Research Article

Soil Extractable Phosphorus Contents as Affected by Phosphatic Fertilizer Sources Applied with Different Levels of Humic Acid

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Abstract | Soil fertility and crop yield can be increased by the combine addition of some organic amendments like humic substances and phosphatic fertilizers. This practice involves an increase in the solubility and availability of P in soils. An incubation experiment was conducted during 2017 to evaluate the impact of various P fertilizers applied with and without humic acid on P availability. Three different rates of humic acid as 0, 5 and 10 kg ha^{-1} with three different P sources as nitrophosphate (NP), single superphosphate (SSP), and di-ammonium phosphate (DAP) at a recommended rate of 90 kg P_2O_5 ha^{-1} were applied. Soils amended with different P fertilizers with and without HA showed mix trend in AB-DTPA extractable P at day zero of incubation and then a rapid mineralization and weekly turnover were increased up to 84 days of incubation period. Maximum mean available P of 14.32 mg kg^{-1} was recorded in soils which were amended with DAP and 10 kg HA ha^{-1}, whereas the lowest available P concentration of 8.09 and 7.82 mg kg^{-1} was recorded in soils where SSP and NP were applied, respectively, without any amendment of HA. Weekly turnover and mineralization potential increased with incubation periods as well as with the application of different HA levels. Maximum weekly P turnover rate and mineralization potential were 1.35 mg kg^{-1} and 67.71 kg P ha^{-1} season^{-1}, were recorded in the soils that were treated with DAP and 10 kg HA ha^{-1}, whereas the lowest were noted in soils that were applied SSP and NP alone. Data regarding the water soluble phosphorus showed significant increased with increasing levels of HA and incubation days with maximum mean available water soluble P of 1.219 mg kg^{-1} in soils treated with DAP and 10 kg HA, while the lowest of 0.565 mg kg^{-1} was noted in soils that were applied with recommended level of NP alone. It was concluded that the application of recommended dose of DAP with HA can be the optimal source for the improvement of P availability and mineralization in given soil conditions.

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Introduction

Soil is known as a basic and essential resource for the presence of terrestrial ecosystem, particularly vital for the sustainable agriculture and provides support for the expanding agriculture (Hermawan and Cameron, 1993; Su et al., 2010). Improvement in the physical and chemical properties of soils plays a significant role in the production of crops for the increasing world population (Nortcliff, 2002). Improved soil qualities are important for good soil fertility, soil production, economic and environmental sustainability. A good quality soil is capable of to yield more as well as sustain a flexible ecosystem in comparison to poor quality soils. Soils with poor quality, like sandy soils, are more vulnerable to water and wind erosion and yield low crop production because of earlier nutrient washing/leaching away from the root-zone of plants (Reynolds et al., 2007).

Phosphorus is the fundamental and crucial element for the plant growth and is termed as the limiting nutrient because of its depleted resources and low availability in agricultural ecosystems (Ding and Pan, 2005; McBeath et al., 2005). It is also used as fertilizer in huge quantities for the production of the crops world widely (Liu et al., 2017). It is a well-known fact that the P resources are very limited as they are depleted day by day. In this regard the availability of P in soil plant system is now become a worldwide challenge (Fink et al., 2016). Increased use of P fertilizers in relation to the increasing food demands is leading towards the accumulation of P in soils by Fe, Al and Ca (Gérard, 2016; Ozanne, 1980), leaching/release from the root zone, eutrophication of aquatic system and ultimately the shortage supply of P in soil. This short supply in forthcoming decades and centuries will be the major reason of limited agricultural production (Van et al., 2017).

Behavior of P depends on its adsorption and desorption to and from the solid phases in soil. Adsorption bound the phyto accessibility of P, whereas desorption permits the release of P from the soil (Lair et al., 2009; Wang and Liang, 2014). Adsorption of P involved the capturing of P by Fe, Al and clay particles (Gérard, 2016) and thus only a small proportion P is available to the plants. The efficiency by which the P is adsorbed by these particles depends on the supply of P to the soil, its desorption and the buffering capacity of the soil. So, the adsorption and desorption processes are of equally importance in relation to the availability of P in soil plant system (Wang and Liang, 2014).

Humic acid, a valuable natural and chemical constituent of the soil organic matter (Lin et al., 2017; Schnitzer, 1982), is obtained from the natural decomposition of plant and animal materials (Spaccini et al., 2006). It has been evaluated that increasing the HA contents results in increased organic matter contents of the soil and also improves the soil fertility and productivity and the yield and quality of crops (Quan-Xian et al., 2008; Zhen-Yu et al., 2013) by producing positive impact on the physical and chemical properties of soil, nutrient uptake efficiency of plants, their root growth and yield (Nikbakht et al., 2008; Tahir et al., 2011). Humic acid contains numerous functional groups like hydroxyl (-OH), carboxyl (-COOH), and phenolic hydroxyl groups and also acts as a leading source of adsorption sites in soil organic matter contents (Lin et al., 2017; Quan-Xian et al., 2008). It also has the capability to affect the P adsorption and its availability by interacting with many metal oxides (like alumina, silicon dioxide, and iron oxide) by making complexes, chelates, and adsorption processes with these elements (Wang et al., 2016; Yan et al., 2016). Addition of humic substances increases the OM contents of soil without going for any humification process of organic matter to happen because it is already present as humified material (Yang et al., 2019). Plants grown in organic matter amended soils can take up P more easily because of its excessive supply in soil solution and the extent with which the P is attached on the exchange sites of organic matter mainly depends on the forms of P present and a range of bio-geochemical and environmental factors including the type of clay contents, organic matter added and the temperature and soil moisture contents of the soil (Zhang et al., 2014). Many of the studies revealed that the addition of organic matter contents to the soil is directly involved in the enrichment of soils with P and other nutrients present in organic matter and it has been documented to be a most important mechanism which affects the P adsorption and desorption directly (Wang and Liang, 2014; Ye et al., 2006). But the results regarding the effect of OM contents on P adsorption and desorption are still not much vibrant because of many of conflicted studies (Hiradate and Uchida, 2004; Zhen-Yu et al., 2013). It has also been investigated that that the organic matter has the ability to increase the P availability in P-fixing soils and enhance its bioavailability in applied fertilizers (Quan-Xian et al., 2008; Yan et al., 2013; Zhen-Yu et al., 2013). Removal of organic matter from the top layer of soil reduced the P adsorption capacity of soil and increase the desorption, thus removing organic matter decreased the P concentrations in soils (Debicka et al., 2016). In disparity, Hiradate and Uchida, 2004 revealed that removing the soil organic matter from an andisol increases the amount of adsorbed P and it suggests that the sites occupied by soil organic matter can absorb P and restrained the P adsorption through aggressive adsorption. Such differing studies indicate that the P adsorption and desorption of different soils depends on the type and nature of soil and organic matter added or present in soil. Keeping in view the importance of humic substances in improving the solubility of soil phosphorus, an incubation experiment was conducted to see the release of extractable P from different sources when applied with and without humic acid.

Materials and Methods

Surface soil was collected from the unfertilized area of the Agricultural Research Farm of the University of Agriculture, Peshawar-Pakistan (Tarnab soil series; fine silty mixed hyperthermic udic Haplustepts) in July 2016 and was brought to the Department of Soil and Environmental Sciences, The University of Agriculture-Peshawar. The soil (silt clay loam) was ground well and sieved through 2mm. Three composite samples were made by this soil and test for different physico-chemical properties before the start of experiment. The soil used was silty clay loam with a pH (1:5) of 7.51 and EC (1:5) was 0.22 dS m^{-1}. This soil was deficient in organic matter contents (0.67%) with low P of 2.05 mg kg^{-1} and lime contents of 14.04% (Table 1). After the analysis of soil an incubation study was conducted in the advanced laboratories of Soil and Environmental Sciences Department of the Agriculture University Peshawar, Pakistan to investigate the release of soil P contents as influenced by the application of different phosphatic fertilizers alone and in combination of different levels of humic acid. Different sources of P fertilizer as nitrophosphate (NP), di-ammonium phosphate (DAP) and single superphosphate (SSP) with a recommended dose of 90 kg P_2O_5 ha^{-1} with and without different levels of humic acid as 0, 5 and 10 kg HA ha^{-1} were applied to 1 kg soil in plastic pots. A total of 9 treatments with 3 replicates arranged in completely randomized design at 25 ^{0}C were incubated for a period of 12 weeks by using the incubation techniques as described by Jenkinson and Powlson (1976). Moisture content of soil under investigation was set at field capacity level with 250 g water per kg soil (25% moisture content). This moisture content was maintained throughout by adding the amount of water daily through a fine water sprayer.

To produced humic acid, 10 kg coal sample was treated with 4 L HNO_3 and 40 L distilled water in three equal intervals each of 15 min. The coal residue was treated with alkali (0.5 N NaOH). The water-soluble salt of HA thus formed was dissolved into a solution which was filtered through Whatman No. 42 filter paper through vacuum suction pump to separate it from insoluble inorganic residues. The solution was then treated with HCl to precipitate HA back and thus sodium-humate (Na-humate) was produced (Hai and Mir, 1998). Humic acid produced was analyzed for pH (McClean, 1982), total N (Bhargna and Raghupathi, 1993), extractable P and micronutrients (Soltanpour and Schwab, 1977) (Table 1).

Table 1: *Physico-chemical properties of soil and humic acid used for the experiment.*

Properties	Units	Concentration
Sand	%	14.00
Silt	%	53.23
Clay	%	32.80
Textural class	-----	Silt clay loam
pH (1:5)	-----	7.51
EC (1:5)	dS m^{-1}	0.22
Organic matter content	%	0.67
P concentration	mg kg^{-1}	2.05
K concentration	mg kg^{-1}	109
Lime ($CaCO_3$)	%	14.04
Humic acid		
pH (1 : 5)	----	5.5-6.0
Organic C	%	50.4-60.3
Total N	%	3.0-5.5
Extractable P	mg kg^{-1}	50.0-52.5
Zn	mg kg^{-1}	05.5-07.3
Mn	mg kg^{-1}	12.2-15.5

Soil texture was determined by standard procedure of Koehler et al., 1984. Soil pH and electrical conductivity were determined in soil and water suspension of 1:5 by Mclean, 1982. Ammonium Bicarbonate–Diethylene Triamine Penta Acetic Acid (AB-DTPA) extractable P was analyzed by the method of Soltanpour and Schwab, 1977, whereas, the water-soluble P was determined by following the same procedure by using distill water instead of AB-DTPA extract solution. Soil organic matter content was determined as per method given by Nelson and Sommers, 1982. Lime was determined by the method of Richard, 1954. To examine the release and accumulation of P contents as influenced by treatments applied, the AB-DTPA extractable and water-soluble soil phosphorus contents were determined on different days intervals i.e. 0, 7, 14, 28, 56 and 84 days of incubation.

Table 2: *Effect of different phosphorus sources alone and in combination of humic acid on AB-DTPA extractable P availability during incubation.*

Treatments		Incubation period (days)						Mean available P (mg kg^{-1})
P sources	HA levels	0	7	14	28	56	84	
(90 kg P_2O_5 ha^{-1})	(kg ha^{-1})	AB-DTPA extractable P (mg kg^{-1} soil)						
NP	0	3.25	7.31	7.24	8.77	9.48	10.86	7.82 f
NP	5	3.63	9.28	10.34	11.44	12.13	12.48	9.88 de
NP	10	3.41	9.43	10.76	12.04	13.48	14.12	10.54 cd
SSP	0	3.37	7.51	7.25	9.68	10.08	10.64	8.09 f
SSP	5	3.47	8.87	9.97	11.37	13.26	14.02	10.16 d
SSP	10	3.35	10.12	11.47	12.54	14.37	15.24	11.18 c
DAP	0	3.81	8.59	8.48	10.02	12.48	13.41	9.47 e
DAP	5	3.73	11.73	14.25	16.26	17.54	17.83	13.56 b
DAP	10	3.59	11.97	14.79	17.27	18.47	19.84	14.32 a
Mean		3.51	9.42	10.51	12.15	13.48	14.27	

Values having different alphabets are statistically ($P \geq 0.05$) different from each other; NP: Nitro phosphate; SSP: Single superphosphate; DAP: Di-ammonium phosphate.

The changes in P contents (weekly-turnover) were calculated by deducting the initial P contents extracted by AB-DPTA at time zero from the final P contents extracted after 12 weeks of incubation and dividing by total numbers of weeks. Mineralization potential in kg P ha^{-1} week^{-1} was calculated by multiplying P content week^{-1} with 2. Mineralization potential season^{-1} was calculated by multiplying mineralization potential week^{-1} with 25.

The data collected were analyzed statistically by using the procedures as mentioned by Steel and Torrie, 1980 with Statistix 8 software (Version 8.1) and least significant difference (LSD) test was applied to know the significant difference among the treatments applied.

Results and Discussion

Concentration of AB-DTPA extractable P at different days of incubation period

Concentration of AB-DTPA extractable P at different intervals of incubation period in Table 2. Data showed a slow and gradual increase in AB-DTPA extractable P up to 84 days of incubation in soils when P sources were applied alone and with combination of different levels of HA and the more prominent effect was observed with each increment of HA level as compared to P sources alone. Maximum mean extractable P value was 14.32 mg kg^{-1} was observed in soils that were treated with 90 kg P_2O_5 ha^{-1} in the form of DAP with 10 kg HA ha^{-1} that was significantly highest then the release of 13.56 mg kg^{-1} obtained from the soils where DAP was applied in combination of 5 kg HA ha^{-1}. Lower extractable P concentrations of 8.09 and 7.82 mg kg^{-1} soil were observed in soils where SSP and NP were applied without HA, respectively.

Data indicate that AB-DTPA extractable P in soils where P sources were applied alone showed decrease after 14 days of incubation and then a rapid mineralization was recorded up to 84 days of incubation, while the P release gradually increased from day 0 to 84 when applied with different HA levels suggesting the role of organic matter contents/ humic substances in P release in soils. When we see the data in regards of incubation days, P release significantly increase with increasing the incubation days signifying the role of humic substances in a variety of way to make soil conditions more conducive for maximum P release with increasing time.

Percent increase with each P source and HA levels indicate that when NP was applied with 5 and 10 kg ha^{-1} HA, the percent increase over NP alone showed an increase from 26.41 to 34.81%, respectively. Similarly, the soils that were treated with SSP and DAP with different levels of HA showed percent increase of 25.61 to 38.23% and 43.22 to 51.30%, respectively with 5 and 10 kg HA ha^{-1} indicating the superiority of high level of HA in P release (Figure 1).

Table 3: *Effect of different phosphorus sources alone and in combination of humic acid on mineralization potential and weekly turnover of the soil.*

Treatments		Incubation period (days)		Weekly turnover (mg kg^{-1} soil)	Mineralization potential (kg P ha^{-1} season^{-1})
P sources	HA levels	0	84		
(90 kg P_2O_5 ha^{-1})	(kg ha^{-1})	AB-DTPA extractable P (mg kg^{-1} soil)			
NP	0	3.25	10.86	0.63	31.71
NP	5	3.63	12.48	0.74	36.88
NP	10	3.41	14.12	0.89	44.63
SSP	0	3.37	10.64	0.61	30.29
SSP	5	3.47	14.02	0.88	43.96
SSP	10	3.35	15.24	0.99	49.54
DAP	0	3.81	13.41	0.80	40.00
DAP	5	3.73	17.83	1.18	58.75
DAP	10	3.59	19.84	1.35	67.71

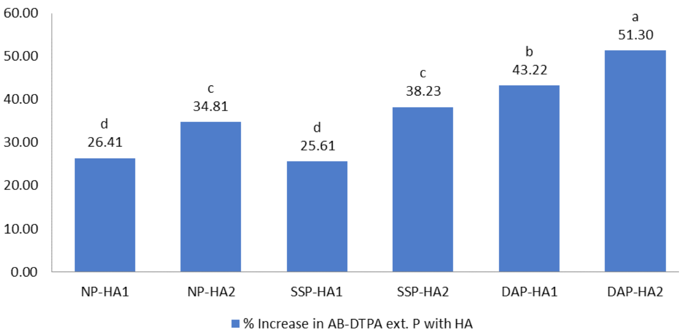

Figure 1: *Percent increase in AB-DTPA extractable phosphorus concentration as affected by different P sources applied with different levels of humic acid. NP: Nitrophosphate; SSP: Single superphosphate; DAP: Di-ammonium phosphate; HA_1: HA@5 kg ha^{-1}; HA_2: humic acid @10 kg ha^{-1}; Bars having different letters are statistically different from each other.*

Overall the effect of di-ammonium phosphate was noted more significant either alone or with 5 and 10 kg HA ha^{-1} when compared with other sources. Maximum P release of 19.84 mg kg^{-1} was noted after 84 days of incubation in soils where DAP was applied @10 kg HA ha^{-1} followed by a release of 17.83 mg P kg^{-1} noted in soils where DAP with 5 kg HA ha^{-1}. After DAP the maximum P release of 15.24 mg kg was given by soils treated with SSP and 10 kg HA ha^{-1}. The increased available P concentrations possibly related to the release of significant amount of CO_2 during the decomposition of OM applied in the form of humic acid which may have complex the cations such as Ca^{+2} and thus reduced the P fixation in calcareous soils (Tolanur and Badanur, 2003). Similar results were quoted by Toor and Bahl, 1997, who stated that the integration of inorganic and organic P fertilizers showed a synergistic effect in increasing the extractable P in comparison to P fertilizers application alone. Adler and Sikora, 2003 stated that addition of organic fertilizers has the ability to enhance the solubility of P through release of some organic acids like humic and fulvic acids in soils which covers the P adsorption sites and accordingly, increases the amount of P contents in soil solution. Improvement in P availability may also be due to some chemical reactions which involved the desorption and mineralization of added and already present P in soil (Akhtar and Alam, 2001; Erich et al., 2002). It is also documented that the initial retention of added P happens due the adsorption mechanism by both; ion and ligand exchange (Sample et al., 1979).

Though, the adsorption and precipitation processes seem to be dependent on P application rate (Sample et al., 1980) but the synergistic effect of organic fertilizers in combination of P fertilizers has been described to enhance the soil P concentrations (Garg and Bahl, 2008; Mkhabela and Warman, 2005). Delgado et al., 2002 also described an increased recovery of applied P with organic mixture of fulvic and humic acids which showed a decrease in precipitation of soluble Ca-phosphate in soil. Yang et al., 2019 stated that the addition of organic matter in soils with P fertilizers can increase the P availability efficiently by increasing the P storage capacity of soil and decrease the P adsorption rate with supreme phosphate buffering capacity.

Turnover and mineralization potential of phosphorus

Data regarding the weekly turnover and mineralization potential in soil as treated with different phosphatic fertilizers alone and in combination of HA is presented in Table 3. Data show that the rate of changes of extractable P (weekly turnover) varied

Table 4: *Effect of different phosphorus sources alone and in combination of humic acid on water soluble P concentration during incubation.*

Treatments		Incubation period (days)						Mean available P (mg kg^{-1})
P sources	HA levels	0	7	14	28	56	84	
(90 kg P_2O_5 ha^{-1})	(kg ha^{-1})	Water soluble P (mg kg^{-1} soil)						
NP	0	0.384	0.524	0.581	0.611	0.634	0.657	0.565 g
NP	5	0.391	0.617	0.645	0.652	0.753	0.764	0.637 f
NP	10	0.398	0.683	0.745	0.765	0.825	0.806	0.704 de
SSP	0	0.373	0.628	0.655	0.703	0.748	0.731	0.640 f
SSP	5	0.403	0.651	0.676	0.794	0.812	0.834	0.695 e
SSP	10	0.411	0.665	0.823	0.847	0.851	0.864	0.744 d
DAP	0	0.456	0.784	0.823	1.202	1.303	1.341	0.985 c
DAP	5	0.478	0.921	0.983	1.208	1.428	1.455	1.079 b
DAP	10	0.471	0.954	1.265	1.513	1.546	1.563	1.219 a
Mean		0.418	0.714	0.800	0.922	0.989	1.002	

Values having different alphabets are statistically ($P \geq 0.05$) different from each other; NP: Nitrophosphate; SSP: Single superphosphate; DAP: Di-ammonium phosphate.

from 0.63-1.35 mg P kg^{-1} soil when the soils treated with different P sources alone and in combination of different levels of HA. Weekly turnover increased with every increment in HA level indicating the importance of HA in increasing the changes in extractable P availability of applied fertilizers. Maximum weekly turnover of 1.35 mg kg^{-1} soil was noted in soils where DAP was applied with 10 kg HA ha^{-1} followed by 1.18 mg kg^{-1} that was noted in soils which were treated with DAP and 5 kg HA ha^{-1}, whereas the lowest weekly turnover of 0.61 and 0.63 mg kg^{-1} soil were observed in pots where SSP and NP were applied alone. Again, when these fertilizers were applied with different levels of HA, an increase in weekly turnover of the soils was observed.

Data regarding the mineralization potential of soils as affected by different P sources when applied alone and in combination of different levels of HA showed the similar results like weekly turnover with highest MP of 67.71 kg ha^{-1} $season^{-1}$ that was produced by pots treated with DAP and 10 kg HA ha^{-1} and lowest of 30.29 kg ha^{-1} $season^{-1}$ in pots where recommended dose of SSP was applied alone. Each and every source of P fertilizer showed increase in weekly turn over and mineralization potential when applied with 5 and 10 kg HA ha^{-1} but when we see the overall effect then the DAP with 10 kg HA ha^{-1} always lies on top indicating the efficiency of humic substances in increasing the mineralization potential and P availability of the soils. Similar findings were given by Sharif et al., 2010 and Jamal et al., 2018, who stated that the addition of P fertilizer reinforced with humic acid was more effective in making the soil conditions more conducive for soil P mineralization and for crop nutrients availability. Our findings are also in agreement with the studies of Sarir et al., 2006 who stated an increase in P recovery and mineralization of P with the application of humic acid.

Concentration of water-soluble P at different levels of incubation period

Data regarding the water-soluble phosphorus contents as affected by different P fertilizers with and without HA is shown in Table 4. The water-soluble P contents showed a significant increase with increased incubation days from minimum P contents of 0.418 mg kg^{-1} at day zero to highest of 1.002 mg kg^{-1} after 84 days of incubation. Mean available water-soluble phosphorus significantly increased with HA levels applied with different P sources from 0.565 mg kg^{-1} in pots where NP fertilizer at a recommended dose was applied, while the highest mean available P of 1.219 mg kg^{-1} was observed in soils which were treated with DAP and HA@10 kg ha^{-1}. With every increase in HA level an increase in mean available P with every P source was observed. Percent increase in available P showed increased with every increment of HA level. Percent increase in mean available water-soluble phosphorus due to different P sources and HA levels were 12.71, 24.51, 8.65, 16.23, 9.54 and 23.74% (Figure 2) when recommended doses of NP, SSP and DAP were applied with 5 and 10 kg HA ha^{-1}, respectively.

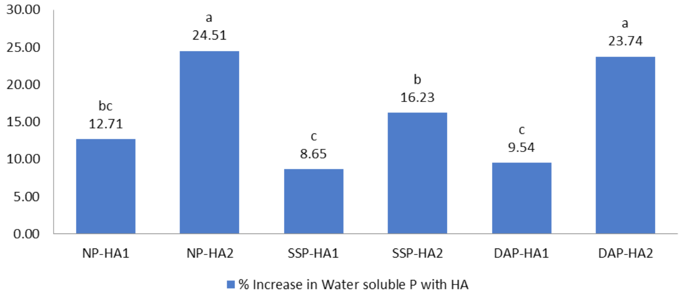

Figure 2: *Percent increase in water soluble phosphorus concentration as affected by different P sources applied with different levels of humic acid; NP: Nitro phosphate; SSP: Single superphosphate; DAP: Di-ammonium phosphate; HA_1: HA@5 kg ha^{-1}; HA_2: humic acid @10 kg ha^{-1}; Bars having different letters are statistically different from each other.*

Data indicate that HA affects the P release in a positive way and this effect can be enhanced by increasing the HA levels. The more appropriate and visible effect among the different P sources used with different levels of HA is noted by NP followed by DAP when applied with 10 kg HA ha^{-1}. Similar findings were quoted by Jamal et al., 2018 and Sharif et al., 2010, who studied the integration used of phosphatic fertilizers and humic acid and stated that their combine use can enhance the solubility of available P in soil.

Conclusions and Recommendations

Based on the results of the study it is concluded that soils treated with different P sources alone and in combination of humic acid exhibit an initial decline in AB-DTPA extractable P in first 7 and 14 days of incubation and after that a rapid mineralization up to 84 days of the incubation period. Among all the P sources, the application of recommended dose of DAP with 10 kg HA ha^{-1} was more effective in making the soil environment more conducive for P mineralization and availability. Adding HA with DAP and SSP to the soils can improve the physical and chemical properties of soils and it may be more feasible for crop productions under sustainable agriculture.

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Novelty Statement

This piece of research work would be helpful in increased use of organic and inorganic fertilizers and will lead towards the sustainable agriculture.

Author's Contribution

Muhammad Izhar Shafi conducted experiment, collected and processed the samples, analyze data and wrote the manuscript. Muhammad Sharif supervised the overall activities and revise the manuscript.

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