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Variability in pyrogenic carbon properties generated by different burning temperatures and peatland plant litters: implication for identifying fire intensity and fuel types

Chuanyu Gao[A], Jinxin Cong[A], Yang Sun[A], Dongxue Han[A] and Guoping Wang[A,*]

For full list of author affiliations and declarations see end of paper

***Correspondence to:**
Guoping Wang
Key Laboratory of Wetland Ecology and Environment, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Shengbei Street 4888, Changchun 130102, China
Email: wangguoping@neigae.ac.cn

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ABSTRACT

Pyrogenic carbon (PyC), generated by fire, acts as a stable carbon deposit in natural ecosystems and is widely used to reconstruct fire history. Fuel type and burning temperature are the two major factors that influence PyC properties and exert variable effects on soil carbon pools, especially for peatlands. However, whether analysis of PyC can identify these two factors remains unclear. To address this knowledge gap, we selected typical peatland plant litters of seven shrub and seven herb plants in the Great Khingan Mountains, China. The properties of PyC produced at 250°C (low-intensity burning) and 600°C (high-intensity burning) without oxygen were evaluated. The results showed that the effects of burning temperature and plant type on δ^{13}C-PyC were not significant. The differences in the initial compositions of herbs and shrubs led to more aromatic and carboxylic compounds in shrub PyC than in herb PyC. A high burning temperature led to less labile components (e.g. aliphatic compounds and acids) and higher thermal stability of high-temperature PyC compared to that of low-temperature PyC. Our results also indicate that several typical PyC chemical composition indicators (e.g. Fourier-transform infrared spectroscopy 1515/1050 ratio and 1720/1050 ratio) can potentially identify PyC sources.

Keywords: carbon, fire history, fire intensity, FTIR, fuel, pyrogenic carbon, soil, stable carbon isotope, thermal stability.

Introduction

Fire is a natural process and an important ecological factor in many ecosystems, as well as a primary disturbance mechanism for sustaining their structure, diversity, and productivity (Battisti *et al.* 2016; Just *et al.* 2017). Regarding the carbon cycle, vegetation fires burn 300–460 million hectares (~4% of the Earth's vegetated land surface) globally per year, emitting 1.6–2.8 Gt carbon to the atmosphere (equivalent to a third of the current annual carbon emissions from fossil fuel), and 12% of the carbon burned is converted to pyrogenic carbon (PyC) (Boden *et al.* 2010; Randerson *et al.* 2012; Jones *et al.* 2019). Thus, the effects of fire on the carbon cycle are substantial, and this significance is forecasted to increase with an increase in fire frequency and intensity under current climate and land cover changes (Flannigan *et al.* 2009; Turetsky *et al.* 2015; Santín *et al.* 2016; Walker *et al.* 2019). An increase in fire frequency and intensity causes more PyC deposition in natural ecosystems, and the importance of PyC in carbon cycling also increases (Santín *et al.* 2015).

Peatlands are arguably the most effective terrestrial ecosystems for sequestering carbon over millennial timescales because of their water-saturated oxygen-limited environments (Loisel *et al.* 2017). Peatlands cover approximately 3% of the total global land area and store approximately 540 Pg of carbon, which accounts for a substantial fraction (30%) of the global soil carbon pool (Gorham 1991; Dise 2009; Yu *et al.* 2010). Peatlands are also affected by wildfires, in addition to management burning in some areas. High fire frequency in peatlands has been reported to decrease peat and carbon accumulation rates; however, it can increase species diversity and abundance of peat-forming species

(Marrs *et al.* 2019). Due to wildfire, peatlands accumulate dead biomass and PyC, which have a higher carbon content and longer residence time than unburnt plant residues (Marrs *et al.* 2019). Recent studies in northern China and Europe have found that PyC represents 5–13% of total peatland soil carbon pools and up to 50% in several special peat soils (Gao *et al.* 2016; Leifeld *et al.* 2018).

Owing to its physicochemical characteristics (e.g. recalcitrance and surface area), PyC is the most stable carbon store in peat soils, preserving a record of fire history, and also affecting the biogeochemical cycles in burnt peatlands, via, for example, priming of native organic matter (OM) decomposition and changes in microbial activity (Gao *et al.* 2018*b*; Könönen *et al.* 2018; Noble *et al.* 2018). Although historical fuel types and fire intensity could provide more palaeoenvironmental information (e.g. vegetation types, atmospheric oxygen concentration), the relationship between PyC properties and its sources is only focused by few studies and it remains unclear, hence recent fire history studies were major focused on fire frequency and fire events (Scott and Glasspool 2006; Gao *et al.* 2018*b*; Karp *et al.* 2018; Wurster *et al.* 2021). Previous studies have found that polycyclic aromatic carbon was composed of approximately 50% stable aromatic carbon when formed at typical vegetation fire temperatures (i.e. around 500°C), with composition dominated by semi-labile carbon when formed below 400°C (Bird *et al.* 2015). As treatment temperature increases, the aromaticity and degree of aromatic condensation in PyC also increased markedly (Wiedemeier *et al.* 2015). Thus, as an important indicator for fire intensity, fire temperature is likely to be a key factor affecting the PyC properties and has a potential to be identified in the palaeorecords.

Flaming and smouldering are two major forms of burning and PyC-producing processes in natural peatlands, and the intensities of these two burning processes are significantly different. As a result of the O_2 limit for smouldering, the peak temperature of a smouldering fire is approximately 500°C and mostly ranges from 200 to 300°C (Huang and Rein 2017), which is considerably lower than that of flaming fire (approximately 600°C) (Santín *et al.* 2017). Typical fuels in peatlands are local surface plant litters, which is mainly composed of shrub and herb plant litters. The lignin content in shrub litter is higher than that in herb plant litters, whereas the carbohydrate content is lower, and these components break down at different temperatures. Thus, changes in both burning type and fuel source in peatlands may result in significantly different PyC properties. However, only few studies have focused on the effects of burning type and fuel source on PyC properties in peatlands.

The Great Khingan Mountains are located in the western region of Northeast China, and peatlands are an important ecosystem type in this region (Xing *et al.* 2015). These mountains have a high percentage of forest and low mean annual precipitation in spring and autumn (460–520 mm) (Fan *et al.* 2017), as a result of due to which wildfires occur more frequently in the Great Khingan Mountains than in other regions of China. In addition, climate change and increase in human activities have markedly increased wildfire frequency and intensity in this region over the last 150 years, with modellings suggesting an increased fire frequency of more than three times than present in this region over the course of the 21st century (Flannigan *et al.* 2013; Gao *et al.* 2018*a*). Increasing the fire frequency results in more PyC deposition in peatlands, which in turn influences the peatland carbon stocks in this region. However, the effects of local peatland fires on the properties of residual PyC remain unclear.

In the current study, we selected typical peatland shrub and herb plants in the Great Khingan Mountains to evaluate the effects of burning type and fuel source on PyC properties in peatlands. An experiment with a selected temperatures of 250°C (low-intensity burning) and 600°C (high-intensity burning) was conducted involving combustion of plant litter (i.e. shrub and herb plants) in the laboratory to simulate the production of PyC, and then determine the properties and stability of PyC produced. Based on this study, we first evaluated the effects of burning temperature and fuel types on PyC properties and stability; second, we aimed to understand whether PyC properties could be used as indicators to reflect fire intensity and fuel types in peatlands enabling use in the development of proxy environmental records.

Materials and methods

Collection of typical peatland plants and PyC production

As mosses are fluffy, spongy, and grow on the moist peatland ground surface, they are burned out more easily under dry conditions and are less influenced by fire under wet conditions than herb and shrub plants. Thus, we selected typical herb and shrub plant litter as mostly likely the major potential PyC source in this study. Based on plant investigation in peatlands in the Great Khingan Mountains, *Vaccinium uliginosum*, *Lonicera*, *Ledum palustre* L., *Betula ovalifolia*, *Betula fruticosa*, *Salix rosmarinifolia*, and *Rhododendron spp*. were selected as typical peatland shrub plants, and *Carex spp*., *Typha orientalis*, *Calamagrostis epigeios*, *Carex appendiculata*, *Eriophorum vaginatum*, *Deyeuxia angustifolia*, and *Glyceria angustifolia* were selected as typical herbaceous peatland plants. All samples were collected in August 2016, and the leaves and stems of each were mixed and stored in paper bags before being transferred to the laboratory. The plant materials were dried at room temperature (20°C) for PyC production and further analysis.

The PyC production method was modified from a previous study (Wurster *et al.* 2015). After drying the plant materials to a constant mass at room temperature (20°C), each type of plant (approximately 1 g) was wrapped with aluminum foil to ensure that the plant materials were not oxidised by air during heating. The samples were placed inside a muffle furnace and heated for approximately 30 min to a final hold temperature (i.e. 250°C for low-intensity fire and 600°C for high-intensity fire) for 1 h. After the reaction, the residual material was cooled in aluminum foil and regarded as PyC from different temperatures of plant incomplete burning. The residual proportion of PyC after reaction (i.e. residual PyC) was calculated using the mass ratio of the residual plant after burning to the original plant mass.

PyC chemical analysis

Carbon abundance and carbon isotope composition of all in plant materials and PyC were analysed using a continuous-flow isotope ratio mass spectrometer (CF-IRMS) at the Analysis and Test Centre of the Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. The CF-IRMS system comprises an elemental analyser (Flash 2000 series) coupled to a Finnigan MAT 253 mass spectrometer. The combustion temperature was set to 960°C and standard samples with known carbon contents (IRMS certified reference: BN/132357) were used to calibrate the measurements and to monitor the working conditions.

Fourier-transform infrared (FTIR) spectroscopy has been widely used to characterise the chemical composition of organic matter (OM) and provide information about the relative abundances of functional moieties in OM. Here, FTIR was undertaken to determine the relative abundances of major moieties normalised to the total area of the FTIR spectra or compared to the polysaccharide peak at 1090 cm^{-1}. The FTIR spectra of PyC samples were obtained using a Cary 670 (Agilent, Santa Clara, CA, USA) FTIR spectrometer in absorption mode with subsequent baseline subtraction on potassium bromide (KBr) pellets (200 mg dried KBr and 2 mg PyC). The measurements were recorded from 4500 to 300 cm^{-1} at a resolution of 2 cm^{-1}. A total of 32 scans were averaged for each sample. The absorption peaks indicative of structural units in the OM were used as an indicator of PyC chemical composition, and the identified and selected peaks are shown in Supplementary Table S1. For example, absorption around 1620 cm^{-1} (1650–1600 cm^{-1}) was interpreted to reflect lignin and other aromatics (aromatic C ΓC stretching and/or asymmetric C–O stretching in COO^{-}) (Cocozza *et al.* 2003). Therefore, the relative abundance of these moieties compared to polysaccharides was expressed as the ratio between the maximum peak height at approximately 1620 and 1050 cm^{-1}.

Thermal stability and heating flow

To generate mass loss, heat flow, and CO_2 production data, thermogravimetric analysis infrared thermographs was undertaken using a Mettler Toledo instrument (PT1000) and a Thermo FTIR analyser at the Engineering Research Centre of Oil Shale Comprehensive Utilisation, Ministry of Education (Jilin, China). Approximately 4 mg of each sample was placed in an aluminum pan under dry air (under O_2 21%/N_2 79%, flow rate 20 mL min^{-1}) at a scanning rate of 10°C min^{-1} (Merino *et al.* 2015). The temperature ranged from 50 to 800°C. Low flow rates were selected to ensure that the CO_2 signal identified by FTIR analysis was sufficiently large. A peak 2357 in FTIR analysis was used to quantify the CO_2 signal, and the height of this peak was used to indicate CO_2 production at different temperatures (Liu *et al.* 2008).

The stability of PyC was evaluated by thermogravimetric analysis (TGA), and the weight loss curve of each sample was divided into three temperature regions to represent the different stabilities of the PyC components. The labile components mainly comprised carbohydrates, whereas proteins and other labile aliphatic compounds were mainly lost in the first temperature region at 150–375°C; recalcitrant OM, such as lignin or other polyphenols, was lost in the second temperature region at 375–475°C, and the highly recalcitrant parts, such as polycondensed aromatic forms were mainly lost at 475–600°C (Merino *et al.* 2015). The mass losses in these three temperature regions were designated as Q1, Q2, and Q3, respectively, and T50 indicates the temperature at which 50% of the overall mass loss was observed. Thus, the amounts of Q1, Q2, Q3, and T50 were used as indicators.

Statistical methods

In addition to the FTIR peak ratio, selected FTIR peaks were also identified based on the minimum in the expected region of the endpoint of each peak or based on the maximum of the second derivative if there was no local minimum. Subtracting the absorbance below the baseline from each selected FTIR peak region (i.e. drawn between the endpoints of each peak) yielded the residual absorbance as the final peak (R code sources: https://github.com/shodgkins/FTIRbaselines). The peak heights of carb (carbohydrates), arom15 (aromatics), arom16 (aromatics or deprotonated COO^{-}), acids (protonated COOH), aliph28 (aliphatic), and aliph29 (aliphatic) were selected as indicators reflecting the chemical properties of PyC in this study (Hodgkins *et al.* 2014). These peak heights were used as area-normalised and baseline-corrected peak heights.

The PyC chemical properties and stability indicators for the two plant types produced at different temperatures were analysed by two-way analysis of variance (two-way ANOVA: different plant types and burning temperature were regarded as two factors) using SPSS 20.0 (SPSS, Inc.). This approach was used to test whether the different plant types and burning temperatures could be identified as distinct factors affecting PyC chemical properties and stability. Significant differences were reported at a probability level of 0.05, unless otherwise stated.

Results

Plant residual rates after burning

At the lower burning temperature, the residual PyC fraction for shrubs averaged 67.55 ± 2.98% (1 s.d.) (ranging from 62.18 ± 0.82 to 70.77 ± 1.54%), which was significantly higher than that for herbs, which was 60.25 ± 2.45% (ranging from 55.24 ± 1.95 to 62.42 ± 3.17%) (Tables 1, 2). At the higher burning temperature, the average for shrub PyC was 21.64 ± 3.55% (ranging from 16.19 ± 3.08 to 24.44 ± 1.23%) and that for herb PyC was 20.65 ± 1.93% (ranging from 19.34 ± 4.24 to 24.50 ± 2.29%) (Tables 1, 2). There was no significant difference in the average residual rates between the shrub and herb PyC at the high burning temperature. Based on two-way ANOVA, the effects of temperature and plant type on residual rates were significant, and the interactions between temperature and plant type also had significant effects on residual amounts of PyC produced (Table 2).

Carbon contents and values of δ^{13}C in PyC

Plant type significantly affected the carbon content of the residual PyC, and the effects of burning temperature on carbon content in residual PyC was also observed to be significant at the $P < 0.1$ level (Table 2). The carbon content of the PyC ranged from 48.36 ± 5.12 to 62.89 ± 0.56% at the low burning temperature, and from 45.43 ± 9.49 to 68.20 ± 1.94% at the high burning temperature (Table 1). Only plant type had significant effects on the δ^{13}C-PyC values in residual PyC at the $P < 0.1$ level (Table 2). The δ^{13}C-PyC values ranged from −29.92 ± 0.21 to −26.95 ± 0.10% in shrub PyC and from −28.77 ± 0.11 to −26.41 ± 0.18% in herb PyC, being similar to those in the original plant, which ranged from −29.71 to −26.88% and from −29.00 to −26.24%, respectively (Table 1).

FTIR spectra of PyC

The FTIR spectra of PyC produced from different types of plants at different temperatures are shown in Fig. 1. The most evident difference between low- and high-temperature PyC is that there is no clear peak at 2850 cm^{-1} or 2920 cm^{-1} in the high-temperature PyC FTIR spectra. The effects of temperature on the FTIR 1625/1050 ratio, FTIR 1720/1050 ratio, and FTIR 3437/1050 ratio were significant (Table 2). These three ratios in the high-temperature PyC were significantly lower than those in the low-temperature PyC. For example, FTIR 1720/1050 ratios in high-temperature herb PyC and shrub PyC were 0.04 ± 0.01 and 0.10 ± 0.08, respectively, whereas those in low temperature were 1.22 ± 0.17 and 1.54 ± 0.41, respectively (Table 2). The effects of plant type on all selected FTIR ratios were significant. In particular, the FTIR 1515/1050 and 1625/1050 ratios were significantly lower for herb PyC than for shrub PyC. The interactions between temperature and plant type only had significant effects on the FTIR 1425/1050 ratio, but not on other FTIR ratios. For FTIR peak identification by baseline correlation, the burning temperature was the key factor that had significant effects on all selected factors, and plant types had significant effects on carb, arom16, acids, aliph28, and aliph29. The interaction between temperature and plant type only had significant effects on arom16, aliph28, and aliph29.

Thermal stability of PyC

The mass loss, mass loss per degree, heat flow, and height of the FTIR CO_2 peak of PyC with increasing temperatures are shown in Fig. 2, 3. Q1, Q2, Q3, and T50 of PyC were used to evaluate the thermal stability of PyC. There are two stages of mass loss for PyC produced at low temperatures and only one stage for PyC produced at high temperatures. The heat flow and CO_2 production from low-temperature PyC were also more complex than those of high-temperature PyC. The results of two-way ANOVA are shown in Table 2, and details of the thermal stability of PyC in different types of plants are presented in Supplementary Table S2. The effects of plant type and the interaction between temperature and plant type had no significant effects on the thermal stability indicators for PyC. Only the burning temperature had a significant effect on the thermal stability of PyC. The effects of temperature on Q1 were evident, with a mass loss of 5.42 ± 2.31% for herb PyC and 5.48 ± 2.54% for shrub PyC under high burning temperature, and 34.39 ± 2.72% for herb PyC and 31.75 ± 3.75% for shrub PyC under low burning temperatures (Table 2). The burning temperature also had significant effects on T50, which increased at the higher burn temperature. For example, T50 in herb PyC increased from 418.60 ± 10.31 to 492.18 ± 15.66°C (Table 2). However, both temperature and plant type had no significant effects on CO_2 production peak time.

Correlation between thermal stability and chemical compositions of PyC

In this study, we chose Q1, Q3, and T50 as indicators to evaluate the thermal stability of the residual PyC, and the peak heights of carb, arom15, acids, and aliph28 as indicators to evaluate the chemical composition of the residual PyC. The correlation between these two groups of indicators is shown in Fig. 4. The correlation between Q1 chemical composition indicators was statistically significant at the 0.001 level. Except for the carb peak, there was a positive correlation between Q1 and the other three chemical composition indicators. The adjusted (adj.) R^2 between Q1 and the acids peak was 0.95, which was the highest of all. In contrast to Q1, T50 was significantly negatively correlated with arom15, acids, and aliph28 and significantly positively correlated with the carb peak. Similar to Q1, the correlation

Table 1. Mean and standard deviation (s.d.) of the mass ratio of residual plant to the original plant (residual rates), δ^{13}C-PyC, and carbon contents in residual PyC under low and high burning temperatures for herb and shrub plant, and values of δ^{13}C-plant in origin plants.

Plant types	δ^{13}C-plant ‰	Low temperature						High temperature					
		Residual rates %		δ^{13}C-PyC ‰		Carbon contents %		Residual rates %		δ^{13}C-PyC ‰		Carbon contents %	
		Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Shrubs													
Vaccinium uliginosum	−29.71	70.77	1.54	−29.58	0.20	60.09	0.08	24.07	2.00	−29.92	0.21	68.20	1.94
Lonicera	−28.41	68.15	1.55	−28.11	0.08	51.81	0.57	24.30	1.45	−28.22	0.04	49.88	0.75
Ledum palustre L.	−28.97	67.75	0.47	−28.85	0.01	62.89	0.56	16.19	3.08	−28.55	0.07	65.81	4.75
Betula ovalifolia	−26.88	65.08	1.12	−26.95	0.10	59.64	1.38	17.55	3.45	−26.97	0.12	61.18	4.15
Betula fruticosa	−28.07	69.18	1.21	−27.92	0.37	57.88	0.49	24.44	1.23	−28.27	0.13	63.75	2.91
Salix rosmarinifolia	−28.03	69.75	1.21	−27.98	0.12	53.01	0.26	24.33	2.96	−27.90	0.09	53.92	9.50
Rhododendron spp.	−29.66	62.18	0.82	−29.50	0.17	61.93	1.61	20.61	2.19	−29.04	0.28	68.17	0.88
Herbs													
Carex spp.	−26.38	59.68	3.45	−26.41	0.18	55.98	0.89	19.11	6.04	−26.57	0.17	67.37	6.60
Typha orientalis	−27.91	55.24	1.95	−27.05	0.75	53.87	4.50	19.46	4.74	−27.56	0.16	45.43	9.49
Calamagrostis epigeios	−26.24	60.56	0.57	−26.65	0.80	48.36	5.12	20.45	2.16	−26.02	0.16	59.98	3.63
Carex appendiculata	−28.90	61.74	0.73	−28.77	0.11	53.11	0.86	21.79	1.54	−28.61	0.13	47.82	0.45
Eriophorum vaginatum	−27.82	62.42	3.17	−27.74	0.12	55.04	1.01	19.89	4.88	−27.80	0.15	62.92	6.66
Deyeuxia angustifolia	−28.63	62.12	5.43	−28.49	0.09	50.48	0.86	24.50	2.29	−28.50	0.05	48.96	3.67
Glyceria angustifolia	−29.00	60.03	0.40	−28.83	0.08	52.82	1.42	19.34	4.24	−28.60	0.22	48.16	8.49

Table 2. Two-way analysis of variance (ANOVA) of mass loss in the different temperature range (i.e. Q1, Q2 and Q3), temperature at 50% of mass lost (T50), CO_2 peak time, the mass ratio of residual plant to origin plant (residual rates), δ^{13}C-PyC, C contents, FTIR 1425/1050 ratio, 1515/1050 ratio, 1625/1050 ratio, 1720/1050 ratio, 3437/1050 ratio, and selected FTIR peak height normalised by total peak area (carb, arom15, arom16, acids, aliph28, and aliph29) in residual PyC. Temperature and plant types were regarded as two factors for the two-way ANOVA, and the mean with the standard division of these factors in residual PyC is shown.

	Tem		Type		Tem × Type		High herbs		High shrubs		Low herbs		Low shrubs	
	F values	*P* values	*F* values	*P* values	*F* values	*P* values	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Residual rate	1642	0.000	15.4	0.001	8.92	0.006	20.65	1.93	21.64	3.55	60.25	2.45	67.55	2.98
δ^{13}C-PyC	0.003	0.955	3.81	0.063	0.002	0.963	−27.67	1.03	−28.41	0.92	−27.71	1.02	−28.41	0.95
C%	3.937	0.059	5.57	0.027	1.76	0.197	54.38	8.80	63.17	5.02	52.81	2.63	55.27	7.06
Q1(150–375°C)	641.2	0.000	1.40	0.248	1.54	0.227	5.42	2.31	5.48	2.54	34.39	2.72	31.75	3.75
Q2(375–475°C)	3.546	0.072	0.374	0.547	0.067	0.797	32.29	5.63	34.32	8.80	37.29	2.03	38.11	6.23
Q3(475–600°C)	9.119	0.006	1.973	0.173	0.055	0.817	28.39	11.57	31.99	10.08	18.38	2.80	23.42	4.64
T50	126.2	0.000	0.218	0.645	1.14	0.296	492.18	15.66	488.59	21.23	418.60	10.31	427.78	14.11
CO_2 peak time	1.714	0.203	0.748	0.396	0.058	0.811	43.57	2.28	44.44	1.69	42.73	2.38	43.22	1.91
FTIR 1425/1050	0.000	0.988	20.5	0.000	7.76	0.010	0.50	0.17	1.50	0.62	0.88	0.12	1.12	0.31
FTIR 1515/1050	2.751	0.110	16.9	0.000	1.94	0.177	0.50	0.18	1.06	0.34	0.81	0.14	1.08	0.35
FTIR 1625/1050	68.56	0.000	7.78	0.010	1.54	0.226	0.38	0.10	0.56	0.15	1.22	0.18	1.70	0.58
FTIR 1720/1050	241.1	0.000	4.89	0.037	2.39	0.135	0.04	0.01	0.10	0.08	1.22	0.17	1.54	0.41
FTIR 3437/1050	62.69	0.000	10.1	0.004	0.043	0.838	0.32	0.11	0.50	0.14	0.78	0.05	0.98	0.25
carb	12.40	0.002	5.78	0.024	1.74	0.199	6.1×10^{-4}	2.0×10^{-4}	3.6×10^{-4}	2.1×10^{-4}	2.9×10^{-4}	8.1×10^{-5}	2.2×10^{-4}	1.8×10^{-4}
arom15	51.53	0.000	0.00	1.00	0.00	1.00	4.4×10^{-6}	2.3×10^{-6}	5.5×10^{-6}	4.0×10^{-6}	3.1×10^{-5}	1.2×10^{-5}	3.1×10^{-5}	1.5×10^{-5}
arom16	454.8	0.000	42.5	0.000	76.8	0.000	1.9×10^{-4}	4.8×10^{-5}	-8.2×10^{-5}	3.8×10^{-5}	4.2×10^{-4}	2.4×10^{-5}	4.6×10^{-4}	6.9×10^{-5}
acids	1741	0.000	7.20	0.013	0.00	1.00	-3.1×10^{-5}	1.9×10^{-5}	-7.0×10^{-5}	2.7×10^{-5}	5.7×10^{-4}	4.1×10^{-5}	5.3×10^{-4}	5.5×10^{-5}
aliph28	126.9	0.000	18.1	0.000	14.1	0.001	2.7×10^{-6}	1.3×10^{-6}	7.1×10^{-6}	4.3×10^{-6}	6.9×10^{-5}	1.2×10^{-5}	1.4×10^{-4}	4.5×10^{-5}
aliph29	160.6	0.000	18.3	0.000	15.7	0.001	3.6×10^{-6}	1.3×10^{-6}	7.2×10^{-6}	4.5×10^{-6}	1.0×10^{-4}	1.8×10^{-5}	2.0×10^{-4}	5.8×10^{-5}

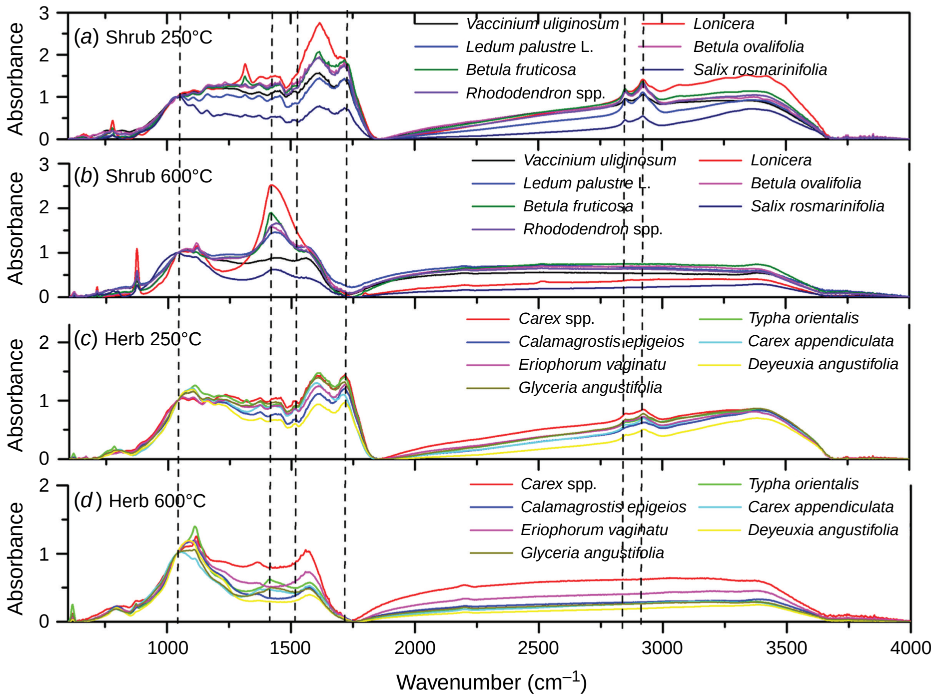

Fig. 1. Fourier-transform infrared spectroscopy (FTIR) spectra of low-temperature shrub pyrogenic carbon (PyC) (*a*), high-temperature shrub PyC (*b*), low-temperature herb PyC (*c*), and high temperature herb PyC (*d*), respectively. The dash lines reflect several relevant peaks, e.g. 1050, 1420, 1515, 1620, 1720, 2850, and 2920 cm^{-1}.

between T50 and the acids peak was 0.80, which was the highest among the four chemical composition indicators. The correlation between Q3 and chemical composition indicators was weak, and there was no significant positive correlation between Q3 and the carb peak. The correlation between Q3 and other three chemical composition indicators were significant, and the highest adj. R^2 were only 0.19 for Q3 and acids peak.

Discussion

Carbon contents and δ^{13}C values of residual PyC

Litter loss as a consequence of burning occurs within a wide range of ecosystems, and the litter loss differences may reflect variations in the flammability of the different litter types (Harvey *et al.* 2012). In this study, the residual amounts of PyC produced from shrubs were higher than those produced from herbs, which indicates that the flammability of the shrubs was lower than that of herbs produced at low burning temperatures. Thus, herb litter would burn more readily, and the fuel would be consumed more rapidly. Based on the residual production of PyC, the most flammable and inflammable plants in peatland systems under low burning temperatures were *Typha orientalis* and *Vaccinium uliginosum*, respectively. For high burning temperatures, the residual production of PyC from several special herb plants (e.g. *Deyeuxia angustifolia*) were even higher than those of shrub plants. This indicates that the flammability of herbs and shrubs was similar under high burning temperatures, which suggests that wildfire could consume both herbs and shrubs because of the high temperature. However, low-intensity burning will mostly consume herbs because of their susceptibility at low burning temperature, and some shrubs may remain.

The effects of burning temperature on carbon content in residual PyC were significant at 0.1 level, whereas plant type exerted no significant effects. The carbon content of the residual PyC ranged from 52.81 ± 2.63% in the low-temperature herb PyC to 63.17 ± 5.02% in the high-temperature shrub PyC. Although PyC and ash are the key products after wildfire (Medvedeff *et al.* 2015), PyC is mainly component produced by incomplete burning, and carbon was the major element at more than 50%. Peat soils are carbon-rich materials, with a carbon content ranging from 40 to 50%, which is lower than the carbon content of the PyC produced in this study (Gao *et al.* 2019). Thus, PyC produced by incomplete burning after wildfire deposited into peatlands could lead to an increase the carbon content of peat soils.

Neither temperature nor plant type had significant effects on the δ^{13}C-PyC values. The difference between δ^{13}C-PyC and δ^{13}C-plant summarised in a previous study showed that δ^{13}C-PyC produced by C_3 grass was slightly lower than that of δ^{13}C-plant. The difference between biomass and PyC was approximately 0–2%, and changes in δ^{13}C-PyC produced from C_3 wood materials were between −2.0 and +0.4% (Bird and Ascough 2012). In other previous studies, no significant difference was observed between δ^{13}C-PyC and δ^{13}C-plant in some PyC production conditions, such as laboratory charring at temperatures of 300–700°C and an exposure time of 0–100 min in a restricted O_2 environment

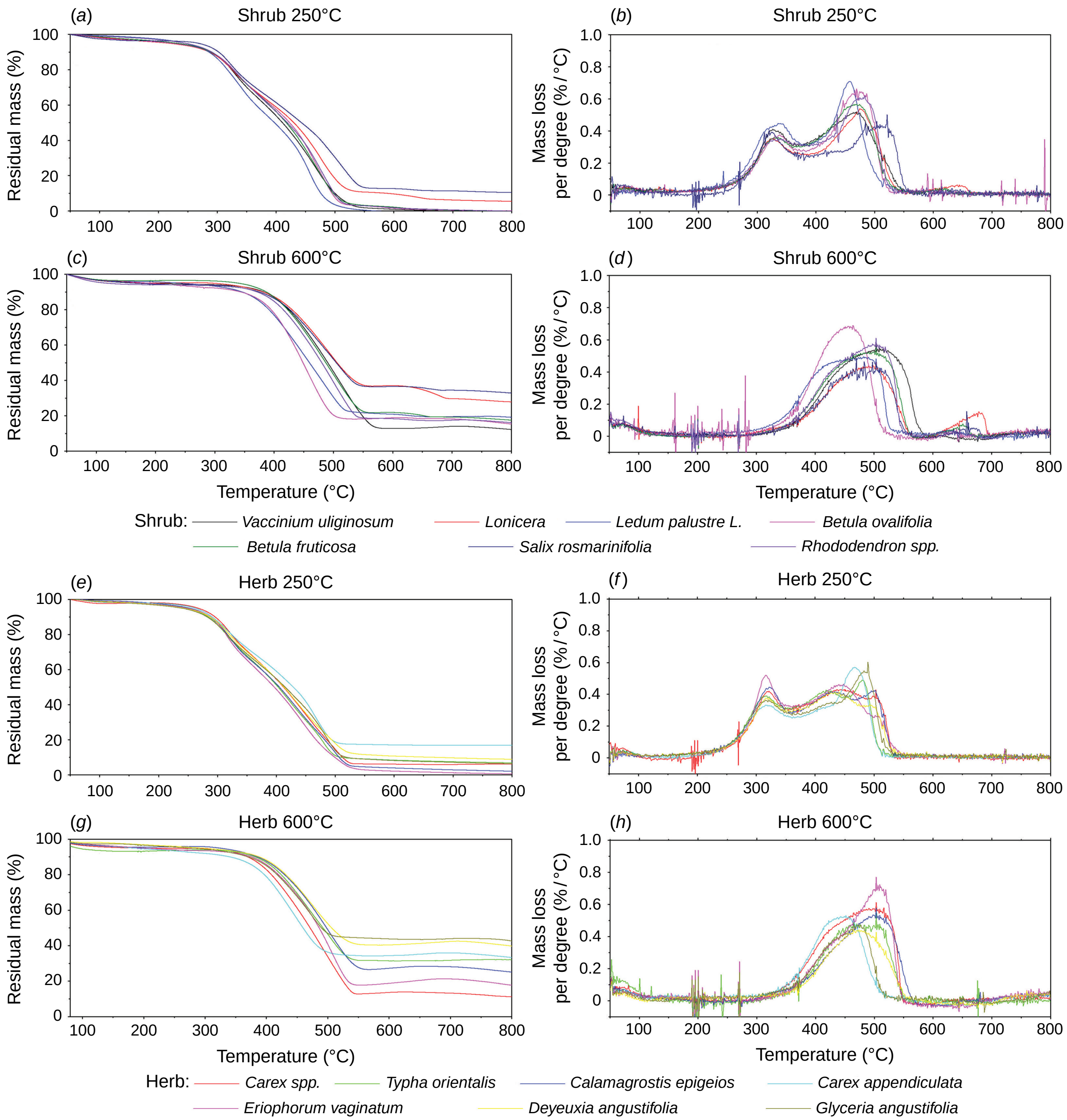

Fig. 2. Mass loss and mass loss per temperature of low-temperature shrub pyrogenic carbon (PyC) (*a*, *b*), high-temperature shrub PyC (*c*, *d*), low-temperature herb PyC (*e*, *f*), and high-temperature herb PyC (*g*, *h*).

(Das *et al.* 2010). These studies suggest that the burning process does not necessarily have a significant effect on carbon isotope fractionation, and in all published cases is ~2%. The δ^{13}C-PyC values may not be a good indicator of the degree (temperature) of wildfires. Most typical peatland plants in temperate environments are C_3 plants, and there is no clear boundary of δ^{13}C-PyC values between typical peatland shrub plants and herb plants. Thus, δ^{13}C-PyC in peatland systems is unlikely to enable discrimination between plant sources.

Effect of plant types on PyC properties

This study revealed differences in the chemical composition of PyC derived from different types of typical peatland plants (Fig. 1). Comparison of the FTIR spectra of herb and shrub PyC, revealed that the FTIR spectra of 1425/1050, 1515/1050, and 1620/1050 ratios were significantly different. These three FTIR ratios in herb PyC were lower than those in shrub PyC at both burning temperatures. The FTIR 1425/1050 ratio reflects carboxylate or carboxylic structures, and

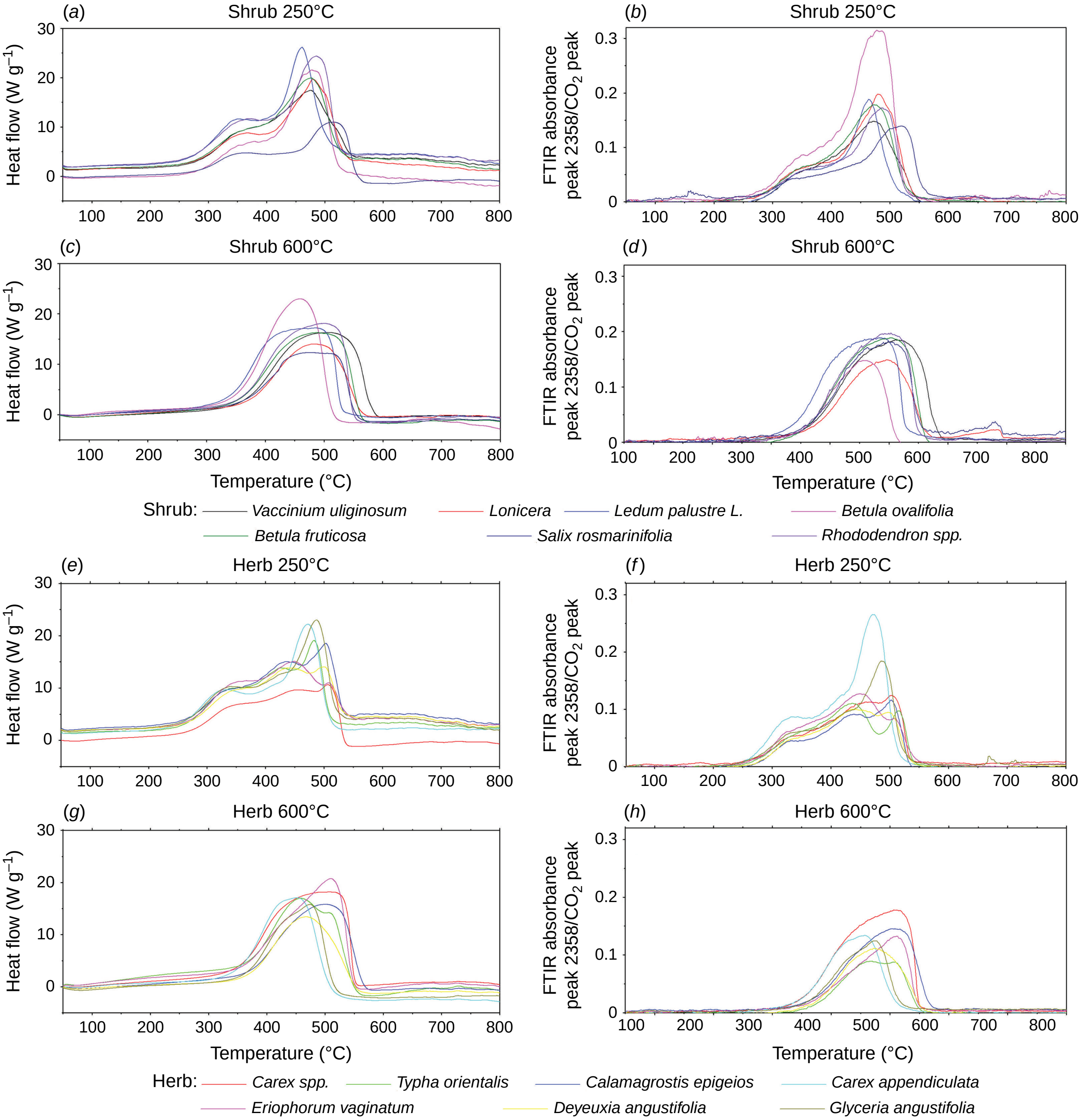

Fig. 3. Heat flow and CO_2 production identified by Fourier-transform infrared spectroscopy 2358 cm^{-1} peak of low-temperature shrub pyrogenic carbon (PyC) (*a*, *b*), high-temperature shrub PyC (*c*, *d*), low-temperature herb PyC (*e*, *f*), and high-temperature herb PyC (*g*, *h*).

the FTIR 1515/1050 ratio reflects the lignin or phenolic backbone (Cocozza *et al.* 2003; Artz *et al.* 2008). The FTIR 1625/1050 ratio is also widely used to reflect aromatic compounds and showed similar results between shrub PyC and herb PyC. Based on the FTIR spectra, more aromatic and carboxylic compounds were present in shrub PyC than in herb PyC. Because the stems were available in shrub plants, it is likely that more aromatic compounds were present in shrub plants than in herb plants explaining this observation.

Previous studies have found a low degree of aromatisation in PyC generated by vegetation fires, and most aromatic compounds were from the original plant materials (McBeath *et al.* 2013; Merino *et al.* 2015). Thus, the aromatic compounds in PyC were similar to the original plant materials, and the high contents of aromatic compounds in the stems of shrub plants resulted in more residual aromatic compounds in shrub PyC.

The thermal stability of PyC is related to its chemical composition. PyC has a high degree of aromatisation, with

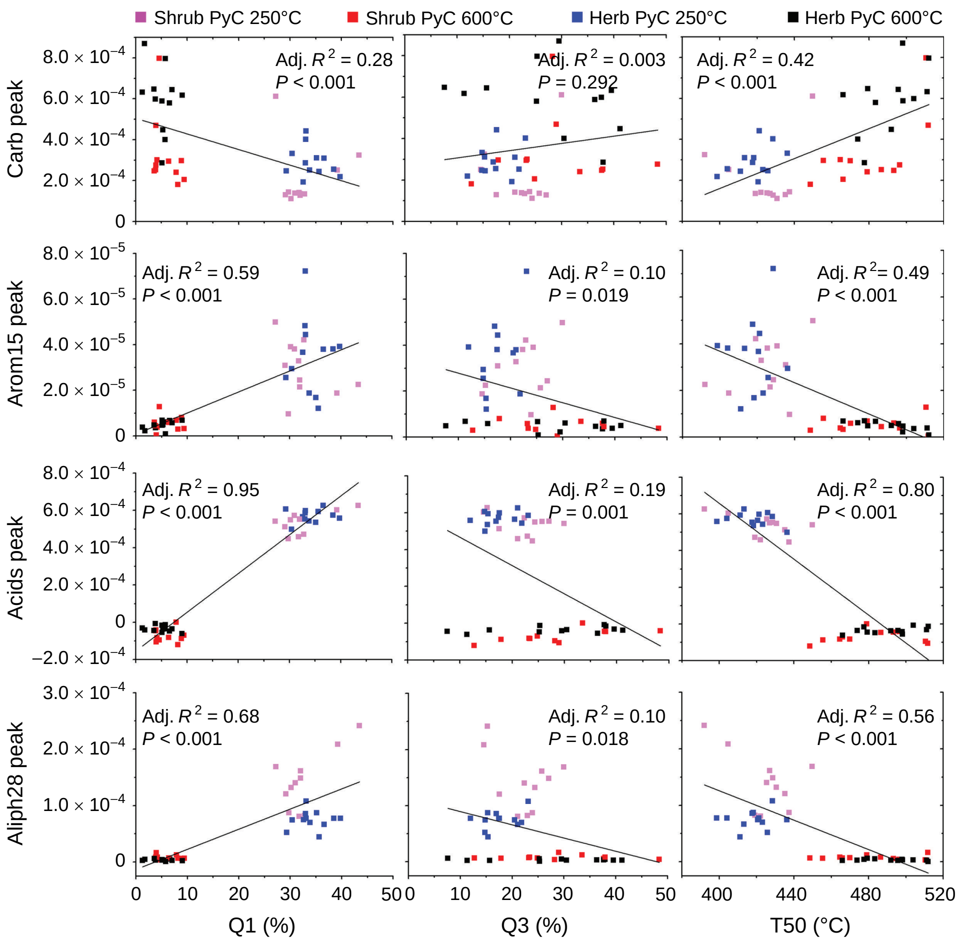

Fig. 4. Correlation relationship between pyrogenic carbon (PyC) chemical compositions indicators (peak height of carb, arom 15, acids, and aliph28) and PyC thermal stability indicators (Q1, Q3, and T50).

high T50 values indicating high thermal stability (Merino *et al.* 2015). In the present study, although the effects of plant type on aromatic compounds in PyC were significant, this resulted is no significant difference in the selected thermal stability indicators (Table 2). For example, Q1 in the low-temperature herb PyC was slightly higher than that in the low-temperature shrub PyC, whereas under high burning temperature Q1 in herb PyC was lower than that in shrub PyC. Conversely, differences in the T50 values were observed between herb and shrub PyC. There was a wide range of T50 and Q1 values for different plants in both the herb and shrub groups, and there was no clear boundary (Fig. 4). Plant type had no significant effects on the thermal stability of PyC, indicating that the effects of chemical composition on the thermal stability of PyC are complex and not easily explained by single chemical compounds. The thermal stability of OM is a good indicator of its biogeochemical stability (Leifeld and von Lützow 2014), and the thermal stability of PyC has also been suggested as a proxy for the biogeochemical stability of PyC (Harvey *et al.* 2012; Leng *et al.* 2019). Thus, the effects of plant type on the biogeochemical stability of PyC were also not significant. Although PyC chemical compositions are closely related to the stability of PyC, PyC chemical compositions was not a good indicator of stability in this study, and the stability is better directly evaluated by the thermal method.

Based on the chemical compositions and thermal stability of PyC from different plant types, we found that it is difficult to distinguish PyC sources based on a single indicator. Vegetation structure and initial plant composition have direct or indirect effects on the composition and properties of PyC. Because aromatic compounds in shrub plants are evidently higher than those in herb plants, FTIR 1425/1050, 1515/1050, and 1620/1050 ratios, which are related to aromatic compounds in PyC, could be used as potential indicators to track PyC sources.

Effect of burning temperature on PyC properties

The effect of temperature on PyC chemical composition was more significant than that of plant type (Table 2). The aliphatic and acid peaks were almost undetectable, and more aromatic compounds were found in PyC produced at high burning temperatures. Aliphatic and acid compounds are active parts of plant materials, and are easily consumed at high-temperature. Previous studies have suggested that as the heating temperature increases during a wildfire, cellulose and hemicellulose in plant biomass are preferentially lost at lower temperature, and with a component subject to chemical transformations involving the formation of aromatics (Keiluweit *et al.* 2010). Although the sources of most of the aromatic compounds in PyC were the original aromatic plant materials (McBeath *et al.* 2013; Merino *et al.* 2015), aliphatic and acid compounds may transform into aromatic compounds, thereby increasing the aromatic compound content in PyC. Compared to the effects of plant types on aromatic contents in PyC, the effects of temperature on arom15, which indicate the phenolic backbone (Cocozza *et al.* 2003; Hodgkins *et al.* 2014), were more prominent. The arom15 values in high-temperature PyC were higher than those in low-temperature PyC (Table 2). Previous studies have also reported that the aromatic compound content increased as the heating temperature increased from 200 to 500°C and the degree of aromatic condensation generally increased as the heating temperature increased from 400 to 1000°C (McBeath *et al.* 2011; Wiedemeier *et al.* 2015). Although the degree of aromatic condensation was not determined analysed in this study, the number and height of the FTIR spectrum peaks in the high-temperature PyC were more concentrated within 800–1800 cm^{-1}, and the number of peaks was lower than that in low-temperature PyC. This result also suggests that the chemical compositions in the high-temperature PyC were simpler than those in the low-temperature PyC, and the degree of aromatic condensation may also be higher.

Although there was no significant effect of plant type on the thermal stability of PyC (Table 2), the effects of burning temperature on the thermal stability of PyC were significant and were similar to those on PyC chemical compositions. An increase in the burning temperature resulted in a considerable decrease in the Q1 and T50 of PyC. However, the effects of burning temperature on the Q3 values of PyC were somewhat complex, with a high variability of Q3 values in high-temperature PyC. The Q3 values in part of the high-temperature PyC were even lower than those of some low-temperature PyC. These results suggest that the increase in thermal stability (T50 values) was mainly caused by the loss of labile OM, such as carbohydrates, proteins, and other labile aliphatic compounds (Merino *et al.* 2015; Santín *et al.* 2017). The rates of mass loss during the thermal treatment PyC also showed two clear peaks (approximately 320 and 470°C) in low-temperature PyC, and only one peak (at approximately 470°C) in high-temperature PyC (Fig. 2*b*, *d*). The heat flow also showed an increasing tendency around 320°C, which was caused by increased mass loss in this temperature range (Fig. 3). The peak in heat flow around 320°C was distinctly lower than that around 470°C, and the difference in the mass loss in these two temperature ranges was weaker than that of heat flow and CO_2 release.

The temperature dependence of CO_2 release was similar to that for heat flow, and no peak was observed around 320°C in the low-temperature PyC. This result indicates that the energy and carbon contents released by the burning of labile parts were lower than those released by the burning of the recalcitrant parts. Despite the mass loss in these two temperature ranges in low-temperature PyC, less carbon loss and lower energy release during burning of the labile components than in the burning of the recalcitrant components. The mass-loss rates and heat flow results also suggest that labile OM acts as one of the major components preferentially consumed by burning to produce in low-temperature PyC, and few of these labile components remain to then be consumed at high burning temperatures. Some of the labile OM may also transform into recalcitrant components during burning at higher temperatures (Keiluweit *et al.* 2010). The Q2 values of PyC, comprised of components such as lignin or other polyphenols, are widely used as a measure recalcitrant OM (Merino *et al.* 2015; Santín *et al.* 2017), but the effects of burning temperature on Q2 values were not significant. These results suggest that high temperatures result in labile OM loss or transformation into recalcitrant compounds, and also result in the loss of some recalcitrant compounds of OM. Similar conditions may also appear for recalcitrant OM (Q2) transforming into highly recalcitrant OM (Q3); thus, the increasing temperature causes the values of Q3 to significantly rise. However, some highly recalcitrant OM may also be lost in a high-temperature environment, which may explain why the variability of Q3 values in high-temperature PyC was higher than for the other thermal stability indicators.

Thus, the major difference in chemical compositions between low- and high-temperature PyC was that there were fewer aliphatic compounds and more aromatic compounds in high-temperature PyC compared to the low-temperature PyC. The effect of temperature on PyC chemical composition and thermal stability was more evident than the effect of plant type. High temperatures may cause the transformation of labile compounds of PyC into recalcitrant compounds and some recalcitrant compounds may also be lost by combustion; thus, the contents of recalcitrant compounds in the final PyC (e.g. aromatic contents) may not act as good indicators for evaluating the burning temperature. As the heating temperature increased, most of the labile part of PyC (e.g. acids, aliphatic) was lost, and the content of the highly recalcitrant part significantly increased. The loss of the labile part of PyC was a good indicator of the increase in burning temperature and PyC thermal stability, as indicated by the T50 values.

Implication for PyC in peatlands produced by the wildfire

Owing to the recalcitrance of PyC and the production of significant amounts of PyC due to high frequency of wildfire, PyC widely acts as an important stable carbon component of peatland soil carbon pools. Plant litter also acts as an important source of soil OM in the peatland soil carbon pool.

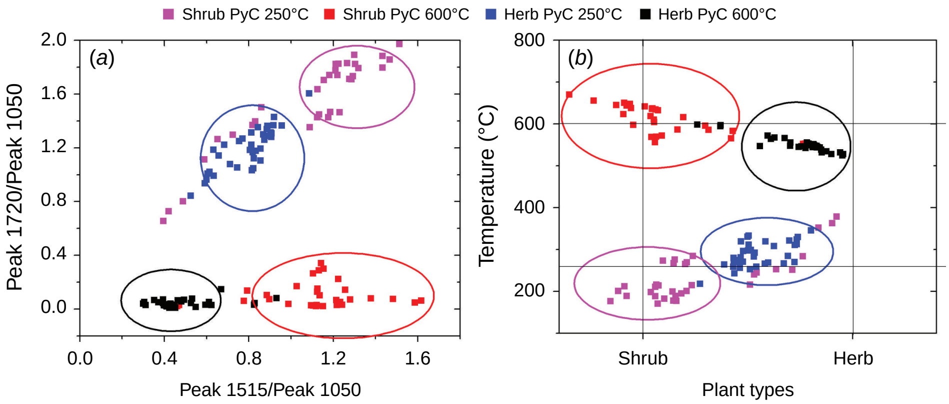

Fig. 5. (*a*) Fourier-transform infrared spectroscopy (FTIR) 1515/1050 ratio vs FTIR 1720/1050 ratio of pyrogenic carbon (PyC) produced from different plant types at 250 and 600°C, and (*b*) Results of transform function calculated by FTIR 15150/1050 ratio and FTIR 1720/1050 ratio. Transform function: plant types (1: shrub, 2: herb) = 2.383 − 1.108 × FTIR 1515/1050 ratio + 0.121 × FTIR 1720/1050. R^2 = 0.478; temperature (250, 600°C) = 499.557 + 128.119 × FTIR 1515/1050 ratio −262.415 × FTIR 1720/1050. R^2 = 0.866.

Wildfire decreases the accumulation of plant litter and increases the accumulation of pyrogenic recalcitrant organic compounds. Thus, the wildfire may have long-term effects on both OM properties and the carbon storage potential of the peatland soil carbon pool. Smouldering and flaming are two major types of wildfires in peatland ecosystems, which are mainly differentiated by different burning temperatures. Based on the above discussion, PyC produced from low-intensity burning at 250°C contains parts with a labile chemical compositions (e.g. aliphatic compounds), and the thermal stability is lower than PyC produced from high-intensity burning at 600°C. The chemical composition and thermal stability of PyC confirm previous reports suggesting that at least some PyC in the soil carbon pool may not be stable in the long term (Fang *et al.* 2014; Kuzyakov *et al.* 2014), and the burning temperature has been proven to be the major factor influencing the stability of PyC. Moreover, plant source also affect the chemical composition of PyC, whereas there were no significant effects on its thermal stability identified in this study.

In peatlands, both herb- and shrub-derived PyC produced at high temperatures act as stable carbon sources that will be sequestered in the peatland carbon pool for a long time. Because labile OM remains a component of PyC that is produced at low temperatures, this form of PyC may be more easily decomposed by microbial metabolism over shorter timeframes than PyC produced at high temperatures. Differences in the stability of PyC from different plant types may help explain the high variability of the long-term effects of PyC on OM properties and carbon storage in the peatland soil carbon pool. Thus, differences in PyC stability may explain the wide range of PyC contents in peatland soil carbon pools in northeast China and Europe reported in previous studies (Gao *et al.* 2016; Leifeld *et al.* 2018). PyC exhibits a range of different chemical compositions depending on the temperature at which it was produced, which may also explain the differences in microbial short-term responses in peatlands after burning (Medvedeff *et al.* 2015).

Although PyC in the peatland soil carbon pool acts as an important indicator of use in reconstructing past fire activity, owing to the limitations of PyC fluxes and δ^{13}C-PyC values, they do not reflect detailed fire information at least in temperate environments (e.g. fire intensity and fuel) (Gao *et al.* 2018*a*, 2018*b*). Recently, researchers have evaluated whether PyC properties can be used to determine historical fire intensity (Belcher *et al.* 2018). In the present study, we found that more phenolic backbones and fewer carboxylic acids are available in high-temperature PyC than those produced at low temperatures (Table 2). Moreover, more lignin compounds are available in the woody parts of shrubs than in herbs, increasing the availability of phenolics in shrub PyC. Thus, FTIR related ratios (e.g. 1050, 1515, and 1720 cm^{-1} peaks) of PyC might be used to estimate fuel types and fire intensity. In Fig. 5, FTIR 1515/1050 and 1720/1050 ratios were selected as two indicators to evaluate whether PyC chemical compositions can be used to reconstruct fire intensity and plant types, and the transform functions were calculated using a multivariate linear model. The original data for these two indicators are shown in Fig. 5*a*, and the final data after the calculation of transform function are shown in Fig. 5*b*. After calculation, the final results of plant types and burning temperatures were close to their real conditions, particularly for the temperature reconstructed results, which means that these two selected indicators of PyC chemical compositions could indicate fire intensity. For plant-type reconstruction results, some data mixtures for herb plants and PyC produced from shrubs were similar to those produced from herbs. These results were positive and showed that higher accuracy can be obtained with the use of more indicators (e.g. PyC chemical compositions and thermal stability) to reconstruct historical fire intensity and plant types. Thus, with detailed information on PyC properties identified in the future, PyC in the peatland soil carbon pool has considerable potential to reflect the fire (e.g. fire intensity) and regional plant history in a more comprehensive manner.

Conclusion

In the present study, the PyC properties of typical peatland plants under different burning temperatures were analysed, and the results indicated that temperature was the major factor influencing PyC properties. The effects of temperature and plant type on carbon content and the δ^{13}C-PyC values were not significant, but both caused substantial effects on PyC chemical composition and thermal stability. The FTIR 1425/1050, 1515/1050, and 1620/1050 ratios, which are related to aromatic compounds in PyC, were significantly higher in shrub PyC than in herb plants, because of the higher amount of aromatic compounds in shrub plants. However, the effects of plant type on the thermal stability of PyC were not significant. The burning temperature had a significant effect on both the chemical composition and thermal stability of PyC. In PyC produced at high temperatures, few labile parts (e.g. aliphatic acids) were available, whereas they could be easily found in low-temperature PyC. Because the properties of PyC from different burning processes varied significantly, they might have contrasting effects on the peatland soil carbon pool. The PyC properties in peatland archives were found to have considerable potential to reflect detailed fire history and regional ecology information, such as fire intensity and plant types.

Supplementary material

Supplementary material is available online.

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Data availability. The data that support this study will be shared upon reasonable request to the corresponding author.

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Author affiliation

[A]Key Laboratory of Wetland Ecology and Environment, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Shengbei Street 4888, Changchun 130102, China.