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Changes of soil phosphorus speciation along a 120-year soil chronosequence in the Hailuogou Glacier retreat area (Gongga Mountain, SW China)

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ABSTRACT

The Hailuogou Glacier (Gongga Mountain, SW China) has been retreating in response to global warming. A soil chronosequence (*Hailuogou Chronosequence*) has developed in the retreat area, and a primary plant succession has developed on it. To investigate the changes of soil phosphorus (P) fractions along the young soil chronosequence in the cold and humid climate, soil samples were collected at seven sites of different ages (0 to 120 years). In all soil samples, concentrations of total P and of different P fractions (Bioavailable P, Al/Fe-bound P (P bound by Al and Fe oxides or hydroxides), Ca-bound P, and residual P) were determined using a sequential extraction technique. Organic P was determined using the high temperature ignition method. For the youngest (0 years, 12 years) soils, P forms were dominated by residual P, and topsoil forms of Ca-bound P, Al/Fe-bound P, organic P, microbial biomass P and bioavailable P were less than 1.86%. From 30 to 120 years, for the topsoil, concentrations of Ca-bound P and organic P gradually increased; the concentration of bioavailable P in surface soil also showed a trend of increase, with percentages of 5–11.5% to total soil P; the concentration of residual P decreased; the concentration of Fe/Al-bound P contributed less than 5% to total soil P at all sites. Ca-bound P and organic P were the dominant P fractions at the older sites (ages: 80 and 120 years). Soil P bioavailability and solubility were influenced by the changes of pH, and concentrations of Fe and Al oxide and hydroxide. The variations of vegetation and microbial activity are also considered as the impact factors of soil P forms. In the later stage of soil development (80~120 years), plenty of soil P was transformed into biomass P pool (299.3 kg ha^{-1}).

1. Introduction

As one of the essential nutrients, phosphorus (P) plays a key role for plant growth and ecosystem development (Schachtman et al., 1998). Insufficient bioavailable P decreases primary productivity, reduces plant growth, and retards ecosystem development (Vitousek et al., 2010). In the long run, P bioavailability in terrestrial ecosystems decreases with time because it is increasingly bound in forms which are hardly bioavailable, resulting in ecosystem degradation (Koerselman and Meuleman, 1996; Ostertag, 2010; Richardson et al., 2004; Walker and Syers, 1976). Although both N and P have been identified as limiting nutrients for the development and biomass accretion of many terrestrial ecosystems (Craine and Jackson, 2010; Cramer, 2010; Elser et al., 2007), recent studies indicate that P rather than N is the main limiting nutrient in some alpine and high-latitude ecosystems, where the climate is cold and humid (Seastedt and Vaccaro, 2001; Wassen et al., 2005).

The principal P source in terrestrial ecosystems is weathering of minerals in parent rock material (Filippelli, 2008; Smeck, 1985; Tiessen et al., 1984). P is released from parent rock material in several fractions which cannot be readily assimilated by plants and soil microorganisms except the part of bioavailable P (Schachtman et al., 1998). Bioavailable P comprises the portion of total P that can be taken up by plants and soil microorganisms (Tiessen and Moir, 1993). The issue of P bioavailability recently has become the focus of many studies of biogeochemical P cycling (Cross and Schlesinger, 1995; Filippelli, 2008; Wang et al., 2007).

Chemical weathering of minerals takes a long time; hence it is hard to investigate this process under close-to-nature conditions in the laboratory. Previous studies generally utilized soil chronosequences to study the processes and mechanisms of P release and P transformation during weathering of parent bedrock and pedogenesis (Eger et al., 2011; Porder and Hilley, 2011; Turner et al., 2007; Föllmi et al., 2009). However, the available information about biogeochemical P

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cycling during the early stage of soil development in high-elevation or high-latitude regions with humid and cold conditions is still sparse.

The Hailuogou Glacier in the Gongga Mountain region (SW China) has retreated continuously since the end of the Little Ice Age (LIA) (Li et al., 2010). A soil and primary vegetation succession chronosequence (*Hailuogou Chronosequence*) has developed in this retreat area. Hailuogou has not been strongly disturbed by human activities, especially in the high-elevation area; it thus is an ideal site to study biogeochemical element cycling in the early stage of soil and ecosystem development at the scale of a few decades. Zhong et al. (1999) established an exact chronosequence for the Hailuogou Glacier retreat area; Li and Xiong (1995) investigated the primary vegetation succession and distinguished it into five stages: (1) bare land; (2) *Salix rehderiana* C.K.Schneid.–*Hippophae rhamnoides* L.–*Populus purdomii* Rehder; (3) *Populus purdomii* Rehder; (4) *Abies fabri (Mast.) Craib*–*Picea brachytyla* (Franch.) E.Pritz.; (5) *Picea brachytyla* (Franch.) E.Pritz.–*Abies fabri* (Mast.) Craib. Luo et al. (2003, 2004, 2005) measured soil respiration at different succession stages and found that soil respiration generally was highest between April and September and lowest in January, and that the *A. fabri* forest's requirement for soil nutrients was great because the nutrient-use efficiency of *A. fabri* was low. He and Tang (2008) investigated the physical–chemical soil properties of the *Hailuogou Chronosequence*, and found that the rate of pedogenesis decreased with time, while a stable state was not achieved during 120 years of soil development. Moreover, soil accumulation rates of organic matter and N were rapid (He and Tang, 2008). However, at the moment no information exists about the changes of total soil P stocks and soil P speciation after different times of deglaciation and soil development, and about the controls of P biogeochemical cycling in the *Hailuogou Chronosequence*. Moreover, it is still unclear whether P is the main limiting nutrient for the forest ecosystems at *Hailuogou chronosequence*.

The bioavailability and transformation of soil P are influenced directly or indirectly by temperature, moisture conditions, lithology of parent rocks, topography, biological factors, climate change, acid deposition, and so on. Devau et al. (2009) suggested that bioavailable P is mainly adsorbed by Fe oxide, gibbsite and clay mineral when soil is acidic, alkaline and neutral, respectively. The decrease in pH can increase Al mobility, as well as increase the solubility of primary minerals P to release bioavailable P to soil (Ohnoa and Amirbahman, 2010). Plants affect P forms by acidification of the rhizosphere, synthesis and release of organic-acid anions, and release of extracellular phosphatases (Richardson et al., 2009). Mycorrhizal fungi, P solubilizing microorganisms, P mineralizing microorganisms and mobilization of P by the microbial biomass can also increase soil P bioavailability (Richardson and Simpson, 2011). Release of Ca–P, interaction among bio-P, Fe–P, and Al–P, leaching of bio-P are geochemical processes, while P uptake by plants, microbial uptake of bio-P, and microbial Po mineralization are biological processes (Cross and Schlesinger, 2001).

Therefore, the first objective of this study is, based on the chronosequence of glacier retreat deposits, to investigate the characteristics and bioavailability of different soil P fractions by using a sequential extraction method. And the second purpose is to analyze the influence of geochemical processes and biological processes on observed temporal trends of the soil P status in the *Hailuogou Chronosequence*.

2. Materials and methods

2.1. Study area

Located at the southeastern edge of the Tibetan Plateau, Gongga Mountain (summit: 7556 m a.s.l.) is the peak of the Great Snow Mountain Range (Fig. 1). Geomorphologically, Gongga Mountain is located in the transition zone of the Tibetan Plateau and the Sichuan Basin; climatically, it is located in the transition zone of two different climate zones: the Tibetan Plateau Frigid Zone and the Warm-humid Subtropic Monsoon Zone. Hailuogou Glacier, which flows down the eastern slope of Gongga Mountain, is a monsoonal temperate glacier (Li et al., 2010). With its more or less constant retreat since late 19th century, *Hailuogou Chronosequence* developed from the terminal moraine and extended to the northeast at a length of about 2 km. A primary vegetation succession has developed on this chronosequence.

The hydrological regime of Hailuogou Watershed is controlled by the southeast monsoon. According to data (1988~2010; Table 1) from the Gongga Mountain Alpine Ecosystem Observation Station, Chinese Academy of Sciences (CAS) (elevation: 3000 m a.s.l.; 29°34′34.69″N,101°59′55.08″E), the mean annual temperature is 4.2 °C. The diurnal temperature range is 20.4 °C. The mean annual precipitation of 1947 mm concentrates in the summer season.

2.2. Sample collection

Soil samples were collected in May 2010 at the seven sites of the chronosequence described by Zhong et al. (1999) according to the "Protocols for Standard Soil Observation and Measurement in Terrestrial Ecosystems" (Sun et al., 2007). A soil profile was hand-dug, and three soil units were divided according to the primary aspects at each site except for the first two sites (Table 2). For the first two sites, only fine moraine material from 0 to 5 cm depth was collected. The three soil units are described as: O horizon which represents litter layer consisting of Oi, Oe and Oa horizons, but the boundaries of the three horizons are unconspicuous, A horizon which represents soil with dark brown color and humus enrichment, and C horizon which represents soil parent material. Due to the immaturity of soil development, none of the soils showed cambic (B), eluvial (E), or illuvial (Bs, Bh) horizons. Soil group on the chronosequence is Regosols according to WRB (World Reference Base for Soil Classification). Soil parent materials are primarily consist of biotite schist, granodiorite, and quartzite, mixed with smaller amount of phyllite, slate and chlorite schist (Yu, 1984).

2.3. Sample analysis

All soil samples were oven-dried (105 °C), sieved (<2 mm) and ground prior to analysis. Total P (TP), Al, Ca, K and Na were measured using a Profile DV (USA Teledyne Leeman Labs) Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (detection limit: 0.02 mg P/l; 0.2 mg Al/l; 0.02 mg Ca/l; 0.8 mg K/l; 0.5 mg Na/l), after digestion by refluxing with the nitric acid, hydrofluoric acid, and perchloric acid, following EPA (2001) Method 200.7. Certified reference materials (GSD-9 and GSD-11) from the National Quality and Technology Supervision Agency of China were analyzed alongside the soil samples to validate the accuracy of the concentration measurements. The measured concentrations for this natural standard were within 10% of the certified values for P, Al, Ca, K and Na.

Soil phosphorus fractionation/speciation was performed using a modified sequential extraction technique developed by Ruttenberg (1992). Duplicate (~0.5 g) samples of oven-dried soil were sequentially extracted with 1 M $MgCl_2$, 0.5 M NH_4F, 0.1 M NaOH–0.5 M Na_2CO_3, and 1 M HCl. The soil samples were shaken end-over-end in 50-ml centrifuge tubes with 30 ml reagent for 16 h at 25 °C and 250 rpm. All extracts were centrifuged at $6000\times g$ ($g\approx 9.8\ m/s^2$) for 20 min at 0 °C, before the supernatant was decanted for analysis of PO_4^{3-}–P. Organic P (Po) in the soils was determined using the high temperature ignition technique (Saunders and Williams, 1955) based on a separate aliquot of the soil sample. The total organic phosphorus calculated as the difference in acid-extractable (1 M H_2SO_4) phosphate between ignited (550 °C) and unignited samples. Concentrations of PO_4^{3-}–P in all extracts were determined using the Murphy and Riley (1962) method on a UV–VIS spectrophotometer (Shimadzu UV2450) at 710 nm. The data obtained for the different P fractions were reported as average values with coefficient of variation less than 10%.