

Loss of phosphorus from soil in semi-arid northern Tanzania as a result of cropping: evidence from sequential extraction and ^{31}P -NMR spectroscopy

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Summary

In semi-arid northern Tanzania, the native woodland is being rapidly cleared and replaced by low input agriculture. This has resulted in pronounced environmental degradation, and in particular loss of phosphorus (P) from the soil. We have used sequential extraction and ^{31}P -NMR to investigate the effects of land use changes, i.e. native woodland, degraded woodland, cultivation for 3 and 15 years and homestead fields where manure was applied, on the amount and structural composition of P in this soil. Clearing and continuous cultivation reduced both organic and inorganic P in the soil. The difference in the amount of organic P from the bulk soil of the fields cultivated for 3 and 15 years was not statistically significant ($P < 0.05$), suggesting that most of the depletion in organic P occurred during the first 3 years of cultivation. By contrast, in the homesteads, there was much organic and inorganic P in the soil. The ^{31}P -NMR revealed that cultivation resulted in a 53% depletion of orthophosphate diester P, whereas only a 30% and 39% reduction of orthophosphate monoester P was found in the bulk soil after 3 and 15 years of cultivation, respectively. These results concur with the suggestion that diester P constitutes more easily mineralizable forms of organic P in soil than does monoester P. Our ^{31}P -NMR also showed that 70% of the inorganic orthophosphate P was depleted from the coarse and fine sand separates as a result of cultivation. The influence of clearing and subsequent cropping on the amount and forms of P was more pronounced in the coarse and fine sand than in the silt and clay, stressing the importance of particle size and chemical properties such as organic matter and oxides in the availability of P in this soil. Our results show that the current low input agricultural practice is not sustainable, and that practices must be developed to combat the ongoing degradation of the soil. A combined use of available organic materials such as animal manure with the judicious use of inorganic fertilizers can replenish the soil's fertility.

Introduction

In many tropical soils, shortage of phosphorus (P) is a major constraint for crop production (Buresh *et al.*, 1997). This deficiency is primarily a result of inherent poverty of the soil in P, depletion of soil P by cropping, and sorption and precipitation involving Fe and Al oxides and hydroxides.

The availability of P in soil is regulated by both geochemical and biochemical processes. In most natural ecosystems, geochemical processes determine the long-term distribution of P in the soil, whereas in the short term, biochemical processes influence the distribution since most of the P available to plants is derived from the soil organic matter.

Natural forest, which relies on nutrient cycling, has developed the necessary mechanisms to obtain its requirements for rapid nutrient cycling (Lal, 1986). However, clearing and cultivation without fertilizer causes significant decrease in soil organic matter and depletion of P (Buresh *et al.*, 1997). In the semi-arid part of northern Tanzania, the indigenous tropical woodland is rapidly being replaced by low input agriculture. In addition, large areas of acacia (*Acacia tortilis* Forsk. Hayne) stands are selectively deforested for charcoal production. This unprecedented rate of deforestation has resulted in environmental degradation in the region. In a previous study we found 56% and 51% reduction of C and N contents in the soil of cultivated fields (Solomon *et al.*, 2000). However, almost no quantitative information exists about the impact of land use changes on the amount and structural composition of P in this soil. The rational choice of cropping systems and supplementary fertilization with P should be based on the understanding of nutrient transformations, and if

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Received 1 December 1999; revised version accepted 30 March 2000

we do not understand these we are likely to manage the land poorly for agriculture.

Several investigators have sought to distinguish fractions of P in soil. Hedley *et al.* (1982) and Tiessen & Moir (1993), for example, used sequential extraction combined with physical fractionation according to particle size to identify different P pools and follow P dynamics in tropical soil. Sequential extraction may isolate pools of P of different potential in relation to plant nutrition, but it does not provide information on the structural composition of the various forms of P in the soil. Newman & Tate (1980) introduced ^{31}P -NMR spectroscopy for characterizing the structural composition of P in alkali extracts of soils. Since their investigation, ^{31}P -NMR spectroscopy has been effectively used to study the influence of cultivation or climate on different forms of P in soil and for characterizing the structural composition of alkali-soluble P in various ecosystems (Tate & Newman, 1982; Hawkes *et al.*, 1984; Zech *et al.*, 1985; Condon *et al.*, 1990; Forster & Zech, 1992; Guggenberger *et al.*, 1996; Sumann *et al.*, 1998).

We have applied sequential extraction techniques and ^{31}P -NMR spectroscopy in bulk soil and particle-size separates of soil under *Acacia* woodland from northern Tanzania (i) to evaluate the effects of clearing of the native tropical woodland and cultivation on the amounts of the various fractions of P in the soil, and (ii) to study the influence of land use changes on the structural composition of P in the semi-arid tropical environment.

Materials and methods

Site description

We studied the soil in the Naberera area of the Masai plains in the northern Tanzanian dry belt which extends from 36–38° east to 3–6° south. The region is a vast plain (1200–1400 m above sea level) with scattered stony outcrops, inselbergs and mountain ridges up to 1800 m. The mean annual temperature is 20°C, and the average annual precipitation ranges between 500 and 600 mm with a maximum between December and April. Geologically the area is associated with Archaean metamorphic rocks with abundant gneiss, schist and quartzite. The plains consists of deep, well-drained soil with a sandy-loam texture and reddish colour which is characterized as Chromic Luvisols according to FAO–UNESCO (1997).

The Naberera area supports a variety of vegetation cover types. On hillsides scattered *Acacia* and *Commiphora* (*Commiphora schimperi* Engl.) bushes occur together with several succulent species such as *Euphorbia candelabrum* Tremat ex Kotschy and *Euphorbia nyikae* Pax ex Engl. The vegetation of the extensive plains ranges from dense *Acacia*–*Commiphora*–*Balanites* (*Balanites aegyptiaca* Delile) woodlands to *Pennisetum* (*Pennisetum mezianum* Leeke) grasslands. The original woodland has been degraded in places where the *Acacia* has been cut for charcoal production. Some fields,

originally woodland, have been manually cleared and cultivated for 3 years and some for 15 years. The size of cultivated fields varies from 1 to 10 ha. In addition, there are traditionally managed homestead fields (0.25–0.5 ha) where animal manure has been regularly applied for about 10 years. Maize (*Zea mays* L.) and beans (*Phaseolus vulgaris* L.) have been grown without fertilizer on the cultivated land. Crop residues that remain after grazing were normally incorporated into the soil.

Sampling

We used a core sampler and collected composite samples in four replicates from the original woodland, degraded woodland, 3 years and 15 years cultivated fields, and from the homestead fields in March 1997. Four representative sites were selected from each land use, and from each site 10 subsamples (200 cm³ core volume at each subsite) were collected in a radial scheme (Wilding, 1985), and bulked into one sample. The spacing between the subsites on the radii ranged from 5 to 20 m depending on the size of the patches. The samples were air-dried and sieved (<2 mm) prior to fractionation.

Particle-size fractionation

Particle-size fractionation was done on <2-mm material (bulk soil) by the method of Amelung *et al.* (1998). After visible root remnants were removed, 30 g of soil was ultrasonically treated with an energy input of 60 J ml⁻¹ using a probe type sonicator (Branson Sonifier W-450) in a soil:water ratio of 1:5. The coarse sand separate (250–2000 µm) was isolated by wet sieving. In order to disperse completely the remaining material in the <250-µm suspension, ultrasound was again applied with an energy input of 440 J ml⁻¹ in a soil:water ratio of 1:10. The clay separate (<2 µm) was separated by repeated centrifuging. The silt (2–20 µm) and fine sand (20–250 µm) separates were separated by wet sieving. The recovery of size separates after ultrasonic dispersion, wet sieving and centrifuging ranged from 968 to 979 g kg⁻¹ of the initial soil mass (Table 1). All fractions were dried at 40°C before grinding them for chemical analysis.

Chemical analysis

Carbon and nitrogen contents of the bulk soil and particle-size separates were analysed by dry combustion with a C/N/H/S analyser (Elementar, Vario EL). Iron and aluminium were extracted following the methods of Blume & Schwertmann (1969) and Mehra & Jackson (1960).

A modified version of the sequential extraction technique of Hedley *et al.* (1982) and Tiessen & Moir (1993) was used to fractionate the P, but with minor modification for the final step: the remaining soil residue, after extraction with concentrated HCl, was heated at 560°C in a furnace, and subsequently the P was extracted after shaking the residue with 30 ml of 0.5 M

H₂SO₄ for 16 h. Inorganic P was determined from 0.5 M NaHCO₃, 0.1 M NaOH, 1 M HCl, concentrated HCl, and 0.5 M H₂SO₄ extracts according to the modified molybdenum-blue method of Murphy & Riley (1962). Total P in NaHCO₃ and NaOH was determined using ICP-AES, and organic P was calculated as the difference between the total and inorganic P.

The NaHCO₃-extractable inorganic and organic P fractions were considered as labile P sorbed on the surfaces of Fe and Al oxides and some microbial P (Bowman & Cole, 1978). The NaOH (0.1 M) extractable P contains secondary inorganic P bound to Fe and Al compounds, as found by Syers *et al.* (1969), and organic P associated with humic and fulvic acids (Tiessen & Moir, 1993) and was therefore considered as moderately labile. Dilute HCl-extractable P was taken as inorganic P associated with Ca (Tiessen & Moir, 1993). The concentrated HCl was intended to remove very stable residual inorganic P. The highly recalcitrant P left after the hot concentrated HCl extraction was removed by combustion followed by 0.5 M H₂SO₄ extraction. Since the labile P (NaHCO₃-P) and moderately labile P (NaOH-P) are not really completely separate pools but represent a continuum of Fe- and Al-associated P extractable with increasing pH (Tiessen & Moir, 1993), we refer to these as labile P fractions, while we regard the concentrated HCl and H₂SO₄ fractions as residual P fractions.

Extracts for ³¹P-NMR analysis were obtained using the method of Newman & Tate (1980). For this purpose, 6.7 g of finely ground samples were ultrasonically dispersed in 20 ml of 0.5 M NaOH (40 ml of 0.5 M NaOH was used for clay separates), and the suspension was centrifuged at 17 700 g at 0°C for 120 min. The resulting supernatant was concentrated to about 2 ml at 40°C in a rotary evaporator. Then 1 ml of D₂O was added and ³¹P-NMR spectra were recorded on a Bruker Avance DRX 500 NMR spectrometer (11.7 T; 202.5 MHz) without proton decoupling at a temperature of 280 K. An acquisition time of 0.1 s, a 90° pulse and a relaxation delay of 0.2 s were used. Preliminary studies with a pulse delay of 2 s resulted in a similar distribution of P forms; however, the resolution of the spectra was poor. The spectra were recorded with a line broadening factor of 20 Hz. Chemical shifts were measured relative to 85% H₃PO₄ and peak assignments were done according to Newman & Tate (1980) and Condrón *et al.* (1990). Intensities of signals were determined by integration of peaks. The total P in the 0.5 M NaOH extract was determined after ignition (560°C) and dissolution of the residues in 0.5 M H₂SO₄. Inorganic P was measured directly from the extracts, and organic P was calculated as the difference of the two. Phosphorus from the alkali extracts was analysed by a modified molybdenum-blue method of Murphy & Riley (1962).

Statistics

Statistical analysis of the data was carried out on the replicates by one-way analysis of variance (ANOVA). If the main effects were significant at $P < 0.05$, a *post hoc* separation of

means was done by univariate least significant difference (LSD) test.

Results and discussion

Sequentially extracted P fractions

Bulk soil. Table 2 shows the amounts of organic, inorganic and total P (mg kg⁻¹ soil) extracted by sequential extraction from the upper 10 cm of the soil under the five forms of land use. The total P contents in the bulk soil ranged from 445 to 955 mg kg⁻¹ soil. These values are similar to those reported by Udo & Ogunwale (1977) for Alfisols in the savannah zone of Nigeria. Although significant differences in the different P fractions were detected among the various land uses, a general distribution pattern was observed in the sequentially extracted P fractions in this soil. The amount of organic P (NaHCO₃-P_o and NaOH-P_o) was generally small and accounted for only 17% of the total extractable P (Table 2). The major portion of it was in the NaOH fraction. The percentage of organic P in this soil is similar to the amounts reported by Udo & Ogunwale (1977) and Sharpley *et al.* (1987) for highly weathered tropical soils and by Agbenin & Tiessen (1995) in semi-arid northeast Brazil. Cross & Schlesinger (1995) showed that a large percentage of the P is organic P in highly weathered tropical soils. However, in the semi-arid tropics where organic matter production is limited by climate, the organic forms of P comprise a smaller portion of total P (Agbenin & Tiessen, 1995; Buresh *et al.*, 1997).

Sequential extraction of this soil showed that the labile inorganic P fractions (NaHCO₃-P_i and NaOH-P_i) accounted for 28% of the total P_i, 69% being from the NaOH-P_i fraction. Calcium-bound inorganic P extracted by dilute HCl accounted for 24% of the total P_i. Residual P (concentrated HCl-P_i and H₂SO₄-P) was the largest fraction, amounting to 48% of the total P_i, of which the majority was in the concentrated HCl-P_i fraction. The existence of appreciable amounts of P in residual fractions was also observed by other investigators. Adams & Walker (1975) demonstrated that residual P constituted 50% of total P in strongly weathered and leached soils of New Zealand and Udo & Ogunwale (1977) recorded the percentage as 54% in the savannah zone of Nigeria.

Particle-size separates. The largest concentration of total P was found in clay, and the concentration decreased with increasing particle size (Table 3). The values in the clay separates were twice as great as that in the bulk soil. The amount of organic P in particle-size separates also increased in the order: coarse sand < fine sand < silt < clay (Table 3), the largest being found in the clay separates characterized by large contents of organic C and N (Table 1). The larger amounts of organic P in clay and silt separates is almost certainly due to the large amounts of organic matter and pedogenic oxides in the finer particle-size separates (Agbenin & Tiessen, 1995;

Table 1 Chemical and physical properties of the A horizon under the five kinds of land use

Land use	CS ^a	FS ^a	Silt	Clay	Bulk density	pH		CEC	Base saturation	Organic C	N	S	C/N	Fe _d ^b	Fe _o ^c	Al _d ^b	Al _o ^c
						H ₂ O	CaCl ₂										
Native woodland	287 (2.3) ^d	206 (1.5)	190 (3.1)	295 (1.0)	1.20 (0.1)	6.6 (0.1)	6.0 (0.1)	16.8 (0.7)	85 (0.9)	18.7 (0.12)	1.83 (0.05)	0.28 (0.02)	10.2 (0.1)	1.02 (0.01)	0.24 (0.03)	0.60 (0.01)	0.17 (0.02)
Degraded woodland	372 (3.1)	304 (2.2)	114 (1.3)	180 (0.7)	1.33 (0.2)	6.9 (0.2)	6.1 (0.1)	15.7 (0.5)	76 (1.0)	13.8 (0.21)	1.22 (0.02)	0.20 (0.05)	11.3 (0.3)	1.09 (0.01)	0.11 (0.05)	0.47 (0.03)	0.15 (0.01)
Cultivated for 3 years	359 (1.9)	233 (2.1)	133 (2.1)	251 (0.9)	1.33 (0.1)	7.0 (0.1)	6.2 (0.1)	14.1 (1.2)	87 (0.5)	8.3 (0.13)	0.90 (0.01)	0.19 (0.02)	9.2 (0.1)	1.14 (0.03)	0.40 (0.01)	0.55 (0.02)	0.15 (0.01)
Cultivated for 15 years	321 (1.5)	261 (1.7)	130 (1.7)	251 (1.8)	1.33 (0.3)	6.7 (0.3)	5.9 (0.3)	11.7 (0.8)	76 (0.9)	8.2 (0.10)	0.90 (0.03)	0.17 (0.03)	9.1 (0.1)	1.18 (0.03)	0.37 (0.02)	0.55 (0.01)	0.16 (0.01)
Homestead	311 (2.3)	356 (2.1)	122 (1.1)	183 (2.3)	1.45 (0.1)	8.4 (0.3)	7.5 (0.1)	21.1 (1.1)	99 (1.5)	19.2 (0.07)	1.95 (0.05)	0.52 (0.03)	9.8 (0.3)	1.02 (0.04)	0.26 (0.01)	0.32 (0.03)	0.17 (0.01)

^aCS, coarse sand; FS, fine sand.^bFe_d and Al_d, dithionite-citrate-bicarbonate-extractable Fe and Al.^cFe_o and Al_o, oxalate-extractable Fe and Al.^dValues in parentheses indicate standard errors of the mean.

Leinweber *et al.*, 1997). Similar patterns of total and organic P distributions in particle-size separates were reported by Syers *et al.* (1969) in New Zealand and Agbenin & Tiessen (1995) in semi-arid northeast Brazil.

Sequential extraction of particle-size separates indicated that clay contains most of the inorganic P fractions. Tiessen *et al.* (1983) indicated that NaHCO₃-P_i and NaOH-P_i consist mainly of inorganic P adsorbed on surfaces, and the largest amount of these inorganic P fractions is therefore in the finer particle-size separates which have the greatest specific surface area. Increasing amounts of residual P with decreasing particle size was also reported for semi-arid soils of northeast Brazil (Agbenin & Tiessen, 1995).

Effects of land use on sequentially extracted P fractions

Bulk soil. Clearing and subsequent cultivation of the native woodland resulted in a marked depletion of all P fractions in this soil. Cultivation led to a 43% and 50% decline in the organic P from bulk soil after 3 and 15 years, respectively (Table 2). The depletion in organic P from the cropped fields could be attributed to the enhanced mineralization of soil organic P caused by cultivation and removal of P in the crops. The difference in the amount of organic P between the fields cultivated for 3 and for 15 years was not statistically significant ($P < 0.05$), and so the rapid depletion of organic matter must have occurred during the first 3 years of cultivation. Bowman *et al.* (1990) demonstrated that total organic P significantly declined during 60 years' cultivation of native North American soils, with almost half of the total loss recorded in the first 3 years of cultivation. Selective removal of *Acacia* for charcoal production resulted in a 28% depletion of the soil organic P in the degraded woodland. This may be attributed to the flush mineralization after removal of the trees which results in a reduction of the organic matter reserves and thus the amount of organic P (Forster & Zech, 1992). In the soil we studied, we found a 14% increase in organic P in the homestead fields, presumably as a result of manuring.

Sequentially extracted P fractions from the bulk soil showed that significantly ($P < 0.05$) more labile inorganic (NaHCO₃-P_i and NaOH-P_i), Ca-bound (1 M HCl-P_i) and residual (concentrated HCl-P_i and H₂SO₄-P) P occurred in the bulk soil of the native woodland than in that of the two cultivated fields (Table 2). Significantly less of NaOH-P_i and concentrated HCl-P_i were extracted from the soil after 15 years of cultivation than after only 3 years ($P < 0.05$). This suggests that with continued cultivation the labile fraction was constantly replenished from moderately labile (NaOH-extractable P) or more resistant P forms such as concentrated HCl-P, and accords with the suggestion of Magid *et al.* (1996). The depletion of acid- and alkali-extractable inorganic P from the bulk soil of the degraded woodland was less than from the cultivated soil. Application of manure seemed to have increased ($P < 0.05$) the content of inorganic P fractions of the homestead fields. Since

Table 2 Phosphorus fractions (mg kg⁻¹) from the sequential extraction of bulk soils

Land use	NaHCO ₃		NaOH		1 M HCl	Conc. HCl ^b	Residual P	Total P
	P _i ^a	P _o ^a	P _i	P _o	P _i	P _i		
Native woodland	55 b ^c	37 b	114 b	106 a	143 b	208 b	77 b	739 b
Degraded woodland	40 b	27 bc	104 c	75 b	129 c	194 c	68 c	636 c
Cultivated for 3 years	24 c	22 c	89 d	60 bc	96 d	150 d	50 e	489 d
Cultivated for 15 years	18 c	16 c	77 e	56 c	88 d	134 e	55 d	445 e
Homestead	121 a	70 a	138 a	93 a	207 a	233 a	94 a	955 a
Mean ^d	52	34	104	78	133	184	69	654

^aP_i, inorganic P; P_o, organic P.

^bConc. HCl, concentrated HCl.

^cDifferent letters within the column indicate significant differences between the means of the different land uses at $P < 0.05$.

^dMean values of each P fraction from the different land uses.

the major portion (>80%) of the P in manure, however, is present in inorganic forms (Bril & Salomons, 1990), most of the increase in total P that we observed in the homestead soil was due to the increase in inorganic rather than organic P fractions.

Particle-size separates. According to Table 3, cultivation of the native woodland resulted in significantly less organic P in all particle-size separates ($P < 0.05$). The largest losses occurred from coarse and fine sand separates. The losses from the silt and clay separates were relatively small. The pattern of organic P depletion in particle-size separates was closely related to the pattern of depletion of soil organic matter (Solomon *et al.*, 2000). In all particle-size separates, the NaHCO₃-P_o fraction reflected the changes in land use systems more clearly than the NaOH-P_o fraction. This indicates that the NaOH-P_o fraction represents a slowly mineralizable pool of P (Buresh *et al.*, 1997). Larger amounts of organic P, particularly from the clay and silt separates, were generally extracted from the fields where manure was applied (Table 3). This could be attributed to the incorporation of additional input of biologically processed organic materials together with manure into the finer separates (Christensen, 1992).

Cultivation affected the amount of inorganic P fractions in all particle-size separates; the greatest losses were from the coarser size separates. Among the inorganic fractions of P, the depletion as a result of clearing and cultivation was most pronounced in the NaHCO₃-P_i followed by NaOH-P_i. Buresh *et al.* (1997) also suggested that in addition to the NaHCO₃-P_i, NaOH-P_i represented an important source of P for plants in tropical soils. Application of manure significantly increased ($P < 0.05$) the amount of inorganic P fractions in all particle-size separates, as seen from the values in the homestead fields (Table 3). The influence was most pronounced in the clay separates.

³¹P-NMR spectroscopy

Bulk soil. We applied ³¹P-NMR spectroscopy to investigate the structure of alkali-soluble forms of P. To facilitate comparisons between samples, signal intensities of the NMR spectra allocated to the different forms of P were converted to amounts of alkali-extractable P on the basis of total P analysed by the wet chemical method. Since different P compounds may be extracted by alkali to different extents, the results cannot be used to calculate total amounts in the soil (Newman & Tate, 1980).

Signals with a chemical shift around $\delta = 6.4$ p.p.m. were assigned to inorganic orthophosphate P (PO₄³⁻). Orthophosphate monoesters (RO.PO₃²⁻) were around $\delta = 5.1$ p.p.m., while signals at $\delta = 1.5$ – 0.5 p.p.m. were considered as orthophosphate diesters [(RO)(R'O).PO₂⁻] peaks. Wet chemical analysis showed that the total alkali-extractable P ranged from 19 to 32% of the total soil P. This accords with the results of Zech *et al.* (1985) for Vertisols in Mexico and Forster & Zech (1992) for weathered tropical soils in Liberia. The relative proportions of inorganic and organic P determined by wet chemical analysis and ³¹P-NMR spectroscopy were similar both in bulk soil and in particle-size separates (Table 4).

Amounts of the different forms of P resolved by ³¹P-NMR indicated that inorganic orthophosphate P was the dominant form of alkali-soluble P (Table 5). It accounted for 51–70% of the total alkali-extractable P. Orthophosphate monoesters were the major organic P species in the upper 10 cm. They accounted for 24–36% of the total P in the alkali extracts, whereas orthophosphate diesters accounted for only 6–7% of total alkali-soluble P. The ratio of diester P to monoester P in the bulk soil ranged from 0.14 to 0.25 (Table 5). This further confirms that in the alkali extracts orthophosphate monoesters were the dominant forms of organic P. These results are similar to those reported by Forster & Zech (1992) for weathered tropical soils in Liberia.

Table 3 Phosphorus fractions (mg kg⁻¹) from the sequential extraction of particle-size separates

Land use	NaHCO ₃		NaOH		1 M HCl P _i	Conc. HCl ^b P _i	Residual P	Total P
	P _i ^a	P _o ^a	P _i	P _o				
CS^c								
Native woodland	11 b ^d	13 a	62 b	32 a	61 b	78 b	9 b	266 b
Degraded woodland	10 b	8 b	55 c	23 b	61 b	70 b	9 b	236 c
Cultivated for 3 years	2 c	2 c	25 d	9 c	41 c	44 c	7 c	130 d
Cultivated for 15 years	3 c	2 c	21 d	10 c	40 c	48 c	7 bc	131 d
Homestead	22 a	12 a	56 a	27 b	97 a	90 a	4 a	318 a
FS^c								
Native woodland	20 b	15 ab	64 b	56 a	79 b	138 a	11 ab	383 a
Degraded woodland	14 c	11 b	55 c	37 b	61 c	132 ab	10 b	318 b
Cultivated for 3 years	4 d	3 c	24 e	25 c	52 d	121 b	7 c	236 c
Cultivated for 15 years	5 d	3 c	37 d	28 c	58 d	119 b	8 c	257 c
Homestead	27 a	22 a	61 a	41 a	96 a	166 a	12 a	425 a
Silt								
Native woodland	55 b	42 b	152 b	148 a	193 b	247 a	71 c	908 b
Degraded woodland	45 c	43 b	131 c	121 b	192 b	224 a	89 b	844 c
Cultivated for 3 years	26 d	29 c	91 d	88 c	111 c	178 b	56 e	579 d
Cultivated for 15 years	20 e	19 d	95 d	91 bc	99 d	195 b	62 d	581 d
Homestead	99 a	69 a	163 a	140 a	212 a	252 a	98 a	1032 a
Clay								
Native woodland	131 b	112 a	242 b	232 b	302 b	349 bc	224 b	1591 b
Degraded woodland	133 b	72 b	266 c	209 c	293 b	379 b	188 c	1540 b
Cultivated for 3 years	57 c	48 c	159 d	125 e	258 c	334 c	164 c	1144 c
Cultivated for 15 years	45 c	40 c	153 e	141 d	234 c	319 c	169 c	1101 c
Homestead	244 a	115 a	301 a	247 a	352 a	396 a	262 a	1916 a
Mean^c								
CS	10	7	44	20	60	66	9	216
FS	14	11	48	37	69	135	10	314
Silt	49	40	126	118	161	219	75	789
Clay	122	77	224	191	288	355	201	1459

^aP_i, inorganic P; P_o, organic P.

^bConc. HCl, concentrated HCl.

^cCS, coarse sand; FS, fine sand.

^dDifferent letters within the column indicate significant differences at $P < 0.05$.

^eMean values of P fractions of each particle-size separate from the different land uses.

Particle-size separates. The amount of orthophosphate monoesters and diesters increased with decreasing particle size, with the largest amount in clay (Table 6). We have found similar results in our investigation of soils from Khyrgyzia (Turrión *et al.*, 2000). According to McKercher & Anderson (1968) and Turrión *et al.* (2000), the larger charge density of monoesters (e.g. inositol phosphate) allows rapid adsorption on clays and interaction with sesquioxides that protect free inositols from degradation and which could account for their enrichment in these separates. Enrichment of diester P species with decreasing size separates might be the result of surface stabilization of orthophosphate diesters produced by microorganisms, possibly due to the closer proximity of microbes to

those surfaces (Sumann *et al.*, 1998). These results are supported by our previous studies on the composition of the organic matter of this soil, in which both microbial-derived carbohydrates (hexoses and deoxysugars) (Solomon *et al.*, 2000) and amino sugars are concentrated in the clay and silt separates. Therefore, these findings strengthen our view that, in general, products of microbial metabolism are enriched in the organic matter associated with the finer size separates (Guggenberger *et al.*, 1994; Solomon *et al.*, 2000).

The contents of inorganic orthophosphate P showed a pattern similar to that of the organic P species (Table 6). On average, 62% of the orthophosphate P was in clay separates, while 33% was associated with the silt. Enrichment of

inorganic orthophosphate P in the clay and silt separates could be attributed to chemisorption and to surface adsorption on finer particles with large specific surface areas. Only 4 and 3% of inorganic orthophosphate P was found in the fine and coarse sand separates, respectively.

In general, the results of ^{31}P -NMR spectroscopy confirmed the influence of particle size and chemical properties such as soil organic matter and pedogenic oxides on the amount and forms of alkali-extractable P as shown by the results of the sequential fractionation.

Effects of land use on different P forms

Bulk soil. Amounts of P species resolved by ^{31}P -NMR spectroscopy indicated that changes in land use resulted in the substantial depletion of P forms from the upper 10 cm of this soil. The cultivated soil contained 53% less orthophosphate diesters than the soil of the native woodland. The depletion of orthophosphate monoesters due to cropping was only 30% after 3 years of cultivation and 39% after 15 years. Hinedi *et al.* (1988) demonstrated that under favourable soil conditions diester P can be quickly converted to inorganic orthophosphate P while monoester P remains stable. Since orthophosphate monoester P includes a substantial amount of inositol phosphates (Tate & Newman, 1982; Condrón *et al.*, 1990) and orthophosphate diester P includes phospholipids and nucleic acids (Newman & Tate, 1980), our results concur with the suggestion that orthophosphate diester P constitutes more easily mineralizable forms of organic P than orthophosphate monoesters. Application of manure, however, led to an increase of orthophosphate diesters and monoesters in the homestead fields.

The contents of inorganic orthophosphate P in the bulk soil decreased in the order: homestead > native woodland > degraded woodland > 15 years' cultivation > 3 years' cultivation. The largest amount was found in the soil of the homestead fields. Studies conducted on animal manure using ^{31}P -NMR spectroscopy indicated that the proportion of inorganic orthophosphate P in animal manure could reach from 84 to 95% of the total P (Leinweber *et al.*, 1997), which could account for the enrichment of this inorganic form of P in the homestead fields.

Particle-size separates. The impact of clearing and cultivation on the amount of organic P was evident in all size separates, with the largest depletion from the coarse and fine sand separates. This accords with the pattern of organic matter depletion observed in this soil (Solomon *et al.*, 2000). We have found the largest decline in organic C and N from coarse and fine sand followed by silt and clay separates. Tiessen *et al.* (1983) suggested that organic matter in the fine separates undergoes a slower change during cultivation than that in the coarser separates. This may be due to the stabilization of microbial metabolites by closer association with the finer

Table 4 Relative proportions (%) of inorganic and organic P in 0.5 M NaOH extracts determined by wet chemical analysis and ^{31}P -NMR spectroscopy in bulk soil and particle-size separates

Land use	Inorganic P		Organic P	
	Wet chemical	NMR	Wet chemical	NMR
Native woodland				
BS ^a	64	68	36	32
CS ^a	51	55	49	45
FS ^a	59	54	41	46
Silt	54	57	46	43
Clay	61	63	39	37
Degraded woodland				
BS	63	65	37	35
CS	80	89	20	11
FS	55	52	45	48
Silt	51	34	49	66
Clay	61	65	39	35
Cultivated for 3 years				
BS	54	52	46	48
CS	45	41	55	59
FS	48	42	52	58
Silt	45	48	55	52
Clay	49	51	51	49
Cultivated for 15 years				
BS	52	55	48	45
CS	31	25	69	75
FS	36	26	64	74
Silt	36	40	64	60
Clay	51	53	49	47
Homestead				
BS	66	70	34	30
CS	71	75	29	25
FS	67	65	33	35
Silt	54	52	46	48
Clay	69	73	31	27

^aBS, bulk soil; CS, coarse sand; FS, fine sand.

particles or by oxides and hydroxides (Guggenberger *et al.*, 1996) which might protect the organic P from rapid mineralization. Similar amounts of organic P resolved by ^{31}P -NMR spectroscopy from the cultivated fields confirmed the results of sequential fractionation. This supports the suggestion that most of the reduction in the organic P of this soil occurred in the first 3 years of cultivation.

Our ^{31}P -NMR spectroscopy from particle-size separates of the soil further revealed that more than 70% of the inorganic orthophosphate P from the coarse and fine sand separates seems to have been lost as a result of cultivation. When compared with the sand-size separates, less orthophosphate P

Table 5 Phosphorus contents (mg kg⁻¹ soil) of NaOH-soluble P forms as determined by integration of ³¹P-NMR signals from bulk soils

Land use	Orthophosphate P	Orthophosphate monoesters	Orthophosphate diesters	Diester/monoester
Native woodland	157 (68%) ^a	62 (27%)	13 (5%)	0.21
Degraded woodland	107 (65%)	47 (28%)	11 (7%)	0.23
Cultivated for 3 years	56 (53%)	44 (41%)	6 (6%)	0.14
Cultivated for 15 years	53 (55%)	38 (39%)	6 (6%)	0.16
Homestead	171 (70%)	59 (24%)	15 (6%)	0.25
Mean ^b	109 (62%)	50 (28%)	10 (10%)	0.20

^aValues in parentheses across the row indicate percentages of P forms in the total alkali-extractable P in the bulk soil of each land use.

^bMean values of each P form from the different land uses.

Table 6 Phosphorus contents (mg kg⁻¹ soil) of NaOH-soluble P as determined by integration of ³¹P-NMR signals from particle-size separates

Land use	Orthophosphate P	Orthophosphate monoesters	Orthophosphate diesters	Diester/monoester
Native woodland				
CS ^a	25 (4%) ^b	14 (5%)	6 (8%)	0.55
FS ^a	32 (6%)	21 (7%)	6 (7%)	0.27
Silt	219 (39%)	132 (44%)	31 (40%)	0.23
Clay	287 (51%)	133 (44%)	34 (44%)	0.26
Degraded woodland				
CS	23 (5%)	2 (1%)	1 (1%)	0.88
FS	19 (4%)	13 (4%)	4 (4%)	0.33
Silt	111 (24%)	151 (51%)	64 (62%)	0.43
Clay	304 (67%)	130 (44%)	33 (32%)	0.25
Cultivated for 3 years				
CS	4 (2%)	5 (2%)	1 (3%)	0.28
FS	9 (3%)	10 (4%)	2 (3%)	0.15
Silt	106 (40%)	94 (41%)	21 (45%)	0.22
Clay	146 (55%)	120 (52%)	23 (49%)	0.19
Cultivated for 15 years				
CS	3 (1%)	7 (3%)	2 (4%)	0.30
FS	5 (3%)	11 (5%)	4 (7%)	0.31
Silt	89 (35%)	109 (45%)	22 (45%)	0.19
Clay	156 (61%)	116 (48%)	22 (44%)	0.19
Homestead				
CS	20 (3%)	5 (2%)	2 (3%)	0.30
FS	30 (4%)	10 (3%)	6 (11%)	0.62
Silt	193 (33%)	157 (52%)	25 (44%)	0.16
Clay	422 (60%)	132 (43%)	24 (42%)	0.18
Mean ^c				
CS	15 (7%)	7 (3%)	2 (4%)	0.46
FS	19 (4%)	13 (5%)	4 (6%)	0.34
Silt	144 (33%)	129 (47%)	33 (47%)	0.25
Clay	263 (62%)	126 (46%)	27 (42%)	0.21

^aCS, coarse sand; FS, fine sand.

^bValues in parentheses within the columns are proportions of P forms in the total alkali-soluble P extracted from the particle-size separates.

^cMean values of P of each particle-size separate.

was lost from the finer particle-size separates. As a result of incorporating animal manure, the amounts of inorganic orthophosphate P, orthophosphate monoester, and orthophos-

phosphate diester P significantly increased, especially in the finer particle-size separates, further indicating the importance of manure for increasing P in this soil.

Conclusions

Based on the results of both sequential extraction and ^{31}P -NMR spectroscopy we can conclude that in this semi-arid region of Tanzania, clear-cutting and subsequent cultivation of the native woodland resulted in a depletion of both organic and inorganic P, thereby causing a decline in the soil's fertility. This might be attributed to the enhanced mineralization of organic P due to the combined effects of cultivation and the removal of soil P in the crops.

A more rapid reduction of organic P occurred from the organic matter bound to the coarse and fine sand than to the finer size separates. Most of this depletion occurred during the first 3 years of cultivation. However, the results from the fields cultivated for 15 years show that depletion of organic P may continue for some further years in this semi-arid agroecosystem.

The effect of clearing and cropping was most pronounced in the $\text{NaHCO}_3\text{-P}_i$ fraction, followed by the NaOH-P_i fraction, suggesting that in this soil, NaOH-P_i also represents an important source of P for plants.

Our ^{31}P -NMR spectroscopy indicated that cultivation led to a marked depletion of both inorganic orthophosphate P and orthophosphate monoester and diester P, especially from sand separates; rather less was lost from the finer separates, which accords with our findings from the sequential extraction. The greatest depletion was from the diester P, suggesting that in this soil, orthophosphate diester P constitutes a more easily mineralizable form of organic P in the soil than does monoester P. There was more organic P and inorganic P in all particle-size separates of the homestead fields. We attribute this to the additions of manure, which contains mainly inorganic P.

Our study clearly shows that the current low input agriculture is not sustainable. Management practices must be developed to combat the ongoing soil degradation. A combined use of available organic materials such as animal manure with the judicious use of inorganic fertilizers can replenish the soil's fertility.

Acknowledgements

We thank Professor W. Zech, the Editor-in-Chief and the two anonymous reviewers for their valuable comments and suggestions which helped to improve our script. We are indebted to the German Academic Exchange Service (DAAD) for providing the fellowship for D. Solomon. We are also grateful to Professor I. Fouda, Dr S. Schade, Dr G.L. Kamukala and Mr S. Decurtins for their help in choosing sites and collecting samples and to Dr L. Haumaier for recording the ^{31}P -NMR spectra. The project was funded by the Tropical Ecology Program of the Deutsche Gesellschaft für Technische Zusammenarbeit, GTZ (Project No 92.2151.7-001.02).

References

- Adams, J.A. & Walker, T.W. 1975. Some properties of a chronotoposequence of soils from granite in New Zealand. 2. Forms and amount of phosphorus. *Geoderma*, **13**, 41–51.
- Agbenin, J.O. & Tiessen, H. 1995. Phosphorus forms in particle-size fractions of a toposequence from Northeast Brazil. *Soil Science Society of America Journal*, **59**, 1687–1693.
- Amelung, W., Zech, W., Zhang, X., Follett, R.F., Tiessen, H., Knox, E. & Flach, K.-W. 1998. Carbon, nitrogen and sulfur pools in particle-size fractions as influenced by climate. *Soil Science Society of America Journal*, **62**, 172–181.
- Blume, H.P. & Schwertmann, U. 1969. Genetic evaluation of profile distribution of aluminum, iron and manganese oxides. *Soil Science Society of America Proceedings*, **33**, 438–444.
- Bowman, R.A. & Cole, C.V. 1978. Transformations of organic phosphorus substrates in soils as evaluated by NaHCO_3 extraction. *Soil Science*, **125**, 49–54.
- Bowman, R.A., Reeder, J.D. & Lober, R.W. 1990. Changes in soil properties in a central plains rangeland soil after 3, 20 and 60 years of cultivation. *Soil Science*, **150**, 851–857.
- Bril, J. & Salomons, W. 1990. Chemical composition of animal manure: a modelling approach. *Netherlands Journal of Agricultural Science*, **38**, 333–351.
- Buresh, R.J., Smithson, P.C. & Hellums, D.T. 1997. Building soil phosphorus capital in Africa. In: *Replenishing Soil Fertility in Africa* (eds R.J. Buresh, P.A. Sanchez & F. Calhoun), pp. 111–149. Special Publication No 51, Soil Science Society of America, Madison, WI.
- Christensen, B.T. 1992. Physical fractionation of soil and organic matter in primary particle size and density separates. *Advances in Soil Science*, **20**, 1–90.
- Condon, L.M., Frossard, E., Tiessen, H., Newman, R.H. & Stewart, J.W.B. 1990. Chemical nature of organic phosphorus in cultivated and uncultivated soils under different environmental conditions. *Journal of Soil Science*, **41**, 41–50.
- Cross, A.F. & Schlesinger, W.H. 1995. A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma*, **64**, 197–214.
- FAO–UNESCO 1997. *FAO–UNESCO Soil Map of the World, Revised Legend with Corrections and Updates*. World Soil Resources Report 60, ISRIC, Wageningen.
- Forster, J.C. & Zech, W. 1992. Phosphorus status of a soil catena under Liberian evergreen rain forest: results of ^{31}P NMR spectroscopy and phosphorus adsorption experiments. *Zeitschrift für Pflanzenernährung und Bodenkunde*, **156**, 61–66.
- Guggenberger, G., Christensen, B.T. & Zech, W. 1994. Land-use effects on the composition of organic matter in particle-size separates of soil: I. Lignin and carbohydrate signature. *European Journal of Soil Science*, **45**, 449–458.
- Guggenberger, G., Haumaier, L., Thomas, R.J. & Zech, W. 1996. Assessing the organic phosphorus status of an Oxisol under tropical pastures following native savanna using ^{31}P NMR spectroscopy. *Biology and Fertility of Soils*, **23**, 332–339.
- Hawkes, G.E., Powlson, D.S., Randall, E.W. & Tate, K.R. 1984. A ^{31}P nuclear magnetic resonance study of the phosphorus species in alkali extracts of soils from long-term field experiments. *Journal of Soil Science*, **35**, 35–45.

- Hedley, M.J., Stewart, J.W.B. & Chauhan, B.S. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Science Society of America Journal*, **46**, 970–976.
- Hinedi, Z.R., Chang, A.C. & Lee, R.W.K. 1988. Mineralization of phosphorus in sludge-amended soils monitored by phosphorus-31-magnetic resonance spectroscopy. *Soil Science Society of America Journal*, **52**, 1593–1596.
- Lal, R. 1986. Conversion of tropical rainforest: agronomic potential and ecological consequences. *Advances in Agronomy*, **39**, 173–264.
- Leinweber, P., Haumaier, L. & Zech, W. 1997. Sequential extractions and ³¹P-NMR spectroscopy of phosphorus forms in animal manures, whole soils and particle-size separates from a densely populated livestock area in Northwest Germany. *Biology and Fertility of Soils*, **25**, 89–94.
- Magid, J., Tiessen, H. & Condron, L.M. 1996. Dynamics of organic phosphorus in soils under natural and agricultural ecosystems. In: *Humic Substances in Terrestrial Ecosystems* (ed. A. Piccolo), pp. 429–466. Elsevier, Amsterdam.
- McKercher, R.B. & Anderson, G. 1968. Content of inositol penta- and hexaphosphates in some Canadian soils. *Journal of Soil Science*, **19**, 47–55.
- Mehra, O.P. & Jackson, M.L. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, **7**, 317–327.
- Murphy, J. & Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, **27**, 31–36.
- Newman, R.H. & Tate, K.R. 1980. Soil characterization by ³¹P nuclear magnetic resonance. *Communications in Soil Science and Plant Analysis*, **11**, 835–842.
- Sharpley, A.N., Tiessen, H. & Cole, C.V. 1987. Soil phosphorus forms extracted by soil tests as a function of pedogenesis. *Soil Science Society of America Journal*, **51**, 362–365.
- Solomon, D., Lehmann, J. & Zech, W. 2000. Land use effects on soil organic matter properties of chromic Luvisols in semiarid northern Tanzania: carbon, nitrogen, lignin and carbohydrates. *Agriculture, Ecosystems and Environment*, **78**, 203–213.
- Sumann, M., Amelung, W., Haumaier, L. & Zech, W. 1998. Climatic effects on soil organic phosphorus in the North American Great Plains identified by phosphorus-31 nuclear magnetic resonance. *Soil Science Society of America Journal*, **62**, 1580–1586.
- Syers, J.K., Shah, R. & Walker, T.W. 1969. Fractionation of phosphorus in two alluvial soils and particle-size separates. *Soil Science*, **108**, 283–289.
- Tate, K.R. & Newman, R.H. 1982. Phosphorus fractions of a climosequence of soils in New Zealand tussock grassland. *Soil Biology and Biochemistry*, **14**, 191–196.
- Tiessen, H. & Moir, J.O. 1993. Characterization of available P by sequential extraction. In: *Soil Sampling and Methods of Analysis* (ed. M.R. Carter), pp. 75–86. Lewis Publishers, Boca Raton, FL.
- Tiessen, H., Stewart, J.W.B. & Moir, J.O. 1983. Changes in organic and inorganic phosphorus composition of two grassland soils and their particle size fractions during 60–90 years of cultivation. *Journal of Soil Science*, **34**, 815–823.
- Turrión, M.-B., Glaser, B., Solomon, D., Ni, A. & Zech, W. 2000. Effects of deforestation on phosphorus pools in mountain soils of the Alay range, Khyrgyzia. *Biology and Fertility of Soils*, **31**, 134–142.
- Udo, E.J. & Ogunwale, J.A. 1977. Phosphorus fractions in selected Nigerian soils. *Soil Science Society of America Journal*, **41**, 1141–1146.
- Wilding, L.G. 1985. Spatial variability: its documentation, accommodation and implication to soil survey. In: *Soil Spatial Variability* (eds D.R. Nielsen & J. Bouma), pp. 166–187. PUDOC, Wageningen.
- Zech, W., Alt, H.G., Zucker, A. & Kögel, I. 1985. ³¹P-NMR spectroscopic investigations of NaOH-extracts from soils with different land use in Yucatan (Mexico). *Zeitschrift für Pflanzenernährung und Bodenkunde*, **148**, 626–632.