

# Sulfur-induced changes in phosphorus distribution in Everglades Agricultural Area soils

Rongzhong Ye · Alan L. Wright · J. Mabry McCray ·  
K. R. Reddy · Linda Young

Received: 28 May 2009 / Accepted: 8 September 2009 / Published online: 18 September 2009  
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**Abstract** Elemental S is used as an amendment for Everglades Agricultural Area soils of south Florida to decrease pH and increase P availability to crops. Our objectives were to determine how S application altered phosphorus distribution and availability in organic soils under sugarcane cultivation. Soils were sampled four times during the growing season at 2, 6, 9, and 13 months after sulfur application and subjected to chemical P fractionation. Sulfur application had minimal effect on soil pH and thus generally failed to increase P supply to sugarcane during the entire growing season at the application rates tested due to the high soil buffering capacity against acidification. Yet, a significant reduction in soil pH did increase P concentrations in labile P and Fe–Al bound P fractions at 2 months for the highest S rate. Concentrations of labile P and Fe–Al bound P declined during the sugarcane growing season. The size of Ca–P fraction remained unchanged during the early season but significantly decreased at the end of

the growing season. Humic–fulvic acid P fluctuated seasonally, averaging 143, 172, 139, and 181 mg P kg<sup>-1</sup> for 2, 6, 9, and 13 months, respectively. Residual P fluctuated in a contrasting pattern to humic–fulvic acid P and contributed approximately 50% to the total P. Overall, S application did not result in large P accumulation in labile pools, thus S application does not appear to enhance potential P export from fields into wetlands.

**Keywords** Everglades Agricultural Area · Histosol · Phosphorus fractionation · Sulfur · Sugarcane

## Introduction

The Everglades Agricultural Area (EAA) in south Florida was drained in the early 1900s and converted to sugarcane and vegetable cropping. The EAA primarily consists of Histosols with high organic matter content, approximately 85% by weight, which contain high N yet low P and micronutrient concentrations that require supplemental fertilization (Snyder 2005; Castillo and Wright 2008). Due to the conversion of land use from seasonally-flooded wetlands to agricultural use, oxidation or subsidence of the drained peatlands has occurred at a rate currently approximating 1.5 cm year<sup>-1</sup> (Shih et al.

R. Ye · K. R. Reddy  
Soil & Water Science Department, University of Florida,  
Gainesville, FL 32611, USA

A. L. Wright (✉) · J. M. McCray  
Everglades Research & Education Center, University of  
Florida, Belle Glade, FL 33430, USA  
e-mail: alwr@ifas.ufl.edu

L. Young  
Statistics Department, University of Florida, Gainesville,  
FL 32611, USA

1998). Consequently, the depth of the soil has declined considerably to the point of causing significant interaction with the underlying bedrock. Cultivation of these drained peatlands, specifically the use of tillage, has resulted in incorporation of bedrock  $\text{CaCO}_3$  into soil, which has gradually increased the pH since drainage from the historic 5.0–5.5 to approximately 7.0–7.5 today (Snyder 2005; Gabriel et al. 2008). Subsequently, these soil pH increases have decreased P and micronutrient availability to crops and necessitated new fertilizer management practices. Sugarcane is the dominant crop grown in the EAA, but it requires approximately 30 kg P  $\text{ha}^{-1}$  year $^{-1}$  and extensive tillage for pre-plant preparation and weed control (Rice et al. 2006). Long-term P application has resulted in P accumulation in soil profile and as well as export into Everglades wetlands through canal systems, which was a major factor contributing to the deterioration of water quality and alterations of the Everglades wetland ecosystem (Childers et al. 2003).

An understanding of P transformations and distribution in soil is necessary to maximize efficient P use by sugarcane, while minimizing potential export from fields into adjacent wetlands. Fractionation schemes have been developed to determine the P distribution and allocation in different pools related to their degree of recalcitrance (Reddy et al. 1998; Harrell and Wang 2007). Such schemes assume that different extractants selectively extract discrete P chemical forms sequentially (Adhami et al. 2007). Though the assumption and procedure is operationally defined, the methods provide a convenient way to characterize the availability and mobility of P in soils and to assess their impacts on the environment (Maguire et al. 2000). Soils with high labile P content indicate high P availability to plants and also potential export by leaching or runoff. Inorganic P associated with  $\text{CaCO}_3$  or bound to Fe and Al oxides are considered relatively stable, but may be susceptible to dissolution and regeneration upon change in environmental conditions (Castillo and Wright 2008). Phosphorus associated with organic pools is unstable in these drained peatlands due to organic matter oxidation and subsequent P mineralization (Wright 2009).

Several factors are capable of influencing P stability and mobility in the soil profile including pH, microbial activity, and soil amendments (Arai et al. 2005; Jaggi et al. 2005). Elemental S is

occasionally applied in the EAA as soil amendment for the purpose of reducing pH and therefore increasing P availability to crops (Gabriel et al. 2008). The microbial oxidation of elemental S to  $\text{SO}_4^{2-}$  produces acidity which reacts with the soil and reduces pH, which in turn releases P bound to Ca and Fe minerals into soil solution. However, the buffering capacity of these calcareous histosols is strong and can counteract the acidifying effects of S oxidation, thus effects of amendments are temporary and may need to be repeated each growing season (Beverly and Anderson 1986). Problems with large scale S application include a potential pulsed P release from soils that may pose runoff or leaching hazards into proximal aquatic ecosystems (Santoso et al. 1995). Additionally, increased nutrient availability resulting from pH reduction can potentially stimulate the microbial population to decompose organic matter and increase soil oxidation rates.

Everglades wetlands of south Florida are traditionally P limited and sensitive to small increases in P loading (Noe et al. 2001). Reducing P export from the EAA is critical to fulfilling the emerging interests of protecting water quality and restoring south Florida ecosystems. Due to the increases in pH and the decreasing depth to bedrock of soils in the EAA, use of S application to counteract the rising pH may increase in the future. Therefore, a better understanding of how S influences pH and P distribution and availability within various pools during the sugarcane growing season is essential and the objective of this study.

## Materials and methods

### Site description

The experimental site is located in the central EAA on Dania muck (euic, hyperthermic, shallow Lithic Haplipsaprist) with a depth to bedrock of approximately 45 cm. The experimental design was a randomized complete block with four S application rates and four field replications. Each field plot measured 9 m × 13 m and consisted of 6 rows of sugarcane (*Saccharum* sp.). Elemental granular S (90%) was applied at rates of 0, 112, 224, and 448 kg S  $\text{ha}^{-1}$  to the furrow and covered after planting sugarcane in the furrow. Other fertilization was

provided using typical guidelines for this region (Rice et al. 2006). All fertilizers were soil-applied just prior to planting and included 17 kg N ha<sup>-1</sup> and 37 kg P ha<sup>-1</sup> as monoammonium phosphate, 228 kg K ha<sup>-1</sup> as KCl, 8.5 kg Mn ha<sup>-1</sup>, 4.5 kg Cu ha<sup>-1</sup>, 5.6 kg Fe ha<sup>-1</sup>, 2.8 kg Zn ha<sup>-1</sup>, and 1.1 kg B ha<sup>-1</sup>. All plots received typical cultural practices including cultivation and herbicide application. Water was applied via seepage irrigation in field ditches approximately 182 m apart. Sugarcane cultivar CP 89-2143 was planted in November 2007 and harvested in February 2009.

### Soil sampling and analysis

Soil samples were collected before planting and fertilizer application and then in January 2008, May 2008, August 2008, and December 2008, corresponding to approximately 0, 2, 6, 9, and 13 months after planting, respectively. Twelve soil (0–15 cm) cores (2.54 cm diameter) were randomly collected from rows within each field plot and composited. Soils were homogenized after the removal of visible plant residues and stored at 4°C.

Soil pH was measured with a soil to water ratio of 1:3 after equilibration for 30 min. Total organic C was measured by loss-on-ignition at 550°C for 4 h after conversion to organic C with a coefficient factor of 0.51 (Wright et al. 2008). Total organic N was measured by Kjeldahl digestion followed by NH<sub>4</sub> analysis (Bremner 1996). Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N were determined by extraction with 2 N KCl followed by colorimetric analysis (Castillo and Wright 2008). Acetic acid extractable nutrients were measured according to guidelines for muck soils (Sanchez 1990) by extracting 4 g soil with 25 ml 0.5 N acetic acid for 1 h, then filtering through Whatman #42 filters. Extracts were analyzed for Ca, Mg, Fe, and Al concentrations by ICP (Perkin–Elmer, Waltham, MA) using EPA method 200.7. Select soil nutrient concentrations and properties before S application are listed on Table 1.

Soils underwent a sequential chemical P fractionation procedure (Reddy et al. 1998; Wright 2009). Approximately 1 g soil was extracted with 25 ml water for 1 h, passed through 0.45 µm membrane filters, and analyzed for P (labile P). The remaining samples were extracted with 25 ml of 0.1 N NaOH for 17 h, filtered and analyzed for Fe–Al bound P

**Table 1** Chemical properties of the Dania soil in the Everglades Agricultural Area before fertilizer application

Soil property	Unit	Concentration
Total organic C	g kg <sup>-1</sup>	416
Total N	g kg <sup>-1</sup>	38
Total P	mg kg <sup>-1</sup>	850
Extractable NO <sub>3</sub> -N	mg kg <sup>-1</sup>	290
Extractable NH <sub>4</sub> -N	mg kg <sup>-1</sup>	16
Extractable Ca	mg kg <sup>-1</sup>	720
Extractable Mg	mg kg <sup>-1</sup>	105
Extractable Fe	mg kg <sup>-1</sup>	13
Extractable Al	mg kg <sup>-1</sup>	1.1

(Fe–Al–P), followed by the extraction of remaining samples with 25 ml of 0.5 N HCl for 24 h and analysis of Ca-bound P (Ca-P). The remaining samples were further digested with 6 N HCl for 1 h at 150°C and analyzed for residual P. Three ml of NaOH extracts was digested with 11 N H<sub>2</sub>SO<sub>4</sub> for 4 h at 350°C and analyzed for NaOH-TP. The humic–fulvic acid fraction was calculated by subtraction of NaOH-Pi from NaOH-TP. Phosphorous concentrations of extracts were measured using the ascorbic acid–molybdenum blue method (Kuo 1996) with an AQ2+ discrete analyzer (Seal Analytical Inc., Mequon, WI).

### Statistical analysis

Analysis of variance (ANOVA) was performed to determine the main effects (S application rate and time) and their interaction. Significant differences among individual treatments and time intervals were analyzed with Tukey's test at  $\alpha = 0.05$ . Pearson correlation and stepwise multiple regression analysis was employed to determine relationships among P fractions and soil properties. All statistical analysis was carried out with SAS 9.1 (SAS Institute).

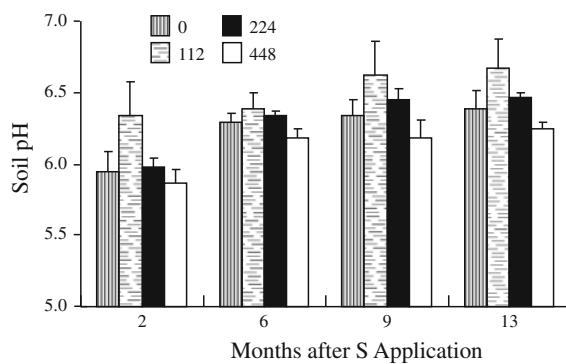
## Results and discussion

### Soil pH

Elemental S is applied in the EAA to lower soil pH for the purpose of improving nutrient availability for crop growth. Sulfur recommendations were

developed many years ago before large increases in soil pH occurred due to soil subsidence, thus, effectiveness of S amendment for the changed soil conditions in the EAA is in question (Schueneman 2001). Oxidation of elemental S to  $\text{SO}_4^{2-}$  produces  $\text{H}^+$  and therefore acts to reduce soil pH, although results may be temporary depending on the soil's buffering capacity (Bloom 2000). Overall, application within the range of 0–448 kg S  $\text{ha}^{-1}$  did not significantly reduce soil pH ( $P = 0.14$ ; Fig. 1). In the present study, the background soil pH prior to S application was 6.2, which was not significantly different from soils collected at any time of the growing season. However, soil pH dropped slightly at 2 months after S addition for the highest S application rate and increased thereafter from 6.0 to 6.4 at the end of growing season, which indicated a lagged effect of soil buffering. Additionally, no interaction effect of S application rate and sampling time ( $P = 0.58$ ) was found.

The limited effect of acidification may result from the relatively low rates of S application and from the high buffering capacity of this organic soil (Bloom 2000; Jaggi et al. 2005; Deubel et al. 2007). Soils with high concentrations of carbonates and bicarbonates are highly buffered against acidification (Bloom 2000; Rogovska et al. 2007). The buffering effects often take place more slowly than the formation of sulfuric acid, therefore, a re-increase of soil pH is possible (Bloom 2000; Deubel et al. 2007). A limited reduction in soil pH after S application was observed



**Fig. 1** Soil pH changes in response to different S application rates (0, 112, 224, and 448 kg S  $\text{ha}^{-1}$ ) throughout the sugarcane growing season. Error bars represent the standard error of the mean

in other studies of calcareous soils (Hassan and Olson 1966).

#### Phosphorus distribution

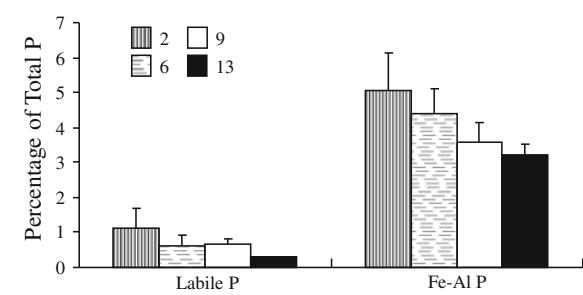
Two-way ANOVA demonstrated that the time effect was significant across all P fractions indicating significant seasonal changes in P distribution (Table 2). The main effect of S application rate was solely found significant on fractions of labile P and Fe–Al–P. No interaction effect of S application rate and time was observed for any of the P fractions.

#### Labile P

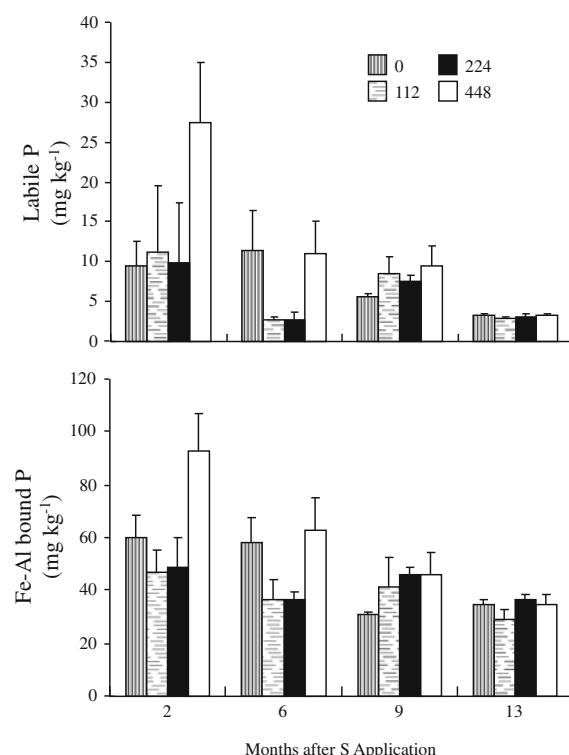
Labile P is commonly considered the most biological available form of P and consistently represented the smallest fraction of total P throughout the growing season, decreasing from 1.1 to 0.3% from 2 to 13 months (Fig. 2). Similar results were also observed in other studies (Maguire et al. 2000; Castillo and Wright 2008). The concentration of

**Table 2** Two-way ANOVA on different pools of P in soils amended with variable S application rates

Variable	P Value		
	Treatment	Time	Interaction
Labile Pi	0.046	0.006	0.258
Fe–Al bound P	0.024	<0.0001	0.077
Ca-bound P	0.289	0.005	0.615
Humic–fulvic acid P	0.469	<0.0001	0.114
Residual P	0.171	<0.0001	0.413
Total P	0.330	0.017	0.600



**Fig. 2** The percentage of labile P and Fe–Al bound P of soil total P throughout the sugarcane growing season. Error bars represent the standard error of the mean



**Fig. 3** Concentrations of labile P and Fe-Al bound P in soils 2, 6, 9, and 13 months after S application for different rates (0, 112, 224, and 448 S kg ha<sup>-1</sup>). Error bars represent the standard error of the mean

labile P decreased from 15 to 3 mg P kg<sup>-1</sup> from 2 to 13 months after S application (Fig. 3). Phosphorus in labile form is highly mobile, unstable, and prone to

loss either by leaching, runoff, or plant uptake, which explains the seasonal decrease observed in this study.

An increase in available P as a result of decreased soil pH has been documented in other studies (Deluca et al. 1989; Codling 2008). In the present study, labile P was significantly higher in soils receiving 448 kg S ha<sup>-1</sup> (13 mg P kg<sup>-1</sup>) when compared to soils receiving 112 (6 mg P kg<sup>-1</sup>) and 224 kg S ha<sup>-1</sup> (6 mg P kg<sup>-1</sup>; Fig. 3). There are two primary mechanisms by which S influences P availability: lowering of soil pH (Gabriel et al. 2008) and replacement of PO<sub>4</sub> with SO<sub>4</sub> and release of PO<sub>4</sub> from association with Fe, Al, and Ca (Jaggi et al. 2005). The significant positive correlations between extractable SO<sub>4</sub> and labile P (Table 3) were likely indicative of a partial stimulatory effect of SO<sub>4</sub> on the release of labile P. Statistical analysis also revealed significant correlations of labile P to Fe-Al-P ( $R^2 = 0.87$ ), Ca-P ( $R^2 = 0.49$ ), humic-fulvic acid P ( $R^2 = -0.36$ ), and soil pH ( $R^2 = -0.33$ ), suggesting possible P replenishment from other pools to the labile fraction (Table 3). Yet, Fe-Al-P ( $R^2 = 0.77$ ) was the major component in explaining the variance in labile P, while Ca-P and humic-fulvic-acid-P contributed to a better prediction.

$$\begin{aligned} \text{Labile P} = & 0.51 + 0.35 (\text{Fe-Al-P}) + 0.01(\text{Ca-P}) \\ & - 0.07(\text{Humic-fulvic-acid-P}) \\ (R^2 = 0.84, Cp = 3, P < 0.0001) \end{aligned}$$

**Table 3** Pearson correlations coefficients for P fractions and soil properties at  $\alpha = 0.05, n = 64$

	Labile Pi	Fe-Al-P	Ca-P	Humic-fulvic acid P	Residual P	Ca	Mg	Al	Fe	Mn	pH
Labile Pi	1										
Fe-Al-P	0.87	1									
Ca-P	0.49	0.34	1								
Humic-fulvic acid P	-0.36	NS	-0.39	1							
Residual P	NS	NS	0.60	-0.58	1						
Ca	0.26	NS	0.56	-0.53	0.65	1					
Mg	0.40	0.37	0.40	-0.44	0.25	0.66	1				
Al	0.62	0.68	NS	-0.29	NS	NS	0.46	1			
Fe	0.36	0.54	NS	-0.27	NS	NS	0.78	0.57	1		
Mn	0.38	0.36	0.47	-0.49	0.26	0.64	0.88	0.38	0.78	1	
pH	-0.33	-0.54	NS	NS	0.52	0.30	-0.3	-0.51	-0.50	NS	1

Ca, Mg, Al, Fe, and Mn = acetic acid-extractable concentrations; NS not significant

### Fe-Al bound P

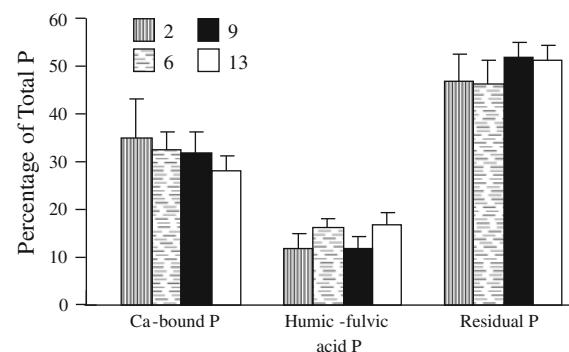
The Fe-Al fraction contains P associated with amorphous and crystalline Fe and Al oxides (Arai et al. 2005). Therefore, it was not surprising to find that Fe-Al-P was strongly correlated to Fe and Al content (Table 3), a finding that was also observed in other studies (Ryan et al. 1984; Maguire et al. 2000). Phosphorus concentrations in the Fe-Al bound fraction displayed a clear declining pattern during the growing season (Fig. 3). Concentrations decreased steadily from the beginning to the end of the season, averaging 62, 48, 41 and 34 mg P kg<sup>-1</sup>, respectively, for 2, 6, 9, and 13 months after S application. This observed decrease indicates that the Fe-Al bound P was a major source of P for sugarcane. Throughout the season, this fraction had the second lowest contribution to total P, averaging 4% (Fig. 2). In acidic soils, the Fe-Al-P is frequently the dominant fraction involved in P retention (Mozaffari and Sims 1996). However, the calcareous nature of this organic soil is likely to encourage more P sequestration in the Ca-bound rather than the Fe-Al bound fraction. Nonetheless, Fe and Al oxides play important roles in controlling P chemistry in soils with high CaCO<sub>3</sub> content (Halajnia et al. 2009). Other researchers also suggested that Fe and Al help to control P loss by leaching and runoff (Arai et al. 2005; Harrell and Wang 2007).

The pools of Fe-Al-P were not affected by S application rates from 0 to 224 kg S ha<sup>-1</sup> (Fig. 3). However, P concentrations in this fraction were significantly higher in soils amended with 448 kg S ha<sup>-1</sup>, averaging 59 mg P kg<sup>-1</sup>, than those receiving lower S rates. The Pearson correlation coefficient between Fe-Al-P and soil pH was significantly negative ( $R^2 = -0.54$ ; Table 3), indicating that a small decrease in soil pH is likely to encourage P retention in this fraction. Inversely, an increase in soil pH may potentially promote P desorption from fixation sites (Gessa et al. 2005), which may explain the continuous losses of Fe-Al-P over time along with increasing soil pH (Figs. 2, 3). Multiple regression analysis, in addition to correlation analysis, showed that 88% of the variance in Fe-Al-P could be explained by labile P, humic-fulvic acid P, and extractable Fe concentrations.

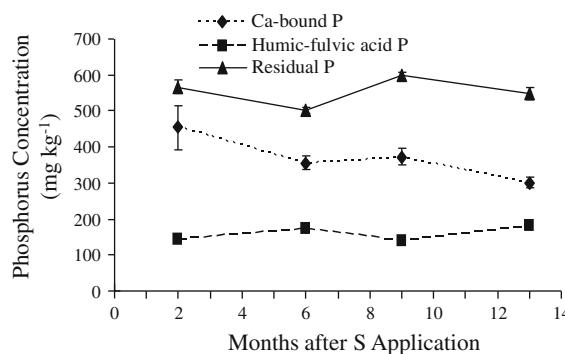
$$\begin{aligned} \text{Fe-Al-P} &= -25.4 + 2.0 \text{ (labile P)} \\ &\quad + 0.2 \text{ (humic-fulvic-acid-P)} + 2.2 \text{ (Fe)} \\ (R^2 &= 0.88, Cp = 4, P < 0.0001) \end{aligned}$$

### Ca-bound P

Phosphorus stocks in the Ca-bound fraction were much higher than those of labile and Fe-Al fractions, contributing 28–35% of the total P (Fig. 4) as a result of high Ca concentrations in the soil. Sugarcane cropping in the EAA requires multiple tillage applications prior to and during the growing season. This consequently results in the incorporation of the bedrock CaCO<sub>3</sub> into soil and promotes P retention in Ca-bound fractions (Castillo and Wright 2008). Correlation analysis revealed that Ca-P concentration was significantly correlated to soil Ca ( $R^2 = 0.56$ ), Mg ( $R^2 = 0.40$ ), and Mn ( $R^2 = 0.47$ ) concentrations indicating that some portion of P in this soil also exists as Mg-P and Mn-P. Association of P compounds with Mn in highly calcareous soils has recently been reported (Adhami et al. 2007), as such P compounds may originate from hureaulite [Mn<sub>5</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O] and reddingite [Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O]. The size of the Ca-P fraction declined gradually during the growing season from 454 mg P kg<sup>-1</sup> to 301 mg P kg<sup>-1</sup> by 13 months (Fig. 5). Previous studies suggested that under cultivated conditions Ca-P, rather than organic fractions,



**Fig. 4** The percentage of three P fractions to total P. Due to lack of significant effects of S, data for S application rates were averaged for presentation. Error bars represent the standard error of the mean



**Fig. 5** Concentrations of P in Ca-bound, humic-fulvic acid, and residual fractions of soils at various times after S application. Due to lack of significant effects of S, data for S application rates were averaged for presentation. Different letters for each fraction represent significant differences between sampling times

represents a stable P pool (Zhang and MacKenzie 1997; Castillo and Wright 2008).

The Ca-P fraction is considered relatively stable under alkaline condition, but unstable under acidic conditions. In the present study, S application did not impact the size of the Ca-P fraction as a result of the limited reduction in soil pH, which implied that Ca-P in this calcareous soil was not sensitive to slight changes in pH as was the Fe-Al-P and labile P fractions (Hassan and Olson 1966).

#### Humic-fulvic acid P

The organic pools are primarily comprised of humic-fulvic acids and the more recalcitrant residual fraction (Turner et al. 2005). Sulfur application did not influence P concentrations in this fraction at any sampling time or alter its proportion to total P. Phosphorus concentrations in the humic-fulvic acid fraction fluctuated during the growing season (Fig. 5). The percentage of humic-fulvic acid P to total P followed the same pattern, varying from 12 to 17% (Fig. 4). Phosphorus distribution in this fraction was negatively correlated to labile P, Ca-P and residual P fractions (Table 3).

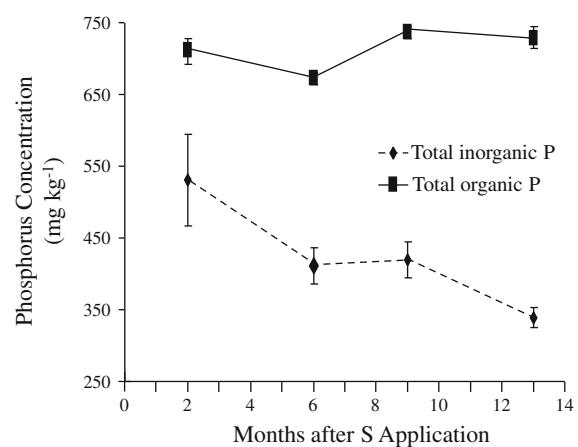
#### Residual P

Residual P was the most abundant P fraction for all sampling times, accounting for 47–51% of the total P (Fig. 4). This fraction is considered unavailable to

crops since the P is in organic form that must be decomposed before becoming available. However, due to subsidence, P contained in this residual fraction will eventually be made available to crops. Sulfur application did not alter P concentrations in this fraction or the contribution of this fraction to total P. Phosphorus concentrations in this fraction fluctuated during the growing season in a contrasting pattern to the humic-fulvic acid fraction, averaging 565, 501, 598 and 547 mg P kg⁻¹, respectively, for 2, 6, 9 and 13 months after S application (Fig. 5).

#### Phosphorus distribution and availability in S-amended soils

Phosphorus concentrations in the top 15 cm of soil averaged 1,244 mg P kg⁻¹ initially and decreased significantly to an average of 1,066 mg P kg⁻¹ at the end of the sugarcane growing season. Soils are capable of releasing P constantly into solution over a long period of time (Arai et al. 2005) due to release of mineral-bound P and decomposition of organically-bound P. However, P release varies with soil properties (Zhou and Li 2001). Active P fractions, such as labile P, Fe-Al-P, and Ca-P, comprise of the primary pools of desorbable P in weekly acidic and calcareous soils (Maguire et al. 2000). In the present study, the size of the inorganic P pools decreased by 13 months and consequently contributed to the decline in total P concentrations and the percentage of inorganic P to total P (Fig. 6). The P



**Fig. 6** Distribution of P among inorganic and organic pools after S application. Error bars represent the standard error of the mean

concentrations in this soil were a net result of the long-term balance between inputs (fertilization, rainfall and soil oxidation) and export (leaching, runoff, and sugarcane uptake). At the current rate of soil oxidation, approximately 60–90 kg P ha<sup>-1</sup> is generated annually (Wright 2009), which is greater than typical P fertilization rates to sugarcane (Rice et al. 2006) and P removed as harvested biomass (23 kg P ha<sup>-1</sup>; Coale et al. 1993). The significant reduction in total P indicates subsidence is a major source of P in runoff from EAA fields, which contributes to deterioration of water quality and modifications to proximal aquatic ecosystems (Childers et al. 2003). Therefore, land management that minimizes soil subsidence is likely to reduce the potential for P export. The majority of P in this soil was retained in organic forms (Figs. 2, 4), indicating the susceptibility of this soil to oxidation under drained conditions typical of sugarcane production in this region (Castillo and Wright 2008; Wright 2009).

Sulfur application at 448 kg S ha<sup>-1</sup> promoted P accumulation in labile P and Fe–Al–P fractions (Fig. 3) suggesting increased P availability to crops and as well as potential increased risk of P export (Codling 2008). However, no significant effects of S addition were found on total P and total inorganic and organic P concentrations. It was likely that the effects of S amendment on labile P and Fe–Al–P were confounded by the non-influential effects of sulfur on Ca–P, and considering the fact that Ca–P was the dominant inorganic fraction. A declining trend in pH for soils receiving 112–448 kg S ha<sup>-1</sup> corresponded to a declining trend in the size of Ca–P pool (Figs. 4, 5). It is reasonable to postulate that application rates beyond 448 kg S ha<sup>-1</sup> would continue to reduce soil pH and reach a point causing significant releases of P from the Ca-bound fraction (Gessa et al. 2005), which may be a cause of concern since Ca–P comprised 32% of total P and more than 80% of total inorganic P in this soil (Fig. 4). Nonetheless, using the current recommended S application guidelines and rates, the risk of P export from the Ca-bound P would be minimal. However, due to the increasing pH problem for EAA soils, there may be a need for greater S application rates in the future, which may overcome the soil's buffering capacity and in fact release large amounts of P from the Ca-bound pool and therefore pose an environmental hazard to nearby aquatic ecosystems.

## Conclusions

Organic P was the major form of P in this soil, averaging 63% of total P, while the Ca–P fraction dominated the inorganic pools, contributing 32% of total P. Total P concentrations in the surface soil decreased significantly at the end of growing season as a result of considerable reduction in inorganic P, especially labile P and Fe–Al–P, which comprised of the majority of available P for crops. Under current sugarcane production, organic P in this soil is susceptible to oxidation and a potential source for P loss. Application of S at rates up to 448 kg S ha<sup>-1</sup> introduced limited effects on reduction in soil pH, yet a small decrease in soil pH promoted P accumulation in labile and Fe–Al bound fractions, which increased P availability and as well as the risk of P export from these two fractions. The pool of Ca–P was relatively stable under current S application guideline and rates. Higher S rates than currently recommended may overcome the soil's buffering capacity and consequently release large amounts of P from the Ca-bound pool and pose an environmental hazard.

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