Phosphorus release dynamics under phosphate rock and ammonium sulphate in soil amendment

Kofi Agyarko a*, Kwame Agyei Frimpong b, Akwasi Adutwum Abunyewa c

a College of Agriculture Education, University of Education, Winneba, Mampong Campus, Ghana
b Department of Soil Science, University of Cape Coast, Ghana
c Department of Agroforestry, Kwame Nkrumah University of Science and Technology, Ghana

Abstract

This study was undertaken to assess the release pattern of available phosphorus in a Togo phosphate rock and ammonium sulphate soil amendment. Treatments were prepared through the combinations of soil, phosphate rock (PR) and ammonium sulphate (AS) fertilizer. The treatments were; Control, 12.5g PR, 25g PR, 12.5g PR+1g AS, 12.5g PR+2g AS, 25.0g PR+1g AS and 25.0g PR+2g AS kg⁻¹ soil. Standard laboratory methods were used to assess pH, available phosphorus (P) and total phosphorus (P). Generally, the pH of treatments decreased to the lowest levels between the 4th and 6th weeks after amendment. The AS fertilizer treatments had significantly (p ≤0.05) lower pH values than those without. Amendments with the 2gAS kg⁻¹ soil had significantly (p≤0.05) lower mean pH values than those with the 1gAS kg⁻¹ soil. The AS fertilizer treatments also had significantly (p ≤ 0.05) higher levels of the available P than those without. The higher the amount of the AS in the amendment, the higher the level of the available P concentration. Increase in the level of AS in the amendment also increased the mean value of the available P released. The peaks of available P released were observed between the 6th and the 8th weeks, after the lowest pH values had been attained. Decreased soil pH relatively increased the amount of phosphorus released (y = -12.47x + 111.4; R²=0.53). Addition of PR in the treatments increased the total P levels. In conclusion, combined application of AS and PR has the potential to increase soil P availability, which is beneficial to crop farmers.

Keywords: Phosphate rock, ammonium sulphate, soil amendment, pH, available phosphorus, total phosphorus.

Introduction

Soils in the sub-humid and humid tropics including sub-Saharan Africa are inherently poor. The inherent low fertility could be attributed to inappropriate land use, poor management and lack of nutrient inputs. These have led to decline in crop production, soil erosion, salinization and loss of vegetation (Bationo, 2009). Improvement of soil fertility and plant nutrition to sustain adequate yield of crops is therefore imperative. The continent has the lowest rate of fertilizer consumption in the world, with an average consumption estimated at 8.3 kg ha⁻¹ (Morris et al., 2007). Farmers lack sufficient money or access to credit to purchase fertilizers, resulting to low fertilizer input and a gradual decrease of soil fertility (Buresh and Smithson, 1997).

The use of alternative sources of nutrient inputs to reduce the cost of synthetic fertilizer application would go a long way in reducing the cost of crop production. One such way of reducing the use of synthetic...
fertilizer is through the use of phosphate rock (PR), which has been considered as cheaper than synthetic phosphate fertilizers for supplying available phosphorus to plants (Lorion, 2004). The problem with PR is, however, its low solubility, particularly in non-acidic soils (Caravaca et al., 2004). Phosphate rock must therefore be treated to convert phosphate to available forms for plant use in soils.

Dissolution of PR to release available phosphorus has been done by some previous studies. Combined application of PR with phosphate-solubilizing microorganisms, which has the ability to bring insoluble soil phosphates in the PR into soluble forms by secreting organic acids have been employed in this sense (Delvasto et al., 2006; Prasanna et al., 2011). The use of organic manure or composting of agricultural wastes with phosphate rock is known to increase the solubility of phosphate rock (Van den Berghe, 1996; Zapata and Roy, 2004; Agyarko et al., 2016). The main principle behind composting of phosphate rock with organic manure or farm wastes is the production of organic and mineral acids as a result of their decomposition. Phosphate dissolution rates can be greatly accelerated in the soil in the presence of these organic acids (Kumari and Phogat, 2008). Various scientists have also tried acidulation of phosphate rock with different acids (usually with sulphuric or phosphoric acid), singly or in combination, in different ratios to enhance the dissolution of phosphate rock.

Ammonium sulphate [(NH₄)₂SO₄] is widely used as a source of nitrogen (N) for crop production by farmers in the sub-Saharan region of Africa. The fertilizer has an acidifying effect on soils due to the nitrification process in warm soils, where microbes will rapidly begin to convert ammonium to nitrate in the process of nitrification [2NH₄+ + 3O₂ → 2NO₂- + 2H₂O + 4H⁺]. During this microbial reaction, H⁺ is released, which ultimately decreases soil pH after repeated use (IPNI, 2016).

Such characteristics of ammonium sulphate fertilizer would be beneficial to farmers when combined with phosphate rock in fertilizer regimes to supply plants with phosphorus. The current study therefore, was to assess the release pattern of available phosphorus in a phosphate rock and ammonium sulphate soil amendment.

Material and Methods

The study was carried out at the College of Agriculture Education, University of Education, Winneba, Ghana (07°04’N, 01°24’W), from the latter part of April to the first week of August, 2015. The experiment was conducted in plastic pots (diameter - 10cm; 5kg soil capacity) with the treatments buried in the soil up to the tip of the pots under field conditions. Treatments were prepared through the combinations of soil (sampled from the top 0 – 15cm top layer of the College’s experimental field and sieved through a 2mm sieve), ground Togo phosphate rock (PR) and ammonium sulphate (AS) fertilizer (Table 1). Treatments were replicated three (3) times. Some properties of the soil and the PR are presented in Tables 2 and 3. Samples were assessed at 0, 2, 4, 6, 8, 10, 12 and 14 weeks after placement of treatments on the field to determine pH, available and total phosphorus (P).

Table 1. Experimental treatments

| Treatment kg⁻¹ soil          |
|-----------------------------|
| Control (Soil only)         |
| 12.5gPR                     |
| 25.0gPR                     |
| 12.5gPR+1gAS                |
| 12.5gPR+2gAS                |
| 25.0gPR +1gAS               |
| 25.0gPR+2gAS                |

The total P of treatment samples was determined by the colorimetric method (Anderson and Ingram, 1989) and available P was determined by the Bray 1 method (Bray and Kurtz No. 1 Method) (IITA, 1985) (Bray and Kurtz, 1945). The pH (H₂O) of samples was also measured (Rowell, 1994). All data were subjected to analysis of variance (ANOVA) and the means were compared with the Least Significant Difference Test (p ≤ 0.05) using the GenStat (11th Edition) statistical software package.

Results

Figure 1 shows the changes of soil pH in phosphate rock (PR) and ammonium sulphate (AS) fertilizer amended soil with weeks of application. Soil pH in all the treatments decreased to their lowest levels
between the 4th and the 6th weeks after amendment. Throughout the 14 weeks following the soil amendment, the AS fertilizer treatments showed lower soil pH curves than those without AS fertilizer additions. The soils amended with 2g AS kg⁻¹ had slightly lower pH curves than those with the 1g AS kg⁻¹ soil. The treatments without AS fertilizer application showed an almost unchanging soil pH values throughout the 14 weeks of amendment.

Table 2. Chemical and physical properties of the soil

| Property of Soil                        | Value and degree |
|----------------------------------------|------------------|
| Chemical                               |                  |
| pH (1:1)                                | 6.33             |
| OC (%)                                  | 1.18             |
| N(%)                                    | 0.12             |
| Ca (                                    | 4.63             |
| Mg (Cmol⁻¹kg⁻¹soil)                    | 1.60             |
| K (Cmol⁻¹kg⁻¹soil)                     | 0.16             |
| Na (Cmol⁻¹kg⁻¹soil)                    | 0.09             |
| OM (%)                                  | 2.04             |
| Avail. P (mg kg⁻¹)                     | 28.14            |
| Exch. A(Al+H)                           | 0.10             |
| TEB (Cmol⁻¹kg⁻¹soil)                   | 6.48             |
| BS (%)                                  | 98.47            |
| Physical                                |                  |
| Sand(%)                                 | 78.28            |
| Silt (%)                                | 2.21             |
| Clay (%)                                | 19.51            |

Source: Agyarko et al. (2016)

Table 3. Chemical properties of the phosphate rock

| Property | Ca (%) | Mg (%) | K (%) | P (%) | N (%) |
|----------|--------|--------|-------|-------|-------|
| Value    | 46.82  | 0.03   | 0.02  | 11.04 | 0.04  |

Source: Agyarko et al. (2016)

The mean soil pH values measured after the 14 weeks of soil amendment varied significantly (p≤0.05) among the different treatments (Figure 2). The AS fertilizer amended soils had significantly (p≤0.05) lower mean soil pH values than those without AS fertilizer application. Amendments with the 2g AS kg⁻¹ soil had significantly (p ≤ 0.05) lower mean soil pH values (5.64 and 5.65) than those with the 1g AS kg⁻¹ soil (5.97 and 6.04). The mean soil pH values in the treatments with the only 12.5g or 25g PR were significant (p ≤ 0.05) the same as the control treatment. Changes in available P concentrations in PR and AS fertilizer treated soil with weeks of application are presented in Figure 3. Treatments with the PR had curves that were conspicuously higher than the control treatment that received no P addition. Treatments with the addition of
the AS had higher levels of the available P than those without. The higher the amount of the AS in the soil, the higher the level of the available P curve. In all the treatments, the peak amounts of available P released were observed between the 6th and the 8th weeks after amendment, generally after the lowest soil pH had been recorded between the 4th and the 6th weeks of amendment.

Figure 3. Changes in available P of treatments with time (PR=Phosphate rock; AS=Ammonium sulphate)

Figure 4. Mean available P of treatments after 14 weeks (PR=Phosphate rock; AS=Ammonium sulphate)

The mean available P concentrations in the different treatments at the end of the 14th weeks of amendment are shown in Figure 4. The combined addition of the AS and PR resulted in significantly (p ≤ 0.05) higher mean available P concentrations than when the PR was applied solely. Mean available P concentrations increased with increased amounts of AS applied, which resulted in a decrease in soil reaction. Thus, soil pH significantly correlated negatively with the amount of available P released (y = -12.47x + 111.4; R²=0.53). The combined additions of 1g AS and the 2g AS with 12.5g PR increased the mean available P concentration by 17.80% and 22.95%, respectively, while the addition of the same amounts of AS to the 25g PR increased the mean available P concentrations by 15.81% and 21.16%, respectively.

Although, PR application increased the total soil P concentrations (Figure 5), the total P curves remained almost constant throughout the study period. All the PR treatments had higher total P curves than the control that received no P source. All the soils amended with 25g PR kg⁻¹ soil had statistically similar mean total P concentrations (18 and 19%), which were significantly (p ≤ 0.05) higher than those found in the soils amended with 12.5g PR kg⁻¹ soil (13 and 14%), which were also not significantly different (Figure 6).

Figure 5. Changes in total P of treatments with time (PR = Phosphate rock; AS = Ammonium sulphate)

Figure 6. Mean total P of treatments after 14 weeks (PR=Phosphate rock; AS=Ammonium sulphate)
Discussion

In agreement with previous studies, soil pH in the different treatments decreased with the addition of the AS, in that ammoniacal or NH₄⁺ containing inorganic fertilizers induce soil acidification through the production of hydrogen(H⁺) ions during the nitrification of NH₄⁺ to NO₃⁻ (Eq. 1 and Eq. 2) (Bolan and Hedley, 2003; IPNI, 2016):

\[
\text{(NH}_4\text{)}_2\text{SO}_4 \leftrightarrow 2\text{NH}_4^+ + \text{SO}_4^{2-} \quad \text{[Eq. 1]}
\]

\[
\text{NH}_4^+ + 2\text{O}_2 \leftrightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \quad \text{[Eq. 2]}
\]

The release of H⁺ during the nitrification process possibly explains why the higher dose of 2gAS kg⁻¹ soil induced lower soil pH values than in the 1gAS kg⁻¹ soil treatments. In other studies, Fageria et al. (2010) and Ferrari et al. (2015) also found the soil pH to decrease with increasing doses of AS fertilizer rates. Ammonium sulphate is an acidic reaction fertilizer and it is stated that it will increase the microflora and S-oxidizing bacteria in the soil as a sulphur containing fertilizer, thus accelerating the pH decrease (Lluch and Olivares, 1979; Müftüoğlu and Sarımehmet, 1993).

According to the Penn State Agronomy Guide (2017), the change of NH₄⁺ to NO₃⁻ in soils becomes complete within a period of 1 month (approximately 4 weeks) after the application of NH₄⁺ compounds. This is indicative that maximum soil hydrogen (H⁺) ions concentrations are recorded when the nitrification reactions (Equations 1 and 2) are completed, leading to a decline in soil reaction. This mechanism is likely to be the underlying reasons for the decrease in soil pH observed in this study between the 4th and the 6th weeks after amendment.

The combined addition of AS and PR enhanced the release of available P, which increased with the amount of the AS in the amendment and the concomitant decrease in soil reaction. Dissolution of PR has been previously achieved through the use of both organic and inorganic materials in soil amendments to reduce soil reaction. For instance, Rodriguez et al. (2006); Kumari and Phogat (2008); Prasanna et al. (2011); Hellal et al. (2012) and Agyarko et al. (2016) have used organic materials in this regard, while Rajan et al. (1994); Chien (1979); Friesen et al. (1987); Ghosal and Chakraborty (2012); Ullah et al. (2012); Osman (2015) and Kumar et al. (2015) used inorganic substances including (NH₄)₂SO₄ and urea along with PR, as in the current study to increase PR dissolution.

The study showed that, the highest available P concentrations were observed between the 6th and the 8th weeks of amendment, after the lowest pH had been attained between the 4th and the 6th weeks of amendment. This trend is line with the observation made by Aithorp et al. (1987) who indicated that, increased dissolution of phosphate rock did not occur until acidity, generated by nitrification or sulphur oxidation of the fertilizer materials, had significantly lowered soil reaction.

The place of hydrogen (H⁺) ion in the dissolution of PR [Ca₅(PO₄)₃(F, OH)] is presented in the following chemical processes (Equations 3 to 6) (Dorozhkin, 2012):

\[
\text{Ca}_5(\text{PO}_4)_3(\text{F, OH}) + \text{H}_2\text{O} + \text{H}^+ \leftrightarrow \text{Ca}_5(\text{PO}_4)_3(\text{H}_2\text{O})^+ + \text{HF}, \text{H}_2\text{O} \quad \text{[Eq. 3]}
\]

\[
2\text{Ca}_5(\text{PO}_4)_3(\text{H}_2\text{O})^+ \leftrightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}^{2+} + 2\text{H}_2\text{O} \quad \text{[Eq. 4]}
\]

\[
\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + 2\text{CaHPO}_4 \quad \text{[Eq. 5]}
\]

\[
\text{CaHPO}_4 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \quad \text{[Eq. 6]}
\]

Generally, inorganic fertilizers and other soil amendments increase the total soil nutrients levels. Therefore, the trend of increased total P concentration in the PR amended soil in the current study is not unexpected.

Conclusion

The combined application of ammonium sulphate (AS) fertilizer and phosphate rock (PR) in soil decreased the soil pH, with the lowest values occurring around the 4th and 6th weeks after amendment. The acidity produced enhanced the release of available P from PR. The highest available P values occurred after the lowest pH values had been achieved, between the 6th and 8th weeks after amendment. The higher the amount of the AS in the amendment the lower the pH and the higher the amount of the available P produced. Combinations of AS and RP in soil amendments would be beneficial to crop farmers.
Acknowledgements

The authors extend their appreciation to the Soil Research Institute (SRI), Kwadaso, Kumasi-Ghana for making their laboratory available for the analyses of samples.

References

Agyarko, K., Abunyewa, A.A., Asiedu, A.K., Heva, E., 2016. Dissolution of rock phosphate in animal manure soil amendment and lettuce growth. *Eurasian Journal of Soil Science* 5(2): 84-88.

Anderson, J.M., Ingram, J.S.I., 1989. Tropical soil biology and fertility: A handbook of methods. CAB International. Wallingford, UK.

Apthorp, J. N., Hedley, M. J., Tillman, R. W., 1987. The effects of nitrogen fertilizer form on the plant availability of phosphate from soil, phosphate rock and mono-calcium phosphate. *Fertilizer Research* 12(3):269–283.

Baticano, A., 2009. Constraints and new opportunities for achieving a green revolution in Sub-Saharan Africa through Integrated Soil Fertility Management. The Proceedings of the International Plant Nutrition Colloquium XVI. Available at [13.01.2017]: http://escholarship.org/uc/item/7hr282j

Bolan, N. S., Hedley, M. J., 2003. Role of carbon, nitrogen, and sulfur cycles in soil acidification. In: Handbook of soil acidity. Rengel, Z. (Ed.). Marcel Dekker. New York, USA. pp. 29–56.

Bray, R. H., Kurtz, L. T., 1945. Determination of total, organic and available forms of phosphorus in soils. *Soil Science* 59(1): 39–46.

Buress, R.J., Smithson, P.C., 1997. Building soil phosphorus capital in Africa. In: Replenishing soil fertility in Africa. Buresh R.J. et al. (Eds.). SSSA Special Publications 51. SSSA, Madison, WI, USA. pp.111-150.

Caravaca, F., Alguacil, M.M., Azzón, R., Díaz, G., Roldán, A., 2004. Comparing the effectiveness of mycorrhizal inoculation and amendment with sugar beet, rock phosphate and *Aspergillus niger* to enhance field performance of the leguminous shrub *Dorycnium pentaphyllosum*. *Applied Soil Ecology* 25(2): 169–180.

Chien, S.H., 1979. Dissolution of phosphate rock in acid soils as influenced by nitrogen and potassium fertilizers. *Soil Science* 127: 371–376.

Delvasto, P., Valverde, A., Ballester, A., Igual, J.M., Muñoz, J.A., González, F., Blázquez, M.L., García, C., 2006. Characterization of brushite as a re-crystallization product formed during bacterial solubilization of hydroxyapatite in batch cultures. *Soil Biology and Biochemistry* 38(9): 2645–2654.

Dorozhkin, S.V., 2012. Dissolution mechanism of calcium apatites in acids: A review of literature. *World Journal of Methodology* 2(1): 1–17.

Fageria, N.K., sos Santos, A.B., Moraes, M.F., 2010. Influence of urea and ammonium sulphate on soil acidity indices in lowland rice production. *Communications in Soil Science and Plant Analysis* 41(13): 1565–1575.

Ferrari, S., Júnior, E.F., Grava de Godoy, J.V., Oliveira de Souza, W.J., Alves, E., 2015. Effects on soil chemical attributes and cotton yield from ammonium sulfate and cover amendment with sugar beet, rock phosphate and *Dorigynium pentaphyllosum*. *Applied Soil Ecology* 17: 371–376.

Friesen, D.K., Sale, P.W.G., Blair, G.J., 1987. Long-term greenhouse evaluation of partially acidulated phosphate rock fertilizers II. Effect of cogranulation with elemental S on availability of P from two phosphate rocks. *Fertilizer Research* 13: 45-54.

Ghosal, P.K., Chakraborty, T., 2012. Comparative solubility study of four phosphatic fertilizers in different solvents and their effect on soil. *Resources and Environment* 2(4): 175-179.

Hellal, F.A., Nagumo, F., Zewainy, R.M., 2012. Influence of phospho-composting on enhancing phosphorus solubility from inactive rock phosphate. *Agricultural Journal of Basic and Applied Sciences* 6(5): 268-276.

IPNI (International Plant Nutrition Institute), 2016. Ammonium Sulphate No. 12. USA. Available at [13.01.2017]: https://www.ipni.net/publication/nss.nsf/0/A9E141566F664341852579AF007640CF/$FILE/NSS-12%20Ammonium%20Sulfate.pdf

IITA (International Institute of Tropical Agriculture), 1985. Laboratory manual for selected methods for soil and plant analysis. IITA, Ibadan, Nigeria.

Kumari, K., Phogat, V.K., 2008. Rock phosphate: its availability and solubilization in the soil – A review. *Agricultural Reviews* 29 (2): 108 – 116.

Kumar, C.S., Rajew, K., Singh, A.K., Rakesh, K., 2015. Effect of acidulated rock phosphate on growth yield attributes and yield of wheat (*Triticum aestivum* L.). *Indian Journal of Agricultural Research* 49(6): 574-576.

Lluch, C., Olivares, J., 1979. Effect of elemental sulphur and sulphate on soil microflora. *Agrochimica* 23(2/3): 273-278.

Lorion, R.M., 2004. Rock phosphate, manure and compost use in Garlic and potato systems in a high Intermontane valley in Bolivia. Master Science Thesis, Washington State University, USA. Available at [13.01.2017]: http://www.dissertations.wsu.edu/thesis/summer2004/r_lorion_071404.pdf

Morris, M., Kelly, V.A., Kopicki, R.J., Byerlee, D., 2007. Fertilizer use in African Agriculture: lessons learned and good practices guide-line. World Bank, Washington, USA. 144p.

Müftüoğlu, N.M., Sarımehmet, M., 1993. Soil acidity of the tea soils of the Eastern Black Sea Region. *Ege University Journal of Agricultural Faculty* 30(3): 41-48.
Osman, M.A., 2015. Studies on the Possible use of Rock phosphate in Agriculture. *International Journal of Chem Tech Research* 8(10): 53 - 68.

Prasanna, A., Deepa, V., Murthy, P.B., Deecaraman, M., Sridhar, R., Dhandapani, P., 2011. Insoluble phosphate solubilization by bacterial strains isolated from rice rhizosphere soils from Southern India. *International Journal of Soil Science* 6(2): 134–141.

Penn State Agronomy Guide, 2017. Nitrogen Fertilizers. Available at [13.01.2017]: http://extension.psu.edu/agronomy-guide/cm/sec2/sec28

Rajan, S.S.S., O'Connor, M.B., Sinclair, A.G., 1994. Partially acidulated phosphate rocks: Controlled release phosphorus fertilizers for more sustainable agriculture. *Fertilizer Research* 37(1): 69 -78.

Rodríguez, H., Fraga, R., Gonzalez, T., Bashan, Y., 2006. Genetics of phosphate solubilization and its potential applications for improving plant growth-promoting bacteria. *Plant and Soil* 287(1): 15–21.

Rowell, D.L., 1994. Soil science: methods and applications. Longman Group Ltd., London, UK.

Ullah, B., Ullah, A., Khan, S. A., Rehaman, A. U., Khan, M. J., Khan, S. A., Irfan, M., 2012. Effect of acidulated rock phosphate on micronutrients uptake by maize. *ARPN Journal of Agricultural and Biological Science* 7(8): 638- 644.

Van den Berghe, C.H., 1996. The effect of Matongo rock phosphate and urea as compared to di-ammonium phosphate in the composting process and the yield of potatoes in the Mugamba region in Burundi. *Fertilizer Research* 45(1): 51-59.

Zapata, F., Roy, R.N., 2004. Use of phosphate rocks for sustainable agriculture. FAO Fertilizer and Plant Nutrition Bulletin 13, Rome, Italy.