



Validation and application of a thermal–optical reflectance (TOR) method for measuring black carbon in loess sediments



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HIGHLIGHTS

- ▶ BC concentrations in the loess samples did vary among the three techniques.
- ▶ Additions of SRM-1649a showed CTO and TOR both yielded good linear correlations.
- ▶ The trend of BC in Luochuan section by TOR was similar to that of susceptibility.
- ▶ High BC happened during the last interglacial and low values in the last glacial.

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ABSTRACT

Three techniques were used to measure black carbon (BC) in samples from Chinese loess–paleosol sequences. The results obtained by (1) chemo-thermal oxidation (CTO, performed two ways), (2) acid dichromate oxidation (Cr_2O_7), and (3) thermal–optical reflectance (TOR) were intercompared because prior studies have shown that the methods can yield disparate results. BC concentrations did vary among the methods, most likely because they measured different components of the BC continuum, but the high-temperature BC (soot) determined by CTO was correlated with the BC and soot obtained by TOR. The CTO and TOR methods both yielded statistically significant linear relationships for loess and lake sediments that had incremental additions of a standard (SRM-1649a). The results also showed that charred material was more abundant in these test sediments than soot carbon. Data for BC in Luochuan loess generated using TOR showed a trend similar to that of magnetic susceptibility, that is, high BC and large susceptibilities during the last interglacial and low values for both variables in the last glacial. The results thus indicate that the TOR method is well suited for studies of sedimentary materials and that more biomass burned during the last interglacial than in the last glacial.

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1. Introduction

Black carbon (BC) is an impure form of the carbon element, and although it is mainly produced by the incomplete combustion of fossil fuels and biomass (Goldberg, 1985), the weathering of graphitic carbon in rocks has been recognized as a minor source (Dickens et al., 2004). One important concept that bears emphasis is that BC is not a single entity but rather a suite of compounds that form a chemical “continuum,” from partially-charred plant material

through char and charcoal to sub-micrometer soot and graphite (Seiler and Crutzen, 1980; Hedges et al., 2000; Masiello, 2004). BC is ubiquitous in the environment, and it has been studied extensively in the atmosphere, soils, waters, ice, and sediments (Kuhlbusch, 1998), in part because of its importance in a wide range of biogeochemical processes. BC preserved in the marine sediments can be thousands to millions of years old because it is both chemically and biologically stable (Bird and Cali, 1998). Indeed, BC has been proposed to be a significant sink in the global carbon cycle (Kuhlbusch, 1998; Schmidt and Noack, 2000).

A variety of approaches have been used to quantify BC, including chemical, thermal, optical, molecular marker and microscopic methods. Some of these methods have been developed for investigations of atmospheric aerosols and cannot be applied to soil or

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sediment samples, and others suffer either from laborious sample pretreatment or a lack of specificity. BC determined by all of these approaches is operationally defined, and it is likely that the methods measure different fractions of the BC continuum (Currie et al., 2002; Hammes et al., 2007). In addition, some methods may be subject to artifacts and measure non-BC materials as BC (Brodowski et al., 2005). Other methods may underestimate BC due to the oxidation of char during pretreatment (Simpson and Hatcher, 2004b).

Methodological problems and advantages and disadvantages in BC quantification have been highlighted in several intercomparison studies. For example, a comparative analysis of soils showed that BC concentrations obtained by different methods can vary over two orders-of-magnitude (Schmidt et al., 2001). An intercomparison using only one material (urban dust) but 18 methods gave quite diverse results as well (Currie et al., 2002).

BC concentrations in loess sediments have been used to reconstruct the history of paleofires (Yang, 2000; Wang et al., 2005, 2012; Zhou et al., 2007). However, published records of BC concentrations have been found to differ greatly even for loess samples taken from the same location. For instance, the BC concentrations reported for the two sections in Lingtai of Chinese Loess Plateau varied by a factor of nine. The average BC concentrations measured by Wang et al. (2005) and Zhou et al. (2007) were 0.18% and 0.22%, respectively, the concentrations in the latter study ranged from 0.05% to 0.43%. More important, the conclusions of the two studies relative to historical trends were in direct contrast: Zhou et al. (2007) concluded that BC abundances were generally higher in interglacial paleosol than in loess but Wang et al. (2005) argued that BC sedimentation in glacial periods was higher than in interglacials. The discrepancies between the studies, which led to differences in conclusions regarding paleofire histories, may be a result of differences in methods, especially the acid treatment procedures and oxidation times. Clearly, a standardized and validated method for BC measurements of loess and other sediments would lead to a better understanding of the long-term variations in BC.

A thermal–optical reflectance (TOR) method was developed for studying black carbon in aerosol particles (Chow et al., 1993, 2004; Cao et al., 2003, 2005), but the method also has been used to study BC in standard reference materials (Currie et al., 2002; Hammes et al., 2007), soils and sediments (Han et al., 2007a, 2009a, 2009c, 2011, 2012; Zhan et al., 2012). Han et al. (2007b) proposed that the TOR method could be used to distinguish between char from soot by oxidizing the various carbon fractions in a stepwise manner. This modification of the procedure has been used to identify sources for aerosol particles (Han et al., 2008, 2009b; Lim et al., 2012). Nevertheless, few studies have compared the TOR method with other approaches for measuring BC, especially in soils and sediments.

In the present study, TOR was used to determine BC contents in loess sediments, and the results were intercompared with the BC values determined by two other commonly used analytical methods, chemo-thermal oxidation (CTO-375) and dichromate oxidation. For the CTO-375 method, we also evaluated the effects of different pretreatment procedures and analytical instrumentation. To test the applicability and accuracy of the TOR method and to evaluate potential matrix effects, standard additions of incremental amounts of urban dust (NIST standard reference material 1649a) were made to loess and lake sediments. The BC results from the CTO-375 and TOR methods were intercompared to further evaluate the applicability of TOR method and to understand the relationships among the different BC fractions measured by these two methods. In addition, the TOR method was applied to studies of BC in a loess-paleosol sequence, with the expectation that the results would serve as a basis for further systematic studies on BC in loess-paleosol sequences.

2. Materials and methods

2.1. Sample collection and preparation

Loess sediment samples were collected from the Luochuan (abbreviated LC, 35°43'N, 109°25'E, 1,212 m above sea level, asl), Zhaojiachuan (ZJC, 35°45'N, 107°49'E, 1250 m asl), and Jingyuan (JY, 36°21'N, 104°36'N, 2210 m asl) sections. These sites are oriented from east to west on the Chinese Loess Plateau (Supplemental Fig. S1) where the East Asian summer and winter monsoons are major influences on seasonal weather patterns on the short term and on climate over longer time-scales. The modern mean annual temperature (MAT) and precipitation (MAP) are 9.2 °C and 623 mm at LC, 8.7 °C and 555 mm at ZJC, 8.9 °C and 240 mm at JY, respectively, and at all three sites, more than half of the annual precipitation falls during the summer. The three sedimentary sequences are all composed of upper loess-paleosol sequences and the lower red-clay deposits. Detailed descriptions of the pedostratigraphy of the LC and ZJC profiles have been presented by Kukla and An (1989), Sun et al. (1998), and Ding et al. (1999), and information on the JY sequence may be found in Sun et al. (2011).

For the present study, seventeen and fourteen samples of loess sediments from the ZJC and JY sections were collected, respectively; and the strata sampled at both sites included the loess-paleosol units L₁, S₁, L₂ and S₂. In addition, we collected a total of 60 samples at 20 cm intervals from the LC profile. Finally, in order to further evaluate and validate the TOR method, a sediment sample previously collected from Huguangyan Marr Lake (21°9'N, 110°17'E), and a loess sediment sample from Shikou (116°9.6'N, 36°54'E, 80–100 cm depth) also were analyzed. All of the environmental samples were air-dried and subsequently sieved (2-mm sieve) to remove plant roots and gravel. Nominally, 3 g of each sample was ground with an agate mortar and pestle, and it was then passed through a 63- μ m sieve for homogenization.

2.2. Elemental analysis

The soil and sediment samples were pretreated with 1 M HCl in order to remove inorganic carbon (Hedges and Stern, 1984), and then dried in an oven at 60 °C. Total organic carbon (TOC) and total nitrogen (TN) were measured in duplicates by dry combustion (950 °C) using a Verio EL III element analyzer (Elementar, Hanau, Germany). Accuracy of the analytical method was calibrated with the analysis of control standards. TOC and TN concentrations of the soil and sediment samples were presented in Table 1.

2.3. Magnetic susceptibility

Low frequency magnetic susceptibility (χ_{LF}) was measured on ~10 g of the LC samples which were packed in separate 10 mL plastic boxes. A Bartington MS2 magnetic susceptibility meter (Bartington Instruments, Ltd., Oxon, England) operating at 470/4700 Hz was used for the susceptibility analyses. For each sample, two independent readings were averaged. Results are expressed as mass-specific, low-frequency, magnetic susceptibility χ_{LF} and reported in units of 10⁻⁸ m³ kg⁻¹.

2.4. Thermal–optical reflectance (TOR)

Detailed methods for extraction, filtration and BC analysis have been described elsewhere (Han et al., 2009a). Briefly, acid pretreatment of the samples was used to remove three types of substances (1) carbonate, (2) silicates, and (3) residual carbonate and some minerals (such as fluorite). After each acid-treatment step, the residue was centrifuged and rinsed with deionized (DI) water. The

Table 1
Sample locations, depths and some chemical properties of the fourteen soils studied.

Location	Sample ID	Depth (m)	TOC (mg g ⁻¹)	TN (mg g ⁻¹)	C/N ratio
Luochuan	L1-8	3.9	1.02	0.38	2.35
	S1-15	8.9	2.88	0.61	4.75
	L2-3	10.9	0.54	0.42	1.27
	S2-12	12.9	0.65	0.45	1.45
Zhaojiachuan	L1-34	9.0	1.02	0.43	2.36
	S1-18	11.8	2.50	0.49	5.10
	L2-5	14.7	0.68	0.37	1.84
	S2-8	23.9	1.60	0.50	3.20
Jingyuan	L1-13	4.5	0.41	0.34	2.39
	S1-27	13.2	1.38	0.42	3.26
	L2-64	17.1	0.88	0.29	3.05
	S2-3	25.2	1.38	0.44	3.16
Huguangyan Marr Lake	MEH-40	0.39–0.40	17.61	1.90	9.23
Shikou	SK-6	0.8–1.0	2.71	0.54	9.57

residue was then passed through a 47 mm quartz-fiber filter (0.4 µm pore size, Whatman Ltd, Maidstone, UK), and the retentate dried in an oven at 50 °C for 6 h before analysis.

Carbon analyses were carried out with the use of a Desert Research Institute (DRI) Model 2001 Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, Chow et al., 1993, 2004). The IMPROVE_A thermal-optical reflectance (TOR) protocol (Chow et al., 2007) was used for these analyses. A 0.526 cm² punch aliquot of each quartz filter sample was heated in a stepwise manner to produce data for four organic carbon (OC) fractions (OC1, OC2, OC3, and OC4) in a helium atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, and three elemental carbon (EC) fractions (EC1, EC2, and EC3) in a 2% oxygen/98% helium atmosphere at 580 °C, 740 °C, and 840 °C, respectively. At the same time, pyrolyzed organic carbon (POC) was produced at <580 °C in the inert atmosphere: this component decreases the reflected light and is used to correct for charred OC. Based on the work of Han et al. (2009a), char is defined as EC1 – POC, soot is EC2 + EC3, and BC is char + soot.

2.5. Chemo-thermal oxidation (CTO-375)

The CTO-375 method was performed in two ways, denoted here as CTO-375/CHN and CTO-375/TOR. The CTO-375/CHN method as used in our study was modified slightly from the procedure described in Elmquist et al. (2004), and it had changes in three steps: (i) demineralization via *ex situ* acidification; (ii) thermal oxidation of organic matter at 375 °C; and (iii) quantification of the residual carbon as BC with a CHN elemental analyzer. Briefly, ~0.5 g loess was treated with 1 M HCl prior to combustion to remove inorganic carbonates and possible metal catalysts. After digestion for 1 h at room temperature, the residues were rinsed with DI water, centrifuged (4000 rpm, 8 min), and the supernatant discarded. This rinsing step was repeated three times, and then the residues were dried at 60 °C for 48 h and reweighed.

The dry samples were ground with a mortar and pestle to a fine powder and homogenized thoroughly to reduce variability between replicates and to reduce any potential charring during thermal treatments. Following these steps, ~0.1 g of each pretreated sample was weighed and spread into a pre-combusted porcelain crucible and then combusted by heating in a muffle furnace under air at 375 ± 5 °C for 18 h. The residual carbon was determined as BC with a CHN elemental analyzer.

Before the thermal oxidation step, the oven temperature of the muffle furnace was increased from room temperature to 300 °C at a rate of 15 °C min⁻¹ and then to 375 °C at 5 °C min⁻¹

and finally held at 375 °C for 18 h. The first (rapid-heating) step was used to avoid charring of non-BC phases, while the second (lower-rate) heating step was designed to minimize the temperature overshoot as the oven approached its target temperature – the latter possibly leading to destruction of less refractory BC particles (Accardi-Dey, 2003). In comparison, method CTO-375/TOR was essentially the same as that described by Han et al. (2011). For this procedure, one-half of each sample filter was placed in a muffle furnace and held at 375 ± 5 °C in air for 18 h, and the instrumental analyses were done with the use of the DRI carbon analyzer as described above for the TOR method.

2.6. Acid dichromate oxidation (Cr₂O₇)

The wet chemical oxidation method for BC was a modification of the procedure used by Lim and Cachier (1996). In brief, ~2 g loess was weighed and then decarbonated with 6 M HCl. The residues were centrifuged, rinsed with DI water, and then treated with 10 M HF/3 M HCl to remove silicate materials. The mixture was subjected to a treatment with 3 M HCl, and after centrifugation (4000 rpm, 8 min), the supernatant was discarded and pellet was rinsed three to four times with DI water, until the pH was 4–5. The sample residues were then oxidized using a solution of 0.1 M K₂Cr₂O₇/2 M H₂SO₄ in water bath at 55 ± 1 °C for 60 h to remove soluble organic matter and kerogen. During the oxidation step, the solution was changed three to five times based on a change in the color of the solution. The solid residue left after these steps was rinsed four times with DI water and dried at 60 °C for 48 h. For this procedure, BC was operationally defined as the organic carbon that survived oxidation with dichromate, and it was determined using a CHN elemental analyzer.

2.7. Standard additions of SRM-1649a

Additions of known amounts of BC to soils and sediment have been used to calibrate BC analytical methods, and they have proven to be especially useful for the analysis of complex sample matrices (Elmquist et al., 2004; Agarwal and Bucheli, 2011). In the present study, standard reference material SRM-1649a was added in incremental amounts to loess and lake sediments. The mixtures were homogenized with an agate mortar and pestle, and subsamples were taken for quantification by the TOR and CTO-375/TOR methods. For the SRM-1649a, the quantified BC concentration using IMPROVE_A TOR method was 37.13 ± 0.05 mg g⁻¹ (Table 2), which is a little lower than the value (41 ± 1.30 mg g⁻¹) reported by Han et al. (2007a), but much lower than the value (76.38 ± 0.35 mg g⁻¹) reported by Currie et al. (2002).

2.8. Quality control and quality assurance

In all cases, each BC sample (quartz filter) was analyzed in triplicate. The DRI carbon analyzer was calibrated with system blanks and known quantities of CH₄ every day the instrument was used. The quantification limits for EC and OC were below 1.0 µg m⁻³, and the difference determined from replicate analyses was <5% for TC and <10% for OC and EC. These relatively high reproducibilities for EC and OC show that the residues on the quartz-fiber filters were acceptably homogeneous.

3. Results and discussion

3.1. BC concentrations quantified by different methods

The BC concentrations in loess and paleosol from the LC, ZJC and JY sections were determined using four methods based on three

Table 2

BC concentration (mg g^{-1}) for Black Carbon steering committee reference material (SRM-1649a) determined by using TOR and CTO-375/TOR methods with two different temperature protocols and compared with other studies.

Analytical method	Temperature protocol	TC (mg g^{-1})	EC (mg g^{-1})	EC/TC (%)
TOR	IMPROVE	169.36 ± 7.94	40.61 ± 1.58	24.02
TOR	IMPROVE_A	162.68 ± 6.06	37.13 ± 0.05	22.82
CTO-375/TOR	IMPROVE_A	20.22 ± 1.44	17.28 ± 1.47	85.46
TOR ^a	IMPROVE	176.8 ± 0.80	76.38 ± 0.35	43.2
TOR ^b	IMPROVE	157 ± 3.20	41 ± 1.30	26.1

^a Currie et al. (2002).

^b Han et al. (2007a,b).

different techniques, and the results of those analyses are presented in Fig. 1. Of the four methods, CTO-375/TOR consistently produced the lowest BC concentrations while the values produced by the Cr_2O_7 method were generally higher than the CTO or TOR results, except for the L2 sample from ZJC. These findings are consistent with those from Currie et al. (2002) and Hammes et al. (2007) who reported that the CTO method usually returned lower BC values than wet chemical methods. The Cr_2O_7 method quantifies the carbon residue that resists oxidation with $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, and therefore pretreatment procedures, especially the duration of the oxidation step, variations in reagent ratios and concentrations, and the final detection technique all may affect the ultimate BC values. Additionally, this method assumes that all of the carbon that survives the oxidation treatment is BC; and this assumption may result in underestimates of BC in soils because: (1) excessive handling of the sample in liquid solutions may lead to loss of sub-micron-sized BC particles (i.e., fine soot BC) (Elmquist et al., 2004); and (2) some BC components may be oxidized over long reaction times (Lim and Cachier, 1996). In a recent intercomparison study of BC in soils, the reproducibility of the wet chemical method was low for sediment and soil samples; indeed, the BC values reported by four different laboratories who used this technique varied by a factor of three or more (Hammes et al., 2007).

The TOR and CTO-375/TOR methods produced similar BC values for some loess samples (Fig. 1), and this leads us to suggest that soot carbon was the major BC component in those samples. Soot is the most condensed and refractory form of BC, and even though some soot may be lost by thermal treatment at 375°C (Nguyen et al., 2004), it is mostly resistant to the thermal oxidation step in the CTO-375 method (Hammes et al., 2007) although. This suggestion is supported by the results of Han et al. (2007a) who pointed out that the TOR method measures several carbon fractions of the BC continuum while the CTO method only measures the high-temperature fraction (soot carbon). Consequently, one would expect the TOR BC values to be higher than those from the CTO-375/TOR analysis if easily oxidized forms of BC were

present and that the two methods would be in better agreement for samples mainly composed of soot. Indeed, labile pyrogenic residues on some of the sample filters most likely were oxidized during the thermal treatment for CTO-375/TOR, and this can explain the lower BC contents compared with the TOR method.

A second comparison shows that results of the CTO-375/CHN analyses were as much as two to four times those measured by CTO-375/TOR. A possible reason for this is the loss of submicron-sized BC particles during the multiple sample-handling steps (e.g. rinsing, centrifugation, and decantation) in CTO-375/TOR method (Gustafsson et al., 1997; Currie et al., 2002; Elmquist et al., 2004). Additionally, the thermal-oxidative CTO-375/CHN method can induce charring of labile organic matter to pyrogenic carbon, therefore causing overestimates in the amount of BC (Simpson and Hatcher, 2004a). A final consideration is that several studies (Gelinis et al., 2001; Gustafsson et al., 2001; Schmidt et al., 2001) have shown that demineralization prior to thermal oxidation, which was part of the CTO-375/CHN procedure but not CTO-375/TOR, results in BC values much lower than those for samples that had not been demineralized. The observed differences in BC concentrations analyzed by the two methods suggest that the combination of charring in CTO-375/CHN and particle loss in CTO-375/TOR were a greater influence on the measured BC than demineralization.

3.2. Standard additions of SRM-1649a

The BC concentrations for the loess and lake-sediment samples that had incremental additions of the SRM-1649a standard and were analyzed by TOR and CTO-375/TOR are presented in Table 3. The loess sediment analyzed by TOR had a high intrinsic BC concentration ($0.34 \pm 0.02 \text{ mg g}^{-1}$), which was approximately three times higher than what was measured using CTO. Similarly, a high BC concentration ($0.67 \pm 0.04 \text{ mg g}^{-1}$) was found for the Marr Lake sediment analyzed by TOR and a much lower BC concentration ($0.17 \pm 0.02 \text{ mg g}^{-1}$) when that sample was analyzed by CTO.

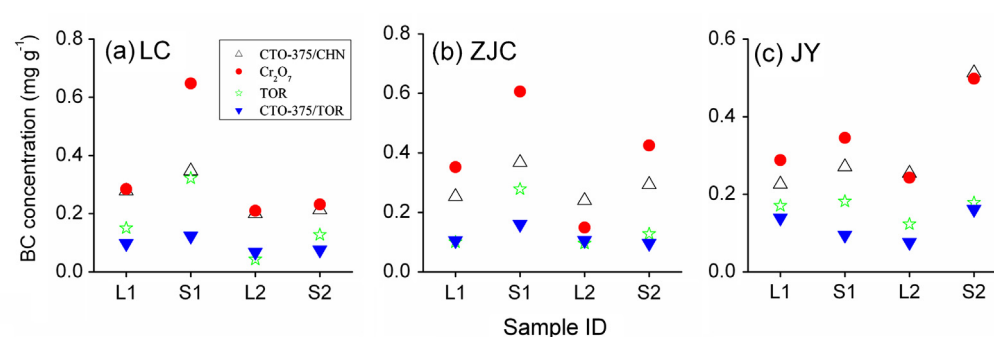


Fig. 1. Concentrations of BC in loess sediments determined by four different methods. L1, S1, L2, and S2 denote the loess-paleosol units of the loess sections: (a) Luochuan (LC), (b) Zhaojiachuan (ZJC) and (c) Jingyuan (JY).

Overall, TOR method gave obviously higher BC content than CTO (Table 3), and as noted above, this is consistent with the results of other studies (Currie et al., 2002; Hammes et al., 2007; Han et al., 2011).

For the standard additions to the loess sample, the CTO method produced only slightly higher BC concentrations compared with the TOR soot contents, but in contrast, the BC concentrations in the lake sediment samples determined by CTO were approximately six times the TOR soot values (Fig. 2c and d). This we attribute, at least in large measure, to the conversion of labile organic matter in the lake sediment into refractory carbon during the CTO thermal pretreatment step; this artifact is known to cause overestimates in the amount of BC (Gelinas et al., 2001; Elmquist et al., 2004; Simpson and Hatcher, 2004a). Indeed, the high TOC content of the Marr Lake sediment (Table 1), makes it likely that some organic matter was converted to BC during the combustion step (Accardi-Dey, 2003). This conversion would lead to much greater between-methods discrepancies for the lake sediment compared with loess because of the much higher TOC in the lake sediment. However, some studies indicate that some soot particles also can be oxidized during thermal pretreatment (Nguyen et al., 2004; Hammes et al., 2007), which would have the opposite effect. Both the extent of charring of organic carbon and the oxidation of soot during thermal oxidation are still poorly constrained, however, and this results in large uncertainties for CTO method and complicates the interpretation of the differences between different methods.

Despite the differences between the CTO and TOR results, x - y plots of the BC values obtained by the two methods showed robust linear relationships for samples with added standards. This was true for both TOR BC vs. CTO375/TOR BC (Fig. 2a and b) and TOR soot vs. CTO375/TOR BC (Fig. 2b and c). In addition, as shown in Fig. 3a and b, strong linear relationships were observed between the amount of standard added and the BC concentrations determined by both methods. The BC concentrations for the loess measured by TOR were slightly lower than those predicted from the standard additions, but the two regression lines were nearly consistent (Fig. 3a). A little lower slope than predicted was obtained by the CTO-375/TOR method for the lake sediments that had incremental additions of SRM-1649a (Fig. 3b), which could be due to the high TOC content of the lake sediment although the mechanism involved is unclear.

Further comparisons of the measured BC concentrations vs. amounts of standard added showed that the CTO method generated much lower BC concentrations than those measured by TOR. For the loess sample, the slope of the BC concentration vs. added standard regression for the CTO analyses was lower than that for

TOR (Fig. 3a); while for the lake sediment, the CTO and TOR lines, though offset, had similar slopes (Fig. 3b). The CTO BC values for the loess and sediment samples were always lower than the TOR or predicted values (Fig. 3a), which is consistent with the study of Agarwal and Bucheli (2011). Moreover, the other reason is that CTO method is viewed as an excellent technology for detecting primarily the presence of soot (Gustafsson et al., 2001; Nguyen et al., 2004; Hammes et al., 2007), but cannot detect the whole BC continuum. Interestingly, for the lake sediment, the CTO and TOR lines, though offset, had similar slopes.

In general, the intrinsic BC contents estimated from the standard addition curves (that is, their y -intercepts) were in reasonable agreement with the concentrations measured in samples without added standards. For the samples with no added standards, soot carbon accounted for about 24% of BC in the loess compared with 9.7% in the lake sediment, and therefore, charred material was found to be more abundant in the loess and lake sediments used in the standards additions test than soot carbon. After the additions of incremental amounts of SRM-1649a, the soot/BC ratio determined using the TOR method varied over a narrow range, not only for the loess sample (17.3–19.2%) but also for the lake sediment (11.1–12.6%, Table 3).

3.3. Variations of BC in the Luochuan profile

The BC concentrations for the Luochuan loess section measured using the TOR method are presented in Fig. 4 along with the magnetic susceptibility results, which are included for comparison. The BC abundances ranged from 0.04 to 0.98 mg g⁻¹ and averaged 0.22 mg g⁻¹ (Fig. 4), which are similar to those in the Lingtai (Zhou et al., 2007) and Weinan (Yang, 2000) sections previously measured using the Cr₂O₇ method, but they are much lower than those in three loess-paleosol sections studied by Wang et al. (2005) who also used the dichromate oxidation method (Table 4).

The LC profile showed the highest BC concentrations in the top 0–0.2 m layer and lower concentrations below although they did not decrease systematically with the depth. As shown in Fig. 4, low BC values corresponded to the low magnetic susceptibilities, and the highest BC co-occurred with the highest susceptibilities. Viewed from a chronostratigraphic standpoint, Fig. 4 shows that the paleosol layers S₀ and S₁ had much higher BC content than the loess layer L₁, and this suggests that more paleofires occurred during times of paleosol development. This finding is consistent with the BC record of Lingtai loess section determined by the Cr₂O₇ method (Zhou et al., 2007), but differs from the results of Wang et al. (2005) who reported that BC variations in the Lingtai

Table 3

BC concentrations for soil and lake sediment samples quantified by the TOR and CTO-375/TOR methods after standard additions of BC from SRM-1649a.

Sample ID	SRM-1649a added (mg g ⁻¹)	TOR			CTO-375/TOR
		TOR	BC content (mg g ⁻¹)	Soot content (mg g ⁻¹)	Soot/BC (%)
SK-6	0.00	0.34 ± 0.02	0.08 ± 0.01	23.99	0.13 ± 0.01
	5.85	0.58 ± 0.01	0.11 ± 0.00	19.24	0.16 ± 0.02
	9.42	0.69 ± 0.03	0.13 ± 0.01	18.20	0.20 ± 0.02
	11.29	0.72 ± 0.02	0.13 ± 0.01	17.56	0.21 ± 0.03
	15.59	0.79 ± 0.00	0.14 ± 0.01	18.48	0.24 ± 0.01
	18.89	1.02 ± 0.00	0.18 ± 0.01	17.26	0.26 ± 0.01
MEH-40	0.00	0.67 ± 0.04	0.04 ± 0.02	9.71	0.17 ± 0.02
	9.13	0.94 ± 0.13	0.12 ± 0.01	12.60	0.36 ± 0.05
	15.79	1.43 ± 0.08	0.18 ± 0.02	12.61	0.64 ± 0.03
	25.44	1.43 ± 0.08	0.17 ± 0.03	12.05	1.02 ± 0.06
	31.98	1.86 ± 0.12	0.21 ± 0.03	11.07	1.03 ± 0.10
	45.31	2.64 ± 0.08	0.32 ± 0.03	12.23	1.81 ± 0.15

The BC concentration of SRM-1649a was 37.13 mg g⁻¹ in this study.

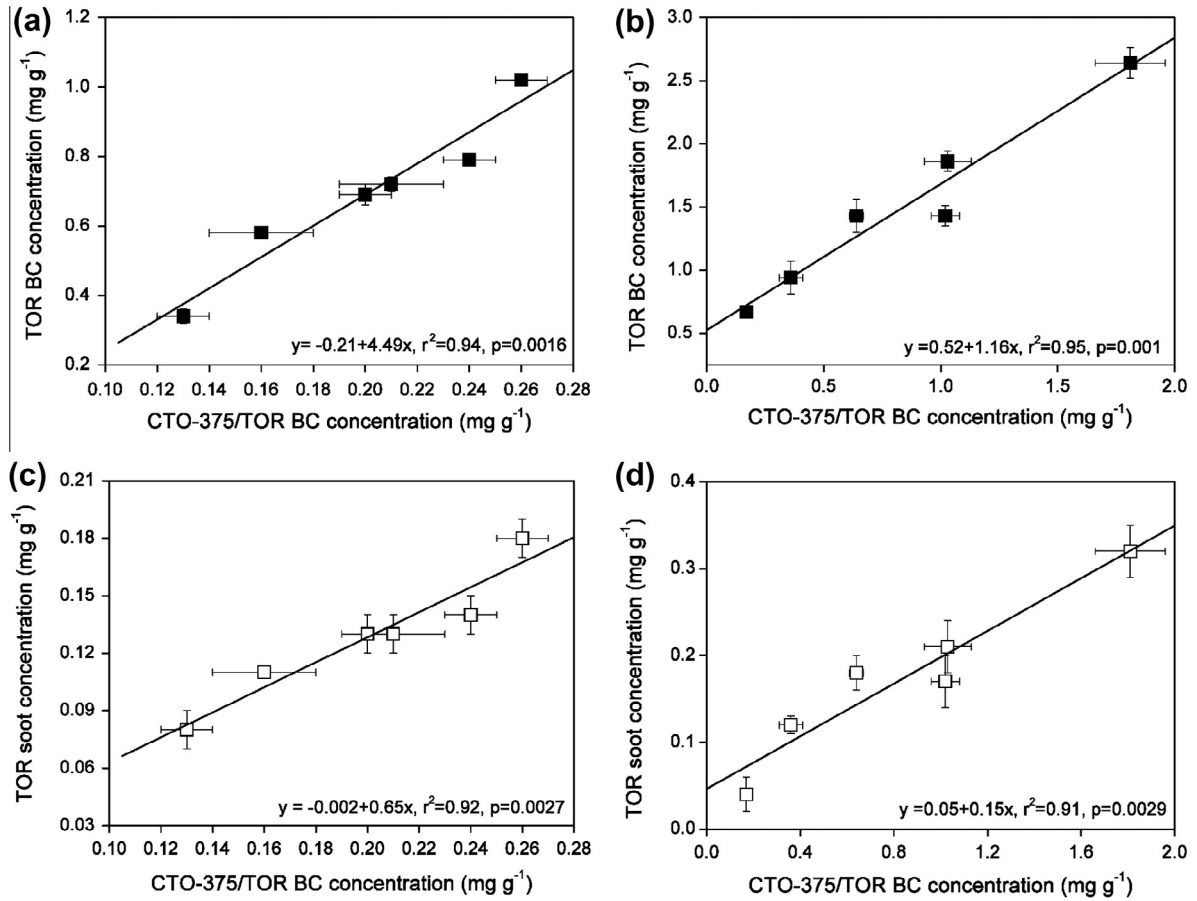


Fig. 2. Correlations between BC and soot concentrations measured by TOR method and BC concentrations quantified by CTO-375/TOR method after standard additions of SRM-1649a: (a) and (c) loess sediments; (b) and (d) lake sediments. Error bars show one standard deviation of triplicate measurements.

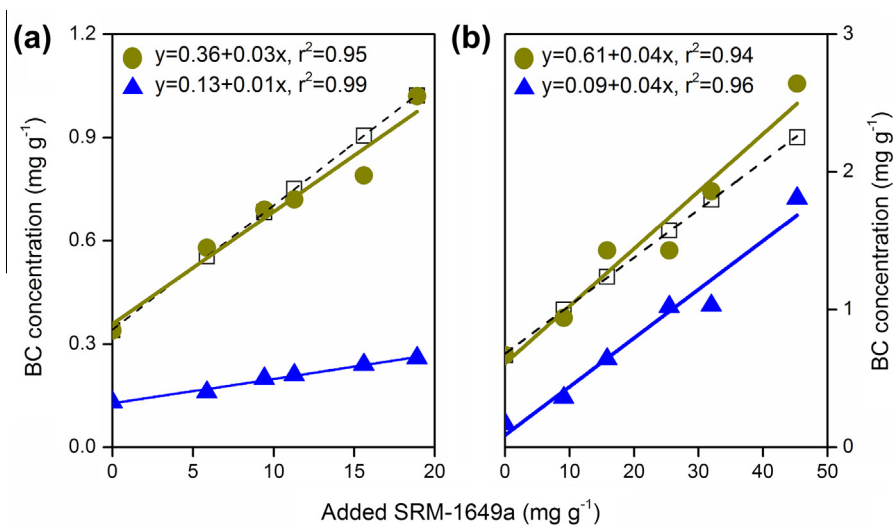


Fig. 3. Standard addition curves for SRM-1649a added to two environmental matrices: (a) loess sediment and (b) lake sediment. Dashed lines and open squares represent predicted BC concentrations from incremental additions of SRM-1649a. Solid lines represent linear regressions for the TOR (filled circles) and CTO-375/TOR (filled triangle) methods.

section did not generally display the same trends as the magnetic susceptibility curve. The discrepancies with the previous studies at Lingtai and those between them are most likely related to the use of the Cr_2O_7 method for the BC analyses. As noted above, intercomparison studies have shown low reproducibility for the Cr_2O_7 method for sediment and soil samples, with BC concentrations

sometimes varying by a factor of three or more (Hammes et al., 2007).

Systematic differences in magnetic susceptibility values between loess horizons and paleosols, have been linked to changes in the strength of the summer monsoon (Kukla and An, 1989; Porter and An, 1995). Paleosols always have significantly higher

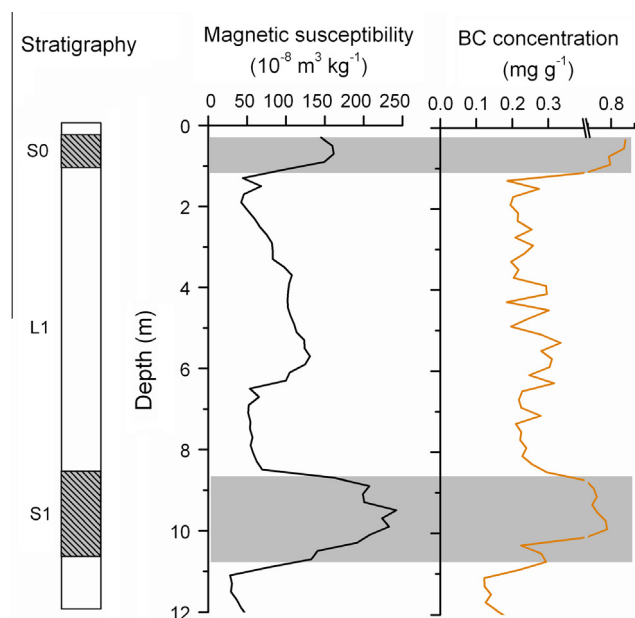


Fig. 4. Comparison of BC concentrations determined by TOR method with magnetic susceptibility in Luochuan loess-paleosol profile. All records are plotted vs. depth. The shaded zones indicate paleosol units.

magnetic susceptibility values than those in coupled loess layers, and this has been attributed to the relatively warm and humid climate during interglacials. Conversely, the low magnetic susceptibility of the loess units indicates cold and dry conditions during glacials (An et al., 1991). The positive relationship between BC and magnetic susceptibility suggests that higher concentrations of BC occurred when the climate was warm and humid and less BC was produced during colder and drier periods.

Furthermore, the co-variance between BC and magnetic susceptibility in the LC profile implies that the abundance and availability of fuels was related to the amount biomass burned. That is, during wetter and warmer periods the increased vegetative cover most likely provided the fuel for larger and more frequent fires. A statistical analysis of a series of global charcoal records (11 marine and 56 terrestrial sites), led Daniau et al. (2010) to reach a similar conclusion, viz., that biomass burning was generally high during interglacials and low during glacials, and this was true for both the Northern and Southern Hemispheres.

In contrast to these results, several studies based on BC in marine sediments indicate higher incidences of paleofires during glacials. For example, a study based on deep-sea core RC24-07, which is from the eastern equatorial Atlantic, indicates that the maximum charcoal concentrations and fluxes occurred during glaciations (Verardo and Ruddiman, 1996). Similarly, analysis of core

SHI-9014 from the Banda Sea showed higher charcoal and BC burial rates during glacials rather than interglacials (van der Kaars et al., 2000). However, the high sedimentation rate of BC during glacials in the open ocean possibly was the result of transportation of BC from the adjacent land by frequent strong winds which were produced during previous interglacials, rather than implying high occurrences of paleofires during glacials on the land (Verardo and Ruddiman, 1996). Of course, contemporary changes in weather and vegetation are known to influence the extent of burning in different regions of the world, with the effects of El Niño being especially dramatic, for example (van der Werf et al., 2004).

Until recently, there have been no continuous, long-term, records of BC concentrations in sediments measured by TOR. Our findings highlight the advantages of applying this technique to studies of loess sediments. The pattern of BC in the Luochuan loess-paleosol section was found to mirror the variations in magnetic susceptibility, and this implies that the paleofires in the region over a ~150 kyr B.P. period were related to the strength of the East Asia summer monsoon. The apparent relationship between BC and climate was likely mediated through the supply of fuel for the fires. That is, the climate was warmer and wetter when the summer monsoon dominated: this stimulated vegetative growth, and as a result, more fuel was available for the fires. In summary, our study demonstrates that the TOR method is well suited for reconstructing the histories of paleofires and relating the observed trends to proxies of paleoclimate. As a tool that facilitates such reconstructions, further applications of the TOR method will improve our understanding of the linkages between fire regimes, fuel loads and climate change at local and regional or even hemispheric to global scales.

4. Conclusions

BC concentrations determined by four analytical methods were systematically different, and those differences can be explained in large measure by the fact that the methods analyzed different components of the BC. However, at the same time, we cannot ignore the inherent limitations of the methods, especially potential artifacts introduced during sample preparation. Standard additions showed that TOR was well suited for measuring BC in complex environmental samples, specifically loess and lake sediments. Although there were offsets in concentrations, the BC measurements obtained using CTO were correlated with both the BC and soot values obtained by TOR.

The application of the TOR method to study the distribution of BC in the Luochuan loess section indicates that BC abundances were generally high during last interglacial and low during last glacial, which is consistent with the findings for the Lingtai section obtained by Zhou et al. (2007) who evaluated the history of paleofires and paleoclimate in this region over the past 150 ka B.P. These authors also stressed the importance of abrupt climate change on

Table 4
Comparison of BC concentrations in different loess sections.

Loess section	Age (ka B.P.)	Analytical method	BC concentration (%)			Reference
			Average	Maximum	Minimum	
Weinan	150	Dichromate oxidation	0.26	0.75	0.1	Yang (2000)
Lijiayuan	220	Dichromate oxidation	1.84	– ^a	–	Wang et al., (2005)
Lingtai	220	Dichromate oxidation	1.78	–	–	Wang et al., (2005)
Weinan	220	Dichromate oxidation	1.24	3.5	0.41	Wang et al., (2005)
Lingtai	420	Dichromate oxidation	0.22	0.43	0.05	Zhou et al., (2007)
Luochuan	~150 ^b	TOR	0.22	0.98	0.04	This study

^a Blank indicates unknown.

^b Source: Heslop et al. (2000).

the incidences and intensities of fires. They proposed that frequent and intense fires occurred during rapid transitions from wet to dry conditions. Continued applications of TOR methods to studies of BC concentrations in loess will provide a basis for better understanding of the relationships between fires and climate over geological time.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.12.011>.

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