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Short communication

Implications of iron solubilization on soil phosphorus release in seasonally flooded forests of the lower Orinoco River, Venezuela

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Abstract

The microbial reduction of Fe oxides is thought to contribute with the release of P in sedimentary environments. However, secondary reactions of the bioproduced Fe(II) with P in solution, can lead to a decrease in the soluble P concentration. In this study, we examined how the reduction of Fe(III) affects the soluble P concentration, when the soils of a seasonally flooded forest gradient are subjected to anaerobic conditions. Soil samples were collected during the dry season from two zones subjected to different flooding intensity: MAX and MIN zones that were inundated 8 and 2 months per year, respectively. When anaerobic conditions were applied to soils from both zones, a clear stimulatory effect on the Fe(III) reduction was observed. However, bioproduced Fe(II) underwent secondary chemical reactions, masking the extend of Fe(III) reduction of these soils. Iron was reduced mainly during the first 15 days of the anaerobic incubation and it was stimulated by a pulse of labile carbon. Iron dissolution did not lead to an increase of the soluble P content. However, in both zones P was high and positively correlated with Fe(II), implying that soil P mobilization was linked to Fe dissolution. In the MIN zone, soluble P concentration decreased, probably as a consequence of the secondary reactions of solubilized P with other non-redox sensitive soils elements. Fe solubilization also had an effect on the activity of acid phosphatase and consequently in the solubilization of P from the organic pool. In conclusion, the P cycle in these soils is strongly coupled to C and Fe cycles.

Keywords: Anaerobic soils; Iron dissolution; Phosphorus mobilization

Extensive areas of river watersheds in the tropics are covered with forests, some of which are seasonally flooded (Kubitzky, 1989). These forests are characterized by annual oscillations between aquatic and terrestrial phases (Junk et al., 1989). The productivity of these forests in the humid tropics is thought to be limited by the phosphorus (P) supply (Vitousek, 1984). Soils in this region are nearly depleted of primary P-containing minerals and most of this element is found predominantely chemisorbed on amorphous minerals and some is also found on crystalline iron (Fe) and aluminum (Al) oxides (López-Hernández, 1977; Hsu, 1977; Schwertmann and Taylor, 1977; Parfitt, 1978; Parfitt and Smart, 1978). For these ecosystems, soil P mobilization has been associated with the biogeochemistry of Fe (Gambrel and Patrick, 1978; Baldwin and Mitchell, 2000; Chacon et al., 2005a).

Water in soil restricts gas diffusion and limits the oxygen availability in soil (Smith and Tiedje, 1979), with a consequent decrease in the soil redox potential (Gambrel and Patrick, 1978). Under such circumstances, microbial dissolution of Fe(III) oxides can take place (Lovley et al., 1991; Baldwin et al., 1997; Baldwin and Mitchell, 2000) and the phosphate anion chemically sorbed to these iron oxides surfaces can be released (Baldwin and Mitchell, 2000). Indeed, several studies have found that P concentration increases when soils become waterlogged (Moore et al., 1992; Szilas et al., 1998; Ferrando et al., 2002). However, Fe(II) produced by the reduction of Fe(III) oxides may undergo chemical transformations, affecting the concentration of P in solution. For example, ferric hydrous oxides can be reduced to amorphous ferrous hydroxide gel complexes ($Fe(OH)_2$) (Ponnamperuma et al., 1967), with a greater surface area than the original ferric compound (Holford and Patrick, 1979). This results in an increase in P sorption capacity (Patrick and Khalid, 1974; Willet and Higgins, 1978; Holford and Patrick, 1979; Phillips and Greenway, 1998). Phosphorus concentration may also decrease during flooding due to the precipitation of ferrous phosphate (vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$) (Zachara et al., 1998).

In a previous study, along a flooded gradient, Chacón et al. (2005a) found that both labile and moderately labile soil P

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concentrations were strongly associated with the amount of crystalline Fe oxides, when the soils were under aerobic condition. Based on this previous study, we hypothesized that any change occurring in the behavior of Fe oxides during the anoxic period, may affect the size of the labile P pool. Therefore, in this study, we examined how the reduction of Fe(III) affects the soluble P concentration when seasonally flooded tropical soils are subjected to anaerobic conditions.

The soil samples were collected from the floodplain of the Mapire River located in south-east Venezuela, between 7° 30′–8° 30′N and 64° 30′–65° 00′W. This river is a northern tributary of the lower Orinoco River, and its basin constitutes a region of low relief covered by the Pleistocene Mesa Formation (Carbón and Schubert, 1994). The Mapire river has been classified as a black-water river due to its brown color and its oligotrophic character in terms of nutrient, sediment load and primary productivity (Vegas-Vilarrúbia, 1988). According to the climatic diagram of the region (Vegas-Vilarrúbia and Herrera, 1993), the annual mean temperature is 27.4 °C and the annual precipitation averages 1333 mm, with the dry season between November and April and the rainy season from May to October. Forests communities of the Mapire river are related to longitudinal and perpendicular gradients of flooding depth and duration, which are associated with local topography.

Soil samples were collected from two zones of a flooded gradient perpendicular to the course of the Mapire River: a low zone close to the river margin where the flood reaches a maximum of 12 m and lasts up to 8 months (from May to December) (MAX zone), and a high zone where the flood reaches a maximum of 1 m for 2 months (from July to September) (MIN zone). In each zone, the surface mineral horizon (0–10 cm) was sampled in six points arranged into three transects with two sampling points in each one. A total of six samples per zone were taken with an auger during the dry season (March 2003). The soil samples were air-dried and passed through a 2-mm sieve.

From each soil sample, four subsamples were taken for the incubation experiment ($n=24$ per zone). Dry soil was placed in glass jars of 500 mL and a slurry was prepared, using a 2.5:1 water/soil ratio. Anoxic condition was created using 100% N_2. Soil samples were then incubated at 25 °C for a period of 2 months. In order to ensure anaerobic conditions, the jars were flushed with N_2 gas every 2 days. At selected times (i.e. 0, 15, 30 and 60 days), six replicate samples from each zone were analyzed for pH, HCl-extractable-Fe (HCl–Fe(II)) and associated inorganic P (HCl–Pi), soil organic carbon (SOC), and acid phosphatase activity (APA). pH was measured in a soil–water mixture at a 1:2.5 soil:water ratio. Acid-extractable Fe(II) was obtained using 0.5 N HCl (Fredrickson et al., 1998) and was considered a measure of the total extent of reduction (Fe^{2+} production). Iron content was determined by absorption atomic spectroscopy and it was assumed that all was ferrous iron. Inorganic P concentration in the acidified extract was determined using the colorimetric method of Murphy and Riley (1962) after adjusting to pH 4 using *p*-nitrophenol. Soil organic carbon was obtained using the Walkley and Black (1934) wet oxidation method. The acid phosphatase activity (APA) was determined using *p*-nitrophenylphosphate (*p*-NPP) as substrate at a temperature of 37 °C (Tabatabai and Bremner, 1969).

Statistical analysis of the data was carried out by a one-way ANOVA. Data were log-transformed when necessary to meet the assumptions for ANOVA. A Tukey honestly significant difference (HSD) test was used when statistical differences ($P<0.05$) were observed. A Kruskal–Wallis non-parametric test was used on data that did not meet assumptions for ANOVA. The relationship between HCl-extractable Fe(II) and inorganic P was analyzed using simple linear regressions and tested for significance at the 5% level. All statistics were computed using STATISTICA for Windows 6.0 (Statistical, 2001).

In the studied soils, the anaerobic condition lead to a decrease in the content of Fe(II), particularly after 15 days of soil incubation, but the decrease was significant only in the soils of the MAX zone (Fig. 1a). Along the incubation period, soil pH increased in both zones, but the increase was slow in the soil of the MAX zone (Table 1). During the first 4 weeks of anaerobic incubation a putrefying odor was present in the soils of the MAX zone. However, at the end of the experiment (day 60), the odor disappeared and the soil pH increased significantly respect to the soil initial condition (Table 1). In the soils of the MIN zone the odor was not present, but a green–blue precipitate, in colloid form, was observed in the early stage of the experiment. This colloid disappeared at the end of the experiment. Soils of the MAX zone did not show precipitate during the incubation period.

In sedimentary environments, two non-enzymatic mechanisms have been postulated for Fe(III) reduction.

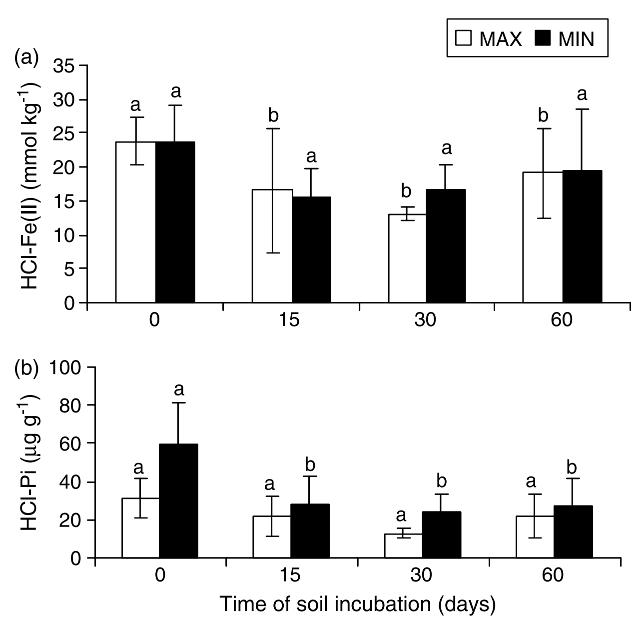

Fig. 1. Fe(II) production (a) and soluble P concentration (b) in the acidified extract. Mean values ± SD. MAX, maximum flooding zone; MIN, minimum flooding zone. Lowercase letters denote significant differences over time within a zone ($P<0.05$).