Characteristics of Soil Phosphorus in Tree Island Hardwood Hammocks of the Southern Florida Everglades

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The Florida Everglades is a P limited, freshwater wetland ecosystem. In many cases, soil P concentrations in tree islands in the Everglades greatly exceed concentrations in the surrounding marsh; however, little information is available regarding the characteristics of P in tree island soil. Surface soil samples from 26 tree islands were analyzed for total elements, distribution of soil P forms, and soil mineralogy. Total phosphorus (TP) concentrations of soil ranged from 0.764 to 88.1 g kg^{-1}. Most (>80%) of the TP in high P hammock soils was bound in an inorganic form (HCl-extractable), while organic P accounted for a relatively small (~10%) proportion. Total P was positively correlated with non-carbonate inorganic soil matter (i.e., non-carbon matter, $r = 0.98$, $p < 0.001$), non-carbonate calcium (NCCa, $r = 0.98$, $p < 0.001$), and HCl-extractable phosphorus (HCl–P, $r = 0.997$, $p < 0.001$). Apatite was identified by X-ray diffraction (XRD) in soils with elevated P concentration. These soils also contained bone fragments. The high proportion of HCl–P observed in tree island soil coupled with a positive relationship between NCCa and P concentration is evidence for an exogenous P source. The presence of apatite and bone fragments in tree island soils indicates that deposition of biogenic apatite contributes to the soil P pool.

Abbreviations: DDI, distilled deionized water; NCM, non-carbon soil matter; NCCa, non-carbonate calcium; OM, organic matter; TC, total carbon; TIC, total inorganic carbon; TP, total phosphorus; XRD, X-ray diffraction.

Phosphorus is an essential element for plants and is present in several forms, or pools, in soil. Different forms are often designated as either inorganic or organic, and commonly further described as exchangeable, labile, and stable or recalcitrant (Ruttenburg, 1992; Nair et al., 1995; Reddy et al., 1998). These descriptions imply differences among P forms with respect to reactivity in the environment. Freshwater aquatic ecosystems, such as much of the Florida Everglades, are typically sensitive to changes in P pools due to naturally low P availability (Schindler, 1977; Davis, 1994; Carpenter et al., 1998; Reddy et al., 1998).

The Florida Everglades is an expansive (~10,000 km^2) and diverse subtropical ecosystem in southern Florida (Sklar et al., 2005; Wetzel et al., 2005). In the interior of the Everglades, emergent marsh dominated by sawgrass (*Cladium jamaicense* Crantz) alternates with areas of open water, characterized by floating aquatic species such as fragrant waterlily (*Nymphaea odorata* Ait.) (Loveless, 1959; Davis, 1994). Within this matrix, tree islands dominated by woody plant species are common inclusions of higher elevation habitat (Loveless, 1959; Sklar and van der Valk, 2002). Island soil surface elevations vary greatly, sometimes exceeding 2.5 m above the soil surface within the adjacent marsh (Wetzel et al., 2008).

The Everglades is a historically oligotrophic wetland ecosystem limited by P (Noe et al., 2001). The system is ombrotrophic, with an annual atmospheric P deposition rate of 0.036 g m^{-2} (Davis 1994). The historic water column P concentration has been estimated as 10 to 11 mg L^{-1} (Noe et al., 2001). The TP concentrations in the P-limited marsh peat soils typically range from 250 to 500 mg kg^{-1} (DeBusk et al., 1994; McCormick et al., 1999), and have been reported at concentrations <200 mg kg^{-1} in marl soils in the southern Everglades (Hanan and Ross, 2009; Liao and Inglett, 2011; Troxler-Gann et al., 2005). Marsh soil is described as P-enriched when TP concentrations exceed 500 mg kg^{-1} (McCormick et al., 1999; DeBusk et al., 2001).

Total P in tree island soil varies from concentrations similar to adjacent marsh soil to levels more than 100 times higher (Wetzel et al., 2011). Variability of P concentration in tree island soils has fostered interest in explaining the formation, function, and potential for restoration of tree islands in the Everglades (Orem et al., 2002; Ross and Sah, 2011; Wetzel et al., 2011). Drainage and flood control projects constructed from the late 19th century through the mid-20th century altered hydrologic and nutrient regimes in the Everglades (Davis, 1994; Light and Dineen, 1994; McVoy et al., 2011). Alteration of hydrologic regime has been attributed to the loss of tree island habitat in the central Everglades during this time period (Hofmockel et al., 2008; Sklar and van der Valk, 2002; Patterson and Finck, 1999; Wetzel et al., 2005). Loss of tree island habitat may affect landscape scale P cycles because tree island soils have been suggested to sequester >65% of historic P inputs to the central Everglades

Fig. 1. Site map depicting tree island locations with hardwood hammock plant communities where soil samples were collected in the Florida Everglades.

marsh (Wetzel et al., 2008). It has been further postulated that storage of P in tree island soils allows low-P conditions to be maintained in the adjacent marsh, and the development of the highly P-limited Everglades marsh (Wetzel et al., 2005, 2008).

The wide difference between tree island and marsh soils, and among tree islands, likely indicates variability in the magnitude of abiotic and biotic mechanisms influencing P distribution across the landscape. The primary hypotheses for the formation of soil P hotspots within the P-limited Everglades marsh, or in similar oligotrophic wetlands in Belize (Macek et al., 2009), focus on the direct or indirect effects of vegetation (Wetzel et al., 2005, 2011; Ross et al., 2006). High rates of evapotranspiration, atmospheric deposition, dissolution of limestone bedrock by root exudates and deposition of animal wastes are theorized to influence the concentration of P in tree island soil (Wetzel et al., 2005; Ross et al., 2006). Each of these mechanisms have been described as influential in transport of nutrients to island habitat in other ecosystems around the world (McCarthy et al., 1993; Frederick and Powell, 1994; Wait et al., 2005; Krah et al., 2006; Ramberg and Wolski, 2007).
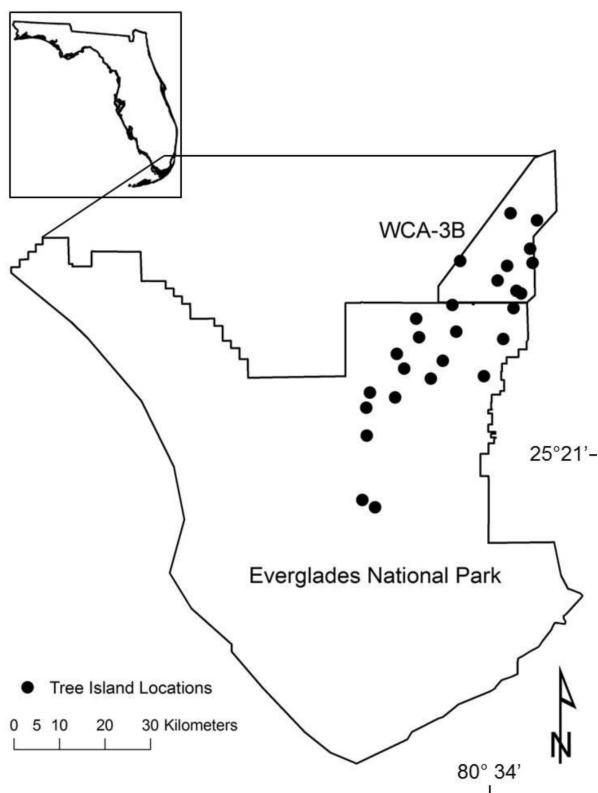
Research related to tree islands in the Everglades has focused primarily on explaining the pattern of general divergence of soil P concentration between the marsh and tree islands (Orem et al., 2002; Wetzel et al., 2005, 2008, 2011). An investigation of organic P forms with nuclear magnetic resonance (NMR) in tree island soil from a wading bird colony in WCA-3 revealed that orthophosphates were the primary form (El-Rifai et al., 2008). Ross and Sah (2011) showed that increases in soil P concentration in tree island hardwood hammock communities might be related to the presence of inorganic P in association with non-carbon soil material, and they theorized this relationship could indicate the presence of phosphate minerals such as hydroxyapatite [apatite, $Ca_5(PO_4)_3OH$]. Phosphate minerals are rare in the Everglades (Harris, 2011), and their accumulation in tree island soil could represent a relatively stable reservoir of P, with implications for restoration.

Little information is available regarding the chemistry, stability, and fate of tree island soil P. Determination of the elemental composition and P characteristics of tree island surface soil will help identify processes of P accumulation and prediction of P availability within tree island soils. We hypothesize that apatite, a Ca phosphate mineral, is the predominant form of P in tree island soils characterized by elevated P concentration. The objectives of this study were to: (i) determine elemental composition of soil in tree islands, (ii) determine correlations among chemical constituents that may elucidate P characteristics, and (iii) identify the P minerals present in tree island soil.

MATERIALS AND METHODS
Site Description and Locations

Composite soil samples, consisting of two surface soil cores each 0- to 10-cm deep, were collected from 26 tropical hardwood hammock plant communities within tree islands from 2005 to 2007 in the southern Everglades, Florida (Fig. 1). Hardwood hammocks are upland forests and differ from other forested areas

in vegetative species composition and geomorphic setting in the Everglades landscape. Tree species that are tropical and subtropical in origin are dominant and generally create a closed canopy within the interior of the island (Ross and Sah, 2011; Saha et al., 2010; Wang et al., 2010b). Species commonly present within the hammock communities include gumbo-limbo [*Bursera simaruba* (L.) Sarg.], *Sideroxylon foetidissimum* Jacq., and sugar hackberry (*Celtis laevigata* Willd.) (Ruiz and Ross, 2004; Saha et al., 2010; Wang et al., 2010b). On average, the soil surface is elevated ~0.9 m above the adjacent emergent marsh habitat and ~0.7 m above the average water table (Ross and Sah, 2011). Most hammock species are intolerant of prolonged periods of soil saturation and soils are typically well-drained due to an elevated landscape position (Saha et al., 2010; Ross and Sah, 2011).

Early categorizations of soils within tree islands in the Everglades describe them broadly as peats (Leighty and Henderson, 1958). Classification of tree island soils is limited and when available these soils are mapped as Histosols of the Dania or Matecumbe series (USDA, 1996). Hammock soils that are occasionally flooded and located within the marl prairie regions of the southern Everglades have been described as somewhat similar to the Folists found in dry hammock forests in the Florida Keys (Ross et al., 2003; Ross and Sah, 2011). Coultas et al. (2008) categorized two nonhydric hammock soils in the southern Everglades as Mollisols, which suggests further mapping and pedological investigation of these soils may provide insight toward tree island soil morphology.

Elemental Analysis

Soil samples were oven dried (70°C) and sieved (<2 mm) before analysis. Soil pH was determined on a slurry with water to soil ratio of 1:1. Total carbon (TC) and nitrogen (TN) were measured by dry combustion using an elemental combustion system (Costech Analytical Technologies, Inc., Valencia, CA). Total P was determined by heating 200 mg of soil to 550°C for 4 h then dissolving the residual material in 6 M HCl (Andersen, 1976). The solution was then analyzed for P concentration on a spectrophotometer (Beckman Instruments, Inc., Fullerton, CA) using the ascorbic acid method of Murphy and Riley (1962). The concentrations of total Al, Ca, Fe, and Mg in the same solution were measured by inductively coupled plasma–optical emission spectroscopy (PerkinElmer, Inc., Waltham, MA).

Percent organic matter (OM) was determined by loss on ignition (LOI, 550°C, 4 h) during the combustion stage of the TP analysis. Total inorganic carbon (TIC) concentration was determined using a pressure-calcimeter, and calcium carbonate ($CaCO_3$) concentration was calculated from measured TIC as described by Wang et al. (2010a). The proportion of soil that was not accounted for by summation of OM and $CaCO_3$ comprised non-carbon soil matter (NCM; Ross and Sah, 2011). The concentration of soil Ca associated with $CaCO_3$ was calculated with the assumption that Ca constitutes 40% of $CaCO_3$ by mass. Non-carbonate Ca was determined by difference between the total soil Ca concentration and the concentration of Ca associated with $CaCO_3$ in soil.

Phosphorus Fractionation

Soil P was partitioned by sequential chemical extraction using a modified fractionation procedure that differentiated six forms of P (Hieltjes and Lijklema 1980; Ivanoff et al., 1998; Reddy et al., 1998; Kuo et al., 2009). The fractionation procedure consisted of four extracting solutions, distilled deionized water (DDI), 1.0 M KCl, 0.1 M NaOH, and 0.5 M HCl. After the soil was treated successively with each of the extracting solutions, the remaining soil residue was analyzed for TP (residual P). A known mass of nominally 0.5 g dry weight soil was combined with 25 mL of each extraction solution in 50 mL centrifuge tubes, to maintain a soil/solution ratio of 1:50 (g mL^{-1}). The tubes were shaken with a reciprocating shaker for 1, 2, 17, and 24 h for DDI, KCl, NaOH, and HCl, respectively (Irick, 2012). After equilibration, sample solutions were centrifuged at 2100 × *g* for 15 min, and supernatants were filtered (no. 42 Whatman) and refrigerated at 4°C before P analysis. Phosphorus measured in filtrates was assumed to be soluble inorganic P (Pi), and was determined colorimetrically as previously described. Sodium hydroxide solutions were also measured for TP by persulfate digestion. Organically-bound P in the NaOH solution (NaOH–Po) was determined as the difference between Pi and TP in solution.

Phosphorus extracted by DDI is defined as water soluble phosphorus (WSP). Extractable P in the KCl solution is available P not solubilized by the DDI extraction. Cumulatively these fractions can be defined as available, exchangeable or labile P. Phosphorus dissolved in the NaOH solutions (NaOH–Pi) is considered Al or Fe bound P. The NaOH–Po fraction is generally attributed to humic and fulvic acid P. Acid extractable P (HCl–P) is presumed as Ca or Mg bound P. The composition of the residual P fraction is unknown, and commonly inferred to contain recalcitrant P associated with minerals and organic matter (Reddy et al., 1998).

Mineralogical Analysis

Mineralogical analyses were performed using oven dried soil (<2 mm) from subset of islands (*n* = 3). The samples were not treated prior analysis to remove carbonates or organic matter. The first stage of mineralogical assessment was observation under a dissecting microscope. Subsequently mineral identification was conducted by XRD using an automated XRD system (Rigaktu Corporation, The Woodlands, TX) equipped with stepping motor and graphite crystal monochromator. Each sample was prepared for XRD analysis using a powder cavity mount (Harris and White, 2008). Samples were scanned from 0 to 60° 2θ using Cu Kα radiation.

Statistical Analysis

All statistical analyses were conducted using SAS version 9.2 (SAS Institute, 2010). Descriptive statistics were determined for measured soil properties and various forms of P. Correlation among soil properties was determined using Spearman's Rank-Order coefficients, with a minimum significance level of 0.05.

RESULTS AND DISCUSSION
Soil Chemical Characterization

Elemental composition of hardwood hammock soil varied widely as indicated by the range of values measured for each parameter (Table 1). Dissimilarity in measured TC and TP is not surprising due to the variety of concentrations reported for Everglades tree island soil (Troxler-Gann et al., 2005; Hanan and Ross, 2009; Wetzel et al., 2011). Carbon, Ca, and P were the primary elements present (Table 1). Total P concentration in tree island soil ranged from 0.764 to 88.1 g kg^{-1} (Table 1).

Total Al, Ca, Fe, and Mg concentrations for Everglades tree island soil were not found in the literature. Measured mean total Al and Fe soil concentrations were lower and total Ca and Mg soil concentrations were greater than marsh soil reported for WCA-3 (Craft and Richardson, 1997). Soil pH for tree island soils was slightly alkaline and the range measured was similar to soil pH reported for other tree islands in the Everglades (Troxler-Gann et al., 2005; Hanan and Ross, 2009). Average soil CaCO$_3$ concentration was intermediate as compared to tree island soils described by Hanan and Ross (2009), and values estimated from inorganic C reported by Ross and Sah (2011). Soil CaCO$_3$ measured in hammock soil was less than half the concentration reported for marl soil in southeastern Everglades (Zhou and Li, 2001).

Low TC values, slightly alkaline pH and low OM concentration measured in the hammock soils (Table 1) suggest that CaCO$_3$ is a significant mineral component. The presence of limestone bedrock in south Florida and outcrops that underlie many tree islands supports this assumption. However, if tree island soils were pure CaCO$_3$, the weight percent of C would be 12%, based on the theoretical molecular mass of the mineral. Organic matter was present in measurable quantity in all samples therefore even at low TC concentrations a portion of the TC is attributable to organic C (Table 1).

The high variability of OM, NCM, Ca, and P are particularly interesting with respect to elucidation of tree island soil biogeochemistry. The range in soil OM, Ca, and TP may reflect varying magnitudes of external contributions of inorganic elements derived from animal wastes to tree islands. Significant negative correlations were determined between soil OM and P, Ca, NCCa, and Fe (Table 2). Negative correlation between OM and P indicates high soil total P is not likely due to the presence of organic bound P.

Precipitation of Ca and P, and association with CaCO$_3$, is often used to explain characteristics of inorganic P in Everglades soil (Koch and Reddy, 1992; Reddy et al., 1998). However, in these hammock soils neither soil CaCO$_3$ nor total Ca concentration were significantly correlated to TP (Table 1). Ross and Sah (2011) reported no significant correlation between TP and inorganic C, but a significant positive correlation between TP and NCM in hammock soils. They theorized that soil P may reflect the presence of Ca phosphate minerals such as apatite, or of P adsorbed to surfaces of non-carbonate minerals (Ross and Sah, 2011). Zhou and Li (2001) showed P sorption with non-carbonate clays in calcareous soils of southern Florida was a significant characteristic of P chemistry. Recruitment of dissolved elements from the surrounding marsh to tree islands, through localized hydrologic pathways mediated by evapotranspiration, is a potential mechanism for accumulation of mineral matter in tree island soil (McCarthy et al., 1993; Wetzel et al., 2005; Ross et al., 2006). The presence of cemented carbonate soil layers in Everglades tree islands may be a product of this mechanism (Coultas et al., 2008). However our findings suggest that carbonate precipitation is not the dominant mechanism of P retention.

Significant positive correlation of soil NCM with P, NCCa, and Mg indicate P chemistry in these hardwood hammock soils may be influenced by Ca and Mg minerals that are not carbonates (Table 2). Jayachandran et al. (2004) reported a general trend of decreasing soil and porewater TP concentration with increasing distance from tropical hardwood hammock vegetation communities in tree islands of Shark Slough and postulated that P biogeochemistry could be influenced by reactions with Ca. Measurement of soil total elements and determination of elemental associations reported here provide new and important insight toward tree island soil chemistry and characteristics of P. Although these findings offer an indication of P association, little can be inferred regarding P availability, distribution of P forms, relative stability, or the presence of specific P minerals.

Soil Phosphorus Fractionation

Sequential chemical P fractionation revealed HCl–P is the dominant P form in these tree island soils, comprising on average

Table 1. Select soil properties from 26 tree islands with tropical hardwood hammock plant communities in the Florida Everglades.

Parameter	Mean	Median	Range
pH†	7.96	8.08	6.36–8.42
Organic matter, g kg^{-1}	403	305	198–899
CaCO$_3$, g kg^{-1}	224	205	56.3–646
Non-carbon matter, g kg^{-1}	373	410	44.8–678
Total Al, g kg^{-1}	2.56	2.11	1.20–7.15
Total C, g kg^{-1}	192	152	93.5–406
Total Ca, g kg^{-1}	195	214	42.8–300
Total Fe, g kg^{-1}	5.04	4.08	1.20–13.4
Total Mg, g kg^{-1}	4.60	3.63	1.53–10.5
Total N, g kg^{-1}	12.4	10.1	5.69–24.6
Total P, g kg^{-1}	47.2	52.2	0.764–88.1

† Subset of data from Ross and Sah (2011).

Table 2. Non-parametric (Spearman's rank-order) correlation coefficients for select tree island soil properties (n = 26).

| Parameter	Total P	Organic matter	Non-carbon matter
Total P		–0.774***	0.977***
CaCO$_3$	–0.197	–0.112	–0.240
Total Al	–0.054	0.156	0.048
Total Ca	0.387	–0.702***	0.312
Non-carbonate Ca	0.977***	–0.791***	0.965***
Total Fe	0.195	–0.400*	0.207
Total Mg	0.439*	–0.190	0.433*

* Significant at the 0.05 probability level.
*** Significant at the 0.001 probability level.

~85% of total P (Fig. 2). Most of the P in the native marsh is organic bound P (Reddy et al., 1998; Bruland et al., 2006). Total P and HCl–P were positively correlated ($r = 0.997$, $p < 0.001$) indicating that mechanisms influencing increases in Ca or Mg bound P are central to P accumulation and storage in Everglades tree islands (Table 3). Reddy et al. (1998) showed that high concentrations of total inorganic P were present in the most P-rich Everglades peat soils. An increase in Ca-bound P is frequently related to increase of inorganic P in marsh soil (Koch and Reddy, 1992; Reddy et al., 1998).

Water-soluble and KCl-extractable P, cumulatively available or exchangeable P, accounted for a very small proportion of the total P pool (Fig. 2) and average P concentration in this pool equates to ~150 mg kg^{-1} of available P. This concentration of available P is approximately one-third the historic TP reported for Everglades marsh soil (Noe et al., 2001). The presence of relatively abundant available P in hammock soil supports the theory that plant productivity in tree islands is enhanced by soil P availability, potentially leading to the expansion of the islands. The origin of the available P remains debatable and is likely the result of multiple sources (Wetzel et al., 2005; Ross et al., 2006).

Both WSP and KCl-extractable P were positively correlated with TP (Table 3). An increase in available P with increasing TP suggests tree island soil with high concentration of TP may release more P than soil with relatively lower P concentration. Water-soluble P was also positively correlated with KCl–P and with HCl–P (Table 3). The relationship between WSP and KCl-extractable P suggests that WSP that is used by plants and microorganisms, or leached from the soil, may be replenished by the exchangeable P pool. The positive correlation between WSP and HCl–P suggests that the dissolution of Ca or Mg P minerals may influence P availability in tree island soil.

Concentration of water and NH$_4$Cl-extractable P was reported to show a similar trend as total P in soils impacted from dairy manure, where higher extractable P was detected in soil with increasing total P concentration (Graetz and Nair, 1995). Water-soluble P was the dominant type of available P in poultry litters and manure (Dail et al., 2007; Codling, 2006; He et al., 2010), accounting for as much as ~55% of the TP in poultry litter (Codling, 2006). Water-extractable P in animal manures (cattle [*Bos taurus*], swine [*Sus scrofa*], chicken [*Gallus gallus*], and turkey [*Melleagris gallopavo*]) has been used to indicate P runoff risk from soils amended with these waste products (Kleinman et al., 2005). Guano collected from wading birds in the Everglades was found to contain ~3,500 mg kg^{-1} of available P, which suggests large amounts of available P may be deposited at islands that birds frequently visit (Irick, 2012). Calcium- or Mg-bound P (HCl-extractable P) accounted for most of TP pool in poultry litter and manure (Dail et al., 2007; He et al., 2010), and ~88% of the TP in wading bird guano (Irick, 2012). Nair et al. (1995) reported that 80% of the Ca or Mg bound P in manure impacted soil may be subject to leaching based on repeated extraction with NH$_4$Cl. Additionally, WSP was not significantly correlated with
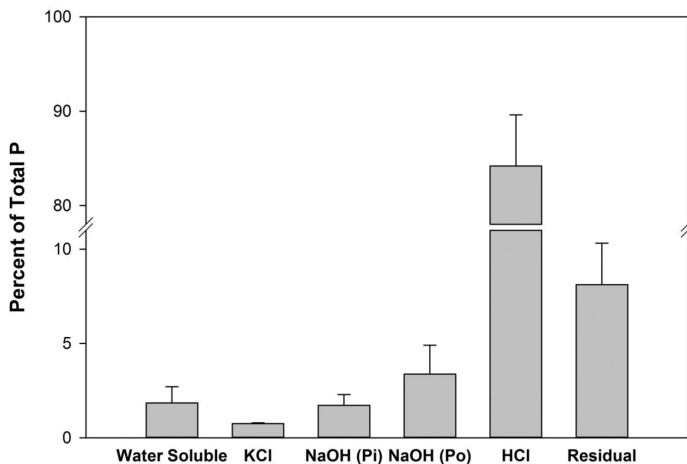
Fig. 2. Distribution of P forms in tree island soil (0–10 cm). Bar values indicate mean ($n = 26$) and errors bars ± 1 SD. KCl, KCl-extractable phosphorus; NaOH (Pi), NaOH-extractable inorganic phosphorus; NaOH (Po), NaOH-extractable organic phosphorus, HCl, HCl-extractable phosphorus; Residual, residual phosphorus.

other forms of P, in particular NaOH–Pi, indicating that Al or Fe bound P is not readily released (Table 3).

Soil OM concentration was positively correlated with NaOH–Po, and negatively correlated with NaOH–Pi (Table 3). Organic matter was also negatively correlated with HCl–P (Table 3). The inverse relationship of NaOH–Po and TP confirms organic P is not the primary P form in tree island soils with high concentrations of P. No significant correlation was determined between residual P, and OM or total P (Table 3). This lack of correlation suggests the residual P is a relatively consistent and stable pool tree island soils. Cumulatively, HCl–P and residual P comprise ~90% of the total P in the hammock soil, and based on the extraction sequence could be considered relatively stable forms of soil P (Fig. 2). However further research is required to describe the potential rate of P release from these soils.

The concentration of HCl-P is positively correlated with soil non-carbon matter (Fig. 3). These findings suggest that elevated P in Everglades tree island surface soil is related to accumulation of Ca–P or Mg–P minerals, and these minerals are not likely carbonates. The total concentration of Ca and Mg in soil suggests

Table 3. Non-parametric (Spearman's rank-order) correlation coefficients for water-soluble phosphorus (WSP), 1.0 M KCl-extractable phosphorus (KCl), 0.1 M NaOH-extractable inorganic phosphorus (NaOH–Pi) and organic phosphorus (NaOH–Po), 0.5 M HCl-extractable phosphorus (HCl), residual phosphorus (Residual), with total phosphorus (TP) and organic matter (OM) for tree island soil ($n = 26$).

Parameter	WSP	TP	OM
WSP		0.487*	−0.149
KCl	0.841***	0.503**	−0.136
NaOH–Pi	0.337	0.896***	−0.862***
NaOH–Po	0.003	−0.475*	0.478*
HCl	0.484*	0.997***	−0.785***
Residual	−0.234	0.136	−0.106

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
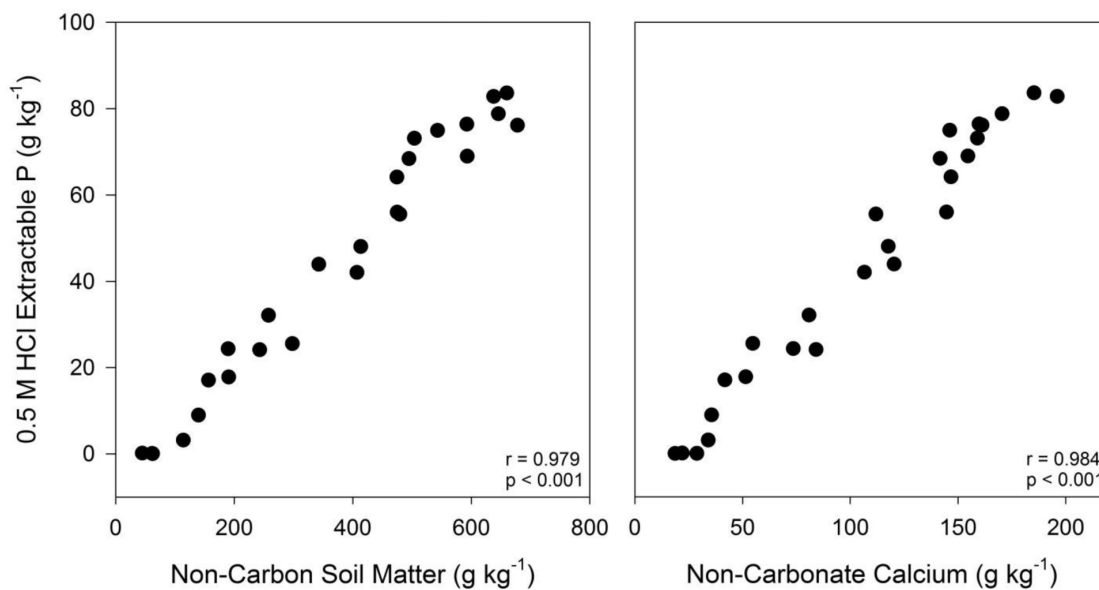*** Significant at the 0.001 probability level.

Fig. 3. Scatter plots depicting relationships between HCl-extractable soil P concentration (g kg⁻¹), and the concentrations (g kg⁻¹) of non-carbon soil matter (NCM) and non-carbonate calcium for tree island soil (_n_ = 26). Correlation coefficient (Spearman), and associated _p_ value denoted for each plot.

Ca is more important in P dynamics because of the abundance of Ca relative to Mg (~40 times greater). Additionally, the positive correlation between NCCa and HCl–P suggests that Ca–P minerals are the dominant forms of P in tree island soil (Fig. 3). These relationships suggest that high soil P content in these subtropical dry forest ecosystems is due to an exogenous source of inorganic P that varies among islands.

Soil Mineral Identification

Apatite and calcite ($CaCO_3$) were present in abundance based on relative XRD peak intensities for each of the high-P samples of tree island soil (Fig. 4). No other phosphate minerals were observed in the soil using XRD. Quartz was identified in two of the samples and aragonite ($CaCO_3$) was identified in one sample (data not shown). Observations under a dissecting micro-

Fig. 4. X-ray diffraction patterns for particles <2 mm in size from three tree island soils (0–10 cm). The arrows indicate primary peaks for apatite and calcite.

scope revealed the presence of bone fragments in many samples with elevated P concentrations, while the presence of calcite in the samples was likely due to fragments of limestone or shell in soil. Aragonite was also probably related to shell fragments, though geochemical analysis of surface and ground water in a hammock in Everglades National Park have shown that tree island ground water is frequently above critical saturation thresholds for these minerals, suggesting that they may precipitate (Sullivan, 2011). Quartz is a common component of nearby marl soil and has been documented to comprise 15 to 40% of the clay-sized minerals of marl prairie soil in the region (Sodek et al., 1990). Investigation of different soil particle size classes may reveal more information regarding soil mineralogy.

Comparison of molar ratios of total Ca and NCCa to P suggests that apatite may be the dominant mineral present as soil NCM and TP increase (Fig. 5). Increase in NCM is negatively correlated with Ca/P and non-carbonate Ca/P ratios (Fig. 5). The theoretical molar Ca/P ratio of hydroxyapatite is 1.67. As NCM and TP concentration in the hammock soils increases the ratio of Ca/P and NCCa/P converges on and conforms to the Ca/P ratio of apatite (Fig. 5). Average molar Mg/P ratio is <<1, further indicating that Mg phosphate interactions are not dictating P chemistry in these soils to the same extent as Ca phosphate minerals. Calcium phosphate minerals tend to be dominant in calcareous soil and Mg phosphates are generally not as abundant or common (Lindsay et al., 1998). Collectively soil elemental analysis, chemical fraction of P, physical identification of soil minerals, and stoichiometric correlation indicate apatite presence is an important characteristic of P biogeochemistry in these tree island hammock soils.

The mechanism for apatite accumulation or transport to tree island soil is likely biogenic based on the consistent presence of bone fragments in many soils with elevated P concentration. Apatite was not observed in the Biscayne, Pennsuco
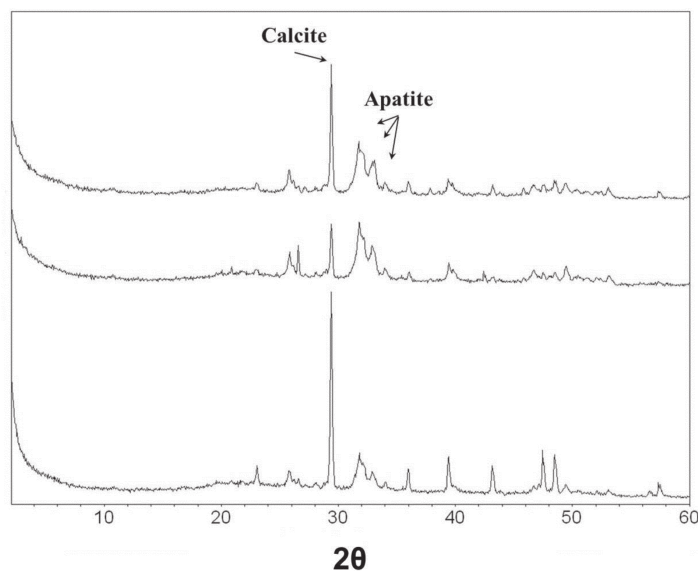
and Perrine Marl, and Chekika and Krome soil types (Sodek et al., 1990). Apatite has been detected in agricultural soils in southern Florida known to be treated with P fertilizer (Harris, 2011). Bates et al. (2010) reported the detection of amorphous apatite in soil from a wading bird colony in northern WCA 3 and attributed the apatite to guano deposition. Multiple apatite peaks were detected in the hammock soil of the present study, indicating that the apatite present in these soils was relatively crystalline. Irick (2012) characterized P forms in wading bird guano from the Everglades. Crystalline P minerals were not detected in the bird guano; however, most of the P in wading bird guano was Ca–P (Irick, 2012). Hydroxyapatite has been proposed as an important constituent of the Ca–P pool in poultry litters, specifically when Ca/P ratios exceed two (Toor et al., 2005; Shober et al., 2006).

Lindsay et al. (1998) described Ca–P mineral in terms of potential solubility in soil solution and apatite species are less soluble than monocalcium phosphates such as brushite and monetite. Sullivan (2011) recently found hydroxyapatite

saturation indices of ground and surface water chemistry of an Everglades hammock did not support in situ precipitation of apatite in tree island soil. Further they suggested that dissolution of inorganic P in surface soil likely contributes to P measured in ground water (Sullivan, 2011). The confirmation of apatite in multiple tree island soils, and observation of bone fragments in these soils indicates that bioapatite contributes to the soil P pool.

Coultas et al. (2008) reported gravel sized (>2 mm) fragments comprised ~22 to 36% of the soil mass in the top 15 cm at two islands in the southern Everglades, and that bone was observed in the gravel. They postulated guano- and bone-derived P could account for the elevated P observed in some tree island soil (Coultas et al., 2008). Apatite presence may also be a result of historic anthropogenic use, as implied by the presence of buried bone and artifacts within the profile of tree island soil from the Everglades (Carr, 2002; Graf et al., 2008; Ross and Sah, 2011).

The accumulation of bone in Everglades tree islands also may be an ongoing process related to wildlife use. Coultas et al. (2008) suggested in addition to anthropogenic focusing, wildlife
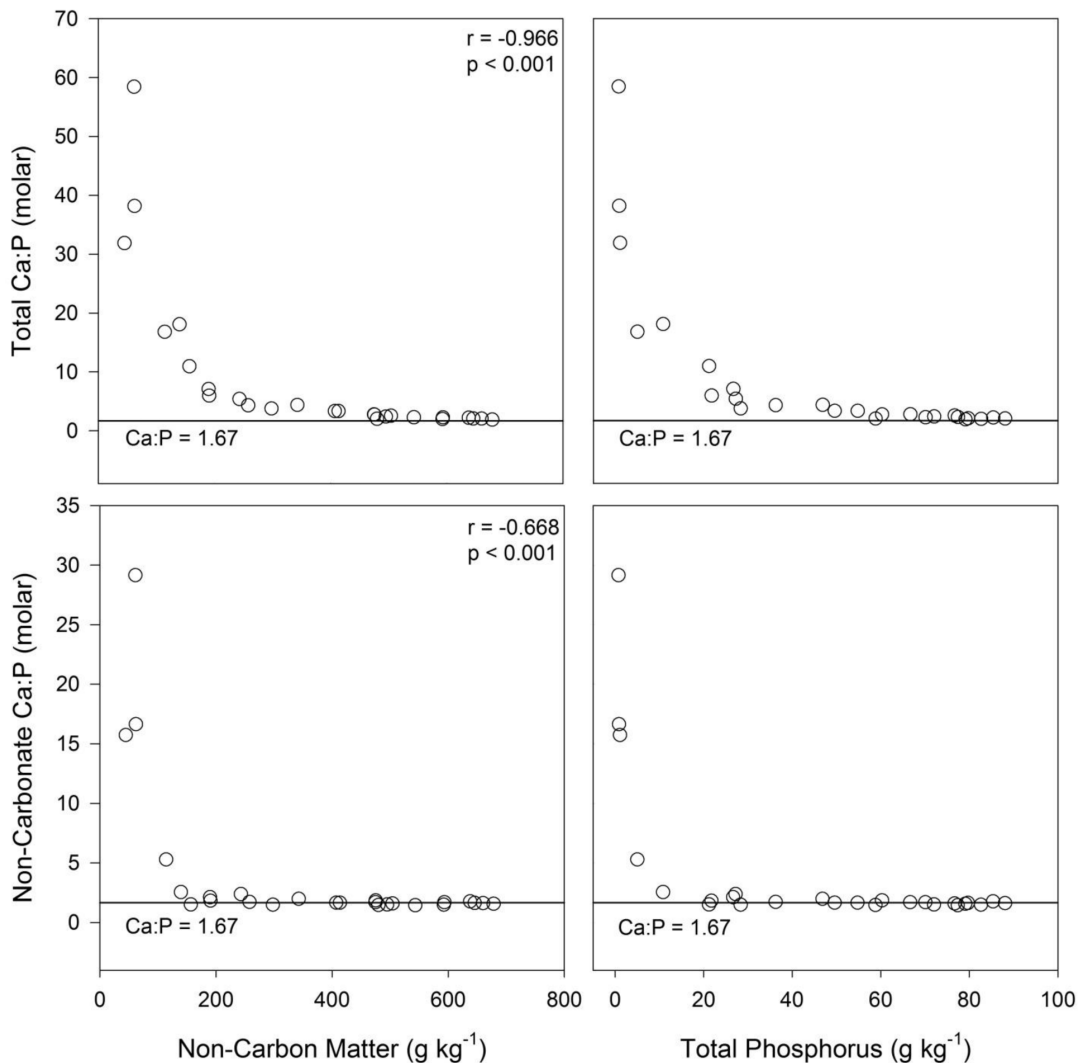

Fig. 5. Scatter plots for stoichiometric molar ratios of total Ca and non-carbonate Ca to total phosphorus (TP) in comparison with non-carbon matter and TP concentration in tree island soil (n = 26). Correlation coefficient (Spearman), and associated p value are denoted for plots comparing Ca/P ratios with non-carbon matter. The solid horizontal line indicates a Ca/P ratio of 1.67.

utilization of islands could also be a vector for bone addition in tree islands. A qualitative assessment of wildlife use in Everglades tree islands noted the presence of avian, mammalian, reptilian, amphibian, and invertebrate species (Meshaka et al., 2002). Until quantitative estimates are developed for habits of animal use in tree islands, determination of potential rates of bioapatite deposition will probably remain unresolved.

Further investigation of phosphate mineral distribution and stability in tree island soils will help elucidate landscape-scale mechanisms influencing differential patterns of nutrient accumulation in the Everglades. In particular, tree islands may play an important role as locations where biogenic soil P minerals are focused, accumulate, and potentially withheld from the P-limited marsh. Protection of tree island habitat is likely an important management approach to maintain mechanisms that promote nutrient accumulation in tree island soil and minimize the potential for ecosystem eutrophication related to loss of island habitat.

CONCLUSIONS

Current theories suggest tree islands are sentinels of nutrients within the oligotrophic Everglades wetland. Our empirical approach is the first to focus on P chemistry in tree island soil. Soil P characteristics in tree islands are dictated by different processes than the surrounding marsh, as evidenced by the high concentration of inorganic P. The high proportion of HCl–P observed in tree island soil coupled with a positive relationship between NCCa and TP concentration is evidence for an exogenous P source. Adsorption of P to Ca in carbonate species is likely not a significant aspect of P chemistry in high P tree island soils. Positive correlation of NCCa with HCl–P, and stoichiometry of total Ca/P, NCCa/P and Mg/P molar ratios is an indication that Ca phosphate minerals are the primary form of P in tree island soil. The presence of apatite and bone fragments in tree island soils confirms that deposition of biogenic apatite contributes to the soil P pool. The source, spatial extent, and timing of this contribution remain unknown. Further quantification of potential soil P constituents will advance development of tree island nutrients budgets and the dynamics of P distribution across the P-limited landscape.

ACKNOWLEDGEMENTS

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