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## Soil pH predominantly controls the forms of organic phosphorus in topsoils under natural broadleaved forests along a 2500 km latitudinal gradient



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#### ABSTRACT

Soil organic phosphorus (P) dynamics is proposed to vary across regions. However, it remains unclear how it is driven by regional variations in environmental conditions. This study examined the variations in the amount and forms of organic P in the top 10 cm of mineral soils in natural broadleaved forests along a latitudinal gradient (18.4–40.8°N) and their environmental drivers. Soil organic P amount (total Po) was expressed in both absolute (i.e. the concentration) and relative (i.e. the proportion of total Po to total P) terms, and soil organic P forms was represented by the proportion of non-residual Po (to total Po) quantified using a modified Hedley P fractionation procedure. Soil total Po amount in both absolute and relative terms were lower at the low-latitude site (18.4°N) than at the high-latitude sites (25.6–40.8°N) and predominantly positively determined by soil total P. The proportion of non-residual Po significantly increased with decreasing latitude and was primarily negatively affected by soil pH, highlighting a strong pH effect on soil organic P forms. Both the amount and forms of soil organic P were also considerably affected by climate (i.e. precipitation and temperature) and some other soil largely through their effects on soil total P, sorption capacity, however they affected soil total P, forms mainly through their effects on soil pH and also via soil cations, organic C, and P saturation status.

#### 1. Introduction

Soil phosphorus (P) availability varies across regions, with generally lower levels in tropical regions than in temperate regions (Harrison, 1987; Turner and Engelbrecht, 2011; Vitousek et al., 2010). In comparison to temperate soils, tropical soils are usually more weathered and contain higher proportions of P in sparingly-soluble crystalline or occluded forms associated with secondary minerals (Yang and Post, 2011). As the occluded P is of limited biological availability (Tiessen and Moir, 2007), P acquisition by plants growing on strongly-weathered tropical soils is suggested to be more strongly dependent on the turnover of organic P than those growing on temperate soils (Gama-Rodrigues et al., 2014; Turner and Engelbrecht, 2011). Improved understanding of spatial variations in soil organic P dynamics and the underlying mechanisms can aid effective management of soil P fertility across regions (Harrison, 1987; Yang et al., 2013).

Organic P in soil is built up during biological immobilization and transformed to inorganic P via biological and biochemical mineralization (McGill and Cole, 1981). While the turnover of soil organic P is primarily participated by plants and soil microbes, the long-term (e.g. decades) dynamics and amount of soil organic P are always determined by environmental factors, such as climate and soil properties, in natural terrestrial ecosystems (Celi and Barberis, 2005; Vitousek et al., 2010). For example, the immobilization of P in soil is driven by the demand of P by plants and soil microbes, which can be further regulated by environmental conditions such as climate and soil nutrients (Augusto

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et al., 2017). Biological mineralization of organic P in soil is driven by the demand for energy of soil microbes that depends on the cycling of soil organic matter (McGill and Cole, 1981). Biochemical mineralization of organic P in soil, participated by phosphatase enzymes, is mainly controlled by the supply and demand of P (Marklein and Houlton, 2012; McGill and Cole, 1981). Soil P supply is determined by soil total P amount and soil properties such as pH and the amount and composition of soil minerals (e.g. iron (Fe) and aluminum (Al)), which further depend on soil forming factors such climate, parent material, and topography (Vitousek and Chadwick, 2013; Vitousek et al., 2010; Walker and Syers, 1976). Soil minerals and organic matter can also affect the stability (or solubility) of soil organic P, which determines the longterm persistence and buildup of organic P in soil (Celi and Barberis, 2005).

Given the complex environmental influences on soil organic P dynamics, inconsistent relationships between environmental factors and soil organic P amount and forms have been reported in previous studies (Murphy et al., 2009; Turner and Engelbrecht, 2011; Siebers et al., 2017). For example, while some studies suggest that climate has a strong effect on soil organic P dynamics at the global scale (Harrison, 1987; Yang et al., 2013), lack of a significant relationship between annual precipitation and the amount or the composition of soil organic P has been reported in lowland tropical rain forests (Turner and Engelbrecht, 2011). At the global scale, soil organic P is found to be generally lower in tropical regions than in temperate regions (Harrison, 1987; Yang et al., 2013). This finding has been mainly attributed to the relatively high precipitation and temperature in tropical regions compared to in temperate regions (Harrison, 1987; Yang et al., 2013). Possible mechanisms underlying this finding include: the relatively high loss of P through leaching and runoff, stronger adsorption of P on secondary Al and Fe minerals, more occlusion of P by Al and Fe minerals, and more rapid decomposition of soil organic matter and mineralization of soil organic P in the tropical regions (Yang et al., 2013). Beside soil organic P concentration, the proportion of organic P to total P has also been found to be generally lower in tropical regions than in temperate regions (Harrison, 1987; Turner and Engelbrecht, 2011). This finding may be explained by the emerging idea that soil P supply controls P nutrition strategies and cycling in forest ecosystems (Lang et al., 2016; Lang et al., 2017). It is proposed that plant and soil microbial communities rely more on the recycle of P, including soil organic P, to sustain sufficient P supply at P poor sites such as lowland tropical forests than at P rich sites such as temperate forests (Lang et al., 2016). However, empirical studies testing these hypotheses have been limited (Lang et al., 2017), and no study has quantitatively examined the direct and indirect effects of climate and soil properties on soil organic P amount and forms along a latitude gradient. Such hypothesis testing and quantitative analysis can provide deep insights into mechanisms underpinning latitudinal variations in soil organic P dynamics. It is also critical for the reliable prediction of spatial variations in soil organic P dynamics using process-based earth system models.

Long-term transformations of P in soil can be examined with sequential extractions such as the procedure of Hedley et al. (1982), which sequentially remove organic P fractions with different solubility (Tiessen and Moir, 2007). NaHCO<sub>3</sub> extractable Po has been found to be related to microbial biomass P (Hou et al., 2016) and plant available P (Bowman and Cole, 1978). NaOH extractable Po is also suggested to be a source for microbial and plant uptake in highly weathered soils (Gama-Rodrigues et al., 2014; Reed et al., 2011). Organic P in the residue is found to mainly consist of *myo*- and *scyllo*-inositol hexakisphosphates that are scarcely available to soil microorganisms and plants, in Andisols (Velasquez et al., 2016). Investigating changes in these soil organic P fractions can provide important insights into the long-term dynamics of soil organic P in terrestrial ecosystems (Cross and Schlesinger, 1995; Gama-Rodrigues et al., 2014; Harrison, 1987; Hou et al., 2016; Reed et al., 2011).

This study collected soils under natural broadleaved forests along a

2500 km latitude gradient in China, and analyzed the fractions of organic P using a modified Hedley P fractionation procedure. The aim was to (1) explore latitudinal variations in the amount and forms of soil organic P, and (2) quantify the relative influences of climate and key soil properties on the amount and forms of soil organic P. We hypothesized that (1) the amount of soil organic P decreased from the temperate regions to the tropical regions, since soil organic P is proposed to be more dynamic in tropical regions than in temperate regions (Turner and Engelbrecht, 2011). (2) The amount of soil organic P would mainly be determined by soil total P amount and also affected by soil organic matter, soil pH, and climate. (3) The forms of soil organic P might be mainly affected by soil pH, given a large range of pH values of the soils studied (3.7–7.1; Cong et al., 2016). Soil pH can potentially affect soil organic P dynamics through several pathways, such as through its effects on the amount and composition of soil minerals (Ulrich, 1991), the composition of soil microbial community (Bünemann et al., 2008), the extracellular activities of phosphatase enzymes (Eivazi and Tabatabai, 1977), and the adsorption/desorption and precipitation/dissolution and thus the solubility of organic P in soil (Celi and Barberis, 2005).

#### 2. Materials and methods

#### 2.1. Site description, soil sampling and sample preparation

Soils were sampled at 26 forest sites along a latitude gradient (18.4–40.8°N) in China during July to October 2012, except the soils at Jianfengling which were sampled in February 2012 (Supplementary Table S1 and Fig. 1). All sites contained natural and mature broadleaved forests (includes temperate, subtropical and tropical forests), with generally similar topographic conditions (elevations of 934-1856 m a.s.l., south aspect, and slopes of 25-35°; Supplementary Table S1). The sites span distinct mean annual temperature (MAT, 1.5–19.6 °C) and mean annual precipitation (MAP, 381-1723 mm yr<sup>-1</sup>) gradients across the approximately 2500 km distance in China (Supplementary Table S1 and Fig. 1). Soils at these sites included Cambisols, Luvisols, Alisols and Combisols, according to the FAO 90 Classification (FAO/Unesco/ISRIC, 1990).

At each forest site, ten plots  $(20 \times 20 \text{ m}^2)$  were selected with distances of about 20 m between adjacent plots. In each plot, ten to fifteen mineral soils at the 0–10 cm depth were sampled using a soil corer (diameter of 4 cm), after forest floor litters were removed. Topsoils were selected in our study, because topsoils are more prone to be affected by environmental factors (e.g. climate) than subsoils (Lang et al., 2017; Jobbágy and Jackson, 2001). The ten to fifteen soils collected from the same plot were bulked together as a composite sample. Soils were sieved through a 2-mm mesh to remove roots and stones and mixed thoroughly. Detailed descriptions of research site and soil sampling are carried out by Zhang et al. (2016). Given that the fractionation of soil P is a laborious task, only four of the ten soils sampled at each forest site were selected (i.e. a total of 104 soils) for the present study.

#### 2.2. Determination of soil properties

Soil pH in water was determined using a glass electrode, soil total organic carbon (C) was determined by the wet combustion method, and soil total nitrogen (N) was determined by micro-Kjeldahl digestion and colorimetric method (Liu et al., 1996). Soil total P was determined with a wet digestion method with concentrated HF and  $HClO_4$  followed by a molybdate blue colorimetric method (Liu et al., 1996).

Soil total Ca, K, Na and Al concentrations were determined by an ICP-AES (Optima 2000, USA) after soils were digested using concentrated  $HCl:HNO_3:HClO_4$  (volume ratios of 8:10:1). Chemical index of alteration (CIA) was calculated as a measure of the degree of soil weathering, according to the modified formula of Nesbitt and Young

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