Review of Sunset Organic and Elemental Carbon (OC and EC) Measurements During EPA's Sunset Carbon Evaluation Project

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U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Research Triangle Park, NC

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1. Executive Summary

As part of an EPA project to evaluate the feasibility of the Sunset Semi-Continuous Organic and Elemental Carbon (OC/EC) monitor, EPA sponsored the deployment of this monitor by local air quality agencies at Chicago, Illinois; Houston, Texas; Las Vegas, Nevada; St. Louis, Missouri; Rubidoux, California; and Washington, D.C. Sunset monitors were collocated with existing 24-hr measurements of OC and EC via filter sampling as part of the Chemical Speciation Network (CSN); at Houston, St. Louis, and Washington, they were also collocated with Aethalometer instruments, which measure black carbon (BC). Sunset data were compared to CSN and Aethalometer data to assess whether the Sunset monitors could be deployed in lieu of making filter measurements at routine monitoring stations. In addition, two Sunset monitors were collocated at EPA OAQPS' on-site monitoring station to assess detection limits and precision via injections of known sucrose standards.

Using injections of known sucrose standards, the coefficient of variation (CV) and bias values of the Sunset were measured; the values ranged between 5%–6% for bias, and 6%–8% for CV, which met the data quality objectives of 15%. The calculated volumetric detection limit was between 1.4 to 1.5 µg/m^3, using a one-hour cycle with 47 minute collection at 8 lpm. Agencies encountered significant operational issues with the Sunset monitors, substantially reducing the number of valid data points for the multi-year deployment. After screening for these issues, and excluding Las Vegas results that were suspect, we found that Sunset OC generally compared well with the CSN OC (r^2=0.73 across five sites); the Sunset/CSN OC ratio was, on average, 1.06, with a range among sites of 0.96 to 1.12. The Sunset instrument measures thermal EC (referred to as "EC") and optical EC ("OptEC"). CSN measurements are thermal EC. Sunset thermal EC and CSN EC did not compare as well, with an overall r^2 of 0.22, in part because 26% of the hourly Sunset EC measurements were below the detection limit. Sunset Optical EC had a much better correlation to CSN EC (r^2=0.67 across all sites), with an average Sunset/CSN ratio of 0.90 (range of 0.7 to 1.08). There was also a high correlation of Sunset Optical EC with Aethalometer BC (r^2=0.77 across all sites), though with a larger bias (average Sunset/Aethalometer ratio of 0.56). There was no systematic difference among the Sunset Optical EC and Aethalometer BC measurements by site location, i.e., Sunset Optical EC was consistently lower than Aethalometer BC at all three sites, with no significant seasonal variation. Somewhat surprisingly, the diurnal pattern of OC was fairly invariant, while EC had a morning peak across all sites. Overall, operational issues with the Sunset monitors were persistent at all sites, but when the instruments were operating well, collected data were comparable to results from CSN.

Implications:

- The Sunset instrument and its software was not robust enough for routine deployment and operation by state/local air quality agencies at the beginning of this study, but a number of improvements have since been made to address the issues encountered in this study.
- When the Sunset instrument was working well, OC and OptEC data were comparable to CSN OC and EC.

2. Introduction

Carbonaceous aerosol is a significant, and often the largest, component of fine particulate matter less than 2.5 microns in diameter ($PM_{2.5}$) in many areas of the United States. It is composed of organic and elemental carbon (OC, EC) (Jacobson et al., 2000), but its composition, sources, and spatiotemporal variations are not well characterized (Jimenez et al., 2009). OC comprises thousands of individual molecules that can be directly emitted as primary emissions or can be formed in the atmosphere from semi-volatile and gaseous precursors over the course of minutes to days. EC is directly emitted from combustion processes, such as from mobile sources or from biomass burning. While it is well established that elevated $PM_{2.5}$ levels are associated with many health effects, such as respiratory and cardiac disease, the complex interaction of specific health effects from individual compounds or $PM_{2.5}$ components such as OC and EC is not well understood.

EPA monitors OC and EC in urban areas as part of the Chemical Speciation Network (CSN), where over 100 monitors across the United States collect filters that are subsequently analyzed for OC and EC on a routine basis. Such measurements have been collected for over 15 years, offering an opportunity to evaluate long-term temporal and spatial trends. As continuous monitoring technology has advanced, EPA and other air monitoring agencies have begun to assess whether continuous monitoring technologies could feasibly be used to reduce the frequency and amount of filter-based measurements. If continuous monitors were used to continue the long-term monitoring, they could provide a significant improvement to the data collected in three main ways: (1) provide data every day, rather than on the 1-in-3 or 1-in-6 day schedule typical for filter measurements; (2) provide hourly data, so that data analyses such as wind direction and diurnal analysis would become feasible; and (3) significantly reduce the cost of sample preparation, shipping, and laboratory analysis. The Sunset OC/EC instrument provides integrated measurements of OC and EC on a customizable sampling time (such as hourly or 2-hour intervals) and flow rate (2 – 9 lpm) via a thermal method similar to that used in CSN, as well as an optical EC (OptEC) measurement that is based on transmission of 660 nm wavelength light through the filter.

The Sunset OC/EC instrument has been widely used in the United States and throughout the world (Snyder and Schauer, 2007; Bae et al., 2004a; Jeong et al., 2004). OC measurements have typically been comparable to other measurements of carbonaceous aerosol, such as from the Aerodyne Aerosol Mass Spectrometer (AMS). At a near-road site in Las Vegas, Nevada, Brown et al. (2013) found that AMS-derived OC and Sunset OC were very consistent, with small bias (r^2 of 0.89, slope of 0.91). In Hong Kong, Lee et al. (2013) also found good agreement between Sunset and AMS measurements (r^2 of 0.87 and slope of 0.88). Other studies had more variation between AMS and Sunset measurements, for example in Riverside (r^2 of 0.53) (Docherty et al., 2011), Tokyo (r^2 range of 0.67-0.83 in two seasons) (Takegawa et al., 2005), and Pittsburgh (r^2 of 0.88) (Zhang et al., 2005). In Riverside, Snyder and Schauer (2007) found the Sunset measurements compared well with filter measurements (r^2 of 0.90 and slope of 1.11). At Atlanta, r^2 values between the Sunset and the Aerosol

Chemical Speciation Monitor (ACSM) were between 0.86-0.92 in summer and fall (Budisulistiorini et al., 2014).

EC from Sunset and BC from Aethalometer instruments have also been compared. In Prague, Zíková et al. (2016) found that Sunset OptEC and BC were fairly comparable (slope of 0.77 and r^2 of 0.99) in winter. In New York, Rattigan et al. (2010) found a consistent seasonal difference in BC/EC ratio over the course of three years of measurements, with a ratio of 1.4 in October–March and ratio of 2.0 in April–September. They also found an average OptEC/EC ratio of 0.88 in October–March and 1.04 in April–September. Throughout the year, there was a high correlation of BC with EC, with a monthly range of 0.82-0.96. In Ontario, collocated EC and BC measurements also had high correlation (r^2 of 0.85 and 0.77 at two sites), with a BC/EC ratio of 1.7 at both sites (Healy et al., 2017).

To evaluate the utility of the Sunset OC/EC instrument as part of the CSN, EPA sponsored the deployment of this monitor by local air quality agencies at CSN sites in Chicago, Houston, Las Vegas, St. Louis, Rubidoux, and Washington, D.C. Monitors were operated at these locations, as well as at EPA in Raleigh, North Carolina, for varying lengths of time during 2012-2017. The primary objectives of the study were to evaluate Sunset instrument performance in various locations and conditions; determine how well the Sunset measurements compare with the CSN and Aethalometer measurements, where available; assess precision and detection limits via injections of a known standard amount of sucrose solution; and determine whether integration of the Sunset OC/EC instrument across a larger number of sites is appropriate for long-term monitoring in the CSN. Results from the study are presented in this report. **Appendix A** documents the operational issues encountered by agencies operating the instrument, and the actions Sunset Labs has taken to address these issues. **Appendix B** provides additional statistics comparing the Sunset data to CSN and Aethalometer data, plus figures showing the ratio between Sunset and CSN or Aethalometer data, diurnal patterns, and time series of data as they exist in the EPA's Air Quality System (AQS) and after additional quality control was done.

3. Methods

3.1 Monitoring Site Locations

Six locations at existing CSN sites were used in this project: Chicago (Com Ed site in Lawndale, AQS ID 17-031-0076); Houston (Deer Park, AQS ID 48-201-1039); Las Vegas (East Las Vegas, AQS ID 32-003-0540); Rubidoux (Rubidoux, AQS ID 06-065-8001); St. Louis (Blair Street, AQS ID 29-510-0085); and Washington, D.C. (McMillan Reservoir, AQS ID 11-001-0043). Two Sunset instruments were operated at St. Louis from August 11, 2016, through January 11, 2017. Table 1 summarizes the site locations and measurements. CSN measurements were collected every third day. Sunset, Aethalometer, and CSN data were acquired from EPA's AQS in summer 2017.

Table 1. Summary of measurements by site; date range indicates the time frame when Sunset data were available in AQS.

City	AQS ID	Site	Operator	Measurements	Dates with Sunset Data
Chicago	17-031-0076	Com Ed, Lawndale	Cook County Dept. of Environmental Control	Sunset, CSN	5/1/14-12/31/15
Houston	48-201-1039	Deer Park	Texas Commission on Environmental Quality (TCEQ)	Sunset, CSN, Aethalometer AE21	8/2/13-12/31/16
Las Vegas	32-003-0540	East Las Vegas	Clark County	Sunset, CSN	8/15/12-12/31/14
Los Angeles	06-065-8001	Rubidoux	South Coast Air Quality Management District	Sunset, CSN	12/17/13-10/14/15
St. Louis	29-210-0085	Blair Street	Missouri Dept. of Natural Resources	Sunset, CSN, Aethalometer AE33	5/7/13-3/30/17
Washington, D.C.	11-001-0043	McMillan Reservoir	District Dept. of the Environment	Sunset, CSN, Aethalometer AE21	10/7/12-8/13/16

3.2 Sunset OC/EC

In this application, the Sunset OC/EC instrument used a thermal optical method similar to NIOSH 5040 (Chow et al., 2001; 2007; Bauer et al., 2009; Park et al., 2005; Bae et al., 2004b; Sin et al., 2004; Birch and Cary, 1996). Other methods, such as IMPROVE-A by TOT, could also be used. Aerosol is drawn through a $PM_{2.5}$ cyclone inlet with a carbon denuder and deposited for 47 minutes at a flow rate of 8 lpm on a quartz fiber filter located in an oven chamber. The collected aerosol is then heated off of the filter during an 8-minute cycle by heating the filter to 850°C for 5 minutes to quantify OC. As the evolved carbon flows through the manganese oxide (MnO_2) oven, it is converted to carbon dioxide (CO_2) gas, which is carried in a helium stream and measured directly by a self-contained non-dispersive infrared (NDIR) detector system. Next, an oxidizing carrier gas (helium with 2% oxygen [O_2]) is introduced at 850°C for 3 minutes to quantify EC, where the EC is detected (similar to the way OC was detected). The remaining 5 minutes is used for cooling down the oven. During the filter heating, carbonaceous material evolves off the filter as CO_2, which is quantified using an NDIR detector. EC is determined as any carbon evolved off the filter after the introduction of He/O_2 once the laser-monitored filter absorbance matches the initial absorbance measured when the filter was first heated. After each hourly analytical cycle, calibration gas of 5% CH_4 with He flushes the system. Manufacturer-specified detection limits are 0.4 µg C/m^3 for OC and 0.2 $\mu gC/m^3$ for EC.

Where reported by the monitoring agency, both thermal EC (referred to as "EC") and optical EC (OptEC) comparisons are provided here. The OptEC is a measurement of transmittance through the filter at a wavelength of 660 nm prior to the thermal analysis, measuring the amount of absorbance in the sp^2 bonds of graphitic carbon. Since the measurements of both OptEC from the Sunset and BC from the Aethalometer are based on optical absorbance methods, we compared how consistent measurements from these techniques were to each other and to the thermal EC from CSN. At Chicago, no OptEC was reported. At St. Louis, thermal EC was not reported after 2014 because the instrument needed very frequent filter replacements; this is likely due to high loadings of metal oxides at the monitoring site. Once only OptEC was measured, the instrument filter did not have to be replaced as often, so only OptEC was reported for the majority of the study.

Two Sunset OC/EC instruments were operated at the EPA site to test instrument setup, and quantify bias, precision, and detection limits using injections of a sucrose standard; the equations used to quantify bias, following EPA guidance, are shown below (Camalier et al., 2007). A known amount (10 uL or 5 uL) of 99.5% sucrose from Sigma Aldrich (product #S9378) was injected into each instrument intermittently over the course of two years. The absolute percent difference (*d*) between the observed response from the instrument and the injected amount of carbon was then calculated. The coefficient of variation upper bound (90th percentile) was calculated as the precision estimate:

$$CV = \sqrt{\frac{n\sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{n} d_i\right)^2}{n(n-1)}} \times \sqrt{\frac{n = 1}{{X^2}_{0.1,n-1}}}$$

Where $X^2_{0.1,n-1}$ is the highest 10th percentile of a chi-squared distribution with $n-1$ degrees of freedom. Bias is calculated as the upper bound of the mean absolute value of the percent differences d across all d_i's, from the mean of absolute values of all ds (*AB*) and the standard deviation of the absolute values of all ds (*AS*):

$$|bias| = AB + t_{0.95,n-1} \times \frac{AS}{\sqrt{n}}$$

$$AB = \frac{1}{n} \times \sum_{i=1}^{n} |d_i|$$

$$AS = \sqrt{\frac{n \times \sum_{i=1}^{n} |d_i|^2 - \left(\sum_{i=1}^{n} |d_i|\right)^2}{n(n-1)}}$$

In addition, the instrument response to clean, blank quartz fiber filters was used to calculate the detection limit. The detection is calculated following 40 CFR Part 136, Appendix B:

$$MDL = \bar{X} + t_{(n-1,1-\propto=0.99)} \times S$$

Where X is the mean of replicate method blank results, $t_{(n-1,1-\propto=0.99)}$ shows the Student's t value at a 99% confidence level, with $n-1$ degrees of freedom, and S is the standard deviation of the blank samples.

3.3 CSN URG 3000N Sampler and Lab Analysis

As part of routine measurements in the CSN, quartz fiber filters are prepared and shipped to monitoring sites. Filters are pre-baked to remove organic vapor and residue. A URG 3000N sampler is used to collect aerosol on filters, but unlike the Sunset instrument, no denuder is used. Aerosol is sampled at a flow rate of 22 lpm through a $PM_{2.5}$ inlet for 24 hours, every third or sixth day. OC and EC are then determined via the IMPROVE_A temperature protocol (Chow et al., 2007) by Desert Research Institute (DRI) using a DRI Model 2001 carbon analyzer. In this protocol, a 0.5 cm^2 circular segment of the filter is removed, and aerosol are thermally evolved off of the filter (similar to the process for the Sunset instrument), where OC is determined under a non-oxidizing atmosphere with He gas, and then EC is found using a mix of 98% He and 2% O_2. Carbonaceous aerosol is volatilized off the filter and converted to CO_2 in an MnO_2 oxidizer, and then reduced to methane via a nickel catalyst and quantified as methane with a flame-ionization detector (FID). For OC, the temperature is ramped to four temperature plateaus at 140°C, 280°C, 480°C, and 580°C, where the temperature is held constant at each plateau until the response in the FID has returned to baseline for 30 seconds (i.e., until there is no more carbonaceous material being volatilized from the filter at that temperature). The He/O_2 atmosphere is then introduced while the temperature is held at 580°C in order to initially quantify pyrolyzed organic carbon (OP), and then the temperature is increased to

740°C and 840°C. The sum of the carbon evolved in the He atmosphere plus the OP is equal to total OC, while the sum of the carbon evolved under the He/O_2 atmosphere minus the OP is equal to total EC. As reported in EPA's 2014 Environmental Technology Verification Report EPA/600/R-14/308, the precision of this instrument based on replicate analyses is greater than 15%, and indicates "a lower degree of data quality than desired."

3.4 Aethalometer

A Magee Scientific Aethalometer was operated at Washington, D.C. (AE21 instrument), St. Louis (AE33 instrument), and Houston (AE21 instrument). The Aethalometer measures BC via an optical method, instead of the thermal method used by the Sunset and CSN (Allen et al., 1999; Weingartner et al., 2003). Aerosol is sampled through a BGI model SCC $PM_{2.5}$ cyclone inlet at 5 lpm and deposited on a filter tape. Every 5 minutes, the Aethalometer measures the light attenuation at 880 nm through the filter tape, and is converted into a BC concentration by assuming an attenuation cross-section of 16.6 m^2/g. The measured BC is subtracted from the prior measurement of BC to determine the BC collected during the 5 minutes of sampling. No post-processing of the raw data was done. For example, when the tape on which aerosol is deposited reaches a given saturation point, the tape advances, so that aerosol is now deposited on a new section of tape. When this occurs, there can be an artifact in the data stream that is not automatically accounted for or corrected without post-processing (Drinovec et al., 2015; Jimenez et al., 2007; Weingartner et al., 2003). The AE33 has two built-in light sources to automatically correct for this (Drinovec et al., 2015), but no correction was made for the AE21 data.

3.5 Data Processing and Quality Control

Sunset and Aethalometer data were reported in both local conditions (LC) and standard temperature and pressure (STP). STP data were converted to LC using local meteorological data; all data reported here are in LC. Daily 24-hr averages were calculated from hourly Aethalometer and Sunset data where at least 75% of the hourly data were available.

During the project, the agencies operating the Sunset instrument encountered instrument component malfunctions such as cracked ovens, NDIR detector failure, heating element failure, and pump failure. These issues were not easily diagnosed during operations and led to shifts in baselines and other data issues that made the data unusable for this analysis. The oven and NDIR problems were typically not found early on, since at the time there was no routine output from the instrument alerting users to these issues, or readily available data from CSN for comparison; this resulted in multiple weeks of data being removed prior to analysis. Data were visually inspected on time series to identify periods where there were sudden shifts in concentration, small quantities of data between data gaps, and unusual outliers.

At St. Louis, starting in January 2015, a filter was stuck, and then during March 2015–January 2016, operators suspected contamination, adjusted the thermocouple, and installed a new photodetector. However, the new photodetector was not working correctly, and data did not return to "normal" until after the oven was replaced in January 2016. There were additional issues with keeping the flow steady in June through July 2016. At Washington, D.C., there were periods where OC or EC concentrations were greater than 100 µg/m^3, even though collocated $PM_{2.5}$ concentrations were low; these data were excluded from analysis here. Prior to May 2014, OC was not reported at this site, so no data were included here for analysis. Only data starting June 2014 were included for analysis, since there were operational issues prior to this time. Data in June 2015 and February–March 2016 were also excluded from analysis because of operational issues associated with a software update in June and a heating coil malfunction at the end of January 2016, which was not fixed until the end of March 2016. Time series graphics of all measurements at each site are provided in Appendix B, and completeness for each parameter is detailed in Table B1.

At Chicago, there was a significant shift in the lowest reported OC values beginning at the end of December 2014, so only data prior to this shift are included here, and only when OC and EC are both reported. Data after January 2015 were excluded from analysis since there was a clear gradual rise in baseline of OC due to degradation of the NDIR. In Houston, there were multiple gaps in the data as NDIR detectors and ovens had to be replaced. Data prior to December 2014 were excluded since older software was used to determine OC/EC and OptEC, the NDIR malfunctioned and was replaced twice, the oven thermocouple malfunctioned and was replaced, there were leaks, and the instrument was sent back to Sunset twice for maintenance. Data during May–August 2015 and July–August 2016 had an unusual shift in OC, and EC was near zero; both of these issues occurred when there were leaks in the sampling line, and neither was seen in the collocated CSN measurements.

Data in Las Vegas were intermittent during the course of operations, resulting in many anomalous data points and shifts in data. Only data with multiple weeks of consistent measurements were included for analysis. For example, in November 2012, OC was consistently reported as less than 0.5 µgC/m^3, and in July and October 2014, the NDIR and heater coils broke and needed to be replaced multiple times, there was vandalism at the site so the shelter air conditioning unit was not working, and instrument software was not routinely updated. The period of December 2012 to May 2013 was the most consistent and complete period of data, and is used here. Given the operational issues at this site, results are not expected to be representative of optimal instrument operations or of other locations, but they are included for completeness. At Rubidoux, there were two periods where there was a significant shift in the lowest reported OC values (May–September 2014 and March–October 2015), when operators found leaks in the sampling line and the oven had to be replaced twice. These data were screened out from further analysis; time series graphs showing the data as reported in AQS and after the subsequent QC described above are provided in Appendix B.

This QC process substantially reduced the number of valid Sunset data points compared to the number reported in AQS. Data availability and summary statistics after data processing and validation is available in Appendix B. After QC, there was a range of coincident, collocated 24-hr

Sunset and CSN values available for comparison, which is detailed in Table 2. Since there were a number of operational issues throughout the project, the quality of data varies by site. For example, data recovery was low at Las Vegas, Chicago, and Rubidoux, so results for these sites are likely less representative than results for Houston, St. Louis, and Washington, D.C. While these latter three sites also had operational issues—in particular, problems with broken ovens and NDIRs not being detected—sufficient data were collected for comparison to CSN data.

Table 2. Available collocated 24-hour Sunset and CSN measurements by site.

Site	N Collocated OC Measurements	N Collocated EC Measurements	Date Range
Chicago	57	60	5/2/2014-12/31/2014
Houston	154	154 OptEC, 152 EC	12/13/2014 – 10/15/2016
Las Vegas	53	53	12/11/2012 – 9/20/2014
Rubidoux	75	75	12/18/2013 – 3/10/2015
St. Louis	198	198 OptEC, 63 EC	9/22/2013 – 1/10/2017
Washington, D.C.	208	211 (OptEC), 208 EC	6/1/2014 – 8/10/2016

3.6 Comparison of Sunset Data to CSN and Aethalometer Data

Detailed measurement quality objectives (MQOs) for comparing Sunset data to CSN and Aethalometer data were discussed in the Project QAPP (U.S. Environmental Protection Agency, 2011). These MQOs include comparison via linear least squares regression, comparison of means including variability, and ratio of the means. In addition, collocated measurements at St. Louis were used to estimate precision, which is the measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions. The MQO for ratio-of-means in CSN measurements was set as 1 ±0.15, where the coefficient of variation (CV) is used as the measure of variability. A recent assessment of collocated CSN data at six sites results in a CV of 8.8% (Rice and Landis, 2016). For all statistics, we report values when the two measurements we are comparing occurred on the same day; e.g., for Sunset and CSN OC, only those days with measurements of both, and for Sunset and Aethalometer, only those days with measurements of both. Thus, there will be some differences in reported values, especially when comparing Sunset EC to either Aethalometer BC or CSN EC, since there are many more days with Aethalometer data than with CSN data. In addition to comparing means within the CV, we also report whether concentrations between two measurements were statistically significant based on a Student's t-test.

4. Results

4.1 Sunset OC Bias and Detection Limit Calculations

Results of CV, bias and detection limit calculations using data from sucrose injections for the two Sunset OC/EC instruments at EPA site are shown in Table 3. The CV and bias values meet the data quality objectives of 15%, ranging between 5% to 6% between the two instruments for bias, and 6%-8% for CV, which is similar to the 8.8% CV across six collocated CSN OC TOR measurements (Gantt et al., 2017). The bias estimates are similar to prior estimates from collocated Sunset OC/EC instrument data, where Bauer et al. (2009) estimated bias of 5.3%-5.6% for OC. The calculated detection limit was between 1.4 to 1.5 µg/m^3, which was higher than the estimate of 0.2 µg/m^3 in Bauer et al. and Sciare et al. (2011), and higher than the estimated MDL from CSN of 0.2 µg/m^3 in Sciare et al. The difference in detection limit calculation methodologies may explain part of the differences among results. The CSN results are calculated as three times the standard deviation of 50 field blanks, while Bauer et al. used a limit of detection calculation as the 95th percentile of the standard deviation across zero air measurements, and Sciare et al. took the average value across 7 blank filter samples. The detection limit found here is similar to an estimated detection limit of 2.0 µg/m^3 from Zheng et al. (2014), who evaluated how results varied under different operational protocols.

Table 3. Calculations of CV (%), bias (%), and detection limit (ug/m^3) based on sucrose injection results for two Sunset OC/EC instruments at EPA OAQPS.

Metric	Sunset 1	Sunset 2
N valid	68	85
Coefficient of variance, CV (%)	7.6%	5.8%
Bias	6.3%	5.4%
Detection limit ug/m^3	1.4	1.5

4.2 Sunset and CSN OC

Figure 1 shows box plots of 24-hr OC concentrations via Sunset and CSN, and Figure 2 shows Sunset versus CSN on a scatter plot. Summary statistics of the Sunset-to-OC comparison are provided in Table 4; only days where both Sunset OC and CSN OC data were available are included. Average Sunset OC concentrations ranged from 2.1 µg/m^3 at Houston to 3.2 µg/m^3 at Rubidoux. Overall, OC concentrations were higher when measured with the Sunset than in CSN, with an average ratio of means (ROM) of 1.13. However, this was largely driven by differences between Sunset and CSN at Las

Vegas, where the means between the two methods are not comparable. At the other five sites, the ROM was 1.06, indicating that on average there was good agreement between the two methods and that MQOs were generally met. As noted earlier, there were significant and frequent operational problems at Las Vegas that likely biases the results there. When the 8.8% precision (CV) of CSN OC is considered, all sites have comparable means between Sunset and CSN except at Las Vegas. Where sufficient samples were available, we also found that there was no significant change in the ROM among seasons, i.e., Sunset and CSN means were comparable in all seasons at each site that had at least 10 24-hr values, except at Las Vegas.

The correlation (r^2) between Sunset and CSN with all measurements was 0.67, and nearly meets the MQO of R=0.90 if Las Vegas is excluded (r^2 = 0.73, R = 0.85). The slope is close to 1 at Rubidoux, Chicago, and St. Louis (0.87 to 0.93), and lower at Las Vegas and Houston (0.62 to 0.66). Grouping all measurements together yields a slope of 0.77, with a bias towards Sunset OC being higher than CSN OC. The scatter plot shows a number of outliers, in particular at Las Vegas and Houston, where both CSN and Sunset measurements initially appeared to be valid and were not removed after initial investigation. Without these outliers, the correlation improves marginally, but the bias between the two measurements would remain relatively unchanged. In fact, even with the multiple operational issues that occurred, the bias between Sunset and CSN measurements is fairly consistent across sites.

Overall, the Sunset and CSN OC concentrations compared fairly well across the sites, with an r^2 of 0.67 and comparable means at all sites except Las Vegas, though with variations in the degree of scatter depending on the frequency of operational issues. There is consistently a bias toward Sunset OC being higher than CSN OC, though this varies by site; however, only at Las Vegas and Houston are the Sunset OC values significantly higher than the CSN OC values. At St. Louis, where there are nearly 200 measurements included in the analysis, the ratio between Sunset and CSN switches from a Sunset/CSN ratio of 1.06 during the early period of operations of 2013 through early-2015 to 0.91 in 2016 and 2017. The differences between the two periods is that new software, a new oven, and a new NDIR detector were installed, so it is unclear which of these specific actions led to a change in Sunset OC readings. At Las Vegas, there were frequent operational issues, and the sample size is relatively small compared to other sites (n = 53), so these results cannot be weighted as heavily as those from other sites. With a somewhat broad range of results, Sunset operations likely play a large role in how well the instrument compares to CSN OC data.

In addition, there are differences in how the two thermal-optical methods determine OC and EC; these differences may play a role in how comparable the Sunset (which used NIOSH) and CSN (which used IMPROVE_A) measurements are, even though the total carbon (OC + EC) typically compares well between the two methods (Chow et al., 2001; 2007). A main difference between the two methods is the temperature regime used to determine OC and EC: in NIOSH; the temperature is ramped to 870°C for determining OC while in IMPROVE_A, it is ramped to 550°C. This means that some carbon that is quantified as OC in NIOSH may be quantified as EC in IMPROVE_A; therefore, for a given sample, the NIOSH OC would be higher than the IMPROVE_A OC, and the NIOSH EC would be lower than the IMPROVE_A EC. In a direct comparison of these different maximum temperature regimes, Piazzalunga confirmed that a "significant amount" of weakly light-absorbing carbonaceous aerosols were evolved off under 870°C (Piazzalunga et al., 2011). In Hong Kong, Wu et al. compared NIOSH and IMPROVE measurements across urban, roadside, and suburban sites over three years, and found that differences between the two methods are mostly from the way the OC and EC split is determined, such that in Hong Kong EC from IMPROVE_A was roughly 2.2 times higher than from NIOSH, with more minor differences for OC between the methods (Wu et al., 2016). They also found that the amounts of biomass burning and metal oxides such as iron and zinc also impacted how well the two methods compared, where higher metal oxide concentrations led to an increase in the difference between IMPROVE_A and NIOSH EC. Similar results were found in the Southeastern United States during 2003-2005, with total carbon comparable between the two methods but with lower EC from the NIOSH method (Cheng et al., 2011).

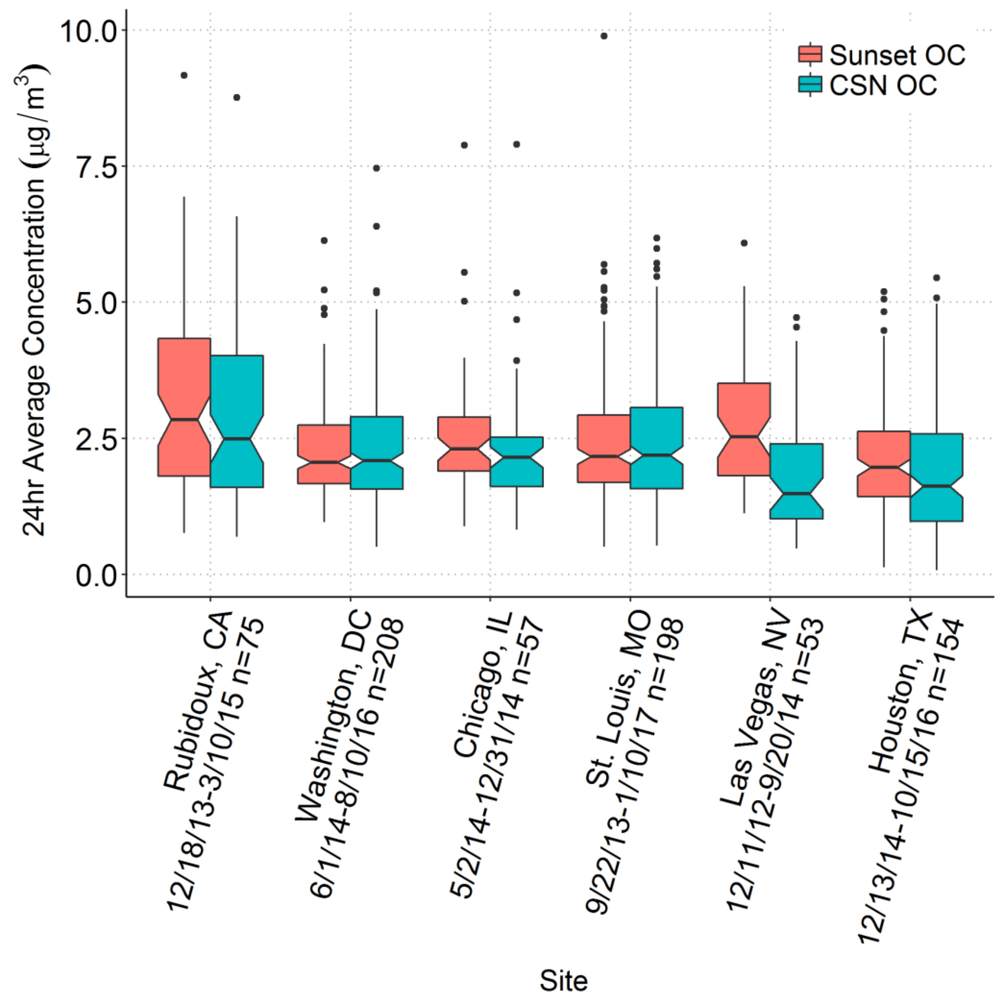

Figure 1. Box plot of OC concentrations at each site via Sunset and CSN measurements.

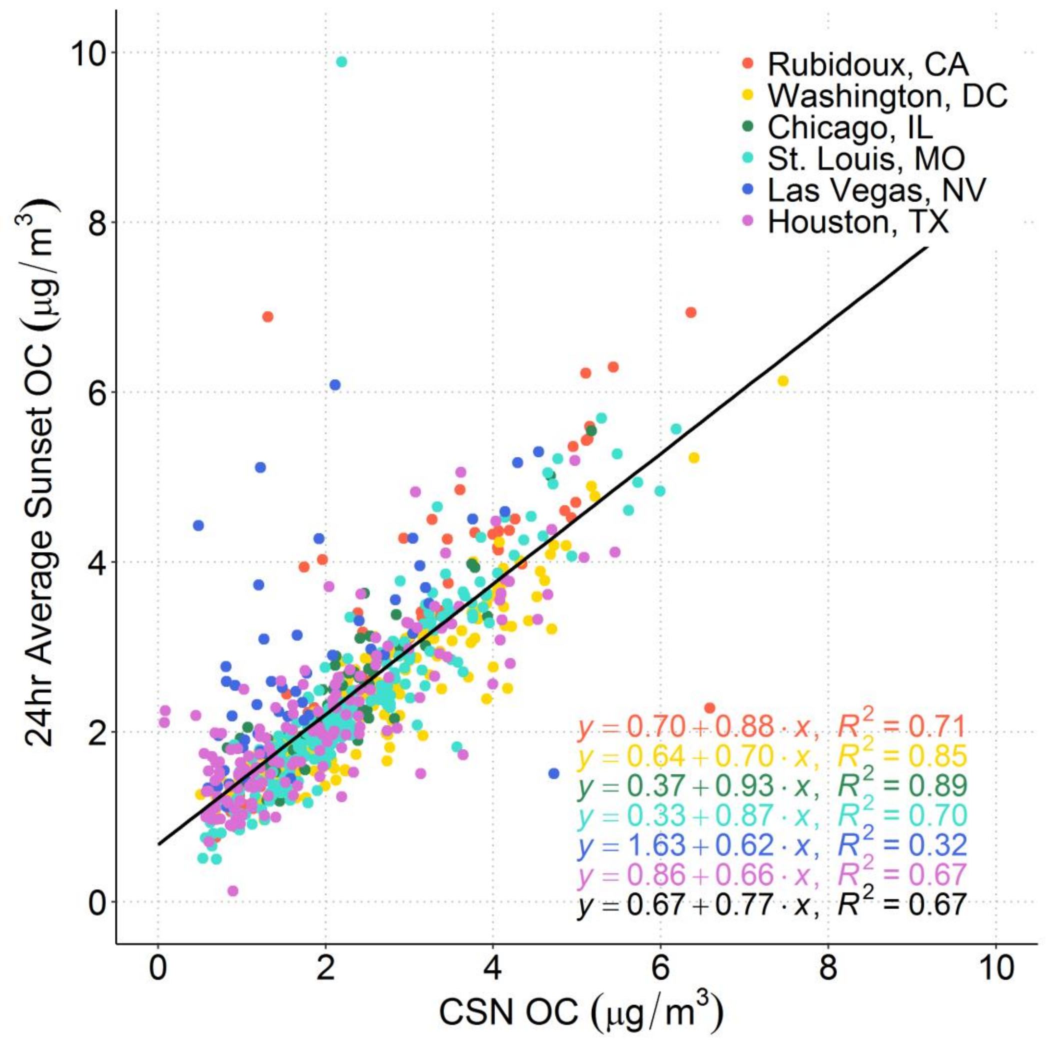

Figure 2. Scatter plot of Sunset and CSN OC concentrations, colored by site; the linear regression equation written in black is for all data at all sites.

Table 4. Summary of Sunset and CSN OC measurements and comparison statistics.

Site	N	Mean Sunset OC	StDev Sunset OC	Mean CSN OC	StDev CSN OC	Ratio of the Means	Comparable Means?	Slope	Intercept	r^2
Rubidoux	75	3.2	1.7	2.8	1.6	1.12	Yes	0.88	0.70	0.71
Washington D.C.	208	2.3	0.8	2.4	1.1	0.96	Yes	0.70	0.64	0.85
Chicago	57	2.5	1.1	2.3	1.2	1.09	Yes	0.93	0.37	0.89
St. Louis	198	2.4	1.2	2.4	1.1	1.01	Yes	0.87	0.33	0.70
Las Vegas	53	2.8	1.2	1.8	1.1	1.52	No	0.62	1.63	0.32
Houston	154	2.1	0.9	1.9	1.2	1.10	Yes	0.66	0.86	0.67

4.3 Sunset and CSN Thermal EC and Sunset Optical EC

Summary statistics of the Sunset-to-CSN EC comparison are provided in **Table 5**; only days where both Sunset EC or OptEC data plus CSN EC were available are included. **Figure 3** shows box plots of 24-hr EC concentrations at each site via Sunset and CSN, and **Figure 4** shows scatter plots comparing CSN EC concentrations with Sunset EC and Sunset OptEC. (For Sunset EC, both thermal EC and optical EC results are shown.) Mean CSN EC concentrations varied between 0.26 µg/m^3 (Houston) and 0.83 µg/m^3 (Rubidoux). Sunset thermal EC was similar to CSN EC on average (1.03 ROM) when excluding Las Vegas and Houston; these latter two had much higher ROM (1.76 and 3.55, respectively) and recorded significantly higher Sunset EC compared to CSN EC. OptEC was consistently lower than CSN EC except at Houston; the average Sunset OptEC/CSN EC ratio when excluding Las Vegas and Houston was 0.90. Houston OptEC was much closer to CSN EC than the thermal EC was (ratio of 1.08 instead of 3.55). Thus, except for OptEC at Las Vegas and the thermal EC at Houston, MQOs were met.

While there is good agreement between the overall EC means at all sites, with the exception of thermal EC at Las Vegas and Houston, the slope and correlation between Sunset and CSN measurements vary widely. For thermal EC, there is relatively high correlation at St. Louis, Rubidoux, and Chicago (r^2 of 0.76 to 0.89 for Sunset EC to CSN EC), but there is poor correlation for the other sites (r^2 of 0.33 to 0.41). Correlations and slopes are more comparable for OptEC to CSN EC, with an r^2 value of 0.67 when all measurements are pooled together, although with a bias toward CSN EC being higher (slope of 0.65).

Overall, OptEC measurements appear to be more in line with CSN EC than the thermal EC measurements are. It is unclear what operational differences occurred at Houston to result in such a large disparity between the site's EC and OptEC results, which was consistent throughout the study. In addition, having fairly consistent results across all five sites with OptEC, despite numerous operational issues, is significant: the OptEC measurement is fairly consistent when compared to CSN EC despite different locations and operations. The difference between OptEC and thermal EC is partially due to differences in detection limits; 26% of hourly concentrations were below the detection limit of 0.2 µg/m^3 for thermal EC. Bauer et al. (2009) estimated that the detection limit for OptEC is lower than for thermal EC, at between 0.02 to 0.1 µgC/m^3; having so many of the observations near or below the detection limit for thermal EC likely impacts these results. Potential interferences in the thermal method from metal oxides may also play a role.

Table 5. Summary of Sunset and CSN EC measurements and comparison statistics.

Site Code	Site Name	N	Mean Sunset EC	StDev Sunset EC	Mean CSN EC	StDev CSN EC	Ratio of the Means	Comparable Means?	Slope	Intercept	r^2
Sunset EC vs. CSN EC											
06 065 8001	Rubidoux, CA	75	0.94	0.57	0.83	0.56	1.13	Yes	0.88	0.21	0.76
11 001 0043	Washington, DC	208	0.40	0.23	0.52	0.42	0.75	Yes	0.35	0.21	0.41
17 031 0076	Chicago, IL	60	0.50	0.26	0.40	0.21	1.24	Yes	1.18	0.02	0.89
29 510 0085	St. Louis, MO	63	0.41	0.35	0.42	0.24	0.99	Yes	1.28	-0.13	0.76
32 003 0540	Las Vegas, NV	53	0.93	0.77	0.53	0.45	1.76	No	0.97	0.42	0.33
48 201 1039	Houston, TX	154	0.93	0.37	0.26	0.14	3.55	No	1.50	0.54	0.33
Sunset OptEC vs. CSN EC											
06 065 8001	Rubidoux, CA	75	0.75	0.52	0.83	0.56	0.90	Yes	0.81	0.07	0.77
11 001 0043	Washington, DC	211	0.44	0.26	0.52	0.42	0.83	Yes	0.45	0.20	0.50
29 510 0085	St. Louis, MO	198	0.42	0.24	0.43	0.25	0.98	Yes	0.89	0.04	0.88
32 003 0540	Las Vegas, NV	53	0.37	0.26	0.53	0.45	0.70	No	0.42	0.15	0.53
48 201 1039	Houston, TX	154	0.28	0.18	0.26	0.14	1.08	Yes	1.06	0.01	0.69

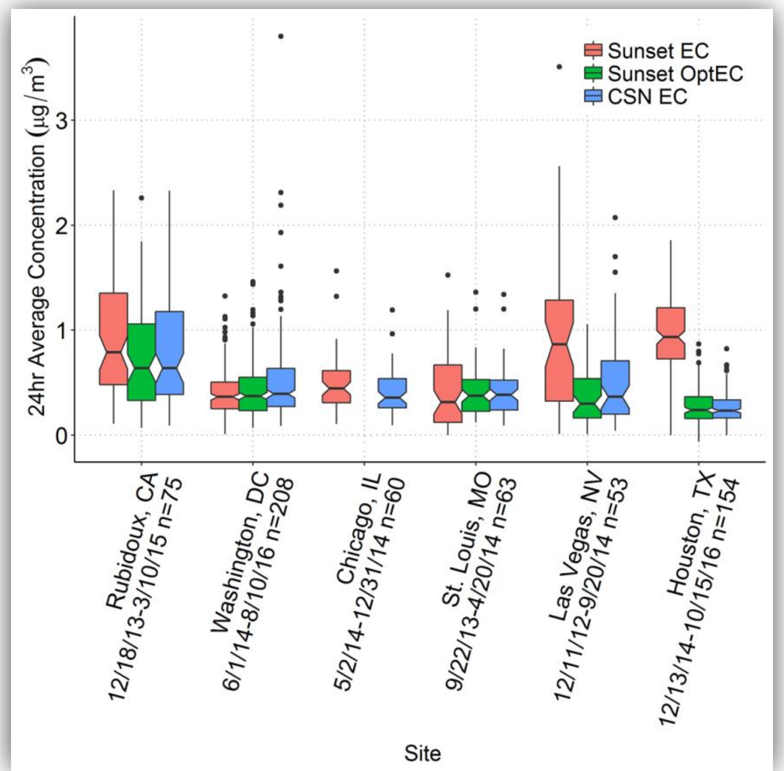

Figure 3. Box plot of Sunset EC, Sunset OptEC, and CSN EC concentrations at each site.

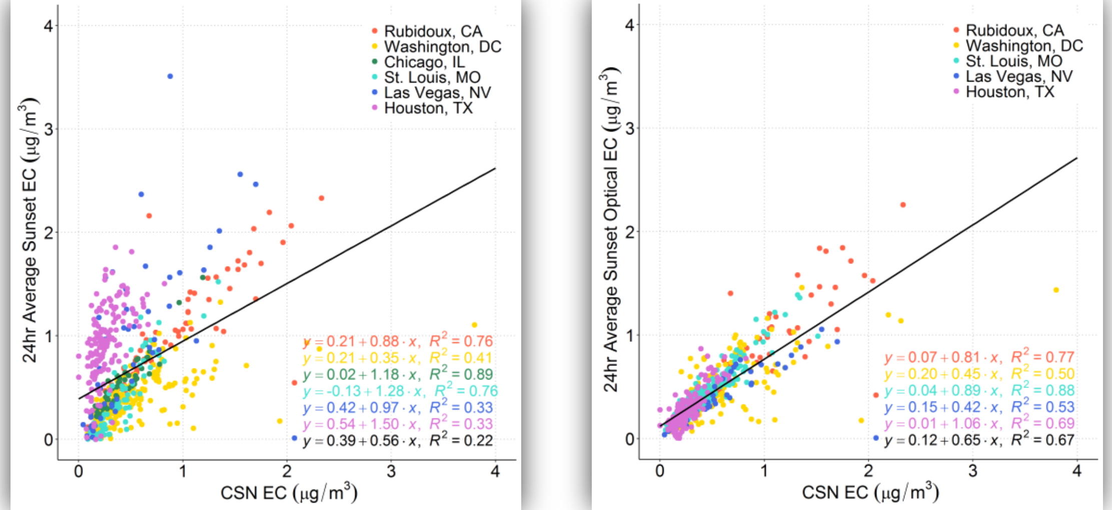

Figure 4. Scatter plot of CSN EC concentrations with Sunset EC (left) and Sunset OptEC (right), colored by site; the linear regression equation written in black is for all data at all sites.

4.4 Sunset OptEC and Aethalometer BC

Summary statistics of 24-hour Sunset OptEC to Aethalometer BC are provided in Table 6, and comparisons between the two measurements are shown in Figures 5 and 6. The Sunset OptEC was consistently lower than the Aethalometer BC at all three of the sites that had data for both measurements (Washington, D.C., St. Louis, and Houston), with a mean ROM of 0.57. This ratio was fairly consistent at each site, with little seasonal variation. For example, the OptEC/BC ratio at Washington, D.C. varied between 0.65 in the winter to 0.70 in the summer. At all three sites, the differences in OptEC and BC measurements were statistically significant, and the measurements were not comparable even when accounting for the precision of the Aethalometer (3.5% for 24-hr measurements).

This consistent offset between the two measurements is clearly seen in the scatter plot at Figure 6, where the r^2 value is higher than 0.82 and the intercept is near zero at all three sites. The relationship between Sunset OptEC and Aethalometer BC is consistent at a range of concentrations, which in this study is up to 2 $\mu g/m^3$ OptEC. However, the slope of the regression, and the ratio of the OptEC/BC means, varies across sites. At St. Louis, the OptEC/BC ratio is 0.47, but at Washington, D.C., it is 0.67. In a multi-year study in New York, similar results were found, with a high correlation between EC and BC, and with BC higher by nearly a factor of 2 during summertime (ratios of 1.3 in winter and 1.8 in summer) (Rattigan et al., 2010; 2013). They also report variation in the BC/EC ratio that we did not see at the sites in this study, with a higher ratio in summer than in winter. In addition, Rattigan et al. (2013) found variation in the BC/EC ratio between the Bronx and Rochester, i.e., between a major urban area and a smaller one. They ascribe part of this variation to changes in optical properties of the ambient aerosol due to emissions from residential wood burning or fuel oil in the wintertime. We do not see the large seasonality in the BC/EC ratio that was observed in Rattigan et al. However, the OptEC/BC ratio is consistently different at each of the three sites here, either due to operational differences among the sites and the sites in Rattigan et al., and/or due to differences in aerosol sources between New York and the sites here.

Table 6. Summary of Sunset OptEC and Aethalometer BC measurements and comparison statistics.

Site	N	Mean Sunset OptEC	StDev Sunset OptEC	Mean Aeth BC	StDev Aeth BC	Ratio of the Means	Comparable Means?	Slope	Intercept	r^2
Washington D.C.	618	0.45	0.27	0.67	0.43	0.67	No	0.59	0.05	0.85
St. Louis	544	0.40	0.22	0.85	0.47	0.47	No	0.44	0.02	0.87
Houston	415	0.31	0.20	0.57	0.26	0.54	No	0.71	-0.10	0.82

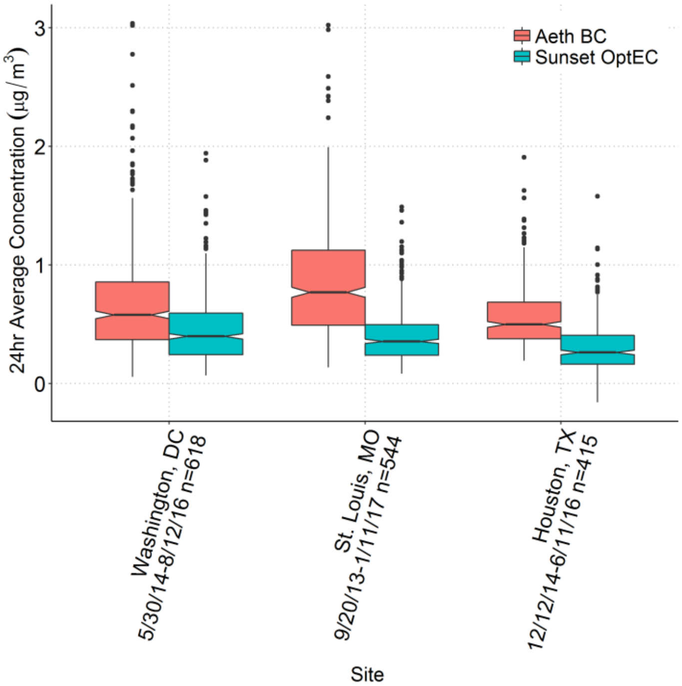

Figure 5. Box plot of 24-hour average Sunset OptEC and Aethalometer BC.

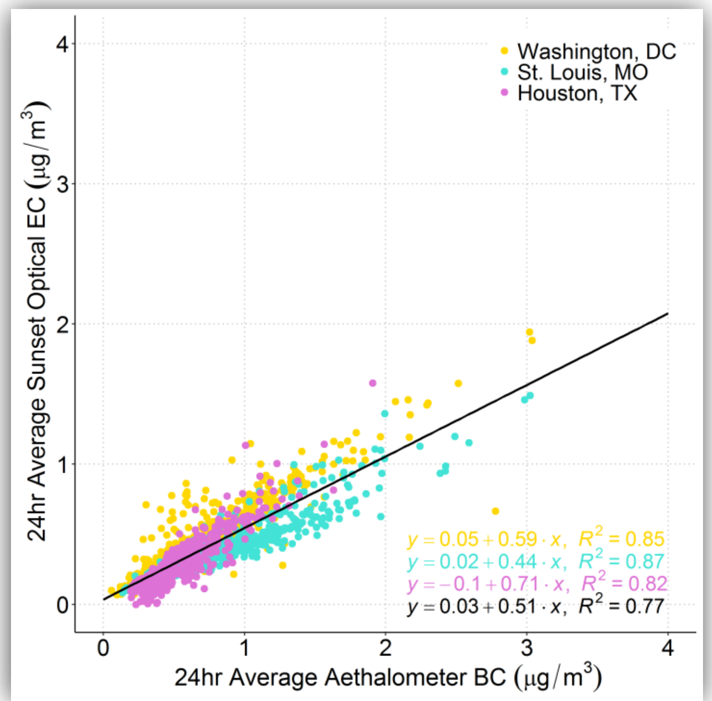

Figure 6. 24-hour averaged Sunset OptEC and Aethalometer BC, colored by site; the linear regression equation written in black is for all data at all sites.

4.5 Precision from Collocated Measurements in St. Louis

Collocated Sunset instruments were operated at St. Louis during August 11, 2016, through January 11, 2017, and offer a way to gauge precision between two relatively well-operating instruments. A scatter plot of the two instruments, termed POC 1 and POC 2, is shown in Figure 7 for 24-hr average OC and Optical EC (n=102); only OptEC was reported at St. Louis during this time period. POC 1, which had been operated during the course of the study, used He as a carrier gas; POC 2 was set up in the summer of 2016 and used zero air as a carrier gas.

OC concentrations varied between 0.6 and 6.7 µgC/m^3, and OptEC between 0.1 and 1.7 µgC/m^3. There is consistent agreement between both OC and OptEC measurements from the two instruments, with r^2 values of 0.93 for OC and 0.91 for OptEC. There is a bias in the slope (1.04 for OC, 1.12 for OptEC), but with an offset (y-intercept) of 0.7 µgC/m^3 for OC and no offset for OptEC (y-intercept of zero). This offset for OC may be due to differences in carrier gas, with small impurities in either the He or zero air carrier gas influencing the OC concentrations but not the OptEC. Results are similar to some of the first series of collocated measurements reported by Bauer et al., which found high correlation (0.97 and 0.98) for OC and OptEC when an ambient sample stream was split and routed to two collocated Sunset instruments (Bauer et al., 2009). They found a lower slope for OptEC (0.82) and magnitude similar to our results for OC (0.95). Their interpretation of results similar to the ones found here at St. Louis was that the instrument produces reliable and reproducible measurements when mass loadings are higher than detection limits. They also note that the instrument needs to be working properly for obtaining such reliable data, similar to the experiences found at multiple sites in this study.

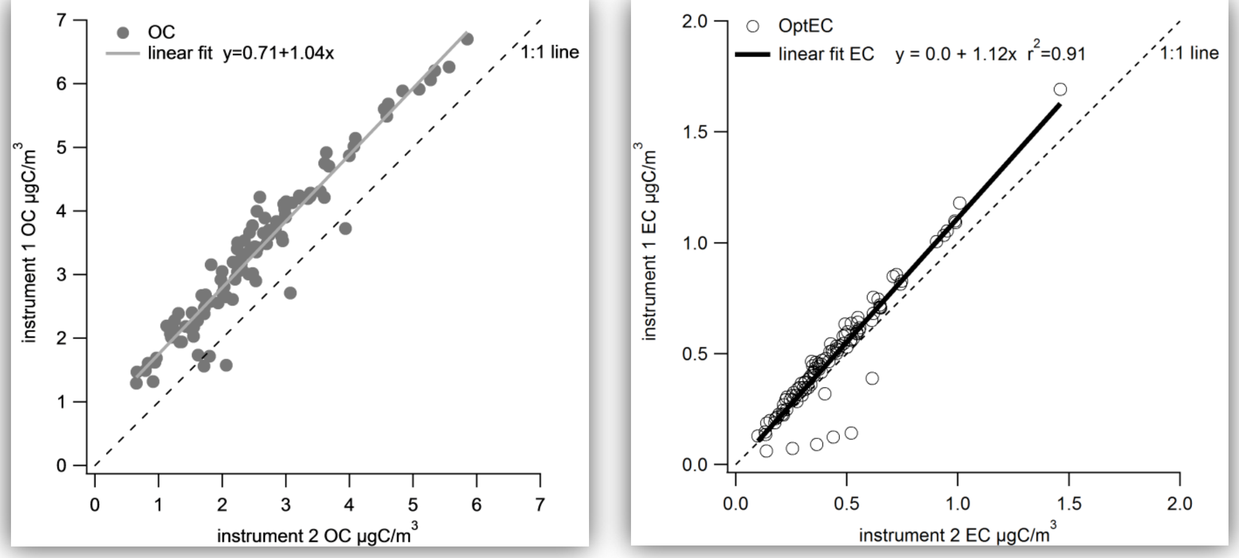

Figure 7. Collocated 24-hour OC (left) and OptEC (right) measurements at St. Louis during August 11, 2016, through January 11, 2017.

4.6 Diurnal Patterns

A strong diurnal pattern was seen at Rubidoux and Las Vegas for both OC and EC, but the average diurnal pattern at other sites was more muted (**Figure 8**). At Rubidoux, OC peaked in the evening while EC peaked in the morning. At the other sites, an overnight peak in OC was also seen, though this overnight peak was only modestly higher than the morning or midday concentrations. EC peaked in the morning at all sites, and was clearly higher on weekdays compared to weekends at all sites. OC was slightly higher on weekends compared to weekdays for nearly all hours at each site. This suggests that while ambient EC concentrations may be more driven by changes in traffic in the morning and on weekdays compared to weekend, ambient OC concentrations are a complex mixture of aerosol and semi-volatile material that varies due to changes in photochemistry, ambient particulate matter concentration levels, and emissions (Jimenez et al., 2009; Donahue et al., 2012; Robinson et al., 2007).

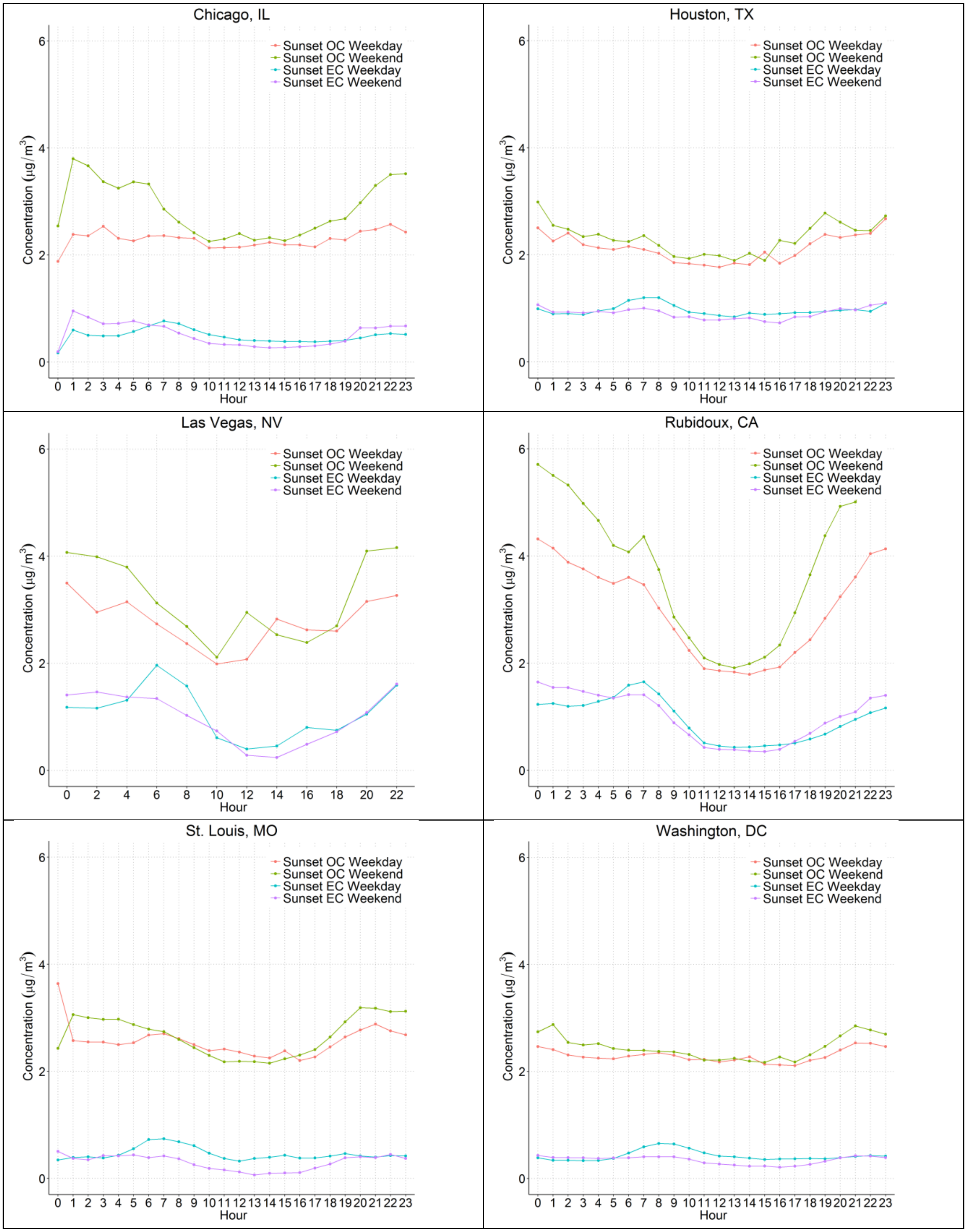

Figure 8. Average hourly OC and EC concentrations on weekdays and weekends at each site.

5. Conclusions

Sunset OC/EC instruments were operated at six sites collocated with CSN measurements, with Aethalometer measurements collocated at three of these sites. Operations were quite variable among the sites, with multiple operational issues at all the sites. Critically, when components of the instrument broke, e.g., the oven or NDIR, it was not clear in the data output that there was a problem. This led to multiple weeks to months of operations with a broken component, resulting in large gaps in quality data. Many of these components have since been upgraded or redesigned by Sunset Labs, including changes to the software that will better alert users when a component is damaged.

Despite the operational problems at all sites, overall Sunset OC and OptEC compared well with CSN and Aethalometer measurements. Sunset OC was consistently higher than CSN OC, with a Sunset/CSN ratio of 1.06. This ratio is well within the precision of the CSN measurements, so the Sunset and CSN OC are comparable. While, on average, the Sunset EC and CSN EC were similar at four of the six sites, there was large scatter and varying biases between these two thermal EC measurements across all sites. This indicates that the thermal EC measurements are not as comparable as the OC measurements are, though part of this may be due to having 26% of Sunset EC measurements below the detection limit. Sunset OptEC data had a much better agreement with CSN EC data, as well as with Aethalometer BC data; Sunset OptEC also has a lower detection limit than Sunset EC, which likely accounts for its improved comparison to CSN EC. The OptEC was consistently lower than the BC, similar to what has been seen previously in the literature, though we did not see seasonal fluctuations in the OptEC/BC ratio. That OptEC is quite comparable to both CSN EC and BC indicates that it is a robust and consistent measurement. Overall, with improvements to the NDIR, oven, and software, the Sunset instrument is a viable instrument for field deployment, though not as “plug and play” as other particulate instruments used in routine monitoring networks.

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Appendix A. Summary of Instrument Operations During the Sunset Carbon Evaluation Project

Sonoma Technology, Inc.
Innovative Environmental Solutions

Technical Memorandum

October 9, 2017 STI-915313-6804-TM

To: Beth Landis, EPA OAQPS

From: Hilary Minor, Steven Brown

Re: Summary of instrument operations during the Sunset carbon evaluation project

Study Overview

The Sunset Carbon Evaluation Project, led by EPA's Office of Air Quality Planning and Standards (OAQPS) Ambient Air Monitoring Group (AAMG), assessed the performance and feasibility of the Sunset Semi-Continuous Organic and Elemental Carbon (OC/EC) instrument at six sites throughout the United States (Chicago, St. Louis, Washington D.C., Houston, Las Vegas, and Los Angeles) during 2012-2017. State and local monitoring agencies operated the Sunset instrument to evaluate instrument performance, gain proficiency in the proper operation and maintenance of the instrument, compare the Sunset thermal OC/EC with the URG 3000N thermal OC/EC sampler, and compare the Sunset optical EC with the Aethalometer optical black carbon (BC) instrument. After the study ended, Sonoma Technology, Inc. (STI) worked with the monitoring agencies that operated the Sunset carbon analyzer, representatives from Sunset, and EPA staff involved in the evaluation project to understand the operational issues encountered during the Sunset Carbon Evaluation Project. This report summarizes the issues experienced during the evaluation study and, if applicable, details of Sunset's improvements to the instrument since the study has ended.

Operational Issues, Analysis, and Resolution

Issue: Users struggled with the sucrose injection process and found it complicated and time intensive.

Sucrose injections were recommended every two weeks, in order to determine the calibration constant (the total mass [µg] of carbon in the instrument's calibration loop at any given time). Users requested guidance on the type of pipette or syringe for easiest application, application technique, and acquisition and storage of the sucrose solution. A system that is more user-friendly would improve their experience. Initially, there was high variability among sucrose injections, so the type of syringe used was changed to an autopipette, and Sunset implemented a drying step to remove variability in the sucrose injections.

- As part of the review of the project, Sunset's representative commented that users were performing sucrose injections more frequently than needed. Sucrose injections are used to determine the calibration constant, which should only change as the calibration gas tank is changed, approximately every 1 to 1.5 years.[1] After the evaluation study, Sunset developed instrument performance filters that can be used instead of the sucrose injections. However, the Sunset manual also indicates that calibration checks should be performed on a weekly basis, which conflicts with the information presented above.
- The non-dispersive infrared (NDIR) detector was improved, negating an interference issue that required the sucrose solution to dry before the sucrose standard analysis was begun.
- The preparation and storage of carbon standard stock solution is detailed in the manufacturer's instrument guide.[2]

Resolution: The NDIR detector was improved and performance filters are now available to users, so sucrose injections do not appear necessary except when calibration gas tanks are changed. However, additional clarification on the frequency of and the procedure for performing sucrose injections is needed in the manual.

Issue: Users experienced hardware issues throughout the evaluation study.

Hardware issues included cracked ovens, NDIR detector failure, heating element replacement, and pump failure. Users noted that the instrument component malfunctions were not easily diagnosed and led to shifts in baselines and other data issues that make the data unusable. These hardware failures were also expensive and time-consuming to fix.

- Sunset improved the NDIR detector, increasing the lifespan of the device from 2 years to 5-7 years.
- The instrument now features extended-life heating coils, so these should not have to be replaced as frequently as the coils in this study.
- The error message screens are designed to minimize errors and report specific hardware or performance-related problems to users. To monitor the functionality of the hardware, Sunset recommends plotting and tracking instrument diagnostic metrics continuously over two- to four-week periods to monitor instrument performance. Specifically, Sunset recommends plotting and tracking the calibration area value, read from the **_Res.txt** results file, for changes of more than 10% that would indicate a leak. Users can also track the **Laser-Temp Correction** value, available on the main screen and in the **_LCRes.txt** results file, for any result below 0.90, which indicates that the filter needs to be changed. The results file, **Local Conditions Results** (**_LCRes.txt**), also contains error flags (1, "review", and 2, "fail") that alert users to problems.

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[1] Sunset Laboratory Inc., Organic Carbon and Elemental Carbon Field Instrument: Model 4 User's Manual (M4-Rev 9), page 43.

[2] Sunset Laboratory Inc. Semi-Continuous OCEC Carbon Aerosol Analyzer: A Guide to Running and Maintaining the Sunset Laboratory Semi-Continuous OCEC Analyser (M5-Rev3), page 83. Available at https://www3.epa.gov/ttnamti1/files/ambient/pm25/spec/Sunset_Manual.pdf.

Resolution: Sunset improved the NDIR and heating coil components and provided guidance on what metrics can be used to track instrument performance.

Issue: Users noted that software updates during the study did not detail the changes made to the software since the last version.

- Sunset's software improvement process first deploys software updates to a laboratory instrument and then, after testing, deploys the software updates to instruments in the field. Software updates during the evaluation study improved the OC/EC split determination and baseline corrections, and added the LC results files and the data validation columns.
- Sunset provided a list of major software changes in an undated manual.[3] Continuing to list major software changes would benefit users in the future.

Resolution: After the study was complete, Sunset provided information on software changes deployed during the evaluation study. Additionally, detailed software update information was provided in an older, undated version of the manual. Sunset should continue to inform users of the details of new software changes when the software changes are made.

Issue: Helium, a carrier gas used to purge the front and back ovens of ambient air, was in short supply and expensive during the evaluation study.

Resolution: A zero air tank, instead of a helium tank, can be used as the carrier gas. Staff at the Missouri Department of Natural Resources (DNR) were successful in running a Sunset with zero air instead of helium.

Issue: Users struggled with filter replacement technique and frequency.

Users noted that there were issues with the filter staying in place: if not tightened enough, the filter flips; if tightened too much, the filter or quartz insert breaks. Furthermore, Missouri DNR staff noted that filters needed to be replaced weekly when the instrument was running in thermal mode, compared to every two weeks when the instrument was running in optical mode.

*Resolution: There was no resolution found for the filter replacement technique, except that users can run the instrument in optical mode to reduce the frequency of filter changes. The **Laser-Temp Correction** parameter, displayed on the instrument's main screen, can be used to determine when the filter needs to be replaced. A value below 0.90 indicates that the filter needs to be changed.*

Issue: In general, operating the Sunset analyzer was relatively time-consuming and challenging.

Users noted that, in general, operating the Sunset analyzer is more time-consuming and challenging than operating other air monitoring instruments.

Resolution: Improved guidance on filter changes, sucrose injection frequency, and on what instrument metrics to monitor will help to reduce the time needed for running the instrument, as will improved NDIR detectors and heating coils.

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[3] Sunset Laboratory Inc. Semi-Continuous OCEC Carbon Aerosol Analyzer: A Guide to Running and Maintaining the Sunset Laboratory Semi-Continuous OCEC Analyser (M5-Rev3), beginning on page 25. Available at https://www3.epa.gov/ttnamti1/files/ambient/pm25/spec/ Sunset_Manual.pdf.

Appendix B. Supplemental Information

- Summary statistics of parameter by site
- Time series of Sunset data available in AQS by site, annotated where data were excluded from the analysis presented here
- Box plots of Sunset to CSN or Aethalometer ratios by site
- Box plots of Sunset and Aethalometer data by hour by site

Table B-1. Summary of 24-hr average valid data by site and variable. Completeness percentage is calculated for Sunset data only; SD is standard deviation.

Site Name	Variable	Count	Mean	Min	Max	Sd	Start Date	End Date	Expected Count	Completeness
Rubidoux, CA	CSN EC	469	0.7	0.0	3.0	0.5	8/1/2012	7/29/2016	1458	
Rubidoux, CA	CSN OC	469	2.7	0.4	9.5	1.3	8/1/2012	7/29/2016	1458	
Rubidoux, CA	Sunset EC	237	1.0	0.1	4.1	0.6	12/17/2013	10/14/2015	666	32%
Rubidoux, CA	Sunset OC	237	3.3	0.7	15.8	1.9	12/17/2013	10/14/2015	666	32%
Rubidoux, CA	Sunset OptEC	237	0.8	0.1	3.5	0.6	12/17/2013	10/14/2015	666	36%
Washington, DC	Aeth BC	1466	0.7	0.1	3.4	0.4	8/1/2012	12/22/2016	1604	
Washington, DC	CSN EC	544	0.5	0.0	3.8	0.3	8/4/2012	3/29/2017	1698	
Washington, DC	CSN OC	544	2.4	0.3	10.4	1.3	8/4/2012	3/29/2017	1698	
Washington, DC	Sunset EC	644	0.4	0.0	1.6	0.2	10/7/2012	8/13/2016	1406	32%
Washington, DC	Sunset OC	644	2.3	1.0	7.1	0.9	8/20/2013	8/13/2016	1089	32%
Washington, DC	Sunset OptEC	649	0.4	0.1	1.9	0.3	5/28/2013	8/13/2016	1173	46%
Washington, DC	Sunset TC	647	2.6	1.0	8.3	1.0	1/1/2013	8/13/2016	1320	59%
Chicago, IL	CSN EC	429	0.4	0.0	1.9	0.2	8/1/2012	7/29/2016	1458	
Chicago, IL	CSN OC	429	2.3	0.1	10.5	1.2	8/1/2012	7/29/2016	1458	
Chicago, IL	Sunset EC	191	0.5	0.1	1.6	0.3	5/1/2014	12/31/2015	609	29%
Chicago, IL	Sunset OC	181	2.5	0.6	7.9	1.1	5/1/2014	12/31/2015	609	29%
Chicago, IL	Sunset TC	182	3.0	0.7	9.2	1.3	5/1/2014	12/31/2015	609	31%
St. Louis, MO	Aeth BC	1501	0.8	0.1	4.7	0.5	8/1/2012	3/30/2017	1702	
St. Louis, MO	CSN EC	539	0.4	0.0	1.5	0.2	8/1/2012	3/29/2017	1701	

Site Name	Variable	Count	Mean	Min	Max	Sd	Start Date	End Date	Expected Count	Completeness
St. Louis, MO	CSN OC	539	2.5	0.5	9.7	1.2	8/1/2012	3/29/2017	1701	
St. Louis, MO	Sunset EC	202	0.4	0.0	1.6	0.4	5/7/2013	4/22/2014	350	32%
St. Louis, MO	Sunset OC	658	2.4	0.5	9.9	1.1	5/7/2013	3/30/2017	1423	32%
St. Louis, MO	Sunset OptEC	658	0.4	0.1	1.5	0.2	1/1/2013	3/30/2017	1549	58%
St. Louis, MO	Sunset TC	658	2.8	0.6	10.2	1.2	1/1/2013	3/30/2017	1549	46%
Las Vegas, NV	CSN EC	378	0.6	0.0	2.9	0.6	8/1/2012	7/26/2016	1455	
Las Vegas, NV	CSN OC	378	2.3	0.0	9.8	1.6	8/1/2012	7/26/2016	1455	
Las Vegas, NV	Sunset EC	207	1.1	0.0	7.6	1.1	8/15/2012	12/31/2014	868	26%
Las Vegas, NV	Sunset OC	211	2.9	1.1	12.6	1.5	8/15/2012	12/31/2014	868	26%
Las Vegas, NV	Sunset OptEC	210	0.4	0.0	1.7	0.3	8/15/2012	12/31/2014	868	24%
Las Vegas, NV	Sunset TC	211	3.9	1.2	14.6	2.2	8/15/2012	12/31/2014	868	24%
Houston, TX	Aeth BC	1398	0.5	0.1	1.9	0.2	8/1/2012	6/11/2016	1410	
Houston, TX	CSN EC	547	0.3	0.0	0.9	0.1	8/1/2012	3/29/2017	1701	
Houston, TX	CSN OC	547	1.9	0.0	10.4	1.3	8/1/2012	3/29/2017	1701	
Houston, TX	Sunset EC	697	0.7	0.0	2.6	0.5	8/1/2013	12/31/2016	1248	32%
Houston, TX	Sunset OC	697	2.4	0.1	8.2	1.1	8/1/2013	12/31/2016	1248	32%
Houston, TX	Sunset OptEC	696	0.3	-0.2	1.6	0.2	8/2/2013	12/31/2016	1247	56%
Houston, TX	Sunset TC	697	3.1	0.1	10.6	1.3	8/1/2013	12/31/2016	1248	56%

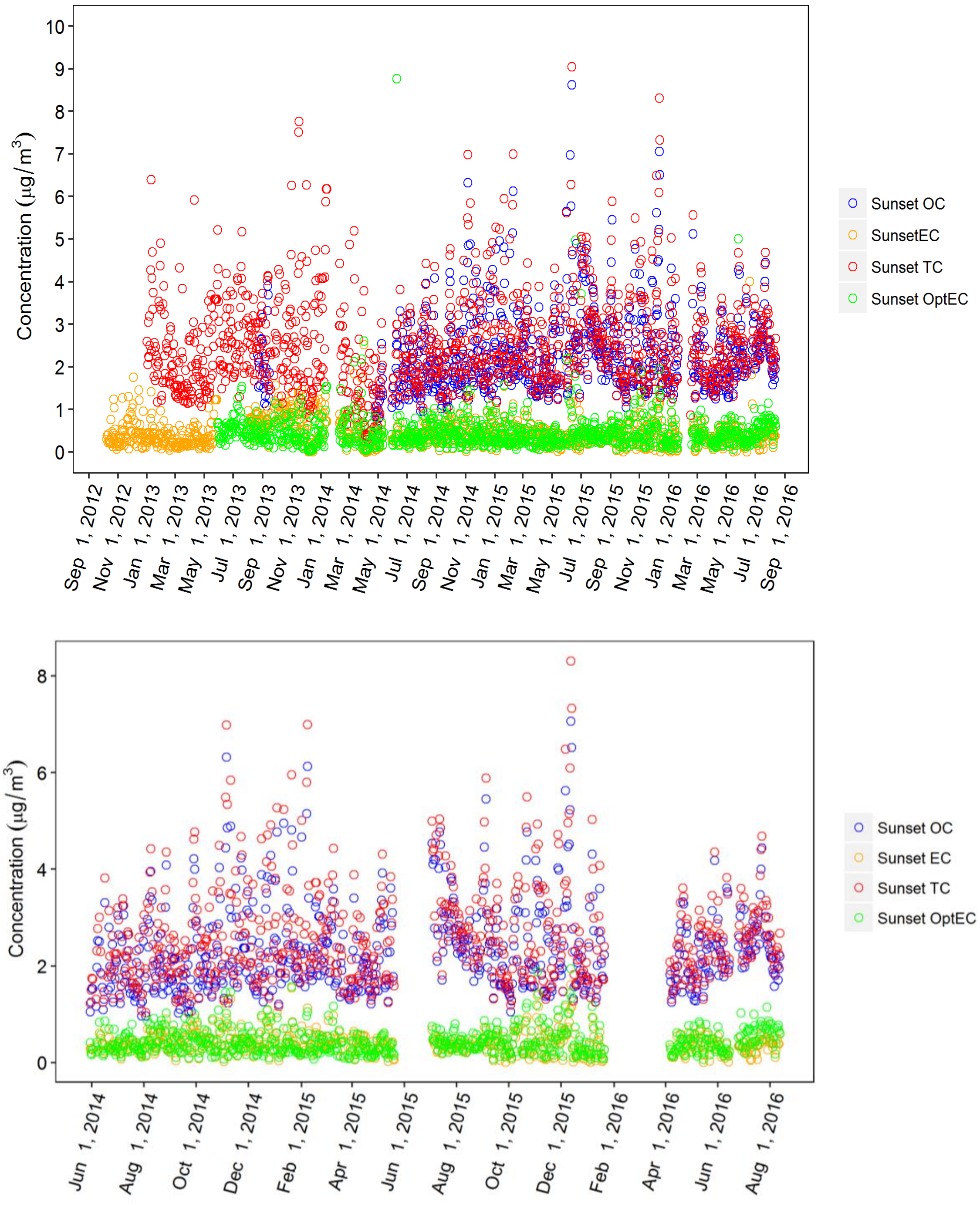
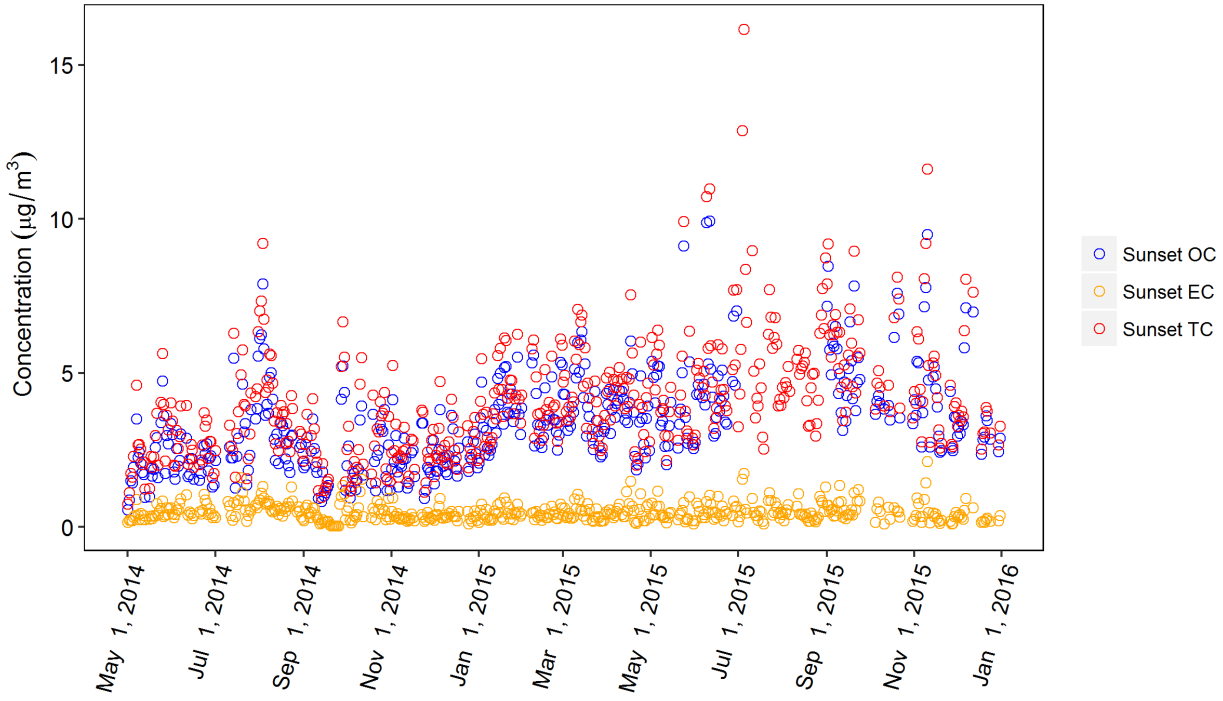


Figure B-1. Time series of Sunset data available in AQS (top) and data used in this work (bottom) for Washington, D.C. Prior to May 2014, OC was not reported, so no data were included here for analysis. Data in June 2015 and February–March 2016 were also excluded from analysis because of operational issues associated with a software update in June and a heating coil malfunction at the end of January 2016, which was not fixed until the end of March 2016.



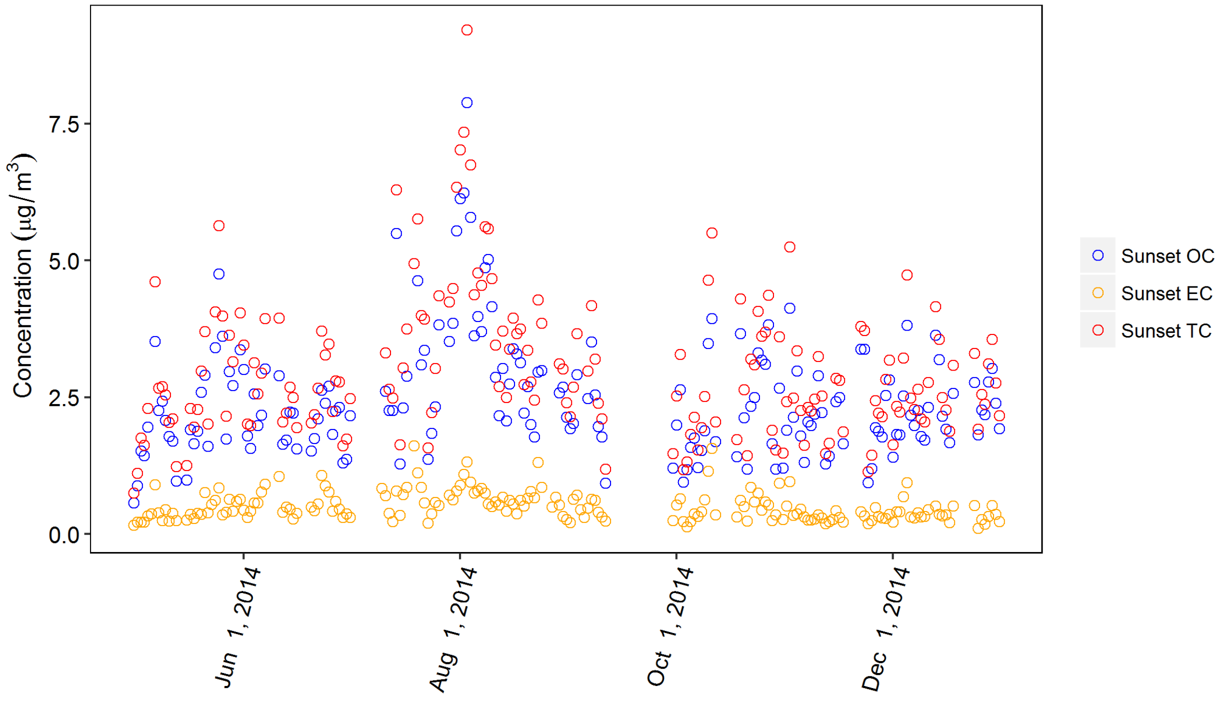
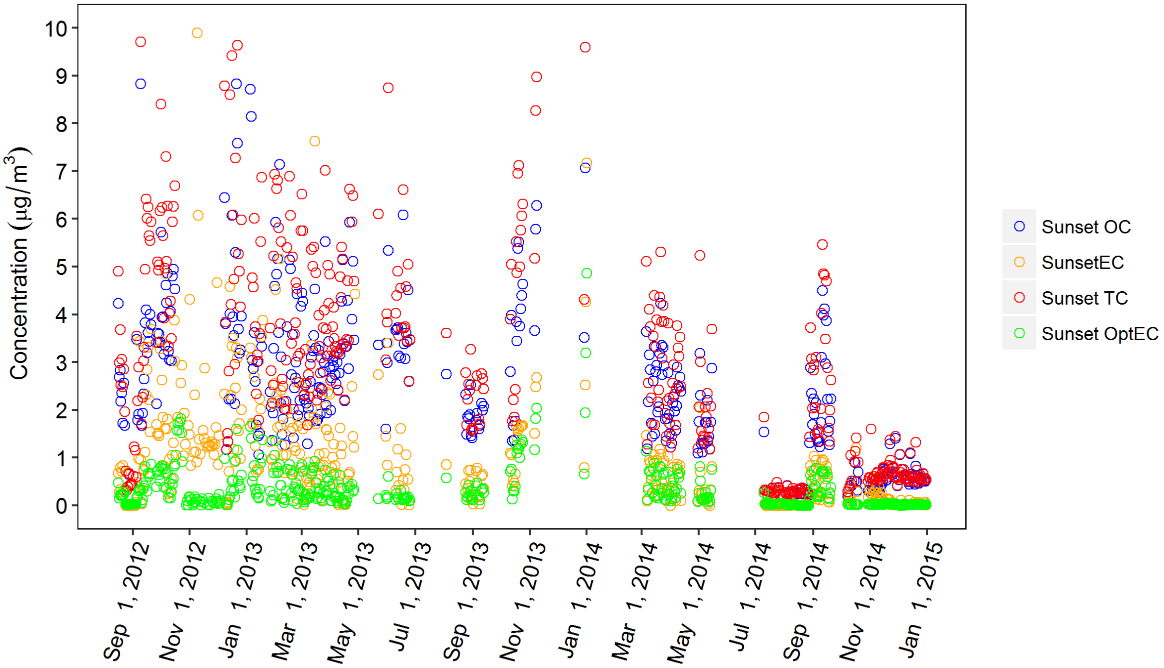


Figure B-2. Time series of Sunset data available in AQS (top) and data used in this work (bottom) for Chicago. Data after January 2015 were excluded from analysis since there is a clear gradual rise in baseline of OC due to degradation of the NDIR.



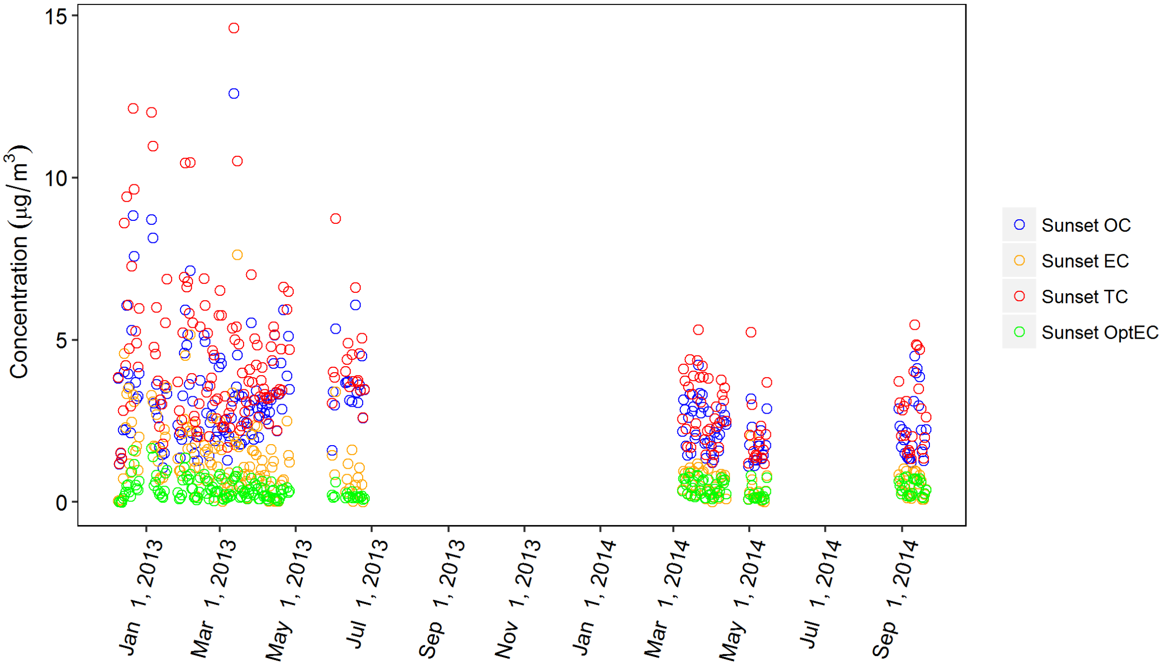


Figure B-3. Time series of Sunset data available in AQS (top) and data used in this work (bottom) for Las Vegas. Data were intermittent due to multiple operational issues. Only data with multiple weeks of consistent measurements were included for analysis. For example, in November 2012, OC was consistently reported as less than 0.5 µgC/m^3, and at other times the NDIR and heater coils broke multiple times, there was vandalism that incapacitated the shelter air conditioning unit, and instrument software was not routinely updated.

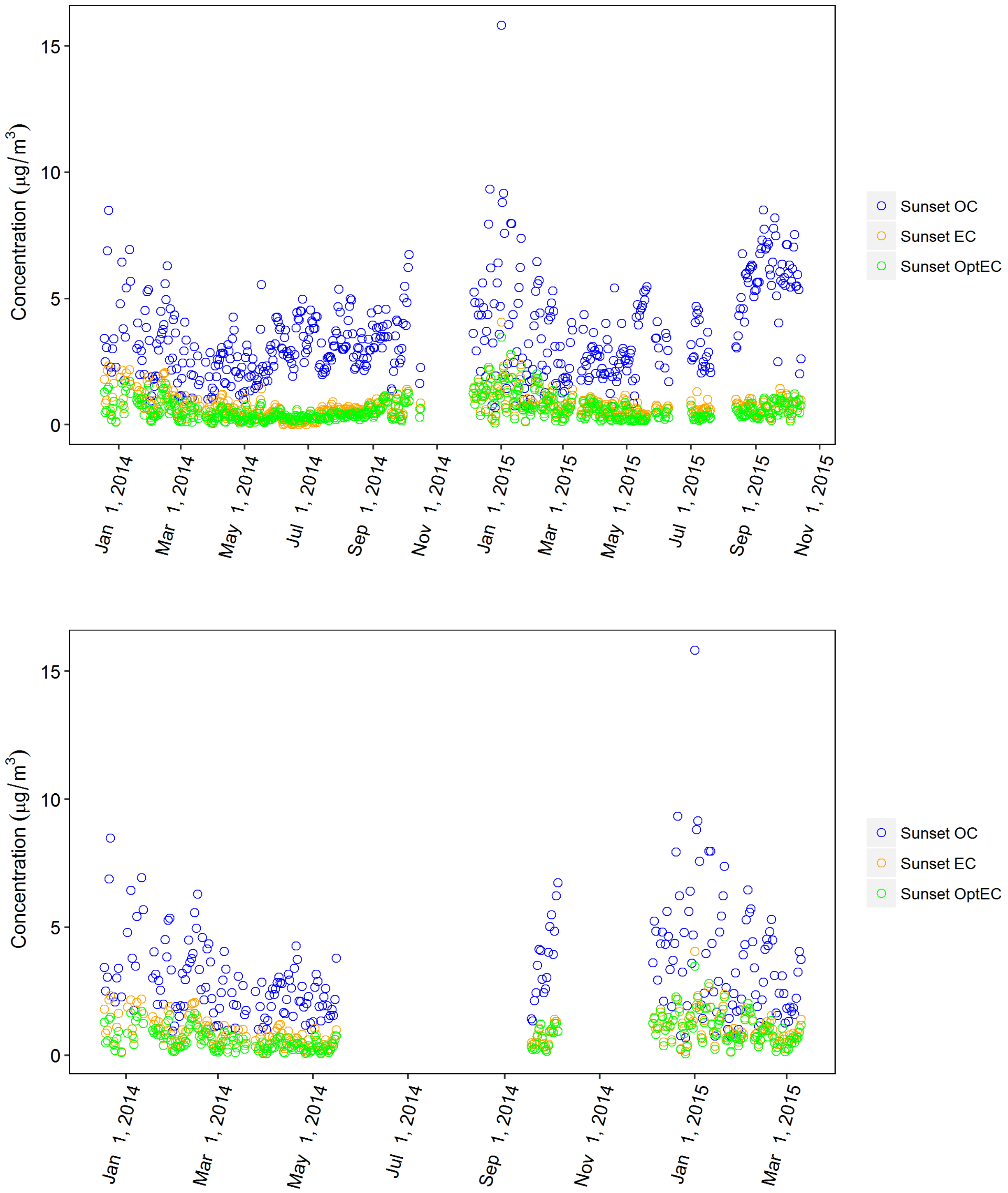


Figure B-4. Time series of Sunset data available in AQS (top) and data used in this work (bottom) for Rubidoux. In May 2014, there was a clear shift in OC upward and a shift of EC downward, and these data were excluded from analysis. During these periods, operators found leaks in the sampling line and the oven was replaced twice.

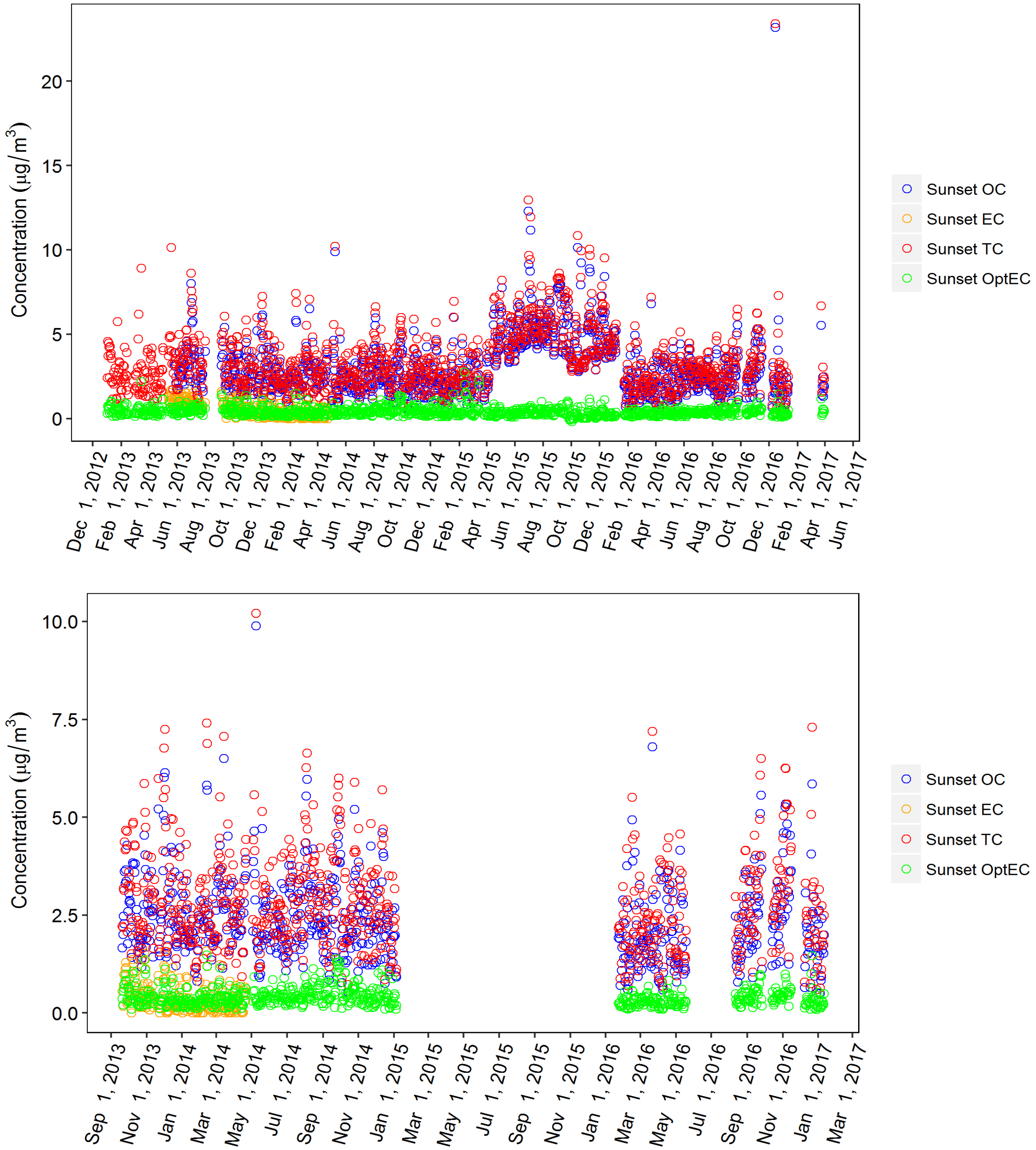
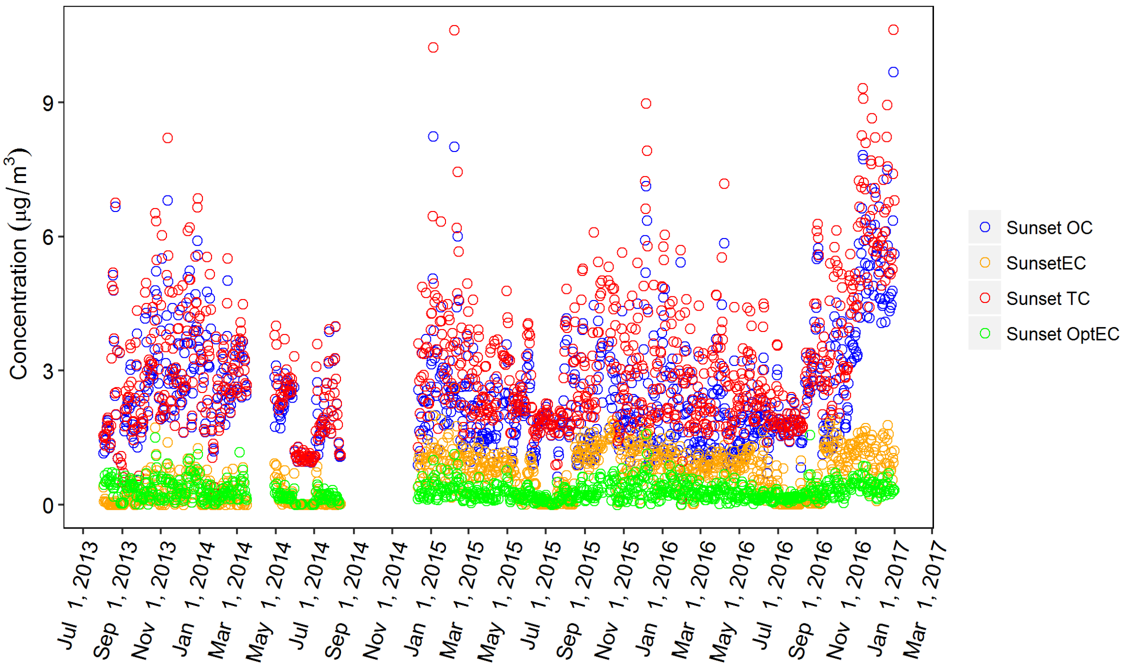


Figure B-5. Time series of Sunset data available in AQS (top) and data used in this work (bottom) for St. Louis. Data prior to September 2013 were excluded from analysis as this was a "warm-up" period when operations were getting settled. There was a sudden shift in OC concentrations starting in January 2015 when the filter was stuck and new calibration calculations were put into place. During March 2015–January 2016, operators suspected contamination, adjusted the thermocouple, and installed a new photodetector. However, data did not return to "normal" until after the oven was replaced in January 2016. There were additional issues with keeping the flow steady in June–July 2016.



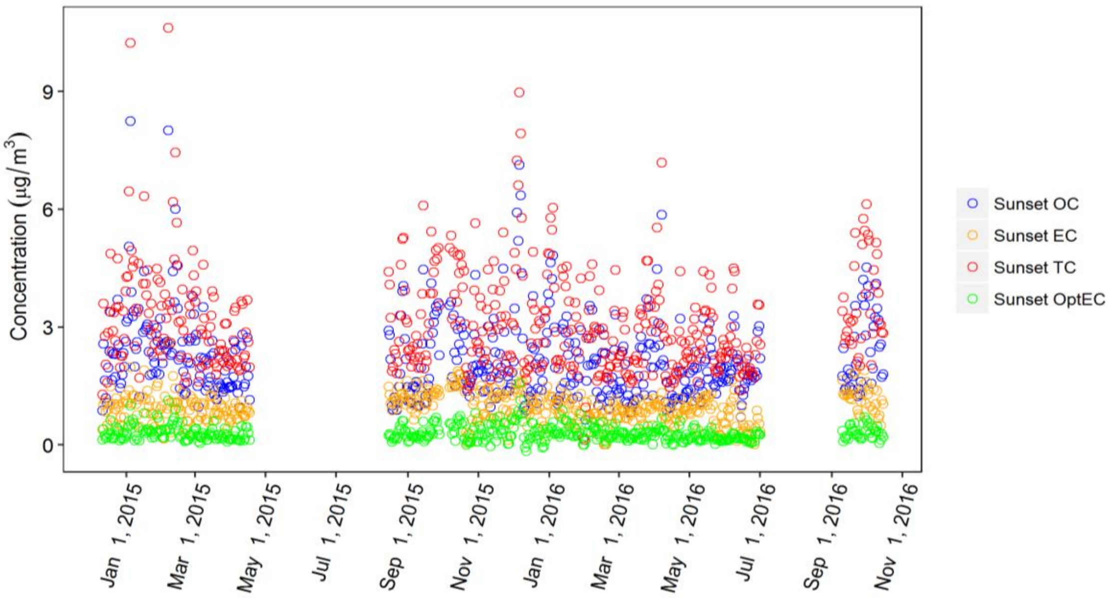


Figure B-6. Time series of Sunset data available in AQS (top) and data used in this work (bottom) for Houston. Data prior to December 2014 were excluded since older software was used to determine OC/EC and OptEC, the NDIR malfunctioned and was replaced twice, the oven thermocouple malfunctioned and was replaced, there were leaks, and the instrument was sent back to Sunset twice for maintenance. Data during May–August 2015 and in July–August 2016 had an unusual shift in OC, and EC was near zero, which were not seen in collocated measurements, and which occurred when there were leaks in the sampling line.

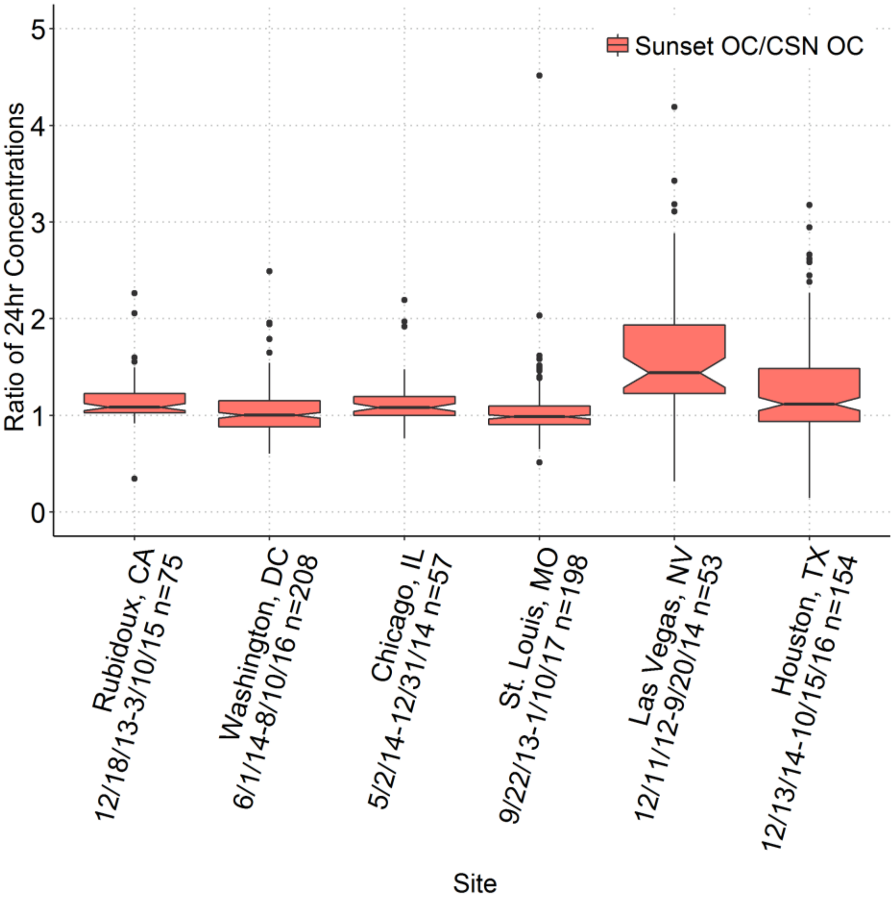


Figure B-7. Box plot of daily Sunset OC/CSN OC ratios by site.

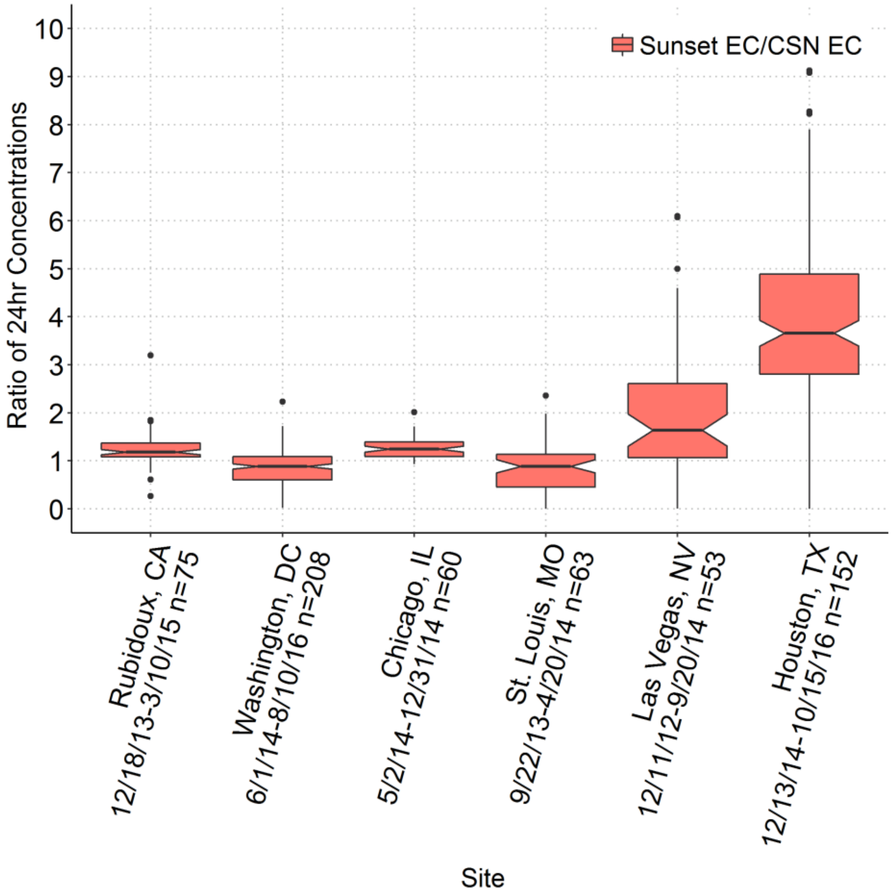


Figure B-8. Box plot of daily Sunset EC/CSN EC ratios by site.

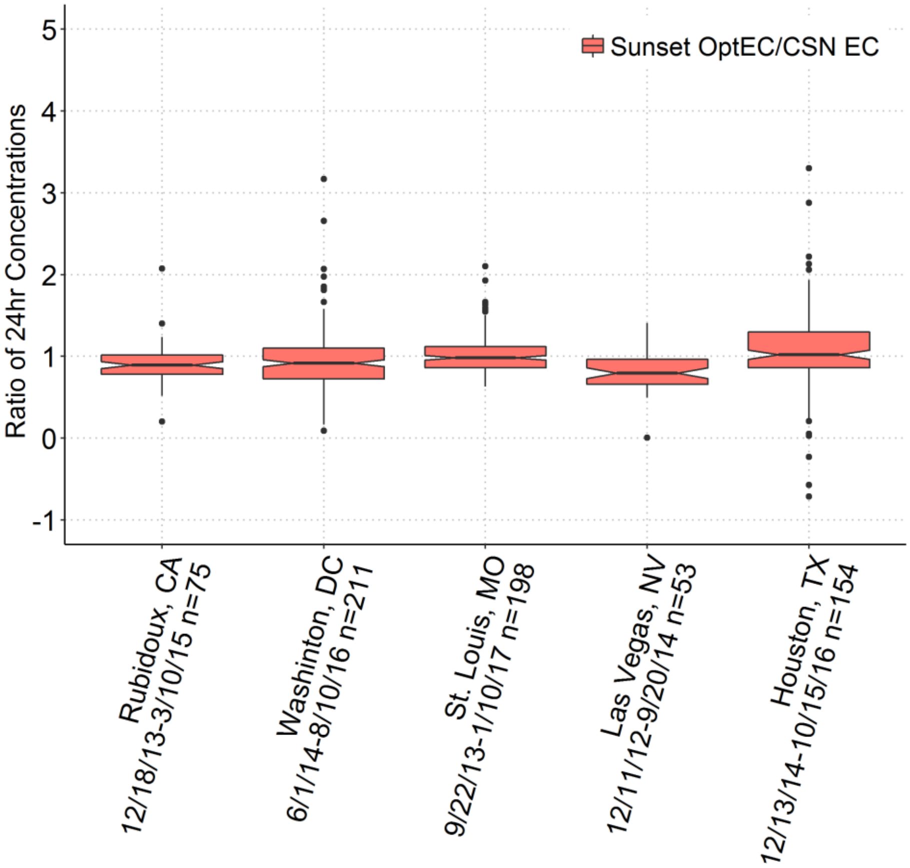


Figure B-9. Box plot of daily Sunset OptEC/CSN EC ratios by site.

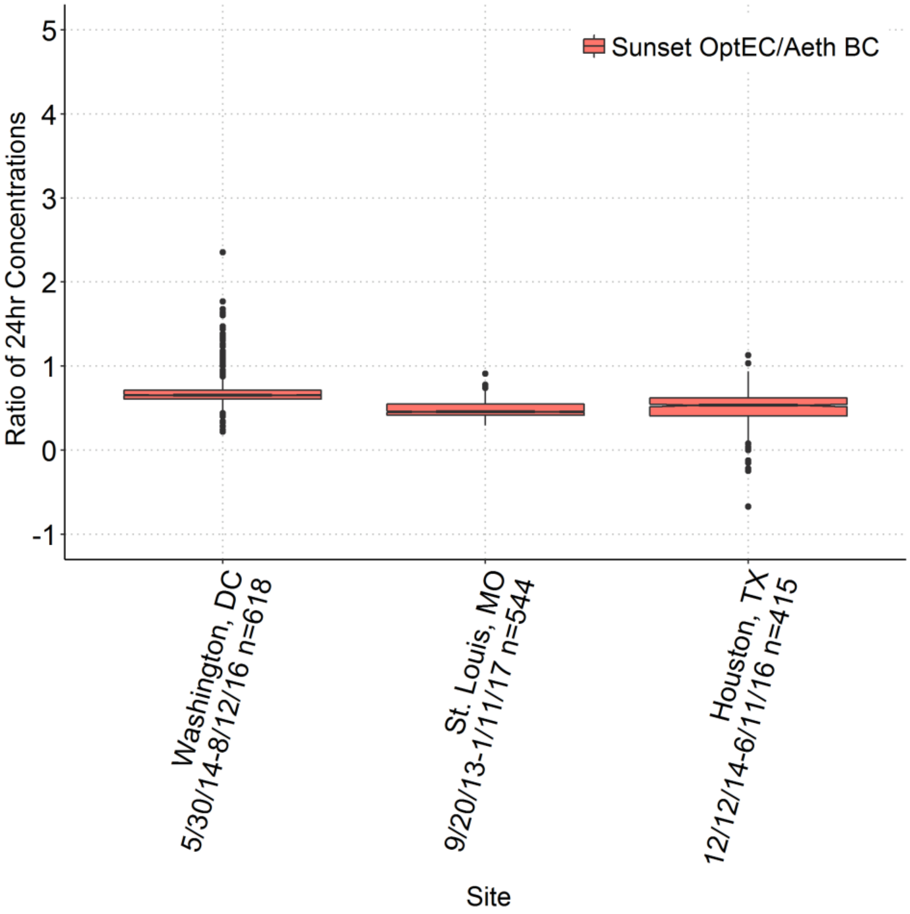


Figure B-10. Box plot of daily Sunset EC/Aethalometer BC ratios by site.

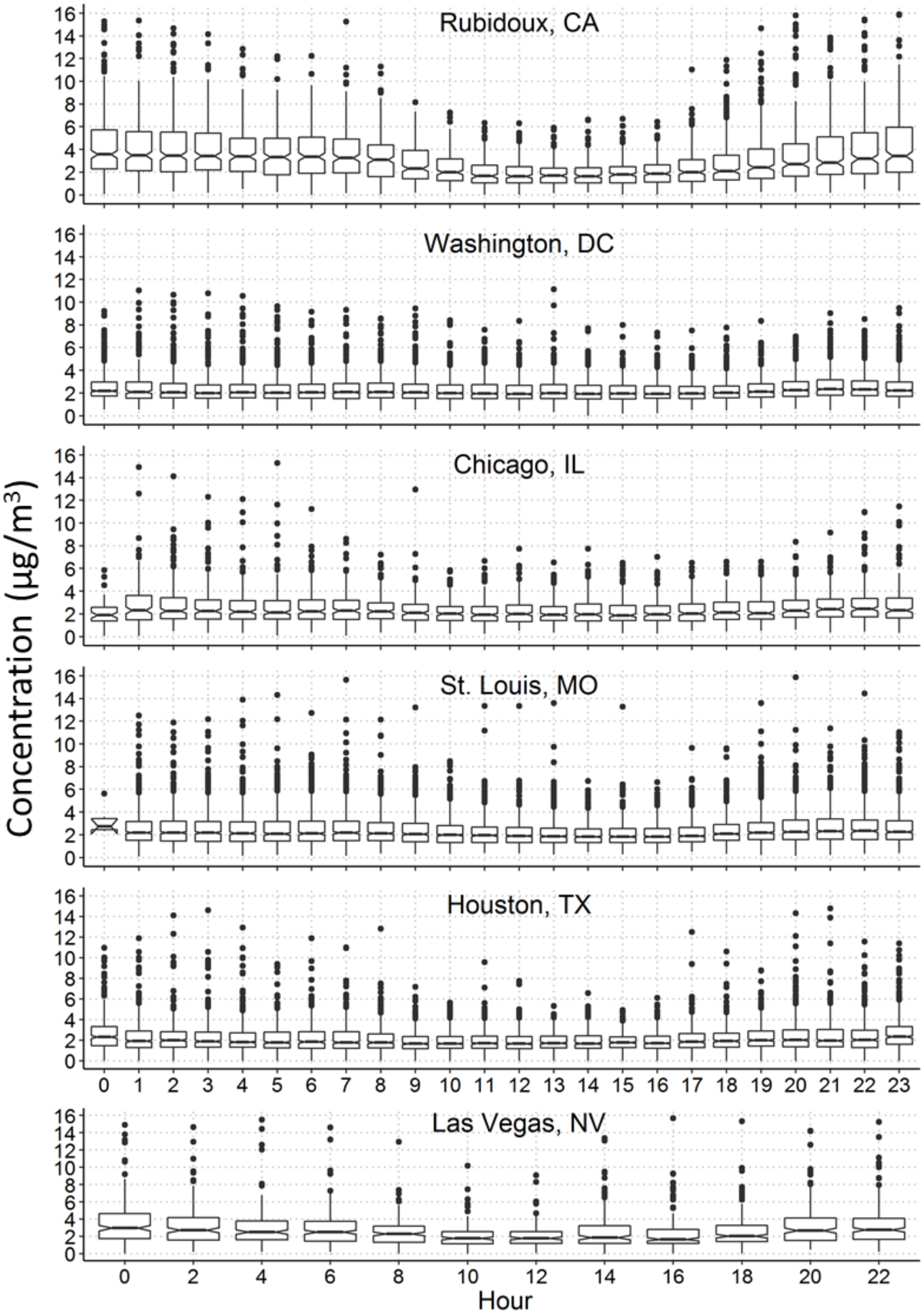


Figure B-11. Box plot of hourly Sunset OC by site.

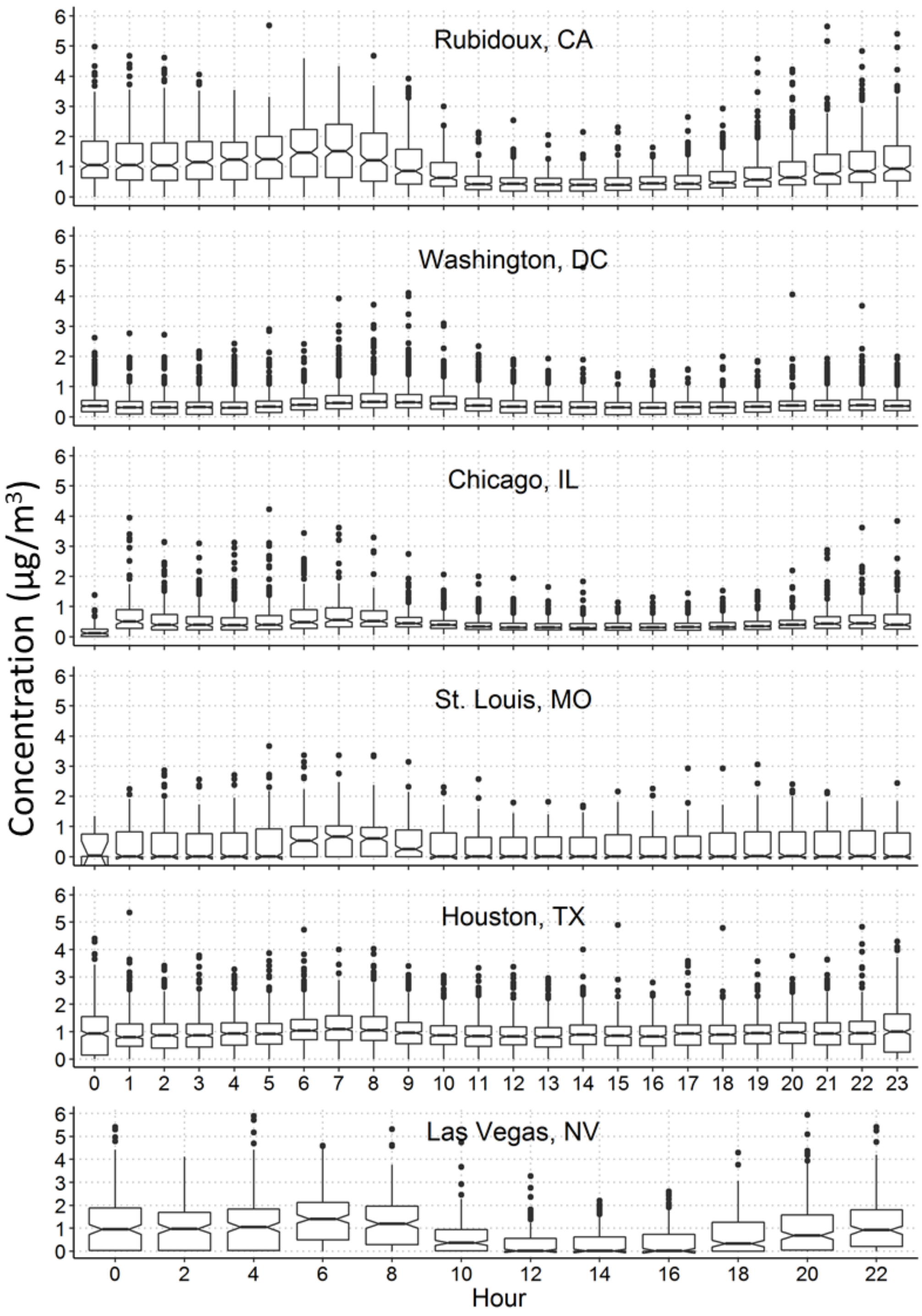


Figure B-12. Box plot of hourly Sunset EC by site.

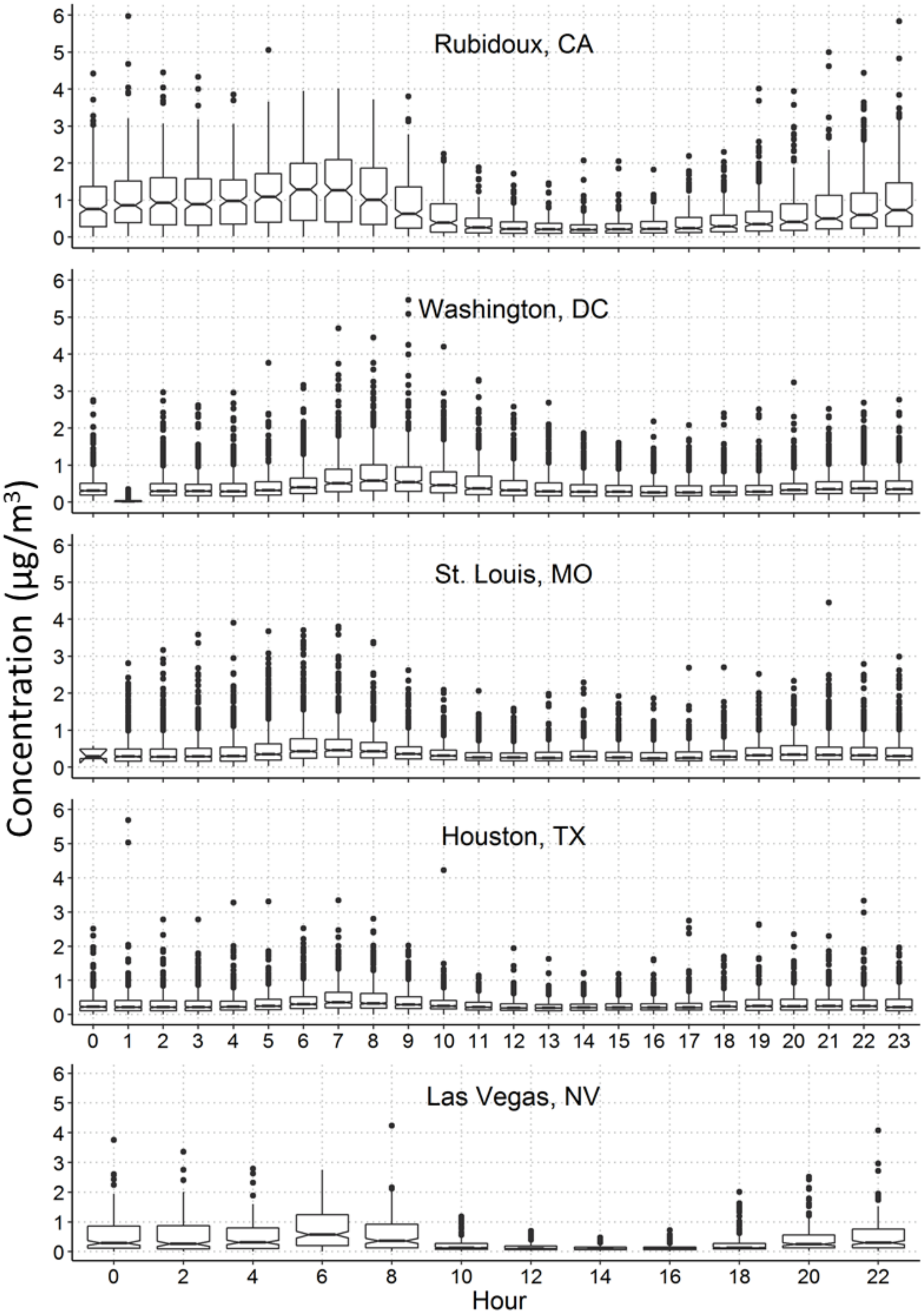


Figure B-13. Box plot of hourly Sunset OptEC by site.

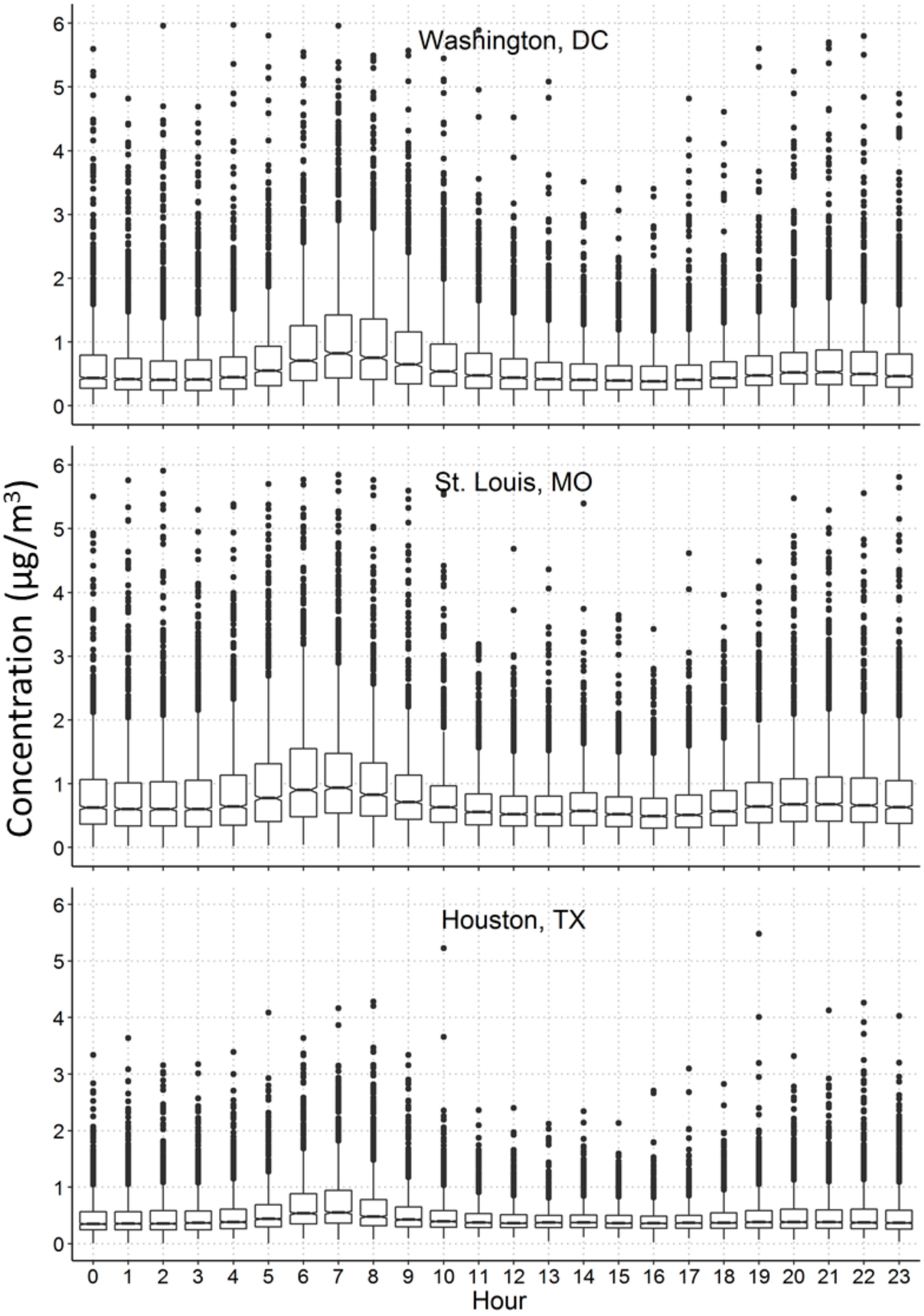


Figure B-14. Box plot of hourly Aethalometer BC by site.

United States
Environmental Protection
Agency

Office of Air Quality Planning and Standards
Air Quality Assessment Division
Research Triangle Park, NC

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