

# SOIL PHOSPHORUS FRACTIONS AS INFLUENCED BY CONCRETIONARY NODULES IN NON-RESPONSIVE SOIL IN THE NIGERIAN SAVANNA

By

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## ABSTRACT

*The soils of Nigerian savanna are enriched with iron (Fe) concretions that have very high affinity for phosphate (P). These soils are extremely poor in P and little is known of the dynamics of P in these Fe-enriched soils. Soil samples were collected from cultivated farmers land in Biye, northern Nigeria and separated into soil fines, soil + concretion and concretions only. Phosphorus fractions (water soluble-P ( $H_2O$ -P), bioavailable-P ( $NaHCO_3$ -P), potentially bioavailable-P ( $NaOH$ -P), acid soluble-P (Ca-bound P/HCl-P), and residual-P) were determined in soil fines, a mixture of soil and concretions and in concretions alone following the Hedley et al fractionation scheme. The concretion contains 2 - 3 times total P more than the associated soil fines ranging, from 604 – 1014 mg/kg. Likewise, the concentration of plant available P was on the average 2 – 3 times higher in soils without concretions or fine soils than in the associated concretions. Similarly, bioavailable P extracted by  $NaHCO_3$  in soil fines (8 – 10.9 mg/kg) is 2 - 3 times greater than available P extracted from concretions. The observed P distribution was thus attributed to preponderance of Fe and manganese (Mn) oxides whose concentrations were twice as high in concretions than in the fine soils. Incorporation of plant residues and other organic materials to increase soil organic P for long- term soil fertility improvement and maintenance is highly recommended in this soil.*

**Key words:** Concretions, Fe-nodules, P-dynamics, P-fixation

## INTRODUCTION

Phosphorus (P) is the next most essential element after nitrogen (N) hindering crop production. It is often regarded as the most unavailable element because of the complexity of its chemistry. Adequate P supply is essential to sustain soil productivity and eventually crop and fodder production. Soils of the Nigerian savannah have been characterized by low P status and high P sorption (Adetunji, 1997; Agbenin, 2003; Abdu, 2006; Abdu and Udofot, 2015; de Campos et al., 2016). These soils have abundance of iron (Fe) and aluminum (Al) oxides, hydroxides and oxi-hydroxides which have high affinity for P, resulting in high rate of P fixation (Agbenin, 2003; Nafiu, 2009; Abdu and Udofot, 2015). High P fixation by these oxides is closely related to their surface charge which is mostly pH-dependent. These oxides are manifested as concretionary nodules in highly weathered tropical soils and are found to be higher in P content than the surrounding soils and hence contain sparingly soluble P fixed to these concretionary nodules (Tiessen et al., 1991b; Zhang et al., 2005). These soils are also characterized by kaolinitic clay type. This 1:1 clay mineral has been reported to retain P more than 2:1 clay minerals (Samadi, 2006; de Campos et al., 2016).

Some soils with apparent P deficiency that have failed to respond to fertilizer P application have been reported (Mokwunye, 1995; Agbenin, 2003). This paradox has never been satisfactorily resolved for most savannah soils because sufficient attention has not been paid to the understanding of P retention mechanisms and the role of concretion and nodules on the soil's P retention and availability. Whereas, Agbenin (2003) demonstrated the role of extractable Fe and Al oxides on P sorption in savannah soils while Tiessen et al. (1991b) provided evidence that nodules/concretions are nutrients and P sink in some savannah soils of Ghana thereby curtailing crop response to fertilization. In these soils with concretionary nodules, applied P was immobilized within the nodules. This explains why it did not respond to fertilizer application as other soils devoid of nodules/ concretions did.

The aim of the present study was to evaluate the nutrient composition and P adsorption of concretionary nodules viz-a-viz the bulk soils in a Plinthic Haplustalf from northern Nigeria that is non-responsive to fertilizer application while the objectives were to investigate the role of concretionary nodules on P sorption and retention in a savanna soil and to determine the effects of concretionary nodules on phosphate fractions and distribution in the soil.

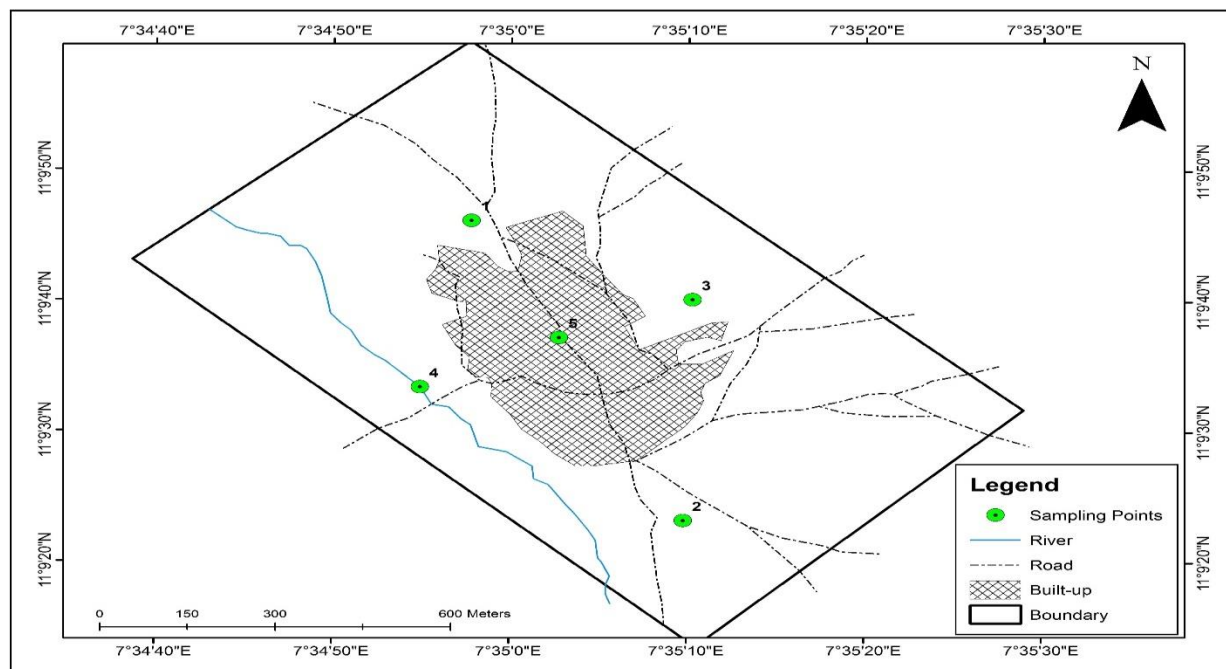
## **THE STUDY AREA**

The study was conducted in Biye village behind Ahmadu Bello University Teaching Hospital, Samaru, Zaria, Nigeria, located between Latitudes 11°9'20"N to 11°9'50"N and Longitudes 7°34'40"E to 7°35'30"E with an altitude of about 686 m above sea level. The area is situated in the Northern Guinea savanna ecology of Nigeria with a monomodal annual rainfall of about 1011±161mm spread over five to six months from May to October.

The soil of the study area is a leached tropical ferruginous soil, classified as Typic Plinthic Haplustalf according to the USDA Soil Taxonomy (Soil Survey Staff, 1984). The soil belongs to the order Acrisols in the FAO system (Valette and Ibanga, 1984) which has developed on deeply weathered Pre Cambrian Basement Complex but overlain by aeolian deposit of variable thickness.

## **MATERIALS AND METHODS**

Soil samples were collected from four experimental fields and one farmer's field in Biye village described above. The sampling sites are further referred to as: Biye north, Biye south, Biye east, Biye west and the farmer's field referred to as Biye central (Fig. 1).



**Fig. 1. Biye showing the four cardinal points where soil samples were collected for the study and a control at the middle**

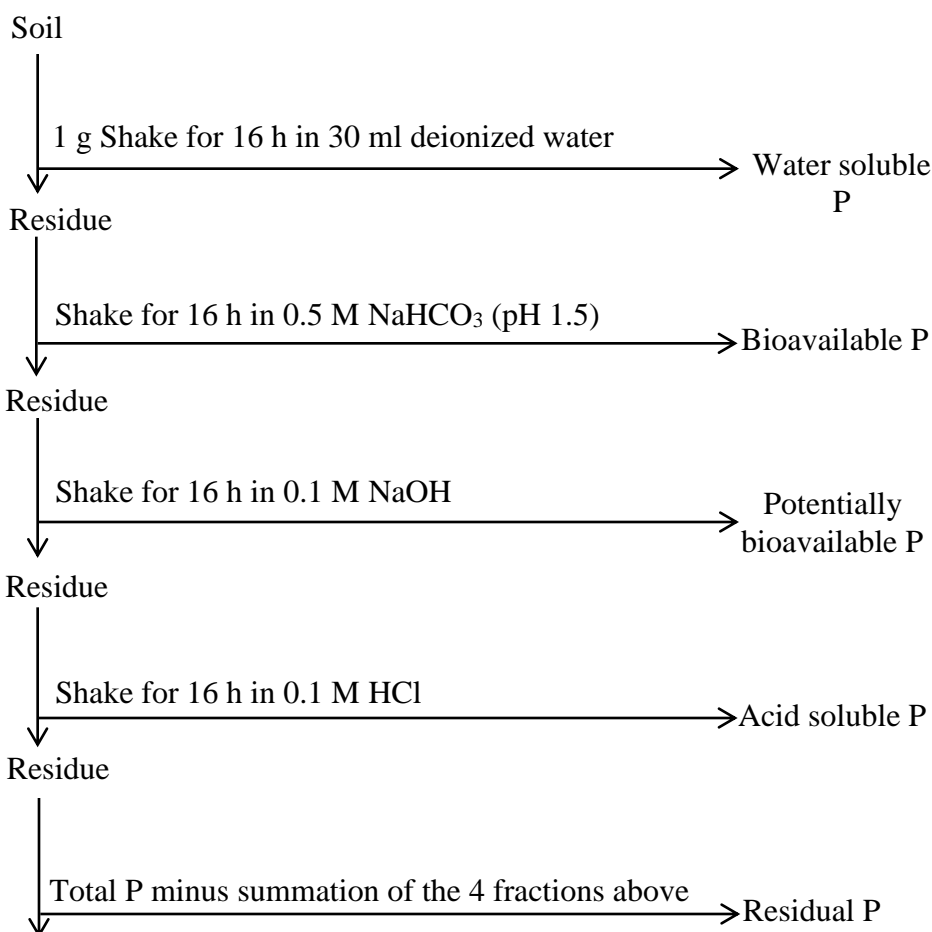
The soil of the study area has been identified to be non-responsive to fertilizer P application based on preliminary survey that was conducted prior to this study (Emmanuel, 2016). Composite soil samples were collected from the top 15 cm layer in each field and replicated three times. Samples collected were air-dried and passed through 2-mm sieve to separate soils from concretions and nodules which were retained on the sieve after removing stones and gravels. The concretionary nodules were divided into two portions. One portion was ground to pass through 2-mm sieve and stored in plastic cups for further chemical analysis. The 2-mm sieved fine soil was also divided into two. One portion was stored in plastic cups for further nutrient analyses. The second portion was mixed with the second portion of the concretions and ground to pass through 2-mm sieve and stored for nutrient analyses.

Chemical characterization was done according to standard analytical procedures. Particle size distribution was determined by the hydrometer method (Gee and Or, 2002). Soil pH was measured in 1:2 water suspension and in 0.01 M  $\text{CaCl}_2$  suspensions using a glass electrode pH meter (Hendershot and Lavkulich, 1983). The organic carbon (OC) was determined by the Walkley-Black dichromate wet oxidation method as described by Nelson and Sommers (1982). Exchangeable  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  were extracted with 1N ammonium acetate buffered at pH 7.0 (Anderson and Ingram, 1993). Total N content of the soils was determined using the micro-Kjeldahl technique as described by Bremner and Mulvaney (1982). Available P was determined using the Bray-1 extraction method (Bray and Kurtz, 1945) and P in solution determined by the method of Murphy and Riley (1962). The cations exchange capacity (CEC) of the soil was determined by the neutral (pH 7.0)  $\text{NH}_4\text{OAc}$  saturation method (Rhoades, 1982). Organic P was determined using the method of Saunders and Williams (1995). Total P was determined by digestion of 1g of soil samples with a mixture of concentrated HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  as

described by Lim and Jackson (1982). Phosphorus in the digest was determined using the method of Murphy and Riley (1962).

### Phosphorus Fractionation

A modified method of Hedley et al. (1982) as describe by Abdu and Udofot (2015) was used to determine soil P fractions in this study. The fractions analyzed include water soluble-P ( $H_2O$ -P), bioavailable-P ( $NaHCO_3$ -P), potentially bioavailable-P ( $NaOH$ -P), acid soluble-P (Ca-bound P/HCl-P), and residual-P. Residual-P was calculated by subtracting the sum of the first four P fractions from the total P content in the soil (Fig. 2).



**Fig. 2. A modified Hedley sequential phosphorus fractionation**

After each extraction, the tubes were centrifuged at 7500 rpm for 30min. The supernatant was then passed through a Whatman No. 42 filter paper. The P concentration in the various filtrates was calorimetrically determined using the molybdenum-blue method of Murphy and Riley (1962).

### Phosphate recovery from soil and concretions

In line with the adsorption study, recovery of phosphate was measured from bulk soil with concretions, sieved soil without concretions and the concretions separately. Ten grams of each sample was weighed into a plastic vial and  $100\mu g$  of  $KH_2PO_4$  in 0.1M KCl was added after

which the suspensions were allowed to equilibrate for 72 hours at field capacity determined gravimetrically. The P saturated soil was air-dried and rescreened through a 2-mm sieve after which 1 g of the air dried soil sample was weighed into a centrifuge tube, P in the soil was extracted using the Bray-1 solution and shaken for 5, 10, 30, 60, 120, 240 and 384 minutes.

### Data Analysis

Analysis of variance (ANOVA) was used to determine significant differences in P dynamics between bulk soil with concretions, sieved soil without concretions and the concretions separately. All statistical data analyses were performed using Excel 2007 and SAS statistical package version 9 (2002).

## RESULTS AND DISCUSSION

### Soil Concretions and Soil Properties

Total weight of soil fines and concretions are shown in Table 1. The weight of concretionary nodules ranged from 65.3 kg - 135.3 kg, accounting for about 7.8 to the 17.7 % of the bulk soil. Physical observation showed that, majority of the concretions was more or less spherical in shape and were tightly packed in the soil matrix. Generally, the soils were shallow due to the presence of plinthites and sandstone underlying the profiles. This could prevent root proliferation and water infiltration thereby reducing plant growth and yield. The abundance of concretion could significantly affect phosphate availability in the soil.

**Table 1. Proportion of soil fine and nodules contents in the study area**

Sampling Location	Bulk Weight (kg)	Soil Weight (kg)	Conc. Weight (kg)	% concretion
Biye North	750	614.67	135.33	17.06
Biye South	796	660.00	136.00	17.10
Biye East	829	763.67	65.33	7.75
Biye West	834	693.67	140.67	16.85
Biye Central	824	679.00	145.00	17.68

The soil pH values across experimental fields in the soil fines (soils without concretions), soils with concretionary and the concretionary nodules were slightly acidic and fairly consistent in all the fields and ranges from 4.9 to 5.9. The average organic carbon (OC) content ranges from 0.85 and 1.10 g/kg across the five fields in both soils with concretions and soils without concretions (Table 1). Sieved soils without concretion (< 2mm) had more OC content than soils with concretions. This can be attributed to coating of the soil surface by concretions thereby limiting OC adsorption. The lowest value of OC (0.81 g/kg) was observed in Biye south, where there occurred highest proportion of concretions.

### Phosphorus Status of the Soil

The total P (Pt) content of soils is of little importance for soil fertility evaluation. However, it has been used as a weathering index to differentiate between highly weathered and less weathered soils (Tiessen et al., 1991a). It is also used as a check on the P balance when soil P is fractionated. Total P concentration ranged from 323 to 840 mg/kg in the mixture of soils and concretions while the soil extractable P ranges from 9.4 - 15.6 mg/kg in all the soils mixed with concretionary nodules (Table 2) suggesting moderate P concentration in these soils. These values were higher than Pt (total P) in soil fines without concretions which ranged from 194 – 624 mg/kg and the available P concentrations that ranged from 8.3 – 13.1 mg/kg.

The Pt levels in concretionary nodules were two to three times higher than those in the soil fine (Table 2). The values ranged from 604 – 1014 mg/kg suggesting enrichment of P in the concretionary nodules and directly influencing P contents of the soil fines.

**Table 2. Mean phosphorus concentration in soil fine, soil and concretions and concretionary nodules**

Location	Colloid type	Total P	Organic P	Available P	Inorganic P
Biye North	Soil fine	401.8c	17.7a	10.6a	24.4a
	Soil + concretion	624.8b	15.7a	10.7a	52.7b
	Concretions	728.2a	13.6b	3.8c	25.7a
Biye South	Soil fine	301.4c	21.5b	13.1a	26.6c
	Soil + concretion	581.2b	47.2a	10.4b	47.0a
	Concretions	710.5a	12.2c	3.5c	30.8b
Biye East	Soil fine	452.1c	17.6b	15.5a	30.3b
	Soil + concretion	717.6b	31.0a	11.7b	53.7a
	Concretions	1014.4a	7.0c	1.6c	29.6b
Biye West	Soil fine	365.9c	20.1b	9.5a	24.6b
	Soil + concretion	452.1b	34.3a	8.3a	56.3a
	Concretions	604.4a	8.5c	1.6b	26.2b
Biye Central	Soil fine	487.9c	15.4b	11.4a	29.9b
	Soil + concretion	531.1b	37.7a	9.7b	43.5a
	Concretions	797.3a	8.5c	1.6c	31.7b

Means followed by same letters are statistically similar at  $P \leq 0.05$  level of significance

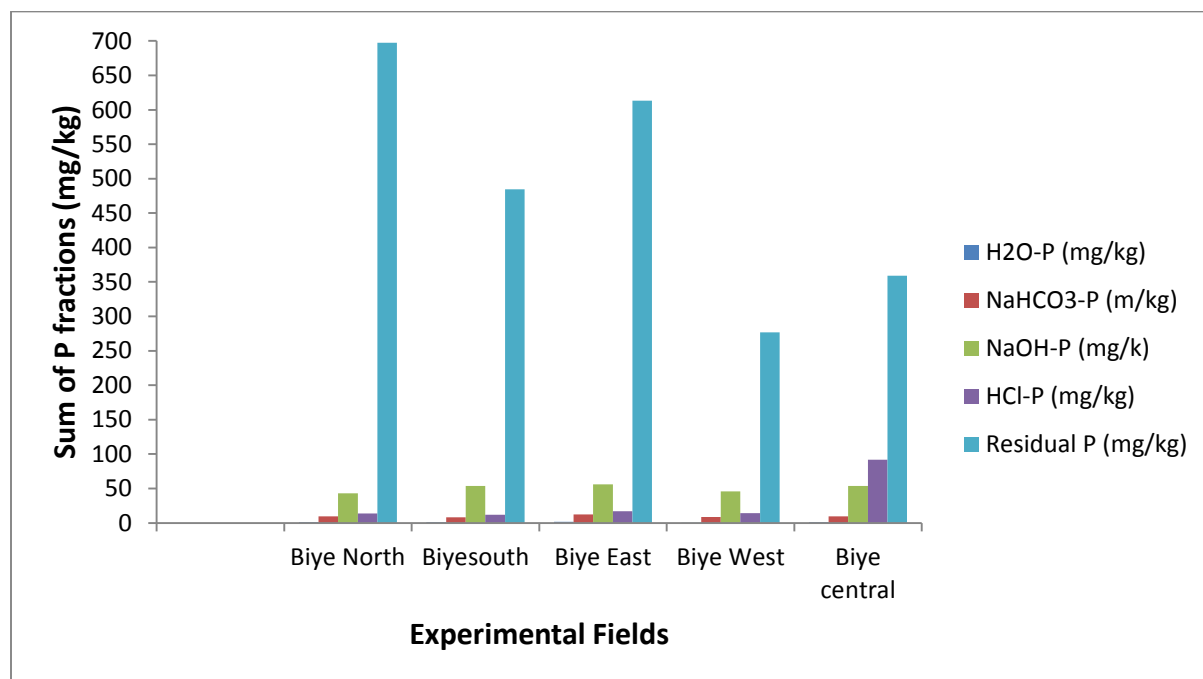
The significance of concretions in P fixation is clearly indicated by the observed difference in P concentrations in soil, a combination of soil and concretion and concretion alone (Table 2). This result corroborates findings of Hauffe (1989) and Tiessen et al. (1991b) in most West African savanna soils. Tiessen et al. (1991b) found that Pt values in ferruginous nodules from semiarid soils in Ghana and Brazil were, on the average, three to four times higher than in the associated soil fines. In top soils with intense P cycling, Fe-enriched concretions were exposed to P from fertilization, which is eventually trapped in the concretions. The amount of available P trapped in concretions during their formation was effectively locked up, indicating that major portions of fertilizer P could be occluded by these soil constituents (Tiessen et al., 1991b).

Phosphorus fixation by Fe, Al and Mn oxides, losses to erosion and crop removal might have also contributed to low P status of the soils. Mean concentrations of Fe in the soils mixed with concretion ranges from 102 to 118 mg/kg as against 76 to 95 mg/kg in soils without concretions.

Similarly, mean concentration of Mn ranged from 24 to 42 mg/kg in a mixture of soils and concretion as against 21 to 29 mg/kg in soils without concretion. Several other studies (Agbenin, 2003; Abdu et al., 2008; Nafiu, 2009) have the attributed low P status of soils of Nigerian savanna to high preponderance of Fe, Al and Mn oxides.

### Phosphorus fractions

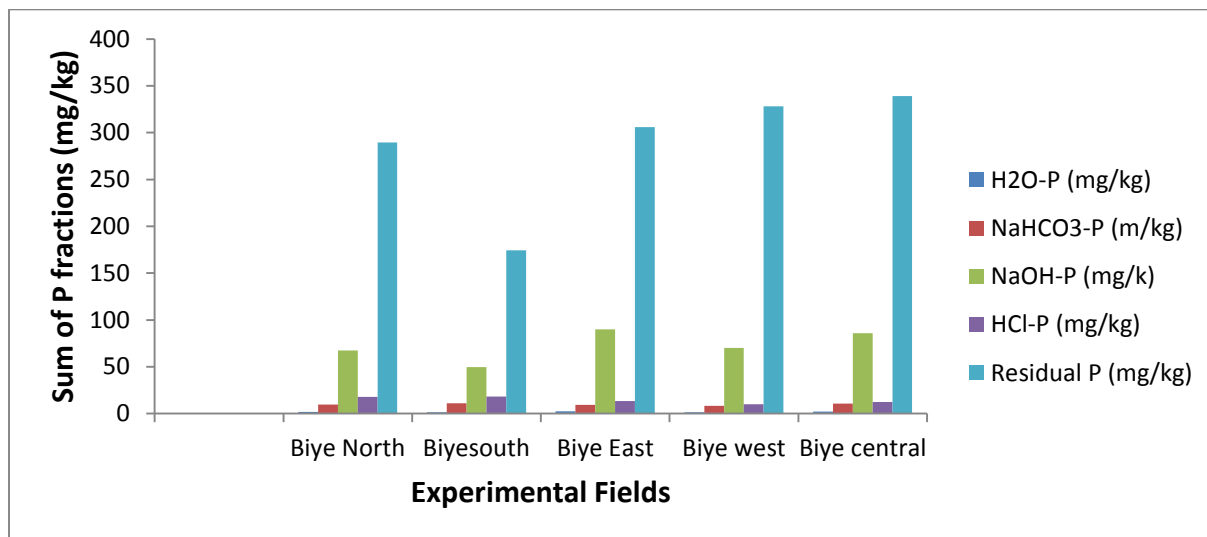
Fractionation results partitioned bulk of the total concentration of P to residual fractions. In soils with concretionary nodules, most P recovered by sequential extraction was in the residual (276 - 697 mg/kg) followed by potentially bio-available fractions (NaOH-P) (43 - 55.8 mg/kg) (Fig. 3). The exchangeable P fraction (NaHCO<sub>3</sub>-P) of soils held lowest percentage (2 - 5%) of the total P in soils with concentrations, ranging from (8 - 12.3 mg/kg) in the entire experimental soils (Fig. 3). The exchangeable P fractions were those released most readily into the soil solution. These fractions correspond with the most available P for plant uptake and can easily be released following any change in the ionic strength of soil solution (Filguerias et al., 2002).



**Fig. 3. Phosphorus fractions in soils with concretions from Biye, northern Nigeria**

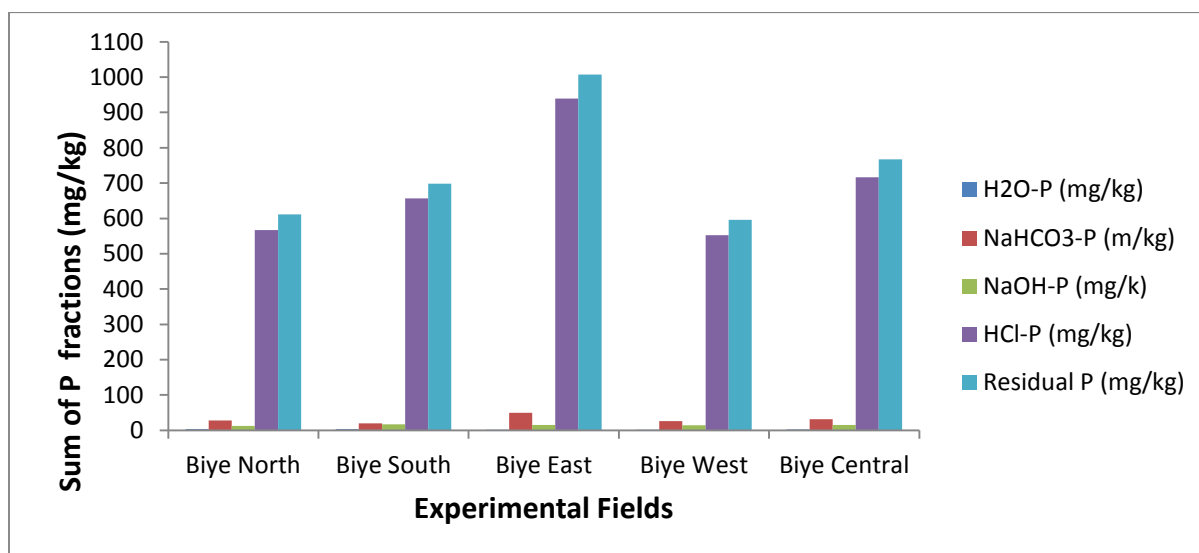
Soils without concretions or soil fines had almost uniform distribution of P fractions with values ranging from 8 - 10.9 mg/kg for plant available P in all the experimental soils. Plant available P was on the average 2 - 3 times higher in soils without concretions or soil fines than in associated concretions with most of differences accounted for by higher residual P level (Fig. 4). HCl-extractable P in soils without concretions ranged from 10.1 - 18.0 mg/kg in all the experimental fields. Although percentage of available P extracted by NaHCO<sub>3</sub> was low in soils without concretions, it was however, 2 -3 times greater than available P extracted from the concretionary nodules. This would suggest that concretionary nodules have some influence on availability of P in soil fines. This result is in agreement with the work of Abekoc (1996) and Tiessen *et al.*

(1991b) who observed that within less than 3 years of fertilizer application, all added P had disappeared from the soil fine, and accumulated in ferruginous nodules. Nearly 90% of the total P recovered from concretions was in the residual fraction (552 – 939.3 mg/kg). Potentially available P (NaOH-P) accounted for a range of 20.2 – 49.3 mg/kg, while plant available P (NaHCO<sub>3</sub>-P) ranged from 1.4 – 3.5 mg/kg; a value 2 – 3 time less than the concentration of available P in soil fines.



**Fig. 4. Phosphorus fractions in soils without concretions from Biye, northern Nigeria**

Whereas the available P was relatively high in soils without concretions, it was however very low in concretion about 2 – 3 times lower than that of soil without concretion (Fig. 5). This suggests that concretionary nodule fixed P in soil solution and transformed them into form not extractable by NaHCO<sub>3</sub> and is not available for plant uptake.



**Fig. 5. Phosphorus fractions in concretionary nodules from Biye, northern Nigeria**



Phosphorus availability depends largely on the forms in which it is held. The modified Hedley fractionation scheme indicated that non-labile P (NaOH-P) was the next dominant P pool after residual fraction in all the soils. This suggests that large amounts of recalcitrant P of limited bioavailability were accountable for poor P supply to plants in Biye soils. According to Tiessen *et al.* (1993) highly weathered soils of the tropics with low available P may be somewhat productive through organic P mineralization which is enhanced by high soil temperatures and distinct wet and dry seasons. Organic P levels were generally low in soils of Biye and local farmers must be encouraged to adopt management practices such as incorporation of plant residues and other organic materials to increase soil organic P for long- term soil fertility improvement and maintenance.

## CONCLUSION

This investigation showed that P levels in the entire studied field were generally low but concretionary nodules contained the highest concentration of P followed by the soils mixed with concretion. The soil fines or soils without concretion have the lowest concentration of P indicating that Fe rich concretions have the ability to trap P and convert it to the forms not available to plant. The bulk of the P fractionation was partitioned into the residual and potentially available fractions which were not immediately available for plant use. Consequently, we can infer that applied soil P from fertilizer may be rendered unavailable by Fe-enriched concretions through fixation and occlusion. The amount of P trapped in concretions was effectively locked up, indicating that major portions of fertilizer P can be occluded by these soil constituents. We hence surmise that P availability is higher and more in soils without concretions, while concretions induces more P fixation and resistant to reversibility of already fixed P than soil fines, lending credence to the importance of ferruginous nodules in P fertilization management. Incorporation of plant residues and other organic materials to increase soil organic P for long-term soil fertility improvement and maintenance is highly recommended in this soil.

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