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Rapid loss of phosphorus during early pedogenesis along a glacier retreat choronosequence, Gongga Mountain (SW China)

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The loss of phosphorus (P) during the early pedogenesis stage is important at the ecosystem level, and it also plays an important role in the global P cycle. The seasonal variation of total P (Pt) and its fractions along a young soil chronosequence (Hailuogou chronosequence) on the eastern slope of Gongga Mountain, SW China, was investigated based on the modified Hedley fractionation technique to understand P loss during the early pedogenesis stage. The results showed that the mineral P (mainly apatite) was the dominant fraction of Pt in the C horizon of the soil, and the seasonal difference in Pt and its fractions was insignificant. In the A horizon, Pt concentrations decreased markedly compared with those in the C horizon, and as the age of the soil increased, the inorganic P (Pi) significantly decreased and the organic P (Po) prominently increased. Seasonally, the P fractions exhibited various distributions in the A horizon. The variation of Pt and its fractions revealed that the P loss was rapid along the 120-year soil chronosequence. The concentrations of Pt in the original minerals decreased more than 50% in the 52 years since the glacier retreated, and the depletion reached almost 80% at the 120-year pedogenesis. The loss of P from the soil of the Hailuogou chronosequence was mainly attributed to weathering, plant uptake, and transport by runoff. The data obtained indicated that the glacier retreat chronosequence could be used to elucidate the fast rate of P loss during the early pedogenesis stage.

Rapid loss of phosphorus during early pedogenesis along a glacier retreat choronosequence, Gongga Mountain (SW China)

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Abstract The loss of phosphorus (P) during the early pedogenesis stage is important at the ecosystem level, and it also plays an important role in the global P cycle. The seasonal variation of total P (Pt) and its fractions along a young soil chronosequence (Hailuogou chronosequence) on the eastern slope of Gongga Mountain, SW China, was investigated based on the modified Hedley fractionation technique to understand P loss during the early pedogenesis stage. The results showed that the mineral P (mainly apatite) was the dominant fraction of Pt in the C horizon of the soil, and the seasonal difference in Pt and its fractions was insignificant. In the A horizon, Pt concentrations decreased markedly compared with those in the C horizon, and as the age of the soil increased, the inorganic P (Pi) significantly decreased and the organic P (Po) prominently increased. Seasonally, the P fractions exhibited various distributions in the A horizon. The variation of Pt and its fractions revealed that the P loss was rapid along the 120-year soil chronosequence. The concentrations of Pt in the original minerals decreased more than 50% in the 52 years since the glacier retreated, and the depletion reached almost 80% at the 120-year pedogenesis. The loss of P from the soil of the Hailuogou chronosequence was mainly attributed to weathering, plant uptake, and transport by runoff. The data obtained indicated that the glacier retreat chronosequence could be used to elucidate the fast rate of P loss during the early pedogenesis stage.

Key words: Phosphorus fractions; P loss; pedogenesis; Hailuogou choronosequence; Gongga Mountain

1 Introduction

Phosphorus (P) is one of the limiting nutrients in diverse natural habitats, including freshwater, marine, and terrestrial biomes (Huang et al., 2013; Elser 2012), especially as nitrogen (N) deposition increases (Elser, et al., 2007; Craine and Jackson, 2010; Cramer, 2010). Mountain regions, especially in some alpine and high-latitude ecosystems where the climate is cold and humid, are the unique terrestrial ecosystems where P rather than N becomes the main limiting nutrient (Seastedt and Vaccaro, 2001; Wassen et al., 2005). The P limitation in terrestrial ecosystems results from the shortage of bio-available P in the soil (Vitousek et al, 2010). Due to the unique global P cycle (Newman, 1995; Fillippelli, 2008), the content of bio-available P in the soil decreases continuously during pedogenesis (Walker and Syers, 1976), resulting in P becoming the limiting nutrient and ecosystem regression in extreme situations (Walder et al, 2004; Vitousek et al, 2010).

In terrestrial ecosystems, the soil bio-available P is generally depleted in two ways. One is by P occlusion over time by biological and geochemical processes in which P is transformed into stable organic forms, which are difficult to mineralize (Walker and Syers, 1976). Another is the direct loss of bio-available P as well as other P fractions by plant uptake, soil erosion, runoff transport, etc. Compared with other ecosystems, the latter cause of P loss should be more significant in mountain ecosystems due to steep slopes, stronger runoff, and well-developed forests that take up more P. Furthermore, compared with occluding immobilization, the direct loss of P in mountain regions was almost completely neglected in former studies, and the loss rate and pathway were also far from clear.

In recently developed soil (younger than one hundred years) where the occluding effect of P is not as remarkable as in well-developed soil (Zhou et al., 2013; Prietzel et al., 2013), the loss of P has not received enough attention so far. In the present study, a young soil chronosequence along the area of retreat of the Hailuogou Glacier was selected to investigate the seasonal variation of total P (Pt) and its fractions. We hypothesized that during the early pedogenesis stage, the seasonal variations of Pt and its fractions in the soil would demonstrate the loss of P with the increasing age of the

soil and vegetation succession. Therefore, the objective of this study is to know whether and how soil P was lost during the early pedogenesis stage according to the seasonal variation of Pt and the composition of its fractions along this 120-year soil chronosequence.

2 Materials and methods

2.1 Study area and soil collection

Hailuogou Glacier, located on the eastern slope of Gongga Mt., southwestern China (Fig. 1), has been retreating since 1890 (Li et al., 2010). A soil chronosequence has developed in the area exposed by the retreat that is approximately 2 km long, 50-200 m wide and has a 150 m altitude difference. The soil development on the chronosquence was described by He and Tang (2008). According to the World Reference Base for Soil Classification (2006), the soils are grouped as Regosols. The mineral composition of the parent materials is similar in the retreat area, including quartz (35.8%), feldspar (33.4%), biotite (12.1%) and hornblende (10.0%) (Zhou, 2014).

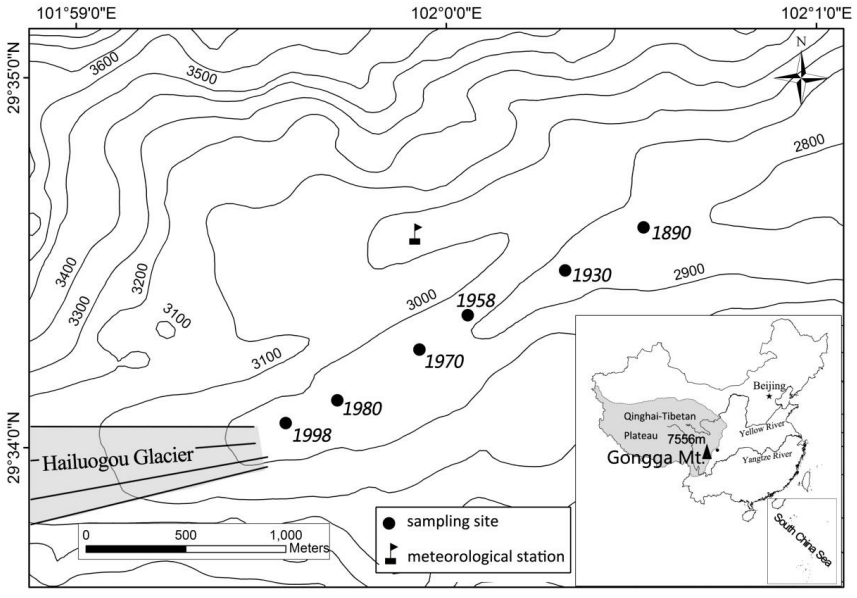

Fig. 1 Sketch map of Hailuogou Glacier retreat area and the sampling sites

A complete primary vegetation successional sequence has formed on the chronosequence, including (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., and (5) *Picea brachytyla* (Franch.) E.Pritz. - *Abies fabri* (Mast.) (Li and Xiong, 1995).

The climate on the Hailuogou chronosequence is controlled by the southeast monsoon with a mean annual temperature of 4.2°C and a mean annual rainfall of 1947 mm (Wu et al., 2013).

The soil samples were collected in December 2010 and July 2011 at the same plots in each site with different ages after the retreat of the glacier (Fig. 1). Three 2×2 m plots were created for each site, and the soil profiles were hand-dug at each plot. The soil profiles were divided into three horizons: the O, A and C horizons, except for the 12-year-old site, where the O horizon was absent.

2.2 Chemical analysis

A modified Hedley fraction extraction technique (Tiessen and Moir 1993) was used to separate the Pt into eight fractions (Fig. 2). Two strips of an anion exchange membrane (BDH 551642S, 9 × 62 mm) were put into the tube. The anion exchange membrane strips were converted to bicarbonate before they were used in the first step. The supernatant of Step 1 - 4 was shaken for 16 h at 25 °C. Thereafter, the supernatant was centrifuged at 25000 × g for 10 min at 0 °C, and then passed through Millipore filters (pore size 0.45 μm). The concentrations of the organic P (Po) were calculated by the differences in the P concentrations between the undigested and the digested samples. The P concentrations were measured with a UV-V spectrophotometer (SHIMAZU UV 2450) using the phosphomolybdate blue method (Murphy and Riley, 1962). Blanks were mixed with the solvents to account for matrix interference during the extraction processes.

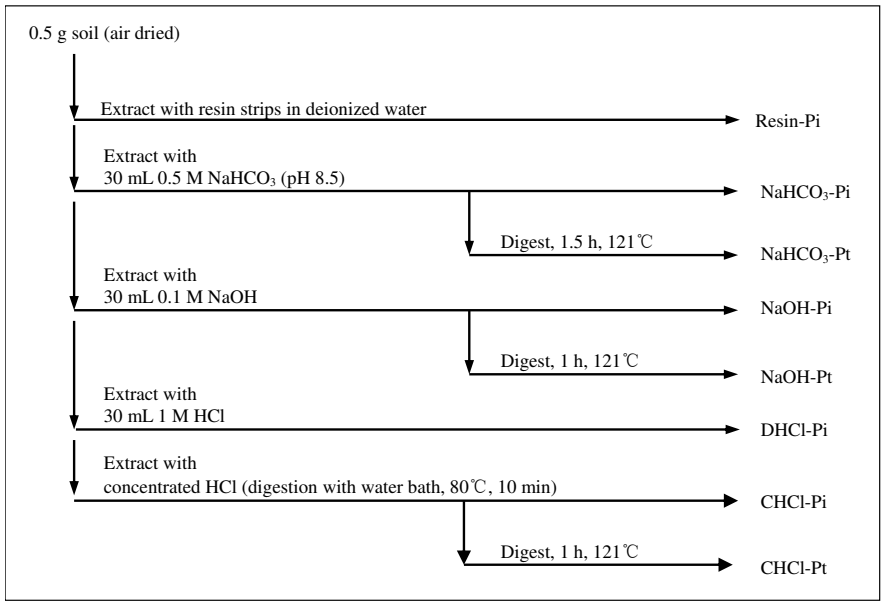

Fig. 2 The extraction procedure of P in soil (modified from Tiessen and Moir, 1993)

The P fractions were defined as follows: (1) Resin-Pi (Resin-inorganic P) = exchangeable P, (2) $NaHCO_3$-P = labile Pi and Po, (3) NaOH-P = moderately bioavailable P, mainly Pi and Po tightly adsorbed and/or fixed by Al and Fe hydroxides, and P in humic and fulvic acids; (4) DHCl-Pi = Pi in primary minerals (mainly apatite); (5) CHCl-P = extractable P by concentrated HCl, refractory P (Tiessen and Moir 1993).

2.3 Depletion factor calculation

The depletion factor (DF) of P proposed by Schroth et al (2007) was used to demonstrate the P loss in the present work. The DF was calculated according to the following equation:

$$DF=[(C_A - C_{Ae})/(C_{Ti,A} - C_{Ti,Ae})]/(C_P/C_{Ti,P})$$

in which C_A and C_{Ae} represent the concentrations of Pt and NH_4Cl extracted P in the A horizon, respectively; $C_{Ti,A}$ and $C_{Ti,Ae}$ represent concentrations of Ti in the bulk soil sample and the NH_4Cl extraction solution of the A horizon, respectively; and C_P and $C_{Ti,P}$ represent concentrations of Pt and Ti in the parent materials, respectively. Both Ti in the bulk soil sample and the NH_4Cl extraction solution were measured using the Inductively Coupled Plasma-Mass Spectrograph (ICP-MS). A standard solution

SPEX^{TM} from the US was used as the standard. Quality control was assured by the analysis of duplicate samples, blanks, and reference materials (GSD-9 and GSD-11, Chinese geological reference materials), and precision was good, with a variability in the repeated analysis of samples and reference materials below 5%. Recovery was 90 ± 6% (error expressed as 95% confidence interval) for the reference materials.

Considering the great increase of the Po in the A horizon, especially at the 80- and 120-year-old sites, the DF was recalculated using a modified function as follows:

$$DF_m=[(C_A - C'_{Ae} - C_{Ao})/(C_{Ti,A} - C_{Ti,Ae})]/(C_P/C_{Ti,P})$$

in which DFm was the modified DF; CA, C'Ae and CAo represent the concentrations of Pt, exchangeable P (RPi + NaHCO3-Pi) and Po (NaHCO3-Po + NaOH-Po + HCl-Po) in the A horizon, respectively; CTi,A and CTi,Ae represent the concentrations of Ti in bulk soil sample and water+ NaHCO3 extraction solution of the A horizon, respectively; and CP and CTi,P represent the concentrations of Pt and Ti in the parent materials, respectively.

3 **Results**

In the C horizon of the soil, the dominant fraction of P was DHCl-Pi, which accounted for over 99% of the Pt. Similar concentrations of Pt and DHCl-Pi were observed at the chronosequence. The seasonal variation in the concentrations of Pt and its fractions in the C horizon was not significant (Fig. 3).

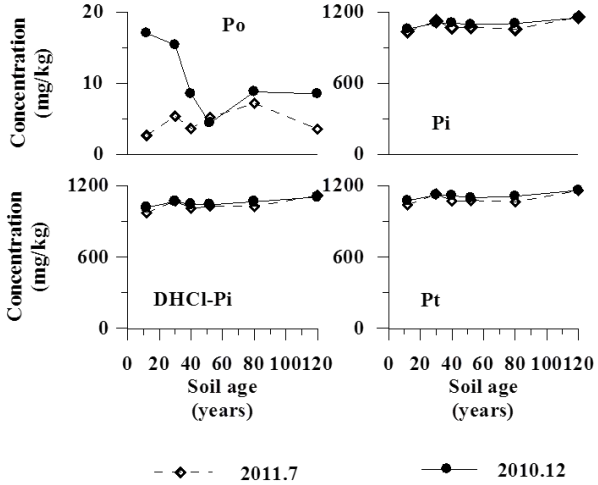

Fig. 3 Variations of the concentrations of Pt and its fractions in C horizon of the Hailuogou

chronosequence

In the A horizon of the soil, the concentration of Pt decreased at all sites compared with those in the C horizon (Fig. 4). At the 12-year-old site, the concentration of Pt in the A horizon was approximately 1000 mg/kg, which was lower than that in the C horizon. This difference became much more marked with the age of soil, and it reached approximately 600 mg/kg at the 120-year-old site. The seasonal differences in the concentrations of Pt were approximately 100 mg/kg, and the concentrations of Pt were a little higher in the winter, except at the 40-year-old site.

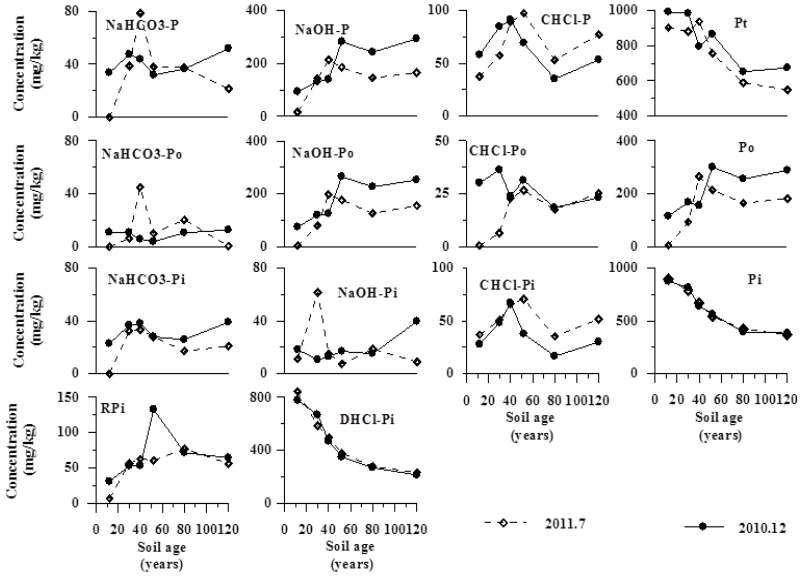

Fig. 4 Variation of the concentrations of P fractions in the A horizon

The concentrations of Po increased continuously with the age of the soil, while the opposite trend was found for Pi (mainly DHCl-Pi) (Fig. 4). The concentrations of bio-available P (RPi+$NaHCO_3$-P) (Tissen and Moir, 1993; Wu et al., 2014), as well as NaOH-P, slightly increased with the age of the soil. The significant seasonal difference in the P fractions was observed for NaOH-P and CHCl-P. The concentrations of NaOH-P in the summer were approximately 100 mg/kg higher than those in the winter, which was mainly attributed to the increase in the concentration of NaOH-Po. On the contrary, the concentrations of CHCl-P in the winter were slightly lower than those in the summer, which was mainly related to the low concentration of CHCl-Pi.

4 Discussion

4.1 Was P lost during the 120 years of pedogenesis?

The ratios of the Pt concentrations in the A horizon to that in the C horizon (Pt-A/Pt-C) revealed the continuous loss of P with soil age (Fig. 5). At the 80- and 120-year-old sites, the ratios were lower than 0.6. The ratios were much lower than those of the chronosequences of similar soil ages. There were no significant decreases of TP at the Morteratsch chronosequence (150 years) and the Damma chronosequence (120 years) in the Swiss Alps (Egli et al., 2012; Prietzel et al., 2013). Meanwhile, these ratios were also lower than those of several older chronosequences. The Pt-A/Pt-C ratio at the 5000-year-old site of the Franz Josef Chronosequence was approximately 72.7% (Walker and Syers, 1976). In a dune chronosequence in New Zealand, the ratio at the 370-year-old site was 59.5% (Eger et al., 2011). There was no obvious change in the TP at a 7800-year-old chronosequence in Northern Sweden (Vincent et al., 2013). Lower Pt-A/Pt-C ratios implied the severe loss of Pt in the soil under the climax community, and the loss rate was faster than other soil chronosequences.

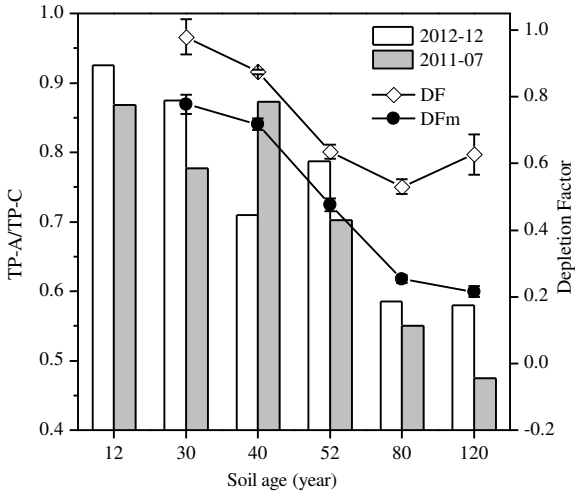

Fig. 5 The ratios of the concentrations of Pt between the A and C horizons and the variations of DF and DF_m along the chronosequence.

Both the DF and DF_m indicated the distinct loss of soil P with soil age (Fig. 5). The rapid loss of P from soil was first observed at the 40-year-old site, and less P was lost at the 120-year-old site than at the 80-year-old site, as was reflected by the DF.

The DF_m calibrated the loss rate and revealed a continuous loss of P along the chronosequence. After 52 years of soil development since the glacier retreated, nearly half of the original mineral P in the parent materials was lost, and the loss of P from the soil reached 78% of the original mineral P at the 120-year-old site. According to the DF and DF_m, the loss of P from the soil at the Hailuogou glacier retreat area was much faster than in other soil chronosequences (Eger et al., 2011).

The loss of soil P might not be as extensive as the DF and DF_m have shown because ecosystems could return P to the soil through continuous Po mineralization. Therefore, the real loss of P from the soil should also take into account the turnover rate, which is a complicated process. Nevertheless, the rapid loss of the original mineral P should cause a shortage of bioavailable P for montane ecosystems in the short-term, compared with the relatively flat region (Walker and Syers 1976, Vitousek et al, 2010; Eger et al., 2011; Vincent et al., 2013). On the other hand, N deposition has dramatically increased in terrestrial ecosystems (Pardo et al, 2011; Fujimaki et al, 2009), which might decrease microbial biomass (Treseder, 2008) and change litter decomposition (Knorr et al, 2005). The P in microbial biomass was regarded as the major P pool (Turner et al, 2013), while the litter decomposition was an important avenue for P return (Fillippelli, 2008). With an increase in the N deposition and its impact on microbial biomass and litter decomposition, the fast loss of P might enhance the shortage of bioavailable P and its limitation for the montane ecosystem.

4.2 **The pathway of P loss along the soil chronosequence**

During the early stage of pedogenesis, P could be released from the parent rocks into the soil by weathering. On the Hailuogou chronosequence, the degree and rate of weathering changed with the age of the soil (Zhou, 2014). The weathering rate at the 120-year-old site was 111 $cmol_c/m^2 \cdot yr$, which was higher than those in Alps and some tropical zones (Egli et al., 2001; Taylor and Blum, 1995; Neat et al., 2004). The rapid weathering process could lead to the dissolution of apatite bound to calcite, biotite,

hornblende, plagioclase and other silicate minerals. The DF_m of soil P at the Hailuogou chronosequence demonstrated that only approximately 22% of the original apatite remained after 120 years of weathering and pedogenesis (Fig. 5). The rapid dissolution of apatite during the weathering process should be ascribed to the fine materials that resulted from strong glaciation and freeze-thaw processes, adequate moisture and rapid vegetation succession.

P released from minerals as phosphate was available for plant assimilation. Along the Hailuogou chronosequence, the primary vegetation succession was quickly established with the weathering and pedogenesis. The increase of biomass, as well as P in biomass, was also prominent along the chronosequence (Table 1). The pool of P in biomass in the forest at the 120-year-old site was 299 kg/ha (Zhou et al, 2013), which was similar to our result (Table 1). Therefore, plant uptake was a significant pathway of P loss from the soil. Moreover, the lower concentrations of bio-available P in July, the growing season, confirmed that plant uptake accelerated the loss of P from the soil.

Table 1 Biomass, biomass P pool and P loss along the Hailuogou chronosequence

Age	Biomass [a]	P conc. [b]	Biomass P	DHCl-Pi C	DHCl-Pi A	A Thickness	Density	P Loss
yrs	t/ha	g/kg	kg/ha	g/kg	g/kg	cm	g/cm^3	kg/ha
30	48.9	1.2	57.5	1.1	0.6	1.0	2.7	117.9
52	184.7	0.9	164.9	1.0	0.4	4.0	2.7	713.4
80	308.0	0.7	225.2	1.0	0.3	8.0	2.7	1643.0
120	382.3	0.8	303.9	1.1	0.2	9.0	2.7	2127.4

a: Biomass was the sum of above and below ground calculated according to Luo et al (2004). b: the P concentration was the average concentration of leaf, trunk, bark and twig.

The concentration of DHCl-Pi decreased in the A horizons, which reflected the great loss of original mineral P from the soil at the relatively old sites (Table 1). Meanwhile, the pool of P in biomass was several times higher at the older sites than at the younger sites. The P in biomass accounted for nearly half of the original mineral P loss from the soil at 30-year-old site, while it reached one seventh at the 120-year-old site. This suggested that in addition to plant uptake, there should be another pathway

for P loss from the soil on the Hailuogou chronosequence.

As P was released from parent rocks, Fe, Al, Ca and other metal ions were released as well during weathering and pedogenesis. Fe and Al ions were apt to form hydroxides. In addition to being assimilated by plants, the released phosphate tended to be adsorbed onto the surface of Fe and Al hydroxides. In the NaOH extracted solution, the P concentrations were significantly positively related with Fe and Al concentrations (Fig. 6). This result implied that the P extracted by NaOH was from Fe and Al hydroxides that bound P, which accounts for more than 30% of the Pt at the 52, 80- and 120-year-old site in December, while it was a little lower in July. A previous study in dark coniferous forests showed that the P bound by Al and Fe was the major fraction of soil P (Wood et al, 1984). Kaňa and Kopáček (2005) confirmed that the adsorption capacity of Fe and Al hydroxides was the dominant factor controlling the transport of soil P to the water body. Šantrůčková (2004) demonstrated that the lower acidity of the forest soil drove the transformation of P and changed the P loss rate. As the vegetation became established and evolved on the Hailuogou chronosequence, the pH of the soil decreased with the soil age (Zhou et al., 2013). In the acidified soil, especially at the 80- and 120-year-old sites, the P bound by Fe and Al was potentially transported by runoff. The annual precipitation was concentrated in the summer (Wu et al, 2013). The P bound by Fe and Al could be more significantly discharged by runoff in the summer than in the winter, which could be interpreted as the reason for the lower contribution of NaOH-P to the Pt in July than in December. Meanwhile, the elevation difference of 150 m along less than 2 km of the Hailuogou chronosequence, led to the strong erosion and great loss of soil P. The mean concentration of Pt in the 32 runoff samples, collected from the 20th to 25th September, 2014 at the Hailuogou chronosequence, was 0.017 ± 0.004 mg/l. The annual runoff was 11.8 m^3/s (Lv and Wang, 2008). The P discharge rate was calculated as 0.2 g/s, which was a very rapid loss.

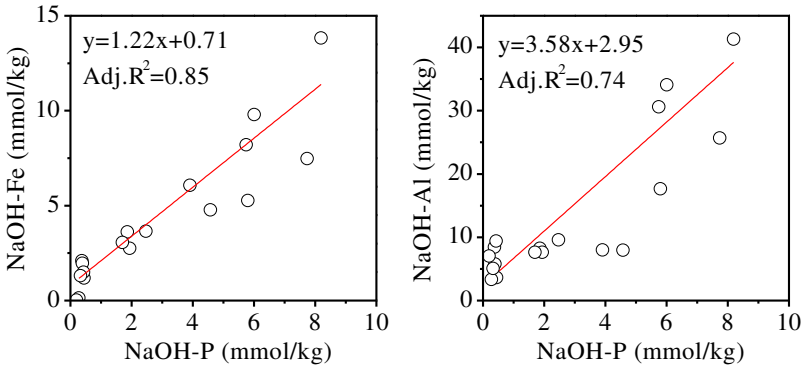

Fig. 6 Correlation between P and Fe, Al in the NaOH extracted solution.

5 Conclusion

During the early stage of pedogenesis at the Hailuogou chronosequence, P was rapidly lost from the soil. The Pt from the original minerals was depleted by over 50% in the 52 years since the glacier retreated, and the loss reached 80% at the 120-year-old site. The fast loss of P from the soil could be attributed to the higher weathering rate, the large amount of plant uptake and transport by runoff.

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