Millennial-Scale Phosphorus Transformations during Diagenesis in a Subtropical Peatland

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The record of ecosystem history preserved in wetland soils is often used to set ecosystem restoration targets but is complicated by diagenetic changes. We examined changes in the forms of soil P in a 4000-yr-old subtropical peat deposit in Florida using sequential fractionation and solution ^{31}P nuclear magnetic resonance spectroscopy. By combining information on changes in soil P composition with ^{14}C dates, our aim was to estimate the long-term rate of P storage in a subtropical peatland. Diagenesis caused a decline in labile compounds and an accumulation of recalcitrant compounds. For example, stable P forms determined by sequential fractionation increased from 23% of total P in surface peat to 48 to 73% of total P at a depth of 1.5 m. In contrast, fulvic-acid bound P declined with increasing depth at a rate of 37 to 65 μg P kg^{-1} yr^{-1}. Solution ^{31}P nuclear magnetic resonance (NMR) spectroscopy showed that the majority of the extractable organic P occurred as phosphodiesters, which declined markedly with depth, indicating recycling of labile organic P in surface sediments. Carbon-14 dating at two soil coring stations indicated a long-term P accretion rate of 1.71 mg P m^{-2} yr^{-1} at both stations, a rate approximately 20-fold lower than previous estimates of long-term P accretion in this wetland. Recently deposited material undergoes rapid biogeochemical transformations that complicate associations between soil properties and extrinsic factors such as nutrient loading. We conclude that studies of P accretion based only on approximately <200-yr-old peat will tend to overestimate long-term sequestration rate of the ecosystem.

Abbreviations: BCMCA, Blue Cypress Marsh Conservation Area; EDTA, ethylenediaminetetraacetate; NMR, nuclear magnetic resonance; SJRWMD, St. Johns River Water Management District.

Anthropogenic nutrient inputs to aquatic ecosystems often result in undesirable changes in flora and fauna, such as algal blooms in lakes and encroachment of pollutant-tolerant vegetation in wetlands (USEPA, 2009). In freshwater ecosystems, P is often the principal nutrient influencing overall community composition (Steward and Ornes, 1975; Davis, 1991; Urban et al., 1993). Restoration of P-enriched ecosystems requires a return to pre-impact loading rates that favored the original biological community, but determining such information is challenging in the absence of long-term water quality records.

The historical trophic status of a water body is commonly assessed by examining the sedimentary record, including analysis of changes in diatoms, invertebrates, and nutrient concentrations over time (Shumate et al., 2002; Whitmore, 1989; Brezonik and Engstrom, 1998; Craft and Richardson, 1998; Brenner et al., 2001). The relationship between time and sediment (or soil) depth is typically determined by measuring the abundance of radioisotopes such as ^{137}Cs, ^{210}Pb, and ^{14}C, allowing recent and long-term P sequestration rates, assumed to reflect

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P loading rates, to be compared. For example, P accretion since 1960 has apparently increased eightfold in nutrient impacted areas of the northern Florida Everglades (Craft and Richardson, 1998), estimated as 0.5 to 1.0 g m^{-2} yr^{-1} using the peak in ^{137}Cs activity (Reddy et al., 1993). Estimates of P accretion in Lake Okeechobee, FL indicate that P loads have increased fourfold since 1910, based on sediment P content and sediment accumulation rate (Brezonik and Engstrom, 1998). Similarly, P accretion rates in marshes of east-central Florida have increased by between 2 and 17 times, when comparing pre-1920 to post-1970 rates (Brenner et al., 2001). This increase was attributed to increased anthropogenic nutrient loading.

Associating changes in soil P with changes in ecosystem loading rate relies on the critical assumption that post-depositional processes have not altered soil organic matter. However, soils and sediments undergo progressive biogeochemical transformations during peat accretion that can complicate the association of historical nutrient loading rates with contemporary soil nutrient levels. For example, researchers examining the depth distribution of soil P in the Everglades found that labile forms of soil P decline with depth, whereas recalcitrant forms increase (Reddy et al., 1998). Other factors in wetlands, such as fire and drought, probably also influence mobilization and distribution of P among pools. It is also suspected that abiotic chemical reactions play a major role in soil humification (Stevenson, 1994). Studies of P transformation in sediments of mesotrophic Lake Erken (Sweden) showed declines in P with depth, and these were associated with loss of P during mineralization (Reitzel et al., 2007). Solution ^{31}P NMR studies of those sediments demonstrated rapid mineralization of polyphosphates, together with accumulation of recalcitrant P-containing teichoic acids and phosphomonoesters.

Although numerous studies have combined dating methods with soil chemical analyses to determine accumulation rates, few have documented long-term changes in soil organic matter in wetlands. An obvious limitation to such a study is that it would require a meaningful elapsed time between measurements, perhaps 10 to 20 yr. The calculation of P accretion rates can also be hindered by analytical limitations. For example, analyses based on ^{137}Cs and ^{210}Pb are limited to relatively recent events: ^{137}Cs to the post-1964 period and ^{210}Pb to approximately the last century. For some peatlands, such as the Everglades, a century of accumulation might represent <30 cm of a peat deposit that can be meters thick. Wetland soil accumulation rates in deep (>1 m) and relatively stable peat have not been well-documented but are the accumulation rates that have most likely been sustained over long time periods. In highly dynamic systems, such as subtropical peat soils, measured accretion rates are partly a function of the time of observation. For example, an estimate of accretion between 1900 and 1975 that was determined in 1980 would differ markedly from an estimate made 20 yr later in 2000, due to diagenetic changes in the 20-yr period. Measured accretion rates are, therefore, not absolute but are relative to the time of sampling. This has important implications for researchers investigating ecosystem history.

Deep peats contain a record of environmental conditions that in some cases span thousands of years and, thus, present a unique opportunity to characterize biogeochemical changes that occur over long time scales. Our objectives were: (i) to determine long-term changes in soil P forms by combining a common sequential fractionation procedure and solution ^{31}P nuclear magnetic resonance spectroscopy, and (ii) to link the changes in P pools with ^{14}C dates to estimate the long-term rate of P sequestration in a subtropical wetland peat soil.

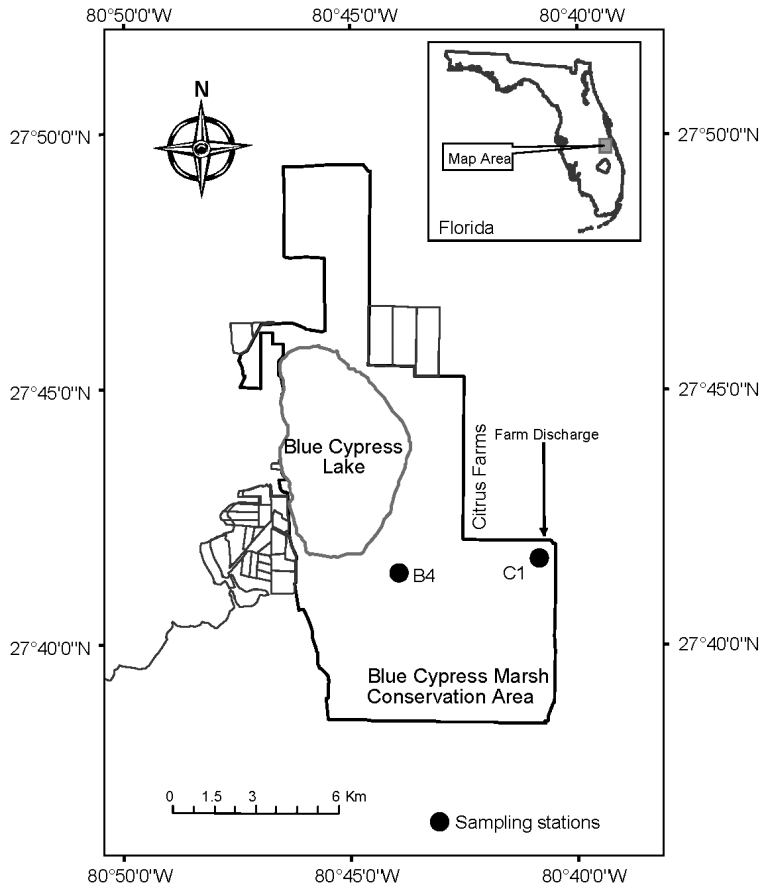

Fig. 1. Location of soil sampling stations in Blue Cypress Marsh Conservation Area.

METHODS

Site Description

Field sampling was conducted in the Blue Cypress Marsh Conservation Area (BCMCA). The BCMCA is a 116-km^2 peat-dominated marsh, located in east central Florida near the headwaters of the St. Johns River (Fig. 1). The region has a subtropical climate and receives approximately 1.5 m of rainfall annually. The BCMCA is used for flood control, recreation, wildlife habitat, and water storage. It is part of a joint St. Johns River Water Management District and United States Army Corps of Engineers floodplain restoration project whose goal is to provide both ecological and flood protection benefits.

The eastern extent of the marsh is characterized by open-water sloughs and tree islands. Typical vegetation in the sloughs is bladderwort (*Utricularia* sp.) and fragrant water-lily (*Nymphaea odorata* Aiton), while the tree islands are characterized by bald cypress [*Taxodium distichum* (L.) Rich.], red maple (*Acer rubrum* L.), and Carolina willow (*Salix caroliniana* Michx.). The western region of the marsh is predominately a sawgrass [*Cladium mariscus* (L.) Pohl subsp. *jamaicense* (Crantz) Kük.] and maidencane (*Panicum hemitomon* Schult.) prairie, with some buttonbush (*Cephalanthus occidentalis* L.), pickerel-weed (*Pontederia cordata* L.), and duck-potato (*Sagittaria lancifolia* L.). The soil at the site consists of well-decomposed peat (Terra Ceia series; euic, hyperthermic Typic Haplosaprists) ranging from 2 m thick in the eastern region to over 5 m thick in the center of the marsh. Surface water in the marsh is characterized as soft and slightly acidic, with a pH of approximately 6.5. The median surface water total dissolved P concentration in the central region of the marsh of 50 $\mu g\ L^{-1}$, which is greater than in the Everglades. Inflows are primarily from rainwater, two small streams on the western side (Padgett Branch and Blue Cypress Creek), and three water control structures on the southern side (Prenger and Reddy 2004). Outflows occur through a large water control structure on the northern end of the marsh. Water level in the marsh typically varies from 7 m (dry) to 9 m above mean sea level (NGVD 1929). This corresponds to surface water depths in the marsh that vary from completely dry to approximately 1.5 m (Lowe, 1986).

Sampling Locations

Agricultural discharges have created a region of elevated soil P in the northeastern area of the marsh, though the discharge ceased in 1994. One sampling location was selected from this region of the marsh, Station C1. Vegetation at this site was a mix of common cattail (*Typha latifolia* L.) and Carolina willow (*S. caroliniana*). A second Station (B4) was selected from the interior, unimpacted marsh, in an area dominated by maidencane (*P. hemitomon*) and sawgrass (*C. mariscus*).

Soil Sampling

Soil samples were collected in triplicate on 18 July 2002 for sequential chemical P fractionation and ^{31}P NMR analysis. Soil cores were collected to a depth of 110 cm at the unimpacted station (Station B4) and 135 cm at the impacted station (Station C1). A second set of cores (one from each station) were collected on 16 Mar. 2004 for radiocarbon dating. Sampling depths for the 2004 radiocarbon samples were 130 and 150 cm for Stations B4 and C1, respectively. Samples were collected to the base of the peat deposit at Station C1 and to the limit of the coring device at Station B4. The peat at Station C1 was underlain by sandy/silty peat. The peat at Station B4 has been estimated as approximately 5 m in thickness and is underlain by clay [St. Johns River Water Management District (SJRWMD), unpublished data, 2005]. Cores collected in 2002 were obtained with a 2 m long by 7.3 cm diameter stainless steel soil corer. A piston-type peat corer was used to collect samples in 2004 (Clark, 2000), which consisted of a steel outer casing and an inner 7.3-cm i.d. thin wall, semi-rigid, polybutyrate core liner. The liner was taken out of the core barrel, cut lengthwise, and the sample removed. The extent to which the soil was compacted during sampling was noted, and this was approximately 15 cm for a 1.5-m sample for both core samplers.

All samples were transferred in the field to Ziploc bags at 10-cm intervals. They were immediately placed into an ice-filled cooler for transport to the laboratory. Samples were processed at the University of Florida's Wetland Biogeochemistry Laboratory. Wet weight was recorded and samples were transferred to rigid polyethylene containers to facilitate thorough mixing by hand and storage. A 50- to 100-g sample was dried at 80°C to constant weight for moisture determination. Total P was determined on all samples by ashing and extraction in 6 M HCl (Andersen, 1976). Total C and N were determined on a dried, ground sample by dry combustion (Nelson and Sommers, 1996) using a Carlo Erba NA-1500 CNS analyzer (Haak-Buchler Instruments, Saddlebrook, NJ)

Sequential Phosphorus Fractionation

Soil P fractions were determined using a sequential extraction technique specifically developed for organic soils (Ivanoff et al., 1998). Briefly, oven dried soils were extracted sequentially using 0.5 M $NaHCO_3$, 1.0 M HCl, and 0.5 M NaOH. The P extracted with 0.5 M $NaHCO_3$ and determined using molybdate colorimetry was considered to consist mainly of labile inorganic P (P_i). Total P of an aliquot of this extraction was determined by digestion with H_2SO_4 and ammonium persulfate. The difference between labile P_i and the total P of the extracted sample is thought to be relatively labile organic P (labile P_o). Phosphorus associated with fulvic acid was determined by acidifying the 0.5 M NaOH extract to precipitate the humic materials. Phosphorus associated with humic acid was then determined by difference between the total P content of the unacidified and acidified extract. Microbial P was determined by the difference between a 0.5 M $NaHCO_3$ extract that received chloroform and labile P_i. The total P content of the residual material remaining at the end of the sequential fractionation is assumed to consist primarily of recalcitrant P. Total P of this residue and total P of a separate unextracted sample were determined by combusting the sample for 4 h at 550°C, followed by dissolution of the ash in 6 M HCl (Andersen, 1976). The P content of each sequential extract fraction was divided by the summed P content of extract fractions to determine the percent P of each extract fraction. The principal goal of the fractionation was to divide soil P among organic and inorganic pools and make operationally defined estimates of environmental lability. Comparison of total soil P measured directly to a summation of the soil P fractions indicated that sequential fractionation underestimated soil total P by approximately 9%.

Solution ^{31}P NMR Spectroscopy

Oven-dried and ground samples from the unimpacted marsh Station (B4) were analyzed by solution ^{31}P NMR spectroscopy. The samples were extracted by shaking the soil for 4 h (20°C) at a 1:20 soil/solution ratio using an extractant solution that consisted of 0.25 M NaOH and 0.05 M Na_2EDTA (ethylenediaminetetraacetate). Samples were centrifuged at 10,000 × *g* for 30 min (Cade-Menun and Preston, 1996) and equal volumes of the extracts were then frozen immediately at −80°C, lyophilized, and ground to a fine powder. Each freeze-dried extract (~100 mg) was redissolved in 0.1 mL of deuterium oxide and 0.9 mL of a solution containing 1 M NaOH and 0.1 M EDTA, and then transferred to a 5-mm NMR tube. The deuterium oxide provided an NMR signal lock and the NaOH raised the pH to >13 to ensure consistent chemical shifts and optimum spectral resolution. Inclusion of EDTA in the NMR tube reduces line broadening by chelating free Fe in solution (Turner and Richardson, 2004). Solution ^{31}P NMR spectra were obtained using a Bruker Avance DRX 500 MHz spectrometer operating at 202.456 MHz for ^{31}P and 500.134 MHz for ^{1}H. Samples were analyzed using a 6 μs pulse (45°), a delay time of 2.0 s, and an acquisition time of 0.8 s. The delay time used ensured sufficient spin-lattice relaxation between scans for P nuclei (Cade-Menun et al., 2002). Between 48,000 and 69,000 scans were acquired depending on the P concentration of the lyophilized extract, although clear signals could not be obtained in all samples. Broadband proton decoupling was used for all samples. Spectra were plotted with a line broadening of 8 Hz, although additional spectra were plotted with a line broadening of 1 Hz to examine signals in the phosphate monoester region. Chemical shifts of signals were determined in ppm (ppm) relative to an external standard of 85% H_3PO_4. Signals were assigned to individual P compounds or functional groups based on literature reports (Turner et al., 2003a) and signal areas were calculated by integration.

Soil Age

Soil dating was determined through ^{14}C analysis of plant macrofossils. Ten centimeter sections of peat to a depth of approximately 1.5 m were carefully examined for plant remains such as stems, seeds, and other woody fragments. Carbon-14 estimates of soil age were determined for six soil depths at Station B4 and eight depths at Station C1. We were careful in avoiding root fragments when collecting plant macrofossils. Samples were sequentially treated with 0.5 M HCl (0.5 h), 0.1 M NaOH (2 h), and again with 0.5 M HCl (0.5 h) to remove carbonates and any soluble organics that may have been transported through the soil profile. Samples were analyzed at University of California, Irvine Keck-CCAMS laboratory by accelerator mass spectrometer (NEC 0.5MV 1.5SDH-2, National Electrostatics Corporation). Carbon-14 dates were converted (or calibrated) to calendar dates using the computer program CALIB, version 5.0.1 (Stuiver and Reimer, 1993). Samples at 35-cm depths at both stations were too recent to obtain accurate ^{14}C data. However, other researchers have dated BCMCA soil using ^{210}Pb dating methodology and found marsh-wide accretion of 0.33 cm yr^{-1} (Brenner et al., 2001). Thus, a sample at a depth of 35 cm is approximately 106-yr-old, and this value was used instead of the ^{14}C age for that sample. Sample ages were determined by subtracting the calibrated calendar date from 2004 AD, the date of sample collection.

Statistical Analysis

Nonlinear regression of ^{14}C dates to soil total P was performed with the JMP statistical program, version 4.0 (SAS Institute, Cary, NC). Linear regression of soil P fractions vs. soil age, and significance (p) of the relationship were calculated using Microsoft Excel, version 2003.

RESULTS

Soil Properties

The soils of BCMCA are highly organic, with organic matter content of approximately 90% (Table 1). Soil pH is slightly acidic, as is surface water in the marsh. Total P declined dramatically with increasing depth at both stations. Total P of surface soil (0–10 cm) at the impacted station was 806 (±82 SD) mg kg^{-1}, compared to 514 (±20 SD) mg kg^{-1} at the interior unimpacted station. Total P declined with depth at both stations, to approximately 70–90 mg kg^{-1} at 100 cm below the soil surface (Fig. 2). The C/N ratio in BCMCA increased from 15:1 in surface soils at both stations to 19:1 at a depth of 90 cm. The C/P increased consistently with depth at both BCMCA stations, from 600:1 to 900:1 in surface soil, to approximately 6000:1 at a depth of 120 cm.

Soil Age and Phosphorus Content

The age of plant microfossils at a depth of 145 cm was 2954 yr at the unimpacted station and 3654 yr at the impacted station (Table 2). There was an abrupt increase (or discontinuity) in age at

Table 1. Physicochemical properties for three soil depths collected from Blue Cypress Marsh Conservation Area in July 2002. Each value is a mean of three replicate samples. Values in parentheses represent one standard deviation. One sample only for Station C1 (100–110 cm).

Station	Depth interval	Bulk density	pH	Organic matter	C	N	P	C/N	C/P
	cm	g cm^{-3}	Units	%	g kg^{-1} dry wt.				
B4 (unimpacted)	0–10	0.085 (0.006)	5.75 (0.01)	91.4 (0.6)	457 (0.5)	30.0 (0.3)	0.514 (0.02)	15.2	890
	50–60	0.089 (0.005)	5.96 (0.04)	93.4 (2.8)	491 (0.3)	30.8 (0.2)	0.193 (0.03)	15.9	2581
	100–110	0.096 (0.000)	6.32 (0.01)	91.7 (0.7)	504 (0.3)	27.1 (0.8)	0.086 (0.02)	18.6	5933
C1 (impacted)	0–10	0.093 (0.024)	6.07 (0.09)	89.4 (1.0)	449 (0.5)	29.8 (0.1)	0.806 (0.08)	15.1	561
	50–60	0.095 (0.016)	5.99 (0.17)	92.0 (2.3)	508 (0.9)	30.2 (0.4)	0.155 (0.05)	17.0	3565
	100–110	0.082 (NA)	6.34 (NA)	91.9 (NA)	530 (NA)	28.8 (NA)	0.074 (NA)	18.4	7184

both stations that occurred somewhere between 75 and 85 cm at station C1 and amounted to an increase in age of 1765 yr. For Station B4, soil age increased by 1345 yr in the interval between 85 and 115 cm. The data from both stations were combined to yield a relationship between soil depth and age, where

$$\text{Soil Age} = 0.656(\text{depth, cm})^{1.69} \quad r^2 = 0.92$$

The age (relative to 2004) for each depth interval was calculated from this model.

Because total P was also determined at these depths, an age was associated with the P content at respective depths. The age and P data were fit to the exponential model:

$$C_t = C_\infty + C_o \exp^{(-k*t)}$$

where C_t = soil total P content at time = t, mg kg^{-1}; C_∞ = asymptotic (background) P for deepest soil, mg kg^{-1}; C_o = increase in P between deepest soil and surface soil, mg kg^{-1}; k = first-order rate constant, yr^{-1}; t = time, yr.

Note that when t = 0 yr, soil total P is simply $C_\infty + C_o$. The data used to calibrate this model consisted of only those depth intervals for which we had both P and ^{14}C data (i.e., six samples at Station B4 and eight samples at Station C1). The model explains approximately 98% of the temporal variability in soil P at both stations and indicates a long-term minimal background soil P content of ~70 mg kg^{-1} at Stations B4 and C1 (Fig. 3).

Soil Phosphorus Fractionation

The majority of soil P was sequestered in organic forms, with total P_o accounting for 72% (±16% SD) of total P. Labile P_i ($NaHCO_3$ extractable P_i) accounted for <1–12% of soil P and declined significantly at the unimpacted station, from approximately 12% in surface soil to 4% at 100 cm. Labile P_i increased slightly with depth at the impacted station. Labile P_o ($NaHCO_3$ extractable P_o) declined slightly with depth at both stations and was highest in surface soils (2–3% of total P). Microbial P also declined with increasing soil depth, from approximately 22% of total P in surface soils (0–20 cm) to 8% at the bottom-most sample at both locations. HCl-extractable P_i (nonlabile P_i) represents inorganic P associated with amorphous and crystalline Ca and Mg compounds and is a relatively stable pool of soil P. This fraction declined significantly at both stations, from approximately 10% of total P in surface soil (0–10 cm) to <2% at the base of the core. Fulvic P declined significantly at approximately the same rate at both stations. Fulvic P accounted for 25 to 30% of total P in surface soils, declining to approximately 15% of total P at both

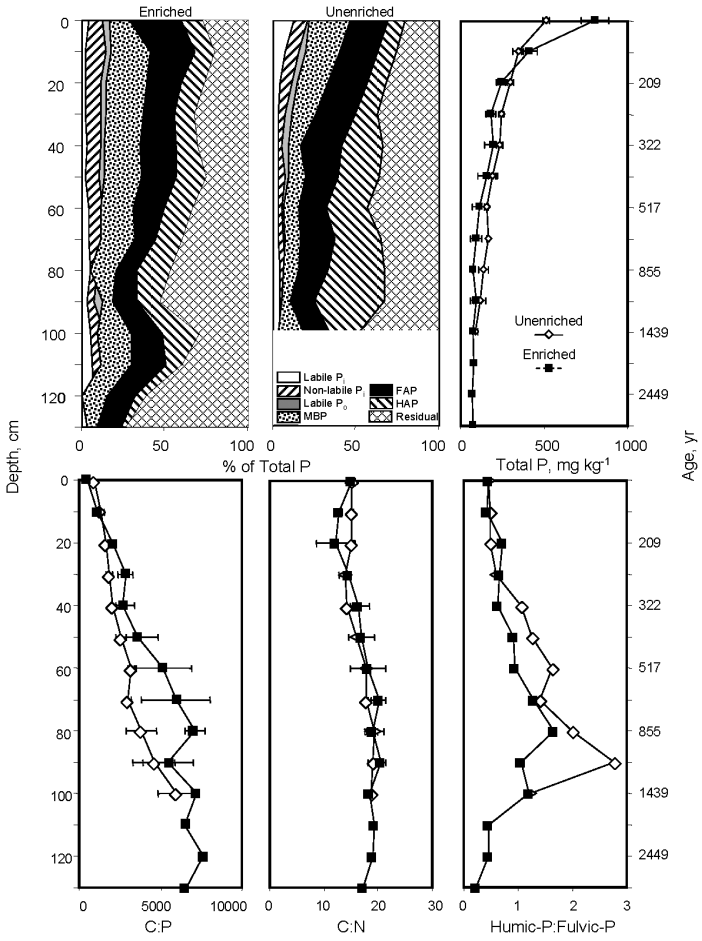

Fig. 2. Results from soil phosphorus fractionation, and total P, C/P and C/N ratios for soils of Blue Cypress Marsh Conservation Area. Phosphorus fractionation data presented as percent of the summation of extractable fractions, including the residual unextractable fraction. Error bars represent one standard deviation. Soil age calculated according to exponential depth vs. age model (see text). Note that soils at unenriched station were fractionated to a depth of 100 cm.

Table 2. The ^{14}C accelerator mass spectrometer (AMS) dates for a variety of samples from the peat cores. Values in parentheses represent standard error of analytical procedure, plus errors associated with calibration dataset used in CALIB software. Conventional radiocarbon age in years before present (YBP) is shown, with 1950 considered as present. Calendar date determined from calibration data set and computer program CALIB.

Station	Soil depth	Sample	Radiocarbon age	Calendar date	Calibrated age
	cm		YBP		
B4	−35	Seed	125 (±20)†	>1800 AD†	106†
B4	−65	Woody husk	345 (±20)	1550 AD (±100)	454
B4	−85	Panicum root	440 (±20)	1440 AD (±50)	564
B4	−115	Stem fragment	1905 (±20)	95 AD (±20)	1909
B4	−125	Pine needle	2930 (±20)	1150 BC (±125)	3154
B4	−145	Seed husk	2790 (±20)	950 BC (±60)	2954
C1	−35	Grass blade	120 (±20)†	>1800 AD†	102
C1	−55	Seed pod case	525 (±25)	1415 AD (±10)	589
C1	−75	Grass blade	1070 (±20)	985 AD (±60)	1019
C1	−85	Twig	2560 (±15)	780 BC (±10)	2784
C1	−95	Nuphar rhizome	2695 (±20)	825 BC (±25)	2829
C1	−125	Nuphar rhizome	3025 (±20)	1290 BC (±30)	3294
C1	−135	Wood fragment	2920 (±20)	1150 BC (±100)	3154
C1	−145	Wood fragment	3365 (±20)	1650 BC (±30)	3654

† Note that age of sample at the 35-cm depth determined from separate ^{210}Pb analysis (Brenner et al., 2001).

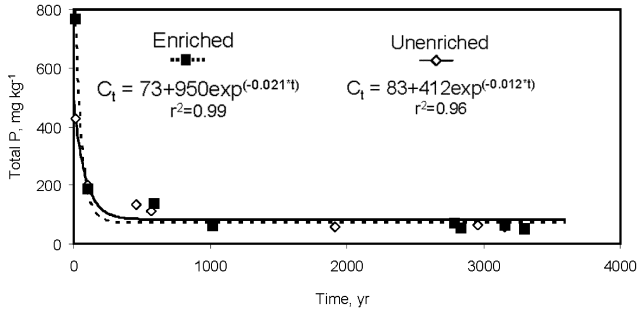

Fig. 3. Relationship between soil age and phosphorus content in Blue Cypress Marsh Conservation Area. Lines represent predictions of exponential model $C_t = C_\infty + C_o\exp^{(-kt)}$, whereas symbols represents actual ^{14}C age and soil P measurements. Time interval is years before 2004 AD.

stations. Phosphorus associated with humic acids averaged 11 to 14% of total P in surface soil at Station B4 and C1, respectively, and increased significantly to a maximum of 42% (B4) and 20% (C1) of total P at a depth of 90 cm. There was no significant change in the concentration of humic P with depth, although the proportion of humic P (i.e., as a percentage of the total soil P) increased significantly with depth.

The ratio of humic P to fulvic P increased from approximately 0.5 in surface soils to a maximum of 2.8 at the unimpacted station in BCMCA. The humic P to fulvic P ratio declined in the lower soil depths at both stations. Residual P showed the greatest increase with depth of all P fractions at both stations, increasing from 23% of total P in surface soils and increasing to between 48% (Station B4) and 73% (Station C1) of total P in the deepest soils. As a rate of change, this amounts to an increase of 0.135% P cm^{-1} at the unimpacted station and 0.289% P cm^{-1} at the nutrient impacted station. When expressed as a temporal rate of change of soil P mass, all fractions declined through time, although the decline in labile P_i at the impacted station was very minor ($p = 0.023$) (Table 3). Fulvic P declined the most rapidly of all the P fractions, at a rate of approximately 0.055 mg kg^{-1} yr^{-1} for both stations.

Solution ^{31}P NMR Spectroscopy

The amount of total P that was extracted in NaOH-EDTA ranged from 70% in surface soils to 11% at 70 cm (Table 4, Fig. 4). Solution ^{31}P NMR spectroscopy confirmed results from the sequential fractionation that showed P is sequestered predominately in organic forms. Within the organic P pool, there was no significant difference between concentrations of phosphate monoesters and diesters (Student's paired *t* test; $p = 0.321$; df = 7). However, it should be noted that NaOH-EDTA extraction degrades some phosphate diesters, such as phospholipids and RNA, to phosphate monoesters, so the actual proportion of phosphodiesters is likely higher and, thus, probably constitutes the dominant form of organic P in these soils. Phosphodiesters were detected to 80 cm. The phosphomonoester region of the NMR spectra did not show signals from higher-order inositol phosphates, including *myo*- and *scyllo*-inositol hexakisphosphate (Turner et al., 2003b; Turner and Richardson, 2004).

Table 3. Regression parameters for rate of change of extractable soil phosphorus fractions with respect to time. Units on slope term are (mg P kg soil^{-1}yr^{-1}. *p* value is significance of regression relationship.

	C1 (Impacted)			B4 (Unimpacted)		
Fraction	Slope	r^2	*p*	Slope	r^2	*p*
Labile P_i	−0.005	0.151	0.023	−0.021	0.249	0.004
Labile P_o	−0.007	0.277	0.001	−0.007	0.592	<0.001
Microbial P	−0.035	0.504	<0.001	−0.053	0.473	<0.001
Nonlabile P_i	−0.020	0.420	<0.001	−0.019	0.475	<0.001
Fulvic acid P	−0.054	0.309	0.001	−0.055	0.690	<0.001
Humic acid P	−0.025	0.368	<0.001	−0.012	0.216	0.007
Residual	−0.038	0.249	0.003	−0.053	0.706	<0.001
Total	−0.179	0.359	<0.001	−0.175	0.667	<0.001

DISCUSSION

It is clear from the ^{14}C data that P content for soil depths of 80–150 cm has been constant for several thousand years. For depths below 75 cm, soil age increased linearly with depth at a rate of 2 mm yr^{-1} and this is the long-term accretion rate at this depth (Table 5). Soil total P asymptotically approached approximately 80 mg kg^{-1} at a depth of 100 cm at both stations, with minimal further change. It is interesting to note that this is approximately the same soil total P concentration of deeper soil samples at both impacted and unimpacted regions of the northern Florida Everglades (Fisher and Reddy, 2010) and that the long term soil accretion rate of approximately 2 mm yr^{-1} is essentially the same as was found for subsurface peat in the Everglades (Craft and Richardson, 1998; Glaser et al., 2013). Combining soil total P content, bulk density, and mass accretion for depths greater than 75 cm yields an annual P accretion rate of 1.71 mg P m^{-2} yr^{-1} at both stations. Note that calculation of this long-term P accretion rate is mostly independent of the soil depth interval over which the calculation is made, provided the selected interval begins at a depth of >70 cm. This P accretion value represents the mass transfer rate of P to very long-term sinks and is quite low compared to previous historical P accretion estimates for wetlands (Table 6). Even though peat wetlands immobilize a large mass of P, they appear to do so over a long time period (Clymo, 1984; Richardson, 1985).

The calculation of wetland P accretion rate is greatly influenced by the depth interval over which the accretion is calculated, particularly during early diagenesis. For example, previous research on historical (pre-human settlement; approximately 1920) P accretion estimates in BCMCA found rates of 40 mg P m^{-2} yr^{-1} (Brenner et al., 2001), or >20-fold higher than rates found in our study. They also found that P accretion had increased from 2 to 17 times the pre-settlement rate. They hypothesized that increased P accretion must be due to increased external P loading, since most of the P in these organic soils is bound in refractory organic forms and is, thus, permanently buried after deposition. However, our results show that over time, the mass of P in the recalcitrant P pool undergoes a relatively high rate of decline relative to other fractions yet still increases as a percentage of the soil

Table 4. Phosphorus compounds in NaOH–ethylenediaminetetraacetate (EDTA) extracts of soils from Blue Cypress Marsh Conservation Area as determined by solution ^{31}P nuclear magnetic resonance spectroscopy. Results are for unimpacted, central marsh station (Station B4). Extraction recovery (shown in parentheses) refers to percentage of total soil P that was extracted with NaOH-EDTA. Depth interval 30–40 cm not analyzed.

Soil depth	Total NaOH-EDTA extractable P	Phosphate	Monoesters	Diesters	Pyrophosphate
cm		mg kg^{-1}			
0–10	361 (70)	164	89	67	42
10–20	213 (58)	81	55	56	21
20–30	176 (55)	69	53	40	16
40–50	76 (35)	31	20	24	0
50–60	64 (29)	23	24	18	0
60–70	106 (67)	37	28	33	9
70–80	18 (11)	5	7	5	0
80–90	55 (41)	28	28	0	0
90–100	35 (34)	7	13	15	0
100–110	25 (26)	0	0	0	0

total P. The difference in P accretion estimates for the two studies is due to the depth interval over which accretion was calculated. For example, the greater estimate of accretion (Brenner et al., 2001) was calculated for a soil depth of 20 to 40 cm, whereas we used a depth of 80 to 150 cm (corresponding to a soil age of 2000–4000 yr). Both studies attempted to measure the "historical" accretion. However, over timescales that span several hundred years or more after organic matter deposition, peat soils appear to undergo relatively rapid transformations, making absolute estimates of accretion during this period problematic. Also note that for BCMCA soils >100-yr-old, soil P was still undergoing major declines with increasing soil depth at both stations, with concomitant changes in individual soil P fractions and C/P ratios (Fig. 1). It is unlikely that this is due to anthropogenic impacts but could be due to changes in plant communities, from shrub or other woody vegetation to a community dominated by emergent or herbaceous plants. For BCMCA, this does not appear to be the case. Analysis of the BCMCA pollen record indicates a historical marsh dominated by herbaceous plants (e.g., Chenopodiaceae-Amaranthaceae) for at least the last 1000 yr (90-cm soil depth), with perhaps recently increasing woody shrub species, such as wax-myrtle [*Myrica cerifera* (L.) Small] and *C. occidentalis* (Brenner and Schelske, 1995). Also, physical inspection of the peat to a depth of 150 cm did not reveal major changes in either peat texture or color.

Reddy et al. (1993) calculated long-term accumulation rates of P at several locations corresponding to P-impacted and unimpacted regions of the Florida Everglades. In their study, "long-term" represented the relatively recent period of 1964–1991, which corresponded to soil depths of <30 cm. They reported P accumulation rates in the range of 110 to 250 mg m^{-2} yr^{-1} for unimpacted regions of the Everglades (Water Conservation Area 2A), a rate between 50- and 100-fold greater than we found for much older soil depths in BCMCA. Craft and Richardson (1998) found P accretion rates that have prevailed over the last century in unenriched regions of Water Conservation Area 2A to be approximately 70 mg m^{-2} yr^{-1}. If there has been little change in nutrient loading in unimpacted regions BCMCA and the Everglades and if soil P is relatively stable after deposition, there should be little change in either P content or accumulation with respect to soil depth (or age), with the possible exception of changes caused by soil compaction. That this is not so is evident from consistent and large declines in soil P that span many centuries and are observed in pristine

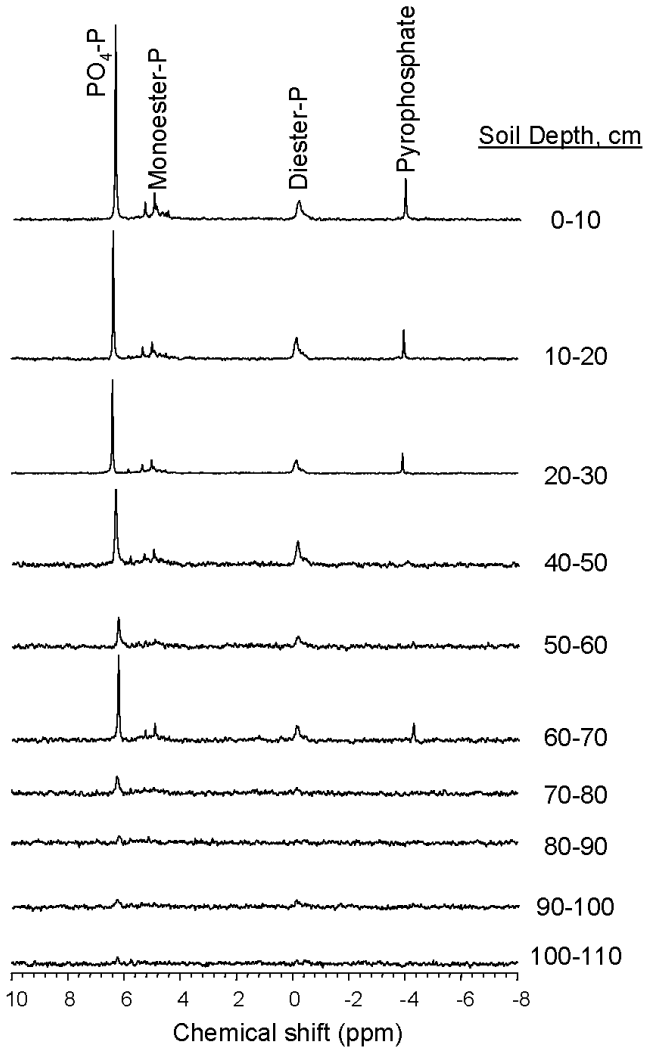

Fig. 4. Solution ^{31}P nuclear magnetic resonance spectra of NaOH-ethylenediaminetetraacetate (EDTA) extracts from Blue Cypress Marsh Conservation Area.

Table 5. Long-term soil and phosphorus accretion at two locations in Blue Cypress Marsh Conservation Area.

Parameter	B4	C1	Units
Depth interval	85–145	75–145	cm
Maximum ^{14}C age	2950	3650	yr
Soil accretion rate†	0.019	0.025	cm yr^{-1}
Mean total P‡	83	73	mg kg^{-1}
Mean bulk density*	0.107	0.092	g cm^{-3}
Historical P accumulation rate	1.71	1.71	mg m^{-2} yr^{-1}

† Slope of best-fit line to ^{14}C vs. depth data.

‡ From model estimate of long-term soil P asymptote; C_{∞}.

regions of wetlands (e.g., in BCMCA; this study), and also the Everglades (Fisher and Reddy, 2010), and this suggests a continuous mineralization of P and loss from the soil profile.

There was an abrupt increase in soil age at both stations. This may have been caused by an extended dry period, leading to organic matter oxidation and perhaps a peat fire. Paleoclimate studies of Caribbean lake sediments indicate a prolonged drought between 770 and 1100 AD (Hodell et al., 2005) and this corresponds closely with the sudden increase in age of BCMCA soils (ca. 985–1440 AD). The sudden increase in soil age may represent renewed organic matter accretion following several hundred years of drought, fire, and soil oxidation. The effect of extreme drought on peat soils is mineralization of organic matter, potentially leading to export and loss of dissolved P. These mostly random climatic events are superimposed on other more gradual biogeochemical processes, and this complicates interpretation of the soil record.

As a percentage of the total P pool, residual P became the predominant soil P fraction over time, comprising between 48% (Station B4) and 73% (Station C1) of the total P at a depth of 110 and 135 cm, respectively. Similar results were reported for other subtropical peatland soils; for example, residual P was found to comprise 70% of total P for peat samples at depths >40 cm in the northern Everglades (Reddy et al., 1998; Fisher and Reddy, 2010). However, the residual fraction showed one of the highest rates of decline in terms of absolute P content. The residual fraction, therefore, appears to constitute a pool of P that is undergoing constant mineralization, demonstrating that resistance to chemical extraction does not necessarily relate to environmental stability or recalcitrance (Turner et al., 2005). A rapid decline of this fraction suggests that it is not highly resistant to degradation, otherwise an increase (in absolute terms) would be expected. The residual fraction might constitute a soil P reservoir (albeit operationally defined) that is accumulating P from the incomplete mineralization of the other P fractions, and then slowly releasing it. This could lead to a more rapid rate of loss from the residual fraction than from any of the other fractions individually, while still causing a relative (as a percentage of total P) increase. The relative decline in labile fractions and increase in residual P was similar for both impacted and unimpacted stations, suggesting that the decline seems to be largely due to mineralization of organic matter and loss (or conversion) of labile fractions. The proportion of P that is associated with humic compounds increased at both stations, though the increase was only significant at the unimpacted station. An increasing ratio of humic acid P to fulvic acid P through most of the soil profile likely reflects increased synthesis and accumulation of humic-type compounds as peat age increases (Stevenson, 1994).

The concentrations of all sequentially extracted P fractions declined markedly with depth (or time), both at the nutrient impacted and unimpacted station. There are two mechanisms that could account for the dramatic declines in P fractions with increasing soil depth. The first is a change in nutrient loading towards greater anthropogenic loading of P over the last century and this scenario is often used to explain the depth distribution of total P in lakes and wetlands (Brezonik and Engstrom, 1998; Craft and Richardson, 1993; Craft and Richardson, 1998; Brenner et al., 2001). The second mechanism involves mineralization of organic P and diffusion of labile organic and inorganic P from the soil profile and loss to the water column (Carignan and Flett, 1981). It is also likely that a portion of the mineralized P is taken up by plants and re-incorporated into a variety of organic P compounds. Organic P mineralization and diffusive loss to the water column can be a major contributor to overall internal nutrient loading budgets and may also represent a significant loss of P from the soil profile (Fisher et al., 2005; Fisher and Reddy, 2001; Moore et al., 1998). Loss mechanisms may also include processes such as plant-mediated enzymatic mineralization of organic P followed by uptake and redistribution to surface soil (Jobbagy and Jackson, 2000). This P is then subject to loss downstream via surface water transport and may play a role in enriching soils in downstream regions (Bostic et al., 2010). These processes would tend to reduce soil total P over time and increase the proportion of recalcitrant forms of P as observed in this study. Further evidence for loss of P from the soil profile is a 10-fold increase in C/P ratio. It is unlikely that the plant community that historically colonized BCMCA and

Table 6. Phosphorus accumulation rates and the soil (or sediment) depth interval used to calculate the rate for selected aquatic ecosystems.

Ecosystem	Site characteristics	Rate	Depth interval	Technique	Reference
		g P m^{-2} yr^{-1}	cm		
Northern Everglades, FL	High P	0.46	0–12	^{137}Cs	Craft and Richardson, 1998
Northern Everglades, FL	Low P	0.06	0–8	^{137}Cs	Craft and Richardson, 1998
Central Everglades, FL	Low P	0.08–0.23	0–6	^{137}Cs	Craft and Richardson, 1998
Northern Everglades, FL	High P	1.10	0–30	^{137}Cs	Reddy et al., 1993
Northern Everglades, FL	Low P	0.20	0–10	^{137}Cs	Reddy et al., 1993
Lake Okeechobee, FL	Center lake, "K8"	0.10–0.40	0–16	^{210} Pb	Engstrom et al., 2006
Blue Cypress Marsh Conservation Area, FL	10 station survey	0.12–1.10	varies	^{210} Pb	Brenner et al., 2001

formed these peat deposits originally had a C/P ratio of 6000:1, as found in our deep soil samples. For example, studies in highly oligotrophic wetlands have found leaf litter and surface soil C/P (mass basis) to be approximately 1000:1 (DeBusk and Reddy, 1998). Thus, these soils have become depleted in P over time, while maintaining relatively constant C and N contents.

The effect of diagenesis alone can best be observed in regions that have not undergone changes in nutrient loading. For example, Lake Erken is a 24-km^2 mesotrophic lake in east central Sweden that has undergone very little change in the catchment for the past century (Rydin, 2000). Intact sediment cores showed marked declines in sediment total P with respect to depth, which were attributed to P that had been mobilized and lost during diagenesis. Other researchers have found similar enrichment of residual P in lake sediment profiles and attributed the increase in residual P to the combined effects of loss of labile fractions and transformation of labile P to more recalcitrant fractions (Carignan and Flett, 1981; Penn et al., 1995). The linkage between nutrient loading, ecosystem trophic status, and sediment properties is not always direct. For example, Torres et al. (2011) examined sediment properties of three lakes of widely varying trophic status, ranging from oligotrophic to hypereutrophic. They found the surface sediment of an oligotrophic lake to have the highest total P (1427 mg P kg^{-1}), as well as highest labile forms of P, of the lakes they studied.

Groundwater inputs may play a role in regulating forms and concentration of soil P, through advective loss of porewater P or through inputs of groundwater P. The soil at Station B4 consists of 5 m of peat underlain by dense clay, so groundwater inputs are unlikely. Also, both stations contained an approximately 20-cm thick layer of highly decomposed sapric peat, which likely has a very low hydraulic conductivity. Finally, the BCMCA is a soft water system, whereas surface water quality in surrounding canals and water bodies has relatively high conductivity, chloride, Ca, and hardness that is three to fourfold greater than the marsh (M. Fisher, SJRWMD, unpublished data, 2006), indicating that the hydrology of the marsh is predominantly driven by precipitation and exchanges with the bordering Blue Cypress Lake.

Few studies have used ^{31}P-NMR to document the long-term fate of phosphate esters in soils, particularly in wetlands. Both phosphomonoesters and phosphodiesters increased slightly with increasing soil age and maintained approximately equal proportions. This increase in organic P forms appeared to be at the expense of alkali-extractable orthophosphate, which declined throughout the profile. Solution ^{31}P-NMR characterization of changes in P forms in plant litter during decomposition in oligotrophic calcareous wetlands have demonstrated marked dissimilarities between plant litter and surface soil (Cheesman et al., 2010). This indicates that factors other than vascular plant community play a major role in peat soil formation and organic P cycling. Phosphodiesters were abundant in these flooded soils as reported for other Florida wetland soils (Turner and Newman, 2005; Turner et al., 2006). This contrasts markedly with most upland mineral soils in which phosphomonoesters typically predominate (Condron et al., 2005). For example, in a study of temperate pasture soils, the ratio of mono- to diester P ranged from 5:1 to 26:1 (Turner et al., 2003c), compared to 1:1 in this study. Notably absent in our ^{31}P-NMR results was *myo*-inositol hexakisphosphate (phytic acid), the dominant phosphate monoester in most upland soils (Turner et al., 2002). The absence of *myo*-inositol hexakisphosphate was also reported in soils from the Florida Everglades and was attributed to low clay content and perhaps decomposition under anaerobic conditions (Turner and Newman, 2005).

CONCLUSIONS

Biogeochemical processes such as weathering, microbial metabolism, loss of labile C and P compounds, and formation of recalcitrant mineral and organic compounds continually alters material originally deposited at the soil surface. Steadily increasing C/P increases in residual P, and an overall decline in total P observed in this study indicate loss of labile fractions and progressive immobilization of remaining P. For the wetland in this study, long-term steady state accumulation of P occurred at a rate of approximately 2 mg m^{-2} yr^{-1}, a rate much lower than observed in more recent deposits in this wetland and other subtropical aquatic ecosystems. These results provide evidence that vertical changes in P are caused in large part by diagenetic processes, in addition to other temporally variable factors such as nutrient loading and climate. It is likely that marked changes in total P in surface soils are often the result of changes in nutrient loading, although factors unrelated to nutrient loading exert a major influence the quantity and quality of P, particularly in organic soils.

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