Bioavailability of slowly cycling soil phosphorus: major restructuring of soil P fractions over four decades in an aggrading forest

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Abstract Although low solubility and slow cycling control P circulation in a wide range of ecosystems, most studies that evaluate bioavailability of soil P use only indices of short-term supply. The objective here is to quantify changes in P fractions in an Ultisol during the growth of an old-field pine forest from 1957 to 2005, specifically changes with organic P (Po) and with inorganic P (Pi) associated with Fe and Al oxides as well as Ca compounds. Changes in soil P were estimated from archived mineral soil samples collected in 1962 shortly after pine seedlings were planted, and on six subsequent occasions (1968, 1977, 1982, 1990, 1997, and 2005) from eight permanent plots and four mineral soil layers (0–7.5, 7.5–15, 15–35, and 35–60 cm). Despite the net transfer of 82.5 kg ha^{-1} of P from mineral soil into tree biomass and O horizons, labile soil P was not diminished, as indexed by anion exchange resins, and $NaHCO_3$ and Mehlich III extractants. An absence of depletion in most labile P fractions masks major restructuring of soil P chemistry driven by ecosystem development. During 28 years of forest growth, decreases were significant and substantial in slowly cycling Po and Pi associated with Fe and Al oxides and Ca compounds, and these accounted for most of the P supplied to biomass and O horizons, and for buffering labile soil fractions as well. Changes in soil P are attributed to the P sink strength of the aggrading forest (at 2.9 kg ha^{-1} year^{-1} over 28 years); legacies of fertilization, which enriched slowly cycling fractions of Po and Pi; and the changing biogeochemistry of the soil itself.

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Introduction

When E.W. Hilgard described Mississippi soils, geology and landscapes in the 1850s (Hilgard 1860, 1906), he based a number of his ecological interpretations on acid extractions of soils. Considering that the availability of soil P in most contemporary studies still relies on relatively simple acid extractions, we do not seem to have moved far beyond Hilgard's analytical approaches, despite the passage of nearly 150 years.

Because nearly all soil P is unavailable for immediate use by soil microbes and plant roots, relationships between labile and recalcitrant P is an important topic for study (e.g., Chang and Jackson 1957; Thomas and Peaslee 1973). Even still, most research and management studies that evaluate bioavailable P continue to characterize P availability using only extractants designed to correlate with yields of P-fertilized agricultural crops grown in the same year as that of the soil sampling and analysis (Bray and Kurtz 1945; Mehlich 1978; Olsen et al. 1954). These correlative methods support a short-term dose–response approach to intensive soil management (Thomas and Peaslee 1973; Richter and Markewitz 2001), and seemingly ignore slowly

cycling fractions of soil P. Over time scales longer than a growing season, slowly cycling fractions of P, in fertilized and unfertilized soils alike, make significant contributions to P bioavailability, and can ultimately determine ecosystem productivity, organic matter storage and sustainability (Walker and Syers 1976; Crews et al. 1995; Schmidt et al. 1996; Townsend et al. 2002). Too often, however, concepts of immediately available P seem to have trapped those of slowly cycling fractions of soil P firmly within labels such as fixed, recalcitrant, resistant, refractory, unavailable, occluded or simply nonlabile, words that clearly marginalize the biological significance of slowly cycling soil P.

In recent decades, however, our understanding of how soil P changes over time has expanded greatly on several fronts (Buol 1995). Walker and Syers (1976) described a now popular concept of progressive P limitation, i.e., that during soil and ecosystem development, P from weatherable minerals is exhausted, leaving residual P to be cycled through organic matter or into occluded and strongly recalcitrant Pi. Garcia-Montiel et al. (2000) proposed an analogous progression of soil P over decadal time scales, following cutting, burning and converting tropical forests on Oxisols to grass pasture. Beyond conceptual models, new analytical methods are prolific, including the use of phosphate sorption isotherms (e.g., Fox and Kamprath 1970; Novak and Watts 2004), radioisotopic labeling and kinetic techniques (McDowell et al. 2001; Hamon et al. 2002), modeling approaches that predict changes in soil P over time with respect to management and pedogenesis (Cox et al. 1981; Karpinets et al. 2004), and chemical and spectroscopic P fractions in long-term soil experiments (Barber 1979; Cope 1981; McCollum 1991; Schmidt et al. 1996; Soloman et al. 2002). These analytical developments generally confirm that, in contrast with other nutrients, chemical compounds associated with soil P lend themselves to sequential chemical extractions that can describe soil P in operationally discrete fractions (e.g., Chang and Jackson 1957; Shelton and Coleman 1968; Dalal 1977; Novais and Kamprath 1978; Hedley et al. 1982a, 1982b; Cross and Schlesinger 1994; Frizano et al. 2002). Moreover, the changes in P fractions in long-term soil experiments provide a special perspective that impacts upon our understanding of how slowly cycling P contributes to P bioavailability over time scales of decades (Schmidt et al. 1996, 1997; Beck and Sánchez 1994; Tiessen et al. 1992; Goh and Condron 1989).

The objective of this paper is to evaluate changes in P fractions and bioavailability in Ultisols that supported the four- to five-decade growth of a forest from seedlings to mature trees. The study is based at the long-term soil experiment at the USDA Forest Service's Calhoun Experimental Forest, in soils historically cultivated and fertilized for cotton.

The Calhoun experiment is well-suited to the methods of Hedley et al. (1982a, 1982b), which are used to examine how organic and inorganic fractions of P contribute to the uptake and circulation of P in long-term systems of land management. In this study, archived samples collected on seven occasions between 1962 and 2005 are available for analyzing the change in soil P during the period in which planted tree seedlings grew to maturity but after the soils had long been cultivated and fertilized for cotton. The aggrading tree biomass and forest floor have been strong sinks for P, hypothetically depleting bioavailable fractions of organic and inorganic soil P as mineral soils are utilized to meet nutritional requirements for growing plant biomass and new O horizons. In long-term soil experiments, P fractions are taken to be sources or sinks of P, to the extent that a fraction of P decreases or increases over time (Schmidt et al. 1996).

Methods

The Calhoun ecosystem

The Calhoun Experimental Forest is located in Union County, South Carolina, at about 34.5°N, 82°W (Richter and Markewitz 2001). Elevation is about 200 m, and the underlying geologic material is part of the Piedmont's most common bedrock, a partly metamorphosed granitic gneiss. Soils that form on broad, geomorphically stable interfluves of the Piedmont's granite gneiss are acidic Ultisols, one of the world's common soil orders, found most often in humid, warm temperate regions and medium to low-elevation tropics (Buol et al. 2003; Richter and Babbar 1991). In the Southern Piedmont, soils on the broad interfluves are typically fine, kaolinitic, thermic Typic Kanhapludults (Soil Survey Staff 2003) of the Appling and Cecil series. Surficial A and E horizons have quartz-dominated mineralogy, and are sandy loams or loamy sands. If not eroded by agriculture, surficial horizons can be relatively deep (>40 cm). Below are acidic, clayey B horizons, dominated by kaolinite clays, quartz and Fe and Al oxides. Physical, chemical and biological data on the soils have been published (Richter et al. 1994, 1999; Markewitz et al. 1998; Richter and Markewitz 1995, 2001), and a summary of information on the soils is provided by Table 1.

The Calhoun ecosystem currently has a warm temperate, humid continental climate with long, hot

Table 1 General physical and chemical information of the Ultisols from the long-term soil experiment at the Calhoun Experimental Forest, South Carolina, USA. Soil data are from 1990s samplings

Horizon	Depth (m)	Bulk density (Mg m^{-3})	pHs[a]	Exchangeable/extractable[b] (mmolc kg^{-1})					SOC (%)	Clay (%)	DCB-extractable (mmolc kg^{-1})	
				Ca	Mg	K	Acidity	SO$_4$			Fe[c]	Al[c]
A	0–0.075	1.52	3.8	0.6	0.2	0.3	10.8	0.2	0.67	10.0	31.0	21.9
E	0.075–0.15	1.52	4.2	0.5	0.2	0.2	6.8	0.2	0.41	13.0	44.5	25.0
BE	0.15–0.35	1.52	4.4	2.3	0.7	0.5	6.5	1.1	0.31	18.0	130.7	76.0
B22	0.35–0.6	1.44	4.4	10.2	3.2	1.1	9.2	7.8	0.33	39.3	373.4	170.9
B23	0.6–1.0	1.44	4.0	7.1	4.7	1.2	16.2	10.2	0.23	48.5	554.1	202.1
BC1	1.0–1.5	1.40	4.0	2.9	2.2	0.7	20.8	10.1	0.23	42.9	512.9	141.2
BC2	2.0–2.5	1.42	4.0	0.3	0.5	0.9	31.0	8.3	0.07	37.7	293.1	80.0
CB1	2.5–3.0	–	4.0	0.4	0.6	1.1	34.1	na	0.08	28.5	202.7	62.0

[a] pHs is soil pH in 0.01 M CaCl$_2$

[b] Exchangeable cations are NH_4–acetate-extractable Ca, Mg and K, and KCl-exchangeable acidity; and SO$_4$ is NH_4VO_3-extractable (adapted from Richter et al. 1994; Markewitz et al. 1998)

[c] DCB-extractable Fe and Al

summers and short, mild winters. Annual precipitation averaged about 1,250 mm between 1973 and 1987 (Whitmire, South Carolina), and hydrologic model simulations have found the evapotranspiration from mature forests to average 880 mm and the drainage to be about 370 mm annually (Gnau 1992). Mean annual air and soil temperature is about 16 °C. Soil temperature ranges between 5 and 25 °C over the year at about 20 cm depth (D.D. Richter, unpublished data).

Site history

On upland sites, vegetation prior to about 1800 was predominantly mixed deciduous forest composed of oaks, hickories and other hardwoods. Upland soils, especially those derived from granitic bedrock, were strongly acidic and relatively low in bioavailable P (Richter and Markewitz 2001). Despite relatively low native fertility, physical soil attributes were attractive for cultivation, and early in the nineteenth century, upland hardwood forests began to be extensively converted to agricultural fields, mainly driven by cotton in upstate South Carolina.

From about 1800 to the U.S. Civil War in the 1860s, fields in the Carolina Piedmont were managed for cotton, corn, tobacco, wheat and other crops, with minimal fertilization. After forests were initially cleared, they were often burned (Ruffin 1852; Gray 1933), and ash effects promoted nutrient bioavailability, including that of P. Following several years of cropping, farmers switched to less demanding uses before abandoning fields and moving onto "fresh soil" (Gray 1933; Richter and Markewitz 2001).

After the Civil War, fields in the Southern Piedmont were more continuously cropped. As systems of share-cropping and tenant farming developed (Vance 1929), fertilization and liming became more standard farm practices, with P and lime originating from mines on the Atlantic and Gulf Coastal Plains (Sheridan 1979). Cotton production increased across the region until the 1920s, when the boll weevil, farm economics and soil degradation combined to create vast areas of abandoned southern farmland. Successional pine forests expanded in area throughout much of the twentieth century, regenerating vigorously in abandoned old fields. In the early twenty-first century, most old fields in the Southern Piedmont are now pine or mixed hardwood–pine forests, hayfields and pastures.

The specific soils under study are located on old upland cotton fields formerly cultivated on the 800-ha Old Ray Place, a nineteenth-century cotton plantation managed by Rev. Thomas Ray and his family from 1820 to 1876. In the early 1930s, the USDA Forest Service purchased the farm property for the Sumter National Forest, and Calhoun Experimental Forest. From the 1930s through to 1955, these fields were cultivated for cotton by a local farmer. In January 1957, after a two-year fallow, the soils were planted with pine seedlings in 16 permanent plots, arranged in four blocks of four plots each. The plots are in close proximity to each other, and blocks were selected to represent different soil-landform conditions.

Soil sampling and general soil analysis

To examine the effects of forest growth on fractions of soil P, we used archived soil collections from the Long-Term Calhoun Soil Experiment, which included eight of the 16 permanent plots in the experiment, repeated and intensive within-plot sampling, and the soil archive

of nearly all samples collected in 1962, 1968, 1978, 1982, 1990, 1997 and 2005 (Richter and Markewitz 2001). The soil sampling areas within four of the eight plots encompassed 388 m², the other four 606 m², until 2005, when sampling in all eight was expanded to nearly 0.2-ha plot areas.

In all collections in the Calhoun archive, mineral soils were sampled similarly by compositing twenty 2-cm-diameter punch-tube cores by depth within each permanent plot. Individual sample points were located within each plot with a stratified random design and samples were taken from four depths (0–0.075, 0.075–0.15, 0.15–0.35 and 0.35–0.6 m). Samples in the archive are stored air-dried, sieved through a 2-mm screen, and were stored in stout cardboard containers until the late 1980s and in capped glass bottles thereafter. Bulk density was sampled with 6-cm diameter cores in the early 1990s (Richter et al. 1994).

General soil properties were analyzed with conventional methods (Page 1982) using surficial 0.6-m samples from the archive collected in 1990 and 0.6–3 m samples collected in 1993. Soil pH was measured in $0.01\ M\ CaCl_2$. Exchangeable base cations were extracted with $1\ M\ NH_4$–acetate at pH 7 (1:10 soil:extractant ratio) and analyzed by atomic absorption spectrometry and flame emission. Exchangeable acidity was extracted with 1 M KCl (1:50 soil:extractant ratio) and extractants were titrated to pH 8.2 with dilute NaOH. Extractable SO_4 was extracted with $0.01\ M\ NH_4VO_3$ and SO_4 analyzed on a Dionex ion chromatograph (Markewitz et al. 1998). Soil texture was estimated by dispersion in Calgon using a standard pipette method (Page 1982). Iron and Al oxides were evaluated with acid ammonium oxalate (AAO) and dithionite–citrate–bicarbonate (DCB) extractions (Carter 1993).

Soil P fractionation

The Hedley sequential fractionation (Hedley et al. 1982a, 1982b) is designed to remove progressively less

available P with each subsequent soil extraction. The approach provides data on both organic and inorganic soil P (Po and Pi, respectively). The specific Hedley procedures used with Calhoun soils closely follow those detailed by Tiessen and Moir (1993) and include the fractions summarized in Table 2, each of which (except the independent total P) result from sequential 16-h extractions.

Hedley procedures were applied to soils collected in 1962 and 1990. Inorganic P was determined colorimetrically in $NaHCO_3$, NaOH and concentrated HCl extractions (Murphy and Riley 1962). Organic phosphate, Po, was determined by subtracting Pi from total P determined after extracts were digested with ammonium persulfate and H_2SO_4 (EPA 1971). Separate unfractionated samples were analyzed for total P via nitric–perchloric acid digestion in order to compare with the recovery of P obtained through summation of all component fractions.

A minor difference between our P fractionation and that described by Tiessen and Moir (1993) was that anion resin extraction was performed separately rather than in sequence (prior to HCO_3 extraction) during the fractionation. In our calculations, the resin-extractable Pi is assumed to be entirely contained in the Pi recovered in the $NaHCO_3$ extract, which we take to be a safe assumption. Mehlich III is an extractant designed to assess relatively bioavailable soil P from acidic, highly weathered Ultisols; Mehlich III-extractable P was estimated on all soils archived from the 1962, 1968, 1977, 1982, 1990, 1997 and 2005 collections (Mehlich 1978).

Forest floor and biomass sampling and analysis

To estimate total P accretion in forest floor and biomass relative to changes in mineral soil P, P was estimated in O horizons and trees in 1962 and 1990. In 1962 (the year of the first mineral soil sampling, when the trees were five years old), P in forest floor and trees was relatively small and estimated at a total of

Table 2 Summary of sequential soil phosphorus fractionations (slightly modified from Tiessen and Moir 1993)

Soil P fractions	Extraction
Readily soluble and exchangeable Pi	Teflon-based anion exchange resin strips saturated with HCO_3
Desorbable Pi and Po at pH 8.5	0.5 M $NaHCO_3$
Fe/Al oxide associated Pi and Po susceptible to alkaline hydrolysis (e.g., ester P)	0.1 M NaOH
Ca-associated Pi	1 and 12 M HCl with the 12 M HCl conducted at 80 °C
Residual Pi and Po	Concentrated H_2SO_4 digestion at 360 °C
Total P (Pi plus Po)[a]	Concentrated HNO_3 and $HClO_4$ digestion

[a] Total P conducted independently of sequential fractionations

6.7 kg ha^{-1}, not from sampling at the Calhoun experiment, but from similar five-year-old loblolly pine forests growing in old upland fields in Mississippi (1.1 and 5.6 kg ha^{-1} P in five-year-old pine forest floor and saplings, respectively; Switzer and Nelson 1972).

Forest floor was collected at the Calhoun experiment in 1991 with five 706-cm^2 samples in each plot. Samples were collected in three layers which approximated the Oi, Oe, and Oa layers that had accumulated during forest development. Relatively little coarse woody debris had accumulated in these stands by 1991 when the trees were 34 years old (Urrego 1993).

In 1990, all trees were measured for total height and diameter at 1.4 m high in each of eight permanent plots ($n \leq 81$ trees per plot depending on tree mortality). Biomass was estimated by a combination of allometric equations depending on the tree component (Kapeluck and Van Lear 1995; Van Lear et al. 1984; Nelson and Switzer 1975; Shelton et al. 1984; Pehl et al. 1984; Baldwin 1987). In 1991, when the stand was 34 years old, ten trees were harvested for nutrient analyses and to estimate site-specific allometric equations that could be used to predict aboveground biomass (Urrego 1993). Foliar biomass was estimated from monthly collections of litterfall (Urrego 1993) over a two-year period. Fine-root biomass (<2 mm diameter) was estimated with 6-cm diameter soil cores (O horizon plus 0–30 cm mineral-soil depth), sampled every three weeks for 12 months. For P in root biomass, P concentrations were taken from Van Lear and Kapeluck (1995) and Shelton et al. (1984). Trees have grown rapidly on these sites, averaging about 8 Mg ha^{-1} year^{-1} of accumulated tree biomass over four decades (Richter et al. 1999).

After air-drying and grinding the plant biomass samples in a Wiley mill, the materials were digested in nitric–perchloric acid and analyzed for total P colorimetrically. Subsamples were oven-dried at 70 °C for at least 24 h to provide an oven-dry basis for the P data.

Results and discussion

Mineral soil description

Soils at the Calhoun soil experiment are acidic, deep and have prominent clayey low-CEC kandic subsoils. Clay (<2 μm) ranges from 10% in surficial A horizons to nearly 50% at 0.6–1 m depths in B horizons (Table 1). Clay mineralogy is almost entirely kaolinite, though quartz is a secondary component. DCB-extractable Fe and Al, which describe the main crystalline framework of Fe and Al oxides, closely track soil clay

fraction within the upper 3 m of the soil (Table 1); i.e., percent clay and DCB-Fe and Al have correlation coefficients >0.89 in samples from the upper 3 m.

These highly weathered Ultisols were likely low in P bioavailability prior to forest clearing and conversion to agriculture (Richter and Markewitz 2001). In the early 1990s, four nearby old hardwood forest soils, that were presumed to have never been cultivated and to be unfertilized, averaged 1.7 μg g^{-1} (SE = 0.3) in Mehlich III-extractable P at 0–0.3 m (and even lower at deeper depths), concentrations so low that uncultivated soils can easily be considered low in bioavailable P (Mehlich 1978; Richter and Markewitz 2001). After the soils had been managed for agriculture for many decades (first cleared of forest and probably burned, periodically cultivated, fertilized and limed), they had accrued considerable P, depending on P inputs, cropping practices and soil properties. Soils from ten old cotton fields in and around the Calhoun experiment were highly variable in Mehlich P and averaged 5.9 μg g^{-1} (SD = 5.0) in 0–0.3 m layers. We attribute the nearly fourfold difference in concentration and the very high variance among the ten soils to be the result of fertilization history across the landscape (Richter and Markewitz 2001).

Net transfer of mineral soil P to tree biomass and O horizons

During the decades of forest development, aggrading tree biomass and organic matter of the forest's O horizons accumulated 39.4 and 45.9 kg ha^{-1} of P, respectively, or a total of 85.3 kg ha^{-1} of P (Table 3). Correcting for an estimated net atmospheric input of about 0.1 kg ha^{-1} year^{-1} (Table 3), the net P transfer from mineral soil to plant biomass and O horizons averaged 82.5 kg ha^{-1}. Atmospheric deposition of P (Chadwick et al. 1999) and soil leaching losses thus had relatively minor effects on the soil and ecosystem budget of P over time scales of several decades (Table 3). Net annual transfer of mineral soil P to aggrading tree biomass and O horizons averaged 2.9 kg ha^{-1} year^{-1} over the 28 years.

Changes in Mehlich III-extractable P

Prior to detailing results from the Hedley fractionation (based on 1962 and 1990 samples), we examine the record of changing Mehlich III P from seven resamplings of the Calhoun archive (1962, 1968, 1977, 1982, 1990, 1997 and 2005), as this extraction indexes relatively labile P in soils with highly weathered mineralogies (Mehlich 1978).

Despite the accumulation of about 82.5 kg ha^{-1} mineral soil P in forest biomass and O horizons, Mehlich

Table 3 Estimated transfers and translocations of mineral soil P over 28 years, compared to statistically significant gains or losses in Hedley fractions of soil P (0–0.6 m depth)
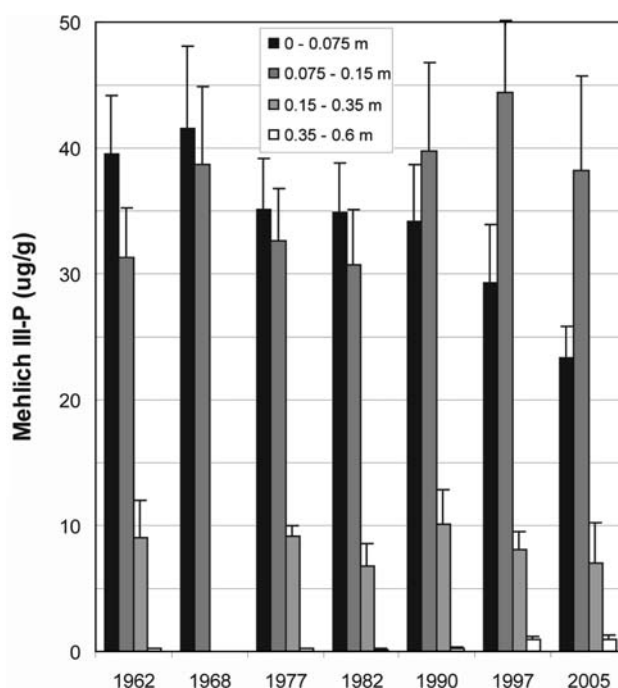
P flux or component		28-year change in soil P ($kg\ ha^{-1}$)
Mineral soil additions (+) and removals (−)		
Vegetation[a]		−39.4
Forest floor[a]		−45.9
Net leaching[b]		+2.8
Total P		−82.5
Observed soil gains (+) and losses (−)		
Resin Pi	Labile, exchangeable	0
$NaHCO_3$ Pi	Labile, adsorbed	+22.0
$NaHCO_3$ Po	Readily mineralizable	0
NaOH Pi	Fe and Al associated	−3.4
NaOH Po	Slowly mineralizable	−22.8
1 M HCl Pi	Ca-associated	−7.6
Conc HCl Pi	Ca-associated	−52.2
Residual P	Recalcitrant organic and mineral	0
Total P	Sum of statistically significant changes	−63.0

[a] Nutrient contents of all vegetation components: foliage, branches, boles and roots; corrected for relatively small P contents in vegetation (5.6 $kg\ ha^{-1}$) and forest floor (1.1 $kg\ ha^{-1}$) at age 5 in 1962 (adapted from Switzer and Nelson 1972)

[b] Net leaching estimates are differences between atmospheric input and leaching at 0.6 m depth, and conservatively represent +0.1 $kg\ ha^{-1}\ year^{-1}$ net accumulation (adapted from Johnson and Lindberg 1992)

Fig. 1 Mehlich III-extractable P has mainly been depth-dependent throughout the 43 years of sampling at the Calhoun Experimental Forest, South Carolina, USA. Recent decreases in Mehlich III P are statistically significant in 0–0.075 m layers. Arithmetic means are illustrated, with *error bars* representing standard errors of the spatial variation among the eight permanent plots. No samples of soil >0.15 m depth were collected in 1968

III P was not greatly diminished during these decades of forest growth (Fig. 1). The 43-year pattern of Mehlich III P illustrates prominent depth effects that are largely invariant through time, depth effects attributed to P additions made directly to surficial plow layers prior to 1955, combined with increasingly strong sorption potential by oxide surfaces with increasing depth (Table 1).

Overall, the relatively minor change in Mehlich III P is most remarkable, especially when considering that surficial layers remained so greatly elevated in extractable P for the 48 years of forest growth, a period of sizeable transfer of P from mineral soil to trees and O horizons. The content of Mehlich III P in the 0.6-m soil totaled 92 and 79 $kg\ ha^{-1}$ of P in 1962 and 2005, entirely comparable to the net transfer of mineral soil P to tree biomass plus forest floor (82.5 $kg\ ha^{-1}$). Rather than suggest that plants do not draw P from fractions extracted by Mehlich III extractant, such time trends in Fig. 1 suggest prominent resupply of the most labile fractions of soil P, hypothetically due to the release of Po and Pi associated with Fe and Al oxides and Ca compounds, fractions likely enriched during the soil's history with cotton prior to 1955.

Although the predominant story of Mehlich III P is its strong depth dependence, which is largely invariant with time, a significant concentration change is increasingly evident, especially in surficial soil layers (Fig. 1). In recent years, Mehlich III P has been significantly decreasing in surficial 0–0.075-m layers and increasing at 0.075–0.15 m. These notable patterns are associated with changes in relatively labile Hedley fractions, and will be important to document as the forest continues to develop in coming decades.

Changes in the most labile Hedley P fractions

The most labile P from Hedley fractionations (resin Pi plus HCO_3 Po and Pi) gives a not dissimilar story to that of Mehlich III extractions. Strong depth dependence is evident, as is the general absence of depletion (Fig. 2), despite the major biomass sink for P. Exchangeable Pi extracted with resin strips was nearly identical in the 1962 and 1990 samplings, with no statistical difference between the two samplings (Table 4). Though a decrease in $NaHCO_3$-extractable Po in the surficial 0.075-m layer was significant at a P value of 0.057, changes were small, i.e., only 1.6 $\mu g\ g^{-1}$ (Table 4). The

most notable observation here is that although NaH-CO_3-extractable Pi hardly changed in surficial 0.075 m layers, this fraction of Pi significantly increased by two-to fourfold in the underlying 0.075–0.35-m soils. For example, in 1962, $NaHCO_3$ Pi averaged 6.9 and 1.0 $\mu g\,g^{-1}$ in 0.075–0.15 and 0.15–0.35-cm layers, yet by 1990, concentrations had increased to 16.6 and 4.6 $\mu g\,g^{-1}$, respectively. This increase in Pi amounted to 22 kg ha^{-1}, a large change relative to the overall P fluxes in the ecosystem (Table 3), and seems likely to be part of the explanation for the observed increases in Mehlich III P in the 0.075–0.15-m soil (Fig. 1).

The major conclusion to be drawn from changes in the most labile fractions of soil P is that, despite relatively large transfers of P from mineral soils into aggrading forest biomass and O horizons, labile fractions of P in the mineral soil remained relatively unchanged (resin Pi, HCO_3 Po) or even increased (HCO_3 Pi) over the several decades of forest development (Table 4). The lability of these fractions cannot be defined by their variation, but rather by their presumed high rate of turnover: i.e., that P removal over the several decades was equaled or exceeded by P input from more slowly cycling fractions. These results lead to the hypothesis that more slowly cycling soil P fractions are not only supplying the P growth requirements of the forest trees, but are also buffering labile fractions against drawdowns.

Changes in slowly cycling but bioavailable fractions of P

Slowly cycling fractions of soil Po and Pi decreased significantly and substantially over the several decades of observations. From the perspective of decades, the dynamics of these fractions suggest we carefully reconsider concepts of labile, bioavailable and occluded P.

In 1990, Po extracted by 0.1 M NaOH was significantly less than that in 1962 throughout 0–0.15-m soil layers (Table 4). The NaOH Po of the uppermost 0.15 m of soil was diminished by about a third of its 1962 concentrations (Fig. 2). In content, this depletion was equivalent to about 23 kg ha^{-1} of P, or >25% of the P accumulated by aggrading tree biomass plus O horizon (Table 3).

The quality of Po, indexed by a ratio of (HCO_3 Po)/(NaOH Po), or highly labile to slowly cycling Po, shifted greatly over these decades (Fig. 3). During the growth of the forest, slowly cycling fractions of Po were especially depleted from surficial A horizons, in contrast to more labile organic pools that remained relatively unchanged (Fig. 2).

In the surficial 0–0.075-m layer of mineral soil, Fe and Al oxide-associated Pi (extracted by 0.1 M NaOH) was significantly less in 1990 than in 1962 (Table 4). The NaOH Pi was diminished in this uppermost layer of mineral soil from 39 to 26 $\mu g\,g^{-1}$, or by about a third

Fig. 2 Overview of changes in soil P fractions for the four layers of soil sampled. *Asterisks* indicate significant differences between collections ($P < 0.05$)
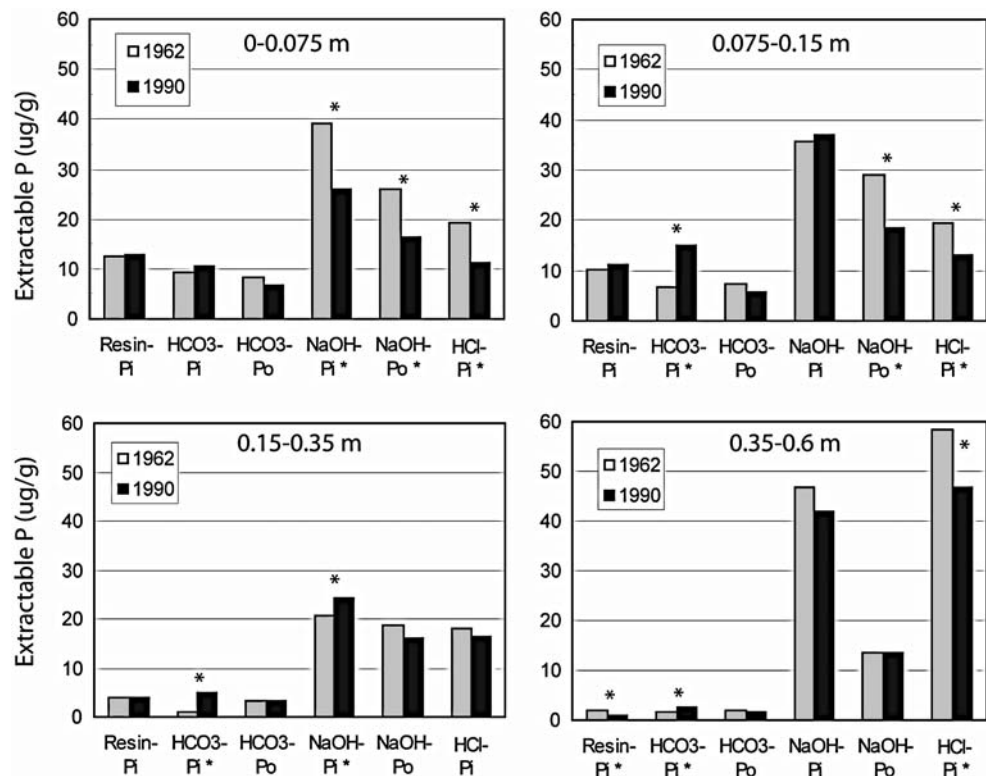
of the 1962 concentration (Fig. 2). In content, the depletion amounted to about 15 kg ha^{-1}. In contrast to this strong depletion of NaOH Pi at 0–0.075 m, there was no change in Fe and Al oxide-associated Pi in soil from 0.075 to 0.15 m, and a modest increase in this fraction of Pi at 0.15–0.35 cm, from 20.6 to 24.4 μg g^{-1}. These changes in NaOH Pi in individual layers indicate much greater dynamics than is suggested by the net budget of NaOH Pi as a whole (Table 3). The 0.6-m soil profile lost 3.4 kg ha^{-1} of NaOH Pi in the 28 years (Table 3) as relatively large depletions in the most surficial layer (about 15 kg ha^{-1}) were compensated by gains at depth (about 12 kg ha^{-1}).

Shifts in Pi indexed by ratios of (resin Pi plus HCO$_3$ Pi)/(NaOH Pi) (Fig. 3) also emphasized major dynamics in Pi on time scales of decades. These ratios for Pi are strongly depth-dependent, due to strong sorption
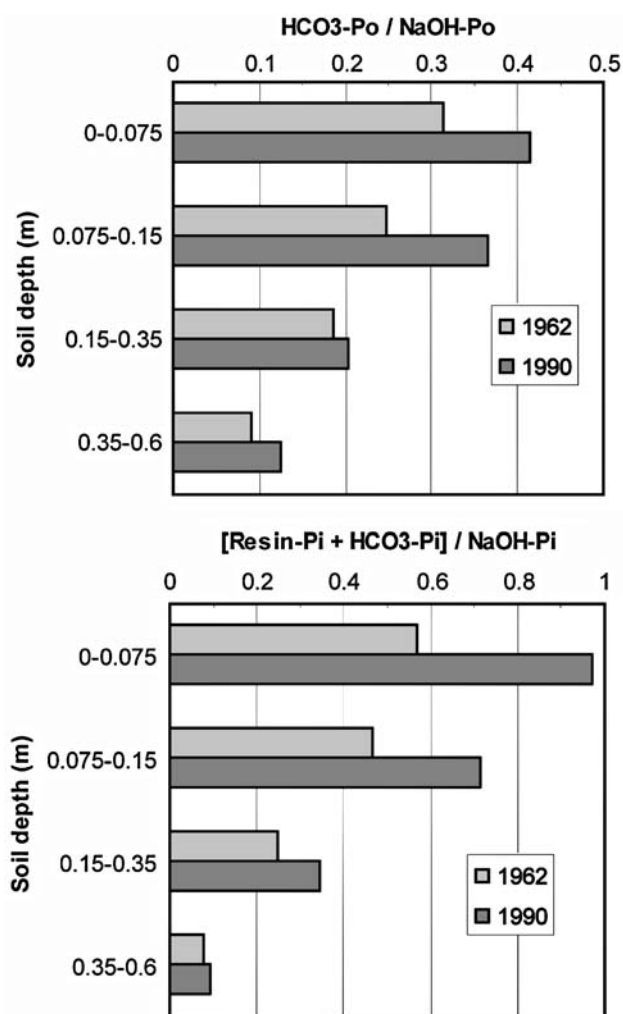
Fig. 3 Decadal changes in ratios of relatively labile fractions of Po and Pi relative to more slowly cycling fractions. Increases mainly result from depletions in slowly cycling Po or Pi, although Pi ratios increase over time at 0.075–0.35-m depths due to increases in relatively labile HCO$_3$-extractable Pi

effects of oxides in subsoils (Table 1), but like Po ratios (Fig. 3) they also shift in favor of more labile fractions over the decades. During the growth of the forest, the increases in relatively labile to more slowly cycling Pi are due to both depletions of NaOH Pi in 0–0.075-m soils and relatively large increases in HCO$_3$ Pi at >0.075 m. Results suggest a translocation of Pi more deeply into the soil profile.

Calcium-associated P compounds, presumed to be extractable by 1 M and concentrated HCl, were drawn down in three of the four layers sampled. Decreases in 1 M HCl-extractable Pi were significant in the two most surficial layers and totaled 7.6 kg ha^{-1}; decreases in P extractable in heated, concentrated HCl were more substantial and were observed in surface soil layers but especially at depth (Table 4). These fractions are attributed to liming and P fertilization prior to 1955, and their decreases to result from the Calhoun's increasingly acidic environment (Fig. 4). Altogether, depletions in HCl Pi totaled 59.8 kg ha^{-1}, or >70% of the P transferred to forest biomass plus O horizons (Table 3). The Ca-associated P fractions appear to be the primary source of P for biological circulation and a buffer of more labile P fractions as well.

We acknowledge our assumption that both 1 M HCl and 80 °C concentrated HCl-extractable Pi fractions are derived from Ca-associated Pi. Some investigators use the concentrated HCl extraction to assess Po (minor in this investigation, Table 4), and add the Pi extracted by concentrated HCl to the residual P pool, presuming both to be strongly occluded from biological cycling (Crews et al. 1995; Townsend et al. 2002). Whatever the specific chemical configuration of this Pi, it clearly needs further exploration, especially given that at Calhoun this fraction of Pi is highly dynamic over time scales of decades and contributes in a major way to the Calhoun's biological P cycle.

Restructuring of soil P fractions during Calhoun ecosystem development

Over nearly five decades, a major restructuring of soil P has been driven by interrelated biogeochemical processes that are transforming many aspects of the Calhoun soil and ecosystem.

First, sustained and substantial net releases of slowly cycling P have persisted within this old field ecosystem throughout these decades. Though the Calhoun ecosystem has developed progressive and acute N deficiency as mineralizable soil N was utilized by the growing forest (Richter et al. 2000; Billings and Richter 2006), P availability remains strikingly high by many measures. Three slowly cycling P fractions have served

Table 4 Changes in soil P fractions (adapted from Hedley et al. 1982a, 1982b) from 1962 to 1990 in eight permanent plots at the Calhoun Experimental Forest, South Carolina, USA

Soil P fraction and depth (m)	1962		1990		Paired-*t* probability[a]
	Mean ($\mu g\ g^{-1}$)	SE ($\mu g\ g^{-1}$)	Mean ($\mu g\ g^{-1}$)	SE ($\mu g\ g^{-1}$)	
Resin strip: labile Pi					
0–0.075	12.57	0.74	12.93	1.12	0.771
0.075–0.15	10.65	1.33	11.08	1.26	0.473
0.15–0.35	3.97	0.25	3.80	0.58	0.793
0.35–0.60	1.86	0.14	1.58	0.57	0.664
Inorganic 0.5 M $NaHCO_3$: labile Pi					
0–0.075	9.23	1.29	10.51	1.68	0.161
0.075–0.15	6.92	1.59	16.65	3.72	0.006**
0.15–0.35	1.05	0.51	4.62	1.36	0.024*
0.35–0.60	1.64	0.50	2.23	0.41	0.190
Organic 0.5 M $NaHCO_3$: readily mineralizable Po					
0–0.075	8.30	1.13	6.69	0.87	0.057
0.075–0.15	7.39	0.85	5.89	0.93	0.160
0.15–0.35	3.43	0.36	3.25	0.51	0.800
0.35–0.60	2.03	0.31	1.64	0.40	0.169
Inorganic 0.1 M NaOH: Fe- and Al-associated Pi					
0–0.075	39.0	2.67	26.0	2.87	0.001**
0.075–0.15	35.6	2.19	37.1	2.69	0.395
0.15–0.35	20.6	1.34	24.4	1.04	0.0001**
0.35–0.60	46.8	4.79	41.2	4.84	0.205
Organic 0.1 M NaOH: mineralizable Po					
0–0.075	25.9	2.95	16.5	2.42	0.001**
0.075–0.15	29.1	2.15	18.6	2.13	0.007**
0.15–0.35	18.6	1.21	16.2	1.06	0.246
0.35–0.60	13.5	2.71	14.6	2.86	0.823
1 M HCl: Ca-associated Pi					
0–0.075	7.49	1.52	2.62	0.36	0.004**
0.075–0.15	4.95	0.76	3.14	0.38	0.009**
0.15–0.35	1.23	0.17	1.07	0.21	0.158
0.35–0.60	0.48	0.08	0.53	0.11	0.099
Inorganic concentrated HCl: Ca-associated Pi					
0–0.075	11.8	1.77	8.7	1.02	0.026*
0.075–0.15	14.5	1.79	10.1	1.02	0.025*
0.15–0.35	16.8	1.87	15.2	2.05	0.243
0.35–0.60	57.8	6.83	45.9	6.46	0.019*
Organic concentrated HCl: Po					
0–0.075	1.23	0.80	1.25	1.00	0.418
0.075–0.15	1.24	0.75	1.36	1.23	0.854
0.15–0.35	1.20	0.79	1.20	0.63	0.989
0.35–0.60	1.84	0.93	1.96	2.74	0.382
Residual: recalcitrant P					
0–0.075	19.7	9.61	22.3	14.5	0.233
0.075–0.15	20.0	6.54	25.2	15.6	0.455
0.15–0.35	30.9	14.8	36.7	24.1	0.329
0.35–0.60	74.6	24.0	82.2	25.1	0.531
Total recovery (sum)					
0–0.075	135.3	31.33	107.3	29.35	0.034*
0.075–0.15	129.8	15.16	128.9	19.10	0.883
0.15–0.35	97.6	18.16	106.7	26.47	0.171
0.35–0.60	200.2	52.03	189.7	53.73	0.619
Independent total					
0–0.075	143.9	29.97	118.0	32.83	0.096
0.075–0.15	152.0	25.07	131.7	28.35	0.037*
0.15–0.35	123.7	28.03	120.0	26.30	0.654

Table 4 continued

Soil P fraction and depth (m)	1962		1990		Paired-*t* probability[a]
	Mean ($\mu g\ g^{-1}$)	SE ($\mu g\ g^{-1}$)	Mean ($\mu g\ g^{-1}$)	SE ($\mu g\ g^{-1}$)	
0.35–0.60	257.7	68.33	228.2	63.56	0.004**

Means and standard errors are reported, with standard errors describing spatial variations among the eight permanent plots

*Significant difference with probability of <0.05

**Significant difference with probability of <0.01

[a] Paired *t*-test used one or two tails depending, respectively, on hypotheses of a decrease over time (HCl-extractable Pi or total P) or of a change with time (resin, HCO_3^-, or NaOH-extractable P, or HCl-extractable Po)

as long-term sources of bioavailable P: Ca-associated Pi, Fe/Al oxide-associated Pi, and Po, all presumed to have been enriched by fertilization and liming, when soils supported cotton. Calcium-associated Pi was the largest Hedley fraction depleted during forest growth, and its slow solubilization over the decades provided most of the P required for forest growth and for buffering the most labile soil P fractions. Utilization of Fe- and Al-associated Pi and net mineralization of Po in A horizons have also been important sources of bioavailable P. Most notable is the rapidly changing quality of Po in surficial A horizons. The total C/Po ratio (using the total Po extracted by both HCO_3 and NaOH) increased from about 160 to 350 during the 28 years between 1962 and 1990, as net mineralization of Po proceeded to draw P from this most surficial soil layer (and c changed but modestly, Fig. 4).

The full 0–0.6 m of soil has however experienced substantial and ongoing acidification (Fig. 4), likely to be especially important to the solubilization of Ca-associated Pi. Base saturation of the 0–0.6-m volume of soil declined from nearly 80% to about 25% in the 43 years from 1962 to 2005 (Fig. 4), a decline closely tracked by soil pH in salt solution (in 0.01 M $CaCl_2$), which ranged from about 4.8 to 4.6 in 1962 and declined to nearly 4.2 in 2005. The lowest pH of 3.6 was observed in the most surficial layer of soil, 0–0.075 m, directly beneath highly acidic O horizons. The acidification has not only been driven by internal ecosystem reactions such as organic acid inputs, nutrient cation uptake and carbonic acid leaching, but also sulfuric acid leaching from acidic deposition (Richter et al. 1994; Markewitz et al. 1998; Richter and Markewitz 2001).

At the same time, oxalate-extractable Fe and Al oxides have significantly increased throughout the upper 0.6 m of soil: AAO-Fe in the surficial three layers, AAO-Al in the deepest three layers (Fig. 4). These
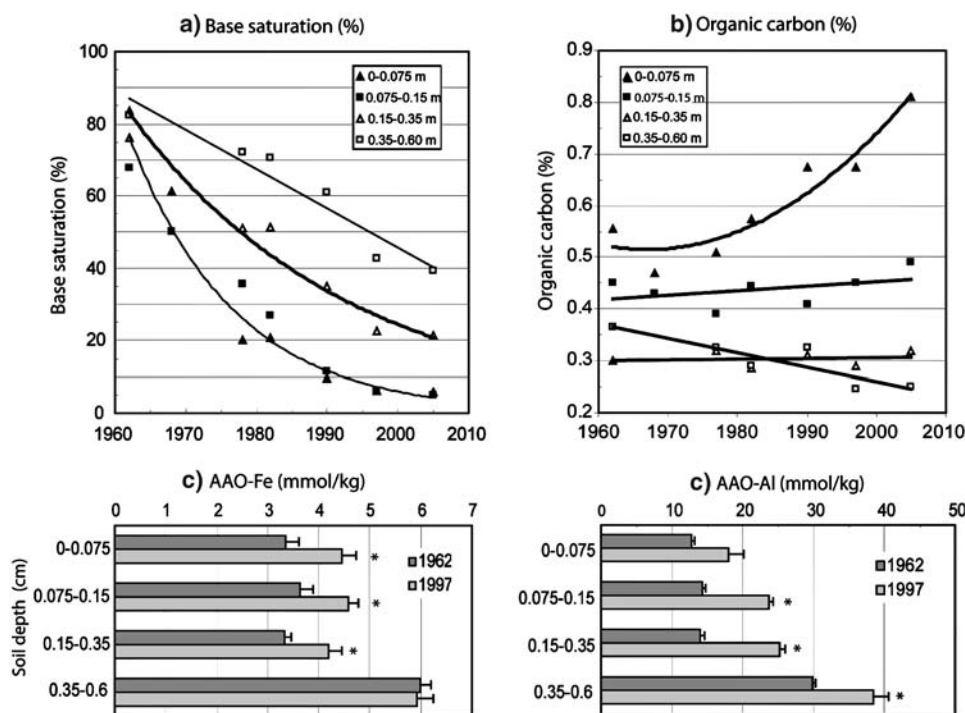
Fig. 4a–c The 48-year development of the old-field Calhoun pine forest has restructured soil chemistry in important ways that directly affect fractions of soil P. **a** The entire 0.6 m volume of soils has acidified substantially, as indexed by base saturation (referenced to effective cation exchange capacity). The most rapid acidification is evident in the 0–0.15-m layers of the soil. Soil pH closely tracks these patterns in base saturation. **b** Sequestration of soil organic carbon during the initial 48 years of forest develop- ment is most prominent in the most surficial soil layer sampled, 0–0.075 m. Only minor changes or even decreases in SOC are observed at 0.075–0.6-m depths. **c** Soil oxalate-extractable Fe and Al oxides have increased significantly during these decades; AAO-Fe in the surficial three layers, AAO-Al in the lower three layers. Oxalate-extractable Fe and Al index amorphous, short-range or- der oxides with high surface area and reactivity to soil P. *Error bars* are standard errors among the eight permanent plots

oxalate-extractable metals index amorphous, short-range order oxides with high surface area and reactivity to soil P. Ongoing acidification protonates these oxide surfaces, rendering them more reactive to a variety of anionic functional groups.

Finally, the growing forest has been rebuilding an A horizon, sequestering organic matter in surficial layers previously depleted of organic matter by cultivation (Richter et al. 1999). Sequestration of carbon is most prominent in the most surficial mineral soil layer sampled, 0–0.075 m (Fig. 4), with remarkably, only minor changes or even decreases in organic carbon observed within soils from 0.075 to 0.6 m in depth. These patterns result from sorption and complexation of a wide variety of organic compounds that originate from O horizons and rhizodeposition, highly acidic compounds that interact with many of the same soil surfaces and reactive sites associated with soil Pi.

We hypothesize that Pi is being slowly displaced by organic acids in 0–0.075-m layers, translocating Pi to deeper soil layers. Indeed, Pi associated with Fe and Al oxides substantially decreased in surficial layers, and Pi extracted by HCO$_3$ (pH 8.5) and by 0.1 M NaOH increased in the two soil layers immediately below, 0.075–0.35 m (Table 4). Many naturally occurring organic acids such as citric and oxalic acids, compete well against phosphate for soil sorption sites (Parfitt 1978; Hu et al. 2001).

Future trends at Calhoun are important and we hypothesize that ongoing organic carbon accrual (Fig. 4), especially in the 0.075–0.15-m layers, will continue to displace Pi more deeply into the soil. Moreover, continued protonation and reactivity of oxides may well substantiate the sink for Pi in 0.15–0.6-m layers, some of which will be recoverable by HCO$_3$, NaOH and Mehlich III extractants. Overall, however, Ca-associated Pi appears relatively large despite draw-downs, and may continue to serve as a long-term source for Pi for many decades to come.

Perhaps most significant is the concentrated HCl fraction of Pi, often considered to be part of the occluded nonbiologically cycling pool of P (Crews et al. 1995; Garcia-Montiel et al. 2000); we not only consider that this fraction is likely associated with Ca compounds in the case of the Calhoun Ultisol, built up by a legacy of fertilization and liming, but that it is very much a part of the

slowly cycling biogeochemical cycle of P that can supply bioavailable P over decadal time scales.

An overview of the changes in P fractions over time scales of decades

The overall pattern of change in P for the Calhoun P cycle is that large transfers of mineral soil P into the forest biological cycle have been accompanied by remarkably little change and even some increase in the relatively labile P fractions in mineral soils. Moreover, depletions in concentrated HCl-extractable Pi, often considered to be part of occluded, unavailable soil P fractions, indicates marked bioavailability on decadal time scales. Depletion rates from slowly cycling P at Calhoun have been more rapid than those required to meet the sink strength of aggrading forest biomass and O horizons. As a result, labile fractions remain well buffered over the period of active forest growth.

That labile P in Calhoun soils has remained relatively constant over several decades not only says much about the buffering by slowly cycling P fractions, but it also indicates the rate at which P is transferred aboveground. In the Calhoun forest ecosystem, the net transfer of P from mineral soil to trees and forest floor (Table 3) averaged about 2.9 kg ha^{-1} year^{-1}, rates that are from two- to more than tenfold less than annual crop harvest removals, which may range from 5 to 30 kg ha^{-1} year^{-1} for cotton or corn (Schmidt et al. 1997; Mitchell et al. 1996). For corn and soybean ecosystems with relatively high removal rates of P from the soil, Schmidt et al. (1997) estimated regressions among P fractions (e.g., resin Pi vs NaOH Pi), and suggested that the regressions' slopes were related to the soil's ability to buffer labile P fractions and to supply P to crop plants as well. Soils with steep slopes between resin Pi and NaOH Pi were able to maintain labile fractions in the face of continued cropping and those with shallow slopes were not (Schmidt et al. 1997). In the Calhoun soil, the sum of the net transfer of P to forest biomass and O horizon (82.5 kg ha^{-1}) and the increase in HCO$_3$ Pi (22.0 kg ha^{-1}) indicates that at least 3.7 kg ha^{-1} year^{-1} has been released from slowly cycling fractions of Po and Pi or has been taken up by roots from deeper than 0.6 m and recycled.

A concluding observation helps explain why soil P bioavailability and long-term soil experiments are such interesting, complex and significant subjects. The concept of P bioavailability has critical temporal dimensions that are directly related to the sink strengths of plants and soil organisms. By definition, the most labile fractions of P are those fractions that actively supply P to plants and microbes and are potentially replenished by mineral dissolution, desorption, and organic mineralization. Historically, to meet the fertilizer needs associated with high crop yields and intensive agriculture, researchers have emphasized the kinetics of P in the soil environment on very short time scales to ensure that sinks can be supplied with P. Bray, Olson and Mehlich extracts have worked well at maintaining high yields of annual crops. However, in order to better manage ecosystems, increase P fertilizer efficiency, and reduce P in runoff water, researchers need to develop kinetics of soil P dynamics that span time scales of decades. This can perhaps only be accomplished using results from long-term soil experiments.

References

Baldwin VC (1987) Green and dry-weight equations for above-ground components of planted loblolly pine trees in the West Gulf region. South J Appl For 11:212–218

Barber SA (1979) Soil phosphorus after 25 years of cropping with five rates of phosphorus application. Commun Soil Sci Plant Anal 10:1459–1468

Beck MA, Sánchez PA (1994) Soil phosphorus fraction dynamics during 18 years of cultivation on a typic paleudult. Soil Sci Soc Am J 58:1424–1431

Billings S, Richter DD (2006) Changes in stable isotopic signatures of soil nitrogen and carbon during forty years of forest development. Oecologia 148:325–333

Bray RH, Kurtz LT (1945) Determination of total, organic, and available forms of phosphorus in soils. Soil Sci 59:39–45

Buol SA (1995) Sustainability of soil use. Annu Rev Ecol Syst 26:25–44

Buol SA, Southard RJ, Graham RC, McDaniel PA (2003) Soil genesis and classification. Blackwell, Oxford, UK

Carter MR (1993) Soil sampling and methods of analysis. Canadian Society of Soil Science, Lewis Publ., Boca Raton, FL

Chadwick OA, Derry LA, Vitousek PM, Huebert BJ, Hedin LO (1999) Changing sources of nutrients during four million years of ecosystem development. Nature 397:491–497

Chang SC, Jackson ML (1957) Fractionation of soil phosphorus. Soil Sci 84:133–144

Cope JT (1981) Effects of 50 years of fertilization with phosphorus and potassium on soil test levels and yields at six locations. Soil Sci Soc Am J 45:342–347

Cox FR, Kamprath EJ, McCollum RE (1981) A descriptive model of soil test nutrient levels following fertilization. Soil Sci Soc Am J 45:529–532

Crews TE, Kitayama K, Fownes JH, Riley RH, Herbert DA, Mueller-Dombois D, Vitousek PM (1995) Changes in soil phosphorus fractions and ecosystem dynamics across a long chronosequence in Hawaii. Ecology 76:1407–1424

Cross AF, Schlesinger WH (1994) A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma 64:197–214

Dalal RC (1977) Soil organic phosphorus. Adv Agron 29:83–113

EPA (1971) Methods of chemical analysis for water and wastes. US Environmental Protection Agency, Cincinnati, OH

Fox RL, Kamprath EJ (1970) Phosphorus sorption isotherms for evaluating the phosphate requirements of soils. Soil Sci Soc Am Proc 34:902–907

Frizano J, Johnson AH, Vann DR, Scatena FN (2002) Soil phosphorus fractionation during forest development on landslide scars in the Luquillo Mountains, Puerto Rico. Biotropica 34:17–26

Garcia-Montiel DC, Neill C, Melillo J, Thomas S, Steudler PA, Cerri CC (2000) Soil phosphorus transformations following forest clearing for pasture in the Brazilian Amazon. Soil Sci Soc Am J 64:1792–1804

Gnau CB (1992) Modeling the hydrologic cycle during 25 years of forest development. Masters Project, School of the Environment, Duke University, Durham, NC

Goh KM, Condron LM (1989) Plant availability of phosphorus accumulated from long-term applications of superphosphate and effluent to irrigated pastures. NZ J Agric Res 32:45–51

Gray LC (1933) History of agriculture in the Southern United States to 1860. The Carnegie Institution of Washington, Washington, DC

Hamon RE, Bertrand I, McLaughlin MJ (2002) Use and abuse of isotopic exchange data in soil chemistry. Aust J Soil Res 40:1371–1381

Hedley MJ, Stewart JWB, Chauhan BS (1982a) Changes in the inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Sci Soc Am J 46:970–976

Hedley MJ, White RE, Nye RH (1982b) Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. III. Changes in L value, soil phosphate fractions, and phosphatase activity. New Phytol 91:45–56

Hilgard EW (1860) Report on the geology and agriculture of the state of Mississippi. State Government of Mississippi, Jackson, MS

Hilgard EW (1906) Soils. Macmillan, New York

Hu HQ, He JZ, Li XY, Liu F (2001) Effect of several organic acids on phosphate adsorption by variable charge soils of central China. Environ Int 26:353–358

Johnson DW, Lindberg SE (1992) Atmospheric deposition and nutrient cycling in forest ecosystems. Springer Berlin Heidelberg, New york.

Kapeluck PR, Van Lear DH (1995) A technique for estimating below-stump biomass of mature loblolly pine plantations. Can J For Res 25:355–360

Karpinets TV, Greenwood DJ, Ammons JT (2004) Predictive mechanistic model of soil phosphorus dynamics with readily available inputs. Soil Sci Soc Am J 68:644–653

Markewitz D, Richter DD, Allen HL, Urrego JB (1998) Three decades of observed soil acidification at the Calhoun Experimental Forest: has acid rain made a difference? Soil Sci Soc Am J 62:1428–1439

McCollum RE (1991) Buildup and decline of soil phosphorus: 30 year trends on a Typic Umbraquult. Agron J 83:77–85

McDowell R, Sinaj S, Sharpley A, Frossard E (2001) The use of isotopic exchange kinetics to assess phosphorus availability in overland flow and subsurface drainage waters. Soil Sci 166:365–373

Mehlich A (1978) New extractant for soil test evaluation of phosphorus, potassium, magnesium, calcium, sodium, manganese, and zinc. Commun Soil Sci Plant Anal 9:477–492

Mitchell CC, Arriaga FJ, Entry JA, Novak JL, Goodman WR, Reeves DW, Runge MW, Traxler GJ (1996) The old rotation. Auburn University Agricultural Experiment Station, Auburn, AL

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36

Nelson LE, Switzer GL (1975) Estimating weights of loblolly pine trees and their components in natural stands and plantations in central Mississippi. Technical Bulletin 73, Mississippi Agricultural and Forestry Experiment Station, MS

Novais R, Kamprath EJ (1978) Phosphorus supplying capacities of previously heavily fertilized soils. Soil Sci Soc Am J 42:931–935

Novak JM, Watts DW (2004) Increasing the phosphorus sorption capacity of Southeastern Coastal Plain soils using water treatment residuals. Soil Sci 169:206–214

Olsen SR, Cole CV, Watanabe FS, Dean LA (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate. United States Department of Agriculture Circular 939. United States Government Printing Office, Washington, DC

Page AL (1982) Methods of soil analysis; chemical and microbiological properties, part 2. Soil Science Society of America, Madison, WI

Parfitt RL (1978) Anion adsorption by soils and soil materials. Adv Agron 30:1–50

Pehl CE, Tuttle CL, Houser JN, Moehring DM (1984) Total biomass and nutrients of 25-year-old loblolly pines (*Pinus taeda* L.). For Ecol Manage 9:155–160

Richter DD, Babbar LI (1991) Soil diversity in the tropics. Adv Ecol Res 21:316–389

Richter DD, Markewitz D (1995) How deep is soil? Bioscience 45:600–609

Richter DD, Markewitz D (2001) Understanding soil change. Cambridge University Press, Cambridge

Richter DD, Markewitz D, Wells CG, Allen HL, April RH, Heine PR, Urrego B (1994) Soil chemical change during three decades in an old-field loblolly pine (*Pinus taeda* L.) ecosystem. Ecology 75:1463–1473

Richter DD, Markewitz D, Trumbore SA, Wells CG (1999) Rapid accumulation and turnover of soil carbon in a re-establishing forest. Nature 400:56–58

Richter DD, Markewitz D, Heine PR, Jin V, Raikes J, Tian K, Wells CG (2000) Legacies of agriculture and forest regrowth in the nitrogen of old-field soils. Forest Ecol Manag 138:233–248

Ruffin E (1852) An essay on calcareous manures. JW Randolph, Richmond, VA

Schmidt JP, Buol SW, Kamprath EJ (1996) Soil phosphorus dynamics during seventeen years of continuous cultivation: fractionation analyses. Soil Sci Soc Am J 60:1168–1172

Schmidt JP, Buol SW, Kamprath EJ (1997) Soil phosphorus dynamics during 17 years of continuous cultivation: a method to estimate long-term P availability. Geoderma 78:59–70

Shelton JE, Coleman NT (1968) Inorganic phosphorus fractions and their relationship to residual value of large applications of phosphorus on high phosphorus fixing soils. Soil Sci Soc Am Proc 32:91–94

Shelton MG, Nelson LE, Switzer GL (1984) The weight, volume and nutrient status of plantation-grown loblolly pine trees in the interior flatwoods of Mississippi. Technical Bulletin 121, Mississippi Agricultural and Forestry Experiment Station, MS

Sheridan RC (1979) Chemical fertilizers in southern agriculture. Agric Hist 53:308–318

Soil Survey Staff (2003) Keys to soil taxonomy. Cornell University, Ithaca, NY

Soloman D, Lehmann J, Mamo T, Fritzsche F, Zech W (2002) Phosphorus forms and dynamics as influenced by land use changes in the sub-humid Ethiopian highlands. Geoderma 105:21–48

Switzer GL, Nelson LE (1972) Nutrient accumulation and cycling in loblolly pine (*Pinus taeda* L.) plantation ecosystems: the first twenty years. Soil Sci Soc Am J 36:143–147

Thomas GW, Peaslee DE (1973) Testing soils for phosphorus. In: Walsh LM, Beaton JD (eds) Soil testing and plant analysis. Soil Science Society of America, Madison, WI, pp 115–132

Tiessen H, Moir JO (1993) Characterization of available P by sequential extraction. In: Carter MR (ed) Soil sampling and analysis. Canadian Society of Soil Science, Lewis Publ., New York, pp 75–86

Tiessen H, Salceda IH, Sampaio EVSB (1992) Nutrient and soil organic matter dynamics under shifting cultivation in semi-arid northeastern Brazil. Agric Ecosyst Environ 38:139–151

Townsend AR, Asner GP, Cleveland CC, Lefer ME, Bustamante MMC (2002) Unexpected changes in soil phosphorus dynamics along pasture chronosequences in the humid tropics. J Geophys Res 107(D20):8067–8076

Urrego MJB (1993) Nutrient accumulation in biomass and forest floor of a 34-year-old loblolly pine plantation. MS thesis, North Carolina State University, Raleigh, NC

Vance RB (1929) Human factors in cotton culture. University of North Carolina, Chapel Hill, NC

Van Lear DH, Kapeluck PR (1995) Above- and below-stump biomass and nutrient content of a mature loblolly pine plantation. Can J For Res 25:361–367

Van Lear DH, Waide JB, Teuke MJ (1984) Biomass and nutrient content of a 41-year-old loblolly pine (*Pinus teada* L.) plantation on a poor site in South Carolina. For Sci 30:395–404

Walker TW, Syers JK (1976) The fate of phosphorus during pedogenesis. Geoderma 15:1–19