

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

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Catena

DOI: 10.1016/j.catena.2023.107108

Published: 15/06/2023

Peer reviewed version

Cyswllt i'r cyhoeddiad / Link to publication

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA): Gao, C., Wang, G., Cong, J., Freeman, C., Jiang, M., & Qin, L. (2023). High intensity fire accelerates accumulation of a stable carbon pool in permafrost peatlands under climate warming. *Catena*, 227, Article 107108. https://doi.org/10.1016/j.catena.2023.107108

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

41 Introduction

42 Globally, fires burn 300-460 million hectares of land annually, representing 4% of the 43 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 44 al., 2017). With global warming and increasing regional human activities, fire intensity and 45 frequency not only increased markedly during the last century also are following an increasing 46 trend that persists into the current century (Flannigan et al., 2013; Gao et al., 2016). Fires not 47 only emit 2200 Tg carbon as CO₂ to the atmosphere but also produce 256 Tg of pyrogenic 48 49 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). 50 The importance of fire in ecosystem carbon cycling is likely to increase further as our climate 51 52 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 53 54 land surface (Yu et al., 2010). Due to its extensively water-logged and anoxic environment, 55 peatlands formed a stable carbon pool and have acted as one of the most important sinks for the 56 carbon capture from the atmosphere during the Holocene (Gallego-Sala et al., 2018; Loisel et 57 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; 58 59 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 60 61 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 62

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.

68 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 69 70 environment and other environmental disturbances (Wright et al., 2011). The high recalcitrance 71 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 72 73 be significantly higher than those in mid-high latitude peatlands, and speculated as the major 74 factor protecting the peatland carbon pool in warmer environments (Hodgkins et al., 2018; 75 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 76 77 peatlands facilitate oxygen diffusion into redox interfaces, increasing Fe(hydro)oxides formation and their association with dissolved organic carbon through coprecipitation and 78 79 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 80 (Riedel et al., 2013; Huang et al., 2021). Climate change and fire in peatlands may also 81 contribute to soil redox conditions and iron phases (Fenner et al., 2011; Norouzi and 82 Ramezanpour, 2013), which may have a strong link to Fe-OC (Eckmeier et al., 2010). 83 Compared to climate factors, fire may clearly also cause serious long-term effects on the 84

stability of peatland carbon pool.

86	As peat soils accumulate under anoxic conditions with continuous inputs, peatlands also
87	serve as an ideal archive for reconstructing historical environmental characteristics (Martini et
88	al., 2007) and are widely used to evaluate the long-term effects of climate on peatland carbon
89	pool (Charman, 2012). PyC, as an important product from fires, is widely used to reconstruct
90	fire history in palaeoenvironment research (Marcisz et al., 2015). Based on PyC fluxes,
91	previous studies also report high fire intensity promoting stable carbon accumulation in the
92	peatland carbon pool with increases in both carbon accumulation rate and the stability of carbon
93	pool (Cong et al., 2020). However, high fire intensity may also destroy PyC and the PyC
94	production may even fall below that of a low-intensity fire, which means there exists
95	uncertainties in fire history reconstructions based on PyC fluxes (Bird et al., 2015; Gao et al.,
96	2022). In addition to PyC fluxes, the chemical properties of PyC are heavily influenced by
97	sources and production process. For example, more aromatic compounds arise in PyC produced
98	from shrubs than that produced from herbs, and higher production temperature significant
99	decrease the labile content of the residual PyC (Wiedemeier et al., 2015; Gao et al., 2022).
100	These results indicate that the chemical properties of PyC could be used to reconstruct a more
101	refined fire history (i.e. fire intensity and fuel sources) than PyC fluxes alone. Thus, in order to
102	improve our understanding of the long term effects of fire on the peatland carbon pool, it will
103	be necessary to reconstruct a more detailed fire history by incorporating chemical properties of
104	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 107 PyC and organic matter, we not only attempted a reconstructed historical fire intensity and fuel 108 109 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 110 111 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 112 emphasis on the stable carbon pool (i.e. aromatic) and the retained labile carbon pool (i.e. Fe-113 OC). This allowed us to evaluate long-term variations in carbon stability and its potential 114 115 forcing mechanisms.

116 2 Materials and methods

117 2.1 Site description and sampling

118 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 119 120 developed on permafrost and threatened by wildfire and climate change. The peat core selected 121 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 122 123 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-124 125 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 126 127 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. 128

129	The peat core covers ca. 700 years, and 7 times fire events were clear identified through PyC					
130	fluxes and the Char analysis software package in total (Gao et al., 2018b).					
131	2.2 FTIR of PyC					
132	Residual PyC in peat soils in each layer was extracted by dichromate oxidation (Gao et al.,					
133	2018b). The FTIR spectra of the residual PyC samples were obtained on a Spectrum Two FTI					
134	spectrometer (PerkinElmer, America) on KBr pellets (150 mg dried KBr and 1 mg peat soil)					
135	The measurements were recorded from 4500 to 300 cm ⁻¹ at a resolution of 1 cm ⁻¹ . A total of 32					
136	scans were averaged for each sample. Absorption peaks indicative of structural units in the OM					
137	were used to identify PyC chemical composition.					
138	2.3 Iron bound organic carbon					
139	The dry sample was extracted with 57.4 mM sodium dithionite in a ratio of 1:120 mass to					
140	the solution, and the samples were shaken for 16 h, then centrifuged. The residues were further					
141	extracted by 0.05 M HCl for 1 h and again centrifuged. In order to account for any organic					
142	carbon released following ion exchange with sulfate (the oxidation product of dithionite), an					
143	equal ratio of soil and 57.4 mM sodium sulfate were processed in parallel (Wagai and Mayer,					
144	2007). The Fe-OC was calculated by the sum of DOC in the total dithionite and acid extractions					
145	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
- 147 iron (Fe_R) contents that contribute to Fe-OC. The Fe in the solution was measured by the
- 148 ferrozine method (Huang and Hall, 2017) while DOC was measured using a total organic
- 149 carbon analyzer (TOC-L, Shimadzu, Japan).

150 **2.4 Indicators of fire factors**

Chemical analysis of residual PyC after burning shows the abundance of typical chemical 151 compounds to have a close relationship with its sources and burning intensity. For example, a 152 153 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 154 155 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 156 burning intensity in this study. The ARs of Fe-OC, aromatics, and total carbon were selected as 157 158 indicators for the accumulation history of different carbon types (i.e. retained labile carbon pool, 159 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 160 contents and peat accumulation rates(Cong et al., 2022). The relationship between selected fire 161 162 indicators and carbon indicators was assessed using the linear regression model.

163 **3 Results**

164 **3.1 Typical FTIR ratios of PyC in HT peat core**

165 Variations in observed FTIR ratios of PyC are shown in Fig. 1, and several characteristic 166 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±1.38 167 (table 1). And the mean value of the FTIR 1720/1050 ratio was 4.02±2.57 and ranged between 168 0.78 and 19.71. Similar to FTIR 1515/1050 and 1720/1050 ratios, other selected FTIR ratios 169 also have a wide range and several clear peaks occurred. Most notably in the layers around 33 170 cm (Fig. S1), the obvious low peak height of 1050 cm⁻¹ causes the selected FTIR ratios to 171 appear markedly higher than the others. High FTIR peaks of selected FTIR ratios almost always 172

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.

176 **3.2** Contents of iron bound organic carbon in HT peat core

177 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 \pm 3.9 mg g^{-1} . From 178 the 30 cm to the bottom layers, the Fe-OC contents are stable with fluctuation around 4 mg g^{-1} 179 (table 1). A markedly increasing trend of Fe-OC occurred from 30 cm to 15 cm, with the highest 180 value of Fe-OC content is 19.4 mg g⁻¹ at 17 cm. In the surface layers, the Fe-OC contents were 181 around 7 mg g^{-1} somewhat higher than those in the bottom layers. The variation trend of Fe_R 182 across depths was similar to Fe-OC contents and markedly increasing from 32cm to 15cm, 183 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 184 4.9 to 13.9. The lowest Fe-OC/Fe_R molar ratio occurred around the 40cm layer, and the highest 185 Fe-OC/Fe_R molar ratio occurred in the surface 5cm layers. An increasing trend of Fe-OC/Fe_R 186 187 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.) R^2 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. R^2 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.

199 4 Discussion

4.1 Fire effects on peatland carbon pool.

Previous studies have highlighted that fire can have serious effects on the peatland carbon 201 pool through burning process and fire residual products (Heinemeyer et al., 2018; Marrs et al., 202 203 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 204 to the surrounding environment, and elsewhere, plant biomass was noticed to significantly 205 206 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 207 208 increased biomass was thus primarily herbs (Marrs et al., 2019). The increasing fire intensity 209 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 210 211 (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 212 213 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 214 215 compounds in the surface peat soils would be more easily consumed or converted to aromatic 216 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 217 shrub stems converted to PyC which results in more PyC being produced from shrub stems that 218 219 contained more aromatic contents (Gao et al., 2022). The higher burning temperature promote 220 the residual PyC to contains more aromatic compounds and higher degree of aromatic 221 condensation (Wiedemeier et al., 2015). Thus, high-intensity fire not only consumed the less 222 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 223 224 aromatic ARs to increase significantly.

225 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 226 peat increased water phenolics concentration from 1mg/L to 4mg/L and contributed to the 227 228 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 229 phenolic with abundant hydroxyl groups promote the Fe-OC formation (Zhao et al., 2020). 230 231 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 232 233 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 239 types indicate the increasing of CARs or aromatic ARs not only came from the PyC, also caused 240 241 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 242 243 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; 244 Nguyen et al., 2018). PyC is rich in condensed aromatic compounds, and soluble aromatic 245 compounds from PyC also deposit in soil after fire (Knicker et al., 2005). Soluble aromatic 246 247 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 248 that increase the CARs and aromatic ARs occurred. High amounts of nutrients also released to 249 250 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 251 al., 2007). With more nutrients available in surface peat soils, more plant growth and the plant 252 253 biomass arises promoting more carbon accumulation in peatland carbon pool (Thormann and 254 Bayley, 1997).

4.2 Historical variation of fire intensity and fuel sources

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 267 700 years. At 650 - 550 cal yr BP, the fire intensity was markedly higher than adjacent periods, 268 269 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 270 periods which indicated the climate in this period was cold and wet (Gao et al., 2018b). During 271 this period, the SST of northeast Atlantic and the δ^{18} O values in speleothem from Dongge Cave 272 also decreased markedly and the solar radiative forcing increased in this period (Mann et al., 273 2005; Wang et al., 2005; Cunningham et al., 2013). The wet climate background was clearly of 274 275 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 276 277 this period. This transition can be speculated as the major factor causing the high PyC fluxes despite wet climate conditions. 278

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

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

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

305	factor that influenced PyC production and increased under the dry/warm environment
306	associated with this period. With the regional increase of human activities from 1900 CE to the
307	present, more serious fires occurred particularly between 1900 and 1980 CE (Gao et al., 2018a).
308	In this period, climate warming and the decreasing precipitation promoted more fire as has
309	occurred in recent years (Novorotskii, 2007). The fire intensity recorded by FTIR 1720/1050
310	ratio increased markedly in recent years with more PyC arising from herb burning. Although
311	the fire intensity in recent years was higher than other periods, the PyC fluxes were lower than
312	in other periods. Thus, it is not easy to evaluate the fire intensity through PyC fluxes directly as
313	high-intensity fire may decrease the amount of PyC production without a serious change in PyC
314	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 327 pathway (Fig. 5a-c). Historical variations in CARs and aromatic ARs were similar over the last 328 329 700 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 330 331 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 332 easily decomposed, especially for unstable carbon (Verbeke et al., 2022). More unstable carbon 333 decomposition caused more stable carbon accumulation in peatland carbon pool and increased 334 335 the aromatic ARs (Hodgkins et al., 2018). Except 550 - 370 cal yr BP, high CARs and aromatic ARs occurred contemporaneously with 336 high degree of fire intensity and the major fuels sources were herbs. The climate characters at 337 338 650 - 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 339 proportions of shrub litters which caused a high amount of carbon with low aromatic contents 340 341 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 342 343 (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. 344 345 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 346

347 consumed during burning and more aromatic contents in fire residual products (Gao et al.,

348 2022), which decreased the unstable carbon source and increased the stable carbon source of

349 peatland carbon pool in totally. Additionally, high-intensity fire also decrease the water 350 retention capacity of surface soils which are more benefit for shrub growth and increase the 351 stable carbon source (Keesstra et al., 2017). Thus, the increasing of fire intensity led more stable 352 carbon accumulated in peatland under cold/wet climate conditions.

353 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 354 climate characters were warm/dry or the degree of fire intensity were high. Under warm/dry 355 climate conditions, more shrub plants growth in peatlands and the plant litters of these plants 356 357 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 358 (Marrs et al., 2019), which may decrease the stable carbon sources from plant litter and 359 360 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 361 increasing of Fe-OC ARs in this period (Fig. 5b). And the Fe_R at 320 - 100 cal yr BP were 362 363 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), 364 365 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, 366 367 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 368 369 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 370

all contributed to high Fe-OC/Fe_R molar ratio, but due to limited Fe_R by plant uptake, the 371 contents seem not high as that at 300-100 cal yr BP. These results suggested that high-intensity 372 373 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 374 375 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 376 degradation and could create probability for long-term carbon storage (Hall et al., 2018). As the 377 fire could promote soil crystalline iron phase formation (Norouzi and Ramezanpour, 2013), 378 379 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 380 than those in warm climate conditions, which further confirmed that the importance of fire 381 382 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. 383 Although the shrubs had higher lignin content compared with herbs, our study showed that 384 385 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.

389

390 5 Conclusion

Based on PyC properties and OM properties in a 700-year peat core from the northern GreatKhingan 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 393 compounds and Fe-OC, the major stable carbon pool and retained labile carbon pool in the 394 peatland, amounting to 278.1±6.2 mg·g⁻¹ and 6.78±3.85 mg·g⁻¹, respectively. Our results shown 395 high intensity herb fires occurred more easily under wet condition and cause more PyC 396 397 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 398 accumulation, and the amount of stable carbon compounds (e.g. aromatic and Fe-OC) 399 increasing along with total CARs. During the last 700 years, both climate warming and high-400 401 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, 402 403 it was interesting that there were no marked changes in aromatic ARs and CARs. While, the 404 Fe-OC ARs were markedly increased around threefold during periods of high fire intensity and warmth. 405

406

407 Acknowledgement

The authors gratefully acknowledge the assistance of the Analysis and Test Center of 408 Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. We thank 409 Prof. Hongwen Yu and Dr. Na Guo for FTIR analysis. Financial support was provided by the 410 National Natural Science Foundation of China (No. 42171103, 42101108, 42230516, 411 42101114), the Young Scientist Group Project of Northeast Institute of Geography and 412 Agroecology, Chinese Academy of Sciences (2022QNXZ01), Jilin Association for Science and 413 (QT202126), Jilin Provincial 414 Technology Science and Technology Department

415 (220220101150JC), and the Youth Innovation Promotion Association CAS (No. 2020235).

416

417 **Conflict of interest:**

- 418 The authors declare no competing financial interests.
- 419

420 **Reference:**

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628	Table 1 Average, maximum and minimum values of FTIR 1515/1050 ratio of PyC, 1/FTIR
629	1720/1050 ratio of PyC, and aromatic content, aromatic AR, Fe-OC content, Fe-OC AR,
630	reactive Fe (Fe_R) content, and Fe-OC/Fe molar ratio in HT peat cores in the northern Great
631	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

634 **Figure captions**

Figure 1. Variation in FTIR 1425/1050 ratios, FTIR 15151050 ratios, FTIR 1620/1050 ratios,
FTIR 1720/1050 ratios, and FTIR 3437/1050 ratios of pyrogenic carbon (PyC) in the HT peat
cores.

Figure 2. Variation in Fe-OC contents, reactive Fe (Fe_R) contents, and molar ratios of Fe-OC COC/Fe_R in the HT peat cores.

Figure 3. Accumulation rates of carbon, aromatic, and Fe-OC versus the fire intensity, fuel
sources, and fire residual products which indicated by 1/FTIR 1720/1050, FTIR 1515/1050,
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.

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

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 and fuel types reconstructed by 1/FTIR 1720/1050 and FTIR 1515/1050 in the HT peat cores

657 (e, f); and the PyC fluxes and the δ^{13} C-PyC values in HT peat cores as indicators to reflect

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

660 Fig. 1





Fig. 2







669 Fig. 4



673 Fig. 5

