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A 2000-year record of phosphorus forms and accumulation in peatland of the Greater Khingan Mountains in Northeast China: Paleoenvironmental implications

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ABSTRACT

To investigate the connection of phosphorus (P) forms with peatland succession and history of fire in Tuqiang peatland, a 57 cm peat core was sampled with high-resolution (1-cm intervals) in the north of the Great Khingan mountain (Northeast China). AMS 14 C dating techniques combined with sequential chemical extraction was used to determine and calculate the accumulation rates of phosphorus fractions. Phosphorus forms were mainly composed with NaOH-P_o, hot concentrated HCl-P (conc. HCl-P) and residual-P. Active phosphorus pools were enriched in the top 8–10 cm of the peat surface. The concentrations of organic phosphorus forms and residual-P were generally high during 1200 to 500 cal yr BP, and the accumulation rate of that gradually decreased since 1600 cal yr BP. Both of concentration and accumulation of organic phosphorus decreased after 600 cal yr BP. The accumulation rate of organic phosphorus forms significantly corresponded with peat development frequency, pollen records and other paleo evidence. The concentration and accumulation of organic phosphorus, especially NaOH-P_o, was positively connected with concentration of pollen and *Cyperaceae*, and decreased when relative abundance of moss or shrubs occurred. Fire changed the vegetation community, decreased the concentration and accumulation of P_o, and reduced inactive P_o/P₁ at the same time. Fire events could also leave geochemical evidence on peat. It is necessary to consider the both changes of inactive P_o/P₁ and organic phosphorus accumulation rate when reflected the fire history by phosphorus in core.

1. Introduction

Wetlands are often seen as pools of nutrients. Phosphorus is one of the major limiting nutrients of primary productivity in terrestrial ecosystems. Therefore, the P demand of plants might be the most important drivers of soil and ecosystem development (Lang et al., 2016). In some dry and cold inland areas, phosphorous, rather than nitrogen, is the nutrient most limiting to the earliest stages of primary succession. Increasing P can also accelerate the rate of plant succession even in extreme climates (Darcy et al., 2018). Global warming may potentially stimulate the mineralization of P, which could have cascading long-term effects on the succession of peatland (Aerts et al., 2001). Vegetation and

fire have also responded to climate changes. Frequent and intensive fires occurred during dry climatic conditions in the paleorecord (Xiao et al., 2015). Fire can ease P limitation and decouple the biogeochemical cycling of nutrients, potentially causing reversion to an earlier stage of ecosystem development. These effects also depend on vegetation and soil types (Butler et al., 2018).

Vegetation is an important participant in the geochemical process of phosphorus cycling. During the process of peatland development, phosphorus in the soil is progressively stored in plant residues or deposited stably in combination with complex organic compounds, which gradually converted into lesser available forms. The reducing bioavailability of phosphorus have limited primary producers in

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terrestrial ecosystems, which are one of the important factors to affect the successions of vegetation community. For example, climax species had higher N: P ratios implied P limitation will be increasing at later succession stages (Zhang et al., 2018a). In addition, long-term climate changes lead to changes of temperature and water level and sequentially change the development of peatland and succession of life both aboveground and underground (Yuan et al., 2011). The environmental changes and natural succession of peatland can be reflected by the succession of the vegetation community, which is recorded in the peat. These processes are recorded in the core through the accumulation of pollen, plant residues and nutrients (Yan et al., 2015a, 2015b). The concentration and state of P change along with all these changes, processes and records in sedimentation. Studying the accumulation of phosphorus in the core may illustrate the succession of productivity in this area.

Fire obviously introduces short-term changes to the environments that lose the most organic phosphorus and changes the biochemical and metrological properties of the plant-soil system (DeLuca and Sala, 2006; Khanna et al., 1994; Romanya et al., 1994; Toberman et al., 2014). Fire impact on P availability is on a similar order of magnitude as mineral weathering and annual P uptake by ecosystems, which enhanced available P 2 to 10 times (Schaller et al., 2016). Different degrees of fire events directly damage the peatland vegetation, and the state of phosphorus existing in plants and surface residues may also undergo drastic changes. The increase of dry matter total P from burn to black carbon was higher than ash, and the most raised form, especially in peat, was inorganic P. (Schaller et al., 2016). In addition, historical fire information is more easily preserved in the peat core, which provides a greater possibility for the reconstruction of fire events in peatlands.

During the Holocene, the timing and duration of long-term climatic phases and abrupt climate changes were different among regions, with close to the monsoon line, treeline and snowline changing climate being especially sensitive to climate changes such as summer monsoons and abrupt climate events (Thamban et al., 2007; Xiao et al., 2015). Northeast China is located on the edge of a monsoon zone, and peatland succession is mainly affected by monsoon activity. The development of peatlands in the Greater Khingan Mountains region was one of the latest in northeastern China, which was related to its high latitude, high elevation and the delayed Holocene climate warming (Xing et al., 2015). Peatlands in this region are characterized by slow rates of decomposition under cold climate conditions and continuous inputs due to deposition, which cause the stable accumulation of phosphorus.

In sedimentology, total phosphorus and active phosphorus are usually determined as basic chemical indicators. However, phosphorus compounds in soil are complex in structure and differ in composition and activity. Therefore, total phosphorus and active phosphorus are unable to reflect the sedimentological characteristics of phosphorus. The Hedley sequence extraction method (Hedley et al., 1982) is an appropriate and widespread method for classifying phosphorus according to its availability and activity. It has been widely applied to research of sedimentation but rarely to reflect the history of peatland succession. It is assumed that the stable phosphorus pools are better to reflect the succession history and fire events of the peatland, and total phosphorus may be affected by active phosphorus such that it cannot reconstruct events clearly. In this paper, phosphorus forms were determined via the Hedley sequence extraction method, and analysed the changes of the concentrations and accumulation in the peat core, aiming to 1) investigate the phosphorus forms accumulation in peatlands 2) reveal the connection between phosphorus forms and succession of peatland, and 3) elucidate the history of fire events indicated by phosphorus forms.

2. Material and method

2.1. Study area

The Great Khingan Mountains are between E $121^{\circ}12'$ – $127^{\circ}00'$ and N

 $50^{\circ}10'-53^{\circ}33'$, where are 180-2029 m above sea level. Bog is the major type of wetland with macrophanerophytes, shrubs, herbs, moss and a young bog creek. The landform structure is simple, and the soil types are meadow soil and marsh soil (Sun et al., 2011). There is a temperate continental monsoon climate with long, cold and dry winters from Nov. to Apr. and short, hot and wet summers from Jul. to Aug. There is also an ice-free period that typically occurs from May to Oct. The mean annual temperature is approximately -2 °C.

The study area (N 52.94295, E 122.85485) is located in a valley 5 km from the east of Tu Qiang (TQ) town and in the north part of the Greater Khingan Mountains and on the north bank of Eermu river (Fig. 1). The mean annual temperature is approximately $-3.9\,^{\circ}$ C, and the mean annual precipitation is approximately 452 mm. The peatland in the TQ area is a typical bog in the Greater Khingan Mountain, which developed from a wide valley. The main plants include shrubs (Betula fruticosa, Ledum palustre, Vaccinium uliginosum, Chamaedaphne calyculata, Salix myricoides).

2.2. Peat core collection

Peat samples were collected in Oct 2016 from TQ in the Great Khingan Mountains. A 57-cm-long profile was collected by a wardenaar peat profile sampler (Eijkelkamp, Netherlands) and was sliced into 1 cm intervals before 40 cm and into 5 cm intervals between 40 and 57 cm in the field. The core was stored in polyethylene plastic bags and then taken back to the laboratory and stored at $-20~^\circ\mathrm{C}$ for laboratory analysis. The profile was divided into 4 sections: peat with roots (0–10 cm), light brown peat (11–25 cm), dark brown peat (26–40 cm) and black peat (41–57 cm).

2.3. Chemical analysis

Samples were combusted at 550 °C for 4 h in a muffle furnace and reweighed to determine loss on ignition (LOI). The data were both presented as percentages. Dry bulk density (DBD) was determined by over-drying at 105 °C for 12 h and weighed. Dry bulk density and LOI analyses were performed at the Analysis and Test Centre, Northeast Institute of Geography and Agroecology (IGA), Chinese Academy of Sciences (CAS). Carbon-14 radiocarbon dating was used for dating sediment samples. Three samples (22, 36, 57 cm) were selected, and calibrated ages were 1065 ± 30 , 1645 ± 30 , and 2020 ± 30 14 C yr BP, respectively (Table 1). The results calibration, age-depth model construction and other details were showed in Han's research (Han et al., 2019)

Phosphorus fractions were analysed by the sequential extraction

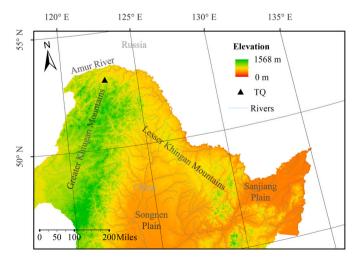


Fig. 1. Location of the sample site in the Great Khingan Mountains.

Table 1
Calibrated Accelerator Mass Spectrometry (AMS) radiocarbon dates and lithology.

Depth (cm)	Lab No.	Dated material	AMS ¹⁴ C age	Calibrated age	Lithology
			(¹⁴ C yr BP)	(cal yr BP) (2σ range)	
22	XA- 7561	Bulk peat	1065 ± 30	968 ± 40	roots
36	XA- 7562	Bulk peat	1645 ± 30	1566.5 ± 50.5	Light brown peat
57	XA- 7563	Bulk peat	$\begin{array}{c} 2020 \ \pm \\ 30 \end{array}$	1973 ± 80	Dark brown peat

method (Tiessen and Moir, 1993). Samples were air-dried and passed through a 0.178 mm diameter sieve and stored in polyethylene plastic at normal temperatures before chemical analysed. Peat samples (0.3000–0.5000 g) were sequentially extracted by anion exchanged resin, NaHCO₃, NaOH, HCl, conc. HCl (hot concentrated HCl), and $\rm H_2SO_4$ –HClO₄. Part of the extracted sample solutions were directly analysed for inorganic phosphorus concentrations, and the residual extracts were digested with HNO₃–HClO₄ for determining total phosphorus. Another peat samples (0.5000 g) were digested by solution of $\rm H_2SO_4$ –HClO₄, and the digested solution was made up to 100 ml to detected the total phosphorus concentration. Phosphorus in the extracts was determined by a SAN++ Continue Flow Analyzer (Manufactured by SKALAR, Netherlands). The determination of phosphorus was performed at the Analysis and Test Centre, Northeast Institute of Geography and Agroecology, CAS.

2.4. Phosphorus accumulation

Accumulation rates of phosphorus forms were calculated by the depth-age model reconstructed from ^{14}C data and the dry bulk density of each depth before 40 cm within the peat cores. Phosphorus accumulation rates (g m $^{-2}$ yr $^{-1}$) were calculated by multiplying the dry bulk density (g cm $^{-3}$) and the phosphorus concentration (mg kg $^{-1}$) for each interval to normalize the data to the annual vertical accretion rate (cm yr $^{-1}$). The percent recoveries were illustrated via Pt and the sum of phosphorus forms. The average recovery ranged from 80 to 120%. The figures are drawn by the software Origin 9.0.

3. Results

3.1. Distribution of phosphorus forms in the peat core

For all samples, the concentrations of phosphorus forms were ranked in the order of NaOH-P $_{\rm o}>$ conc. HCl-P $_{\rm o}>$ Residual-P> conc. HCl-P $_{\rm i}\approx$ NaOH-P $_{\rm i}\approx$ NaHCO $_{\rm 3}$ -P $_{\rm o}>$ Resin-P \approx NaHCO $_{\rm 3}$ -P $_{\rm i}\approx$ HCl-P $_{\rm i}.$ The average concentration of total phosphorus was 1069.36 mg kg $^{-1}$, ranging from 195.10 mg kg $^{-1}$ to 2031.67 mg kg $^{-1}$. Phosphorus forms content curves for the peat core showed that the concentration of phosphorus decreased and remained stable from 2000 to 1300 cal yr BP, were highest from 1300–400 cal yr BP, and then decreased since about 400 cal yr BP.

Since about 250 cal yr BP to now (10–0 cm), the percentages of inorganic and organic phosphorus were nearly equally, except for HCl–P and NaOH-P_i. The percentages of forms of resin-P, NaHCO₃-P_i and NaHCO₃-P_o increased, which were higher than that of in non-surface peat which approximately 16%, 9% and 3%, respectively (Fig. 2a). However, the organic phosphorus increased and kept stable between 60%–70% after 8 cm, and the inorganic phosphorus showed the opposite regular distribution. NaOH-P_o and conc. HCl-P_o became the main forms in the phosphorus pools (Fig. 2b and c). In particular, the percentage of NaOH-P_o increased about from 15% to 40% with increasing depth, but labile phosphorus forms showed the opposite tendency.

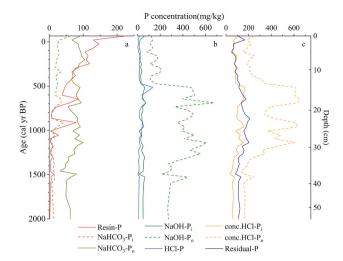


Fig. 2. Distributions of phosphorus forms in TQ peat profile(a) concentrations of resin-P, NaHCO₃-P₁ and NaHCO₃-P₀ (b) concentrations of NaOH-P₁, NaOH-P₀ and HCl-P (c) concentrations of conc. HCl-P₁, conc. HCl-P₀ and residual-P.

3.2. Accumulation of phosphorus forms in the peat core

Phosphorus always existed in stable phosphorus pools in peat land. such as humic organic phosphorus and residual phosphorus (Graham et al., 2005). The accumulation acceleration over 1600 years (40 cm) in the TQ area was calculated by the concentrations of phosphorus forms, DBD and the ¹⁴C method for the peat core at less than 40 cm. The accumulation of phosphorus below 40 cm was not be calculated due to lack of DBD data. The total phosphorus accumulation rate ranged from $1.25 \text{ mg m}^{-2} \text{ y}^{-1}$ to $15.75 \text{ mg m}^{-2} \text{ y}^{-1}$, which the average was 7.16 mgm⁻² y⁻¹. Total phosphorus accumulation rates continued to decline from 1.6 cal ka BP to now. The results were similar to other researches (Graham et al., 2005; Wang et al., 2012). The phosphorus forms with the highest accumulation rates were conc. HCl-Po and NaOH-Po, and the forms of residual-P and conc. HCl-Pi followed (Fig. 3b and c). The accumulation rate of phosphorus sharply decreased at about 600 cal yr BP. Inorganic phosphorus decreased 57.20% and organic phosphorus decreased 81.46%, respectively. The accumulation rates after 600 cal yr BP was similar with Mt. Changbai but was higher than that of Songnen Plain (Wang et al., 2006, 2012).

3.3. Phosphorus accumulation during successions of TQ peatland

In order to analyse the phase of phosphorus forms during successions of TQ peatland, the cluster analysis results of pollen in TQ peatland was introduced in this paper, and the successions of TQ were divided into four stages (Han et al., 2019).

Zone 1 (2000–1200 cal yr BP, 57–29 cm): The concentrations of phosphorus forms were 4.42–301.50 mg kg $^{-1}$, the NaOH-P $_{\rm o}$ and conc. HCl-P $_{\rm o}$ were steadily increased 100.4% and 169.0%, respectively. The concentrations of forms were NaOH-P $_{\rm o}$ > conc. HCl-P $_{\rm o}$ > residual-P. The accumulations of NaOH-P $_{\rm o}$ and conc. HCl-P $_{\rm o}$ decreased with fluctuation. All concentrations and accumulation rates of forms were the lowest at approximately 1400 cal yr BP. During this period, the concentration of pollen showed a similar trend with organic phosphorus accumulation.

Zone 2 (1200–600 cal yr BP, 29–16 cm): The concentrations of organic phosphorus forms were the highest during this period. And the accumulation rates for all phosphorus forms were lower than that of zone 1, and remained stable. The highest accumulation rates of phosphorus forms was 5.65 mg m $^{-2}$ y $^{-1}$. NaOH-P $_{\rm 0}$ accumulation state was less than that in the zone 1 with a continual decline trend. While the conc. HCl-P $_{\rm 0}$ displayed the opposite trend. The concentration of NaOH-P $_{\rm 0}$ fluctuation period was approximately 80 years, and other forms were

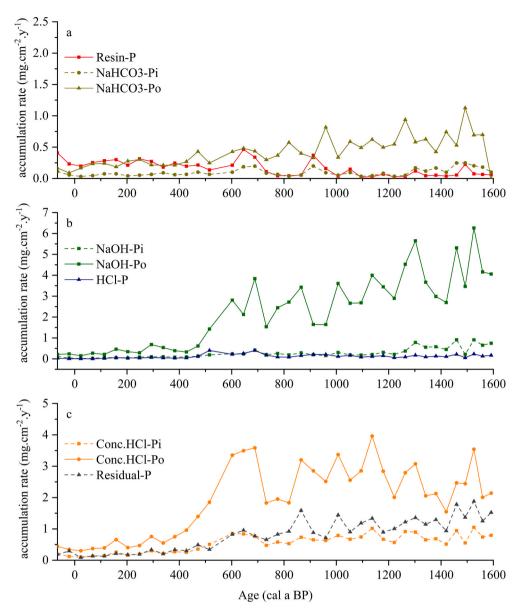


Fig. 3. Accumulate rates of phosphorus forms nearly 2000 years in TQ area calculated by concentration before 40 cm of the peat core(a) accumulation rates of resin-P, NaHCO₃-P_i and NaHCO₃-P_o (b) accumulation rates of NaOH-P_i, NaOH-P_o and HCl-P (c) accumulation rates of conc. HCl-P_i, conc. HCl-P_o and residual-P.

approximately 130 years, which showed similar changes but were lower than NaOH-P_o. All fraction accumulation rate reached the lowest at 900 and 700 cal yr BP. In this zone, the percentage of *Cyperaceae* was generally high, displaying an opposite trend with *Sphagnum*.

Zone 3 (600–300 cal yr BP, 15–9 cm): The concentrations of stable phosphorus forms such as NaOH-P $_{\rm o}$, conc. HCl-P $_{\rm o}$, residual-P declined rapidly, but labile forms began to increase since this zone. Accumulation rates of all forms declined dramatically. In this zone, the *Cyperaceae* decreased with increased *Ericaceaee* and *Sphagnum*.

Zone 4 (since 300 cal yr BP, about 9 cm): The concentration of NaOH- P_0 was lower than that of other zones, but conc. HCl- P_0 was higher than that during 2000 to 1600 cal yr BP. The accumulation rates of phosphorus forms in this phase were the lowest. In addition, the accumulation of NaOH and conc. HCl extracted-forms exhibited two peaks at approximately 300 cal yr BP and 170 cal yr BP. There was remarkable increase of *Ericaceaee* and notice decrease of *Cyperaceae* and *Sphagnum*.

In this study, NaOH-P $_{\rm o}$, conc. HCl-P $_{\rm o}$ and residual-P showed a similar trend. The concentrations of them were higher during 1400–600 cal yr BP (34-15 cm) than that during 2000–1400 cal yr BP (57-34 cm) and 600 cal yr BP to now (15-0 cm). The concentrations of inorganic

phosphorus forms showed no apparent regularity.

4. Discussion

4.1. Distribution and accumulation of phosphorus forms

The peatland in the TQ area was a typical bog in the Greater Khingan Mountains developed in a wide valley. The concentration of total phosphorus was similar that of alpine meadow soil (Makarov et al., 1997, 2004; Solomon et al., 2002; Wang et al., 2012). The concentration of total phosphorus increased significantly since 250 cal yr BP (10 cm). The main factor for distribution changes among forms was the migration effect of the labile fraction. Plant roots absorbed the labile phosphorus forms to satisfy plant growth needs, which enriched the labile phosphorus fraction (such as resin-P and NaHCO₃–P) on the peat surface. These results were similar with other researches (Cassagne et al., 2000; Wang et al., 2012). The distributions of phosphorus forms were stable at more than 40 cm, which were weakened by the way of sample per 5 cm.

HCl-P was generally referred to as calcium-combined phosphorus, while NaOH-P_i was generally referred as Fe and Al-combined

phosphorus. Organic phosphorus contributed the largest portion of phosphorus in the sub-alpine zones. The alpine zones were sensitive to changes in Ca–P forms and were significantly influenced by the altitudinal, vegetation and soil organic matter, respectively (Zhou et al., 2016). In this study, the phosphorus mainly combined with organic matters, while the concentrations of inorganic forms did not appear regular. HCl-P₀ had no significant correlation with Ca²⁺, Fe³⁺ or Al³⁺. NaOH-P₀ and residual-P displayed positive correlation with Ca²⁺ (Wang et al., 2006). In peatland, the phosphorus mainly combined with organic matter, and the Ca²⁺, Fe³⁺ and Al³⁺ might be adsorbed by negative charge on the surface of organic matter. Thus, the NaOH-P₀, conc. HCl-P₀ and residual-P were stable enough to possibly preserve the changes on the accumulation of phosphorus along with successions.

The autogenic succession of peatland may occur from wet to dry phase or in the reverse process. Vegetation succession also presented corresponding with succession and was recorded in the core (Yan et al., 2015a, 2015b). Additionally, the alterations in vegetation evolution caused by long-term climatic evolution could change the accumulation

of phosphorus (Cross and Schlesinger, 2001). Diverse developmental (successional) histories might lead to different accumulations of phosphorus in bogs (Wang et al., 2012). Similarly, fire occurrence is influenced by climate change, which also affects vegetation type and coverage. As a result, the significant differences in phosphorus accumulation rates in the three stages implied the succession and change of peatland, though organic phosphorus forms were the similar trends as a whole.

4.2. Changes of phosphorus forms in relation to peatland succession

During successions of peatland, especially in the early stages of pedogenesis, the accumulation of phosphorus decreased slowly along the chronosequence because most of the phosphorus was depleted gradually, increasing the limiting effect of phosphorus on vegetation (Coomes et al., 2013). Vegetation communities, which sensitive to environmental variations during development of peatland, will undergo different changes with the successions. Therefore, different

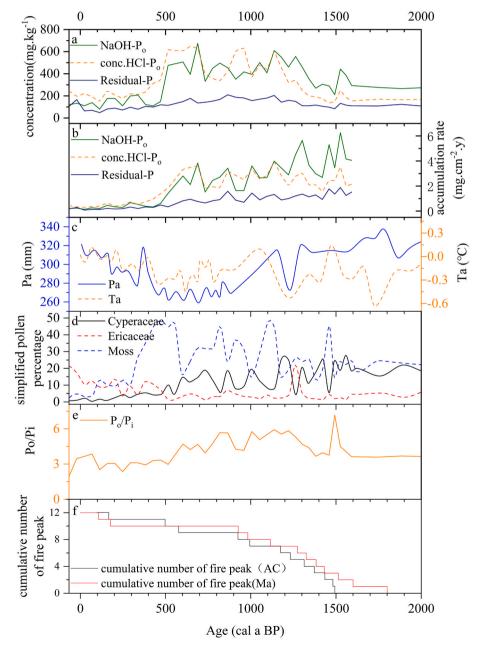


Fig. 4. Phosphorus forms, peatland initiation frequency, fire frequency and paleorecords during 2000 years in TQ area (a) concentrations of NaOH-P_o, conc. HCl-P_o and residual-P (b) accumulation rates of NaOH-P_o, conc. HCl-P_o and residual-P (c) Mean annual precipitation (Pa) and mean annual temperature (Ta) over the Hulun Lake (Wen et al., 2010) (d) Simplified pollen percentage diagram of TQ profile (Han et al., 2019) (e) P₁/P_o of the peat core in TQ area (f) Cumulative number of fire peak of TQ area based on particle concentration of macroscopic charcoal (MaN) and area concentration of microscopic charcoal (AC) (Xu and Li, 2015).

characteristics and trends of phosphorus forms may reflect different stages of succession in peatland. Though phosphorus availability limited the plant growth, organic phosphorus forms (especially stable forms) were accumulated after combined with part of organic matters which derived from plant residues. Organic phosphorus pools were mainly combined with organic compounds, and all forms of organic phosphorus and residual-P were strongly positive correlated with contain of organic matter. In lake sediment, Re-OP could be accumulated in lake sediment corresponding to phosphorus inputs coupled with organic matter and environmental conditions (Lu et al., 2018; Wang et al., 2006). Therefore, recalcitrant forms of organic phosphorus have been accumulated potentially in the peat core after successions of plant community.

From 2000–1500 cal yr BP, the climate of Greater Khingan Mountains region turned cold and wet (Wen et al., 2010; Xu et al., 2010). The concentrations of NaOH-P_o, conc. HCl-P_o and residual-P were relatively low. The majority of peatlands in northeast of China were initiated and developed intensive during 4.2–0.8 ka. The percentage of Herbs was relatively high and dominated by *Cyperaceae*, while percentage of shrubs was minor (Fig. 4d) (Han et al., 2019). All organic forms and residual-P record a dramatic change at about 1500 cal yr BP. Similarly, the same changes of recalcitrant phosphorus fraction were recorded in Hulun lake sediment (Lu et al., 2018). And the mean annual temperature (Ta) was relatively high about 1500 cal yr BP (Fig. 4c). The *Cyperaceae* and *Sphagnum* decreased in this period (Fig. 4d).

From 1300-500 cal yr BP, the east Asian summer monsoons weakened, the climate in northeast of Khingan Mountain turned to cold and dry, peatlands development reached the last peak during the Holocene (Xing et al., 2015, 2016). Cyperaceae decreased while sphagnum slightly increased. The NaOH-Po, conc. HCl-Po and residual-P were the highest, which implied the peatland intensive development in TQ region with high concentrations and accumulation rates of organic phosphorus forms in this period (Fig. 4a and b). The accumulation of phosphorus was affected by concentration of phosphorus and peat accretion process (Craft and Richardson, 2008), to reflect the comprehensive variations of phosphorus forms during the peatland succession. Pollen concentration reflected the state of plant community in generally. Accumulation rates of phosphorus forms were high when the concentration of pollen concentration was increased (Han et al., 2019), and Picea and Abies reached maximum values in the pollen assemblage at about 1200 cal yr BP (Li et al., 2011), showing cold climates (Fig. 4c), and phosphorus fraction accumulation and concentration were commonly raised when the temperature was decreased.

Temperature and Precipitation promote the change of geochemical characteristics, accumulation of peatlands and vegetation successions (Lu et al., 2018). Strengthened flooding caused a decline of vegetation species richness while increasing plant biomass when the *Cyperaceae* was the dominant vegetation (Garssen et al., 2017). Cold climatic conditions could limit degradation rate of vegetation residual productivity, rising accumulation and degradation rate of carbon and organic phosphorus forms (Mauquoy et al., 2002). Therefore, proper cool and moist climate enhance the accumulation of stable organic phosphorus in the Great Khingan Mountain.

From 600 cal yr BP, *Cyperaceae* sharply dropped and *Sphagnum* increased (Fig. 4c), marking the herbaceous communities turned to shrub communities (Han et al., 2019), and the concentrations and accumulation rates of NaOH-P $_{0}$ and conc. HCl-P $_{0}$ decreased rapidly (Fig. 4a and b). The distinction was similar with concentrations of phosphorus in depressional wetland between sedges and shrubs (Wang et al., 2006). Peatland development rapidly slowed at 600 cal yr BP due to two sides. Firstly, *Cyperaceae* was easier decreased along with the increase of phosphorus limitation in peatland succession. Secondly, the vegetation growth was limited by inappropriate climate conditions.

4.3. Historical fire events indicated by phosphorus forms

The organic phosphorus directly turned into inorganic phosphorus

forms by fire, which increased degree of conversation rate to inorganic phosphorus with the increasing burning temperature. As a consequence, most of the organic phosphorus were lost and the availability of phosphorus was increased (Santín et al., 2018; Wang et al., 2015). The concurrent decline in P accumulation rates and Po/Pi were used as indicators of fire event occurrence in this article. To avoid unusually high accumulation rates of P_i in topsoil caused by the active phosphorus concentrated in peat surface profile, we eliminated resin-P, NaHCO₃-P and residual-P for the Po/Pi calculation (inactive Po/Pi). Charcoal fragments were used to reconstruct fire history throughout the Holocene (Scott and Damblon, 2010). Xu et al. (2015) studied three kinds of charcoal for Char Analysis and the reconstructions of fire history in the TQ area (Fig. 4f). Research showed that fire return intervals (FRIs) varied smoothly and the mean FRI was 81-124 years per fire. Fire concentrated during 1500 to 1200 cal yr BP, 1000-900 cal yr BP, 600 to 500 cal yr BP and 300-200 cal yr BP, respectively (Xu and Li, 2015).

Correspondingly, the accumulation rates of phosphorus forms and inactive P₀/P_i decreased during the period of charcoal appearance. The inactive P_o/P_i ratio decreased at 1450 to 1370 cal yr BP, 1200 cal yr BP, 1100 cal yr BP, 970 to 900 cal yr BP, 700 cal yr BP, 650 cal yr BP, 240 cal vr BP and 100 cal vr BP, respectively (Fig. 4e). Among them, the accumulation rates of organic phosphorus and inactive Po/Pi ratio decreased significantly about 1370-1450 and 900-970 cal yr BP. It was possibly occurred severe fire or higher fire frequency in these two periods, which implying organic phosphorus transformed into inorganic phosphorus and reducing the accumulation of organic phosphorus forms. These results were similar with Butler et al. (2018), who observed that fire could improve the concentration of inorganic phosphorus through heat-induced mineralization, which leads to the increased phosphorus solubility and the decreased phosphorus accumulation (Bayley et al., 1992; Butler et al., 2018; Serpa et al., 2020). In present study, inorganic phosphorus with strong mobilization capacity could not be used to reconstruct fire history clearly due to its accumulation on the near-surface layer of peatland under vegetation absorption (Figs. 2 and 3). Furthermore, fire reduced the biomass and dead mass of vegetation, which reduced the origin of the organic phosphorus (Xu et al., 2011).

Burning released the phosphorus biochemistry limitation. The buffering of soil and the growth of vegetation kept from the geochemical elements dramatically changes in the aquatic system. These factors indistincted boundary among fire events when the intensive fire occurred, shorten the period of frequent fire. The prior phenomenon was demonstrated by the accumulation of phosphorus around 1400 to 1300 cal yr BP. In addition, lower inactive $P_{\rm o}/P_{\rm i}$ always combined with the decrease of *Cyperaceae*, the accumulation rate of NaOH-Po and the increase of moss, which were same with the variation of vegetation after fire several years (Noble et al., 2018).

From 600 cal yr BP, the climate had changed to a relatively warm and dry, and the type of vegetation had changed from sedge to shrub, and fire events were simultaneously recorded by charcoal and black carbon at around 600 cal yr BP (Gao et al., 2018; Zhang et al., 2018b). Fire combined with arid climate caused dramatic changes in vegetation types and the accumulation of organic phosphorus. The accumulation of organic phosphorus was relatively low with high $P_{\rm i}/P_{\rm o}$ when peatland developed into oligotrophic peat.

The result suggested that fire events left geochemical evidence on sediment. Frequent fire often accompanied with decrease in precipitation lead to reduce the accumulation of organic phosphorus forms. However, the burning declined inactive $P_{\rm o}/P_{\rm i}$, the concentration and accumulation of $P_{\rm o}$, changing the vegetation community at the same time. Both changes of inactive of $P_{\rm o}/P_{\rm i}$ and accumulation rate must be considered when the fire history was reflected by phosphorus in core. The deposition of phosphorus forms would be utilized as evidence of fire history.

5. Conclusion

Phosphorus forms of peat were mainly composed of NaOH-Po, conc. HCl-P and residual-P. Active phosphorus pools were enriched above 8-10 cm on the peat surface. The accumulation rates of organic phosphorus forms, especially NaOH-Po, showed good correspondence with peat development frequency, climate change, pollen records and other paleo evidence. The concentrations of organic phosphorus forms and residual-P were generally high during 1200 to 500 cal yr BP, and the accumulation rates of that gradually decreased since 1600 cal yr BP. Both of concentration and accumulation of organic phosphorus sharply declined after 600 cal yr BP. The wet and cold climate improved the accumulation of organic phosphorus. The concentration and accumulation of NaOH-Po displayed positive connection with concentration of pollen and Cyperaceae which was raised when Cyperaceae was dominant plant, and decreased with relative abundance of moss or shrubs. Fire combined with arid climate caused remarked changes in vegetation types and the accumulation of phosphorus around 600 cal yr BP. The concentrations and accumulations of organic phosphorus forms were relatively low when succession of peatland into oligotrophic peat since 600 cal yr BP. Fire events left geochemical evidence on sediment. The buffering capacity of soil and the growth of vegetation released biochemistry limitation of P after burning, shorten period of frequent fire which reflected by the phosphorus forms in the core. Fire changed the vegetation community, decreased the concentration and accumulation of Po and reduced inactive Po/Pi at the same time. Therefore, both changes of inactive Po/Pi and organic phosphorus accumulation rate must be considered when the fire history was reflected by phosphorus in core. The relationship of phosphorus forms with vegetation biomass and types is clearly needed. In addition, it is necessary to investigate more regions to confirm the universality and limitations of reconstructing the peatland succession and fire history by phosphorus forms.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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