

Spatial patterns, storages and sources of black carbon in soils from the catchment of Qinghai Lake, China

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Summary

Black carbon (BC), composed of char and soot, is an important component of soil organic carbon (SOC), and these materials are potentially important for the global carbon cycle and global climate. A thermal-optical reflectance method was used to determine the spatial patterns of SOC, BC, char and soot in nine soil types collected from 152 sites in the Qinghai Lake catchment. All of the analytes showed large spatial variability: SOC, BC and char were most abundant in bog soils and least abundant in aeolian soils, while soot concentrations in alpine frost desert and in aeolian soils were about half of those in the other soils. The average BC concentration in the 0–20-cm soil layers was 1.3 g kg⁻¹, and BC amounted to 5.6% of the SOC. Char, SOC and BC all decreased with soil depth, but soot showed little variation. The proportions of BC to SOC and char to BC showed contrasting trends in four soil profiles; the former increased and the latter decreased with depth. The quantity of SOC sequestered in topsoils of the catchment area was estimated to be 191 Tg; BC accounted for approximately 4.8% of this, and char made up approximately 85% of the total BC stock. The burning of animal dung for domestic cooking apparently was an important source of soil BC: combustion of other biofuels and fossil fuels was the other main source.

Introduction

Carbon cycling in the terrestrial ecosystem plays a key role in the global carbon budget, and interest in the terrestrial carbon cycle has increased in a variety of disciplines, including ecology, climatology, soil science, physiology and geology. This is largely because of the sharp rise in atmospheric CO₂ concentrations caused by human activities and concerns over future changes in climate. Nevertheless, there are still many large uncertainties in the quantification of the terrestrial carbon cycle. This is because the quantities of soil organic carbon (SOC) stored in terrestrial environments and the rates at which carbon is deposited and lost are affected by diverse and interconnected factors, such as pollution emissions (Kopacz *et al.*, 2011), soil properties (Zhan *et al.*, 2013a), land use (Wu *et al.*, 2003), climate and vegetation (Jobbágy & Jackson, 2000). Moreover, the diversity and complexity of terrestrial ecosystems also contribute to the variability of SOC in soils.

Black carbon (BC), composed of char and soot, is an important component of organic carbon in soils and sediments, and is produced from the incomplete combustion of fossil fuels and biomass (Goldberg, 1985). Generally, char has a low formation temperature and retains the morphology of its source material, while soot is produced by condensation of gas phase intermediates at temperatures of > 600°C (Lim & Cachier, 1996). Char and soot have different physical and chemical properties and different environmental and climatic impacts; therefore it is essential to be able to differentiate them. The most commonly used methods, such as chemo-thermal oxidation (CTO-375), benzene polycarboxylic acid (BPCA) marker and acid dichromate oxidation (Cr₂O₇), detect different fractions of the BC continuum, which can lead to differences spanning about two orders of magnitude for a given sample (Hammes *et al.*, 2007). However, they cannot differentiate between char and soot: it has been suggested that CTO-375 can measure a specific BC fraction such as soot carbon but fails to identify the char fraction (Hammes *et al.*, 2007). At present there is no widely accepted method to quantify BC.

The thermal optical reflectance (TOR) method is widely used for BC analysis in atmospheric aerosols (Cao *et al.*, 2005; Chow *et al.*, 2007). It is based on stepwise oxidation of different carbon

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fractions at different temperatures and under different atmospheres, and has been shown to differentiate between char and soot (Han *et al.*, 2007). This differentiation has been used to identify different sources in aerosol studies (Han *et al.*, 2010; Lim *et al.*, 2012), yielding some interesting results. For example, Han *et al.* (2010) reported seasonal variations in char and soot concentrations in Xi'an city and proposed that char:soot ratios may be effective in source identification of carbonaceous aerosols. Lim *et al.* (2012) reported that char:soot ratios could serve as an indication of continental effects and confirmed that char was emitted from smouldering combustion and soot produced from motor vehicle emissions and coal combustion.

The TOR method also has recently been applied to BC quantification in both soils and sediments (Han *et al.*, 2009, 2011, 2012; Zhan *et al.*, 2013a). Application of this method in lake sediments showed that variation of BC and soot concentrations is consistent with the industrialization of eastern China (Han *et al.*, 2011) in the past 150 years, and is indicative of the history of regional biomass burning in China (Han *et al.*, 2012). Scientific comparison of the TOR results with CTO-375 results in soils and sediments showed good correlations with BC (Han *et al.*, 2007; Zhan *et al.*, 2013b), further confirming that CTO-375 specifically measures soot carbon (Hammes *et al.*, 2007). Stepwise addition of standard reference materials (SRMs) to soils and sediment also confirmed the applicability and accuracy of the TOR method (Zhan *et al.*, 2013b).

The BC component is stable and has a large chemical adsorption capacity; hence, it plays important roles in global biogeochemical cycles and affects environmental systems in complex ways. It sequesters carbon into a chemically and microbiologically refractory pool that would otherwise be converted into CO₂, and therefore is an important reservoir for atmospheric CO₂ (Forbes *et al.*, 2006). Studies have shown that BC concentrations in German chernozems may reach up to 45% of the SOC (Schmidt *et al.*, 1999), and the percentages are as large as 82% in soils from the Australian National Soil Archive (Lehmann *et al.*, 2008). These results demonstrate the potential importance of BC as a terrestrial soil C sink. However, the spatial patterns and stocks of BC in soils over regional scales are poorly known, and this limits our understanding of how and why carbon moves through ecosystems.

The Qinghai-Tibet (Q-T) Plateau, the highest and largest plateau in the world, is covered by an extensive area of permafrost, and seasonally frozen soils also are widely distributed. Permafrost is particularly sensitive to climate change and therefore conditions on the Q-T Plateau are important within the framework of global climate. Studies have shown that permafrost soils not only sequester large amounts of SOC (Zimov *et al.*, 2006), but also store large quantities of BC (Guggenberger *et al.*, 2008).

Qinghai Lake is a prominent feature of the Q-T Plateau and the catchment area of the lake is about 3×10^4 km² (Li *et al.*, 2007). Most of the soils in the catchment are subject to seasonal freezing and thawing, but little basic research has been conducted to investigate the spatial patterns or stocks of soil BC in this high-altitude ecosystem. For the study presented here, we used a thermal-optical reflectance (TOR) method to investigate the

distribution and sequestration of BC and related substances in soils from the catchment area of the Qinghai Lake. Furthermore, we identified the likely sources of selected carbonaceous species, estimated the pools of SOC, BC, char and soot, and discuss some implications of the decomposition of soil BC on the plateau.

Materials and methods

Study area

Qinghai Lake is the largest saline lake in China. The lake is located on the north-eastern side of the Tibetan Plateau at an altitude of 3194 m a.s.l. The catchment area forms a closed intermontane basin, covering an area of about 4260 km² (Li *et al.*, 2007) extending between longitudes 99°36'–100°47' and latitudes 36°32'–37°15'. The types of soils in the catchment are shown in Figure 1, and the dominant types of vegetation are montane shrub and alpine meadow.

Qinghai Lake is subjected to the effects of the East-Asian summer monsoon and Indian monsoon at various times of the year, as well as the prevailing westerlies, and therefore the lake is extremely sensitive to climatic change. The mean annual temperature is about –0.7°C, and the mean annual precipitation is about 250 mm, with more than 70–80% of the precipitation falling during the summer and early autumn (Li *et al.*, 2007). The mean annual evaporation capacity of the lake is 800–1000 mm. The lake is typically covered with ice from late November to early April each year.

Soil sample collection and preparation

In July 2008, a total of 152 surface soil samples (0–20 cm) were collected from the Qinghai Lake catchment at the locations shown in Figure 1. These samples can be grouped into nine different soil types: (i) alpine meadow soils, (ii) castanozems, (iii) bog soils, (iv) aeolian soils, (v) alpine steppe soils, (vi) mountain meadow soils, (vii) chernozems, (viii) mountain solonchaks and (ix) alpine frost desert soils. Moreover, four soil cores were also sampled with a soil auger at two different locations (Figure 1). These cores were taken from the surface to a depth of 100 cm at 10-cm depth intervals. The terminology for the soil types in this study is matched to the IUSS Working Group (2006) as far as possible in Table 1.

For the first step of sample preparation, coarse fragments, such as roots and other plant and animal materials, were removed from the soil samples with forceps. Then the samples were air-dried and sieved to 2 mm. The bulk density of each sample was determined by weighing a known volume of an air-dried aliquot of the sample after drying at 105°C for 8 hours. The subsamples were ground, sieved (< 2 mm) and stored in plastic bags until analysis.

Chemical analysis

Before analysis, the air-dried soil samples were pretreated with HCl to remove inorganic carbon according to the method of Zhan *et al.* (2013a). The residue was washed in deionized water three times, with centrifugation (3680 g for 12 minutes) and decantation

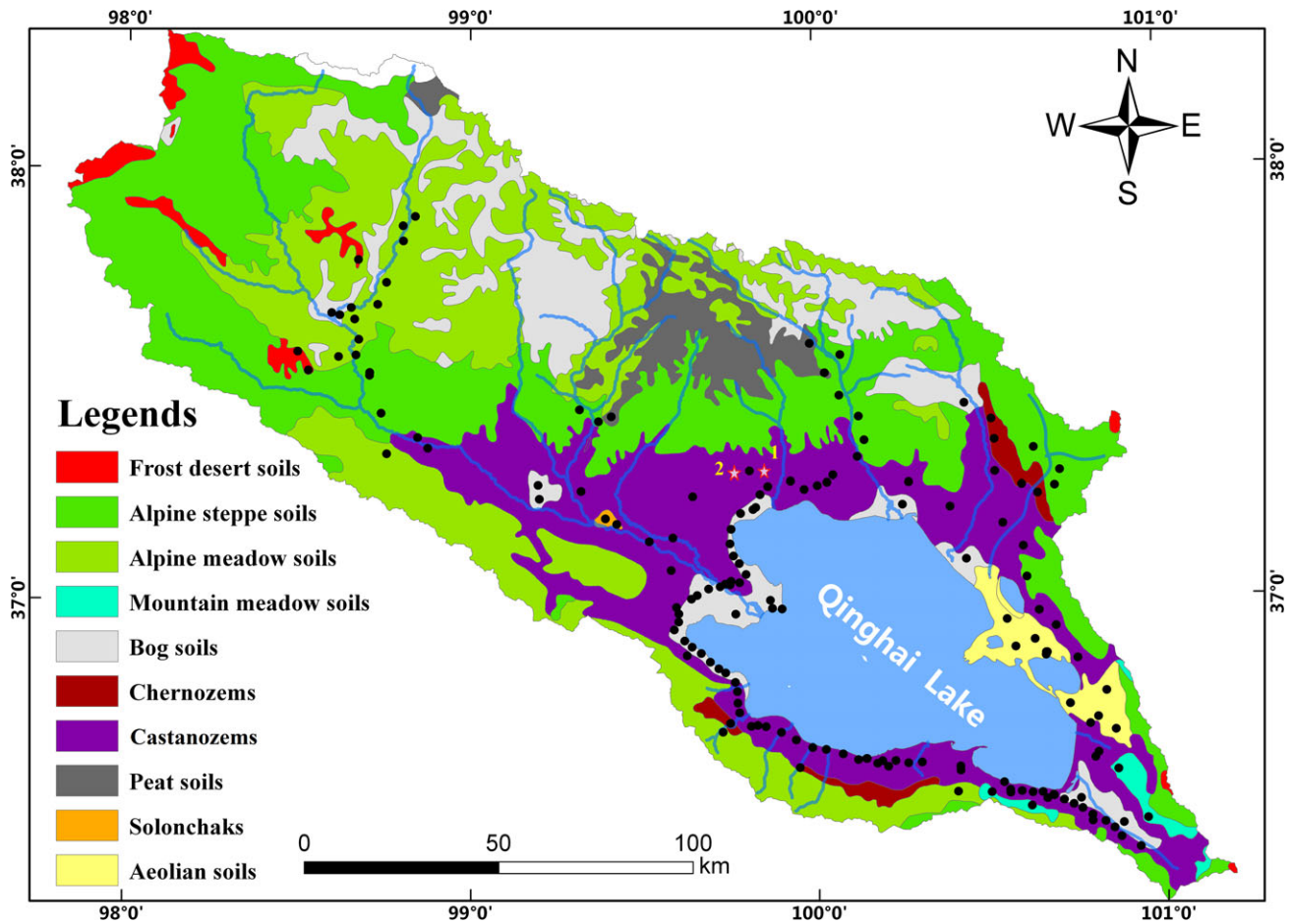


Figure 1 Schematic map of the Qinghai Lake catchment showing the locations of the sampling sites. The black circles mark the topsoil sampling stations and the stars numbered 1 and 2 represent two sites where the soil profiles, two at each site, were collected.

of the supernatant after each washing step. The pellets were removed and then dried at 60°C to constant mass. Soil organic C content was determined by CuO-catalysed dry combustion using a CHN elemental analyser (Elementar Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany).

The BC was measured using the thermal-optical reflectance (TOR) method developed by Han *et al.* (2007). Briefly, inorganic carbonates, minerals and metal oxides were removed from the soils by digestion with hydrochloric acid and hydrofluoric acid (HF). The residues were filtered through pre-fired (850°C, 3 hours) 47-mm quartz filters (Whatman International Ltd, Maidstone, England). The BC analyses were conducted with the use of a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE_A protocol (Chow *et al.*, 2007; Han *et al.*, 2009; Zhan *et al.*, 2013b). During the heating steps, four OC fractions (OC1, OC2, OC3 and OC4 at 140, 280, 480 and 580°C in a pure He atmosphere) and three elemental carbon (EC) fractions (EC1, EC2 and EC3 at 580, 740 and 840°C in 2% O₂/98% He) were produced. One pyrolyzed organic carbon fraction (POC) was produced in the heating process, and this was monitored by measuring the return to the initial values of the laser reflectance. Here, BC

is defined as EC1 + EC2 + EC3 – POC. Char and soot are defined as EC1 – POC and EC2 + EC3, respectively (Han *et al.*, 2007).

Storage estimation

The BC density for each soil profile was calculated using the following equation:

$$BCD = \sum_{i=1}^n \rho_i \times C_i \times H_i \times (1 - \delta_i) / 100, \tag{1}$$

where *BCD*, ρ_i , C_i , H_i and δ_i are BC density (kg m⁻²), bulk density (g cm⁻³), soil organic carbon content (g kg⁻¹), thickness (cm) and volume percentage of the fraction > 2 mm in layer *i*, respectively.

The BC storage (BCS, Tg) can then be estimated by:

$$BCS = \sum_{j=1}^n area_j \times BCD_j, \tag{2}$$

where *area_j* and *BCD_j* are the surface area (km²) and BC density (kg m⁻²) of the different soil groups, *j*, respectively.

Table 1 Soil organic carbon (SOC), black carbon (BC), char and soot concentrations, BC:SOC and char:BC ratios in catchment soils from the Qinghai-Tibet Plateau

Soil type	FAO/UNESCO classification	N ^a	Statistic	Mass concentration / g kg ⁻¹				BC:SOC / %	Char:BC / %
				SOC	BC	Char	Soot		
Bog	Gleysols	35	Range ^b	25.71–148.70	0.61–8.72	0.32–8.32	0.07–0.41	1.06–9.25	51.61–98.70
			Mean ± SD	48.16 ± 25.71	2.66 ± 1.53	2.44 ± 1.52	0.23 ± 0.09	5.56 ± 1.40	88.71 ± 8.22
Alpine meadow	Cambisols	14	Range	21.95–56.74	0.47–2.80	0.23–2.63	0.15–0.37	0.82–7.01	48.49–94.24
			Mean ± SD	36.51 ± 10.21	1.70 ± 0.69	1.47 ± 0.72	0.23 ± 0.06	4.82 ± 1.63	85.28 ± 12.41
Mountain meadow	Umbric leptisols/ dystric cambisols	4	Range	20.36–32.12	1.06–2.87	0.81–2.63	0.22–0.28	5.15–8.94	76.37–91.63
			Mean ± SD	24.84 ± 5.26	1.59 ± 1.06	1.34 ± 0.87	0.25 ± 0.02	6.11 ± 1.89	81.71 ± 6.81
Chernozems	Chernozems	5	Range	28.01–38.63	1.15–2.11	0.87–1.94	0.17–0.50	3.56–6.05	73.84–91.82
			Mean ± SD	31.98 ± 4.11	1.61 ± 0.39	1.34 ± 0.39	0.27 ± 0.14	5.03 ± 0.92	82.85 ± 7.80
Castanozems	Kastanozems	68	Range	3.57–42.87	0.21–2.05	0.05–1.85	0.09–0.41	1.06–47.50	23.66–90.82
			Mean ± SD	17.76 ± 8.72	0.87 ± 0.46	0.66 ± 0.44	0.21 ± 0.06	5.96 ± 6.06	70.32 ± 14.40
Alpine steppe	Cambisols	11	Range	11.80–23.85	0.42–0.95	0.19–0.76	0.11–0.23	3.18–5.32	45.87–81.79
			Mean ± SD	16.32 ± 3.77	0.73 ± 0.14	0.54 ± 0.14	0.20 ± 0.03	4.57 ± 0.76	72.00 ± 9.59
Solonchaks	Solonchaks	2	Range	10.81–12.51	0.58–0.66	0.42–0.43	0.16–0.24	5.30–5.35	64.43–72.05
			Mean ± SD	11.66 ± 1.21	0.62 ± 0.06	0.42 ± 0.01	0.20 ± 0.05	5.32 ± 0.03	68.24 ± 5.39
Frost desert	Gelic arenosols	3	Range	3.60–9.32	0.22–0.50	0.13–0.38	0.09–0.15	5.40–6.03	58.17–75.42
			Mean ± SD	7.05 ± 2.59	0.39 ± 0.13	0.26 ± 0.11	0.13 ± 0.03	5.61 ± 0.29	65.23 ± 8.21
Aeolian	Arenosols	10	Range	0.62–9.44	0.07–0.45	0.01–0.33	0.05–0.15	3.17–11.04	19.79–71.91
			Mean ± SD	4.31 ± 2.85	0.22 ± 0.11	0.13 ± 0.09	0.09 ± 0.03	6.20 ± 2.18	52.57 ± 16.67

^aN is the number of samples.

^bRange, mean and standard deviation (SD) in g kg⁻¹ dry weight.

Statistical analysis

Statistical analyses were performed using the SPSS 16.0 software package for Windows (SPSS Inc., Chicago, IL, USA). Soil data were analysed by one-way analysis of variance (ANOVA) and the means were considered significantly different for *P*-values less than 0.05.

Results

Concentrations and spatial characteristics of SOC, BC, char and soot

The summary statistics for SOC, BC, char and soot contents in soils from the catchment of Qinghai Lake are presented in Table 1. The SOC concentration in the soils ranged from 0.62 to 149 g kg⁻¹, with a weighted mean value of 26 ± 11.6 g kg⁻¹. On average, the largest SOC concentrations (48 g kg⁻¹) in the surface layer (0–20 cm) were found in the bog soils while the smallest (4.3 g kg⁻¹) were in the aeolian soils. The average SOC concentrations in the other types of soils ranked as follows: alpine meadow soils > chernozems > mountain meadow soils > castanozems > alpine steppe soils > solonchaks > frost desert soils (*P* < 0.001, Tables 1 and 2).

The BC, char and soot contents in the soils from all sites in the catchment area ranged from 0.07 to 8.7, 0.01 to 8.3, and 0.05 to 0.5 g kg⁻¹, respectively. The average BC content for all soils in the 0–20-cm layer was 1.3 ± 1.2 g kg⁻¹; the largest BC was

in the bog soils (2.7 ± 1.5 g kg⁻¹), followed by alpine meadow soils (1.7 ± 0.7 g kg⁻¹), while the smallest was in the aeolian soils (0.22 ± 0.11 g kg⁻¹, *P* < 0.001, Tables 1 and 2). Similarly, the largest char concentrations were found in the bog soils and the smallest in aeolian soils (*P* < 0.001, Tables 1 and 2). The spatial distribution of char was similar to those of SOC and BC. In contrast, the mean soot concentrations in bog soils, alpine meadow soils, mountain meadow soils, chernozems, castanozems, alpine steppe soils and solonchaks showed little difference, but the concentrations in these soils were about twice those in the alpine frost desert and aeolian soils (*P* < 0.001, Tables 1 and 2). The concentration ratios of BC to SOC varied widely, from 0.8 to 48% (mean 5.6%). The percentage of char in BC varied from 20 to 99%, with a mean value of 75%, indicating that char is a significant component of BC in most of the soils.

Spatial distributions of SOC and BC concentrations and estimation of stocks

The frequency distributions of the SOC, BC, char and soot concentrations are shown in Figure 2. More than 90% of the soils had SOC concentrations that ranged from 0 to 60 g kg⁻¹ (Figure 2a). The BC and char concentrations had similar distributions, and > 90% of the BC and char concentrations were < 3 g kg⁻¹ (Figure 2b,c). Statistically, the soot concentrations approximated a normal distribution and approximately 80% of the observations were in the range of 0.1–0.3 g kg⁻¹ in the upper 20 cm of the catchment soils (Figure 2d).

Table 2 Summary results for soil organic carbon (SOC), black carbon (BC), char and soot concentrations, BC:SOC and char:BC ratios from ANOVA

		Sum of squares	Degrees of freedom	Mean square	F	P-value
SOC	Between groups	30 542.365	8	3817.796	20.73	< 0.001
	Within groups	26 336.101	143	184.169		
	Total	56 878.466	151			
BC	Between groups	98.475	8	12.309	17.23	< 0.001
	Within groups	102.158	143	0.714		
	Total	200.633	151			
Char	Between groups	93.229	8	11.654	16.40	< 0.001
	Within groups	101.624	143	0.711		
	Total	194.853	151			
Soot	Between groups	0.203	8	0.025	5.46	< 0.001
	Within groups	0.665	143	0.005		
	Total	0.868	151			
BC:SOC	Between groups	36.242	8	4.530	0.213	0.988
	Within groups	3042.860	143	21.279		
	Total	3079.102	151			
Char:BC	Between groups	14 734.366	8	1841.796	11.88	< 0.001
	Within groups	22 162.083	143	154.980		
	Total	36 896.449	151			

The total SOC and BC stocks that were calculated for the upper 20 cm of the catchment soils were estimated to be 191 and 9.1 Tg, respectively (Table 3). This shows that BC accounted for only 4.8% of the estimated SOC stock in the surface soils. The total stock of char-C in the upper 20 cm of the soils (7.7 Tg) was approximately five times greater than the soot-C stock (1.4 Tg), and this was equivalent to 85% of the total BC (Table 3). Among the nine different soil types, the largest topsoil char-C pool was in the alpine meadow soils; these soils accounted for more than 70% of the char-C stock in the Qinghai Lake catchment. Moreover, the char stored in the alpine meadow soils accounted for almost 60% of the BC stock.

Vertical distributions of SOC, BC, char, soot, BC:SOC and char:BC

The concentrations and vertical distributions of SOC, BC, char, soot, BC:SOC and char:BC in two profiles from each of two locations are shown in Figure 3. Generally, the SOC, BC and char concentrations all decreased with increasing soil depth, except at B1 where the largest value was found in the 20-cm soil layer at this site. The SOC concentrations in the 10–100-cm soil layer averaged 10 g kg⁻¹, with values ranging from 3.9 to 17 g kg⁻¹. The SOC concentrations in the 0–30-cm depth interval declined sharply and then varied within a narrow range in the deeper 40–100-cm layers.

The average BC concentrations in profiles A1 and A2 (0.85 and 1.2 g kg⁻¹, respectively) were much larger than those at B1 (0.52 g kg⁻¹) or B2 (0.46 g kg⁻¹). Furthermore, the variations in BC concentrations with depth at A1 and A2 were smaller than those at B1 and B2; indeed, the concentrations of BC in each soil layer at B1 and B2 were less than those in the corresponding

layers at A1 and A2. It is noteworthy that the vertical distribution of char was similar to the pattern exhibited by BC while the soot concentrations, in contrast, were small and showed almost no systematic variation with depth at any of the sites. The fraction of BC as a percentage of SOC increased irregularly with depth in the soil profiles, from a minimum of 4% up to 16%. The largest percentages of BC relative to SOC were always found in the 60–100-cm interval. Char accounted for more than 50% of BC in the four different soil profiles, with a maximum value of 91% at the A2 site. The proportion of char to BC generally decreased with soil depth.

Discussion

Variations in BC concentrations

The concentrations of BC in the soils from the Qinghai Lake catchment showed a spatial distribution similar to that of SOC. The average concentration of BC in the 0–20-cm soil layer was 1.3 g kg⁻¹; this is slightly larger than the BC concentrations in a temperate mixed-grass savanna in Texas (Dai *et al.*, 2005), but much smaller than those in German chernozemic soils (Schmidt *et al.*, 1999). The range of BC concentrations (0.07–8.7 g kg⁻¹) was comparable to the results reported by Rovira *et al.* (2009) for soils from a Mediterranean shrubland.

These differences may be misleading because BC was measured by different analytical methods in the various studies. Recent inter-comparison studies have shown that different methods can give widely disparate BC results, largely because BC is not a single entity but rather a continuum of carbonaceous compounds (Hammes *et al.*, 2007). Nonetheless, the amounts of BC in our samples appear to be much larger than in soils from the Chinese Loess Plateau (0.02–5.5 g kg⁻¹; Zhan *et al.*, 2013a) or urban soils

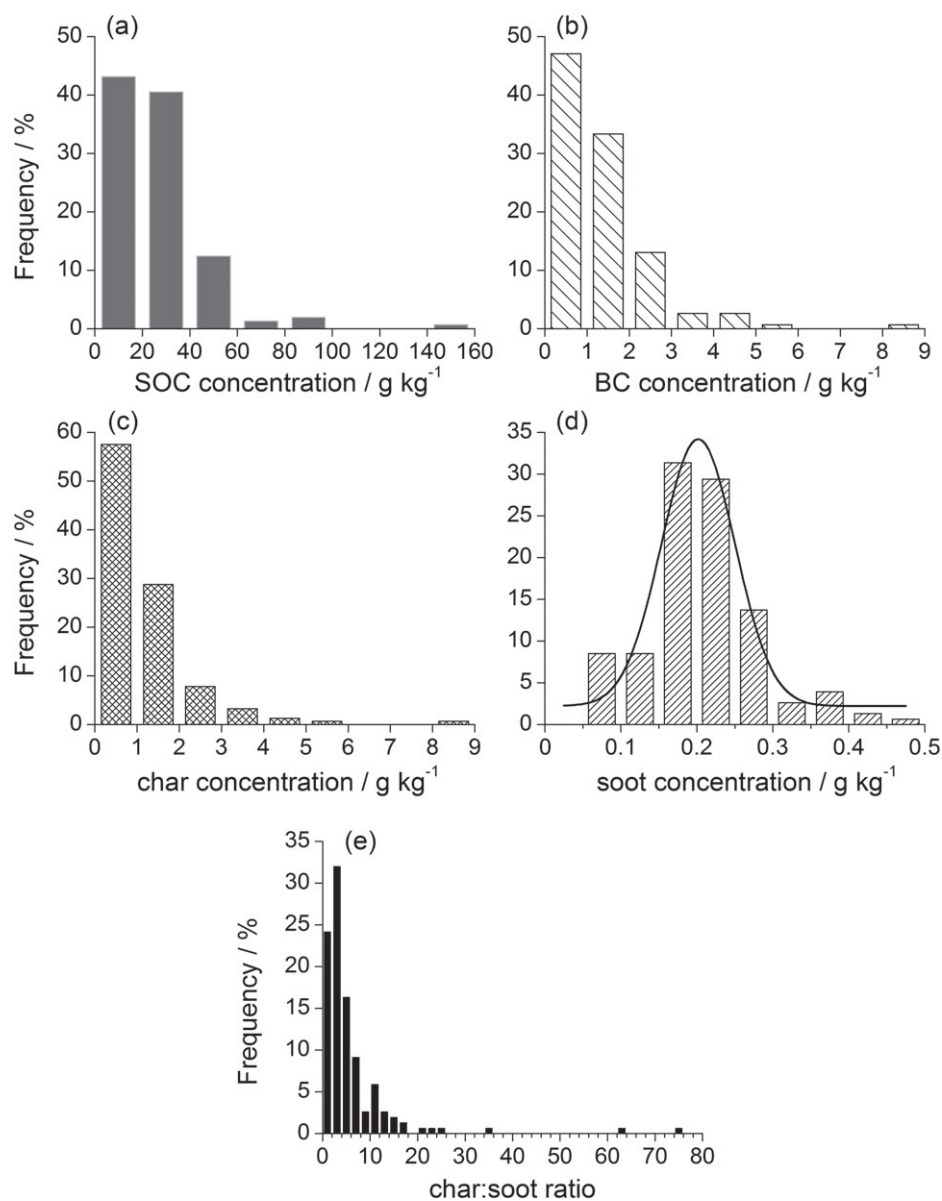


Figure 2 Frequency distributions of (a) soil organic carbon (SOC), (b) black carbon (BC), (c) char and (d) soot concentrations and (e) char:soot ratios in topsoils (0–20 cm) from the Qinghai Lake catchment on the northeast Qinghai-Tibet Plateau.

from Xi'an (0.17–2.1 g kg⁻¹; Han *et al.*, 2009) that were analysed using the thermal-optical reflectance method.

One possible reason for these differences is the high elevation of the plateau and the associated differences in climate, biomass and fuel loadings. Moreover, fire (Dai *et al.*, 2005), anthropogenic activities (Glaser *et al.*, 2001) and soil properties, such as mineral composition and organic C content (Czimczik & Masiello, 2007), also could be factors that influence the soil BC distributions. Microbial communities in frozen soils are normally in a metabolic state approaching dormancy, and significant biotic oxidation of char is likely only when the soils thaw (Guggenberger *et al.*, 2008). This implies that the BC deposited in some topsoils may record the original atmospheric BC deposition.

The variations of BC with soil depth were similar to those of SOC, and this suggests a possible connection between these two pools of C. In contrast to several studies that have shown the largest BC concentration in deep soil layers (Hammes *et al.*, 2008), the BC concentrations in our study generally decreased with depth and reached a minimum at 100 cm. This result is consistent with the findings of Glaser *et al.* (2001), who studied 'Terra Preta' soils from Central Amazonia (Brazil) and observed a rapid decrease in BC concentrations with soil depth. At our B1 site, the maximum BC concentration occurred at a depth of 20 cm, and this may have been caused by the leaching of oxidized BC species (Rumpel *et al.*, 2009) or bioturbation (Czimczik & Masiello, 2007). The patterns of BC:SOC in the four profiles were very similar to those reported by

Table 3 Storage of SOC, BC, char and soot in the 0–20-cm layer of soils from the Qinghai Lake catchment

Soil type	Area ^a / ×10 ³ km ²	Carbon pool / Tg			
		SOC	BC	Char	Soot
Bog	0.96	10.86	0.60	0.55	0.05
Alpine meadow	14.38	136.96	6.42	5.56	0.86
Mountain meadow	0.47	5.59	0.22	0.19	0.03
Chernozems	0.86	7.56	0.38	0.32	0.06
Castanozems	2.27	12.38	0.62	0.47	0.15
Alpine steppe	2.75	14.17	0.64	0.47	0.17
Solonchaks	0.06	0.23	0.01	0.008	0.002
Frost desert	1.37	3.31	0.18	0.12	0.06
Aeolian	0.22	0.34	0.02	0.01	0.01
Total	23.34	191.40	9.05	7.66	1.39

^aThe area data are from Liu *et al.* (2006).

MacKenzie *et al.* (2008). This may be explained by the stabilization or preservation of BC particles recovered from the sand and the coarse silt fractions (Brodowski *et al.*, 2007).

Our data showed little variation of soot concentrations with depth (Figure 2), and one can infer from this that the decomposition of soot was slow, presumably because of its inherent chemical recalcitrance (Goldberg, 1985). Several other studies have reported a similar lack of variability in vertical profiles of soot (Han *et al.*, 2009; Zhan *et al.*, 2013a), and taken together these results provide some direct support for the refractory nature of soot. Therefore, we would expect that soot in soils should be considered a relatively inert C pool in the context of global biogeochemical cycles. If one assumes that soil soot concentrations for the various types of soils on the Q-T Plateau are similar to those reported here, it can be estimated that about 154 Tg of soot may be stored in the upper 20-cm soils of the plateau. Unfortunately, the data on BC stocks in high-altitude soils in other areas of the world are limited, so it is difficult to evaluate the status and role of soot carbon in the global C cycle. Nevertheless, this estimate of soot sequestered on the Q-T Plateau is equivalent to 12% of the topsoil SOC pool in China's paddy soils (Pan *et al.*, 2004).

Possible sources for BC in soils

Several studies have shown that the char:soot ratio can be used as a tool for distinguishing the primary carbon emissions from biomass burning, coal combustion, motor vehicle exhausts and cooking (Chow *et al.*, 2004; Cao *et al.*, 2005; Han *et al.*, 2009). Generally, the char:soot ratio from biomass burning is larger than that from the burning of fossil fuels, and the ratio from coal combustion is larger than that from vehicle exhausts (Chow *et al.*, 2004; Cao *et al.*, 2005). For example, Cao *et al.* (2005) reported that the char:soot ratio for biomass burning in Xi'an was 11.6, compared with 1.9 for coal combustion. Chow *et al.* (2004) found that biomass burning produced a ratio of 22.6, and emissions from residential cooking had ratios ranging from 2.0 to 6.0.

The ratios in the upper 0–20-cm soils from the Qinghai Lake catchment ranged from 0.25 to 76, with a mean value of 6.1. About

25% of the topsoil samples had ratios of <2, about 50% were between 2 and 6, and values larger than 10 accounted for about 15% of the samples (Figure 2e). This suggests that the main sources of soil BC in the Qinghai Lake catchment were emissions from biomass burning, such as dung combustion and wildfires.

Dung from yak, sheep and cows and wood are commonly used for cooking in these regions. In rural areas of the plateau, wood, straw and yak dung account for about 75% of the total energy consumed, and yak dung accounts for about 50% of this (Kang *et al.*, 2009). Although the average BC emission factor for burning dung (0.25 g kg⁻¹) is significantly less than that for wood fuel (0.41 g kg⁻¹) or forest biomass (0.98 g kg⁻¹) (Reddy & Venkataraman, 2002), the contribution of burning dung to soil BC should not be overlooked. At some sample sites in our study, the char:soot ratios were larger than 10, which is strong evidence that the main source for soil BC was biomass burning.

In addition to wildfires and dung combustion for residential cooking and heating, the byproducts of fossil fuel combustion, especially from western and central China and middle-eastern and southern Asia, probably contributed to the soil BC on the Q-T Plateau (Kopacz *et al.*, 2011). The weathering of continental rocks also may have contributed to the soil BC in the form of petrogenic graphite (Dickens *et al.*, 2004), but it is difficult to estimate either of these effects even semi-quantitatively. Strong winds and dust storms are very prevalent during spring on the plateau, which could result in erosion and re-deposition of BC in topsoils. Water erosion also may contribute to the transport of soil BC in some regions (Rumpel *et al.*, 2009).

BC decomposition and its implications for the carbon cycle

During the past 50 years, meteorological data have shown that the temperatures on the Tibetan Plateau have been increasing (Li *et al.*, 2007). Some studies have demonstrated an effect of temperature on SOC; that is, when temperatures increase, SOC contents decrease (Fang *et al.*, 2005). Nonetheless, there is still no consensus concerning the temperature dependence of organic C decomposition, and this is largely because soil organic compounds exhibit a wide range of physicochemical properties, and these determine their susceptibility to decomposition (Davidson & Janssens, 2006).

Whether a warming climate will significantly enhance BC decomposition is still not well known, but higher temperatures accelerate the breakdown of recalcitrant organic matter. Recently, a study conducted by Cheng *et al.* (2008) indicated that climate warming could increase BC decomposition, but there is little if any direct evidence that the concentrations of BC in soils have been affected over timescales of centuries.

Permafrost regions are large reservoirs for carbon, and the Q-T Plateau is particularly important in this context because most of the plateau is covered by permafrost or seasonally freezing soils. The soils surrounding Qinghai Lake are subjected to seasonal freezing (up to 6 months) and thawing. The freeze-thaw cycling of the soils is potentially important for the cycling of carbon because it may affect the stability of SOC and BC. Several studies have indicated that the

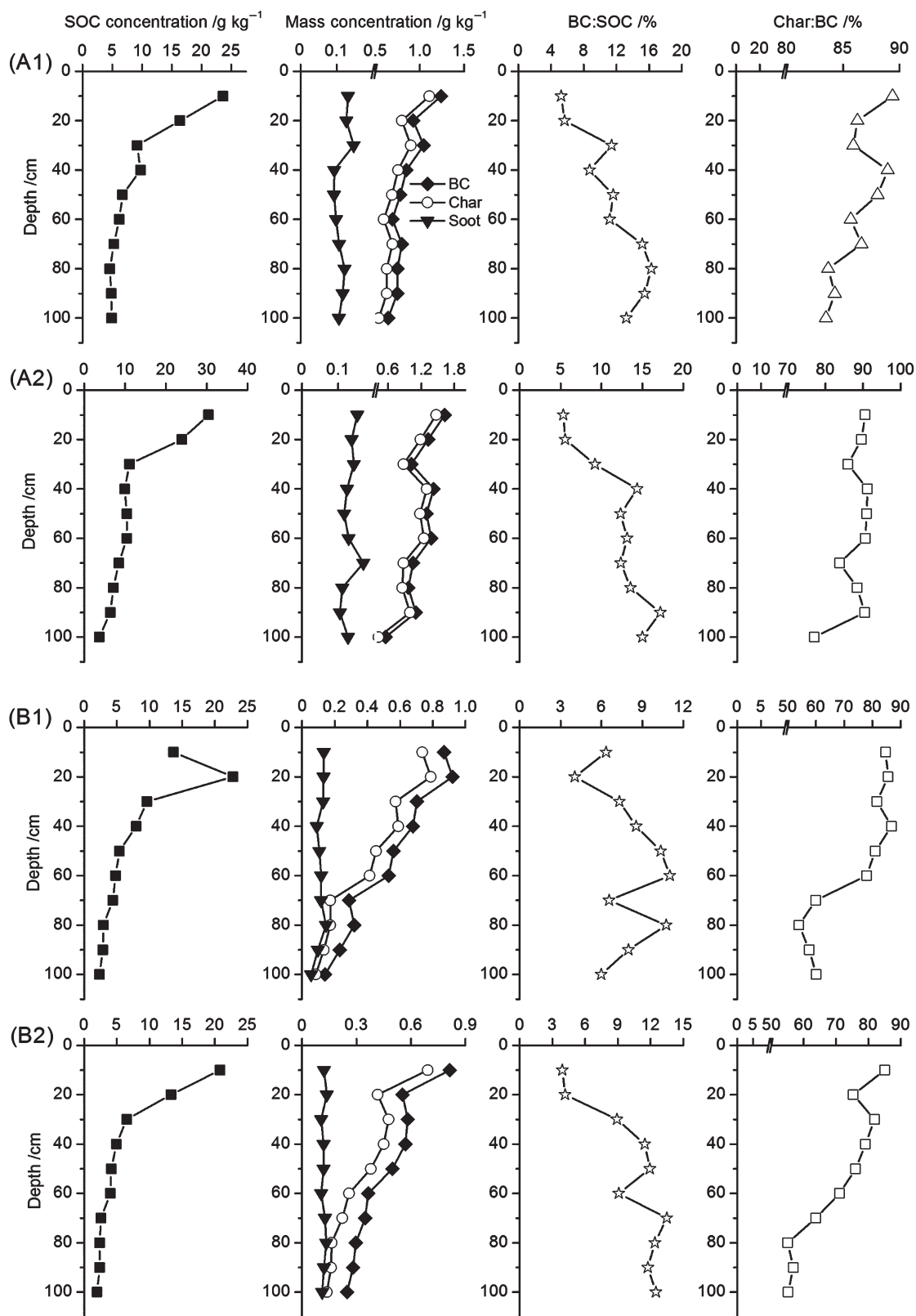


Figure 3 Vertical distributions of soil organic carbon (SOC), black carbon (BC), char and soot concentrations, and BC:SOC and char:BC ratios. A1 and A2 represent the two profiles from one sampling site and the same is true for B1 and B2 at a second site.

thawing and degradation of permafrost may result in the loss of SOC from the carbon pool (Zimov *et al.*, 2006), and this is considered one of the most potentially significant positive feedbacks between terrestrial ecosystems and a warmer world.

Black carbon, which our studies and others have shown forms a significant fraction of the SOC, can be preserved in soils for tens of thousands of years or possibly even longer (Schmidt *et al.*, 1999). Hammes *et al.* (2008) investigated the turnover time of soil BC produced from biomass burning and indicated that BC could survive unchanged in soils over timescales of decades to centuries. Additionally, some studies have shown that the mineralization of BC could occur over timescales of weeks to years (Bruun *et al.*, 2008), and this process also would lead to the sequestration of carbon in sedimentary materials.

Soot evidently persists for long periods of time in sediments of the Q-T Plateau. This conclusion is based on the fact that the soot concentrations were relatively constant with soil depth. This result also implies that the soot C pool sequestered in soils from the Qinghai Lake catchment and the larger Q-T Plateau may be relatively insensitive to increasing temperatures. Our results seem to be in conflict with those from some incubation and modelling studies (Fang *et al.*, 2005) that showed no difference in temperature sensitivity between young and old or labile and recalcitrant carbon species.

In any case, it is important to reiterate the point that BC has been operationally defined in the sense that different analytical methods have been used to determine the concentrations of this material in environmental samples. Although BC is widely considered to be relatively inert, it is possible that some BC trapped in the seasonally frozen soils, particularly in the form of fire-derived char, could at some point be converted into forms of carbon that would be released into the atmosphere. Any increases in the rates at which carbon is cycled in soils could affect the atmospheric CO₂ concentrations, and this in turn could lead to a significant positive feedback to climate change.

Conclusions

This study investigated the spatial distribution of SOC, BC, char and soot in 152 topsoil samples collected from the catchment area of Qinghai Lake. Values of SOC, BC, char and soot all varied greatly among the different types of soils. Overall, BC was a relatively minor fraction of the SOC. The BC content always accounted for < 10% of the SOC, except for in castanozems (the percentage of BC to SOC was over 47%). The study also shows that char comprised a larger fraction of the soil BC than soot, and unlike the patterns exhibited by char (and SOC and BC) in the four soil profiles analysed, the soot concentration showed little variation with the depth. This implies that soot is likely to be more chemically recalcitrant compared with char and therefore less likely to be affected by climate change; the larger implication is that soot probably functions as a carbon sink in these soils.

Therefore, it is of great importance to understand the dynamics of the various BC fractions in terrestrial soils. This is equally true for the SOC components that were not studied in detail here; we

note that even though BC:SOC was variable, the average percentage of BC in SOC was only 5.6%, and we think that research on the non-BC fraction of SOC is needed. Once this information is obtained we should eventually be able to predict how much CO₂-C will be released to the atmosphere over the short and long term.

The results also suggest that the soil BC in the Qinghai Lake catchment was mainly derived from biomass burning, especially the emissions from dung combustion and wildfires. Emissions from fossil fuel combustion could also make a contribution. This is quite different from the case of urban environments where the major sources of BC in soils are emissions from coal combustion and motor vehicles (Han *et al.*, 2009). Although the magnitudes of the estimated SOC and BC stocks in the 0–20-cm soil layer in the catchment soils of Qinghai Lake do not appear to be especially large, it is important to note that the data presented here are preliminary and that there remain significant gaps in our understanding of the cycling of carbon on the Q-T Plateau. The mechanisms of BC transport, deposition and decomposition in the high-altitude regions are perhaps least known and need more attention. To predict further changes to the climate system reliably, it is important to understand the connections and feedbacks between global climate and all forms of C stored in the permafrost and seasonally freezing soils on the Q-T Plateau and other high-altitude regions.

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