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Phosphorus Fractions of a Chronosequence of Stabilized Contiguous Sand Dune in the Semi-arid Savanna of Nigeria

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Abstract: In the study of pedogenetic processes, knowledge of soil phosphorus transformation can be regarded as a valuable tool. This research was conducted to study the suitability of soil phosphorus as an index of soil weathering in strongly acid soils in the semiarid savanna of Nigeria. Phosphorus fractions from selected modal soil profiles formed on contiguous Tertiary and Quaternary sand dune of a chronosequence that ranges in age from 5,000 to over 100,000 years were studied. Using chemical extraction methods, total phosphorus, organic phosphorus and the various active inorganic phosphorus fractions were determined. The phosphorus fractions showed clear developmental trends in the A horizons than in the subsoils. In the surface horizons, calcium phosphate (Ca-P), and iron phosphates (Fe-P) tended to decrease over time while organically bound phosphorus (Po) and residual phosphorus (residual-P) increased over time. The most prominent features of the P transformation are the loss of about 7650 kg ha⁻¹ m⁻¹ profile of calcium phosphate and 10,100 kg ha⁻¹ m⁻¹ profile of total phosphorus (TP), both in 10⁵ years. Increase in Po was 760 kg ha⁻¹ m⁻¹ profile and that of residual-P was 2,929 kg ha⁻¹ m⁻¹ profile, also in 10⁵ years, thereby, giving a fairly low rate of P transformation. The relative order of P transformation was: Po > residual-P > Ca-P > Fe-P and Al-P. The results of this study showed that factors other than chronological age also influenced the trends. The strongly weathered nature of the parent materials prior to deposition most probably limited the usefulness of P-fractions as an index of soil weathering in the chronosequence and also, most probably, was responsible for the slow rate of P transformation. The results of this study showed that the P fractions in the surface horizons exhibited clearer developmental trends, but in the subsoil the trend was irregular with chronological age.

Key words: Phosphorus fractions, chronosequence, sand dune, semi-arid savanna

Introduction

The usefulness of phosphorus fractions as an indicator of soil fertility and the degree of pedogenesis have long been established (Ridley, 1984; Loganathan and Sutton, 1987). Phosphorus is the one major element in soil which must be supplied almost entirely by the parent material of unfertilized soils because of low atmospheric returns. Phosphorus is cycled mainly in geologic time (Smeck, 1985). It is therefore, obvious that the transformation and losses of P during pedogenesis will be influenced by the nature of the P in the parent material. The relative abundance of the various phosphorus fractions affects the degree of soil weathering and development. Calcium phosphate (Ca-P), aluminium phosphate (Al-P), iron phosphate (Fe-P) and residual-P occur in the order of increasing weathering status (Walker and Syers, 1976). The active (extractable) fractions of phosphorus are the most available to plants, with the degree of availability increasing in the order of Ca-P, Fe-P and Al-P under well-drained conditions (Walker and Syers, 1976).

Table 1: Basic site information and classification of the soils

Sand dune	Dune form*	Years*	MAR+ (mm)	Landuse/vegetation	Dune height	Soil classification
Illela	Fortress	5,000	500	Shifting cultivation/Combretum nigricans, Anogeissus	Pronounced, 10-20 m high	Ustic Quartzipsamments
Sokoto	Longitudinal	20,000	650	Semi-permanent cultivation/Accacia albida, Combretum nigricans	Low-nearly flat, Less than 1 m	Typic Kanhaplustults
Sangiwa	Transversal	100,000	600	Virgin to shifting cultivation/Combretum nigricans	Moderate, Less than 3 m	Ustic Quartzipsamments

*Sombroek and Zonneveld (1971), + MAR = mean annual rainfall

Acid soils of the humid tropics are known to be generally deficient in phosphorus. These soils have been reported to be highly weathered (Buol *et al.*, 1980) and low in available P (Loganathan and Sutton, 1987). Total active phosphorus is also low and dominated in most cases by Al-P and Fe-P fractions, indicative of the highly weathered nature of the soils. Similarly, Walker and Syers (1976) found acid-extractable Ca-P to form a high fraction of total phosphorus (TP) in loess freshly derived from present-day river beds in Canterbury, New Zealand. With increasing weathering of soils, total phosphorus decrease along with pH, whereas organic phosphorus (Po) and nearly insoluble P increase at the expense of acid-extractable P. Fractions of P may however, be changed by pre-weathering of parent materials. Walker and Syers (1976) analyzed the effect of pre-weathering of parent materials on fractions of phosphorus. They found out that acid-extractable Ca-P declined markedly from 503 mg kg⁻¹ (TP = 624 mg kg⁻¹) in the least weathered sample, to 3 mg kg⁻¹ (TP = 587 mg kg⁻¹) in the strongly weathered greywacke rock at a depth of 3 m in North Auckland. In northwestern (NW) Nigeria, sandy deposits whether aeolic or fluvial occur extensively in the Early Pleistocene. Aeolian deposits are however, more widespread in the region and in the Sahelian region of West Africa (Jones and Wild, 1975). Sombroek and Zonneveld (1971) using heavy minerals revealed that the sandy deposits in NW Nigeria were all derived from the same original local sources, namely the sandy Cretaceous and Tertiary sedimentary rocks of the Gundumi, Gwandu and Rima formations. The sandy deposits are in effect formed one from the other through weathering and re-deposition. Deposition, in the Pleistocene, started with the poorly sorted aeolic deposit of Sangiwa dunes and was followed by a period of irregular rainfall when fluvial deposition occurred. A return to desert conditions, still in the Pleistocene, resulted in the deposition of well-sorted sand (Sokoto) deposits. The cyclic deposition continue with more fluvial depositions and finally a long and pronounced dry season, but no true desert conditions, in Recent times, resulted in the deposition of the fleecy-cloudlike Illela dunes (Table 1). All the sand dunes are presently stabilized and exhibit varying degree of inherent meso-relief. They are all predominantly quartz rich and are made-up of kaolinitic clay, oxides of Fe and Al (Raji *et al.*, 2000). Sombroek and Zonneveld (1971) reported the ages of the dunes based on stratigraphic correlation of the sand dune with similar dune formations within the region, where absolute age determination has been carried out. They gave the ages as about 5,000 years for Illela, 20,000 years for Sokoto and 100,000 years for Sangiwa dunes. Chronologic effects on P fractions are complicated by such weathering and re-deposition of parent material.

There have been few investigations of soils in these complicated weathering and re-deposited parent material to understand the genesis, P fractions variation and pedogenic processes that have shaped them. Study of the chronological variations in P fractions is not only important from the standpoint of soil fertility, genesis and development but also in soil management. Phosphorus distribution has also been used to identify Paleosols (Runge *et al.*, 1974), develop landscape models

(Washer and Collins, 1988) and even distinguish forest-derived from Prairie-derived soils. Studies of polysequences, providing an example of a setting, have been valuable for the understanding patterns of soil development and soil processes. Such studies have stimulated the search for monosequences as envisaged by Jenny (1941). Stevens and Walker (1970) and Walker and Syers (1976) opined that if sufficient chronosequences could be found with different constellations of the other state factors, there would be little need to study climo-, litho-, topo- and bio-sequences. Phosphorus transformations in soils are best characterized in temperate regions, whereas little is known about the P dynamics in soils of semi-arid regions. This study reports on P fractions in a chronosequence of three soils in the semi-arid savanna region of NW Nigeria with ages ranging from 5,000 years to over 100,000 years. The objective was to determine whether chronological age or pedogenesis influence the contents of P fractions in the surface horizons and subsoil of the stabilized sand dune soils of northwestern Nigeria.

Materials and Methods

Description of Study Area

The study site was selected from the stabilized contiguous sand dune formations in the Sokoto River Basin in the northwestern tip of the Federal Republic of Nigeria. The Sokoto basin falls between latitude 12° 00'N and 13° 45'N and longitude 4° 00'E and 6° 45'E. The present day climate of the area is hot and semi-arid. The total annual rainfall is about 690 mm decreasing northwards while ustic soil moisture and hyperthermic temperature regimes prevail in the area (Raji *et al.*, 1996a). Vegetation is largely that of the Sudan zone, which contains savanna woodland on better soils and tree and shrub savanna on the poorer. Presently the natural vegetation is sparse but the land is cultivated to cereals such as millet (*Pennisetum typhoideum* Rich) and guinea corn (*Sorghum bicolor* (L) Moench) and legumes such as cowpea (*Vigna unguiculata* (L) Walp).

Field Studies

A stratified purposive sampling procedure was adopted. A chronosequence of three stabilized contiguous sand dune soils (5,000, 20,000 and over 100,000 years), representing different geological ages, dune morphology, degree of weathering and pedogenesis was selected. The three soils, derived from the stabilized sand dunes, are Illela, Sokoto and Sangiwa. For each soil type, three profiles were sampled as replicates. The profiles were sampled by genetic horizons. Multiple samples from each horizon were bulked while core samples were used for bulk density determination (Blake and Hartge, 1986). In this study, the A-horizon is equated to the surface horizon while from the AC/AB to all horizons at depth are taken as the subsoil.

Laboratory Analysis

Bulk soil samples were air-dried and passed through 2 mm sieve while the core samples were oven-dried at 105°C for 24 h. Sub-samples were ground to pass through 0.5 mm sieve. All chemical analyses were carried out in duplicates. Particle size was by the hydrometer method after pre-treating the soils with 35% H₂O₂ to oxidize the organic matter and calgon (sodium hexametaphosphate) to disperse them. Soil pH was determined in 1:2.5 soil/water suspension. Organic Carbon (OC) was determined by the Walkley-Black wet oxidation method (Nelson and Sommers, 1982). Amorphous Fe and Al (Feox and Alox) were extracted in the dark by ammonium oxalate (pH 3) procedure outlined by McKeague and Day (1966). Dithionite citrate extractable Fe and Al (Fed and Ald) were determined by the method of Mehra and Jackson as described by McKeague *et al.* (1971). Calcium carbonate (CaCO₃) equivalent was determined by the acid neutralization methods as described by Nelson (1982).

One-half gram samples of soils were weighed in duplicate into 40-ml centrifuge tubes and inorganic P fractions were determined by the method of Chang and Jackson as modified by Williams *et al.* (1967). In the P-fractionation scheme, the soil samples were extracted in sequence using different extractants for different P fractions. The easily soluble P (adsorb-P) was extracted with NH₄Cl, the Al-P fraction by NH₄F, the Fe-P fraction by NaOH, the residual P fraction by citrate-dithionite-bicarbonate reagent and the Ca-P fraction by HCl. The citrate-dithionite-bicarbonate extract was digested with concentrated HNO₃ until colourless and then evaporated to dryness to remove acidity. The evaporated material was dissolved in water for P determination. The NH₄F extract was treated with boric acid/HCl. For the boric acid/HCl treated NH₄F extract and for a second HCl extract, pH was adjusted to about 2.0 using quinaldine red indicator before the P determination. Active inorganic phosphorus was taken as the summation of the adsorb-P, Ca-P, Fe-P and Al-P fractions. Total P was determined by the sodium bicarbonate fusion method (Walker and Syers, 1976). The organic P was determined by the ignition method outlined by William *et al.* (1970). The P in the extract at each step was determined by the ascorbic molybdenum blue colour method of Muphy and Riley (1962). The degree of P-transformation in the surface horizon and the subsoil in the sand dune soils was calculated for the period of 10⁵ years by comparing the P levels in the youngest Illela (5,000) and the oldest Sangiwa (100,000) dune soils. This was done by multiplying the weight of soil calculated to a meter depth (Table 5) by the appropriate mean P values in the surface horizon or in the subsoil. The calculation to a meter depth was to serve as a common reference level for the purposes of discussion which was however, carried out by comparing the contents of the P-fractions of the whole soil (both surface and the subsurface horizons) together. The extracted P fractions do not necessarily correspond exactly to soil P pools (Daroub *et al.*, 2000). However, because it is more meaningful to relate the P fractions to P pools (Ca-P, Al-P etc.) in the soils, extracted P fractions have been assigned to P pools described in the literature. The limitation imposed by this approach was taken into consideration in the discussions that follow.

Statistical Analysis

Means and standard deviation of P contents in sand dunes were calculated. The mean difference by chronological age and soil type was evaluated by analysis of variance. Correlation coefficients and simple regression analysis between P fractions or pools and selected soil properties were calculated. All statistical analyses were carried out using SAS (1998) software programme.

Results and Discussion

Soil Characteristics

The soils were generally strongly acidic with pH values decreasing with depth (Table 2) except in pedon 2 (data not shown) on Illela dunes where phosphatic rich sediments have been reported to occur at depth (Sombroek and Zonneveld, 1971; Kogbe, 1979). Organic carbon contents were generally very low, less than 2.0 g kg⁻¹ in all the soils. There were no significant differences in the organic carbon contents between the soils. Texturally, all the soils were sandy in their Ap horizon, a reflection of their siliceous parent material. In the subsoil horizons, the texture was sandy, sandy loam and loamy sand for the Illela, Sokoto and Sangiwa dunes, respectively. Soils on Illela and Sangiwa dunes were classified as Ustic Quartzipsamments while those on Sokoto dunes were classified mainly as kanhaplic Haplustults (Raji *et al.*, 1996a, b, 1999).

Table 2: Selected properties averaged across horizons from the profiles of the chronosequence

Soil properties	Youngest soil		Intermediate soil		Oldest soil	
	Surface* (n = 6)	Subsoil* (n = 8)	Surface (n = 6)	Subsoil (n = 5)	Surface (n = 6)	Subsoil (n = 6)
Sand (g 100 g ⁻¹)	94	91	92	82	89	84
Silt (g 100 g ⁻¹)	1.5	1.7	2.5	5.1	7.5	6.0
Clay (g 100 g ⁻¹)	4.5	7.6	6.0	13.1	4.0	10.5
pH	5.8	6.2	5.9	5.0	5.4	4.5
OC (g kg ⁻¹)	0.9	0.4	1.1	0.7	1.1	0.3
CaCO ₃ (g kg ⁻¹)	7.8	6.7	3.5	2.2	5.8	5.9
Feox (g kg ⁻¹)	0.1	0.1	0.2	0.2	0.1	0.1
Fed (g kg ⁻¹)	0.5	0.5	0.5	1.1	0.2	0.3
Al _{ox} (g kg ⁻¹)	0.1	0.1	0.1	0.1	0.1	0.1
Al _d (g kg ⁻¹)	0.2	0.9	0.1	0.1	0.1	0.2
Bulk density (Mg m ⁻³)	1.7	1.6	1.6	1.5	1.6	1.3

* Surface = A-horizon; Subsoil = AC/AB + Bt or C horizons

Total Phosphorus (TP)

The means of TP for the surface horizons ranged between 493 and 1226 mg kg⁻¹ while the subsoil values ranged from 579 to 1715 mg kg⁻¹ (Table 4). The total phosphorus contents of the sand dune soils were generally high when compared with figures reported for temperate or tropical acid soils (Meixner and Singer, 1985; Loganathan and Sutton, 1987). These values are however, much lower than values reported by Agbenin and Tiessen (1994) for Lithosols and Cambisols from semi-arid northeastern Brazil. The high phosphorus levels in the parent materials are probably responsible for this high soil phosphorus content despite the ages of the soils and their strongly weathered nature. Kogbe (1979) reported a widespread occurrence of phosphatic nodules in sediments within the study area especially in areas overlain by the Illela dunes. Loganathan and Sutton (1987) have reported similar findings for Onne acid soils, in southeastern Nigeria, where they attributed the high phosphorus levels to the occurrence of remains of marine organisms.

Total phosphorus contents increases from about 500 mg kg⁻¹ in the youngest and intermediate soils to over 1200 mg kg⁻¹ in the oldest soil (Table 4). In the subsoil, TP decreased from the youngest soil to the oldest consistent with P transformation models (Smeck, 1985). The trend in the surface horizons suggested that the effect of chronological age on TP accounts for over 90% of the total variance (Table 6). The pre-weathering of the parent material means that even the youngest soil would be low in total phosphorus. The significantly higher TP value in the surface horizon of the oldest soil (Sangiwa) (Table 4), contrary to expected trend, could not easily be attributable to any obvious factor, but probably to its relatively high Po and OC contents. Total phosphorus contents of the youngest soil (Illela) were also highly variable, which reflect the complexity of the occurrence of the phosphates nodules in the underlying geological materials. As a result of this variation in TP, the data on phosphorus fractions were presented as percentages of TP and as weight per unit volume as recommended by Meixner and Singer (1985) (Fig. 1 and Table 5) to remove inherent variation in value.

Total phosphorus values increased regularly down the soil profile in the youngest soil but with soil development, there was a decrease in the eluvial horizon (AC) while in the oldest soil, TP contents decreased down the profile (Table 3). The lowest A-horizon values in the youngest soil was consistent with trends reported for such soils which are virtually devoid of organic matter and therefore low Po contents (Walker and Syers, 1976). With soil development, leaching of P, plant uptake, and lower OC accounts for the lowest values in the AC/AB horizons. The increase in the Bt horizons might be due to the capacity of the clay minerals to adsorb and retain illuvial P as coatings on Fe and Al oxides.

Table 3: Mean phosphorus fractions of the chronosequence (mg kg⁻¹)

Soil horizon	Depth (cm)	TP	Ca-P	Po	Residual-P	Fe-P
Youngest (Illela)						
Ap	0-28	505	77	20	197	96
AC	28-63	578	92	5	275	52
C1	63-142	1550	395	0	430	51
C2	142-175	1881	407	0	582	78
Intermediate (Sokoto)						
Ap	0-22	485	35	70	305	50
AB	22-39	505	25	45	347	65
Bt1	39-56	1011	1	20	983	1
Bt2	56-85	977	2	5	965	2
Oldest (Sangiwa)						
Ap	0-33	1214	15	121	1008	32
AC	33-65	1238	13	5	1150	43
C1	65-108	627	1	0	571	39
C2	108-185	532	2	0	480	30

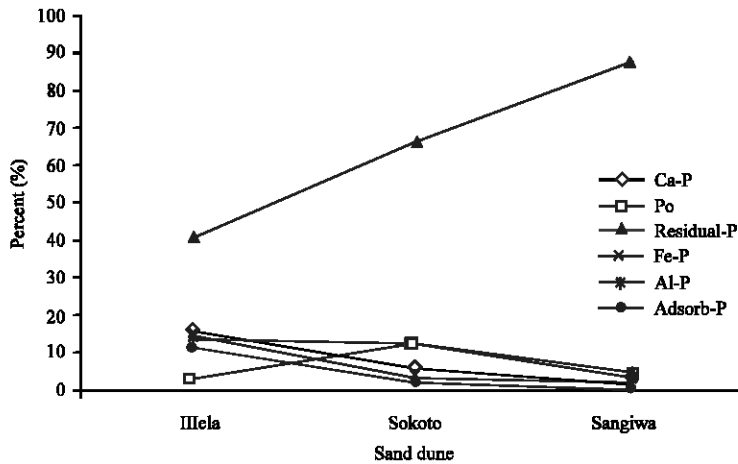
Day *et al.* (1987) reported strong association between TP and clay in soils of Florida. Raji *et al.* (2000) also reported significantly higher contents of oxides of Fe and Al in the subsoil of the intermediate soil (Sokoto) than the other two.

Organic P (Po)

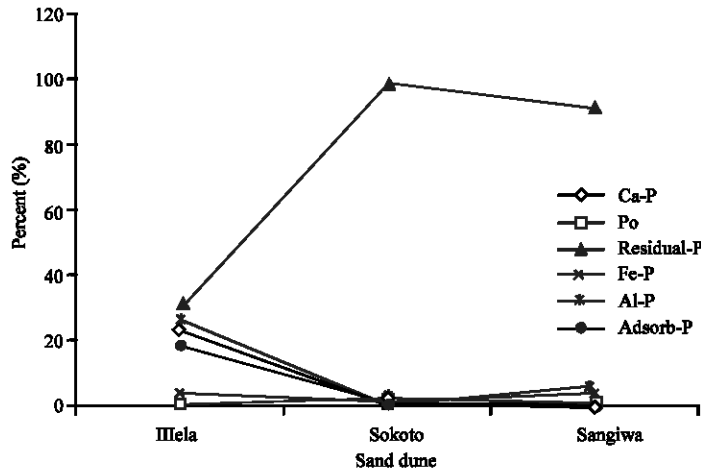
Organic phosphorus content, in the surface horizons, increased along the sequence from 14 mg kg⁻¹ in the youngest soils through 57 to 63 mg kg⁻¹ in the oldest soils. The trend indicates an asymptotic increase in relative abundance and an approach to a steady state condition in these sand dune soils devoid of any initial organic matter. Distribution with profile depth showed the A horizons as having the highest values and this decreased to undetectable levels at about 50 cm depth (Table 3). Heakal *et al.* (1995) also reported undetectable amounts of Po below 45 cm in semi-arid sandy soils of Saudi Arabia. Similar to the result obtained by Walker and Syers (1976), the C: Po ratio also showed a consistent decrease with profile depth. Organic phosphorus had a positive significant correlation with organic matter ($r = 0.5150$, $p = 0.01$) as also reported by several workers (Walker and Syers, 1976; Heakal *et al.*, 1995).

The Po contents of the sand dune soils were generally low but compared well with results reported for other sandstone derived acid soils in the savanna region of Nigeria (Udo and Ogunwale, 1977). The Po values which ranged from traces to 121 mg kg⁻¹ (Table 3) were far less than the range of values (0-318 mg kg⁻¹) reported by Agbenin and Tiessen (1994) for Brazilian soils with higher organic matter contents. Organic phosphorus accounted for less than 15% of TP (Fig. 1) despite the high levels of active inorganic P. Walker and Syers (1976) showed that the build up of organic matter and Po in soils is influenced positively by the amounts of active inorganic P. Total P did not correlate with either organic carbon or Po. This could be ascribed to the low and non-significant contents of organic matter and Po in these soils (Table 4). Moisture deficit and high temperatures limit the productivity and organic matter accumulation in this semi-arid ecosystem. The most prominent feature of the P transformation (between Illela and Sangiwa dunes) was the increment in Po of 760 kg ha⁻¹ m⁻¹ profile in 10⁵ years.

The low C: Po ratios of less than 50 in all the soils should signify potential contribution of Po to P availability and crop nutrition through organic matter mineralization (Tisdale *et al.*, 1985; Lekwa and Whiteside, 1986). However, Agbenin and Tiessen (1994) reported stabilization of Po in



a. Surface horizon



b. Subsoil

Fig. 1: P fractions as a percentage of total phosphorus (TP)

soils with C: Po ratios less than 30. They ascribed this to the presence of the organic fractions in the resistant humified organo-mineral complex fractions. The low C: Po ratios would, therefore, not necessarily lead to mineralization.

Active Inorganic Phosphorus

To facilitate the discussion, P fractions were grouped into total phosphorus (TP), organic phosphorus (Po), primary Ca-P, active inorganic-P and residual-P. Calcium phosphates (Ca-P) contents decreased along the sequence. Ca-P values decreased from about the 400 mg kg⁻¹ in the youngest soils to a near constant level of about 1.0 mg kg⁻¹ in the intermediate 20,000 years old soil (Table 4). The Ca-P values in the youngest soil were significantly higher than values in the intermediate soils which in turn were also statistically higher than values in the oldest soil (Table 4). Within profiles, the distribution of Ca-P did not conform wholly to the expected trend (Smeck, 1985).

Table 4: Means and standard variation (in parentheses) of P fractions in the surface horizon and subsoil

Soil	TP	Ca-P	Po	Residual-P	Fe-P	Al-P	Adsorb-P
Surface							
Youngest (n = 6)	516 (114.3)b	84(12.1)a	14(9.7)a	211(127.9)b	74(36.2)a	75(12.5)a	58(16.4)a
Intermediate (n = 6)	493(18.3)b	30(10.5)b	57(16.4)a	326(33.0)b	57(12.1)a	15(9.2)b	8(2.7)b
Oldest (n = 6)	1226(15.9)a	14(1.1)c	63(63.8)a	1079(78.3)a	37(10.8)a	28(11.1)b	4(1.1b)
Subsoil							
Youngest (n = 8)	1715(266.3)a	401(11.1)a	0b	506(168.4)b	64(17.3)a	442(58.2)a	301(21.2)a
Intermediate (n = 5)	994(20.7)b	10(0.5)b	12(10.4)a	974(13.3)a	1(0.5)c	1(0.5)b	3(1.1)b
Oldest (n = 6)	579(52.8)c	1(0.5)b	0b	525(50.6)b	34(10.2)b	15(2.2)b	3(0)b

Means followed by the same letter is not significantly different for the surface and subsoil

Table 5: Mean weights of P fractions calculated over a meter depth (kg ha⁻¹ m⁻¹)

Soil	Bulk density (Mg m ⁻³)	Weight of soil (<2mm)	PT	Ca-P	Po	Residual-P	Fe-P
Surface							
Youngest (n=6)	1.7	17000	9205	1426	240	3587	1258
Intermediate (n=6)	1.6	16000	7920	480	920	5216	920
Oldest (n=6)	1.6	15900	19493	222	1001	17156	596
Subsoil							
Youngest (n=8)	1.6	16100	27619	6456	0	8146	1038
Intermediate (n=5)	1.5	15200	15108	22	190	14804	22
Oldest (n=6)	1.3	12400	7185	18	0	6516	427

Table 6: Simple regression analysis between phosphorus fractions and chronological age

Horizon	Equation	R
TP		
Surface	444.15 + 7.581×10 ⁻³ X	0.923***
Subsoil	1452.23 - 9.16×10 ⁻³ X	0.833***
Ca-P		
Surface	66.25 - 5.62×10 ⁻⁴ X	0.748***
Subsoil	251.67 - 2.81×10 ⁻³ X	0.621**
Po		
Surface	29.64 + 3.66×10 ⁻⁴ X	0.369
Subsoil	6.33 - 5.19×10 ⁻⁵ X	0.269
Residual-P		
Surface	193.01 + 8.72×10 ⁻³ X	0.960***
Subsoil	691.88 - 1.18×10 ⁻³ X	0.193
Fe-P		
Surface	64.22 - 2.69×10 ⁻⁴ X	0.473*
Subsoil	36.58 - 7.38×10 ⁻⁵ X	0.111
Al-P		
Surface	50.85 - 2.76×10 ⁻⁴ X	0.417
Subsoil	275.86 - 2.95×10 ⁻³ X	0.594**
Adsorb-P		
Surface	40.41 - 4.02×10 ⁻⁴ X	0.639**
Subsoil	189.92 - 2.10×10 ⁻³ X	0.620**

Significant levels * = 5%, ** = 1% and *** = 0.1%

The surface horizons and subsoil usually are respectively the most and least weathered of a soil (Boul *et al.*, 1980). Therefore, primary Ca-P contents are expected to decline with time, more rapidly in the surface horizons. In contrast, the subsoil of all the sand dune soils showed a marked decline in the quantity and proportion of Ca-P (Table 3 and Fig. 1) except in the youngest soil which conforms to the expected trend. A possible cause for the high Ca-P in the surface horizons of the older soils could be the pre-weathered nature of the soil parent materials. Walker and Syers (1976) reported a general pattern of decline for Ca-P with time. In the series they studied at New Zealand, Ca-P had declined to zero throughout the profile by 22,000-23,000 years. The higher contents in the A horizons

could most probably be due to immobilization of the little P in aeolian dust prevalent in the study area (Moberg and Esu, 1991) by CaCO_3 . The close to neutral pH conditions in the A horizons, higher CaCO_3 contents (Table 2) and limited leaching of the semi-arid ecosystem all enhanced such immobilization (Heakal *et al.*, 1995). The potential role of CaCO_3 is supported by the high significant correlation it had with Ca-P ($r = 0.5400$, $p = 0.01$). Free calcium carbonate was less than 5 g kg^{-1} in all the soils, indicating that apatite is the only likely sources of the Ca-P in these soils (Williams *et al.*, 1980). However, the apparent absence of weatherable minerals (apatite inclusive) in these soils further confirms the suggestion of a parent material that is strongly weathered, considering that the present semi-arid climate is unfavourable to intense weathering (Sombroek and Zonneveld, 1971). The near total loss of Ca-P, when the surface and subsurface horizons values were combined, from 7892 to $502 \text{ kg ha}^{-1} \text{ m}^{-1}$ in 20,000 years (Table 5) is comparable to the findings reported by Walker and Syers (1976) for soils in New Zealand.

Fe-P contents decreased regularly in the surface horizons from 74 mg kg^{-1} in the youngest soil to 37 mg kg^{-1} in the oldest (Table 4). Effect of chronological age was therefore, significant and accounted for close to 47% of the total variance (Table 6). In the subsurface horizons, Fe-P showed no consistent trend. The intermediate soil, a Kanhaplustult, pedologically the oldest had most of its sesquioxide converted into laterite. This could explain its relatively low Fe-P since the bulk of it is in the residual form (Williams *et al.*, 1980). Aluminium phosphate unlike the Fe-P showed no consistent trend in both surface and subsurface horizons (Table 4 and 6). This is probably for the same reasons adduced for Fe-P in the subsurface horizons.

Residual-P (Residual-P)

In the surface horizon, residual-P increased with increasing age from 211 mg kg^{-1} in the youngest soil to 1079 mg kg^{-1} in the oldest (Table 4) with chronological age tending to accounts for over 90% of the total variance (Table 6). This trend is consistent with conceptual models of residual-P transformation in a chronosequence (Walker and Syers, 1976; Smeck, 1985). In general, residual-P also increased with profile depth. This is in contrast to account given by Walker and Syers (1976) which showed that during the course of soil development, the surface horizons have higher secondary inorganic P contents, a reflection of increased weathering at the soil surface. Better moisture condition in the clay-rich subsoil horizons, could provide the needed zone for enhanced chemical weathering in these highly porous sand dune soils. Residual-P accounted for over 30% of TP in the youngest soils (Fig. 1). This percentage is high for young soil in a semi-arid ecosystem (Smeck, 1985) and tends to further highlight the pre-weathered nature of the parent material. As a percentage of TP (Fig. 1), residual-P generally increased along the sequence and had an inverse relation to trends exhibited by Ca-P. This trend may indicate a probable conversion of the active and available Ca-P to the unavailable residual-P.

Conclusions

The relative abundance of the inorganic-P fractions was in the order of residual-P >> Fe-P > Al-P > Ca-P in the Sangiwa and Sokoto dunes and residual-P >> Al-P > Ca-P > Fe-P in the Illela dunes. This sequence of abundance further confirms the strongly weathered nature of the parent materials, but the dominance of Ca-P over Fe-P in the Illela dunes also tend to support the theory that they are the youngest both pedologically and chronologically. The dominance of Ca-P over Fe-P could also be more of geological rather than pedological in origin. The sequence signifies the relative importance of the low initial level of organic matter and their high rate of mineralization, abundance of oxides of iron and aluminium that occlude phosphorus over the low rates of chemical weathering and leaching. It

is apparent that aside from the conversion of the Fe-P, Al-P and Ca-P losses to residual-P and Po a large portion of these losses are likely to be precipitated as coatings on the oxides of iron and aluminium.

The trend in distribution of the various fractions along the chronosequence was statistically significant for all P fractions except for Po where the trends were non significant for both surface and subsoil values. The P fractions showed clearer developmental trends in the surface (Ap) horizons than in the subsurface horizons. In the surface horizons, Ca-P, Fe-P and adsorb-P decreased with increasing chronological age while Po and residual-P increased. With increasing age, in the subsoil horizons, Ca-P, TP and adsorb-P all decreased. Organic phosphorus, residual-P, Fe-P and Al-P in the subsoil and TP and Al-P in the surface horizons, all exhibited irregular trends with increasing chronological age. This seems to suggest that the contents of the phosphorus fractions depend not only on chronological age but also on other factors, especially in the subsoil. Differences in the meso-relief of the dune induced differences in the moisture contents and on the level of weathering and leaching. The pre-weathered nature of the soil parent material and the occurrence of phosphate nodules especially underlying the Illela dune (youngest soil) must have confounded the influence of age on the P transformation trends.

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