value of bulk density (1.41 g cm^{-3}) were recorded with application of MRP 200 kg ha^{-1} followed by MRP 150 kg ha^{-1}. However particle density of post harvest soil slightly increased from 2.63-2.65 gcm^{-3} with increasing levels of MRP up to 200 kg ha^{-1} MRP.

The soil pH ranged from 7.67 to 7.68, EC of the soil ranged from 0.42-0.44 dSm^{-1}, with the increasing levels of MRP up to 200 kg ha^{-1}. The soil organic carbon content increased slightly (0.58 to 0.59) by the application of different levels of MRP, which was over their respective control. This could be envisaged due to increase in nutrition of the soil and growing crops resulting in vigorous root and shoot growth which produces higher biomass, consequently leading to increased accumulation of organic matter in soil. Lowering of bulk density and increased particle density is due to increase organic carbon content which results in more porosity and better soil aggregation [10-11].

Cation exchange capacity of the post harvest soil improved significantly with MRP application and maximum value of CEC (15.68 cmol kg^{-1}) was recorded with MRP 200 $kgha^{-1}$, which was over the control. This may be due to the enhancement of mineral matter of the leading to increase cation exchange capacity [12].

3.4 Status of primary (N. P. K.) and secondary (Ca, Mg) nutrients in soil after crop harvest

The results clearly indicate that increasing levels of MRP significantly increase the status of available, N. P. K, exchangeable Ca and Mg. Which were over their respective control. The maximum increases of these nutrients were recorded with treatment receiving MRP 200 kg ha^{-1}. The soil status of available N, ranged from (195.54 – 197.79 kg ha^{-1}), available P (18.43-30.10 kg ha^{-1}), and available K (240.28-246.95 kg ha^{-1}) with application of MRP 0-200 kg ha^{-1}. The maximum available soil nitrogen content (197.79 kg ha^{-1}), phosphorus (30.10 kg ha^{-1}) and potassium (246.95 kg ha^{-1}) were recorded with treatment receiving MRP 200 kg ha^{-1} which was over their respective control. The appreciable build up of available N, P & K in post harvest soil with application of MRP could be attributed to supply of these nutrients to soil, mineralization of organic bound N. P and K due to microbial action with time and enhanced its mobility due to complexing of important cations specially responsible for the phosphate fixation. [13-15]. Among the different levels of MRP maximum exchangeable Ca and Mg (4.87 and 3.59 $meq100^{-1}g$) respectively were recorded with treatment receiving MRP 200 kg ha^{-1}. Which was over their respective control. This could be explained on the basis of as MRP contain considerable amount of Ca^{++} and Mg^{++} leading to release of these nutrients during decomposition & mineralization of soil organic matter and partly due to production of organic acids which brought down the pH of soil and ultimately lead to higher availability of exchangeable Ca^{++} and Mg^{++}.

Table 2: Physico-chemical properties of post harvest soil as influenced by mussorie rock phosphate (mean of 2 years)

Mussoori rock phosphate (kg ha^{-1})	Bulk density (gcm^{-3})	Particle density (gcm^{-3})	pH	Electrical conductivity (dSm^{-1})	Organic Carbon (%)	Available Nitrogen (kg ha^{-1})	Available Phosphorus (kg ha^{-1})	Available Potassium (kg ha^{-1})	Exchangeable Calcium (meq $100^{-1}g$)	Exchangeable Magnesium (meq $100^{-1}g$)	Cation exchange capacity (cmol kg^{-1})
0	1.43	2.63	7.67	0.42	0.58	195.54	18.43	240.28	2.73	2.02	15.57
100	1.42	2.64	7.67	0.43	0.59	196.77	22.18	242.96	4.13	2.74	15.61
150	1.42	2.64	7.67	0.43	0.59	197.33	25.34	244.18	4.50	2.97	15.64
200	1.41	2.65	7.68	0.44	0.59	197.79	30.10	246.95	4.87	3.59	15.68
SE(d)	0.006	0.003	N5	0.003	NS	0.46	0.71	0.94	0.46	0.55	0.007
CD(P=0.05)	0.012	0.005	N5	0.007	N5	0.99	1.51	2.009	0.098	0.12	0.02

3.5 Build of micronutrients & heavy metals in soil after crop harvest

The data related to DTPA-extractable micronutrient & heavy metals (Fe, Zn, Cd, Pb& Cr) in soil after crop harvest as influenced by application of MRP are presented in Table-3. The results clearly indicate that the content of all these micronutrients and heavy metals (Fe, Zn, Cd, Pb& Cr) in soil after crop harvest were tends to reduce gradually with every enhancing levels of MRP application from 0-200 kg ha^{-1}. The maximum reduction was noted with MRP 200 kg ha-1. Where the value were (DTPA-Fe 3.37 ppm, Zn- 0.84 ppm, Cd - 0.57ppm, Pb - 0.65ppm and Cr - 0.90ppm) respectively. This could be ascribed due to the antagonistic effect of phosphorus applied through MRP to fix and form complexes with these micro nutrients and heavy metals and decrease their content. The low-grade rock phosphate of Jhabua, Madhya Pradesh (India), was investigated for its possible application in the removal of lead (Pb), copper (Cu), zinc (Zn) and cobalt (Co) ions from aqueous solutions. Effects of contact time, amount of absorbent and initial concentration of metal ions were studied. Adsorption of heavy metal ions was found to follow the order: Pb^{2+}> Cu^{2+}> Zn^{2+}> CO^{2+}. The probable mechanism of metal ions removed by rock phosphate was found to be by its dissolutions followed by subsequent precipitation [16].

Table 3: Soil content of DTPA-extractable micronutrients & heavy metals as influenced by Mussoorie rock phosphate (mean of 2 year's)

Mussoori rock phosphate (kg ha^{-1})	DTPA- extractable iron (ppm)	DTPA- extractable zinc (ppm)	DTPA-extractable cadmium (ppm)	DTPA- extractable lead (ppm)	DTPA -extractable chromium (ppm)
0	3.59	0.94	0.78	0.71	1.13
100	3.51	0.91	0.74	0.70	1.10
150	3.48	0.88	0.65	0.65	1.03
200	3.37	0.84	0.57	0.65	0.90
SE(d)	0.019	0.030	0.01	0.02	0.008
Cd(P=0.05)	0.040	0.060	0.03	0.03	0.018

3.6 Yield

The green foliage and dry matter yield of fenugreek crop was increased significantly with every enhancing levels of MRP up to 200 kg ha^{-1} over control (Table-4). The increase in green foliage yield with levels of MRP ranged from 59.03 to 92.56 qha-1 over control and that of dry matter yield ranged from 12.34 to 19.11 qha^{-1}. The maximum yield of green foliage (92.56qha^{-1}) and dry matter (19.11qha^{-1}) yield were recorded with treatment receiving 200 kg ha^{-1} MRP. This could be explained on the basis of MRP provide better nutritional environment of soil consequently release of various plant nutrient from soil at a better pace and increasing the availability and uptake of nutrients by growing plants, responsible for the improvement of green foliage and dry matter yield of the crop [17-19].

Table 4: Yield attributes and plant content of heavy metals and micronutrient (mean of 2 year's)

Mussoori rock phosphate (kg ha^{-1})	Fresh weight (qha^{-1})	Dry weight (qha^{-1})	Plant content of heavy metals & micro nutrient			
			Cadmium (ppm)	Lead (ppm)	Chromium (ppm)	Zinc (ppm)
0	59.03	12.34	0.13	0.20	0.24	0.37
100	78.84	15.86	0.13	0.20	0.25	0.37
150	84.13	17.74	0.13	0.18	0.24	0.36
200	92.56	19.11	0.12	0.17	0.24	0.34
SE(d)	15.58	2.96	0.005	0.005	0.005	0.004
CD(P=0.05)	33.21	6.31	0.012	0.012	0.010	0.008

3.7 Heavy metals content in plant after crop harvest

The data pertaining to the plant content of heavy metals (Cd, Pb, Cr& Zn) are depicted in Table-4. Results clearly indicate that the plant content of heavy metals were tend to reduce with every increasing levels of MRP up to 200 kg ha^{-1} and thus the higher reduction were observed with treatment receiving 200 kg ha^{-1} MRP followed by 150 kg ha^{-1} MRP. Cadmium (Cd) content in plants reduced from 0.13 ppm at control to 0.12 ppm at 200 kg ha^{-1} MRP. The corresponding decrease in lead (Pb) content was from 0.20 to 0.17 ppm, Chromium (Cr) content ranged from 0.24-0.24 ppm and Zinc content ranged from 0.37 to 0.34 ppm. Over all highest reduction in plant metal contents (Cd - 0.12 ppm, Pb - 0.17, Cr -0.24 and Zn - 0.34 ppm) were observed with MRP 200 kg ha^{-1}, which were the below the tolerance levels of the crop and critical level of toxicity. This may be attributed to the antagonistic effect of phosphorus to fix and form complexes with different toxic metals and decrease their bioavailability to the growing plants. Research work shows that PR was effective in increasing arsenic uptake and decreasing metals uptake by P. Vittata and thus can be used as a cost effective amendment for phytoremediation of metals polluted soils [20]. Fenugreek is extremely sensitive to metals added to soils. The fenugreek crop is consumed in food as leafy vegetable, seed as a spice and fodder too, crop uptake studies are essential in the assessment of hazards due to metals in soil and plants because of their relevance to phytotoxic effects and to contamination of the food chain. Therefore, lower content of these heavy metals in fenugreek leave obtained in the present study is good for consumption.

4. Conclusion

From the results of the present study, it may be concluded that MRP can be used as a source of plant nutrients with special reference to phosphorus. Its application to soil brought about an increase in green foliage and dry matter yield of fenugreek over control without any detrimental effects and critical levels of heavy metals in soil and plants structure were protected. It showed significant positive effect on soil physic-chemical properties, nutrient availability in soil and plant. Thus MRP at this level can be used for crop production without any detrimental effects.

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