



A newly identified calculation discrepancy of the Sunset semi-continuous carbon analyzer

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Abstract. The Sunset semi-continuous carbon analyzer (SCCA) is an instrument widely used for carbonaceous aerosol measurement. Despite previous validation work, in this study we identified a new type of SCCA calculation discrepancy caused by the default multipoint baseline correction method. When exceeding a certain threshold carbon load, multipoint correction could cause significant total carbon (TC) underestimation. This calculation discrepancy was characterized for both sucrose and ambient samples, with two protocols based on IMPROVE (Interagency Monitoring of PROtected Visual Environments) (i.e., IMPshort and IMPlong) and one NIOSH (National Institute for Occupational Safety and Health)-like protocol (rtNIOSH). For ambient samples, the IMPshort, IMPlong and rtNIOSH protocol underestimated 22, 36 and 12 % of TC, respectively, with the corresponding threshold being ~ 0 , 20 and 25 μgC . For sucrose, however, such discrepancy was observed only with the IMPshort protocol, indicating the need of more refractory SCCA calibration substance. Although the calculation discrepancy could be largely reduced by the single-point baseline correction method, the instrumental blanks of single-point method were higher. The correction method proposed was to use multipoint-corrected data when below the determined threshold, and use single-point results when beyond that threshold. The effectiveness of this correction method was supported by correlation with optical data.

1 Introduction

Carbonaceous aerosol, usually fractionated into elemental carbon (EC) and organic carbon (OC), is of increasing interest due to its important roles in human health and the environment. The most widely used method for aerosol OC / EC measurement is thermal–optical analysis, which classifies OC and EC based on their differences in both thermal and optical characteristics. The IMPROVE (Interagency Monitoring of PROtected Visual Environments) (Chow et al., 1993) and NIOSH (National Institute for Occupational Safety and Health) (Birch and Cary, 1996) protocols, as well as their variants (Watson et al., 2005; Chow et al., 2007b), are typically adopted in modern thermal–optical analysis. Compared with low time-resolution results (usually 24 h averages), hourly OC / EC data is more suitable for investigating the short-term patterns due to the variations of emission, transportation, gas-particle partitioning, chemical reaction, etc. Therefore, several (semi-)continuous instruments have been developed for carbonaceous aerosol measurement (e.g., aerosol mass spectrometer and single particle soot photometer). Among these instruments, the semi-continuous carbon (or OC / EC) analyzer (SCCA) manufactured by Sunset Laboratory Inc. (Beaverton, Oregon, USA) is the only one commercially available that could measure OC and EC simultaneously, and thus it was widely used in field measurements (Lin et al., 2009; Hu et al., 2012; Docherty et al., 2011).

The initial design of the SCCA was described in Birch and Cary (1996). The products have gone through several generations since then, and the newest version is

Model 4 developed in 2000 (Sunset Laboratory, 2014, <http://www.sunlab.com/about/about-us.html>). Several improvements have been made, such as the change from a flame ionization detector (FID) to a flow-through non-dispersive infrared (NDIR) system to reduce the requirement for consumable gases (air or hydrogen) at the field site (Bauer et al., 2009). The US EPA (Environmental Protection Agency) has recently launched the Sunset OC / EC Evaluation Project to evaluate the performance of Sunset Model 4 SCCA in various locations and conditions, as part of the preparation work for the use of Sunset SCCA as the routine instrument for long-term monitoring in the Chemical Speciation Network (Sunset OC / EC Evaluation Project, 2013, <http://www.epa.gov/ttnamti1/spesunset.html>).

Identified factors that affect the accuracy of SCCA results generally fall into two categories: namely, artifacts produced during the sampling process and those that interfere the thermal–optical analysis. The positive and negative sampling artifacts can be largely reduced with efficient denuders and a backup quartz filter (Lin et al., 2009; Arhami et al., 2006). Identified analysis interferences included (a) the inorganic carbonate particulate matter. The concentration of carbonate carbon was generally small compared to total carbon (TC, sum of OC and EC). When needed, it could be quantified manually since the SCCA allows it to appear as a unique peak (Karanasiou et al., 2011). (b) Refractory metal oxides, which influence thermal–optical analysis results in two ways. The first of which is that they are usually colored, which does not cause problems except for samples collected near ore-producing industries (Sunset Laboratory, 2014, <http://www.sunlab.com/about/technology.html>). The second mechanism was that they were found to cause premature EC evolution in the inert mode. Suggested measures to avoid this artifact included frequent change of filters, lowered maximum temperatures in the inert mode, and automated laser-temperature correction (Jung et al., 2011). (c) Colored organic materials, the errors caused by them was found to be minimal. (d) Secondary organic aerosol and biomass burning organic aerosol (Cheng et al., 2011). Organics from these two sources tend to be relatively refractory and easy to pyrolyze, and thus complicated the OC / EC split.

Previous efforts on artifact identification and correction have improved the accuracy of SCCA results to a large extent. However, as far as we know, no work about the SCCA has focused on the possible calculation discrepancy during the processing of raw signals. In this paper we reported a newly identified type of calculation discrepancy produced by the baseline correction of raw signals. This discrepancy was characterized under several conditions. Also, possible influencing factors and reduction measures were discussed.

2 Experimental method

2.1 Sunset SCCA

The Sunset Model 4 semi-continuous OC / EC analyzer measures aerosol OC and EC simultaneously. The detailed configuration has been well documented elsewhere (Birch and Cary, 1996; Lin et al., 2009; Arhami et al., 2006; Jung et al., 2011; US Environmental Protection Agency, 2012, <http://www.epa.gov/ttnamti1/spesunset.html>). Briefly, with a flow rate of 8 L min^{-1} , the air was drawn through two quartz-fiber filters packed together, and ambient $\text{PM}_{2.5}$ was collected onto a sampling spot of 1.31 cm^2 . The collected sample was subsequently analyzed by the thermal–optical method. Aerosol carbon thermally evolved during each heating step and was converted to CO_2 and detected by the NDIR sensor. Optical charring correction by light transmittance was based on a tuned diode laser (660 nm). At the end of each analysis, methane gas (5.0%; UHP (ultra-high purity) He balance) was injected as an internal standard. After deduction of the determined baseline signals, raw NDIR signals in each step were integrated and converted to carbon mass with a calibrated constant. Then the analytical result was normalized to the response of the methane standard, in order to adjust for the slight variations in flow rates.

In addition to the thermal–optical analyzed OE/EC data (referred to as thermal OC / EC below), the SCCA also provided optical EC by recording the laser attenuation every minute throughout the sampling period. This data was related to EC mass via a predetermined conversion factor (see detailed working curve and the algorithm in Jeong et al., 2004). Optical OC was then defined as thermal–optical analyzed TC minus optical EC. Since optical EC was determined independently, it is insusceptible to any calculation discrepancy produced during the thermal–optical analysis.

2.2 Temperature protocol

Three temperature protocols were applied in this work (Table 1). RT-IMPROVE (referred to as IMPshort hereinafter) was an instrument-included IMPROVE-like SCCA protocol, with the setting in He mode simplified to one step (550°) based on the idea that detailed separation of OC peaks was less meaningful in the SCCA. RT-IMPROVE-A (referred to as IMPlong hereinafter) was modified from an offline version of IMPROVE-A (Chow et al., 2007a) protocol. It differs from IMPshort with more temperature steps in He mode, and the prolonged hold time of He mode in total, especially step OC4. RT-NIOSH5040 (referred to as rtNIOSH hereinafter) was an SCCA protocol comparable to NIOSH5040, and was well validated against offline samples (Bae et al., 2004).

Table 1. Temperature protocols used for the Sunset semi-continuous OC / EC analyzer.

Step	Gas	RT-IMPROVE (IMPshort)		RT-IMPROVE-A (IMPlong)		RT-NIOSH5040 (rtNIOSH)	
		Temperature (°)	Hold time (s)	Temperature (°)	Hold time (s)	Temperature (°)	Hold time (s)
OC1	He	550	110	140	60	340	60
OC2	He	–	–	280	60	500	60
OC3	He	–	–	480	60	615	60
OC4	He	–	–	580	240	870	90
Cooling oven	He	–	–	–	–	Oven off	60
He time			110		420		330
EC1	He /O ₂	550	75	580	90	550	45
EC2	He /O ₂	700	75	740	90	625	45
EC3	He /O ₂	850	90	840	240	700	45
EC4	He /O ₂	–	–	–	–	775	45
EC5	He /O ₂	–	–	–	–	850	45
EC6	He /O ₂	–	–	–	–	900	120
He /O ₂ time			240		420		345
Total time			350		840		675

3 Results and discussion

3.1 Calculation discrepancy identification

The calculation discrepancy was initially observed during the sucrose tests conducted as external calibrations with the IMPshort protocol. Sucrose recovery decreased to only 78 % (blue markers in Fig. 1a), far beyond the uncertainty range of 5 % (Polidori et al., 2006). To examine the possible influence of the calibration constant used to convert NDIR signals to carbon mass, we further conducted that calibration with another two protocols, i.e., IMPlong and rtNIOSH, with identical constants and conditions. For these two protocols, however, sucrose recoveries were satisfactory (blue markers in Fig. 1b, c), indicating the calibration constant was acceptable. For the IMPlong protocol, a slight deviation ($\sim 2\%$) seemed to occur when more than 42.07 μgC of sucrose was loaded, while that was well within the uncertainty range. For rtNIOSH, sucrose was fully recovered within the tested range, i.e., up to 100.97 μgC of sucrose.

To clarify the underlying mechanism responsible for the underestimated sucrose recovery by the IMPshort protocol, we examined the raw signals, and found that the baseline correction method appeared to be a likely cause. In Model 4 SCCA, a multipoint baseline correction method (MP) was adopted in the included instrument-calculation software (RT-calc, version 522) to improve the linearity of NDIR detectors. This method determined the baseline according to signals at the start point, the center point (the lowest datapoint around the introduction of He /O₂) and the end point (datapoint just before the methane calculation peak). It was designed to deal with an increasing or rounded NDIR baseline, which, rather than a horizontal one, is more often the case observed in the instrumental blank tests (Bauer et al., 2009). MP was the default method and should have been used by

all previous SCCA-related work. However, the MP-corrected baseline was appropriate only if the NDIR signals have truly returned to baseline level at the center datapoint, which we suspect was not the case especially under heavy carbon loads, due to the incomplete evolution of OC within the limited residence time (Chow et al., 2005). In this case, the baseline would be biased to a higher level, therefore TC being underestimated. A schematic diagram of the suspected mechanism was depicted in Fig. 2.

To confirm the relationship of MP and the calculation discrepancy, we reanalyzed the raw signals of sucrose tests with another baseline correction method, namely the single-point method (SP). SP equaled the signal at the starting point as the baseline all through the analysis. Results of quantified TC with the MP and SP methods were referred to below as TC_{MP} and TC_{SP}, respectively. When SP correction was applied, recovery of sucrose spikes were statistically indistinguishable from unity for all protocols (red markers in Fig. 1), confirming the assumption that the “lost” sucrose with the IMPshort protocol was caused by MP correction.

3.2 Evidence from ambient samples

Although no difference was observed in the sucrose tests of IMPlong and rtNIOSH protocols, their performance in ambient samples was unknown. To examine the possibility of the calculation discrepancy occurrence in ambient samples, field sampling was conducted in Tsinghua University (40°19' N, 116°19' E), a site in the urban area of Beijing without major industrial sources nearby. Three protocols were used sequentially, with IMPshort from mid-July to November 2011, rtNIOSH in January and February 2012, and IMPlong in June, July, and November 2012. Time resolution (sampling time + analysis time) was 1 h (45 min + 15 min) for IMPshort, and 2 h (100 min + 20 min) for IMPlong and rtNIOSH.

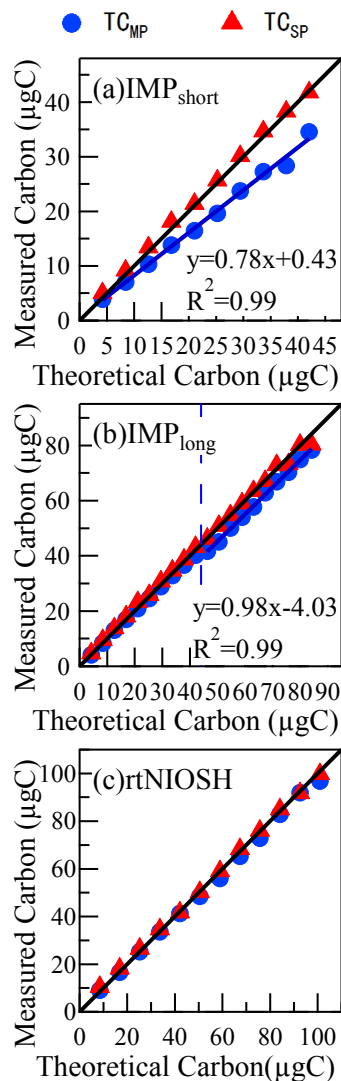


Figure 1. Sucrose calibration results of (a) IMPshort (b) IMPlong and (c) rtNIOSH protocols, baseline corrected with MP and SP, respectively. The 1 : 1 line was shown for reference. Linear regression of TC_{MP} was indicated in blue line for reference.

Filters changing and sampling cyclone cleaning were done every 4–7 days, and the sucrose calibration was conducted monthly. Raw signals were analyzed with both MP and SP. The adopted detection limit here was $2.0 \mu\text{g m}^{-3}$ for OC and $0.5 \mu\text{g m}^{-3}$ for EC, and data below this value was screened out. TC concentrations ($\mu\text{gC m}^{-3}$) were then converted into mass (μgC) by multiplying the sample volume (m^3), to avoid the ambiguity caused by different sampling time in one cycle. As the accurate TC value of ambient samples was unknown, TC_{SP} was used as reference of true TC based on results from the sucrose tests. The calculation discrepancy was thus defined as $-(TC_{MP} - TC_{SP})$; the negative sign indicating that a TC underestimation was expected. Accordingly, the relative

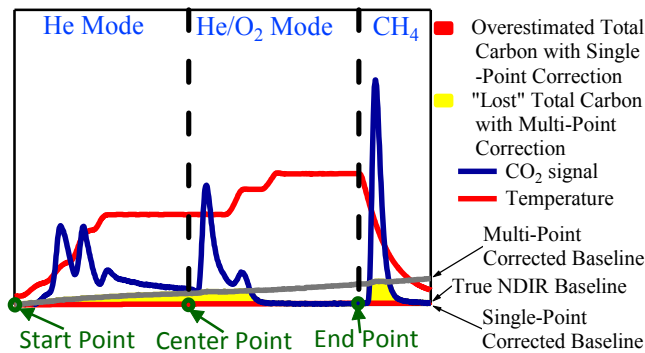


Figure 2. Schematic diagram of the suspected mechanism of the calculation discrepancy produced by the multipoint baseline correction method.

magnitude of the discrepancy was defined as the percentage of underestimated TC to TC_{SP} .

For ambient samples, this calculation discrepancy was observed with all protocols (Fig. 3) in a similar pattern to that of sucrose; namely, being present only when above a certain threshold of carbon load, and being positively correlated with a carbon load once above that threshold. The discrepancy emerged gradually, with no obvious discontinuity before and after the threshold. However, detailed characteristics could differ much among protocols. For the IMPshort protocol, ambient samples and sucrose performed much alike. The threshold carbon levels were both less than the detection limit, with magnitude of underestimation almost the same (22 %). For the IMPlong protocol, however, the performance of ambient samples was in sharp contrast with that of sucrose. The threshold carbon for ambient samples was determined to be about $20 \mu\text{gC}$. Although the difference was present even before that threshold, it was thought to be caused by the systematic error resulted from the significantly higher instrumental blanks associated with SP, as discussed in Sect. 3.3. This was further supported by the sharp increase in discrepancy magnitude of up to 36 % once after that threshold. In comparison, for sucrose, an insignificant underestimation of 2 % was seen only when over $42 \mu\text{gC}$ was loaded. As for the rtNIOSH protocol, although the threshold was not detected up to $100 \mu\text{gC}$ of sucrose, it was seen at only $25 \mu\text{gC}$ of ambient samples. Nevertheless, the magnitude of its discrepancy (12 %) ranked the lowest among three protocols. The distinct SCCA performance on sucrose and ambient samples suggested the need of a more refractory calibration substance to better represent ambient samples.

The characteristics of this discrepancy, i.e., the discrepancy-emerging threshold carbon load and the magnitude of TC underestimation, varied with the type of samples as well as temperature protocols. The underlying reason of these variations could come down to the thermal stability distribution of carbonaceous samples. Compared with sucrose, TC underestimation in Beijing

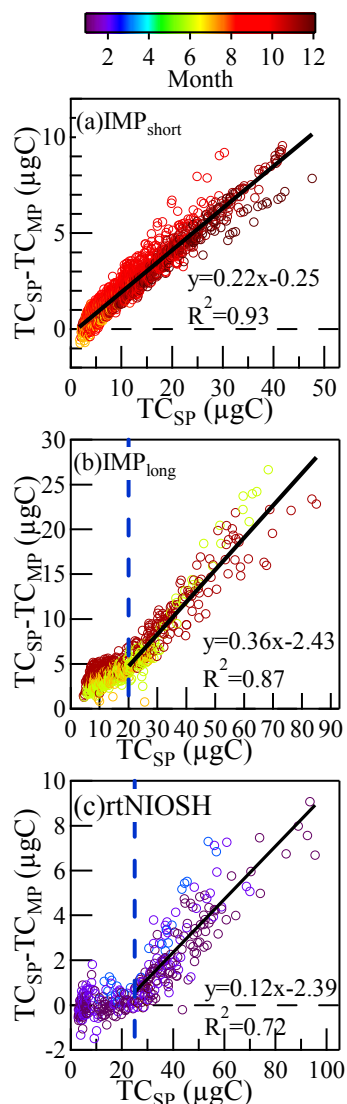


Figure 3. Calculation discrepancy quantification for ambient samples analyzed with (a) IMPshort, (b) IMPlong and (c) rtNIOSH protocol.

ambient samples was generally seen at a significantly lower threshold and larger magnitude. In addition, the magnitude of TC underestimation varied with seasons as well. Generally, the discrepancy tends to be larger with a lower threshold in summer (June–August) samples than winter (November–February next year) ones. The seasonal bifurcation in magnitude was seen for all protocols (Fig. 3, Fig. S3 in the Supplement). For IMPshort, as the threshold was close to zero even in winter, its seasonal variation could not be seen. For IMPlong (Fig. 3b) and rtNIOSH (Fig. S3 in the Supplement), however, the threshold both dropped from a rather high value (~ 20 and ~ 25 μgC , respectively) in winter to near zero in summer. These differences could be largely explained by variation of thermal properties among

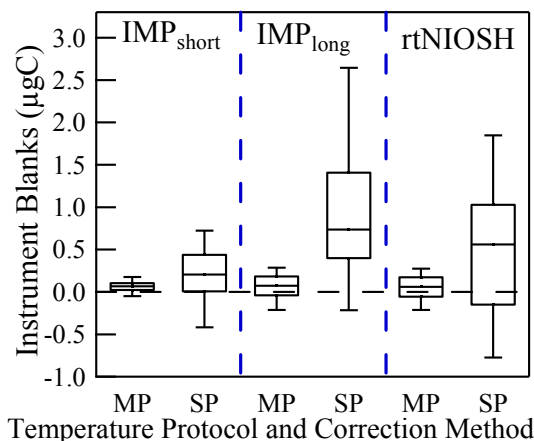


Figure 4. Instrumental blank distributions for the three protocols respectively corrected with two baseline correction methods. The box-and-stem plots depict the 5th, 25th, 50th (median), 75th, and 95th percentiles for instrumental blanks. See text for detailed explanation of the abbreviations.

sample types. The significantly lower threshold for sucrose than ambient samples suggested a more refractory nature of ambient OC. More refractory OC needed more time or higher temperature to evolve completely, and thus increased the possibility that the signal did not return to baseline level at the center point. Compared with sucrose of the same TC, the increased portion of refractory OC in ambient samples made it more sensitive to this calculation discrepancy. The seasonal variation of this discrepancy could be explained similarly. It was well proven that summer samples contained a larger portion of water soluble organic carbon (Lin et al., 2009; Cheng et al., 2011), which was an important source of organic compounds that was relatively refractory and easy to pyrolyze during the inert mode. The increased proportion of water soluble organic aerosol could push the thermal properties of the whole ambient sample towards a more refractory direction, thus increasing the possibility of discrepancy occurrence. For a fixed sample type, the threshold was always in the increasing order of IMPshort, IMPlong and rtNIOSH, indicating a prolonged time or an increased temperature in the step just before the center point (i.e., the highest temperature step of He mode) could reduce the possibility of discrepancy occurrence.

Although frequently exceeded in the heavily polluted Beijing samples, the observed threshold carbon load was a rather high value for American samples. That could largely explain why previous validation work failed to identify this type of calculation discrepancy. For example, Bae et al. (2004) examined the rtNIOSH protocol against offline instruments and found good agreement. However, the maximum TC concentration in their work was ~ 20 $\mu\text{g m}^{-3}$ (corresponding to 9.6 μgC), well below the rtNIOSH threshold of 25 μgC . In addition, the semi-continuous carbon analyzer used in their

work was an older version equipped with the FID detector. Also, the validation work of Bauer et al. (2009) adopted a protocol similar to rtNIOSH, the performance of which was also expected to be similar. Maximum TC in that work was even lower, corresponding to only $3.24 \mu\text{gC}$. In another interprotocol comparison work (Arhami et al., 2006), a modified-IMPROVE protocol was shown to agree well with a modified-NIOSH protocol. In that modified-IMPROVE protocol, the total hold time in He mode was 315 s, with a 125 s residence time in the temperature plateau of 550° . The threshold of that protocol was thus expected to be a little lower than the IMPLong threshold of $20 \mu\text{gC}$. In comparison, the maximum TC concentration in that study was only $\sim 30 \mu\text{g m}^{-3}$ (corresponding to $10.8 \mu\text{gC}$). Moreover, the difference of thermal properties between Beijing and American aerosols may also contribute to the different picture.

3.3 Instrumental blanks

To examine the influence of true baseline signals, instrumental blanks measured daily at 00:00 local time were respectively calculated with MP and SP corrections. The distribution was shown in Fig. 4. Based on MP-corrected results, the upper limit of instrumental blanks was suggested to be $0.3 \mu\text{gC}$ in the standard operating procedure. This criteria was met for all protocols tested. By contrast, SP-corrected instrumental blanks were distributed with much higher means and larger variances than MP results. The higher means indicated the incapability of SP to exclude true baseline signals, while the large variances implied that it was not appropriate to correct SP results simply by deducting a constant instrumental blank value. In addition, both the variances and means of SP-corrected results were in the increasing order of IMPshort, rtNIOSH, and IMPLong. The TC_{SP} blank level of IMPLong was the highest, reaching $0.99 \pm 0.86 \mu\text{gC}$ (average \pm one standard variation). In comparison, the blank level of rtNIOSH as $0.48 \pm 0.78 \mu\text{gC}$ was more acceptable. As IMPshort could not provide accurate TC estimation, rtNIOSH was recommended over IMPLong in terms of a more stable blank level.

3.4 Reduction and correction method

When ambient carbon load exceeded a certain threshold value, the default MP baseline correction could cause significant TC underestimation. Although this TC underestimation could be corrected with the SP method, the SP method could not exclude the influence of fluctuating true baseline signals, and thus would introduce a TC overestimation which can be significant under low carbon load. Since no single correction method is valid under all circumstances, a thorough solution should include measures to avoid this calculation discrepancy, as well as a systematic procedure for discrepancy detection and correction.

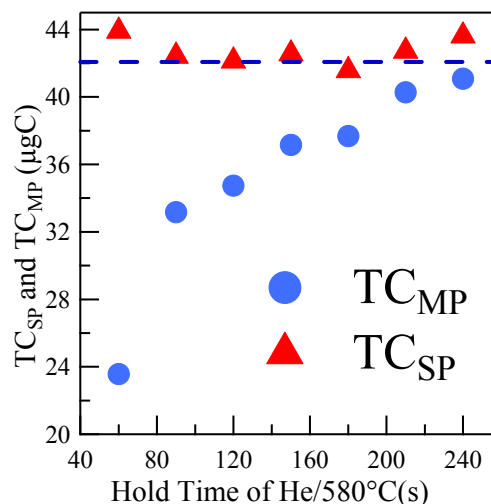


Figure 5. TC recoveries of sucrose with a series protocols based on the IMPLong protocol, with the only differences among these protocols being the hold time of step OC4. Target sucrose mass ($42.07 \mu\text{gC}$) is shown with a dashed line for reference.

One possible measure to avoid this calculation discrepancy was to shorten the sampling time within a cycle. As discussed above, we have

$$\begin{aligned} \text{carbon load}(\mu\text{gC}) &= \text{ambient concentration}(\mu\text{gC m}^{-3}) \\ &\times \text{sampling volume in a cycle}(\text{m}^3) \end{aligned} \quad (1)$$

and

$$\begin{aligned} \text{sampling volume in a cycle}(\text{m}^3) &= 8 \text{ L min}^{-1} \\ &\times \text{Sampling time in a cycle}(\text{min}), \end{aligned} \quad (2)$$

where 8 L min^{-1} was the fixed sampling flow rate. Under the same ambient concentration, shortening sampling time in a cycle could effectively reduce the carbon load through reducing sampling volume, and thus increasing the threshold of TC concentration. Take rtNIOSH as an example, when the sampling time was 2 h (100 min sampling plus 20 min analysis), the threshold carbon load of $25 \mu\text{gC}$ corresponded to an ambient TC concentration of $31.25 \mu\text{gC m}^{-3}$. When changed to 1 h cycle (40 min sampling plus 20 min analysis), the threshold-corresponding concentration was increased to $78.13 \mu\text{gC m}^{-3}$, which was close to the maximum TC concentration observed in this work. However, this was at the cost of reducing the proportion of effective sampling time, thus the representativeness of reported concentration. Moreover, this measure could solve only part of the problem for the IMPLong and IMPshort protocols, the threshold carbon load of which was much lower than rtNIOSH.

Another choice was to increase the temperature plateau and/or prolong the hold time in the step just before the center point (i.e., the highest temperature step of He mode), so as to increase the possibility that the CO_2 signal returned to

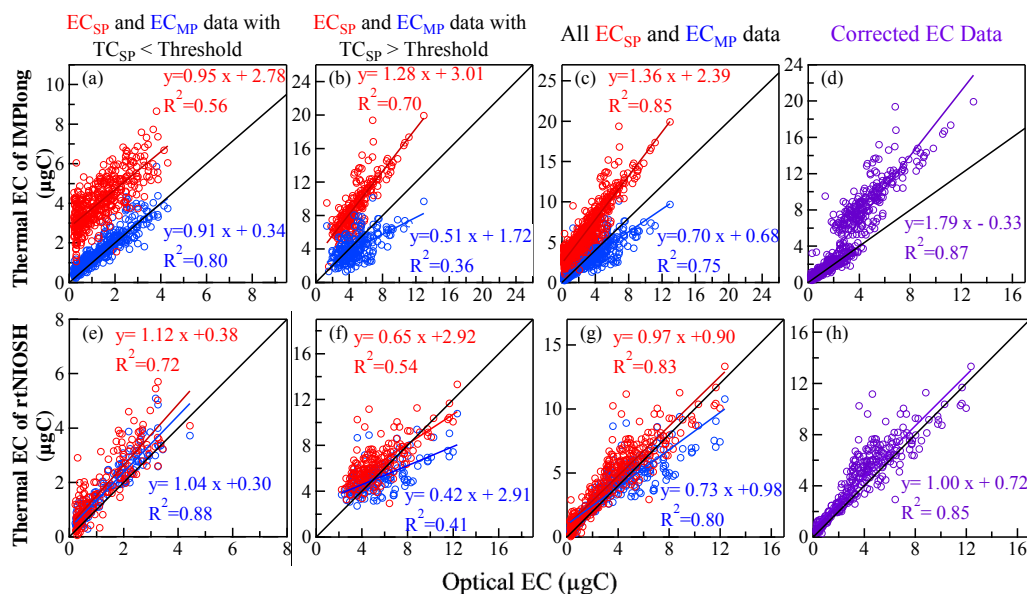


Figure 6. Thermal EC data, including EC_{SP}, EC_{MP} and corrected EC, plotted against optical EC for (a)–(d) IMPlong protocol, and (e)–(h) rtNIOASH protocol. Linear regression of both EC_{SP} and EC_{MP} with optical EC was done for (a, e) data with corresponding TC_{SP} < threshold, (b, f) data with corresponding TC_{SP} > threshold carbon, and (c, g) all data, respectively. The correlation of corrected EC with optical EC (d, h) is also shown for comparison. The 1 : 1 line is shown for reference.

baseline at center point. The effectiveness of increasing temperature was validated by the better performance of rtNIOASH over IMPshort and IMPlong. The effectiveness of prolonging the hold time in the He mode was examined with an additional series of sucrose experiments. Filters loaded with a certain sucrose mass (42.07 µg) were analyzed with a series of IMPlong-like protocols. This series of protocols differs only in OC4 hold time, which varied from 60 s to 240 s with a 30 s interval. Checks were repeated 3 times, and the averaged results are shown in Fig. 5. The differences of TC_{MP} to target mass was found to decrease with prolonged hold time, and down into the uncertainty range when hold time was longer than 210 s. This measure was an effective solution for the application of IMPROVE protocols on the SCCA, while it also suffers from the less efficient sampling time ratio.

Since this calculation discrepancy is inevitable under high ambient concentrations, we propose a systematic procedure for check and correction of this discrepancy, as described below. (i) Analyze raw data with both SP and MP correction. (ii) Plot the difference between TC_{SP} and TC_{MP} against TC_{SP}, as illustrated in Fig. 3. (iii) If the difference is distributed randomly around a certain value (true baseline signals), then the threshold is not reached. Under this circumstances, MP-corrected results are suggested. (iv) If the difference increased positively with TC_{SP} when above a certain threshold, the data should be treated separately. Use MP-corrected results for data below that threshold, and SP results when beyond that threshold.

As the correlation between thermal and optical EC was observed to be rather good in previous SCCA validation work (Arhami et al., 2006; Yu, 2011), it provided another criteria to testify the validity of the suggested correction method. Since the TC underestimation existed nearly all the time for IMPshort, this protocol was not considered here. For the other two protocols, the correlation was tested between optical EC and thermal EC including MP-corrected EC (referred to as EC_{MP} hereinafter), and SP-corrected EC (referred to as EC_{SP} hereinafter) (Fig. 6). The general pattern was the same for both protocols. Although EC_{SP} correlated better with optical EC compared to EC_{MP} in terms of overall performance (Fig. 6c, g), EC_{MP} correlated better with optical EC when the threshold was not reached (Fig. 6a, e). We also checked the performance of EC data corrected with the method we proposed above (Fig. 6d, h), i.e., using EC_{MP} when below the threshold and EC_{SP} when above that threshold. A stronger correlation between optical and thermal EC was found, with R^2 reaching 0.87 and 0.85 for IMPlong and rtNIOASH protocols, respectively. However, an obvious gap in corrected EC data was observed for the IMPlong protocol, caused by the significantly higher EC_{SP} data than EC_{MP} data. In comparison, corrected EC showed good continuity for the rtNIOASH protocol. In addition, the absolute values of corrected EC data given by the rtNIOASH protocol were very close to optical EC (with slope equaling 1.00). Thus the rtNIOASH protocol was recommended over the IMPlong protocol.

The instrument manufacturer has recently released an updated version of the calculation software (version 629), while it could not thoroughly solve this calculation discrepancy,

even with the NIOSH-like temperature protocol. As shown in Figs. S1 and S2 in the Supplement, the current calculation program used a piece-wise baseline correction method. When total carbon concentration determined by the multipoint correction method exceeded a predetermined threshold concentration ($\sim 25 \mu\text{gC m}^{-3}$), the baseline correction method changed from the multipoint method to a new method similar to the single-point method. However, the arbitrary choice of the threshold concentration was the problem. As we have explained above, the threshold carbon load could vary with temperature protocols as well as sample types. For the two IMPROVE-like protocols the threshold was too large (Fig. S2). For the rtNIOSH protocol, we supplemented some experiments of summer ambient samples from 1 June to 31 August 2013, with a time resolution of 1 h (40 min sampling + 20 min analysis). The threshold carbon load in summer was found to be significantly lower (close to zero) than that in winter ($\sim 25 \mu\text{gC}$) (Fig. S3 in the Supplement). Although the current calculation program performed better for winter samples, it failed to identify and correct the calculation discrepancy in summer samples. Thus we recommend that the occurrence of this calculation discrepancy should always be checked when this instrument was applied to new temperature protocols or ambient samples with unknown distribution of thermal stability.

4 Conclusion and implications

The widely use of the Sunset SCCA in carbonaceous aerosol studies required high data accuracy. Previous validation work has focused on the artifacts associated with sampling and analytical methods. The results of this study suggested the significance of taking the calculation discrepancy produced during data processing into consideration. Under high ambient aerosol concentrations, the default multipoint baseline correction method could generally result in a TC underestimation of 12–36 %, depending on the temperature protocol used. This indicated the potential need of reanalysis of previous reported data, especially those with IMPROVE-like protocols (e.g., Pan et al., 2012), and/or under heavily polluted period or areas (e.g., Lin et al., 2009; Andreae and Gelencsér, 2006). Single-point correction combined with the rtNIOSH protocol could give the most reliable results under a high carbon load. A framework to identify and avoid this calculation discrepancy was suggested. The effectiveness of this framework was supported by correlation with optical data.

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