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

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## Abstract

Sunset Semi-Continuous Carbon Analyzer (SCCA) is an instrument widely used for carbonaceous aerosol measurement. Despite previous validation work, here we identified a new type of SCCA calculation discrepancy caused by the default multi-point baseline correction method. When exceeding a certain threshold carbon load, multi-point correction could cause significant Total Carbon (TC) underestimation. This calculation discrepancy was characterized for both sucrose and ambient samples with three temperature protocols. For ambient samples, 22 %, 36 % and 12 % TC was underestimated by the three protocols, respectively, with corresponding threshold being  $\sim 0$ , 20 and 25  $\mu\text{gC}$ . For sucrose, however, such discrepancy was observed with only one of these protocols, indicating the need of more refractory SCCA calibration substance. The discrepancy was less significant for the NIOSH (National Institute for Occupational Safety and Health)-like protocol compared with the other two protocols based on IMPROVE (Interagency Monitoring of PROtected Visual Environments). Although the calculation discrepancy could be largely reduced by the single-point baseline correction method, the instrumental blanks of single-point method were higher. Proposed correction method was to use multi-point corrected data when below the determined threshold, while 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 environmental effects. 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

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rate of 8 L per minute, the air was drawn through two back-to-back quartz-fiber filters, and ambient  $\text{PM}_{2.5}$  was collected onto a sampling spot of  $1.31 \text{ cm}^2$ . The collected sample was subsequently analyzed with thermal-optical method. Aerosol carbon thermally evolved during each heating steps was converted to  $\text{CO}_2$  and detected by 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 He balance) was injected as an internal standard. After deduction of the determined baseline signals, raw NDIR signals in each step was integrated and converted to carbon mass with a calibrated constant. Then the analytical result is 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), 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 (Arhami et al., 2006; Jeong et al., 2004). Optical OC was then defined as thermal-optical analyzed TC minus optical EC. Since optical EC was determined independently, it's 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 setting in He mode simplified to one-step ( $550 \text{ }^\circ\text{C}$ ) based on the idea that detailed separation of OC peaks was less meaningful in SCCA. RT-IMPROVE-A (referred to as IMPlong hereinafter) was modified from offline version of IMPROVE-A (Chow et al., 2007a) protocol. It differs from IMPshort in the 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 off-line samples (Bae et al., 2004).



underestimated. A schematic diagram of the suspected mechanism was depicted in Fig. 2.

To make sure 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 MP and SP method 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 IMPshort protocol was caused by MP correction.

### 3.2 Evidence from ambient samples

Although no difference was observed in sucrose tests of IMPlong and rtNIOSH protocols, their performance in ambient samples was unknown. To examine the possibility of calculation discrepancy occurrence in ambient samples, field sampling was conducted in Tsinghua University (40°19' N, 116°19' E), a site in 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. Filters changing and sampling cyclone cleaning were done every 4–7 days, and 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<sup>5</sup>, and data below this value was screened out. TC concentrations ( $\mu\text{g C m}^{-3}$ ) were then converted into mass ( $\mu\text{g C}$ ) by multiplying the sample volume ( $\text{m}^3$ ), to avoid the ambiguity caused by different sampling time in one cycle. For ambient samples, the accurate TC value of which being unknown,  $TC_{SP}$  was used as reference of true TC based on results in sucrose tests. The calculation discrepancy was thus defined as  $-(TC_{MP} - TC_{SP})$ , the negative sign indicating that a TC underestimation was expected.

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Accordingly, the relative 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 with that of sucrose, namely being present only when above a certain threshold carbon load, and being positively correlated with carbon load once above that threshold. However, detailed characteristics could differ much among protocols. For 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 IMPlong protocol, however, performance of ambient samples was in sharp contrast with that of sucrose. 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 up into 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 to 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 thermal stability distribution of carbonaceous samples. Compared with sucrose, TC underestimation in Beijing ambient samples was generally seen at significantly lower threshold and larger magnitude. In addition, the magnitude of TC underestimation varied with seasons as well. rtNIOSH was applied only in winter, thus its seasonal variation was not available. While for IMPshort and IMPlong, a bifurcation

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in magnitude was both seen among seasons (Fig. 3a and b). Generally, the discrepancy tend to be larger in summer (June to August) samples than winter (November to February next year) ones. These differences could be largely explained by variation of thermal properties among sample types. The significant 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, thus increased the possibility that the signal not returning to baseline level at center point. Compared with sucrose of same TC, the increased portion of refractory OC in ambient sample made it more sensitive to this calculation discrepancy. The seasonal variation of this discrepancy could be explained similarly. It was well proved 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 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 off-line instrument and found good agreement. However, the maximum TC concentration in their work was  $\sim 20 \mu\text{g m}^{-3}$  (corresponding to  $9.6 \mu\text{g C}$ ), well below the rtNIOSH threshold of  $25 \mu\text{g C}$ . 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

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3.24  $\mu\text{gC}$ . In another inter-protocol 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 °C. 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 LT were respectively calculated with MP and SP correction. 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 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. TC<sub>SP</sub> 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

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underestimation could be corrected with SP method, the SP method could not exclude the influence of fluctuating true baseline signals, 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.

One possible measure to avoid this calculation discrepancy was to shorten the sampling time within a cycle. As carbon load equals ambient concentration multiplies sampling time in a cycle, this could effectively reduce the carbon load with the same ambient concentration, thus increasing the threshold TC concentration. Take rtNIOSH for 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 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 reduction of proportion of effective sampling time, thus the representativeness of reported concentration. Moreover, this measure could solve only part of the problem for IMPLong and IMPshort protocol, 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 center point (i.e. the highest temperature step of He mode), so as to increase the possibility that  $\text{CO}_2$  signal having returned to baseline at center point. The effectiveness of increasing temperature was validated by the better performance of rtNIOSH over IMPshort and IMPLong. The effectiveness of prolonging hold time in He mode was examined with an additional series of sucrose experiment. Filters loaded with a certain sucrose mass ( $42.07 \mu\text{g}$ ) was 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 averaged results were shown in Fig. 5. The differences of  $\text{TC}_{\text{MP}}$  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 application of IMPROVE protocols on SCCA, while it also suffers from the low 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 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). 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 and g),  $EC_{MP}$  correlated better with Optical EC when the threshold was not reached (Fig. 6a and e). We also checked the performance of EC data corrected with the method we proposed above (Fig. 6d and h), i.e. using  $EC_{MP}$  when below the threshold and  $EC_{SP}$  when above that threshold. Stronger correlation between optical and thermal EC was found, with  $R^2$  reaching 0.87 and 0.85 for IMPlong and rtNIOSH protocol, respectively. However, an obvious gap in corrected EC data was observed for IMPlong protocol, caused by the significantly higher  $EC_{SP}$  data than  $EC_{MP}$  data. In comparison, corrected EC showed good continuity for rtNIOSH protocol. In addition, the absolute values of corrected EC data given by rtNIOSH protocol was

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very close to optical EC (with slope equaling 1.00). Thus rtNIOSH protocol was recommended over IMPlong protocol. In addition, the instrument manufacturer has released an updated version of the calculation software (version 629), while the detailed instruction has not been available. Thus we just compared the result from the new software and that based on the single-point method in Fig. S1 without further discussions.

#### 4 Conclusion and implications

The widely use of 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 to take calculation discrepancy produced during data processing into consideration. Under high ambient aerosol concentrations, the default multi-point baseline correction method could generally result in a TC underestimation of 12% to 36%, depending on the temperature protocol used. This indicated the potential need of re-analysis 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 Gelencser, 2006). Single-point correction combined rtNIOSH protocol could give the most reliable results under 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.

**Supplementary material related to this article is available online at**  
**[http://www.atmos-meas-tech-discuss.net/7/377/2014/  
amtd-7-377-2014-supplement.pdf](http://www.atmos-meas-tech-discuss.net/7/377/2014/amtd-7-377-2014-supplement.pdf)**

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## References

- 5 Andreae, M. O. and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, 6, 3131–3148, doi:10.5194/acp-6-3131-2006, 2006.
- Arhami, M., Kuhn, T., Fine, P. M., Delfino, R. J., and Sioutas, C.: Effects of sampling artifacts and operating parameters on the performance of a semicontinuous particulate elemental carbon/organic carbon monitor, *Environ. Sci. Technol.*, 40, 945–954, doi:10.1021/es0510313, 10 2006.
- Bae, M. S., Schauer, J. J., DeMinter, J. T., Turner, J. R., Smith, D., and Cary, R. A.: Validation of a semi-continuous instrument for elemental carbon and organic carbon using a thermal-optical method, *Atmos. Environ.*, 38, 2885–2893, doi:10.1016/j.atmosenv.2004.02.027, 2004.
- 15 Bauer, J. J., Yu, X. Y., Cary, R., Laulainen, N., and Berkowitz, C.: Characterization of the sunset semi-continuous carbon aerosol analyzer, *J. Air Waste Manage.*, 59, 826–833, doi:10.3155/1047-3289.59.7.826, 2009.
- Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Tech.*, 25, 221–241, 20 2010. doi:10.1080/02786829608965393, 1996.
- Cheng, Y., Duan, F.-K., He, K.-B., Zheng, M., Du, Z.-Y., Ma, Y.-L., and Tan, J.-H.: Intercomparison of thermal-optical methods for the determination of organic and elemental carbon: influences of aerosol composition and implications, *Environ. Sci. Technol.*, 45, 10117–10123, doi:10.1021/es202649g, 2011.
- 25 Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies, *Atmos. Environ. A-Gen.*, 27, 1185–1201, 1993.
- Chow, J. C., Watson, J. G., Chen, L.-W. A., Paredes-Miranda, G., Chang, M.-C. O., Trimble, D., Fung, K. K., Zhang, H., and Zhen Yu, J.: Refining temperature measures in thermal/optical 30 carbon analysis, *Atmos. Chem. Phys.*, 5, 2961–2972, doi:10.5194/acp-5-2961-2005, 2005.

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- 5 Chow, J. C., Yu, J. Z., Watson, J. G., Ho, S. S. H., Bohannan, T. L., Hays, M. D., and Fung, K. K.: The application of thermal methods for determining chemical composition of carbonaceous aerosols: a review, *J. Environ. Sci. Heal. A*, 42, 1521–1541, doi:10.1080/10934520701513365, 2007b.
- 10 Docherty, K. S., Aiken, A. C., Huffman, J. A., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Worsnop, D. R., Snyder, D. C., Peltier, R. E., Weber, R. J., Grover, B. D., Eatough, D. J., Williams, B. J., Goldstein, A. H., Ziemann, P. J., and Jimenez, J. L.: The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition, *Atmos. Chem. Phys.*, 11, 12387–12420, doi:10.5194/acp-11-12387-2011, 2011.
- 15 Hu, W. W., Hu, M., Deng, Z. Q., Xiao, R., Kondo, Y., Takegawa, N., Zhao, Y. J., Guo, S., and Zhang, Y. H.: The characteristics and origins of carbonaceous aerosol at a rural site of PRD in summer of 2006, *Atmos. Chem. Phys.*, 12, 1811–1822, doi:10.5194/acp-12-1811-2012, 2012.
- 20 Jeong, C. H., Hopke, P. K., Kim, E., and Lee, D. W.: The comparison between thermal-optical transmittance elemental carbon and aethalometer black carbon measured at multiple monitoring sites, *Atmos. Environ.*, 38, 5193–5204, doi:10.1016/j.atmosenv.2004.02.065, 2004.
- Jung, J., Kim, Y. J., Lee, K. Y., Kawamura, K., Hu, M., and Kondo, Y.: The effects of accumulated refractory particles and the peak inert mode temperature on semi-continuous organic carbon and elemental carbon measurements during the CAREBeijing 2006 campaign, *Atmos. Environ.*, 45, 7192–7200, doi:10.1016/j.atmosenv.2011.09.003, 2011.
- 25 Karanasiou, A., Diapouli, E., Cavalli, F., Eleftheriadis, K., Viana, M., Alastuey, A., Querol, X., and Reche, C.: On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols, *Atmos. Meas. Tech.*, 4, 2409–2419, doi:10.5194/amt-4-2409-2011, 2011.
- Sunset Laboratory: Sample Analysis Method for Organic and Elemental Carbon Aerosols: available at: <http://www.sunlab.com/about/technology.html> (last access: 15 January 2014), 2014.
- 30 Sunset Laboratory: <http://www.sunlab.com/about/about-us.html>, last access: 15 January 2014.
- Lin, P., Hu, M., Deng, Z., Slanina, J., Han, S., Kondo, Y., Takegawa, N., Miyazaki, Y., Zhao, Y., and Sugimoto, N.: Seasonal and diurnal variations of organic carbon in PM<sub>2.5</sub> in Beijing

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and the estimation of secondary organic carbon, *J. Geophys. Res.-Atmos.*, 114, D00G11, doi:10.1029/2008jd010902, 2009.

Pan, X. L., Kanaya, Y., Wang, Z. F., Taketani, F., Tanimoto, H., Irie, H., Takashima, H., and Inomata, S.: Emission ratio of carbonaceous aerosols observed near crop residual burning sources in a rural area of the Yangtze River Delta Region, China, *J. Geophys. Res.*, 117, D22304, doi:10.1029/2012jd018357, 2012.

Polidori, A., Turpin, B. J., Lim, H.-J., Cabada, J. C., Subramanian, R., Pandis, S. N., and Robinson, A. L.: Local and regional secondary organic aerosol: insights from a year of semi-continuous carbon measurements at Pittsburgh, *Aerosol Sci. Tech.*, 40, 861–872, doi:10.1080/02786820600754649, 2006.

US Environmental Protection Agency: Sunset OC/EC Evaluation Project, available at: <http://www.epa.gov/ttnamti1/spesunset.html> (last access: 15 January 2014), 2013.

US Environmental Protection Agency: Standard Operating Procedure (SOP) For the Analysis of Organic and Elemental Carbon (OC/EC) Using the Sunset Laboratory Semi-Continuous Carbon Aerosol Analyzer, <http://www.epa.gov/ttnamti1/spesunset.html> (last access: 15 January 2014), 2012.

Watson, J. G., Chow, J. C., and Chen, L.-W. A.: Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, *Aerosol Air Qual. Res.*, 5, 65–102, 2005.

Yu, X.-Y.: Measurements of Carbonaceous Aerosols Using Semi-Continuous Thermal-Optical Method, Pacific Northwest National Laboratory (PNNL), Richland, WA (US), 2011.



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**Table 1.** Temperature protocols used for sunset semi-continuous OC/EC analyzer.

Step	Gas	RT-IMPROVE (IMPshort)		RT-IMPROVE-A (IMPlong)		RT-NIOSH5040 (rtNIOASH)	
		Temperature (°C)	Hold Time (s)	Temperature (°C)	Hold Time (s)	Temperature (°C)	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 <sub>2</sub>	550	75	580	90	550	45
EC2	He/O <sub>2</sub>	700	75	740	90	625	45
EC3	He/O <sub>2</sub>	850	90	840	240	700	45
EC4	He/O <sub>2</sub>	–	–	–	–	775	45
EC5	He/O <sub>2</sub>	–	–	–	–	850	45
EC6	He/O <sub>2</sub>	–	–	–	–	900	120
He/O <sub>2</sub> Time			240		420		345
Total Time			350		840		675

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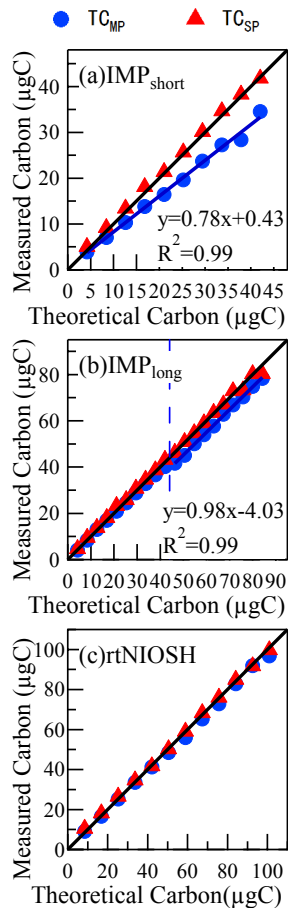
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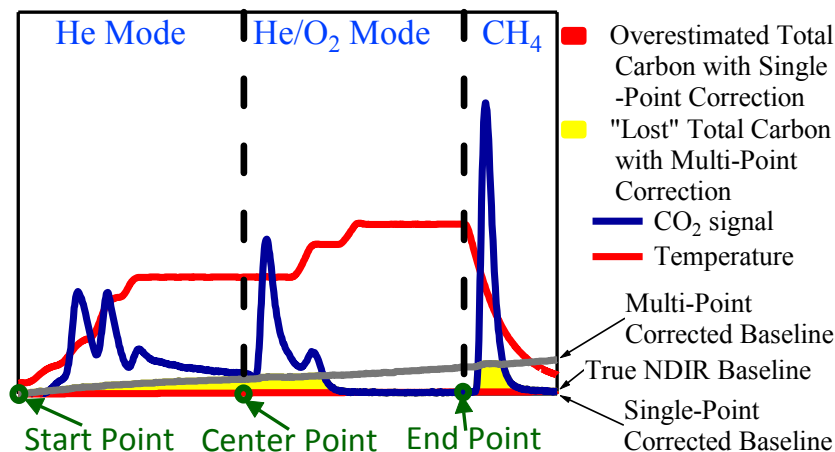
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**Fig. 1.** Sucrose calibration results of **(a)** IMP<sub>short</sub> **(b)** IMP<sub>long</sub> and **(c)** rtNIOSH protocol, base-line corrected with MP and SP, respectively. The 1 : 1 line was shown for reference. Linear regression of  $\text{TC}_{\text{MP}}$  was indicated in blue line for reference.

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**Fig. 2.** Schematic diagram of the suspected mechanism of the calculation discrepancy produced by Multi-Point baseline correction method.

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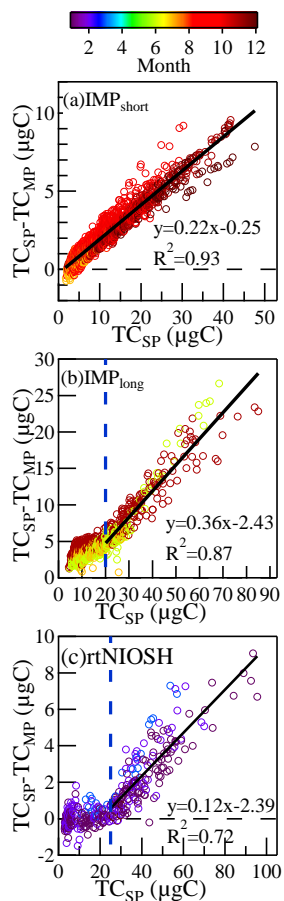
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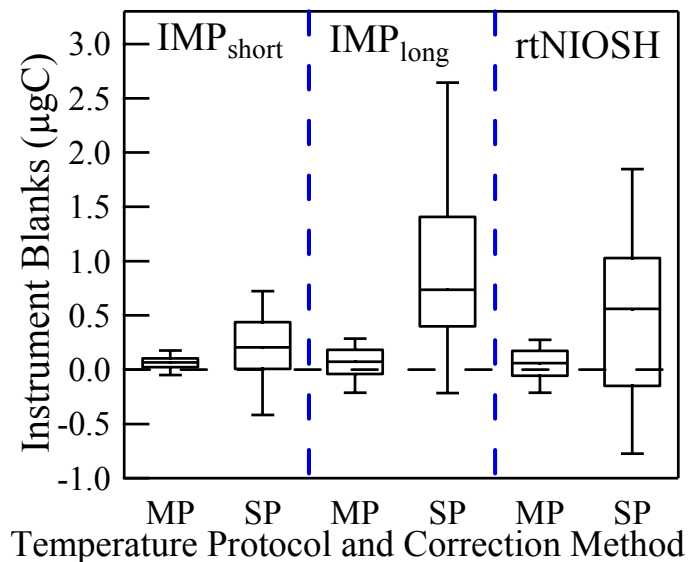
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**Fig. 3.** Calculation discrepancy quantification for ambient samples analyzed with **(a)** IMP<sub>short</sub>, **(b)** IMP<sub>long</sub> and **(c)** rtNIOSH protocol.

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**Fig. 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 percentile for instrumental blanks. See text for detailed explanation of the abbreviations.

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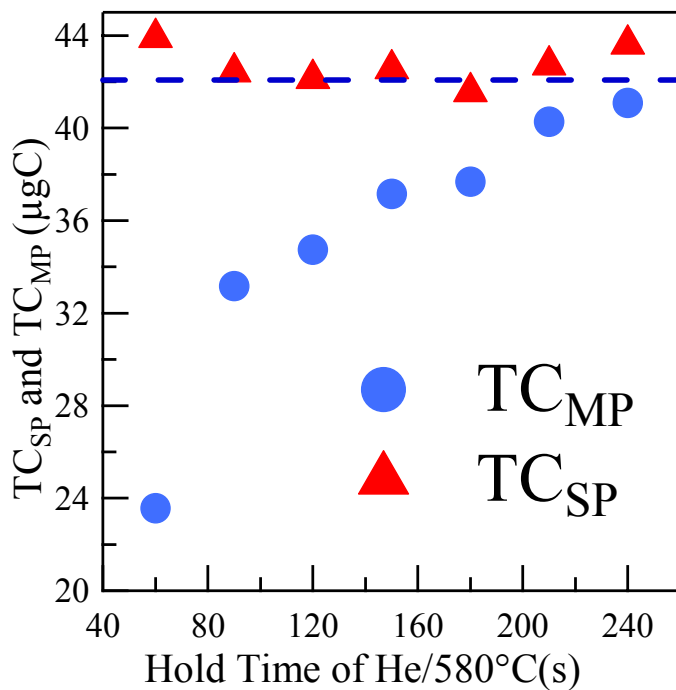
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**Fig. 5.** TC recoveries of sucrose changed with hold time of Step OC4 in IMPLong protocol. Target Sucrose mass (42.07 µgC) was shown in dash line for reference.

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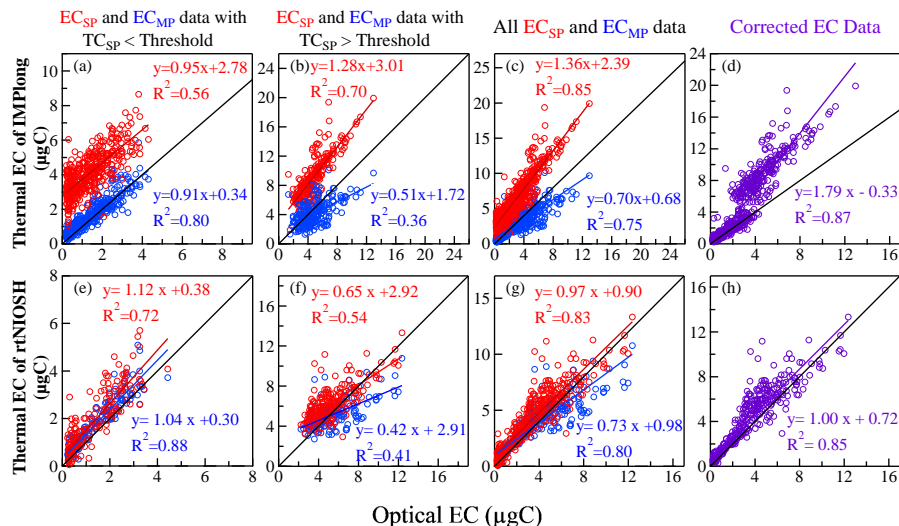
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**Fig. 6.** Thermal EC data, including  $EC_{SP}$ ,  $EC_{MP}$  and corrected EC, plotted against Optical EC for (a–d) IMPlong protocol, and (e–h) rtNIOSSH protocol. Linear regression of both  $EC_{SP}$  and  $EC_{MP}$  with Optical EC was done for (a and e) data with corresponding  $TC_{SP} < \text{Threshold}$ , (b and f) data with corresponding  $TC_{SP} > \text{Threshold}$  carbon, and (c and g) all data, respectively. Correlation of corrected EC with Optical EC (d and h) was also shown for comparison. The 1 : 1 line was shown for reference.