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Carbon concentration and isotope composition of black carbon in the topsoil of the central and southeastern Qinghai-Tibetan Plateau, and their environmental significance

Lian Liu[a,*], Quan Li[b,**], Min Huang[a], Yan Yang[a]

[a] Chinese Academy of Geological Sciences, Beijing 100037, PR China
[b] Key Laboratory of Land Surface Pattern and Simulation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, PR China

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ABSTRACT

The carbon concentration and carbon isotope of black carbon (BC) have been widely used to reconstruct fire history and vegetation change. In order to establish the relationship between BC, contemporary vegetation and climate at the high altitudes of the Qinghai-Tibetan Plateau (QTP), we investigated the carbon concentration and carbon isotope composition of BC and soil organic carbon (SOC) (%BC, %SOC, $\delta^{13}C_{BC}$ and $\delta^{13}C_{SOC}$) in 29 topsoil samples from the central and southeastern QTP. In general, the %SOC and %BC of topsoil show generally similar variations, indicating a common controlling factor for SOC and BC production, i.e., vegetation. The relatively small BC/SOC ratios fall in the range of BC/OC for pyrogenic particles from biomass burning, indicating a minor contribution of BC from fossil fuel combustion. The $\delta^{13}C_{SOC}$ of topsoil can effectively indicate local vegetation in the QTP. The $\delta^{13}C_{BC}$ and $\delta^{13}C_{SOC}$ are positively correlated, whereas the $\delta^{13}C_{BC}$ values are more negative than those of $\delta^{13}C_{SOC}$. This could due to fire season and fractionation processes during post-deposition, but not carbon isotope fractionation during combustion or exogenous BC input. Therefore, BC in topsoil of the QTP mainly records 'local' environmental information, and the $\delta^{13}C_{BC}$ can be used in paleovegetation reconstruction in combination with the local climate.

1. Introduction

As an important component of the Earth system, fire is tightly coupled to climate, vegetation and human activities (Bowman et al., 2009). Black carbon (BC) is a continuum produced by the incomplete combustion of vegetation and fossil fuels. More than 80% of the BC stays on Earth's surface after fire events, whereas the rest is emitted into the atmosphere with smoke (Kuhlbusch and Crutzen, 1995). Because of its strong resistance to microbial degradation and its ability to sequester carbon, BC is considered to be an important sink for biospheric carbon at the scales of short-term biospheric processes in the long-term geological carbon cycle (Lehmann et al., 2008).

Previous research has revealed that carbon concentration of BC (%BC) can be used to recover the fire history in terms of the frequency and intensity of fire events (Chylek et al., 1995; Bird and Cali, 1998; Clark et al., 2001; Wang et al., 2005; Eva et al., 2015; Tan et al., 2015). In addition, the carbon isotope composition of BC ($\delta^{13}C_{BC}$) has been used to document vegetation change because it is controlled mainly by source plants in many areas around the world (Turney et al., 2001; Hall et al., 2008; Wang et al., 2012; Zhou et al., 2014; Liu et al., 2013, 2016a, 2016b). In reconstructing past vegetation, the $\delta^{13}C_{BC}$ has some advantages over the carbon isotope composition of SOC ($\delta^{13}C_{SOC}$), as follows: BC is chemically inert and resistant to alteration by acid treatment (Bird and Cali, 1998), while the $\delta^{13}C_{SOC}$ can potentially be biased by pre-analysis acid preparation (Brodie et al., 2011); BC is biochemically inert enough to resist biodegradation (Masiello, 2004),

Abbreviations: BC, black carbon; OC, organic carbon; SOC, soil organic carbon; QTP, Qinghai-Tibetan Plateau; %BC, carbon concentration of black carbon; %SOC, carbon concentration of soil organic carbon; $\delta^{13}C_{BC}$, carbon isotope composition of black carbon; $\delta^{13}C_{SOC}$, carbon isotope composition of soil organic carbon; $\Delta\delta^{13}C$, variable between 'before burning' and 'after burning'; $\Delta^{13}C_{SOC\text{-}BC}$, difference between the $\delta^{13}C_{SOC}$ and $\delta^{13}C_{BC}$ values for the same sample; a.s.l., above sea level; UTC, Universal Time Coordinated; MAT, mean annual temperature; MAP, mean annual precipitation; YZR, Yarlung Zangbo River; CAM, Crassulacean acid metabolism; RESDC, Resources and Environmental Sciences, Chinese Academy of Sciences

* Correspondence to: L. Liu, Chinese Academy of Geological Sciences, 26 Baiwanzhuang Road, Beijing 100037, PR China.
** Correspondence to: Quan Li, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, PR China.
E-mail addresses: liulian198394@163.com (L. Liu), liquan@igsnrr.ac.cn (Q. Li).

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whereas pedogenic degradation may exert an additional effect on $\delta^{13}C_{SOC}$ (Zech et al., 2007; Wang et al., 2008). However, the $\delta^{13}C_{BC}$ has received limited study and its vegetation indication remains ambiguous although it is supposed to reflect the carbon isotope of burnt plants. Therefore, it is necessary to carry out systematic and detailed modern process studies of BC, in order to establish a sound basis for using $\delta^{13}C_{BC}$ in the study of paleovegetation and paleoenvironment.

At high altitudes, the carbon isotope composition of plant and organic carbon in topsoil is controlled by a number of factors, such as species composition, environmental temperature, and moisture availability (Körner et al., 1988, 1991; Lü et al., 2004; Li et al., 1999). To date there is still a lack of investigation into topsoil BC at the high-altitude regions of the Qinghai-Tibetan Plateau (QTP), where alpine vegetation changes dramatically with the altitude gradient and responds sensitively to climate changes (Lü et al., 2004; Wei and Jia, 2009). The question remains as to whether or not the characteristics of BC in the QTP are closely related to local vegetation and climate.

The QTP, known as the 'roof of the world', is the largest elevated landscape in the world with an average altitude of over 4000 m above sea level (m a.s.l.). The climate and vegetation are clearly zonal. The QTP covers several climatic zones, from alpine temperate extreme dry zone in the north to alpine sub-temperate, alpine sub-cold in the middle, and alpine temperate zones in the south. The vegetation ranges from forest, shrub, alpine meadow, steppe, desert steppe and alpine desert from the southeast to the northwest (Investigation Team of Chinese Academy of Science, 1988; Institute of Geography, 1990, 1999; Li et al., 2016b). Because the QTP has these unique environmental and vegetation characteristics, it provides a crucial place to research BC in the topsoil at high altitudes. However, the BC characteristics of the topsoil in the QTP are still poorly known. Recently, the BC concentration in ice cores from five widely-spaced glaciers in the QTP were measured (Ming et al., 2008; Xu et al., 2009; Wang et al., 2015), and the results indicated that black soot aerosols deposited on the QTP were different between the northern and southern plateaus, which reflected regional differences in source strength and transport pathways for atmospheric black soot between Europe and Asia. These limited studies aroused our interest in the study of BC in the QTP. What are the specific characteristic and environmental indications of the BC? What is the impact degree of exogenous BC in the QTP?

In this study, we conducted an investigation into the characteristics of BC in samples of topsoil from central and southeastern QTP. We analyzed the carbon concentration and carbon isotope composition of BC (%BC, $\delta^{13}C_{BC}$) and the soil organic carbon (%SOC, $\delta^{13}C_{SOC}$) of topsoil samples in those districts. Our aim was to investigate how the BC varies with vegetation types and climate, and whether the BC in the QTP topsoil records only 'local' environmental information or is likely to be strongly influenced by exogenous BC.

2. Study region

Topsoil samples used in this study were collected from two transects across the central and the southeastern QTP (Fig. 1). The central QTP covers the vast interior plateau at an average elevation of 4500–5200 m to the south of the Kunlun Mountain and north of the Himalayan Mountains (Tibetan Investigation Group, 1966). The mean annual temperature (MAT) decreases from 8 to 10 °C in the south to −6–0 °C in the north. The mean annual precipitation (MAP) decreases from > 600 mm in the east, to 100–200 mm in the west (Lü et al., 2011; Li et al., 2016b). Vegetation in the central QTP shows a distinct southeast-northwest gradient, from alpine meadow zone and temperate subalpine steppe zone, to alpine steppe zone (Hou, 2001; Editorial Committee of Vegetation Map of China, Chinese Academy of Sciences, 2007). Our sampling sites at a mean elevation of 5003 m a.s.l. in the northern region of the central QTP are covered by alpine steppe with dominant Poaceae (e.g., *Stipapurpurea*) and *Artemisia* spp. The MAT is −1.2 °C at the sites, with a July average of 8.6 °C and a January average of −12.1 °C. The MAP is 301 mm, and about 90% of the rainfall occurs in June to September (Chinese Meteorological Data Sharing Service System, http://cdc.cma.gov.cn).

Topsoil samples in the southeastern QTP were collected from the valleys of Shannan and Mainling in the drainage system of the Yarlung Zangbo River (YZR). The YZR has a drainage area of 2.4×10^5 km^2 within the southern QTP. The average elevation of topsoil samples there is 3338 m a.s.l. The moisture vapor in the region comes mainly from the warm/moist Southwest Monsoon originating from the Indian Ocean. Thus, the precipitation gradually decreases from east to west due to the weakening of the Southwest Monsoon. The Shannan valley in the midstream area of the YZR is covered by temperate subalpine steppe and shrub, whereas the Mainling Valley in the downstream area supports subalpine coniferous forest and evergreen broad-leaved forest under relatively warm/humid climatic conditions (MAT of 8.79 °C, and MAP of 676.70 mm) (Hou, 2001). The MAT is 5.2 °C at the sites, and the average temperature is higher than 0 °C in March to October and below 0 °C in other months. The MAP is 413 mm, and about 87% of the rainfall occurs in June to September (Chinese Meteorological Data Sharing Service System, http://cdc.cma.gov.cn).

3. Samples and methods

3.1. Sampling

A total of 29 topsoil samples were collected from the central (CQT-1 to CQT-11) and southeastern (SEQT-1 to SEQT-18) QTP at altitudes of 2944–5326 m in the summer of 2012 (Table 1, Fig. 1). The sampling locations are located far from the impact of human activity. All samples were collected from the top 5–10 cm of the topsoil. All air-dried samples were screened to remove plant residues such as rootlets and leaves, and then ground to a fine powder for measurement (see Section 3.2) of the concentrations of BC and SOC, as well as the values of $\delta^{13}C_{BC}$ and $\delta^{13}C_{SOC}$.

3.2. Carbon concentration and isotope analysis

To extract SOC for measurement, the soil samples were treated with HCl (1 M) for 48 h to remove carbonates. Then the residues were washed to near-neutral pH and freeze-dried. The remaining carbon in the residues after this process was the SOC (Liu et al., 2013).

The BC in the topsoil samples was extracted by the chemical oxidation method, following Lim and Cachier (1996). In order to remove carbonates, silicates, Ca^{2+} and Mg^{2+}, topsoil samples were treated with HCl (3 M), HF (10 M)/HCl (1 M), and HCl (10 M) for 24 h, respectively. Then the residues were treated with an oxidizing solution (0.1 M $K_2Cr_2O_7$/2 M H_2SO_4) at 55 °C for 60 h to remove soluble organic matter and kerogen. The remaining refractory carbon in the residues was the BC.

Analyses of carbon concentration and isotope composition were performed at the Key Laboratory of Cenozoic Geology and Environment in the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. The carbon concentration and isotope composition were measured using a thermo-elemental analyzer (Flash EA 1112) integrated with a ConFlo III system with a Thermo MAT253 isotope ratio mass spectrometer. An external standard sample UREA ($\delta^{13}C_{VPDB} = -49.1‰$) and USGS24 ($\delta^{13}C_{VPDB} = -16.049‰$) were introduced as the reference standards for $\delta^{13}C$ analyses. All carbon isotope results are exhibited as a permil deviation relative to the VPDB standard with a precision of ± 0.2‰.

4. Results

4.1. Carbon concentration of SOC and BC in topsoil samples

In the central QTP, the %SOC values of the topsoil samples ranged