

Comparison of Elemental Carbon in Lake Sediments Measured by Three Different Methods and 150-Year Pollution History in Eastern China

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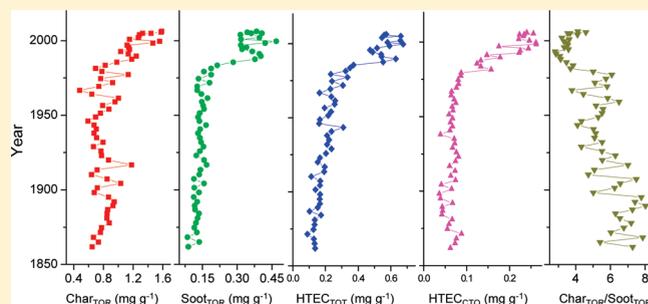
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S Supporting Information

ABSTRACT: Concentrations of elemental carbon (EC) were measured in a 150 yr sediment record collected from Lake Chaohu in Anhui Province, eastern China, using three different thermal analytical methods: IMPROVE_A thermal optical reflectance (TOR), STN_thermal optical transmittance (TOT), and chemothermal oxidation (CTO). Distribution patterns for EC concentrations are different among the three methods, most likely due to the operational definition of EC and different temperature treatments prescribed for each method. However, similar profiles were found for high-temperature EC fractions among different methods. Historical soot_{TOR} (high-temperature EC fractions measured by the IMPROVE_A TOR method) from Lake Chaohu exhibited stable low concentrations prior to the late 1970s and a sharp increase thereafter, corresponding well with the rapid industrialization of China in the last three decades. This may suggest that high-temperature thermal protocols are suitable for differentiating between soot and other carbon fractions. A similar soot_{TOR} record was also obtained from Lake Taihu (~200 km away), suggesting a regional source of soot. The ratio of char_{TOR} (low-temperature EC fraction measured by the IMPROVE_A TOR method, after correction for pyrolysis) to soot_{TOR} in Lake Chaohu shows an overall decreasing trend, consistent with gradual changes in fuel use from wood burning to increasing fossil fuel combustions. Average higher char_{TOR}/soot_{TOR} was observed in Lake Taihu than in Lake Chaohu in the past 150 years, consistent with the longer and more extensive industrialization around the Taihu region.



INTRODUCTION

Elemental carbon (EC) in the atmosphere absorbs light and plays a role in Earth radiative balance and climate change.¹ However, EC is not a well-defined constituent, but a collective term, which refers to a combustion continuum, ranging from slightly charred, degradable biomass to highly condensed, refractory soot.² EC can be formed fundamentally by two pathways, corresponding to two types of EC: char and soot. Char is combustion residue formed directly from the partial burning or heating of carbonaceous material in a low-oxygen (O₂) environment and can retain the morphology of its source material.³ Soot is composed of submicrometer particles of grapelike clusters formed from the condensation of hydrocarbon radicals at high temperature (>600 °C).³ Although char and soot may share common combustion sources, the two constituents have different physical and chemical properties.²⁻⁴ For example, the typical particle size distributions of char (generally 1–100 μm) and soot (submicrometer) are different,² which result in different

transport modes and distances^{2,3,5} and different light absorption characteristics.⁶ Thus, it is essential to differentiate between char and soot in the environment to gain a better understanding of their environmental and climatic impacts.

There are many established methods for EC quantification. However, the results vary greatly for a given material because the detection efficiency of different methods may vary across the EC continuum, and some methods may incorrectly identify organic carbon (OC) as EC.⁷⁻⁹ It is also unclear how selective different methods are with regard to identifying specific EC components (e.g., char and soot). Both laboratory-produced EC-rich materials and environmental matrices such as soils and sediments have been tested to evaluate the effects of potential

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interference on EC determination.^{7,8} Although studies on EC pollution (e.g., refs 10–13) and the historical reconstruction of atmospheric EC deposition using lake sediments^{14,15} have been conducted, it has yet to be determined if there is a preferred method for these types of studies.

In this study, we compare EC results from previously dated sediment samples from Lake Chaohu in Anhui Province, eastern China,¹⁸ using three analytical methods: chemothermal oxidation (CTO);¹² thermal optical reflectance (TOR) following IMPROVE_A protocol;¹⁶ and thermal optical transmittance (TOT) following STN protocol.¹⁷ The CTO method was chosen because of its widespread use in sediment studies and for its ability to provide estimates of soot carbon concentrations.^{12,19,20} The TOR method was selected because of its ability to quantify both char and soot based on its stepwise oxidation of different carbon fractions under different temperatures and atmosphere,²¹ and the TOT method was chosen because of its recent application to reconstruct atmospheric EC deposition using lake sediments.^{14,15} This article elaborates the suitability of the different methods for reconstructing the EC pollution history, presents historical char and soot reconstructions from both Lake Chaohu and Lake Taihu (~200 km away in Jiangsu Province), and discusses the possibility of a regional source of soot.

2. EXPERIMENTAL SECTION

Two sediment cores were recovered from Lake Chaohu in 2006 and Lake Taihu in 2003, respectively, in eastern China (Figure S1 of the Supporting Information for a detailed description of the research sites). Details regarding sampling sites, core collection, sample processing, and the establishment of deposition chronology were published elsewhere.^{18,22} The sediments cores were subsampled continuously at 1 and 0.5 cm intervals for Lake Chaohu and Lake Taihu, respectively. Both natural (²¹⁰Pb and ²²⁶Ra) and anthropogenic (¹³⁷Cs) radionuclides were measured and used to establish deposition chronologies of the two cores.^{18,22}

Sediment samples from Lake Chaohu were measured for EC concentrations using three protocols: IMPROVE_A TOR^{16,23,24} (with Thermogram shown in Figure S3 of the Supporting Information), STN_TOT^{14,17} (with Thermogram shown in Figure S4 of the Supporting Information), and CTO,^{19,20} whereas samples from Lake Taihu were measured only with the IMPROVE_A TOR method. For all sediment samples, acid pretreatment is needed before EC analysis. Although there are some differences in the pretreatment among the three protocols,^{15,19,24} the principles are similar, that is, to remove carbonate, mineral dust, and metal oxides to minimize the interference on carbon analysis. Only the procedure by Han et al.²⁴ was used in this study. Briefly, sediment samples were oven-dried, homogenized, and pretreated with hydrochloric (HCl) and hydrofluoric (HF) acids (Figure S2 of the Supporting Information for a schematic). The residues were then filtered onto pre-fired quartz filters and analyzed using the different EC protocols (Table S1 of the Supporting Information). Carbon liberated at different temperature protocols and analysis atmospheres was quantified using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc. Calabasas, CA).

Thermal evolution methods assume that low-volatility EC fractions are not liberated in an inert He atmosphere, allowing it to be separated from the more volatile OC.^{17,23} IMPROVE_A TOR

and STN_TOT apply low- and high-temperature protocols, respectively, to separate OC from EC. Heating in an O₂-free environment, however, can cause some OC to pyrolyze and form nonvolatile, light-absorbing char that could be misclassified as EC. To ensure that POC produced in the inert atmosphere is measured as part of OC instead of EC, the reflectance or transmittance of a filter is monitored during thermal analysis. POC is defined as the carbon measured after the introduction of a He/O₂ atmosphere but before reflectance or transmittance returns to its initial value (Figures S3 and S4 of the Supporting Information). The most important difference between the two methods is the duration of heating steps. IMPROVE_A TOR uses flexible time length; each consecutive step of heating occurs when the flame ionization detector (FID) returns to baseline or remains constant for more than 30 s such that to make sure that each kind of carbon with similar refractory properties can be completely evolved in each temperature. STN_TOT applies fixed time length of 45–120 s for each heating step (Table S1 of the Supporting Information). For both protocols, EC is defined as the sum of the carbon liberated as a result of heating in a He/O₂ environment minus POC.

The CTO protocol preheats samples for 16–24 h in an ambient air at 375 °C^{19,20,25,26} and assumes that there is no losses in EC. For samples analyzed using the CTO protocol in this study, filter residues were combusted for 18 h in a muffle furnace after the acid pretreatment.²⁰ Because only a small amount of carbon residues were available after CTO-375 pretreatment, the filter samples were analyzed following the IMPROVE_A TOR protocol.²⁴ In essence, our evaluation of the CTO method is specifically limited to the effects of sample combustion prior to EC determination.

3. RESULTS AND DISCUSSION

3.1. Comparison of EC Concentrations and Distributions Measured with the Different Methods. The different terms and their definitions used in this study are presented in Table 1. TC_{TOR} and TC_{TOT} are total carbon (TC, the sum of all OC and EC fractions) measured by the IMPROVE_A TOR and STN_TOT methods, respectively, after the acid pretreatment. EC_{TOR} and EC_{TOT} are EC measured with the IMPROVE_A TOR and STN_TOT methods, respectively, after acid pretreatment, whereas EC_{CTO} is defined as TC measured with the IMPROVE_A TOR method after both acid and CTO-375 pretreatments, following the definition of Gustafsson et al.¹⁹ According to Han et al.,²¹ char_{TOR} and soot_{TOR} are low- and high-temperature EC respectively measured by the IMPROVE_A TOR method, and char_{TOR} is defined as EC1 (evolved at 580 °C) minus POC; whereas soot_{TOR} is defined as the sum of EC2 (evolved at 740 °C) and EC3 (evolved at 840 °C). Similar to soot_{TOR}, HTEC_{TOT} is also high-temperature EC measured with the STN_TOT method (the sum of EC3, EC4 and EC5, which are evolved at 750, 850, and 925 °C, respectively), whereas HTEC_{CTO} is high-temperature EC measured with the IMPROVE_A TOR method (the sum of EC2 and EC3, which are evolved at 740 and 840 °C, respectively) after both acid and CTO-375 pretreatments.

For samples from the Lake Chaohu core, TC_{TOR} and TC_{TOT} are highly correlated ($R = 0.99$), with a near-unity slope (1.005) (Figure S5 of the Supporting Information), confirming an even distribution of residues on filter.

The comparison of the three different EC profiles (Figure 1) indicates that they are not consistent to each other in detail,

Table 1. Terms and Their Definitions Used in This Study

terms	pretreatment	protocol	temperature	atmosphere	definition
TC _{TOR}	acid	IMPROVE_A TOR	<840 °C	He and O ₂ /He	TC after acid pretreatment
TC _{TOT}	acid	STN_TOT	<925 °C	He and O ₂ /He	TC after acid pretreatment
EC _{TOR}	acid	IMPROVE_A TOR	<840 °C	O ₂ /He	EC1 + EC2 + EC3 – POC ^c
EC _{TOT}	acid	STN_TOT	<925 °C	O ₂ /He	EC1 + EC2 + EC3 + EC4 + EC5 – POC ^c
EC _{CTO} ^a	acid + CTO-375	IMPROVE_A TOR	<840 °C	He and O ₂ /He	TC after CTO-375 pretreatment ^d
char _{TOR} ^b	acid	IMPROVE_A TOR	<580 °C	O ₂ /He	EC1 – POC ^c
soot _{TOR} ^b	acid	IMPROVE_A TOR	>580–840 °C	O ₂ /He	EC2 + EC3
HTEC _{TOT}	acid	STN_TOT	>675–925 °C	O ₂ /He	EC3 + EC4 + EC5
HTEC _{CTO}	acid + CTO-375	IMPROVE_A TOR	>580–840 °C	O ₂ /He	EC2 + EC3

^aThe EC_{CTO} is the total carbon (TC, the sum of all OC and EC fractions) measured by the IMPROVE_A TOR protocol after the CTO-375 pretreatment following its original definition from Gustafsson et al.¹² ^bThe definition of char_{TOR} and soot_{TOR} are from Han et al.²¹ Char_{TOR} reflects low-temperature EC (EC1 evolved at 580 °C in a 2% O₂/98% He atmosphere, after correction for pyrolysis), whereas soot_{TOR} means high-temperature EC, i.e. the sum of EC2 (evolved at 740 °C) and EC3 (evolved at 840 °C). ^cPyrolyzed organic carbon (POC) is produced in the inert atmosphere and defined as the carbon that evolves to the time at which the laser reflectance (or transmittance) achieves its initial value after 2% of O₂ is added to the He atmosphere. ^dCTO-375 pretreatment means that samples were combusted at 375 °C for 18 h in air before carbon analysis.

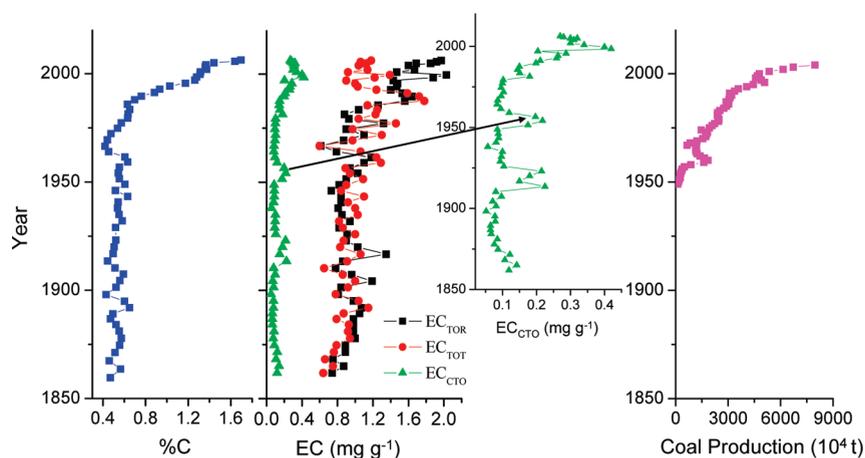


Figure 1. Comparison of historical EC variations measured with the IMPROVE_A TOR, STN_TOT, and CTO methods in Lake Chaohu, as well as total organic carbon (TOC) profiles.¹⁸ The coal production from 1949 to 2004 in Anhui Province, China, is also presented to indicate its contribution to EC profiles.

which may be partly associated with that all EC methods are operationally defined with clear-cut but different boundaries and developed for specific scientific questions. For example, in aerosol studies the TOR method was originally designed for an ambient environmental OC/EC measurement, whereas the TOT method was thought to measure, mainly source samples²³ with small influence from ambient solid particles. The CTO method intends to quantify soot carbon,^{12,19} whereas another chemothermal method was designed for combustion residues.²⁷ In fact, there is no clear-cut line between some forms of macro-organic carbon such as the humiclike materials and kerogen and so forth, and char, which is located in the end of the EC combustion continuum with low chemical refractiveness.² Previous studies^{7–9} had suggested that different methods can result in large EC differences, and the differences are not consistent with some methods showing higher EC for one set of samples and lower EC for other sets.

Average EC_{TOR} is about 10% higher than that of EC_{TOT} (Table S2 of the Supporting Information). However, similar concentrations and temporal trends were found from preindustrial

period to the early 1990s, with average values of 0.97 mg g⁻¹ for EC_{TOR} and 0.99 mg g⁻¹ for EC_{TOT}, respectively, at this period. After 1990, the difference between EC_{TOR} and EC_{TOT} became apparent with increasing EC_{TOR} and decreasing EC_{TOT} trends (Figure 1). This may be attributed to the incomplete removal of some metal oxides in the pretreatment. Because the STN_TOT method applies a high-temperature protocol (OC4 at 900 °C, Table S1 of the Supporting Information) to evolve OC in pure He atmosphere, metal oxides, if existing in the pretreated filter samples, can release O₂ and thus oxidize EC and POC.²⁸ Examining carbon thermograms reveals that transmittance signals returning to its initial value can occur during high-temperature OC analysis (OC4 stage), leading to negative POC values, confirming the oxidization of EC or POC in the inert atmosphere. It is strange that this phenomenon was only observed in the lower part samples (before ~1990) rather than in the upper part samples. We suggest that the upper part samples should also contain some, maybe more, metal oxides in filter residues because they contain higher concentrations of major and most trace elements.¹⁸ For the lower part samples, the negative POC values can partly offset the losses

of EC and POC when they return as an EC part. However, the upper part samples have higher OC contents (Figure 1), and thus can produce more POC in the analysis procedure, which would obscure the signal of POC oxidation, resulting in positive POC values. As the mixed signal of OC charring and EC oxidation due to existing metal oxides cannot accurately reflect the real POC, the measured EC may not be correct. In contrast, because the IMPROVE_A TOR method applies a relatively low-temperature protocol (580 °C for OC4) to evolve OC in inert atmosphere, the EC and POC oxidation, even when metal oxides exist in the samples, would be minimized.²⁸

The average EC_{CTO} , which was suggested as soot carbon in previous studies,⁷ is the lowest one among the three methods, accounting for one-seventh of that of EC_{TOR} (Table S2 of the Supporting Information), indicating the long-term (18 h) combustion effect. Temporal trends showed an abrupt increase in both EC_{TOR} and EC_{CTO} concentrations after the late 1970s. However, before the late 1970s, EC_{TOR} showed relatively small fluctuation, whereas two high-concentration periods occurred for EC_{CTO} during 1913–1922 and 1951–1956 (Figure S6 of the Supporting Information). The 1951–1956 peak may be coincident with the beginning of extensive coal usage in Anhui Province due to the establishment of the People's Republic of China (Figure 1). However, the reason for the 1913–1922 peak remains unknown. During the three EC_{CTO} peak periods, that is 1913–1922, 1951–1956, and post-1970s (Figure S6 of the Supporting Information), EC_{CTO} concentrations are much higher than their corresponding $HTEC_{CTO}$ concentrations. Examining carbon thermograms finds abundance of high-temperature OC (OC4 at 580 °C in inert He atmosphere) and low-temperature EC (EC1 at 580 °C in 2% O₂/98% He atmosphere) occurring for these samples. This suggests that some highly polymerized and aromatic materials were not fully oxidized in CTO-375 pretreatment.

The comparison of the three EC historical profiles with the historical coal production in Anhui Province, which mainly serves the eastern China (Figure 1), indicates that EC_{TOR} seems much more consistent with the coal usage in eastern China. However, this does not get the conclusion that the IMPROVE_A TOR method is better than the other two to reflect EC pollution history. Biomass burning is another source of EC, especially for char, in Lake Chaohu region, which is surrounded with agricultural land, and fire wood is still commonly used as fuel. However, historical fire wood consumption cannot be estimated, which limits our evaluation of which is the better method for EC pollution. In addition, char is easily incorporated into local soils, and thus a small fire event can significantly influence EC concentrations in lake sediments.

3.2. Comparison of Soot_{TOR} with HTEC_{TOT} and HTEC_{CTO}. Compared with char, the structure of soot carbon is more graphitic,³ leading to a higher temperature combustion. Figure 2 shows similar profiles among the three high-temperature EC, including soot_{TOR}, HTEC_{TOT}, and HTEC_{CTO}, in Lake Chaohu, with high correlation coefficients among the three parameters (Table S3 of the Supporting Information). Although HTEC_{TOT} evolves at a higher temperature (>675 °C) than soot_{TOR} (>580 °C), its average concentration ($0.30 \pm 0.18 \text{ mg g}^{-1}$) is ~ 1.5 times that of soot_{TOR} ($0.20 \pm 0.11 \text{ mg g}^{-1}$). This is mainly due to the different time setting of the two protocols. In contrast to a flexible time setting of the IMPROVE_A TOR method, which ensures a complete combustion of each carbon fraction, the STN_TOT method allows a fixed time length

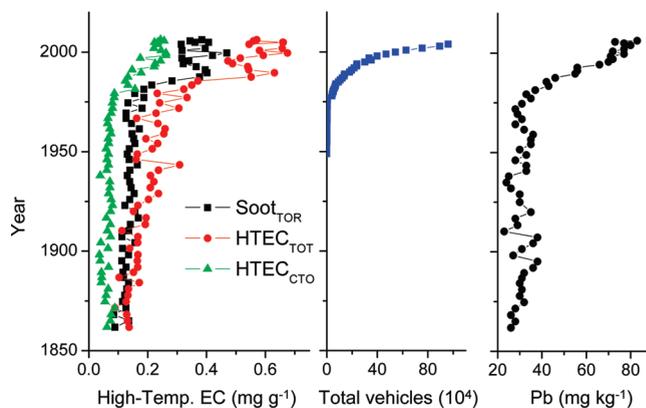


Figure 2. Comparison of historical variations of soot carbon measured by the IMPROVE_A TOR method (soot_{TOR}, the sum of EC2 and EC3, which are evolved at 740 and 840 °C in 2% O₂/98% He atmosphere, respectively) with high-temperature EC measured by the STN_TOT method (HTEC_{TOT}, the sum of EC3, EC4, and EC5, which are evolved at 750, 850, and 925 °C in 2% O₂/98% He atmosphere, respectively) and by the IMPROVE_A TOR method after the CTO-375 pretreatment (HTEC_{CTO}, the sum of EC2 and EC3, which are evolved at 740 and 840 °C in 2% O₂/98% He atmosphere, respectively) in Lake Chaohu, with the total number of vehicles (from 1949 to 2004) in the Anhui Province and lead concentration profile¹⁸ presented here to reflect the gasoline consumption.

(45–120 s) to evolve each carbon fraction, which is possibly not enough for a complete combustion of a certain carbon fraction, especially when carbon content is high.^{23,29} Those unburned carbon will evolve in the next heating steps, causing higher EC values in the high-temperature fractions. Greater discrepancies between soot_{TOR} and HTEC_{TOT} (Figure 2) occurred after the late 1970s, when TOC concentrations are relatively high (Figure 1), suggesting that this is a case.

The CTO protocol uses low temperature and very long-term (16–24 h) heating to separate soot from other carbon fractions; some soot particles can also be oxidized in this pretreatment.^{7,30} The averaged 150-year EC_{CTO} concentration ($0.16 \pm 0.09 \text{ mg g}^{-1}$) is even lower than that of soot_{TOR} ($0.20 \pm 0.11 \text{ mg g}^{-1}$). The average concentration of HTEC_{CTO} ($0.11 \pm 0.07 \text{ mg g}^{-1}$) is only approximately half that of soot_{TOR} ($0.20 \pm 0.11 \text{ mg g}^{-1}$), confirming the oxidation of soot in the CTO-375 pretreatment. All three profiles of high-temperature EC showed low but slowly increasing concentrations before 1978, and an abrupt increase thereafter, which are consistent with the time trends of coal consumption and motor vehicle emissions associated with the industrialization of China, reflected from the lead profile¹⁸ and the total number of motor vehicles in Anhui Province (Figure 2). This suggests that high-temperature thermal protocols may be more suitable for soot determination.

3.3. Different Sources for Char and Soot. The temporal variations of char_{TOR} and soot_{TOR} and their ratios in Lake Chaohu are presented in Figure 3. Through out the core, char_{TOR} is a dominant component of EC_{TOR} (>70% in average) (Table S2 of the Supporting Information) and has a similar vertical profile to EC_{TOR} (Figure S7 of the Supporting Information). However, soot_{TOR} exhibited a different profile from char_{TOR}.

Though combustion produces both char and soot, the ratio of char_{TOR} to soot_{TOR} differs among sources.^{6,31,32} Biomass burning and coal combustion have a wide range in the ratio

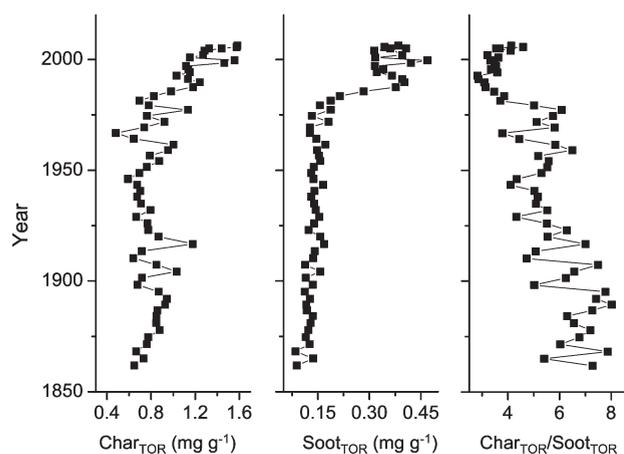


Figure 3. Historical variations of char_{TOR} and soot_{TOR} measured by the IMPROVE_A TOR method, as well as their ratio ($\text{char}_{\text{TOR}}/\text{soot}_{\text{TOR}}$) in Lake Chaohu.

of $\text{char}_{\text{TOR}}/\text{soot}_{\text{TOR}}$ (from 1.2 to ~ 68),⁶ depending on the fuel type, combustion temperature, air to fuel ratio, and so forth. For example, bituminous coal produces a much higher $\text{char}_{\text{TOR}}/\text{soot}_{\text{TOR}}$ ratio than anthracite coal (ratio < 4).⁶ In contrast, motor vehicle exhausts have a ratio typically lower than unity.^{6,31} Therefore, the $\text{char}_{\text{TOR}}/\text{soot}_{\text{TOR}}$ ratio may be useful in source identification. As shown in Figure 3, there is an apparent decrease of $\text{char}_{\text{TOR}}/\text{soot}_{\text{TOR}}$ ratios from the preindustrial period to the 2000s, reflecting the shift of energy usage in the past 150 years, from biomass burning to the increasing coal combustion, and from the late 1970s motor vehicle emissions increase.

Whereas char_{TOR} still increased after the early 1990s (Figure S7 of the Supporting Information), coincident with the increase in coal consumption, the soot_{TOR} fluctuated around 0.34 mg g^{-1} . The nonincrease in soot_{TOR} concentration is likely associated with the implementation of the pollution emission control policy by the Chinese government after the beginning of the 1990s. The implementation results are plausible. For example, the energy consumption per unit (ton standard coal per 10^4 RMB) decreased from 13.2 in 1980 to 2.8 in 1994, and decreased continually thereafter (<http://tongji.cnki.net>). Streets³³ also observed the reduction in China's EC and greenhouse gas emissions in the 1990s.

3.4. Long Range EC Pollution History Reconstructed from Soot_{TOR} Variations. Historical variation of sedimentary char_{TOR} and soot_{TOR} concentrations in Lakes Chaohu and Taihu (Figure 4) reveals different profiles for char_{TOR} but similar trends for soot_{TOR} . The areas surrounding Lake Taihu were much more industrialized than Lake Chaohu, especially in the past 30 years (Supporting Information). Average char_{TOR} in Lake Taihu (0.60 mg g^{-1}) in the past 150 years was lower than that in Lake Chaohu (0.93 mg g^{-1}), consistent with more intense residential wood combustions surrounding Lake Chaohu. Several studies suggested that biomass burning produces much more char than fossil fuels,^{31,32} and the overall $\text{char}_{\text{TOR}}/\text{soot}_{\text{TOR}}$ ratios (Figure S8 of the Supporting Information) are considerably lower at Taihu than Chaohu (Figure 3).

Char_{TOR} showed large variability in Lake Taihu (Figure 4). The lowest char_{TOR} concentrations appeared in the period of 1850 to 1870, with a rapid increase afterward and peaked around 1890, consistent with the timing of the Westernization Movement in China (1861–1894).³⁴ The decrease of char_{TOR} concentrations

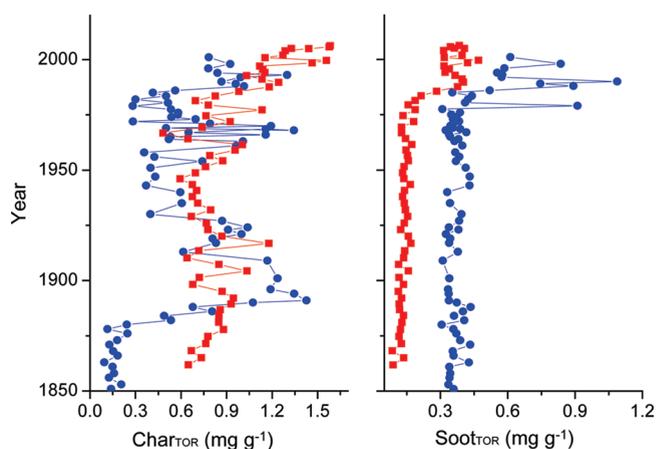


Figure 4. Comparison of char and soot measured by the IMPROVE_A TOR protocol (char_{TOR} and soot_{TOR}) in Lake Chaohu (red squares) and Lake Taihu (blue cycles). The similarity of soot_{TOR} profiles in the two lakes suggests the regional dispersion of soot particles.

after 1890 is consistent with the long-term war activities that occurred in China from 1895 to 1949. Char_{TOR} in Lake Taihu also increased during the late 1960s and the early 1990s. Because char is produced mainly in low-temperature combustion processes and has a large particle size,² a high concentration of char_{TOR} can be attributed to local biomass burning and pollution events (i.e., industrial activities).

Because of the longer and more extensive industrialization occurring around Taihu region,³⁴ the average 150-year soot_{TOR} concentration in Lake Taihu (0.42 mg g^{-1}) is about twice that of Lake Chaohu (0.20 mg g^{-1}) (Figure 4). However, a similar historical pattern of soot_{TOR} was observed in both lakes (Figure 4), with stable low concentrations before 1978, and a rapid increase thereafter. Average post-1978 soot_{TOR} concentration (0.35 mg g^{-1}) was ~ 2.5 times higher than that of pre-1978 (0.14 mg g^{-1}) in Chaohu region; this increase rate is similar to the atmospheric EC variations recorded in the Tibetan Plateau from an ice core of the Zouqiupu region.³⁵ Lake Taihu displays a relatively large variation in soot_{TOR} concentrations at the top of the core, which may be attributed to postdepositional disturbance.^{22,36}

Soot particles enter waters generally through the three pathways, that is, atmospheric deposition, riverine inputs, and surface runoff. Atmospheric soot is normally widespread dispersed.^{3,5} For example, our 14 city air quality investigations found similar soot_{TOR} levels among different cities despite different pollution mixtures.³⁷ Riverine inputs and surface runoff would entrain elevated soot from urban areas.³⁸ However, this part of soot can be redistributed in big lakes such as Lakes Daihai and Taihu with large drainage areas (Supporting Information). In addition, as soot is generally of submicrometer size, it is easily lofted by fires and emitted to the air,^{3,5} and some soot from local combustions can also be redistributed in the atmosphere. Thus, it is reasonable to suggest that the temporal soot trend reflects the variation of regional soot pollution.

■ ASSOCIATED CONTENT

S Supporting Information. The research site provides the basic information of Lakes Chaohu and Taihu. Figures show the locations of the two sediment cores, with sample pretreated

processes for the three EC analysis methods illustrated; thermograms for the IMPROVE_A TOR and STN_TOT methods, respectively, and the correlation between TC_{TOR} and TC_{TOT} in Lake Chaohu; comparison of EC_{CTO} and HTEC_{CTO}, and EC_{TOR} and char_{TOR}, respectively, in Lake Chaohu, and historical variation of char_{TOR}/soot_{TOR} ratio in Lake Taihu. Tables of details the three carbon analysis protocols used to compare the IMPROVE_A TOR, STN_TOT, and CTO methods; a summary of different carbon fraction concentrations in Lake Chaohu; and the correlation matrix among different carbon contents and lead in Lake Chaohu. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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