Soil phosphorus bioavailability assessed by XANES and Hedley sequential fractionation technique in a glacier foreland chronosequence in Gongga Mountain, Southwestern China

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The primary productivity of terrestrial ecosystems is influenced by soil phosphorus bioavailability, which depends largely on chemical fractions of phosphorus. The sequential fractionation technique developed by Hedley et al. or its subsequent modification is a well-known method to determine soil phosphorus forms. Hedley sequential fractionation technique separates the phosphorus into fractions based on their different chemical solubilities in extractants with certain chemical properties. Recently, synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy has been employed to measure soil phosphorus species directly and non-invasively. The XANES method provides information concerning local structure and chemical information of target elements at a molecular level. Thus, it can distinguish phosphorus fractions bound by metal oxides or hydroxides (such as Fe, Al, and Ca). In this present work, the phosphorus speciation of topsoil along a glacial foreland chronosequence in Gongga Mountain is determined using these two methods. The changes in soil phosphorus bioavailability along the 120-year-old chronosequence are assessed based on comparisons of the results obtained by these two methods. The results indicate that Hedley sequential fractionation technique shows a greater ability to determine soil bioavailable phosphorus (Resin-P and $NaCHO_3$-P), while XANES is effective in distinguishing phosphorus bound by metal compounds. In the chronosequence, Ca- and Al-bound phosphorus were derived mainly from primary minerals, whose phosphorus contents decreased within 120 years of moraine weathering and soil development. The content of soil bioavailable phosphorus increased rapidly after 30 years since deglaciation. The increasing phosphorus bioavailability promoted the colonizing and primary succession vegetation.

soil, phosphorus forms, Hedley sequential fractionation technique, XANES, Hailuogou

As one of the important nutrients, phosphorus (P) often is considered a limiting or a co-limiting nutrient together with nitrogen (N) for the primary productivity of terrestrial eco-systems (Vitousek et al., 2010). Meanwhile, in addition to climate, P may play a key role in the formation of vegetation belts and timberlines (Sala et al., 2000; Ducić et al., 2011). Soil P and its bioavailability also affect the primary plant succession in soil chronosequences formed in glacier forelands (Chapin et al., 1994; Wu et al., 2013).

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There are two forms for P in soils: inorganic (minerals and/or mineral bound P) and organic (organic matter and/or organic bound P). Soil P can also be separated into dissolved and particle P on the basis of its solubility. The former consists of mainly free phosphate ions ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}), which are only a very small proportion of the total P in natural systems. The latter includes mainly P adsorbed onto metal oxides (e.g., Fe and Al) and mineral edges of clay particles, or precipitated as secondary Ca-, Fe-, or Al-minerals. Bioavailable P is the sum of all P that can be assimilated by plants and microbes, the chemical fractions of which are dominated by dissolved orthophosphates. The remaining P fractions cannot be directly taken up by plants partly or completely (termed occluded P) (Walker and Syers, 1976; Gonsiorczyk et al., 1998; Reynolds et al., 2001). Therefore, determination of soil P fractions and bioavailability is a precondition for evaluating the influence of P on terrestrial ecosystems and for revealing the relationship between P and the formation of vegetation belts and plant succession.

Several sequential fractionation methods have been developed to categorize soil P using solvents with different selective chemical properties. The most widely used P extraction method is the one proposed by Hedley et al. (1982) and its modifications (e.g., Tiessen and Moir, 1993; Cassagne et al., 2000; Zhou et al., 2013). Hedley sequential fractionation technique separates soil P into Resin-P, NaHCO$_3$-P, NaOH-P, and HCl-P according to different extractants. However, the P fractions divided by Hedley sequential fractionation cannot represent definite chemical forms of P. Moreover, the method cannot distinguish Fe-bound, Al-bound, or Ca-bound P (Hunger et al., 2005; Kar et al., 2011). Thus, Hedley sequential fractionation technique cannot give an accurate evaluation of P bioavailability. Recently, synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy has been developed to bridge this gap. The XANES method can indicate the structure and chemical group of target elements at the molecular level (Hesterberg et al., 1999; Beauchemin et al., 2003; Lombi et al., 2006; Liu et al., 2011; Prietzel et al., 2013). Therefore, it is able to discriminate P fractions associated with different metals. So far, there are only two reports that compare soil P fractions determined by Hedley sequential fractionation technique and XANES (Beauchemin et al., 2003; Kruse and Leinweber, 2008). Their results indicate that, in contrast to the Hedley technique, XANES can directly divide inorganic P into definite chemical forms (Beauchemin et al., 2003; Kruse and Leinweber, 2008). However, XANES cannot accurately discriminate the P absorbed by certain minerals and organic matter (Ajiboye et al., 2008) because these P species have similar energy spectra (Peak et al., 2002). Hence, several studies have measured P speciation using the two methods simultaneously to understand the soil P fraction synthetically (Kruse and Leinweber, 2008).

Consequently, the present study uses both the modified Hedley sequential fractionation technique and XANES to measure soil P speciation of a 120 year-old chronosequence in Hailuogou Glacier foreland, Gongga Mountain, China. The first objective is to characterize changes of soil P speciation with respect to soil development, which is helpful to reveal the relationship between primary plant succession and pedogenesis in glacier retreat areas. The second objective is to explore advantages and disadvantages of the two techniques in discrimination of the various forms of soil P.

1   Study area

Gongga Mountain (summit: 7556 m a.s.l.) is located in the middle part of the Hengduan Mountain Range in the transition zone of the Tibetan Plateau and the Sichuan Basin. This mountain represents the peak of the southeastern edge of the Tibetan Plateau where geological formations are complex and the neo-tectonic movement is intense. Geomorphologically, Gongga Mt. (101°30′–102°15′E and 29°20′–30°20′N) is a typical alpine valley landform. Around Gongga Mt., there are dozens of glaciers, which collectively form the largest modern marine glacier in Asia. In response to global warming, the Hailuogou Glacier on the eastern slope of Gongga Mt. has markedly retreated since the end of the Little Ice Age and left several lateral moraines and terminal moraines. The Hailuogou chronosequence developed from the current terminal moraine having a length of about 2 km and an altitude drop of about 100 m. Primary plant succession has developed on this chronosequence, ranging from shrubs (*Astragalus adsurgens* Pall. and *Hippophae rhamnoides* L.), to broadleaf tree forest (*Populus purdomii* Rehder), to coniferous forest (*Picea brachytyla* (Franch.) E. Pritz. and *Abies fabri* (Mast.) Craib) (Li and Xiong, 1995; Zhong et al., 1999; Li et al., 2010) (Figure 1).

2   Sampling and methods

According to the field investigation, seven sites were selected in September 2010 based upon considerations of soil development and chronosequence (representing 0, 12, 30, 40, 52, 80, and 120 years) (Zhong et al., 1999), and three soil profiles at each site were hand dug. Because of the short time allowed for pedogenesis, the B horizon is absent in all profiles. Soil samples were collected from two horizons in each profile. The A horizon represents dark brown soil containing humus, while the C horizon represents the parent materials. Fine moraine materials from depths ranging from 0 to 10 cm were collected at the first two sites (0 and 12 years) due to the lack of soil development. About 1 kg of soil in total was sampled from each site and kept in the polyvinyl chloride plastic bags. All samples were dried at 45°C and sieved (< 2 mm) for analysis.
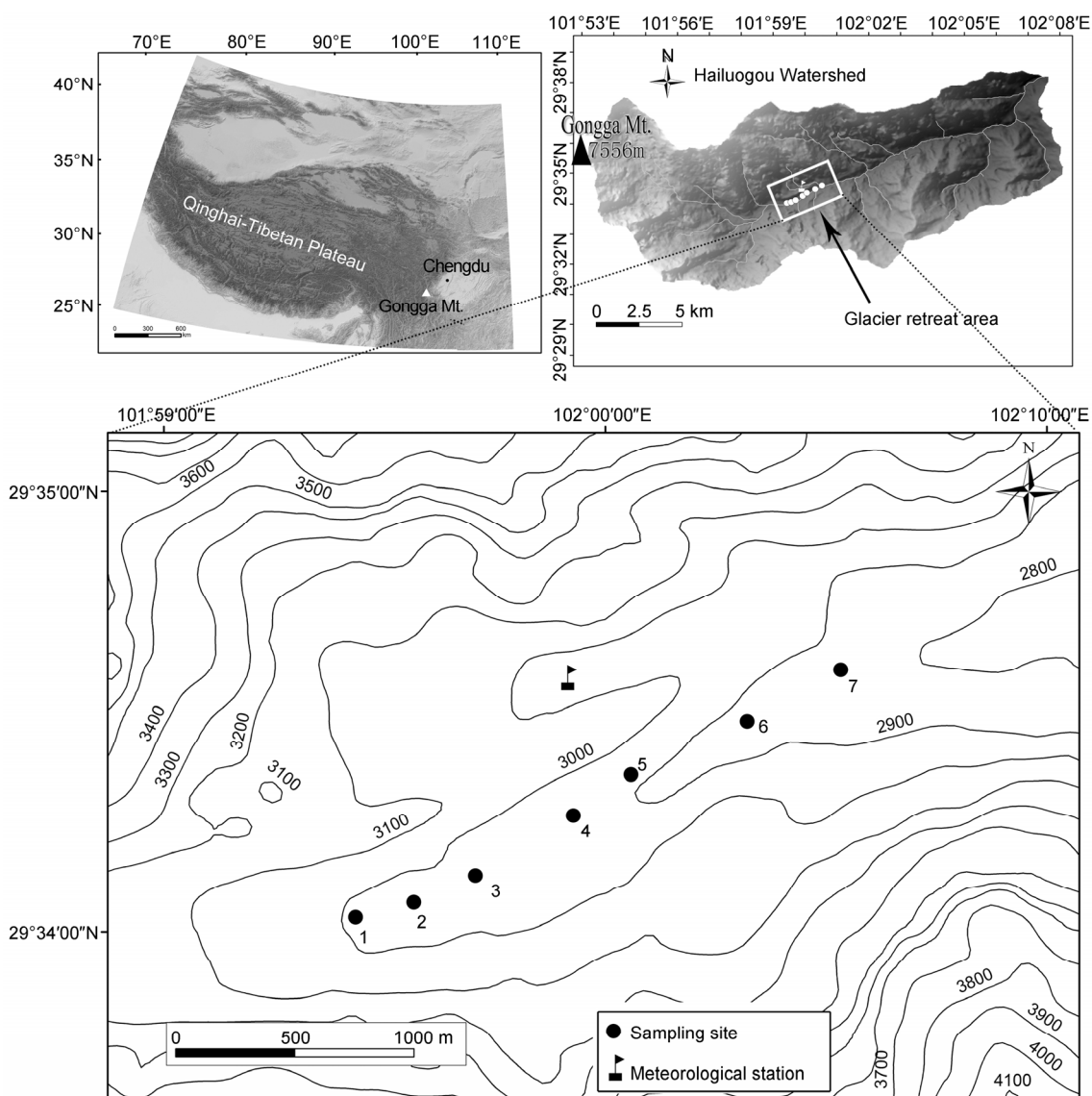
Figure 1   Sampling site.

The pH values were measured (soil∶solution ratio [w/w] = 1∶2.5) with a glass electrode. The concentration of total N (TN) was analyzed with an element analyzer. After digesting the sample with nitric acid, hydrofluoric acid, and perchloric acid, the concentration of total P (TP) was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Acidic NH_4 oxalate solution was used to extract amorphous Al and Fe (Al_o, Fe_o). The concentrations of Fe_o and Al_o in the extracts were also measured by ICP-AES (Teledy Leeman Labs Procigy DC Arc). A standard SPEX^TM solution (SPEX Industries, Edison, NJ, USA) was used as the standard.

Soil phosphorus fractions were obtained using a modified sequential extraction technique (Tiessen and Moir, 1993). The dried and sieved soil (~0.5 g), with two duplicates, was loaded into a 50 mL polyvinyl chloride centrifuge tube. The following reagents were used in the P sequential extraction.

Resin-P: two resin strips of anion exchange membrane (AEM, BDH®, 55164S, 9 mm × 62 mm) within a saturated HCO_3^- solution and 20 mL deionized water; $NaHCO_3$-P: 30 mL of 0.5 mol/L $NaHCO_3$ solution; NaOH-P: 30 mL of 0.1 mol/L NaOH solution; DHCl-Pi (inorganic P): 30 mL of 1 mol/L HCl solution; and CHCl-P: 10 mL of concentrated HCl solution in a water bath boiling under 80°C for 10 min. Except for the CHCl-P extraction, all other P fractions were extracted via end-to-end shaking for 16 h (25°C). Two sub-extractions of $NaHCO_3$-P, NaOH-P, and CHCl-P were separated. One was used to analyze the concentrations of $NaHCO_3$-Pi, NaOH-Pi, and CHCl-Pi. The other was autoclaved at 121°C for 2 h, and then the P concentration was measured. The $NaHCO_3$-Po (organic P), NaOH-Po, and CHCl-Po concentrations were obtained by subtracting the concentration values for the autoclaved extract from their corresponding values in the un-autoclaved extract. All

PO_4^{3-} concentrations in the extracts were measured using the molybdenum blue colorimetric method using a spectrophotometer (Shimadzu UV1750) at 700 nm. The residual P concentration was calculated using the difference between the TP and the sum of all P fractions.

XANES: The method has been described in detail by Prietzel et al (2013). Six standard compounds were used to indicate different P fractions. The measurements were conducted at the Synchrotron Light Research Institute (SLRI).

3   Results

3.1   Soil properties

Soil physiochemical properties are closely related to soil age (He and Tang, 2008). The soil in the retreat area of the Hailuogou Glacier is in the early stage of pedogenesis, and thus, the soil is thin and displays no obvious horizons. The initial stage of pedogenesis is shown in the 0 and 12 year sites where the A horizon has not formed. Therefore, the soil properties in the surface layer of these two sites are used for comparison with those of the A and C horizons of other sites (Figure 2). Generally, the pH values decrease with pedogenesis. The highest value of 7.3 was recorded at both the 0 and 12 year sites, while the lowest value was recorded in the A horizon at the 80 year site (pH 3.6). The pH values are generally higher in the C horizon than in the
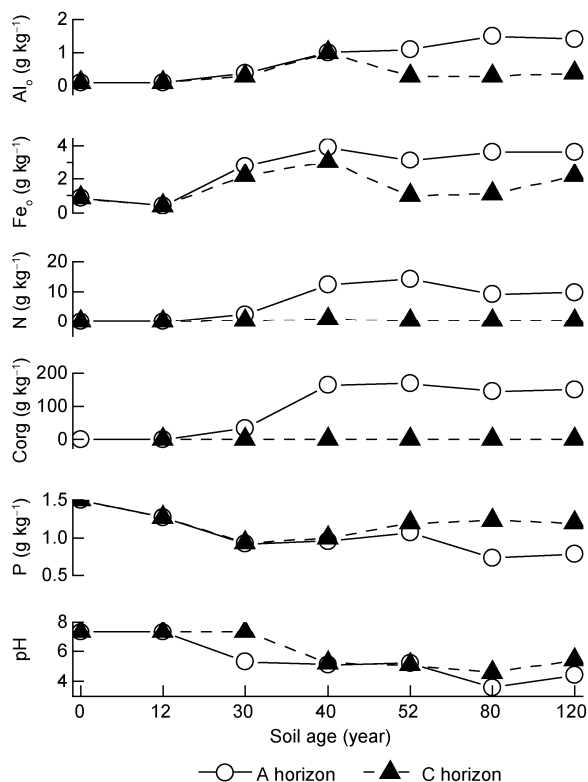
A horizon at a given site. The TP concentrations in the soil also decrease with time. There is no significant difference in TP concentrations in the A and C horizons at the sites located before 52 years in the chronosequence. Owing to the ongoing process of pedogenesis, the TP concentrations in the C horizon are uniformly higher than in the A horizon at the 80 and 120 year sites. The concentrations of the organic C (OC) and TN in the A horizon increase with soil development. At the 40 year site, the OC and TN concentrations reach 165.6 and 12.5 g kg^{-1}, respectively, and those high values are retained at the older sites. There are relatively low OC and TN concentrations in all of the C horizon samples without obvious variations. The concentrations of Fe_o and Al_o in the soil increase with pedogenesis, and a more remarkable increase occurs in the A horizon, while these concentrations decrease a little in the C horizon for sites older than 40 years.

3.2   Phosphorus fractions in the retreat area of Hailuogou Glacier as determined by the Headley sequential fractionation method

The main phosphorus fractions in the C horizon are DHCl-P, CHCl-P, and NaOH-P. The DHCl-P fraction is dominant, accounting for 92%–97% of the TP, while CHCl-P accounts for 3%–5%, and NaOH-P accounts for 1%–3%. However, the concentrations of Resin-P and $NaCHO_3$-P are very low (Figure 3). The organic P concentration in the C horizon (mainly in the form of NaOH-Po) is also very low, which accounts for 1%–3% of the TP.

The P fractions in the A horizon vary widely with pedogenesis, which demonstrate a marked decrease for DHCl-P and an increase for all other P fractions. Due to the absence of the A horizon at the 12 year site, the P fractions in the C horizon are used for comparison with those in the A horizon of the other sites. The DHCl-P fraction decreases from 86.1% at the 12 year site to 52.7% at the 52 year site and then to 38.9% at the 120 year site. The Resin-P fraction increases from 2.1% at the 12 year site to 13.0% at the 80 year site. Although a little decrease occurs in the 120 year site, the Resin-P fraction there still reaches 7.5%. The variation trend of $NaCHO_3$-P is similar to that of Resin-P. The concentrations of NaOH-P at the 30 and 40 year sites are two times higher than that in the initial stage of soil development, and a similar increasing trend is observed at the 52 year site and at the 80 and 120 year sites. The NaOH-P concentration reaches 28.1% of the TP concentration in the 120 year site (Figures 4(a) and (b)).

Another remarkable feature of the P fractions observed is the clear increase in organic P in the A horizon, wherein the organic P increases from 8.1% in the 12 year site to 44.0% at the 120 year site. The NaOH-Po fraction is the main source of organic P, which displays a similar variation trend as that of NaOH-P (Figure 4(c)).
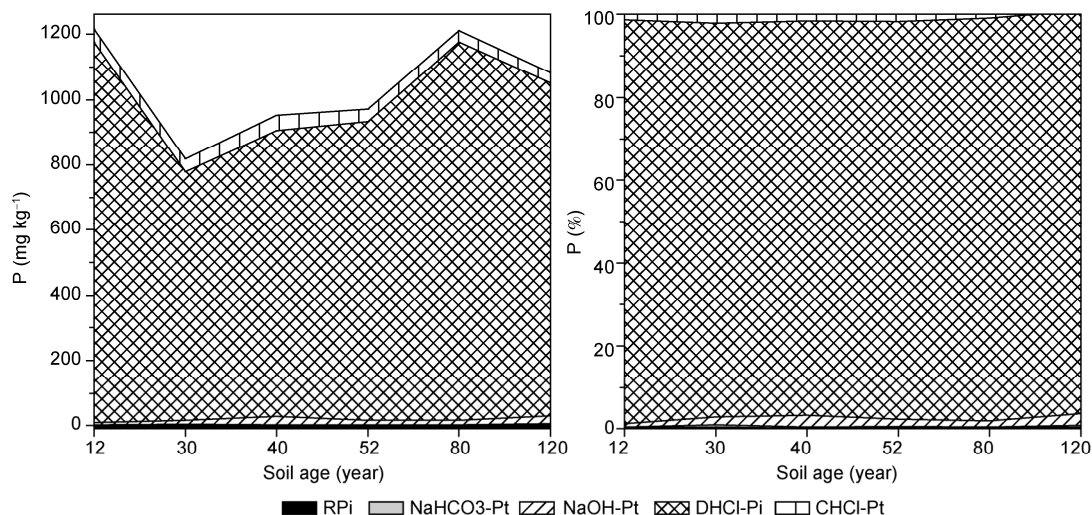

Figure 2   Changes in soil properties with pedogenesis.

Figure 3   P fractions determined by Hedley sequential fractionation.

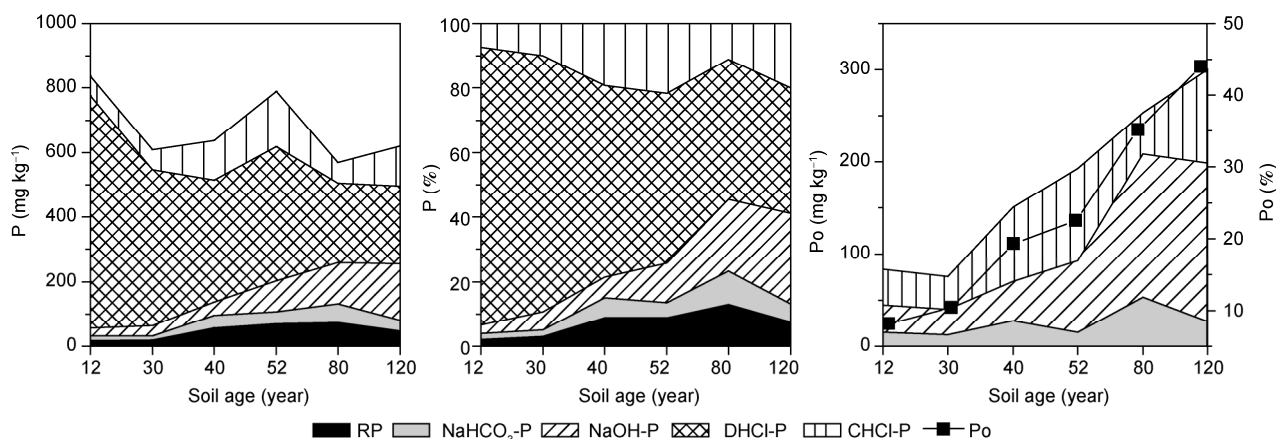**Figure 4**   Composition of P fractions in the A Horizon. (a) Concentration of P fractions; (b) percentage of P fractions; (c) fractions of organic P.

3.3   Phosphorus fractions in the retreat area of Hailuogou Glacier measured by XANES

There are two main P fractions in the C soil horizon in the retreat area of the Hailuogou Glacier according to XANES: Ca-bound P and Al-bound P. The Ca-bound P concentration accounts for about 70% of the TP and the main component is hydroxyapatite ($Ca_5(PO_4)_3(OH)$), based on the standard reference. The Al-bound P concentration accounts for about 30% of the TP (Figure 5(c) and (d)).

The P fractions in the A horizon also vary widely, with a marked increase of organic P and a decrease of Ca-bound P. The concentrations of organic P increase rapidly for sites older than 30 years, and nearly all P at the 80 year site exists as organic P, which may be partly attributable to the error induced by the use of a small amount of samples. The fact that XANES cannot effectively detect organic P may be another reason (See Section 4.1). Al-bound P nearly disappears at the 40 year site, where Fe-bound P emerges with

the highest concentration of 199.5 g kg^{-1}. Although Fe-bound P has a relatively low concentration of 14.6 g kg^{-1} at the 80 year site, it is the main P fraction in the soil except for organic P. The other two Ca-bound P minerals are dicalcium phosphate and monocalcium phosphate, which have minor concentrations at the 30, 40, and 50 year sites (Figure 5(a) and (b)).

4   Discussion

4.1   Comparison of Hedley sequential fractionation technique and XANES for P fraction analysis

Bioavailable P is the portion of P that can be assimilated and utilized directly by organisms. Bioavailable P includes both the dissolved and particle phosphates (weakly bounded, exchangeable fractions that are easily released from particles). The potential bioavailable P is the portion of inorgan-
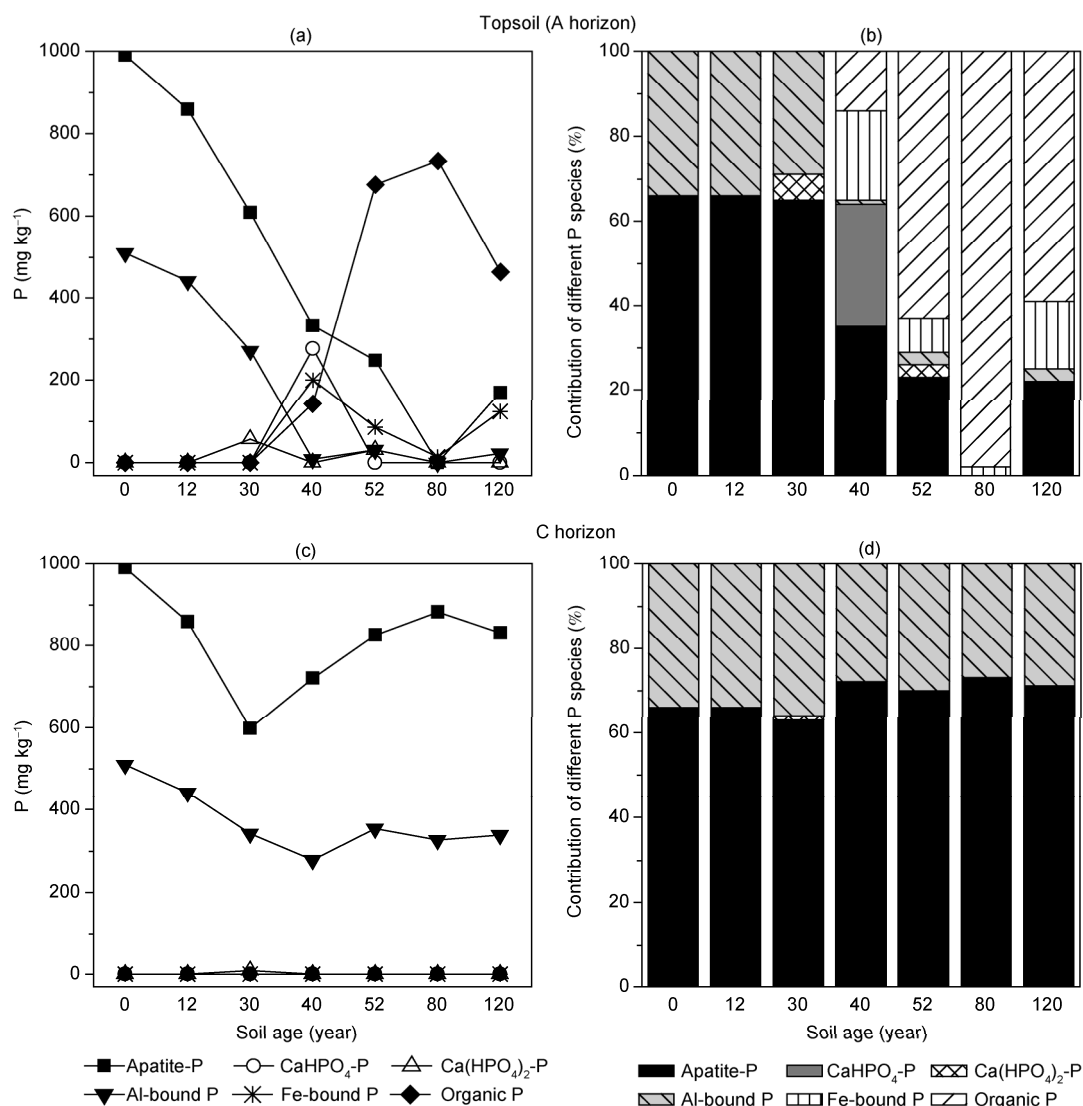
Figure 5 Composition of P fractions determined by XANES.

ic P and polymerized phosphate adsorbed on the particles. Phosphates adsorbed on metallic oxyhydroxides (Fe_o, Al_o) cannot be utilized directly by organisms. When the metallic oxyhydroxides are transformed, the potential bioavailable P is released and becomes bioavailable. Organic compounds and polymerized phosphate can release bioavailable P when they are decomposed and mineralized. However, the process of mineralization and desorption is not well understood and requires further study. Other fractions of P, including Al- and Fe-bound phosphate, cannot be utilized because they are always combined in the mineral crystal lattice and are not readily released (Abrams and Jarrell, 1992; Gonsiorczyk et al., 1998; Smil, 2000; Reynolds and Davies, 2001).

The P fractions determined by Hedley sequential fractionation technique cannot accurately distinguish the concrete chemical forms of P or the P adsorbed by certain metallic oxyhydroxides (Hunger et al., 2005). Nevertheless,

this method can estimate the fractions of dissolved orthophosphate (Resin-P) and weakly bound P ($NaHCO_3$ extracted P) more accurately than XANES can. These two fractions were classified as bioavailable P, which can be assimilated by plants directly during the growing season (Johnson et al., 2003). We define these two fractions as readily bioavailable P. Other fractions, such as Al-bound and Ca-bound, which can be transferred into bioavailable P (Johnson et al., 2003), as well as occluded P (Walker and Syers, 1976), are difficult to separate by Headley sequential fractionation technique.

As it is a technique for measurement in a solid form, XANES cannot detect dissolved orthophosphate (Resin-P). On the other hand, it can ascertain the chemical structure and the information of metal elements around P (Hesterberg et al., 1999; Beauchemin et al., 2003; Lombi et al., 2006; Liu, 2011; Prietzel et al., 2013). Therefore, XANES can estimate the concentration of metallic oxyhydroxide bound

P. We define this metallic oxyhydroxide bound P as potentially bioavailable P. Part of the organic P can be transferred into bioavailable P when it is mineralized (Cross and Schlesinger, 2001; Johnson et al., 2003). However, it is difficult to distinguish the organic P by XANES, because this method cannot differentiate the structural P in an organic compound from the P adsorbed by organic matter. Theoretically, the soil organic P detected by XANES is the structural P of organic compounds, because the standard reference for the organic P is $(CH_3)_6 (PO_4)_6 \cdot xNa + yH_2O$. However, the organic P content obtained by XANES is as high as 99% of the TP, whereas Hedley sequential fractionation technique gives the organic P content as 35.2% of the TP. Therefore, the XANES value seems unreasonable. One possible interpretation is that XANES cannot distinguish the P adsorbed by organic matter and organic-metal complexes from the structural P.

There is a strong relationship between the Al-bound and Ca-bound P determined by XANES (Table 1). Meanwhile, the Al-bound and Ca-bound P are negatively correlated with the soil age (Table 2) and with the concentrations of Fe_o and Al_o. These relationships demonstrate that the Al-bound and Ca-bound P decrease with the extent of pedogenesis and indicate that the Al-bound P and Ca-bound P represent the initial P or initial mineral P in the parent material of the Hailuogou glacial retreat chronosequence. This deduction corresponds with the result of P fraction compositions in the C horizon.

Table 1 Correlations among P fractions determined by Hedley sequential fractionation technique and XANES[a]

	Ca-P1	Ca-P3	Al-P	Fe-P	org-P
Ca-P1	1				
Ca-P3	0.04	1			
Al-P	0.89	0.18	1		
Fe-P	−0.63	−0.23	−0.74	1	
org-P	−0.93	−0.09	−0.82	0.62	1
RPi	−0.83	−0.10	−0.83	0.46	0.93
NaHCO₃-Pi	−0.46	−0.05	−0.46	0.82	0.59
NaHCO₃-Po	−0.6	−0.85	−0.83	0.49	0.55
NaHCO₃-Pt	−0.71	−0.51	−0.89	0.58	0.81
NaOH-Pi	−0.6	0.07	−0.43	0.75	0.64
NaOH-Po	−0.94	−0.27	−0.71	0.58	0.81
NaOH-Pt	−0.94	−0.27	−0.71	0.58	0.81
DHCl-Pi	0.89	0.44	0.83	−0.70	−0.70
CHCl-Pi	0.43	0.54	0.31	0.23	−0.23
CHCl-Po	−0.6	−0.34	−0.43	0.81	0.58
CHCl-Pt	−0.54	−0.17	−0.37	0.75	0.64

a) Ca-P1 represents apatite P; Ca-P3 represents $Ca(H_2PO_4)_2$. Because $CaHPO_4$ is only detected at the 40 year site with a very low content, it is not included in the correlation analysis.

The correlational analyses of P fractions determined by the two methods show that Al-bound and Ca-bound P are positively correlated with DHCl-P ($r = 0.89$ and 0.83, respectively). Fe-bound P is positively correlated with NaHCO₃-Pi, NaOH-Pi, and CHCl-Po ($r = 0.82$, 0.75, and 0.81, respectively), which indicates that weakly bound particle inorganic P and hard decomposable organic P are apt to be adsorbed on Fe oxyhydroxides. The organic P measured by XANES has a positive relationship with Resin-P and NaOH-Po. Because Resin-P is inorganic P, the remarkable relationship between Resin-P and organic P indicates that an increased concentration of bioavailable P is the result of higher biomass and more organic P being returned from litter decomposition. The results of the two methods show that organic P clearly increases in the A horizon during the pedogenesis process. At the 80 and 120 year sites, the concentration of NaOH-Po accounts for more than 50% of the TP. This is the reason for the good relationship between the concentration of organic P determined by XANES and the NaOH-Po fraction.

4.2 Change in soil P fractions during the pedogenesis process and its driving factors

The dominance of apatite in the recently deglaciated soils reported by our study has also been reported for other glacier forefields (Turner et al., 2007; Föllmi et al., 2009). In addition, some granite deposits contain childrenite $[(Fe,Mn)AlPO_4(OH)_2 \cdot H_2O]$, eos-phorite $[MnAl(PO_4)(OH)_2 \cdot H_2O]$, amblygonite $[(Li,Na)Al[(F,OH)PO_4]]$, and montebrasite $[LiAl(PO_4)(OH)]$ (Neiva et al., 2000).

The moraine deposit of Hailuogou Glacier is the major parent material of soil composed of granite and granitoidite[1]. The Al-phosphate and apatite are the major source of soil, and thus Al-bound P and Ca-bound P are the two main fractions during the early stage of pedogenesis (<12 years). The P in Al-bound P is easier to be decomposed and released compared with the P in Ca-bound P (Flicoteaux and Lucas, 1984); therefore, there is almost no Al-bound P after 40 years of pedogenesis. Weathering is weak during the early stage of pedogenesis; therefore, the release of P from minerals and the fraction of Resin-P in early soil do not meet the demands of vegetation development.

After 12 years since the glacier retreat, with the increasing strength of weathering and development of vegetation, the soil becomes more acidic and Al-Phosphate and apatite are dissolved gradually, resulting in the rapid decrease of Al-bound and Ca-bound P fractions. In contrast, the organic P fraction increases rapidly. The Fe-bound P fraction emerges at the 30 year site. Afterwards, the Fe-bound P fraction varies at a low level and becomes positively related

1) He Y R, Zhang B H, Liao C L, et al. 2005. Soil features, taxonomy and its eco-environmental effect on the east slope of Gongga Mountain (unpublished document).

Table 2   Correlations between the soil properties and the P fractions in the A horizon

	Age	pH	C_{iorg}	C_{org}	N_{tot}	P_{tot}	Fe_o	Al_o
Ca-P1	−0.96	0.95	0.63	−0.68	−0.67	0.86	−0.74	−0.99
Ca-P3	−0.04	0.18	0.39	0.22	0.22	−0.04	−0.18	−0.04
Al-P	−0.82	0.95	0.63	−0.68	-0.67	0.82	−0.90	−0.88
Fe-P	0.70	−0.71	−0.66	0.85	0.86	−0.41	0.90	0.64
org-P	0.85	−0.86	−0.66	0.70	0.71	−0.63	0.67	0.93
RPi	0.66	−0.77	−0.39	0.66	0.66	−0.49	0.64	0.83
NaHCO3-Pi	0.52	−0.41	−0.53	0.99	0.99	0.06	0.62	0.46
NaHCO3-Po	0.49	−0.77	−0.65	0.14	0.14	−0.49	0.72	0.60
NaHCO3-Pt	0.54	−0.77	−0.65	0.54	0.54	−0.37	0.75	0.71
NaOH-Pi	0.71	−0.49	−0.39	0.94	0.94	−0.14	0.55	0.60
NaOH-Po	1	−0.89	−0.39	0.54	0.54	−0.71	0.64	0.94
NaOH-Pt	1	−0.89	−0.39	0.54	0.54	−0.71	0.64	0.94
DHCl-Pi	−0.94	0.94	0.39	−0.49	−0.49	0.77	-0.81	−0.89
CHCl-Pi	−0.37	0.49	0.13	0.54	0.54	0.66	-0.06	−0.43
CHCl-Po	0.77	−0.54	−0.65	0.77	0.77	−0.14	0.58	0.6
CHCl-Pt	0.66	−0.43	−0.65	0.89	0.89	0.03	0.49	0.54

with the Fe_o content (Table 2). If taking apatite, Al-phosphate, and Fe-bound P as potentially releasable P, it decreases remarkably after 40 years since the glacier retreat on the soil chronosequence. The primary mineral contributes little to the soil P pool after 40 years since the glacier retreat, even being negligible at the 80 years site.

The bioavailable P (Resin-P and $NaCHO_3$-P), which increases dramatically after 30 years, especially the Resin-P, shows an opposite trend to that of potentially releasable P. With an increase in readily bioavailable P, vegetation develops, after which, litter decomposition becomes the main source of the increase in organic P, while the organic matter content of the soil increases as well. On the other hand, the development of vegetation, especially the growth of coniferous forest (*Picea*, *Abies*), changes the soil properties, such as soil pH. As a result, changes in soil properties and the development of vegetation promote the decomposition of P minerals and the release of the bioavailable P.

On the basis of the above results, the soil P fraction composition is closely related with soil and vegetation development. The fractions of Al-bound P and Ca-bound P are markedly correlated with soil age (Table 2). Correspondingly, the DHCl-P fraction decreases with soil age, whereas the concentrations of Fe_o and Al_o increase gradually, which promote P adsorption. Al_o, in particular, exhibits a high capacity to adsorb organic P and Resin-P, indicated by remarkably positive correlations ($r = 0.93$ and 0.83, respectively). The strong relationships between Al_o, Fe_o, and P fractions demonstrate that Fe and Al hydroxides in the soil are crucial factors that control the P retention ability of the soil (Kaňa and Kopáček, 2005).

5   Conclusion

Hedley sequential fractionation technique and XANES have their respective advantages for P fraction analyses in topsoil along a glacial retreat chronosequence in Hailuogou Glacier. Hedley sequential fractionation technique can evaluate the concentration of readily bioavailable phosphorus more accurately. XANES can indicate the concentration of potentially bioavailable P as it can accurately distinguish between different metal-bound P.

The Al-bound P and Ca-bound P in the soil along the glacial retreat chronosequence of Hailuogou Glacier, which are the sources of mineral P, decrease with the soil age, and Al-bound P almost disappears after 40 years. The concentrations of soil Al_o and Fe_o increase during the pedogenesis process, which mainly adsorb organic P. The Resin-P and $NaHCO_3$-P fractions rapidly increase after 30 years and promote the development of vegetation. The development of vegetation impacts the soil P fraction composition and is shown as an increase in organic P and a decrease in Al-bound P and Ca-bound P.

Abrams M M, Jarrell W M. 1992. Bioavailability index for phosphorus using nonexchange resin impregnated membranes. Soil Sci Soc Am J, 56: 1532–1537

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