

High intensity fire accelerates accumulation of a stable carbon pool in permafrost peatlands under climate warming

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2	peatlands under climate warming
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High intensity fire accelerates accumulation of a stable carbon pool in permafrost

Abstract

Herbs

Peatland carbon pools store one-third of global soil carbon, but are increasingly threatened
by wildfires, particularly high intensity wildfires, as a consequence of climate warming
However, with only a limited understanding of fire history reconstruction available, the long-
term impacts of fire intensity on the stability of the peatland carbon pool remains poorly
understood. Here, based on Fourier transform infrared spectroscopy and chemical analysis of
PyC and organic matter in Hongtu (HT) peat core in the northern Great Khingan Mountains
(China), historical fire intensity and fuel sources during the last 700 years were reconstructed
and their effects on carbon stability evaluated. Our results showed that the major stable carbon
pool (i.e. aromatics) and the retained labile carbon pool (i.e. iron-bound organic carbon, Fe-OC)
in HT peatland are 278.1±6.2 mg·g ⁻¹ and 6.78±3.85 mg·g ⁻¹ , respectively. High-intensity herb
fires in peatlands occurred more easily under wet conditions and caused more PyC
accumulation than shrub fires. Both climate warming and high-intensity fire promoted more
aromatics and Fe-OC accumulation, increasing the overall stability of peatland carbon pool.
High-intensity fire under warm climate conditions resulted in Fe-OC accumulation rates
threefold higher (ca. 0.02 mg·cm ⁻² yr ⁻¹ to ca. 0.06 mg·cm ⁻² yr ⁻¹) but had no marked effects on
the aromatic and PyC accumulation rates. Overall, our results suggest that high-intensity fires
can accelerate stable carbon pool accumulation in peatlands during climate warming.
Keywords: Peatlands; Fire intensity; Aromatic; Iron bound organic carbon; Climate change;

Introduction

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Globally, fires burn 300-460 million hectares of land annually, representing 4% of the Earth's vegetated land surface and act as an important ecological factor in many ecosystems, such as forests, peatlands, and savanna (Battisti et al., 2016; Just et al., 2017; van der Werf et al., 2017). With global warming and increasing regional human activities, fire intensity and frequency not only increased markedly during the last century also are following an increasing trend that persists into the current century (Flannigan et al., 2013; Gao et al., 2016). Fires not only emit 2200 Tg carbon as CO₂ to the atmosphere but also produce 256 Tg of pyrogenic carbon (PyC) that acts as the most stable carbon source in the soil carbon pool with serious implications for carbon cycling in natural ecosystems (Schmidt et al., 2011; Jones et al., 2019). The importance of fire in ecosystem carbon cycling is likely to increase further as our climate changes further in the future (Flannigan et al., 2009; Turetsky et al., 2015; Walker et al., 2019). Peatlands store more than 30% of the world's soil carbon, while only covering 3% of the land surface (Yu et al., 2010). Due to its extensively water-logged and anoxic environment, peatlands formed a stable carbon pool and have acted as one of the most important sinks for the carbon capture from the atmosphere during the Holocene (Gallego-Sala et al., 2018; Loisel et al., 2020). The permafrost peatlands are mainly distributed in mid-high altitude regions that are highly sensitive to climate change and increasingly threatened by wildfires (Gibson et al., 2018; Voigt et al., 2019). Fires not only consume surface biomass and peat soils, but also may produce stable carbon and increase the abundance of plants the following growing season which has been observed to promote additional carbon accumulation (Marrs et al., 2019; Gao et al., 2021; Gao et al., 2022). Furthermore, the PyC and ash produced under incomplete burning, also

promotes decomposition of organic matter by increasing the microbial activities due to its high surface area and absorbed nutrients (Noble et al., 2018; Saarnio et al., 2018; Zhao et al., 2022). Thus, the effects of fire on peatland carbon cycling can be complex, but the need for us to more completely understand the complex effects on the peatland carbon pool are increasing as our climate changes.

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Increased organic matter recalcitrance following the initial rapid decay of plant litter could be hypothesized as a major factor protecting the peatland carbon pool under a warmer environment and other environmental disturbances (Wright et al., 2011). The high recalcitrance of aromatic compounds in peat soils is widely used as an index to the stability of peatland carbon (Cong et al., 2020). The aromatic content of low-latitude peatlands have been found to be significantly higher than those in mid-high latitude peatlands, and speculated as the major factor protecting the peatland carbon pool in warmer environments (Hodgkins et al., 2018; Verbeke et al., 2022). In addition to the stable carbon pool, fixed labile carbon can also contribute to stable carbon storage in peatlands. Climate warming and water level decline in peatlands facilitate oxygen diffusion into redox interfaces, increasing Fe(hydro)oxides formation and their association with dissolved organic carbon through coprecipitation and adsorption (iron-bound organic carbon, Fe-OC), creating stable Fe-OC complexes that act as retained labile carbon pool that protects labile carbon against microbial degradation and export (Riedel et al., 2013; Huang et al., 2021). Climate change and fire in peatlands may also contribute to soil redox conditions and iron phases (Fenner et al., 2011; Norouzi and Ramezanpour, 2013), which may have a strong link to Fe-OC (Eckmeier et al., 2010). Compared to climate factors, fire may clearly also cause serious long-term effects on the

stability of peatland carbon pool.

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As peat soils accumulate under anoxic conditions with continuous inputs, peatlands also serve as an ideal archive for reconstructing historical environmental characteristics (Martini et al., 2007) and are widely used to evaluate the long-term effects of climate on peatland carbon pool (Charman, 2012). PyC, as an important product from fires, is widely used to reconstruct fire history in palaeoenvironment research (Marcisz et al., 2015). Based on PyC fluxes, previous studies also report high fire intensity promoting stable carbon accumulation in the peatland carbon pool with increases in both carbon accumulation rate and the stability of carbon pool (Cong et al., 2020). However, high fire intensity may also destroy PyC and the PyC production may even fall below that of a low-intensity fire, which means there exists uncertainties in fire history reconstructions based on PvC fluxes (Bird et al., 2015; Gao et al., 2022). In addition to PyC fluxes, the chemical properties of PyC are heavily influenced by sources and production process. For example, more aromatic compounds arise in PyC produced from shrubs than that produced from herbs, and higher production temperature significant decrease the labile content of the residual PyC (Wiedemeier et al., 2015; Gao et al., 2022). These results indicate that the chemical properties of PyC could be used to reconstruct a more refined fire history (i.e. fire intensity and fuel sources) than PyC fluxes alone. Thus, in order to improve our understanding of the long term effects of fire on the peatland carbon pool, it will be necessary to reconstruct a more detailed fire history by incorporating chemical properties of PyC. To evaluate the long-term effects of fire on peatland carbon, we identified a representative

peatland core in the northern Great Khingan Mountains (China), located in a permafrost region

that is seriously threatened by wildfires (Gao et al., 2018b). Based on chemical properties of PyC and organic matter, we not only attempted a reconstructed historical fire intensity and fuel sources, but also reconstructed historical variation of carbon stability in the permafrost peatlands in the northern Great Khingan Mountains. Based on these data, we evaluated the impact of climate changes on fire intensity and fuel sources in our study region. We then evaluated the effects of these fire factors on the stability of peatland carbon, with a particular emphasis on the stable carbon pool (i.e. aromatic) and the retained labile carbon pool (i.e. Fe-OC). This allowed us to evaluate long-term variations in carbon stability and its potential forcing mechanisms.

2 Materials and methods

2.1 Site description and sampling

The study area is located in the east side of northern part of the Great Khingan Mountains (Northeast, China), at the margins of the summer monsoon. Peatlands in this region are developed on permafrost and threatened by wildfire and climate change. The peat core selected for this study was located at Hongtu peatland (HT; 51.62 ° N, 124.24 ° E, altitude 550 m, depth 59 cm) a site used in our previous studies, with the *Vaccinium uliginosum* as the dominant species at the site (Gao et al., 2018b; Cong et al., 2022). The water table in HT peatland was close to the surface layer of the peat core, and the peat soils accumulated under the water-saturated conditions. The peat core was collected from a dug profile and bottom samples were collected using a Russian corer. The stainless steel knife was used to section the samples into 1-cm intervals in the field directly, and 59 samples were collected in total. The age-depth model was built through three AMS ¹⁴C dating samples within the same peat core in previous studies.

The peat core covers ca. 700 years, and 7 times fire events were clear identified through PyC fluxes and the Char analysis software package in total (Gao et al., 2018b).

2.2 FTIR of PyC

Residual PyC in peat soils in each layer was extracted by dichromate oxidation (Gao et al., 2018b). The FTIR spectra of the residual PyC samples were obtained on a Spectrum Two FTIR spectrometer (PerkinElmer, America) on KBr pellets (150 mg dried KBr and 1 mg peat soil). The measurements were recorded from 4500 to 300 cm⁻¹ at a resolution of 1 cm⁻¹. A total of 32 scans were averaged for each sample. Absorption peaks indicative of structural units in the OM were used to identify PyC chemical composition.

2.3 Iron bound organic carbon

The dry sample was extracted with 57.4 mM sodium dithionite in a ratio of 1:120 mass to the solution, and the samples were shaken for 16 h, then centrifuged. The residues were further extracted by 0.05 M HCl for 1 h and again centrifuged. In order to account for any organic carbon released following ion exchange with sulfate (the oxidation product of dithionite), an equal ratio of soil and 57.4 mM sodium sulfate were processed in parallel (Wagai and Mayer, 2007). The Fe-OC was calculated by the sum of DOC in the total dithionite and acid extractions after subtracting the DOC in sulfate extractions. Similarly, we also measured the Fe contents in total dithionite and acid extractions as well as the sulfate extractions, and calculated the reactive iron (Fe_R) contents that contribute to Fe-OC. The Fe in the solution was measured by the ferrozine method (Huang and Hall, 2017) while DOC was measured using a total organic carbon analyzer (TOC-L, Shimadzu, Japan).

2.4 Indicators of fire factors

Chemical analysis of residual PyC after burning shows the abundance of typical chemical compounds to have a close relationship with its sources and burning intensity. For example, a high FTIR 1515/1050 ratio indicates PyC is predominantly produced from shrubs which contain more aromatic compounds than herbs, while a low FTIR 1720/1050 ratio indicates PyC is mainly produced under high fire intensity (Gao et al., 2022). Thus, the FTIR 1515/1050 ratio and FTIR 1720/1050 ratio were used as indicators to reflect the historical fuel source and burning intensity in this study. The ARs of Fe-OC, aromatics, and total carbon were selected as indicators for the accumulation history of different carbon types (i.e. retained labile carbon pool, stable carbon pool, and total carbon pool) in peatland carbon pools. The ARs of Fe-OC, aromatics, and total carbon were calculated by the multiply results of the selected carbon contents and peat accumulation rates (Cong et al., 2022). The relationship between selected fire indicators and carbon indicators was assessed using the linear regression model.

3 Results

3.1 Typical FTIR ratios of PyC in HT peat core

Variations in observed FTIR ratios of PyC are shown in Fig. 1, and several characteristic FTIR spectrums associated with the PyC in different layers of the HT peat core Fig. S1. The range of FTIR 1515/1050 ratio varied from 0.09 to 9.34 with the mean values of 1.09±1.38 (table 1). And the mean value of the FTIR 1720/1050 ratio was 4.02±2.57 and ranged between 0.78 and 19.71. Similar to FTIR 1515/1050 and 1720/1050 ratios, other selected FTIR ratios also have a wide range and several clear peaks occurred. Most notably in the layers around 33 cm (Fig. S1), the obvious low peak height of 1050 cm⁻¹ causes the selected FTIR ratios to appear markedly higher than the others. High FTIR peaks of selected FTIR ratios almost always

appeared in the layers from 36 to 46 cm, and most of the low FTIR peaks occurred in the layers below 51 cm. From 30 cm to the surface, there exists a weak increasing trend of FTIR 1720/1050 ratios, which increased from ca. 2.0 to ca. 5.0.

3.2 Contents of iron bound organic carbon in HT peat core

Variations in Fe-OC content, Fe_R content, and Fe-OC/Fe_R molar ratio are shown in Fig 2. The range of Fe-OC was from 3.0 to 19.4 mg g⁻¹, and the average value is 6.9±3.9 mg g⁻¹. From the 30 cm to the bottom layers, the Fe-OC contents are stable with fluctuation around 4 mg g⁻¹ (table 1). A markedly increasing trend of Fe-OC occurred from 30 cm to 15 cm, with the highest value of Fe-OC content is 19.4 mg g⁻¹ at 17 cm. In the surface layers, the Fe-OC contents were around 7 mg g⁻¹ somewhat higher than those in the bottom layers. The variation trend of Fe_R across depths was similar to Fe-OC contents and markedly increasing from 32cm to 15cm, which increased from ca. 2.3 mg g⁻¹ to 8.3 mg g⁻¹. The molar ratio of Fe-OC/Fe_R ranged from 4.9 to 13.9. The lowest Fe-OC/Fe_R molar ratio occurred around the 40cm layer, and the highest Fe-OC/Fe_R molar ratio occurred in the surface 5cm layers. An increasing trend of Fe-OC/Fe_R molar ratio was also found with the depth decreased from 60 cm to 50 cm.

3.3 Relationship between fires and peatland carbon pool

Regression model statistics for selected fire indicators and carbon indicators were calculated and the scatter plot best-fit lines were shown in Fig. 3. With the decreasing of 1/FTIR 1720/1050 ratios, the ARs of both carbon, aromatic, and Fe-OC significantly increased. While the adjusted (adj.) R² between 1/FTIR 1720/1050 ratios and these carbon indicators were low and ranged from 0.19 to 0.22. The increase of FTIR 1515/1050 ratio only has significant effects on the Fe-OC AR with the adj. R² was 0.10. The increasing of PyC ARs also significantly

increased the ARs of both carbon, aromatic, and Fe-OC. The adj. R² shows that the effects of PyC ARs on CARs (0.64) and aromatic ARs (0.66) more markedly than Fe-OC AR which was only 0.23. And these values were also higher than the relationship between fire intensity and carbon indicators.

4 Discussion

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4.1 Fire effects on peatland carbon pool.

Previous studies have highlighted that fire can have serious effects on the peatland carbon pool through burning process and fire residual products (Heinemeyer et al., 2018; Marrs et al., 2019; Cong et al., 2020). With the fire intensity increasing, the ARs of both carbon, aromatic, and Fe-OC significantly increased were found in current study (Fig. 3). Fire releases nutrients to the surrounding environment, and elsewhere, plant biomass was noticed to significantly increase greater in a burnt site compared to those in an unburnt site (Gao et al., 2021). With the burning frequency increasing, herb growth is rapid compared to the recovery of shrubs and the increased biomass was thus primarily herbs (Marrs et al., 2019). The increasing fire intensity was associated with higher burning temperature and burning duration, which promoted more nutrients to be converted from organic to inorganic compounds that are easily utilized by plants (Wang et al., 2015a). Fires promote more carbon accumulation in peatland had been widely found in previous studies (Heinemeyer et al., 2018; Cong et al., 2020), and the subsequently greater availability of plant litter in burnt sites acted as the important carbon source may explain this phenomenon (Gao et al., 2021). Under the high-intensity fire, the unstable carbon compounds in the surface peat soils would be more easily consumed or converted to aromatic compounds which are more stable than other chemical compounds of carbon (Zhao et al., 2012).

Additionally, with burning intensity increasing, herbs would be more easily consumed and more shrub stems converted to PyC which results in more PyC being produced from shrub stems that contained more aromatic contents (Gao et al., 2022). The higher burning temperature promote the residual PyC to contains more aromatic compounds and higher degree of aromatic condensation (Wiedemeier et al., 2015). Thus, high-intensity fire not only consumed the less stable compounds in residual carbon, also promoted more residual PyC with high aromatic contents accumulated in peatland carbon pool. Importantly, both of these factors promote the aromatic ARs to increase significantly.

The positive relationship between Fe-OC and fire intensity indicates that the fire intensity promotes formation of Fe-OC. Previous studies found that the combusted near-surface boreal peat increased water phenolics concentration from 1mg/L to 4mg/L and contributed to the formation of condensed phenolic compounds within two days (Wu et al., 2022). Phenolic acid with hydroxyl groups have an affinity with Fe_R (i.e. Fe(hydro)oxides), and the condensed phenolic with abundant hydroxyl groups promote the Fe-OC formation (Zhao et al., 2020). Furthermore, fire increased hydrophobicity of the soil surface after fire (Knicker, 2007). The water-repellent layer thickness also depend on fire intensity and increase diffusion of oxygen into anoxic solution, which also may promote the Fe-OC formation (Chen et al., 2020).

PyC is a carbon rich material and approximately 50% aromatic carbon available in PyC which formed at typical vegetation fire temperature (Bird et al., 2015; Wiedemeier et al., 2015; Gao et al., 2022). The increasing of PyC ARs could direct increase the ARs of carbon and aromatic in peatland carbon pool. However, the values of PyC ARs only ranged between 0.02 and 0.12 mg cm⁻² yr⁻¹, much lower than the 0.8 to 2.8 mg cm⁻² yr⁻¹ for aromatic ARs and from

1 to 4 mg cm⁻² yr⁻¹ for CARs (Fig. 3). The markedly different of PyC ARs and other carbon types indicate the increasing of CARs or aromatic ARs not only came from the PyC, also caused by the effects of PyC on biogeochemical cycles in peatlands (Noble et al., 2018). The accumulation of PyC with high surface area also increases microbial activities and promotes decomposition of more labile carbon which was speculated as a major reason that stable carbon (i.e. aromatics) accumulated in burnt peatland with the accumulation of PyC (Awad et al., 2018; Nguyen et al., 2018). PyC is rich in condensed aromatic compounds, and soluble aromatic compounds from PyC also deposit in soil after fire (Knicker et al., 2005). Soluble aromatic compounds released from PyC have been noted to inhibit carbon decomposition and the peatland carbon pool (Fenner and Freeman, 2020), and this was speculated as a major reason that increase the CARs and aromatic ARs occurred. High amounts of nutrients also released to the surrounding environment as ash during burning and co-emitted with PyC, which means more PyC residual is accompanied by more nutrients at the surface of the peatland (Blank et al., 2007). With more nutrients available in surface peat soils, more plant growth and the plant biomass arises promoting more carbon accumulation in peatland carbon pool (Thormann and Bayley, 1997).

4.2 Historical variation of fire intensity and fuel sources

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To identify the potential factors influencing fire intensity and fuel sources, the PyC fluxes and δ^{13} C-PyC values of our previous study were selected which reflected basic fire history and local climate characteristics and shown in Fig. 4. In addition to local forcing factors, global climate factors also need to be considered as potential forcing mechanism on fire history. Solar radiative forcing has been widely used as an indicative global climate forcing factor (Mann et

al., 2005), along with sea-surface temperature (SST) in the northern Atlantic Ocean and the δ^{18} O values in speleothem from Dongge Cave. Each were used to reflect historical variation of the westerlies and the East Asian monsoon which have serious effects on the climate characters in the monsoon margin regions (Wang et al., 2005; Cunningham et al., 2013). These factors were selected as global potential forcing factors to be suggestive of whether these factors cause serious effects on fire history in northern Great Khingan Mountains (Fig. 4d, e).

There are four interesting periods of fire history in Great Khingan Mountain during the last 700 years. At 650 - 550 cal yr BP, the fire intensity was markedly higher than adjacent periods, and the fuel sources in this period were mainly from herbs, indicating strong herb burning occurred in this period (Fig. 4a, c). The δ^{13} C-PyC values in this period were lower than adjacent periods which indicated the climate in this period was cold and wet (Gao et al., 2018b). During this period, the SST of northeast Atlantic and the δ^{18} O values in speleothem from Dongge Cave also decreased markedly and the solar radiative forcing increased in this period (Mann et al., 2005; Wang et al., 2005; Cunningham et al., 2013). The wet climate background was clearly of benefit to herb growth in peatlands (Lou et al., 2015). The greater herb growth promoted high intensity peatland herb fires and more herb PyC accumulated in peatland carbon pool during this period. This transition can be speculated as the major factor causing the high PyC fluxes despite wet climate conditions.

At 550 - 350 cal yr BP, the fire intensity decreased markedly and the increasing of FTIR 1515/1050 ratio indicates the proportion of shrub PyC increased, suggesting fires in this period were low intensity shrub fires. During this period, the δ^{13} C-PyC values were higher than those in period around 600 cal yr BP, and the highest value occurred at ca. 550 cal yr BP before

decreasing gradually between 550 - 350 cal yr BP (Gao et al., 2018b). The precipitation and solar radiative forcing continuously decreased and were lower than those around 600 cal yr BP (Mann et al., 2005; Wang et al., 2005). These indicate that the climate characters in this period were drier than nearby periods and more shrub growth in peatlands resulted in the major PyC sources becoming shrubs. Due to the changed fuel source and fire intensity, PyC fluxes also decreased markedly over this period (Gao et al., 2018b). Interestingly, the strongest intensity of herb fire occurred (and cause high amount of PyC accumulation) in the peatland around 380 cal yr BP, and a clear decrease of fire intensity and fuel source conversion followed around 350 cal yr BP. Wet climate conditions indicated by the $\delta^{18}O$ values in speleothem from Dongge Cave around 400 cal yr BP would benefit herb growth (Wang et al., 2005). As the precipitation decreased gradually at 400 - 370 cal yr BP, more herb growth and low precipitation caused herb fires to occur more easily in this period. The serious fire and low precipitation could then support shrub growth in peatlands (Marrs et al., 2019). High fire intensity would also decrease available fuels for further high intensity of fires (Knapp et al., 2009; Gao et al., 2022). Thus, after this serious fire event, the fire intensity markedly decreased around 370 cal yr BP and the fuel types shifted towards shrubs.

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After the low fire intensity period around 350 cal yr BP, the fire intensity again increased gradually between 300 - 100 cal yr BP, and the variation trend was similar to those of δ^{13} C-PyC values and PyC fluxes (Gao et al., 2018b). During this period, the values of FTIR 1515/1050 ratio fell between the first two periods indicating the sources of PyC were from a mixture of herbs and shrubs. Solar radiative forcing also increased gradually at this time, indicating temperatures gradually increased (Mann et al., 2005). Thus, the fire intensity was the major

factor that influenced PyC production and increased under the dry/warm environment associated with this period. With the regional increase of human activities from 1900 CE to the present, more serious fires occurred particularly between 1900 and 1980 CE (Gao et al., 2018a). In this period, climate warming and the decreasing precipitation promoted more fire as has occurred in recent years (Novorotskii, 2007). The fire intensity recorded by FTIR 1720/1050 ratio increased markedly in recent years with more PyC arising from herb burning. Although the fire intensity in recent years was higher than other periods, the PyC fluxes were lower than in other periods. Thus, it is not easy to evaluate the fire intensity through PyC fluxes directly as high-intensity fire may decrease the amount of PyC production without a serious change in PyC fluxes.

Fuel sources and fire intensity have shown a close relationship with regional climate change over the last 700 years. High intensity herb fire occurred more easily under wet conditions and caused more PyC accumulation in peatlands. Wet climate condition benefitted herb growth in peatland, however, extreme drought events following long wet period supported high intensity herb fires and accumulated high amounts of PyC in peatlands. With regional human activities increasing during the 20th century, more frequent local anthropogenic fires were of high fire intensity causing a major change in the PyC FTIR 1720/1050 ratios.

4.3 Historical stability of peatland carbon pool and its controls

Not only fires, but historical variations in temperature and precipitation also have potential to influence the peatland carbon pool (Cong et al., 2020; Cong et al., 2022). Here, in contrast to the CARs reported in previous studies (Cong et al., 2022), we also used the aromatic ARs to indicate historical variation of carbon pool stability, and the Fe-OC and Fe-OC/Fe_R molar ratio

to indicate historical variation of retained labile carbon pool respectively in the C retention pathway (Fig. 5a-c). Historical variations in CARs and aromatic ARs were similar over the last 700 years, and four periods with markedly high values were found. Low fire intensity occurred at 550 - 370 cal yr BP and the major fuel sources were shrubs. In this period, the PyC ARs were also lower and climate character was drier than nearby periods (Fig. 5g, h). Under the dry and warm environment, the biomass of peatland plants increased and the soil carbon pool more easily decomposed, especially for unstable carbon (Verbeke et al., 2022). More unstable carbon decomposition caused more stable carbon accumulation in peatland carbon pool and increased the aromatic ARs (Hodgkins et al., 2018).

Except 550 - 370 cal yr BP, high CARs and aromatic ARs occurred contemporaneously with high degree of fire intensity and the major fuels sources were herbs. The climate characters at 650 - 550 cal yr BP and from 0 cal yr BP to the present were wet/cold (Gao et al., 2018b), which not only decrease the net primary productivity of surface plants and CARs, also decrease the proportions of shrub litters which caused a high amount of carbon with low aromatic contents in herb plant litters accumulated in the peatland carbon pool (Wang et al., 2015b; Lou et al., 2018). While, the changes of fire intensity may alter the accumulated process of the carbon pool (Cong et al., 2020). Weak stability and low CARs of carbon pool in HT peatland only occurred under the wet/cold climate conditions and low-intensity fire period, such as 100 - 0 cal yr BP. When the degree of fire intensity was higher than nearby periods, the CARs and aromatic ARs were also markedly higher than nearby periods. High-intensity fire promoted more herbs consumed during burning and more aromatic contents in fire residual products (Gao et al., 2022), which decreased the unstable carbon source and increased the stable carbon source of

peatland carbon pool in totally. Additionally, high-intensity fire also decrease the water retention capacity of surface soils which are more benefit for shrub growth and increase the stable carbon source (Keesstra et al., 2017). Thus, the increasing of fire intensity led more stable carbon accumulated in peatland under cold/wet climate conditions.

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At 320 - 100 cal yr BP, the climate characters were warm/dry and the degree of fire intensity were high, and the CARs and aromatic ARs were similar to those in periods which the climate characters were warm/dry or the degree of fire intensity were high. Under warm/dry climate conditions, more shrub plants growth in peatlands and the plant litters of these plants were also act as another stable carbon source for peatland carbon pool (Hodgkins et al., 2018). Compare to shrub plants, herbs more easily recover after high intensity and frequency fires (Marrs et al., 2019), which may decrease the stable carbon sources from plant litter and weakened the impact of high amount of aromatic compounds (i.e. PyC) accumulated in peatland carbon pool under warm/dry climate conditions. However, there existed significant increasing of Fe-OC ARs in this period (Fig. 5b). And the Fe_R at 320 - 100 cal yr BP were threefold higher than that at 650-550 cal yr BP (wet/cold, high-intensity fire). Furthermore, the Fe-OC/Fe_R molar ratio in deep layers of the HT peat cores was stable and around 7.8 (Fig. 5c), which represented the coprecipitation form of Fe-OC was the major retained type of Fe-OC and stores in peatland carbon pool due to its low decomposing rate (Wagai and Mayer, 2007). While, the Fe-OC/Fe_R molar ratio at both 650-550 cal yr BP and 300-100 cal yr BP periods were higher than the average levels (i.e. fitted line), implying that high-intensity fire promotes higher labile OC retained by Fe_R. From 50 cal yr BP to present, more fires caused by regional human activities and prescribed fire also cause serious influence on soil redox condition, these factors

all contributed to high Fe-OC/Fe_R molar ratio, but due to limited Fe_R by plant uptake, the contents seem not high as that at 300-100 cal yr BP. These results suggested that high-intensity fire under warm climate create an additional effect on Fe-OC ARs. In the waterlogged conditions, Fe often acts as an electron acceptor and couple iron reduction, which could dissolve short ranged Fe(hydro)oxides and increase carbon release from Fe-OC (Chen et al., 2020), while more crystallinity Fe(hydro)oxides showed a strong resistance against microbial degradation and could create probability for long-term carbon storage (Hall et al., 2018). As the fire could promote soil crystalline iron phase formation (Norouzi and Ramezanpour, 2013), hence implying that fire intensity increasing the amount of labile carbon retained by Fe_R.

Thus, high Fe-OC/Fe_R molar ratio more easily occurred under high fire intensity periods than those in warm climate conditions, which further confirmed that the importance of fire intensity on the quantity of Fe-OC. The changes of fuel sources only cause the Fe-OC ARs significant changing, and more PyC from herbs burning significant increase the Fe-OC AR. Although the shrubs had higher lignin content compared with herbs, our study showed that whatever high fire intensity in herb or low fire intensity in shrub they also contribute to similar effects on soil aromatic ratio. This is mainly due to low fire intensity decrease lignin contribution to aromatic compounds in residual wildfire products (Knicker, 2007), hence further confirming that the importance of fire intensity to Fe-OC formation.

5 Conclusion

Based on PyC properties and OM properties in a 700-year peat core from the northern Great Khingan Mountains, we reconstructed a detailed fire history and evaluated the impact of fire

intensity and fuel types on the stability of peatland carbon pool under climate change. Aromatic compounds and Fe-OC, the major stable carbon pool and retained labile carbon pool in the peatland, amounting to 278.1±6.2 mg·g⁻¹ and 6.78±3.85 mg·g⁻¹, respectively. Our results shown high intensity herb fires occurred more easily under wet condition and cause more PyC accumulation in the peatland than shrub fires. The fuel sources only had weak effects on Fe-OC ARs in the peatland carbon pool, with increased fire intensity leading to more PyC accumulation, and the amount of stable carbon compounds (e.g. aromatic and Fe-OC) increasing along with total CARs. During the last 700 years, both climate warming and high-intensity fires promoted more stable carbon compounds in the peatland carbon pool. During periods of high fire intensity and warmth, both of which benefitted stable carbon accumulation, it was interesting that there were no marked changes in aromatic ARs and CARs. While, the Fe-OC ARs were markedly increased around threefold during periods of high fire intensity and warmth.

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Table 1 Average, maximum and minimum values of FTIR 1515/1050 ratio of PyC, 1/FTIR 1720/1050 ratio of PyC, and aromatic content, aromatic AR, Fe-OC content, Fe-OC AR, reactive Fe (Fe_R) content, and Fe-OC/Fe molar ratio in HT peat cores in the northern Great Khingan Mountains.

	Mean	S.D.	Min	Max
FTIR 1515/1050 ratio	1.09	1.38	0.09	9.34
1/FTIR1720/1050 ratio	0.33	0.17	0.06	0.87
Aromatic content mg.g ⁻¹	278.1	6.2	263.0	290.4
Aromatic AR mg.cm ⁻² .yr ⁻¹	1.55	0.41	0.89	2.65
Fe-OC content mg.g ⁻¹	6.78	3.85	3.07	19.4
Fe-OC AR mg.cm ⁻² .yr ⁻¹	0.04	0.02	0.01	0.10
Fe _R content mg.g ⁻¹	3.74	1.77	1.61	8.30
Fe-OC/Fe _R molar ratio	8.40	1.79	4.93	13.9

Figure captions

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Figure 1. Variation in FTIR 1425/1050 ratios, FTIR 15151050 ratios, FTIR 1620/1050 ratios, 635 FTIR 1720/1050 ratios, and FTIR 3437/1050 ratios of pyrogenic carbon (PyC) in the HT peat 636 cores. 637 Figure 2. Variation in Fe-OC contents, reactive Fe (Fe_R) contents, and molar ratios of Fe-638 OC/Fe_R in the HT peat cores. 639 Figure 3. Accumulation rates of carbon, aromatic, and Fe-OC versus the fire intensity, fuel 640 sources, and fire residual products which indicated by 1/FTIR 1720/1050, FTIR 1515/1050, 641 642 and PyC AR, respectively. The fitting functions show the overall trends of the combined data and the significant (P<0.05) adj. R² were reported. 643 Figure 4. (a) Historical variation of FTIR 1515/1050 of PyC in the HT peat cores, and high 644 645 FTIR 1515/1050 ratio indicate the fuel sources are shrubs. (b) Historical variation of FTIR 646 1720/1050 of PyC in the HT peat cores, and high FTIR 1720/1050 ratio indicate low degree of fire intensity. (c) Historical variation of 1/FTIR 1720/1050 of PyC in the HT peat cores, and the 647 increasing trend indicate the fire intensity increasing. (d) PyC fluxes (black line) and δ^{13} C-PyC 648 values (blue line) in the HT peat cores (Gao et al., 2018b). (e) Solar radiation forcing in the 649 650 tropical Pacific (blue line, Mann et al., 2005), and Sea surface temperature (SST) in the North Atlantic Ocean (black line, Cunningham et al., 2013). (f) Dongge Cave speleothem δ^{18} O records 651 652 (Wang et al., 2005). Figure 5. Historical variation of aromatic accumulation rates, Fe-OC accumulation rates, and 653 654 molar ratios of Fe-OC/Fe_R in the HT peat cores (a-c); (d) Historical variation of carbon accumulation rates in the HT peat core (Cong et al., 2022); Historical variation of fire intensity 655 656 and fuel types reconstructed by 1/FTIR 1720/1050 and FTIR 1515/1050 in the HT peat cores (e, f); and the PyC fluxes and the δ^{13} C-PyC values in HT peat cores as indicators to reflect 657

accumulation rates of fire residual products and regional climate characters (g, h).









