

Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound

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Abstract. The affinity of iron oxides and hydroxides for phosphorus is thought to contribute to phosphorus limitation to net primary productivity in humid tropical forests on acidic, highly weathered soils. Perennially warm, humid conditions and high biological activity in these soils can result in fluctuating redox potential that in turn leads to considerable iron reduction in the presence of labile carbon and humic substances. We investigated the effects of reducing conditions in combination with the addition of labile carbon substrates (glucose and acetate) and an electron shuttle compound on iron reduction and phosphorus release in a humid tropical forest soil. Glucose or acetate was added to soils as a single dose at the beginning of the experiment, and as pulsed inputs over time, which more closely mimics patterns in labile carbon availability. Iron reduction and phosphorus mobilization were weakly stimulated by a single low level addition of carbon, and the addition of the electron shuttle compound with or without added carbon. Pulsed labile carbon additions produced a significant increase in soil pH, soluble iron, and phosphorus concentrations. Pulsed labile carbon inputs also promoted the precipitation of ferrous hydroxide complexes which could increase the capacity for P sorption, although our results suggest that rates of P solubilization exceeded re-adsorption. Plant and microbial P demand are also likely to serve as an important sinks for released P, limiting the role of P re-adsorption. Our results suggest that reducing conditions coupled with periodic carbon inputs can stimulate iron reduction and a corresponding increase in soil phosphorus mobilization, which may provide a source of phosphorus to plants and microorganisms previously undocumented in these ecosystems.

Introduction

Highly weathered, humid tropical forest soils are often characterized by a dominance of iron (Fe)-rich minerals, high rates of carbon (C) cycling, and variable or fluctuating redox conditions. These characteristics lead to the potential for rapid rates of Fe reduction and re-oxidation. Old, wet tropical forest soils also tend to have low concentrations of labile phosphorus (P) due in

large part to minerals with high P sorption capacities (Sanchez 1976). Crystalline and non-crystalline oxides of Fe and aluminum (Al) are considered the main geochemical sinks of phosphate in acidic soils (Parfitt et al. 1975; Hsu 1977; López-Hernández 1977; Schwertmann and Taylor 1977; Parfitt 1978); non-crystalline Fe and Al oxides tend to control soil sorption reactions due to their large specific surface area (Parfitt 1989). Standard P extraction procedures conducted under aerobic conditions often yield low labile inorganic P pools from tropical forests soils (Johnson et al. 2003), and have led to the assumption that tropical forests obtain the majority of their P from soil organic matter (Herrera et al. 1978; Jordan 1982; Tiessen et al. 1994; Chacon and Dezzeo 2004). The organic P pool is generally small in relation to the inorganic P pool (Cross and Schlesinger 1995); for example, the amount of the inorganic P in resistant form typically ranges between 40 and 80% of the total P in the soil (Tiessen et al. 1994).

The high affinity of soil Fe and Al minerals for P is thought to be a primary mechanism responsible for P limitation of net primary productivity (NPP) in humid tropical forests (Vitousek 1984; Vitousek and Sanford 1986). This notion contrasts with high aboveground C density (Mackensen et al. 2000; Dezzeo and Chacon 2005), large P pools in forest soils and vegetation (Scatena et al. 1993; Silver 1994; Silver et al. 1996; Mackensen et al. 2000), and high rates of P cycling (McGroddy et al. 2004) reported for these forests. Although P retention by Fe and Al oxides has been considered a process of low reversibility in highly weathered tropical soils (Gijsman et al. 1996), undoubtedly the transfer of even modest amounts of P from this appreciable pool to the soil solution can play an important role in maintaining soil P bioavailability.

There are several mechanisms that could result in the release of P from geochemical pools under low redox conditions, including reduction of Fe(III) phosphates, hydrolysis and dissolution of Fe and Al phosphates, and release of clay-associated phosphates (Ponnamperuma 1972; Gambrell and Patrick 1978; Baldwin and Mitchell 2000; Chacon et al. 2005). Under reducing conditions bacteria obtain energy for growth by coupling the oxidation of organic matter to the reduction of different electron acceptors (Quantin et al. 2002; Stemmler and Berthelin 2003; Weiss et al. 2004). Manganese and Fe oxides are among the main electron acceptors in soils under anaerobic condition (Lovley and Phillips 1986; Quantin et al. 2002). As Fe(II) production occurs, phosphate anions chemically associated to Fe(III) oxides are released (Baldwin and Mitchell 2000).

These processes are likely to be stimulated by the availability of labile C and fluctuating redox conditions associated with high NPP, and warm perhumid conditions typical of wet tropical forests (Figure 1). Iron reduction is fueled by the availability of organic acids of low-molecular weight such as acetate (Küsel et al. 2002). More complex organic substrates such as glucose can also be used by Fe(III) reducers, however, it has been suggested that less than 5% of the reducing equivalents are transferred to Fe(III), while most of the glucose is degraded by fermentation (Lovley 1991). Humic substances can affect patterns

of Fe reduction and re-oxidation in soils. Several studies have shown that *Geobacter metallireducens* and *Shewanella alga* can use humic substances and quinones to transfer electrons between electron donors and acceptors (Lovley et al. 1996, 1998). For example, experiments with anthraquinone-2,6-disulfonate (AQDS), an analog to the humic acid, have shown that it can increase the rate and amount of Fe(III) reduction (Fredrickson et al. 1998; Zachara et al. 1998).

In this study we conducted a laboratory experiment to investigate the effects of reducing conditions on Fe reduction and soil P release in a humid tropical forest soil. We examined the effects of changes in redox alone, and in combination with the addition of an easily fermentable C substrate (acetate), a less fermentable C substrate (glucose), and an electron shuttle compound (AQDS) with and without an additional C substrate. We added glucose and acetate as a single dose and as a pulsed input over time. Pulsed inputs of organic substances to the soil are likely to have a different impact on microbial processes and biogeochemical cycling than static inputs, particularly if inputs effectively replenish resources depleted by biological or biogeochemical processes. In humid tropical forests, inputs of labile C tend to be pulsed, as opposed to constant over time or strongly seasonal and are driven by patterns in rainfall, wind, and plant and microbial growth and mortality (Lodge et al. 1994). We hypothesized the microbial reduction of Fe(III) can be an important mechanism for increased bioavailability of soil P due to frequent reducing conditions, and abundant labile C and Fe minerals.

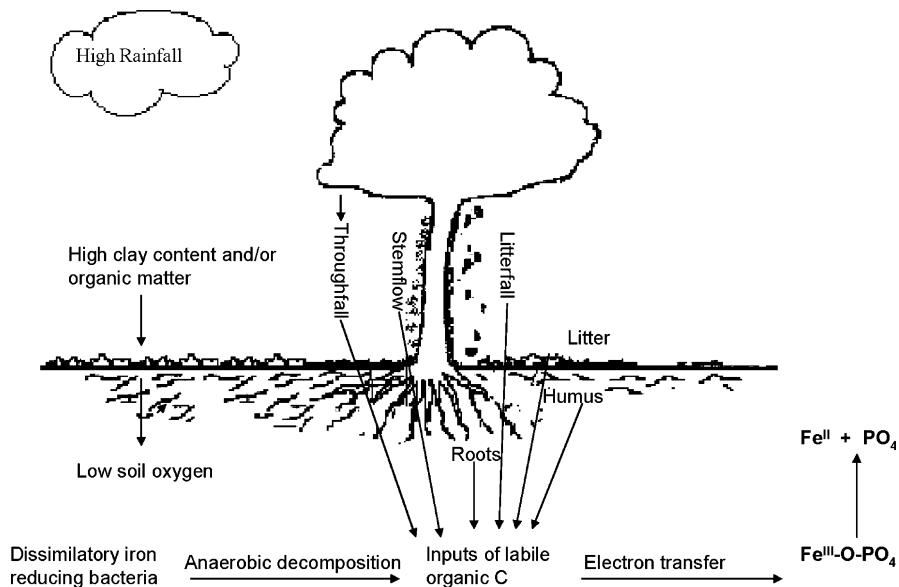


Figure 1. Schematic model of Fe(III) reduction and P release in humid tropical forests soils.

Materials and methods

Study area

The study was conducted with soils sampled from the Bisley Research Watersheds, part of the NSF-Sponsored Long Term Ecological Research Program in the Luquillo Experimental Forest (LEF) in northeastern Puerto Rico (18°18' N, 65°50' W). The Bisley Watersheds occur between 350 and 550 m above sea level, receive approximately 3500 mm of rainfall per year relatively evenly distributed throughout the year, and have an average annual temperature of 23 °C with little seasonal variation (Brown et al. 1986; Scatena 1989). Soils in the LEF are derived from volcanic sediments with Tertiary-age quartz-diorite intrusions of the Rio Blanco stock (Frizano et al. 2002). Soils at the study sites are characterized as acidic with high clay, Al, and Fe content. The labile P fraction considered most accessible to plant roots (Cross and Schlesinger 1995) was not detectable in these soils, while the moderately labile NaOH-extractable pool and the recalcitrant concentrated HCl-extractable pool represent the 20 and 67% respectively of the total P in the soil (McGroddy and Silver 2000). These soils are classified as Ultisols in the Humatus-Cristal-Zarzal series.

Soil sample and incubation

We collected a composite soil sample (about 10 kg) from the 0–10 cm depth. The sample was shipped immediately to U.C. Berkeley and maintained at room temperature in order to avoid detrimental impacts to microbes (Verchot 1999). Upon arrival, roots were manually removed and the samples were evenly split into seven treatments with 35 replicates each (Table 1). Our additions of labile C amounted to 0.09 mg C g dry soil⁻¹. This represents only a small percentage of the total labile C pool (4.7 mg C g dry soil⁻¹) as reported in McGroddy and Silver (2000). Our goal here was to add small pulses of labile C typical of weekly C inputs to the soil.

Table 1. Description of the experimental treatments.

Treatment	Description
Control	Without additional C source
Acetate	1 mM sodium acetate added at a rate of 0.960 mg C/20 g fresh soil
Acetate-3T	1 mM sodium acetate added in three installments on days 0, 2 and 7
Glucose	0.33 mM glucose added at a rate of 0.959 mg C/20 g fresh soil
Glucose-3T	0.33 mM glucose added in three installments on days 0, 2 and 7
AQDS	0.10 mM AQDS added at a rate of 0.672 mg C/20 g fresh soil
AQDS + glucose	0.10 mM AQDS added at a rate of 0.672 mg C/20 g fresh soil plus 0.33 mM glucose added at a rate of 0.959 mg C/20 g fresh soil

The samples were incubated as a slurry in amber 100 ml serum vials ($n = 5$ per treatment, total $n = 245$), using a 2:1 water to soil ratio. Anoxic conditions were created by flushing the vials for several minutes with 100% N_2 . Incubations were conducted at 25 °C for a period of 13 days. At selected times (0, 1, 2, 3, 6, 10, 13 days) five replicate samples from each treatment were destructively harvested in a glove box for gas production or consumption and chemical determinations. We measured the production of carbon dioxide (CO_2) and methane (CH_4) as indices of microbial activity.

Chemical measurements

We measured acid-extractable Fe(II) using 0.5 N HCl (Chao and Zhou 1983). It was used here as a measure of the total extent of reduction (Fe^{2+} production). Ferrous iron (Fe(II)) in the acidified extract was determined using the ferrozine assay (Lovley and Phillips 1987). Oxalate-extractable Fe and Al and the associated P pool were extracted using 0.2 M ammonium oxalate at pH 3 in the dark (McKeague and Day 1966). In reduced soils, oxalate extracts have been shown to extract poorly crystalline ferrous hydroxides compounds $Fe(OH)_2$, ferrosiferrous hydroxide, ferrous carbonate and soluble Fe(II) (Willet and Higgings 1978). Phosphorus in the oxalate extract was determined following Szilas et al. (1998) to avoid interference of the oxalate reagent. A 10 ml aliquot of extract was combined with 5 ml concentrated HNO_3 , evaporated at 100 °C, and digested. The residue was dissolved in 2 ml 0.3 M H_2SO_4 . Phosphorus concentrations were measured using a colorimetric method (Murphy and Riley 1962) after adjusting the solution to pH 4 using *p*-nitrophenol. Iron and Al concentrations in the oxalate extract were measured on an inductively coupled plasma spectrophotometer (Thermal Jarrel Ash, Framingham, MA) at U.C. Berkeley. A second soil subsample was extracted in 0.10 N NaOH and analyzed for PO_4 according to Murphy and Riley (1962). Soil pH was obtained in a 1:1 soil to water ratio.

Gas production

The headspace of each jar was sampled before harvesting to estimate the production of CO_2 and the production and/or consumption of CH_4 as an integrated measure of microbial activity. Twenty-five milliliters of gas samples were collected from each vial, transferred to 22 ml serum bottles and sealed with geomicrobial septa and silicon. Carbon dioxide and CH_4 were analyzed simultaneously on a SRI 8610C gas chromatograph using a thermal conductivity detector (CO_2) and a flame ionization detector (CH_4) at University of California, Berkeley. Standards of 100 ppm CO_2 and 10 ppm CH_4 were run every 10 samples to check for instrument drift.

Statistical analyses

Statistical analyses were performed using STATISTICA for Windows 6.0 (Statistica 2001). We used a one-way analysis of variance (ANOVA) to determine if treatments differed in pool sizes or rates. Data were log-transformed when necessary to meet the assumptions for ANOVA. We used a Tukey's test as a means separation procedure. We used a Kruskal–Wallis non-parametric test on data that did not meet assumptions for ANOVA (pH, HCl–Fe, oxalate-extractable Fe and P, and P_{sat} index). Simple linear correlations were used to assess the relationship between Fe(II) production and pH. Exponential ($y = e^x$), logarithmic ($y = \ln(x)$) and linear ($y = m + bx$) models were used to assess the relationship between Fe(II) production and oxalate-extractable Fe. In each case the model with the highest r^2 value was selected as the best fit to the experimental data. The relationship between Fe(II) production and CO_2 or CH_4 effluxes was analyzed using Pearson correlation coefficients. All the correlations were tested for significance at the 95% level.

Results

Effects of labile carbon and an electron shuttle compound

An anoxic headspace alone and in combination with labile C and AQDS additions resulted in a small, but significant immediate increase in HCl-extractable Fe(II) and oxalate-extractable P (Table 2). Oxalate extractable Fe and NaOH-Pi increased in all treatments except the control and single dose glucose addition, and pH increased in all treatments except the single dose acetate and AQDS additions (Table 2). After this initial phase (day 3) HCl-extractable Fe (II), soil pH, and oxalate-extractable Fe continued to increase with the pulsed C inputs, but did not show a similar pattern in controls or with

Table 2. *F*-statistics for ANOVAs of changes in Fe, P and pH pools over the first 3 days of the anaerobic soil incubation.

Treatment	Studied parameters				
	P_{ox}	Fe_{ox}	NaOH-Pi	HCl–Fe(II)	pH
Control	3.83*	ns	ns	11.90***	8.67**
Acetate	4.28*	3.39*	7.19**	34.42***	ns
Acetate-3T	3.39*	17.28***	9.48**	31.73***	8.23**
Glucose	5.14*	ns	ns	3.61*	5.70**
Glucose-3T	9.58**	15.49***	9.27**	27.78***	8.06**
AQDS	5.39*	3.45*	8.86**	13.94***	ns
AQDS + glucose	4.02*	7.03**	4.23*	12.37***	10.86***

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

single-dose C additions (Figures 2 and 3). A short term increase in oxalate-extractable Fe occurred between the 6th and 10th day after a single acetate addition and there was no effect of a single dose of glucose. Soil pH was strongly positively correlated with Fe(II) concentrations in the pulsed C

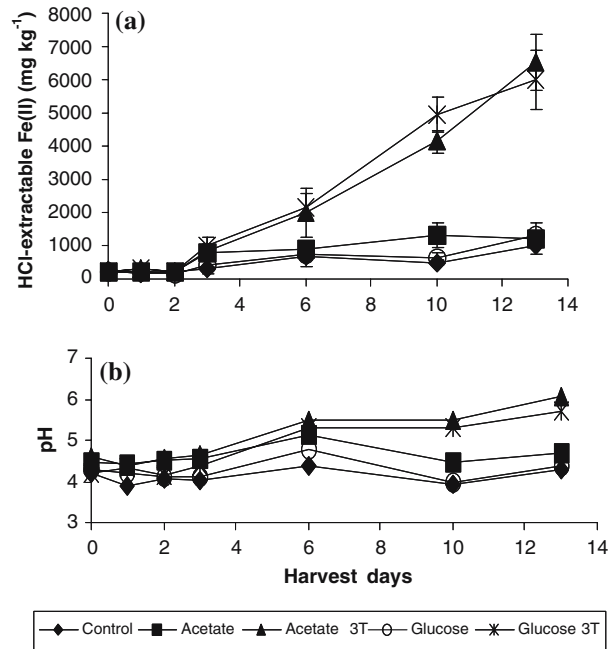


Figure 2. Effect of labile C source on Fe(II) production (a) and pH (b). Acetate-3T and glucose-3T = labile C added in three installments. Values are means \pm 1 standard deviation.

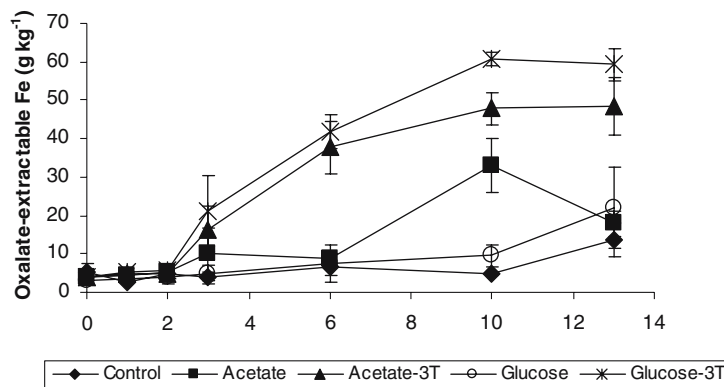


Figure 3. Effect of labile C source on the content of oxalate-extractable Fe. Acetate-3T and glucose-3T = labile C added in three installments. Values are means \pm 1 standard deviation.

addition treatments (Table 3). In all the treatments, oxalate-extractable Fe was strongly and positively correlated with Fe(II) (Figure 4). With pulsed C additions the relationship approached saturation near 2000 $\mu\text{g g}^{-1}$ Fe(II) and

Table 3. Relationship between pH and Fe(II) production in experimental treatments (significance was determined at the 95% level).

Treatment	R^2	Significance level	Equation
Control	0.32	0.001	$\text{pH} = 3.96 + 0.0004\text{Fe(II)}$
Acetate	0.18	0.05	$\text{pH} = 4.48 + 0.0002\text{Fe(II)}$
Acetate-3T	0.83	0.001	$\text{pH} = 4.53 + 0.0002\text{Fe(II)}$
Glucose	0.14	0.05	$\text{pH} = 4.15 + 0.0002\text{Fe(II)}$
Glucose-3T	0.83	0.001	$\text{pH} = 4.25 + 0.0002\text{Fe(II)}$
AQDS	0.10	ns	$\text{pH} = 4.14 + 0.0002\text{Fe(II)}$
AQDS + glucose	0.48	0.001	$\text{pH} = 4.13 + 0.0003\text{Fe(II)}$

ns = not significant.

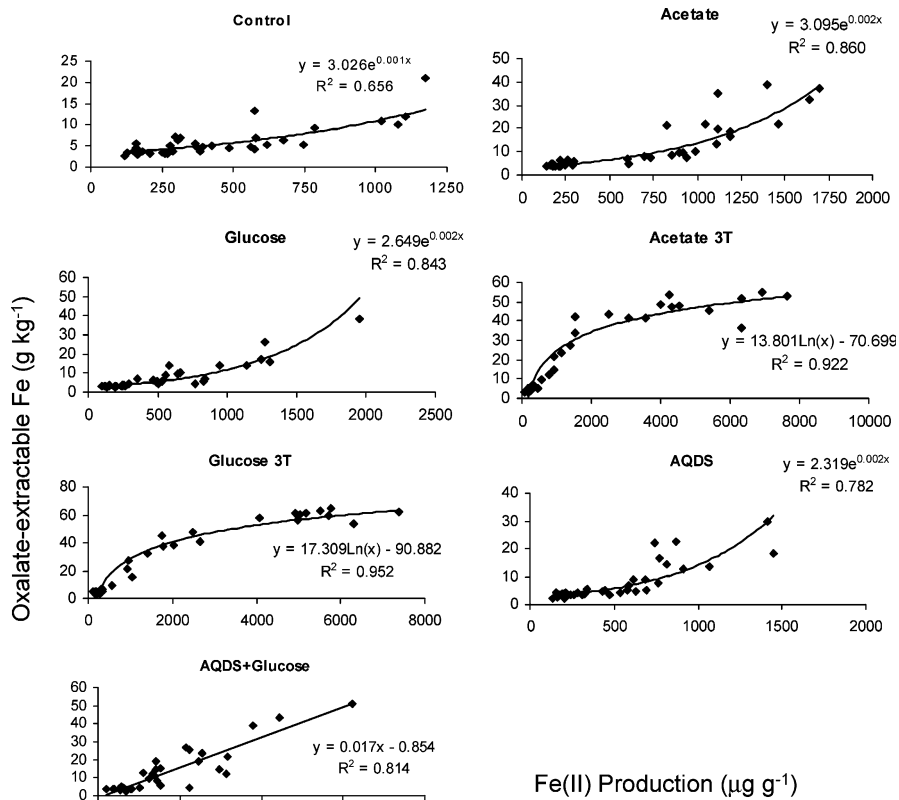


Figure 4. Relationships between Fe(II) production and oxalate-extractable Fe.

40 g kg⁻¹ oxalate-extractable Fe (Figure 4), while in the control, single C dose, and AQDS treatments oxalate-extractable Fe increased linearly.

Changes in the behavior of Fe oxides were reflected in the soil P fractions. Oxalate-extractable P followed the same trend as oxalate-extractable Fe (Figure 5a) with the largest effect in the pulsed C treatments after the 3rd day of soil incubation and little or no significant effect from a single dose of glucose or acetate. The alkaline-extractable inorganic P fraction (NaOH-Pi) was only sensitive to the pulsed glucose additions (Figure 5b); this fraction is associated with the strongly chemisorbed P on amorphous and some crystalline Al and Fe phosphates (Tiessen et al. 1983).

The molar ratio of oxalate-extractable P:(oxalate-extractable Fe + oxalate-extractable Al) can be used as an index of the P saturation (P_{sat}) status of soils. High values of P_{sat} are indicative of a low P sorption capacity where P can be released after dissolution of Fe oxides and resorbed under oxidizing conditions (Szilas et al. 1998). In this study, the P_{sat} index range from 0.005 to 0.001. Pulsed C additions quickly led to low values of P_{sat} (after the 3rd day of soil

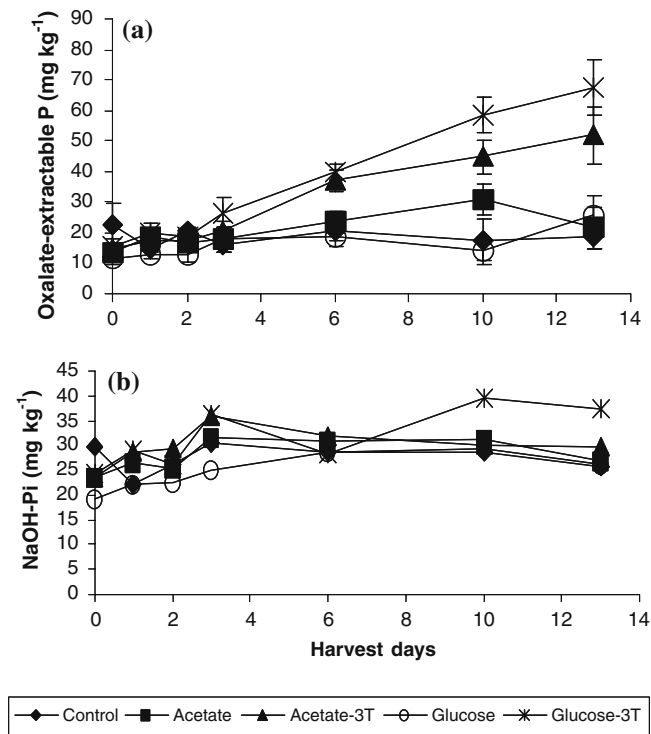


Figure 5. Effect of the labile C source on oxalate-extractable P (a) and alkali-extractable P (b). Acetate-3T and glucose-3T = labile C added in three installments. Values are means \pm 1 standard deviation.

incubation), while in the other treatments P_{sat} decreased only at the end of the experiment (days 10 and 13).

The addition of AQDS alone did not produce significant changes in Fe(II), oxalate-extractable Fe, or pH with respect to the control (Figure 6a and b; Table 3). Glucose + AQDS increased Fe(II) and oxalate-extractable Fe, but Fe dissolution did not result in a significant release of oxalate-extractable P or NaOH-Pi (Figure 7a and b).

Biodegradation of organic matter

Both CO_2 and CH_4 production peaked during the 1st day of soil incubation in all treatments (Figure 8). After the 2nd day of soil incubation, rates of CO_2 production decreased and stayed relatively constant throughout the rest of the experiment (2 and 6 $\mu\text{g g dw}^{-1} \text{day}^{-1}$). Methane production declined after the 1st day in all treatments, and then increased significantly in the pulsed C treatments after the 6th day of soil incubation (Figure 8b). The increase was greater in the glucose additions than in the acetate additions. Fluxes of CO_2

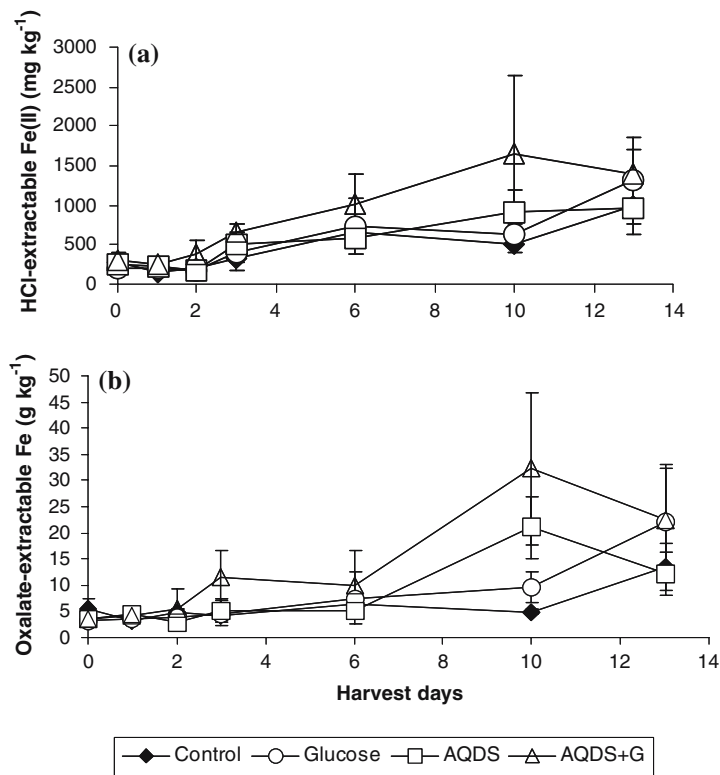


Figure 6. Effect of AQDS and AQDS + glucose on HCl-extractable Fe (a) and oxalate-extractable Fe (b). Values are means \pm 1 standard deviation.

and CH_4 were negatively correlated with Fe(II) production in the control and following a single dose of labile C (Table 4).

Discussion

Effects of added C and AQDS on Fe and P dynamics

Humid tropical forest soils are often characterized by heterogeneous physio-chemical environments (Lodge et al. 1994), where the availability of soil oxygen (O_2), C, and electron couples fluctuate over short temporal scales (hours to days) and small spatial scales (centimeters to meters) (Silver et al. 1999; Pett-Ridge and Firestone 2005). Periodic depletion of soil O_2 availability coupled to high Fe content and inputs of labile C are likely to make to these ecosystems suitable sites for bacterial Fe(III) reduction, which can increase the solubility of P associated with Fe oxides.

In this study, the decline in soil O_2 availability alone and in combination with the addition of C or an electron shuttle compound led to Fe(III) reduction during the first 3 days of soil incubation. After this initial period, pulsed C inputs in combination with reducing conditions were necessary to increase

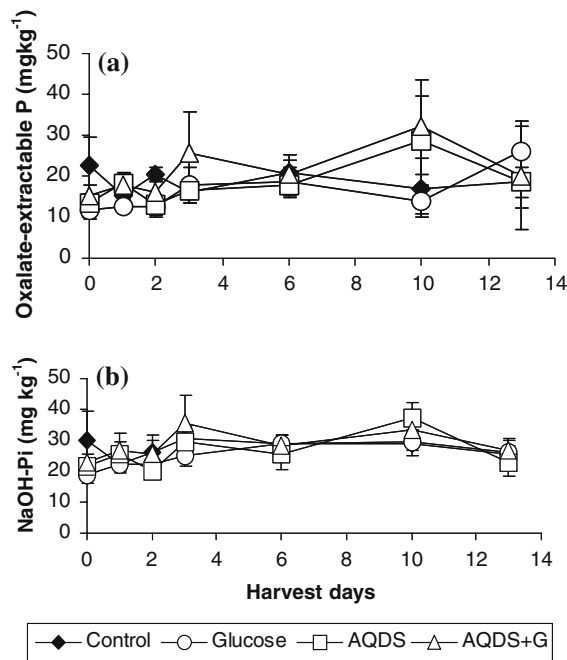


Figure 7. Effect of AQDS and AQDS + glucose on oxalate-extractable P (a) and alkali-extractable P (b). Values are means \pm 1 standard deviation.

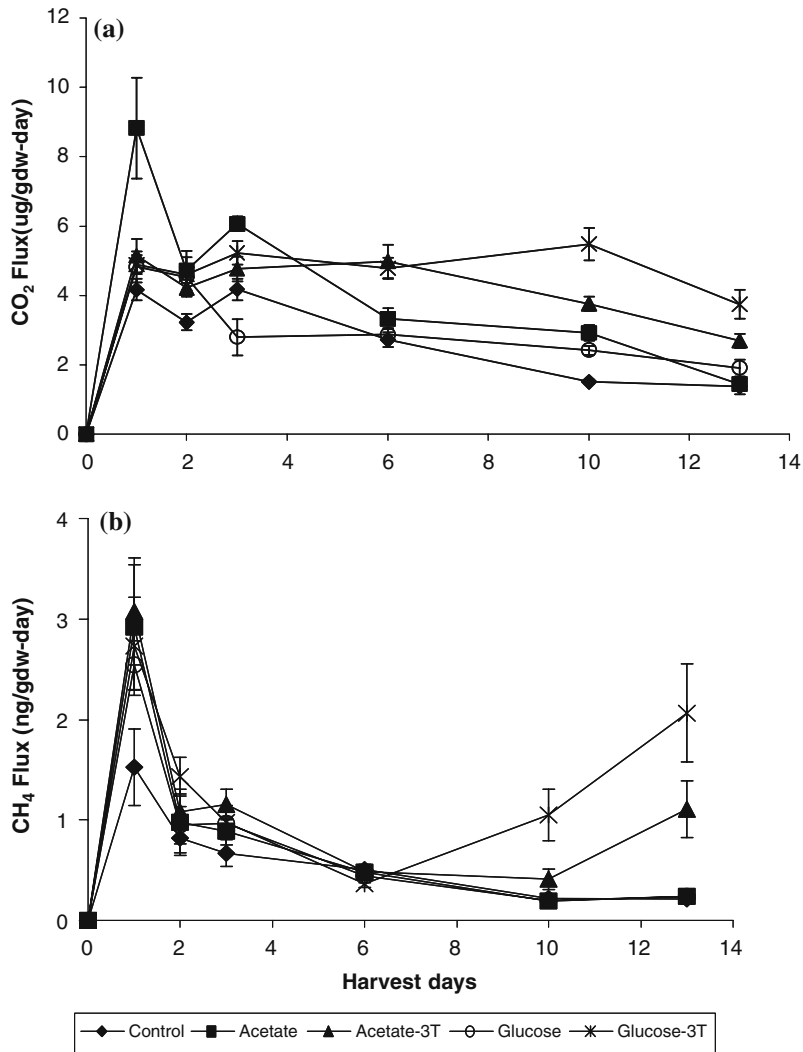


Figure 8. Effect of labile C source on CO₂ (a) and CH₄ (b) fluxes. Acetate-3T and glucose-3T = labile C added in three installments. Values are means \pm 1 standard deviation.

rates of Fe(III) reduction. The production of Fe(II) was positively correlated with soil pH in most treatments, due to the general tendency of proton consumption during microbial reduction of Fe(III) (Ponnamperuma 1972). The lack of correlation between Fe(II) production and pH in the AQDS treatment, and the weak correlations obtained in the control and single dose C additions suggests that Fe(III) reduction was not a significant pathway for organic matter decomposition in those treatments. Our data also suggest that C

Table 4. Pearson coefficient correlation between CO₂, CH₄ flux and Fe(II) production.

Treatment	CO ₂ flux vs. Fe(II) production	CH ₄ flux vs. Fe(II) production
Control	-0.71	-0.57
Acetate	-0.70	-0.63
Acetate-3T	ns	ns
Glucose	-0.60	-0.57
Glucose-3T	ns	ns
AQDS	-0.51	-0.43
AQDS + glucose	-0.42	-0.59

ns = not significant.

availability may have limited Fe(III) reduction rates in the control and single dose treatments.

We can estimate the potential for C limitation to Fe reduction under natural conditions using some simplifying assumptions. The amount of labile C added to our soil is equivalent to 0.06 Mg C ha⁻¹ (using a bulk density of 0.64, Silver et al. 1994), and 4.7 Mg C ha⁻¹ y⁻¹ assuming three pulsed inputs every 2 weeks. This amount is similar to the standing stock of labile C reported in McGroddy and Silver (2000). In this a seasonal ecosystem, C inputs are distributed throughout the year; storm events and treefalls could increase C inputs to the soil surface resulting in large pulses of labile C (Ostertag et al. 2003). Thus, the pulsed C additions for this experiment are comparable to natural C inputs at the study site and suggest that Fe(III) reduction under natural soil conditions is not likely to be C-limited. Furthermore, we speculate that disturbance events that result in strong C pulses could result in significant P release via Fe reduction if coupled with reducing conditions.

Bacterially generated Fe(II) undergoes secondary chemical reactions, which lead to the precipitation of ferrous Fe solids as vivianite (Fe₃(PO₄)₂·8H₂O) and siderite (FeCO₃) (Fredrickson et al. 1998; Zachara et al. 1998; Dong et al. 2000). Both minerals can be an effective sink for Fe(II) (Dong et al. 2000). In this study we did not observe either a decrease in pH or the formation of purplish-blue precipitate characteristic of vivianite formation. It is possible that siderite was formed, particularly given the high concentration of CO₂ during the later phases of the experiment. Future studies should investigate the possibility of siderite formation and implications for Fe and P cycling.

In addition to the precipitation of Fe(II) minerals, ferric hydrous oxides can also be reduced to ferrous hydroxide gel complexes (Ponnamperuma et al. 1967). Freshly precipitated Fe(OH)₂ would be in amorphous form (Shukla et al. 1971) and have a greater surface area (Holford and Patrick 1979) than the original ferric compound, potentially resulting in greater P sorption capacity (Patrick and Khalid 1974; Willet and Higgings 1978; Holford and Patrick 1979). As mentioned above, oxalate extracts have been shown to extract poorly crystalline ferrous hydroxides compounds such as Fe(OH)₂. In this

study the observed increase in oxalate-extractable Fe as progressive Fe(III) reduction took place with C pulses could be ascribed to the extraction of freshly precipitated Fe(OH)₂ compounds. The relationship between Fe(II) and oxalate-extractable Fe suggests that the formation of ferrous compounds from the dissociated Fe(II) reached a saturation level in the treatments with pulsed C inputs. This saturation state suggests that the production of Fe(II) surpasses the precipitation of ferrous hydroxide complexes.

Pulsed C inputs also led to an increase in oxalate-extractable P with increasing oxalate-extractable Fe, reaching high levels of extractable P by the end of the experiment. This high mobilization of P, associated with inputs of labile C and Fe dissolution, supports observed patterns in soil P fractions in this ecosystem (McGroddy and Silver 2000). Moderately labile P fraction (NaOH-Pi), which is likely to include P that is sorbed on Fe and Al oxides, was positively correlated with soil moisture and the light C fraction. Soil moisture (often negatively correlated to soil redox) and labile C availability increase, Fe(III) reduction is enhanced and P is released.

The high P mobilization from the reduction of Fe(III) in humid tropical forests could result in an increase in soil P availability and plant uptake. A recent study by Wood et al. (2005) showed that the leaf litter P concentrations in tropical forests were positively correlated with rainfall. The authors suggest that this positive relationship could be a response to increased P availability associated with higher soil moisture.

It is possible that some of the P released via Fe reduction was re-adsorbed to freshly precipitated Fe(OH)₂ due to the large reactive surface area of these compounds. In this study pulsed C inputs accelerated the reduction of Fe(III) to ferrous compounds and the mobilization of P, while at the same time increasing the P sorption capacity of the soil evidenced by the decrease in the P_{sat} index over time. Although P mobilization increased over time, the rate of P release may be an underestimate if some of the mobilized P was simultaneous re-adsorbed on Fe surfaces. Several authors have shown a decrease in water-soluble PO₄ in anaerobic soils due to P re-adsorption on ferrous hydroxide gel complexes (Patrick and Khalid 1974; Willet and Higgings 1978; Holford and Patrick 1981; Phillips and Greenway 1998). Plant and microbial P demand may effectively compete with P re-adsorption, particularly if re-adsorption is delayed as suggested by our results.

Biodegradation of C coupled with Fe(III) reduction

Under anoxic soil conditions the final step of organic C mineralization leads to the production of CH₄ in methanogenic environments or to CO₂ production if inorganic electron acceptors (NO₃⁻, Fe(III), SO₄²⁻) are available. In this study, we measured rapid microbial utilization of the easily metabolizable C substrates and resulting fluxes of CO₂ and CH₄. With the progressive solubilization of Fe(II), the production of CH₄ and, to a lesser extent, that of CO₂

was inhibited in the control and single C dose treatments. This inhibition was corroborated by the negative correlation between Fe(II) production and CO₂ or CH₄ flux. In the treatments with pulsed C inputs ferric iron reducers and methanogenic bacteria were able to utilize the fermentable C substrate, thus CH₄ efflux increased after the second dose of acetate and glucose without a delay in Fe(II) production. Previous studies have shown that ferric iron reducers can compete with methanogenic bacteria, causing the inhibition of CH₄ production (Lovley and Phillips 1986; Achtnich et al. 1995; Chidthaisong and Conrad 2000). Our data suggest that at low levels of available C, Fe reducers inhibited CH₄ production, but at higher levels of substrate availability CH₄ production did not compete with Fe reduction.

Conclusion

Our results suggests that in ferralitic soils characteristic of humid tropical forests, soil P availability is strongly coupled to C and Fe cycles. Spontaneous pulses of organic acids of low molecular weight, when coupled with periodic reducing conditions, are a suitable source of energy to Fe-reducing bacteria. Microbial reduction of Fe(III) led to the release of P strongly sorbed on the surfaces of Fe oxides. However, under periodic labile C inputs ferric hydrous oxide can be reduced to ferrous hydroxide gel complexes. High concentrations of freshly precipitated Fe(OH)₂ may lead to an increase in the P sorption capacity, although results from our study suggest that P solubilization exceeded rates of re-adsorption. High plant and microbial P demand under natural conditions could also limit rates of P re-adsorption. Our results highlight the importance of Fe(III) reduction as a potential source of available P under short-term anoxic conditions in humid tropical forest soils, and the role of periodic C inputs to fuel the process in these highly productive ecosystems. Phosphorus release via Fe reduction is likely to provide an important and poorly documented source of labile P in highly weathered tropical soils and may in turn contribute to the high NPP observed in these ecosystems.

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