

Harmonizing Aerosol Carbon Measurements between Two Conventional Thermal/Optical Analysis Methods

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S Supporting Information

ABSTRACT: Although total carbon (TC) can be consistently quantified by various aerosol carbon measurement methods, the demarcation of TC into organic carbon (OC) and elemental carbon (EC) has long been inconsistent. The NIOSH and IMPROVE protocols are most widely used for thermal/optical analysis (TOA), but current knowledge rests in the description that the NIOSH protocol usually gives lower EC values than does the IMPROVE protocol. This study seeks to explore the possibility of quantitatively linking the difference between the two TOA protocols. Residential coal-burning samples that had been collected and analyzed following the NIOSH protocol in previous studies were directly reanalyzed following the IMPROVE protocol for this study. A comparison of each pair of NIOSH and IMPROVE EC values reveals the dynamic relation between the two protocols, which can be expressed as a regression equation, $y = (1-x)/(1 + 4.86x^2)$ ($R^2 = 0.96$), where the independent x is the EC/TC ratio ($R_{EC/TC}$) for the IMPROVE protocol, and the dependent y is the difference between IMPROVE and NIOSH $R_{EC/TC}$ relative to IMPROVE $R_{EC/TC}$. This regression equation may be the first effort in formulating the relationship between the two TOA protocols, and it is very helpful in harmonizing inconsistent TOA measurements, for example, source characterization, ambient monitoring, and atmospheric modeling.

INTRODUCTION

The inconsistency of aerosol carbon measurements due to the diversity of operationally defined analytical methods brings about considerable uncertainties in combustion source characterization, ambient monitoring, and atmospheric modeling.^{1–3} With its growing importance in anthropogenic emissions, carbonaceous aerosol will attract more scientific attention in atmospheric studies, especially in climate change analysis.²

Thermal-optical analysis (TOA) is a conventional technique for the determination of carbonaceous aerosol collected on quartz-filters. Based on the differences between organic carbon (OC) and elemental carbon (EC) in thermal and optical properties, TOA is defined using two progressive heating stages: The first stage is characterized by an inert atmosphere in which OC on a quartz-filter is volatilized or pyrolyzed; the second stage is conditioned in an oxidizing atmosphere where all the remaining carbonaceous particles are burned off. Carbon evolving from the filter is catalytically oxidized into CO₂, reduced to CH₄, and finally detected by a flame ionization detector. A laser beam is employed to monitor the real-time transmittance through or reflectance from the aerosol-laden filter during the thermographic analysis to correct for the overestimation of EC due to charring. The time when laser intensity regains its initial

value is construed as a split point, before and after which the carbon that evolves is designated as OC and EC, respectively.^{4,5}

The IMPROVE (Interagency Monitoring of Protected Visual Environment) and NIOSH (U.S. National Institute for Occupational Safety and Health) protocols are the most widely used TOA protocols in the atmospheric science community. The IMPROVE protocol⁵ has traditionally been applied to samples from nonurban background sites in the U.S. IMPROVE network and in 2005 was amended to the IMPROVE_A by elevating each step's apparent temperature about 20–40 °C.⁶ The NIOSH 5040 protocol was originally designed for assessment of the risk of diesel exhaust with EC as the surrogate for diesel particulate matter,⁴ and is used by the US Environmental Protection Agency (EPA) in the PM_{2.5} Chemical Speciation Trends Network (STN).^{7,8} Unlike the IMPROVE protocol, which specifies the temperature at every step, the NIOSH protocol only outlines the necessary principles for operation without detailing individual temperature parameters. As a result, there exist several NIOSH-derived

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programs that are usually referred to as a NIOSH protocol, for example, EPA-NIOSH (STN),^{7,8} EMEP/NIOSH,⁹ ACE-Asia,^{10–12} and Birch/NIOSH.¹³

Previous pillar papers have demonstrated that the NIOSH protocol always reports a lower EC value than the IMPROVE protocol,^{12,14–19} but there remains a major problem that the EC difference between NIOSH and IMPROVE measurements is not fixed, but is variable at even more than an order of magnitude from sample to sample, depending on the physical, morphological, and chemical properties of the samples originating from various fuels, sites, or processes.^{12,18} This leads to an ambiguous understanding of ambient measurements and inventory estimates of aerosol carbon, and it calls for a novel way to determine the relation between the two TOA results.

The present study tries to capitalize on the samples having been previously collected separately for other studies.^{20–22} Carbon results had previously been obtained by using a NIOSH-derived instrumental program^{20,23} similar to the Birch/NIOSH protocol.¹³ These samples had been kept in a refrigerator at a temperature below $-20\text{ }^{\circ}\text{C}$ until they were reanalyzed for this study following the IMPROVE protocol. As a result, each of the samples has two EC values measured respectively by the IMPROVE protocol in this study and by the NIOSH protocol in previous ones.^{21,23} Based on the comparison of paired-EC values, we were able to identify an EC/TC ratio ($R_{\text{EC/TC}}$) that was dictated by the relating model and thereby harmonize TOA-relevant OC/EC data in ambient monitoring, inventory estimates, and modeling results.

MATERIALS AND METHODS

Samples. Only a brief introduction of the samples used in this study will be made as all of them have been detailed in previous papers.^{20–22} In total, 61 samples were treated in two groups (Table 1). The first group contained 27 coal-burning samples that had been utilized in two of our studies addressing emission factors from residential coal burning in China.^{20,21} They were used to deduce a regression equation linking the two TOA methods. The second group had 34 samples, including 14 source samples and 20 urban samples; they had been employed in a study investigating the impacts of maximum temperature (T_{max}) and residence time on OC/EC measurements (NIOSH protocol)²² and can be used to verify the validity of the conclusions of this study. According to source apportionment studies, coal was a major contributor to PM10 or TC (second only to traffic emissions) in both Shanghai and Guangzhou, where urban samples in Group II were collected.^{24,25}

Analysis. This study employed the two popular TOA protocols: One is derived from Birch/NIOSH¹³ and has been used in two of our previous papers;^{20,23} the other is the IMPROVE protocol, established by Chow et al.^{5,6} (Table 2). Note that the IMPROVE protocol in Table 2 is an amended version of the original. It has been confirmed that the utilization of the amended version in a new generation of hardware (model 2001) does not shift the separation of OC/EC, maintaining the long-term consistency of the IMPROVE database.⁶ The data having been analyzed by a TOT carbon analyzer (Sunset Laboratory Inc., Forest Grove, OR) according to the NIOSH protocol were brought into direct use for this study. IMPROVE-data were newly acquired using a DRI model 2001 carbon analyzer following the IMPROVE protocol, with only the reflectance-corrected data being considered.

Table 1. Samples Used

Group I					
coal ID ^a	V_{daf}^b (%)	rank ^c	combination ^d		
			HEB/BRI	HEC/CHU	SEB/CHU
ZG	38.42	HVB	C1	C10	C19
YL	37.34	HVB	C2	C11	C20
XW	30.83	MVB	C3	C12	C21
DT	30.36	MVB	C4	C13	C22
CX	30.08	MVB	C5	C14	C23
XA	20.74	LVB	C6	C15	C24
CZ	16.00	LVB	C7	C16	C25
YQ	12.19	SA	C8	C17	C26
AY	8.09	SA	C9	C18	C27
Group II ^e					
source samples			ambient samples		
S1	anthracite coal burning		S15	SH-JD-20051012	
S2	raw bituminous smoke		S16	SH-JD-20051019	
S3	bituminous briquette smoke		S17	SH-JD-20051022	
S4	wood burning		S18	SH-JD-20051026	
S5	plastic burning		S19	SH-JD-20051030	
S6	tire burning		S20	SH-JD-20051102	
S7	paper combustion		S21	SH-JD-20060117	
S8	rice straw burning		S22	SH-JD-20060408	
S9	charcoal burning		S23	SH-JD-20060726	
S10	cigarette smoke		S24	SH-JD-20060805	
S11	idle diesel vehicle exhaust		S25	SH-YC-20051012	
S12	road vehicle exhaust		S26	SH-YC-20051015	
S13	charbroiling exhaust		S27	SH-YC-20060217	
S14	cooking exhaust		S28	SH-YC-20060423	
			S29	GZ-TH-20070110	
			S30	GZ-TH-20070111	
			S31	GZ-TH-20070113	
			S32	GZ-TH-20070114	
			S33	GZ-TH-20070115	
			S34	GZ-TH-20070117	

^a These coal IDs are the same as those in ref 20. ^b Volatile matter content on a dry and ash-free basis. ^c Rank by ASTM standard classification of coal (2004), SB is for semibituminous coal, HVB for high-volatile bituminous coal, MVB for medium-volatile bituminous coal, LVB for low-volatile bituminous coal, and SA for semianthracite. ^d Coal-stove types: SEB is for simple low-efficiency briquette-stove, HEB for high-efficiency briquette-stove, HEC for high-efficiency chunk-stove; burning styles: BRI is for honeycomb-coal-briquette, CHU is for raw-coal-chunk. ^e Refer to ref 22 for more details; ambient samples were collected in Shanghai's Jiading district (SH-JD), Yangchang Campus of Zhabei district (SH-YC), and Guangzhou's Tianhe district (GZ-TH).

RESULTS AND DISCUSSION

Paired $R_{\text{EC/TC}}$ Results for Group I and Inferred Deficiency in Current Knowledge. It has been proven many times that almost all heating-based methods have good agreement regarding TC, yet often disagree on how to divide TC into OC and EC.²⁶ Chow et al.¹⁸ found that the NIOSH EC was typically less than half of the IMPROVE EC. Our paired results for Group I are

Table 2. Thermal/Optical Analysis Protocols Used for This Study

carrier gas	carbon fractions	NIOSH ^a		IMPROVE ^b	
		temperature (°C)	time (s)	temperature (°C)	time (s)
He	OC1	250	60	140	160–580
	OC2	450	60	280	160–580
	OC3	650	60	480	160–580
	OC4	850	90	580	160–580
charring correction		transmission		reflection	
He/O ₂	EC1	550	45	580	160–580
	EC2	650	60	740	160–580
	EC3	750	60	840	160–580
	EC4	850	40		
	EC5	870	40		

^a Similar to Birch¹³. ^b Protocol used in IMPROVE aerosol data set for DRI Model 2001 since 2005. Residence time for each step is not fixed, but varies from 160–580 s, which is sufficient for each FID carbon peak to be well-defined.

shown in Table 3, indicating that NIOSH derived $R_{EC/TC}$ was 0.51 ± 0.30 (average \pm s) times IMPROVE EC.

The reason why NIOSH EC is usually lower than IMPROVE EC has been considerably investigated. There are three main factors that contribute, individually or jointly, to the inconsistency in EC results. The first factor, possibly the most important, relates to T_{max} .¹⁴ T_{max} for the NIOSH protocol is 850 °C or higher,^{4,8,13} whereas for the IMPROVE protocol, it is 580 °C or lower.^{5,6} Thus, there is a temperature difference of about 300 °C for the two protocols: Carbon released within this temperature range is defined as OC by NIOSH^{13,27} and is recognized as EC by IMPROVE.¹⁸ Zhi et al.²² found that the EC measurement with T_{max} at 850 °C accounted for about 60% of that at a T_{max} of 550 °C when the NIOSH protocol was used, demonstrating the critical importance of T_{max} in aerosol carbon fractioning. The second factor relates to charring. The NIOSH protocol tends to generate more pyrolytic carbon (PC) than the IMPROVE protocol does.^{14,15,17,22,27} PC generally has a higher light-absorbing efficiency than native EC, which mostly demands that, prior to the split point in the He/O₂ mode, more light-absorbing carbon (LAC, including native EC and PC) be burned to compensate for the charring-caused laser signal decreases, resulting in a lower EC in the NIOSH protocol.¹⁵ The third factor is the laser pattern for the charring correction (reflection or transmission). Studies have revealed that PC is always distributed throughout the filter section rather than only on or close to the filter's outer surface.^{16,17} When heated in oxygen, LAC near the filter surface (mainly native EC) is released earlier than that imbedded in the filter (mainly PC). As a result, the reflectance usually returns to the initial intensity more rapidly than transmittance does; in other words, the IMPROVE protocol tends to give an earlier OC/EC cut-point than the NIOSH protocol does,¹⁹ and possibly contributes to the higher EC values.

However, the above understanding that the IMPROVE protocol typically gives a higher EC than the NIOSH one does is at most a qualitative description instead of a quantitative prediction. The TOA protocol-caused biases on EC values are not consistent

Table 3. Measurements for Group I Samples

filter no.	IMPROVE $R_{EC/TC}$ (x)	NIOSH $R_{EC/TC}$	relative difference to IMPROVE $R_{EC/TC}$ (y)	predicted y	residual
C1	0.114	0.022	0.806	0.833	-0.028
C2	0.088	0.008	0.905	0.879	0.026
C3	0.121	0.015	0.878	0.821	0.058
C4	0.151	0.030	0.798	0.764	0.034
C5	0.131	0.021	0.842	0.802	0.040
C6	0.111	0.019	0.828	0.839	-0.011
C7	0.122	0.020	0.836	0.819	0.017
C8	0.159	0.043	0.730	0.749	-0.019
C9	0.188	0.049	0.741	0.693	0.048
C10	0.370	0.153	0.586	0.378	0.208
C11	0.613	0.552	0.100	0.137	-0.037
C12	0.810	0.757	0.066	0.045	0.020
C13	0.616	0.545	0.116	0.135	-0.019
C14	0.783	0.739	0.056	0.055	0.002
C15	0.547	0.456	0.167	0.185	-0.017
C16	0.463	0.364	0.213	0.263	-0.050
C17	0.342	0.215	0.371	0.420	-0.048
C18	0.137	0.045	0.672	0.791	-0.119
C19	0.152	0.044	0.709	0.762	-0.053
C20	0.400	0.242	0.396	0.338	0.058
C21	0.516	0.436	0.155	0.211	-0.056
C22	0.566	0.477	0.157	0.170	-0.012
C23	0.514	0.423	0.177	0.213	-0.036
C24	0.527	0.420	0.202	0.201	0.001
C25	0.301	0.138	0.540	0.485	0.054
C26	0.162	0.060	0.629	0.743	-0.114
C27	0.278	0.143	0.487	0.525	-0.038

but irregular depending on the sample's features, and thus, there is no simple relationship between each pair of measurements. It is still impossible for us to interchange EC values quantitatively between NIOSH and IMPROVE.^{12,18} Typical examples in Table 3 are C21 and C3, which in fact originated from the same bituminous coal (XW) but burned in chunk and briquette styles, respectively. The IMPROVE EC for C21 is only about 1.18 times the NIOSH EC, whereas for C3, it is elevated to more than 8.21 times. Of the 27 samples tested, IMPROVE EC is 1.07–10.48 times the NIOSH EC, which is indicative of a significant variability in the EC relationship. Schmid et al.²⁶ also showed that biases were not consistent from sample to sample for paired measurements from several thermal/optical protocols. There is a clear need in developing a dynamic relationship between the two measurements.

Bridging the Gap between the TOA-Caused EC Difference and IMPROVE $R_{EC/TC}$. Table 3 includes a derived column of “relative difference to IMPROVE $R_{EC/TC}$ ” denoting the difference between IMPROVE $R_{EC/TC}$ and NIOSH $R_{EC/TC}$ with respect to IMPROVE $R_{EC/TC}$. This column was assigned as a dependent variable, y , and IMPROVE $R_{EC/TC}$ was assigned as an independent variable, x . Note that assigning IMPROVE $R_{EC/TC}$ as x does not mean IMPROVE protocol is “truer” than NIOSH or other methods. As shown in Figure 1, an ordinate was accordingly set up, aimed at developing a formula or equation linking x and y . The target equation is supposed to conform to the following conditions: (i) the higher x , the lower y , which can

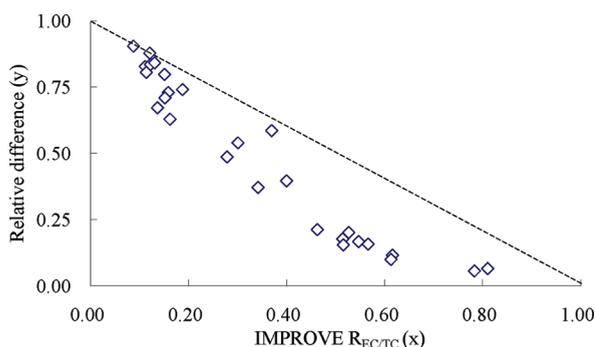


Figure 1. Group-I data layout used to deduce a regression equation linking two TOA $R_{EC/TC}$ values. All samples in Group-I are from coal-combustion. The dashed line is for $y = 1 - x$.

be clearly seen from Figure 1; (ii) when x approaches 0, y approaches 1, which applies to pure organic matter, and when x approaches 1, y approaches 0, which applies to graphitic carbon; and (iii) all the measured y values are below the line $y = 1 - x$. These conditions constrain the equation to be nonlinear, expressed as $y = (1 - x)/(1 + mx^n)$, where m is a positive constant and n is a positive whole number. With the help of the professional statistical analysis software SPSS16.0, we obtained a nonlinear regression equation, $y = (1 - x)/(1 + 4.86x^2)$ ($R^2 = 0.96$). According to this equation, the intertranslation of the TOA measurements becomes feasible; in other words, knowing either x or y makes it possible to determine y or x through the application of this equation.

The trend reflected in the formula is directly substantiated by the paired data in Table 3 since bituminous coal-chunks usually have higher $R_{EC/TC}$ than others, and their EC values as a result show less sensitivity to TOA protocols. By summary of the methods and comparisons, Watson et al.²⁸ found that many of the methods agreed on EC from diesel exhaust or powdered graphite samples, but they often disagreed for ambient and biomass-burning samples. This can possibly be attributed to the fact that $R_{EC/TC}$ for diesel exhaust (let alone powdered graphite) is usually higher than that for ambient and biomass burning samples.^{18,29}

The equation was developed via a statistical fit to measured data for China's coal burning rather than based on physical or chemical properties of the samples, yet its validity may result from the effects of OC fraction in carbonaceous aerosols. Total carbonaceous aerosols comprise a complex mixture that is classified mainly in two fractions: EC and OC. EC is the refractory fraction and is released only by oxidation at a certain temperature, for example, above 500 °C, whereas OC is the volatile fraction that is thermo-sensitive.²⁸ Samples with different OC fractions behave differently under the two TOA protocols characterized by different T_{max} values. First, it is OC instead of EC that pyrolyzes when heated in an inert atmosphere. As a result, higher OC/TC ratios (lower $R_{EC/TC}$) generally have more opportunity for charring, particularly using the NIOSH protocol that tends to generate more char than the IMPROVE protocol.^{14,22} As has just been pointed out, more charring in the NIOSH protocol usually leads to a decreased EC value, which exerts a greater influence on samples with a higher OC/TC ratio (lower $R_{EC/TC}$) in changing the $R_{EC/TC}$ measurement. Considering a sample with an OC/TC ratio of 0.9 ($R_{EC/TC} = 0.1$), if a tenth of the OC fraction is pyrolyzed, the measured $R_{EC/TC}$ will be fundamentally biased. By contrast, even if a sample with an OC/TC ratio of 0.1 ($R_{EC/TC} = 0.9$) pyrolyzed all of its OC, the

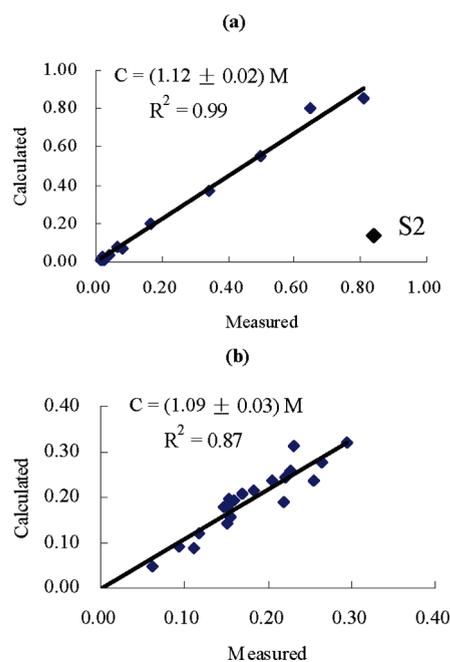


Figure 2. Agreement between measured and calculated NIOSH $R_{EC/TC}$ values for Group II samples. C and M stand for calculated and measured $R_{EC/TC}$, respectively. (a) Source samples (S1–S14, excluding S2); (b) urban samples (S15–S34). The regression equations were obtained through SPSS (intercepts were both set to zero). Included in each parentheses is slope \pm standard error.

measured $R_{EC/TC}$ would hardly be swayed remarkably. Second, brown carbon is often more abundant in biomass-burning samples or bioaerosol particles than it is in fossil fuel samples,³⁰ and biomass samples usually have a lower $R_{EC/TC}$ (higher OC/TC ratio) than fossil fuel samples do.^{29,31} Since brown carbon requires a higher combustion temperature than nonlight-absorbing OC does,^{30,32,33} the IMPROVE protocol tends to define more brown carbon as EC than the NIOSH protocol does. This is in part evidenced by Reisinger et al.³⁴ who found that the discrepancy between the thermal methods is linked to the percentage of brown carbon in total LAC. In summary, the between-protocol difference is enlarged by a higher OC abundance.

Experimental results also support the equation. First, for Group II samples, the directly measured NIOSH $R_{EC/TC}$ and the calculated NIOSH $R_{EC/TC}$ (through the equation) of each sample are plotted in Figure 2. They display a good correlation ($R^2 = 0.98$ for source samples and $R^2 = 0.87$ for urban samples). Note that the fitting in Figure 2a excludes S2, of which the measured NIOSH $R_{EC/TC}$ is significantly different from the calculated NIOSH $R_{EC/TC}$. Further examination indicated that, due to the overloading for S2, the monitored reflectance during IMPROVE evolution suddenly leveled off prior to the achievement of the initial value and thus resulted in a delayed OC/EC splitting, even much later than the transmitted laser did. As a result, IMPROVE reported a lower $R_{EC/TC}$ than NIOSH did, followed by an extremely low calculation of NIOSH $R_{EC/TC}$, shown in Figure 2. Chow et al.¹⁸ also noticed that the point at which the initial reflectance or transmittance was attained was uncertain for heavily loaded filters. Second, according to Chow et al.,¹⁸ for the total of 60 samples (41 ambient samples and 19 source samples) that were analyzed, the average $R_{EC/TC}$ was 23% for the IMPROVE protocol; by contrast, the

average $R_{EC/TC}$ dropped to 9% for the NIOSH protocol, coinciding with the 9% calculated from the regression equation. Third, Schauer³⁵ compiled the typical measurements for both the NIOSH and IMPROVE protocols and found that, for biomass emissions, the IMPROVE protocol typically measured the $R_{EC/TC}$ to be around 20% (15–25%) of the particle carbon, and, by contrast, the NIOSH method measured the $R_{EC/TC}$ to be around 5% (2–10%), which is very close to the 7% that was predicted by the regression equation. Fourth, examining the $R_{EC/TC}$ for reference material 8785⁸ it can be noted that the measured NIOSH $R_{EC/TC}$ 0.279 ± 0.023 can be converted to 0.440 ± 0.036 for IMPROVE $R_{EC/TC}$, in close agreement to one of the IMPROVE $R_{EC/TC}$, 0.465 ± 0.019 . It is also not significantly different from the recommended information value for the IMPROVE $R_{EC/TC}$ of 0.490 ± 0.050 (95% confidence). Note that the T_{max} of 900 °C in STN/NIOSH is 50 °C higher than the T_{max} of 850 °C for our experiment and was dealt with by extrapolation according to another paper.²²

Harmonizing TOA Measurements through the Recommended Equation. For the first time, the relationship between the two TOA protocols has been quantitatively characterized other than just qualitatively described, facilitating the data conversion between the TOA methods. This is very helpful in the fields that need uniform aerosol carbon fractioning.

First, the recommended formula can find its application in atmospheric aerosol carbon characterization. IMPROVE and NIOSH are both widely used in characterizing ambient carbonaceous aerosols in many sites for temporal or spatial variations. The protocol dependence of the measurement data discounts the intercomparability among different observation campaigns or efforts since many researchers have to ignore such an inconsistency when compiling their data. For example, Novokov et al.,³¹ aiming to correct for the positive artifacts of filter sampling, presented an analysis of OC/EC ratios derived from published OC and EC concentrations measured in mostly urban and some nonurban locations in Asia, Europe, and North America. However, they neglected the impact of different TOA protocols on the $R_{EC/TC}$ or OC/EC ratios. In a review on OC and EC in Asia from 1996 to 2006, although carbon concentrations were presented mainly from IMPROVE criteria, there was also one citation from NIOSH.³⁶ Yu et al.³⁷ attempted to compare the average EC level in Hong Kong with levels in other cities. Although the measured average EC concentration in Hong Kong (by NIOSH) was obviously lower than the EC concentrations reported for other cities (by IMPROVE), the authors still did not feel confident to determine whether the average EC concentration in Hong Kong was lower than or similar to the concentration in other cities. For the comparability of OC or EC data, some researchers had to choose data that were measured by a single protocol, for example, IMPROVE or NIOSH, rejecting other protocol data. This was seen when Feng et al.³⁸ intended to compare the ambient OC and EC levels in Shanghai with some other cities. They only took NIOSH data into account. Actually, with the regression equation, it is now possible to conduct an intertranslation between the NIOSH and IMPROVE protocols. Back to Yu et al.,³⁷ assuming that all of the EC values were measured with the IMPROVE protocol, the Hong Kong EC would be almost in the middle (Figure 3).

Other applications involve source apportionment, secondary OC (SOC) calculations, and the harmonization of inventory estimates. Current apportionment models or methods include EC in the list of source attribution, and the inconsistent EC

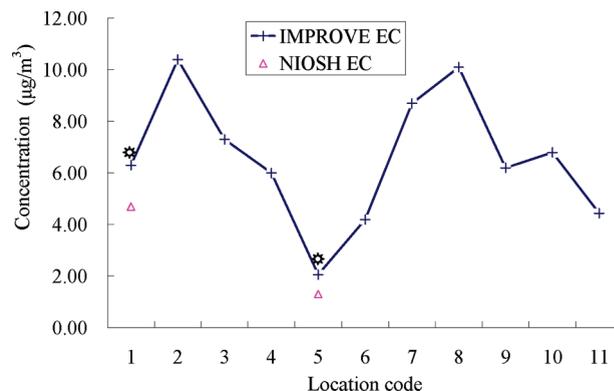


Figure 3. An example for harmonizing EC measurements through the recommended formula. IMPROVE EC concentrations for location-1 and -5 (labeled by star) are the conversions from NIOSH values (represented by red triangle). Data points without star marks are measured results tabulated in Yu et al.³⁷ (Table 3 therein). Locations are as follows: 1. Hong Kong; 2. Guangzhou; 3. Shenzhen; 4. Zhuhai; 5. Helsinki, Finland; 6. Los Angeles downtown, U.S.; 7. Beijing, Chengongzhuang; 8. Beijing, Tsinghua; 9. Shanghai, Tongji Univ.; 10. Shanghai, near downtown; 11. Chongju, Korea. Please consult the Supporting Information for more details.

concentrations from different methods may lead to a differed interpretation of the source contribution, particularly for wood smoke.³⁹ Secondary organic aerosol (SOA) plays an important role in atmospheric haze, visibility, climate, and human health, and the estimation of the contribution of SOA to the total ambient aerosol OC (TOC) is essential to the shaping of effective control strategies for particulate matter.⁴⁰ However, the typical method for estimating SOC is based on the measurement of OC/EC ratio. For example, Turpin and Huntzicker⁴¹ assumed: $SOC = TOC - EC \times (OC/EC)_{primary}$, where $(OC/EC)_{primary}$ is the ratio for primary source emissions. The observed OC/EC ratios exceeding 2.0 were used as $(OC/EC)_{primary}$ to identify the presence of secondary organic aerosols^{42–45} for the summertime afternoon samples at downwind receptors, suggesting the critical importance of the OC/EC ratio on SOA studies. Regarding inventory estimates, the current emission inventories usually include a mixture of EC and OC estimates/sources from different TOA protocols, or carbon content estimates roughly derived from mass.²⁹ The net climate effect of carbonaceous aerosols (warming or cooling) depends on the aerosol's single scattering albedo, which is the ratio of incoming solar radiation that is scattered to the incoming radiation that is absorbed by aerosols.³¹ Therefore, the lack of uniformity generates uncertainties when emission inventories' estimates are fed into atmospheric models and when finally the model outputs are compared to atmospheric results.¹ Relations obtained in the present study could be useful in harmonizing estimates in emission inventories, that is, translating them into a "single measure type".

Further Considerations. This study suggests a new approach to the old problem of how to reconcile EC measured with NIOSH protocol to EC measured with IMPROVE protocol. This is of particular importance when researchers on carbonaceous aerosols are theoretically and practically difficult to establish a standard method or accept an existing protocol (e.g., NIOSH, IMPROVE) as the "standard" worldwide. In fact, even after a standard TOA protocol is assigned, this bridge is still useful in linking existing data sets.

It should be noted that the equation is subject to modification or refinement through future concerted efforts. First, apart from OC abundance, there are also other possible causes for the discrepancy between NIOSH and IMPROVE protocols. For example, brown carbon can badly influence the OC/EC split,³⁰ metals in the sample can start to remove EC already in the inert gas mode,¹⁸ heavily loaded filter can change laser attenuation coefficient and charring rate,^{15,27} and differing abundances of SOA may have inconsistent influence on laser correction.⁴⁶ More importantly, the equation was deduced from coal-burning samples (Group I) and was directly verified by only 13 source samples and 20 urban samples (Group II), and more comprehensive and systematic verifications should be carried out for ambient samples with various regional features, difficult as this may be. For example in China, urban samples are usually heavily influenced by coal combustion,^{24,47} whereas in the U.S., most of the EU, or Africa, coal burning contributes little to urban samples (e.g., ref 48). So it will not be surprising if the constant ($m = 4.86$) in the equation is recalibrated after more comprehensive and rigorous experiments are conducted in pursuit of a wider applicability. In this respect, this study is more an advancement than finality for harmonization of aerosol carbon fractioning.

■ ASSOCIATED CONTENT

S Supporting Information. A table including more details about the samples in this paper's Figure 3 is provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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