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Solubility of phosphorus in subtropical forest soils as influenced by low-molecular organic acids and key soil properties

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ABSTRACT

Low phosphorus (P) solubility in soil limits primary productivity in terrestrial ecosystems worldwide. However, our understanding about drivers of soil P solubility is still incomplete. This study examined the levels of water soluble inorganic P (Pi) and organic P (Po) in soils under mature subtropical forests in China, and how they can be influenced by three low-molecular organic acids (LOAs, i.e. citric, malic and oxalic acids) and key soil properties (e.g. organic C concentration). Water soluble Pi (mean 0.05 mg kg^{-1}) and Po (0.32 mg kg^{-1}) in the soils studied were generally low, compared to in many other areas of the world. While all three LOAs significantly solubilized P from the soils studied as a whole, the solubilized amount varied greatly among soils and also varied largely with the type of LOA and P forms. Solubilized Po by the three LOAs were > 2.5 times of the solubilized Pi. Soluble total P (Pi + Po) increased in the order of oxalic acid < malic acid < citric acid and was positively related to the soluble aluminum and iron. Rock fragment (4–50 mm) content explained 69%, 51%, and 31%, respectively, of the variations in water, oxalic acid, and malic acid soluble Pi. Efficiencies of the three LOAs in solubilizing Pi, but not Po, generally increased with soil organic C, total N, total P, and microbial biomass C concentrations. Our results suggest that interplay among P forms, LOAs, and soil properties control soil P solubility.

1. Introduction

Phosphorus (P) limits primary productivity in terrestrial ecosystems worldwide (Augusto et al., 2017). Soil is the major source of P for plant growth in terrestrial ecosystems. Despite large total amounts of P in soils (typically between 50 and 1500 mg kg^{-1}), soil P is always in short supply (Augusto et al., 2017; Hou et al., 2012; Vitousek et al., 2010), as only soluble inorganic P in soil is directly available to plants (Frossard et al., 2000). Soil soluble inorganic P represents a small but variable fraction of soil total P. For example, soluble inorganic P extracted by resin ranges from < 0.1 to 222.0 (mean 17.2) mg kg^{-1}, accounting for 0.02 to 48% (mean 4.12%) of total P, in worldwide natural soils (Hou et al., 2016). Thus, improved understanding about variability in soil P solubility and its drivers is critical for better understanding plant strategies to cope with P deficiency and spatial variations in P limitation on primary productivity in terrestrial ecosystems (Jones et al., 2003; Reed et al., 2015; Sun et al., 2017).

Soil P solubility is directly controlled by sorption/desorption and precipitation/dissolution (Frossard et al., 2000), which can be further affected by soil physiochemical properties such as soil pH, organic matter content, and texture, and biological activities such as biological immobilization and the secretions of low-molecular organic acids (LOAs) and phosphatase enzymes (Frossard et al., 2000; Jones, 1998; Richardson et al., 2009; Vitousek et al., 2010; Sinsabaugh and Follstad Shah, 2012). Iron (Fe), aluminum (Al), and calcium (Ca) oxides are the major soil minerals affecting P solubility in soils, with Fe and Al oxides playing the dominant roles in acidic soils and Ca oxides in alkaline soils (Celi and Barberis, 2005; Vitousek et al., 2010). The solubility of P in acidic soils is always low relative to neutral or alkaline soils, due to its sorption to Fe and Al oxides in acidic soils (Celi and Barberis, 2005).

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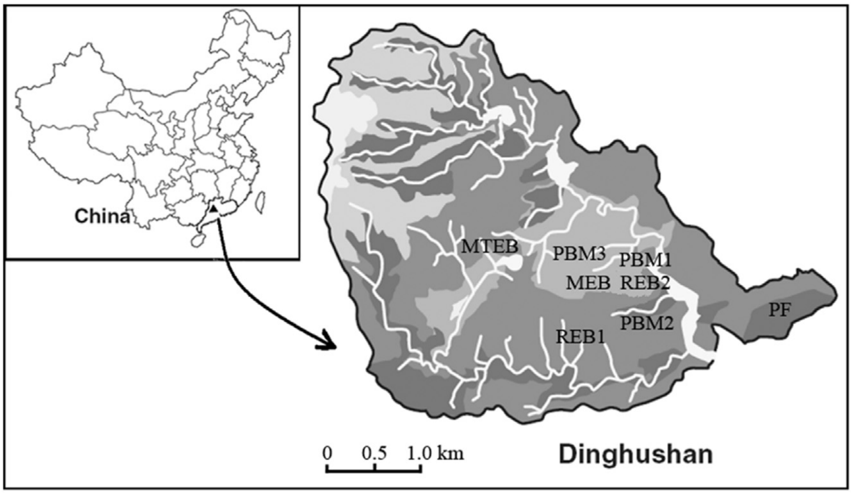

Fig. 1. Location of the eight study forest sites in south China. Full name of the eight forest sites and their basic site characteristics are summarized in Table S1.

Coarse soil particles feature low P sorption capacity relative to fine soil particles; therefore, P solubility may vary with soil texture (Wuenscher et al., 2015). Soil organic matter and secondary minerals can form organic matter-mineral complexes to provide bonding sites for phosphate (Kang et al., 2009). Soil organic matter content can also affect soil P solubility indirectly through its effects on microbial P immobilization and the extracellular activities of phosphatase enzymes (Liptzin and Silver, 2009; Hou et al., 2015; Sinsabaugh and Follstad Shah, 2012). Meanwhile, dissolved soil organic matter can competitively inhibit P sorption to improve soil P solubility (Guppy et al., 2005). Dissolved organic matter, including LOAs, can be produced during the decomposition of plant litter and soil organic matter (Adeleke et al., 2017). A range of LOAs such as citric, malic and oxalic acids can also be derived from plant root and soil microbes, in response to P deficiency (Adeleke et al., 2017; Guppy et al., 2005; Jones, 1998). LOAs may affect the solubility of P in soils through several mechanisms, such as direct ligand exchange between LOAs and phosphates, ligand-promoted mineral dissolution, and impacts on microbial activity (Guppy et al., 2005; Oburger et al., 2011; Wei et al., 2010).

Many studies have demonstrated the potential of LOAs in solubilizing P in soil (Adeleke et al., 2017; Jones et al., 2003). However, impact of LOA on soil P solubility depends on the type and concentration of LOA and the type of soil (Jones et al., 2003; Menezes-Blackburn et al., 2016). The amount of P solubilized by LOA typically increases with the concentration of LOA, however there could be a critical threshold of LOA concentration necessary to solubilize sorbed and precipitated P (Menezes-Blackburn et al., 2016). Tri-carboxylic acids such as citric acid generally show higher potentials in solubilizing inorganic P than di-carboxylic acids such as oxalic acid (Bolan et al., 1994; Oburger et al., 2011). However, oxalic acid is found to be more effective than citric acid in calcareous soils due to the stronger ability of oxalic acid to chelate calcium (Ca) (Wang et al., 2015). In a screen of 20 contrasting soils, Jones et al. (2003) found that 1 mM citric acid and 1 mM oxalic acid both significantly solubilized inorganic P in 65% of the tested soils but not in the other soils; moreover, the amount of P solubilized (in comparison to water) did not correlate well with either total soil P, soil pH, P sorption capacity or total Fe (Jones et al., 2003). More research on factors affecting the response of soil P solubility to LOAs is required for improved understanding about organic acid-mediated nutrient release in different soil types (Adeleke et al., 2017; Jones et al., 2003). Moreover, most previous studies have focused on the impacts of LOAs on the solubility of inorganic P in soil, with much less attention on the impacts of LOAs on the solubility of organic P in soil (Menezes-Blackburn et al., 2016; Wei et al., 2010). Some studies proposed that LOAs can affect the solubility of organic P in soil via similar mechanisms to those for inorganic P, as organic P reacts with metal ions in similar ways as the free phosphate ions (i.e., via phosphorus-oxygen single or double bond) (Celi and Barberis, 2005; Wei et al., 2010).

Subtropical forest is an important component of the world forests (Hansen et al., 2013). Previous studies suggest that P limits primary productivity and soil microbial activities in mature subtropical forests in China (Hou et al., 2012; Liu et al., 2012; Zhu et al., 2014). In response to P deficiency, plants may exude LOAs to solubilize P from soil. However, little is known about whether and how LOAs and soil properties may affect P solubility in soils in this area. To address this question, this study determined the concentrations of water and LOAs (including citric, malic and oxalic acids) soluble inorganic P and organic P in soils under mature subtropical forests in China, and explored linkages between these soil P measures and soil physiochemical properties such as soil pH, organic C concentration, and rock fragment (diameter 4–50 mm) content. The aim of this study was to (1) examine the level of water soluble P in soils and the efficiencies of three common LOAs in solubilizing P from soils in mature subtropical forest ecosystems, and (2) to identify key soil properties that affect P solubility in strongly acidic soils. We hypothesized that (1) water soluble P (both inorganic P and organic P) concentrations in soils were generally low in mature subtropical forests, relative to in many other areas of the world, because soils in the study area are strongly acidic and contain relatively low amounts of total P (Hou et al., 2012). (2) All three selected LOAs could significantly solubilize P from soils, but with variable solubilization efficiencies among organic acids, soils, and P forms. (3) Efficiencies of the three LOAs in solubilizing P from soils were linked to key soil properties such as soil pH and organic C concentration.

2. Materials and methods

2.1. Site descriptions and soil sampling

The studied soils were collected from Dinghushan Biosphere Reserve (DBR; 112°31′–112°34′ E, 23°09′–23°12′ N; Fig. 1) in Guangdong province, southern China. The DBR has a mean annual temperature of 21 °C and a mean annual precipitation of approximately 1900 mm. The vegetation consists mainly of evergreen broadleaf forests and also of pine and broadleaf mixed forests and pure pine forests which were all > 60 years old. Soils are Ferralsols according to the FAO classification (FAO-UNESCO, 1974) and have developed from Devonian sandstone and shale during the Holocene.

A total of 32 soils at 0–15 cm mineral depth were collected from eight regional representative forests in the DBR (Fig. 1 and Table S1). In brief, at each forest site four plots ($20 \times 20\ m^2$) were established. In each plot, three mineral soils at the 0–15 cm depth were randomly