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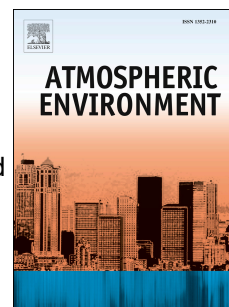
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Comparison of Elemental and Organic Carbon Measurements between IMPROVE and CSN Before and After Method Transitions

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Abstract

During a transition period from 2007 to 2009, the Chemical Speciation Network (CSN) altered its carbon sampling instrumentation and analysis methods to be more consistent with the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. CSN and IMPROVE operated collocated samplers spanning the transition at eight sites. This paper compares elemental, organic, and total carbon (EC, OC, and TC, respectively) measurements at these collocated sites from 2005 through March 2016. Prior to the changes, the concentration measurements between the two networks had imprecisions of 17, 17, and 16% and biases of 0.22, -1.93, and -1.69 $\mu\text{g m}^{-3}$ for EC, OC, and TC, respectively, with CSN measuring higher OC and TC than IMPROVE. After the sampling equipment and analytical methods were changed, the imprecision improved to 14, 12, and 10% and biases decreased to -0.02, -0.12, and -0.15 $\mu\text{g m}^{-3}$ for EC, OC, and TC, respectively. The increased comparability, particularly the smaller biases, between the two networks facilitates comparisons between urban and rural aerosols in geospatial analyses.

Keywords: particulate matter, elemental carbon, organic carbon, IMPROVE, CSN

1. Introduction

Carbon in atmospheric particulate matter is difficult to measure because many carbon compounds are semi-volatile and can change state as the conditions (e.g., temperature and pressure) vary within the sampling system and during sample handling (Chow et al., 2010). Various techniques, such as denuders and backup filters, are used to condition the air stream to avoid positive artifacts and to account for negative artifacts (Maimone et al., 2011; Subramanian et al., 2004; Watson et al., 2009). In addition to the collection issues, there are uncertainties in the analytical techniques used to quantify fractions of the carbon. In the field of atmospheric chemistry, “organic” and “elemental” carbon fractions are routinely quantified by an operationally defined technique. The distinction between “organic” and “elemental” is not based on molecular structure but on the optical absorption of the particulate matter sample during thermal evolution. The analytical technique involves heating the sample first in a helium (oxygen-free) environment to quantify “organic carbon (OC)”, followed by an oxygenated environment to quantify “elemental carbon (EC)”. In the high-temperature, helium environment, some carbonaceous material is pyrolyzed, resulting in an increase in optical attenuation. This pyrolyzed carbon (abbreviated as OP) is subsequently burned when oxygen is introduced and the optical attenuation signal is used to partition the pyrolyzed carbon into OC rather than into EC (Chow et al., 2001). Multiple variations of this analytical technique - involving different temperature steps, timing, and optical measurements - have been developed by various agencies (Countess, 1990); two variations have primarily been used in the United States (US), referred to as the Interagency Monitoring of Protected Visual Environments (IMPROVE_A) and National Institute for Occupational Safety and Health (NIOSH) protocols. Details on the techniques and comparisons of the two methods can be found in (Bae et al., 2009; Chow et al., 2007; Chow et al., 2001; Wu et al., 2012). Two major US programs monitoring particulate matter (PM) chemistry, the

IMPROVE and Chemical Speciation Network (CSN), used these two different methods until CSN decided to modify their sampling and analytical techniques to increase comparability between the networks (Air Resource Specialists, 2007). Analyses often incorporate data from both networks, in which case it is important that the measurements be comparable. The potential disadvantage of using the same techniques is that both networks may perpetuate the same sampling and analytical biases and thus not provide an independent check for each other.

The two networks are described in depth elsewhere (Solomon et al., 2014) and briefly as follows. Both networks collect PM_{2.5} samples for 24 hours every three days on quartz filters for carbon analysis. The IMPROVE network was established in 1988 to aid in the protection of visibility in Class I areas in accordance with the 1977 amendments to the Clean Air Act. As of 2017, 155 IMPROVE sites operate across the US along with three international sites (two in Canada and one in the Republic of South Korea). The IMPROVE carbon sampler collects PM_{2.5} aerosols on a 25 mm diameter quartz fiber filter with a nominal flow of 23 L min⁻¹. Samples and field blanks are installed and remain in the samplers for one week and are shipped to/from the sites every three weeks in uninsulated boxes. The potential sampling artifacts associated with the IMPROVE sampler have been described in several publications (McDade et al., 2009; Turpin et al., 1994; Watson et al., 2009). Starting in 2005, the IMPROVE_A analytical protocol was used to measure carbon in the IMPROVE network, and the carbon concentrations are blank corrected using the median field blank carbon concentration from the corresponding month (Dillner, 2015); prior to 2005, the IMPROVE protocol was used to measure carbon and backup (or secondary) quartz filters were used to correct for positive sampling artifacts. IMPROVE carbon analysis has always been performed by Desert Research Institute (Reno, NV).

The CSN was created to support implementation of the 1997 PM_{2.5} National Ambient Air Quality Standards (NAAQS) (EPA, 1997). There are currently 136 CSN sites. CSN used varied sampler designs for collecting carbon samples prior to the 2007 - 2009 changeover, when the entire network switched to using the URG-3000N samplers (Air Resource Specialists, 2007). The replaced samplers are listed in Table 2 and include the Spiral Ambient Speciation Sampler (SASS, Met One Instruments, Inc.) with a flow rate of 6.7 L min⁻¹, the Reference Ambient Air Sampler (RAAS, Andersen Instruments, Inc.) with a flow rate of 7.3 L min⁻¹, the Mass Aerosol Speciation Sampler (MASS, University Research Glassware Corporation) with a flow rate of 16.7 L min⁻¹, and the Partisol 2300 (R&P 2300, Rupprecht and Patashnick Co., Inc.) with a flow rate of 10.0 L min⁻¹. All the replaced samplers collected PM_{2.5} samples on 47 mm diameter quartz filters. The URG-3000N is nearly identical to the IMPROVE carbon sampler with the addition of active flow control. The URG-3000N has a nominal flow rate of 22.8 L min⁻¹ and collects PM_{2.5} samples on 25 mm diameter quartz filters (EPA, 2011). From inception, CSN used the NIOSH thermal/optical transmission (TOT) protocol to measure carbon (Birch, 2003), but between 2007 and 2009, the CSN sites converted to using the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow et al., 2007). The analytical change coincided with the sampler change at each site. Historically, the CSN carbon concentrations were not blank corrected; as of November 20, 2016, the CSN carbon concentrations are available uncorrected and blank corrected with the median carbon field blank concentration for the corresponding month. Figure 1 presents a timeline of network changes. CSN samples were installed the day before and removed the day after sampling occurred. CSN field blanks are removed from the shipping container and exposed to ambient air only while the samples are loaded and unloaded; CSN field blanks are not left in the sampler for any amount of time. CSN samples are shipped to/from the site in coolers with ice packs.

Differences between carbon measurements in the two networks prior to the changes are well documented (Chen et al., 2010; Chow et al., 2010; Solomon et al., 2014). Differences in sample filter size, flow rate, and screen hole size result in substantial differences in face velocity (McDade et al., 2009). Increases in face velocity are anti-correlated with measured carbon concentrations, especially when significant concentrations of semi-volatile species are present (McDow and Huntzicker, 1990; Viana et al., 2006). Prior to the equipment change, the CSN network collected carbon samples at lower flow rates and on larger diameter filters, translating to lower face velocities, which resulted in the retention of more volatile OC species (Chow et al., 2010). Additionally, the analytical protocols for the thermal/optical measurement of OC and EC were different between the two networks. This is described in depth elsewhere (Chow et al., 2001), but the most significant difference is that more of the total carbon is partitioned towards OC than EC by the NIOSH method compared to the IMPROVE_A method. These differences resulted in systematic biases between CSN and IMPROVE OC and EC data, with IMPROVE reporting lower OC values than CSN and higher EC values than CSN prior to the changes. To unify the two networks, CSN converted to using sampling and analysis techniques almost identical to the IMPROVE methods, including the same analytical laboratory, DRI. Rattigan et al. (2011) compared the IMPROVE and CSN data pre- and post-changes at the New York site. The current analysis supports their results with more sites and significantly more data.

From 2009 to 2015, the CSN and IMPROVE networks have been operating with consistent sampling and analysis methods. The remaining differences between the two networks were:

- 1) blank subtraction on IMPROVE measurements (CSN started blank subtraction in November 2015),
- 2) the CSN sampler is mass flow controlled,
- 3) CSN filters are transported to and from sampling sites in coolers with ice packs,
- 4) sample handling is performed in different laboratories, and
- 5) the time that the samples remain at the sites.

The purpose of this effort is to compare the carbon measurements from the two networks before and after the change in equipment and analysis method as well as quantify any remaining additive or multiplicative biases.

2. Data Collection

2.1. IMPROVE

The IMPROVE network data were collected directly from the University of California, Davis IMPROVE database so both blank subtracted (Dillner, 2015) and raw values could be calculated and the difference resulting from this correction could be assessed. The blank subtracted values were compared with the publicly available IMPROVE data (FED, 2017) and were found to be identical. The raw data can be made available upon request from the authors. Data were retrieved for samples collected from January 1, 2005 through March 31, 2016. All valid data (i.e. no AQS null code) values were included in this analysis.

Irrespective of method or network, EC, OC, and TC concentrations are the resulting sums of measured carbon fractions (i.e., $OC = O1 + O2 + O3 + O4 + OP$, $EC = E1 + E2 + E3 - OP$, $TC = OC + EC$).

Consistent with network data reporting protocols, the monthly standard deviations of field blank filter measurements were used to calculate method detection limits (MDLs). The MDLs are calculated as two times the standard deviation of field blanks (σ_{dbf}) collected during the same month as the samples.

Additionally, a floor value (t) is implemented corresponding to the analytical detection limits quoted by the laboratory, found in the IMPROVE SOP 351 Table 3 (Cheng, 2016). Mathematically, $MDL = 2 * (Max(\sigma_{dfb}, t)) / (Air\ Volume)$.

2.2. CSN

CSN data were collected from the Air Quality System (AQS) database (EPA, 2017a). Since MDL and uncertainty values were not reported to AQS after the instrument change, MDL values were filled in using values reported in Appendix A of the Annual Data Summary Reports, spanning 2007 to 2015 (EPA, 2017b). Multiple AQS parameter codes have been used to report EC and OC concentrations throughout CSN's duration to account for changes in sampling, analysis, and reporting methodology (EPA, 2008). In this analysis, parameters have been restricted to those listed in Table 1 to retain only the most reported and representative values. To compare total carbon (TC), the sum of EC and OC was calculated when it was missing from the AQS database. As with IMPROVE, all valid data values were included in this analysis. There appeared to be a small study in 2010 at the New York site that used pre-change methods; these data were not included in the analysis.

ParameterName	Network	AQS Parameter Code	Reporting Timeline
OC CSN Unadjusted PM2.5 LC TOT	CSN	88305	Pre-Change
EC CSN PM2.5 LC TOT	CSN	88307	Pre-Change
OC PM2.5 LC TOR	IMPROVE	88320	Continuous
EC PM2.5 LC TOR	IMPROVE	88321	Continuous
OC CSN_Rev Unadjusted PM2.5 LC TOR	CSN	88370	Post-Change
EC CSN_Rev Unadjusted PM2.5 LC TOR	CSN	88380	Post-Change
Total Carbon PM2.5 LC TOT	CSN	88312	Continuous

Table 1. Parameter codes used in analysis.

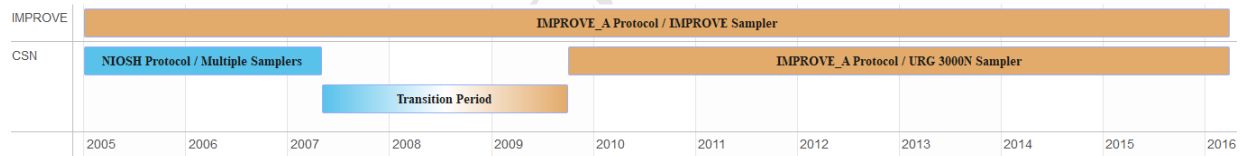


Figure 1. Timeline of instrumental and analytical methods.

2.3. Site Selection

All collocated samplers operating during the analysis period were included. CSN had six sites with duplicate samplers for intra-network comparison while IMPROVE had seven sites with duplicate carbon samplers (Table 2). Eight sites were used for inter-network comparison; however, the New York IMPROVE site was shut down on June 5, 2010. The Phoenix site is unique in that it has a CSN sampler and two complete IMPROVE samplers.

Location	Site ID	Latitude	Longitude	Instrument Change	Replaced Instrument	Collocation
Bakersfield, CA	06-029-0014	35.356	-119.041	May 3, 2007	SASS	CSN – CSN
Rubidoux, CA	06-065-8001	34.000	-117.416	May 3, 2007	SASS	CSN – CSN
Roxbury, MA	25-025-0042	42.329	-71.053	October 1, 2009	SASS	CSN – CSN
New Brunswick, NJ	34-023-0006	40.473	-74.422	October 1, 2009	SASS	CSN – CSN
G.T. Craig, OH	39-035-0060	41.492	-81.679	October 1, 2009	SASS	CSN – CSN

Deer Park, TX	48-201-1039	29.670	-95.129	April 1, 2009	MASS/SASS	CSN – CSN
Atlanta, GA	13-089-0002	33.688	-84.290	April 1, 2009	RAAS/SASS	CSN – IMPROVE
Birmingham, AL	01-073-0023	33.553	-86.815	May 3, 2007	SASS	CSN – IMPROVE
Detroit, MI	26-163-0001	42.229	-83.208	April 1, 2009	SASS	CSN – IMPROVE
Fresno, CA	06-019-0008(11)	36.785	-119.774	April 1, 2009	SASS	CSN – IMPROVE
New York, NY	36-005-0110	40.816	-73.902	May 3, 2007	R&P 2300/SASS	CSN – IMPROVE
Phoenix, AZ*	04-013-9997	33.504	-112.096	October 1, 2009	SASS	CSN – IMPROVE- IMPROVE
Pittsburgh, PA	42-003-0008	40.465	-79.961	October 1, 2009	SASS	CSN – IMPROVE
Seattle, WA	53-033-0080	47.568	-122.308	May 3, 2007	MASS/SASS	CSN – IMPROVE
Everglades NP, FL	12-089-0030	25.391	-80.681	–	–	IMPROVE – IMPROVE
Medicine Lake, MT	30-091-9000	48.487	-104.476	–	–	IMPROVE – IMPROVE
Hercules Glades, MO	29-213-0003	36.614	-92.922	–	–	IMPROVE – IMPROVE
Hoover, CA	06-051-9000	38.088	-119.177	–	–	IMPROVE – IMPROVE
Seney NWR, MI	26-153-9000	46.289	-85.950	–	–	IMPROVE – IMPROVE
Saguaro West, AZ	04-019-9000	32.249	-111.218	–	–	IMPROVE – IMPROVE

Table 2. Collocated Sites. Note: Phoenix has two full sets of IMPROVE modules collocated as well as CSN samplers.

3. Results and Discussion

Figure 2 shows a time-series of the scaled relative differences, D_i , $D_i = \left(\frac{([IMPROVE_i] - [CSN_i]) / \sqrt{2}}{([IMPROVE_i] + [CSN_i]) / 2} \right)$, at each collocated CSN-IMPROVE site (Hyslop and White, 2009). Here $[CSN_i]$ and $[IMPROVE_i]$ represent the measured concentrations on each day (i), and the differences are divided by $\sqrt{2}$ to account for the presence of errors in both measurements. The vertical black lines in each graph of Figure 2 indicate when the new CSN carbon samplers and analytical techniques were employed at each collocated site. The magnitude of the differences between the EC and OC measurements decreased significantly as the instruments and analysis methods were changed at each site, trending towards average values that are slightly below zero. The Birmingham IMPROVE monitor frequently experienced low flow episodes from mid-2009 through early 2015. These data were demarcated with qualifier codes but were not invalidated. Additionally, CSN Birmingham data during 2013 was found to be an outlier when compared to IMPROVE and Southeastern Aerosol Research Characterization (SEARCH) data (Weakley et al., 2016). A solid gray line in Figure 2 appearing on November 20, 2015 indicates when blank correction was applied and the sample handling and analysis laboratories were changed for CSN. Future analyses will be performed to understand any impacts these additional changes may have on the CSN data.

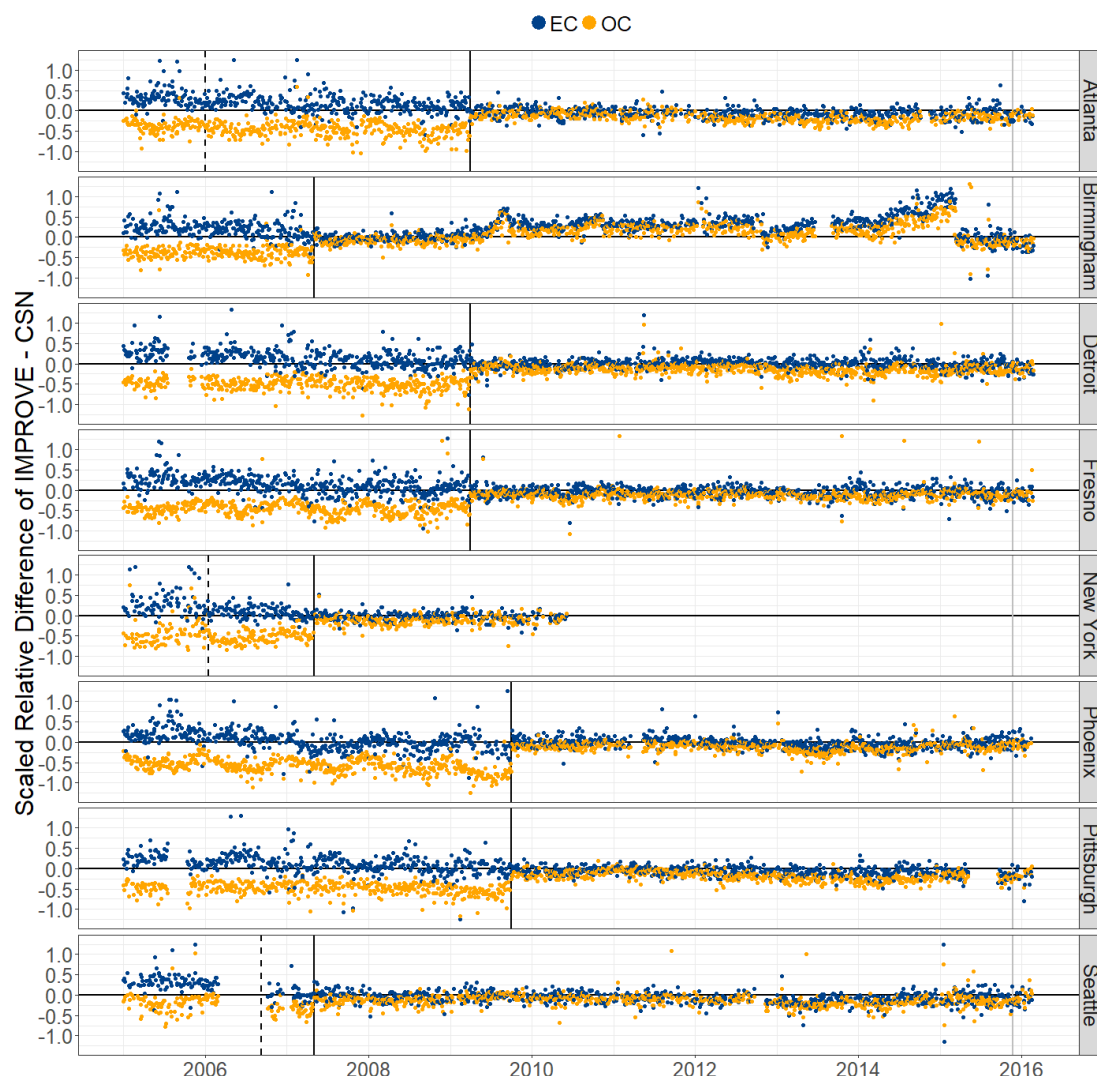


Figure 2. Temporal comparison of IMPROVE and CSN collocated samplers by site (indicated on the right). The vertical dashed line indicates a change to the Met One SASS instrument while the vertical solid black line indicates the date of sampler and analytical method changes described in the text. The vertical solid gray line indicates the recent change of sample handling and analytical laboratories.

Two metrics were calculated to summarize the distribution of scaled relative differences between the collocated samplers: imprecision and bias. Imprecision was calculated using a robust estimate for the standard deviation of the measurement differences, *Percentile Imprecision* = $\frac{1}{2}(P_{84}(D_i) - P_{16}(D_i)) * 100\%$, where P_X is the X^{th} quantile and D_i is the scaled relative difference, as plotted in Figure 2 (Hyslop and White, 2009). Imprecision provides a measure of the randomness or spread of the concentration differences but does not account for systematic differences (bias) between CSN and IMPROVE. This robust percentile imprecision calculation is used because it focuses on the bulk of the data and minimizes the influence of outliers. The second metric, bias, provides an estimate of the systematic measurement differences (e.g., calibration, particle capture efficiency, semi-volatile retention, etc.) and was calculated as the signed median scaled relative difference, $\text{Bias} = P_{50}(D_i)$. To provide context for comparability between networks, collocated imprecision values were calculated for within-network pairings; sites with

two colocated CSN samplers (listed in Table 2) were used to calculate intra-network CSN imprecision and bias, and sites with colocated IMPROVE samplers were used to calculate intra-network IMPROVE imprecision and bias. The intra-network biases are expected to be zero because the colocated measurements are identical to the routine measurements, and thus provide a measure of the uncertainty in the inter-network bias estimates. Only sample pairs where both concentration values were greater than three times the MDL were used in the calculations. For sites with colocated CSN and IMPROVE samplers, the same formula was used to calculate the analogous inter-network statistics. The intra-network imprecisions place a lower bound on the inter-network imprecision. The results are shown in Tables 3a and 3b.

Inter-network imprecision estimates improved for all three species after the network changes. Bias was reduced by an order of magnitude but remained higher than the intra-network biases, indicating that they are significant. For the CSN intra-network comparison, the OC and TC imprecision estimates did not change and the bias estimates remained low ($<0.03 \mu\text{g m}^{-3}$ absolute bias). The EC imprecision estimates for CSN (9%) were better than IMPROVE (13%) before the change and degraded to the same level as IMPROVE after the change. The degradation of EC in CSN led us to look more closely at the colocated CSN colocated measurements (Figure 3). Both the Cleveland and Riverside-Rubidoux CSN colocated sites experienced periods of abnormally high differences in the EC measurements after the change; however, only five data points during this period had qualifier flags, while the rest were marked as valid with no qualifier flags. Therefore, we chose to leave the data in the calculations.

The trends observed in the present analysis are consistent with an initial comparison between the two methods by Chow et al. (2001) who reported 10% and 14% imprecision for NIOSH and IMPROVE EC, respectively, as well as more recent assessments (Solomon et al., 2014). Although previous studies employed different methods for calculating imprecision, the resulting interpretations are equivalent.

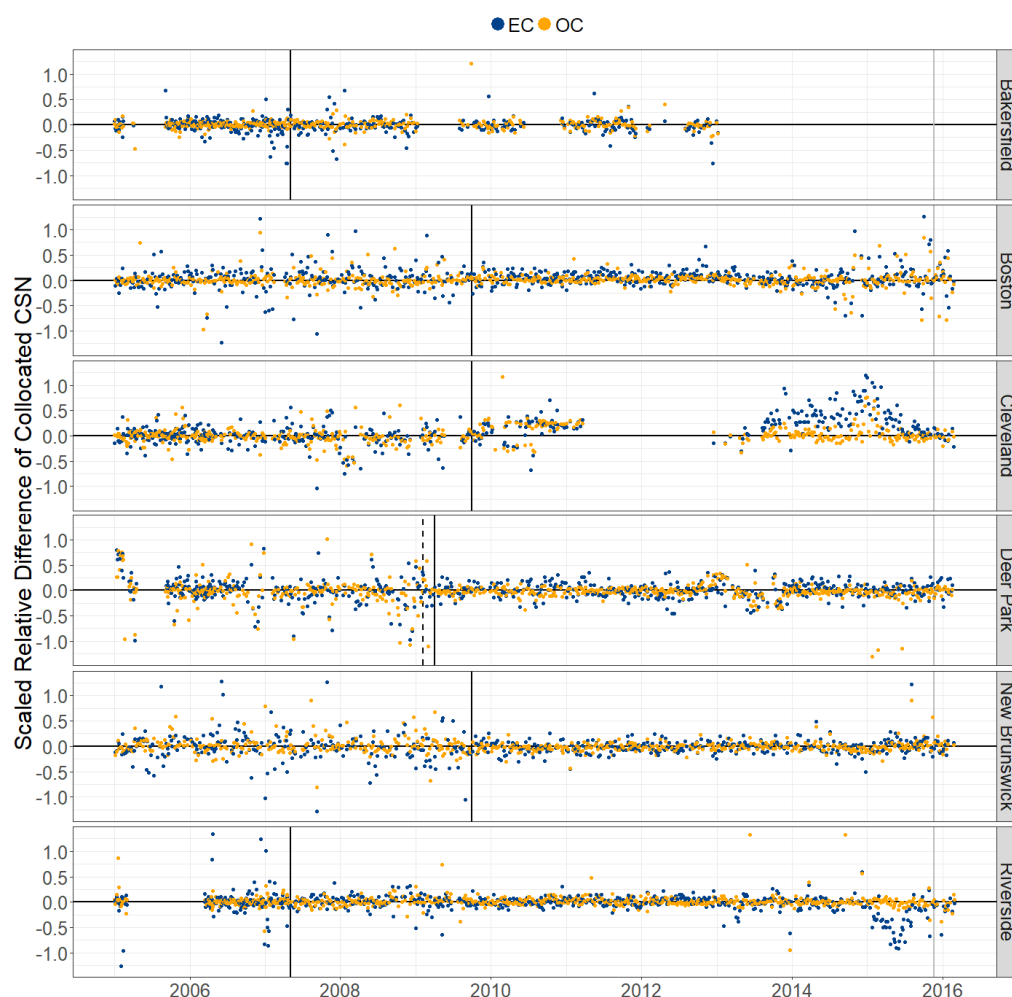


Figure 3. Temporal comparison of collocated CSN samplers by site (indicated to the right). The vertical lines have the same meaning as in Figure 2.

To better understand the differences between the two networks after the change, we accounted for a remaining known difference between the measurements, blank subtraction. To do this, the IMPROVE data were modified to remove the blank subtraction from the concentrations, and Table 3b summarizes those results. Since the EC content of field blank filters is typically zero, the difference between subtracted and non-subtracted EC was negligible. For OC, this difference was 0.22 and $0.14 \mu\text{g m}^{-3}$ for pre-change and post-change, respectively. Similar to OC, the TC differences were 0.25 and $0.14 \mu\text{g m}^{-3}$. We chose to account for blank-correction on the IMPROVE concentrations instead of the CSN concentrations because the IMPROVE field blank concentrations are 4-5 times higher than the CSN field blank concentrations; this is a result of the differences in handling discussed in the Data Collection Section. If CSN left the field blanks out in the ambient air for the same amount of time as the samples, the CSN field blank concentrations would be higher and may help explain more of the differences between the IMPROVE and CSN concentrations, particularly prior to the changes.

		EC	OC	TC
IMPROVE–IMPROVE	(Continuous)	Imprecision: 13% Bias: 0.00 $\mu\text{g m}^{-3}$ Pairs: 6624	Imprecision: 10% Bias: 0.04 $\mu\text{g m}^{-3}$ Pairs: 6195	Imprecision: 9% Bias: 0.04 $\mu\text{g m}^{-3}$ Pairs: 6455
	(Pre-Change)	Imprecision: 9% Bias: 0.01 $\mu\text{g m}^{-3}$ Pairs: 594	Imprecision: 8% Bias: -0.02 $\mu\text{g m}^{-3}$ Pairs: 1327	Imprecision: 7% Bias: -0.01 $\mu\text{g m}^{-3}$ Pairs: 1339
CSN–CSN	(Post-Change)	Imprecision: 13% Bias: 0.01 $\mu\text{g m}^{-3}$ Pairs: 1939	Imprecision: 8% Bias: 0.01 $\mu\text{g m}^{-3}$ Pairs: 1983	Imprecision: 7% Bias: 0.02 $\mu\text{g m}^{-3}$ Pairs: 2023
	(Pre-Change)	Imprecision: 17% Bias: 0.22 $\mu\text{g m}^{-3}$ Pairs: 1482	Imprecision: 17% Bias: -2.15 $\mu\text{g m}^{-3}$ Pairs: 2807	Imprecision: 16% Bias: -1.94 $\mu\text{g m}^{-3}$ Pairs: 2811
IMPROVE–CSN	(Post-Change)	Imprecision: 14% Bias: -0.02 $\mu\text{g m}^{-3}$ Pairs: 5018	Imprecision: 12% Bias: -0.26 $\mu\text{g m}^{-3}$ Pairs: 5128	Imprecision: 10% Bias: -0.29 $\mu\text{g m}^{-3}$ Pairs: 5142

Table 3a. Percentile precision, bias, and number of valid pairs used in comparison (blank subtracted IMPROVE values).

		EC	OC	TC
IMPROVE–CSN	(Pre-Change)	Imprecision: 17% Bias: 0.22 $\mu\text{g m}^{-3}$ Pairs: 1482	Imprecision: 15% Bias: -1.93 $\mu\text{g m}^{-3}$ Pairs: 2811	Imprecision: 14% Bias: -1.69 $\mu\text{g m}^{-3}$ Pairs: 2811
	(Post-Change)	Imprecision: 14% Bias: -0.02 $\mu\text{g m}^{-3}$ Pairs: 5018	Imprecision: 11% Bias: -0.12 $\mu\text{g m}^{-3}$ Pairs: 5147	Imprecision: 10% Bias: -0.15 $\mu\text{g m}^{-3}$ Pairs: 5149

Table 3b. Percentile imprecision, bias, and number of valid pairs used in comparison (non-blank subtracted IMPROVE values).

Using the reported data, the TC bias between networks after instrument and method changes was $0.29 \pm 0.77 \mu\text{g m}^{-3}$. Blank subtraction for TC contributed $0.14 \mu\text{g m}^{-3}$ of the bias. The remaining bias may be related to logistical differences between network operations. The duration of filter exposure to field conditions as well as shipping temperatures has been considered in previous studies (Solomon et al., 2014). CSN filters are shipped to and from sites on a per-sample basis in coolers maintained below 4°C (Note: In 2013, CSN started performing sequential sampling at some sites). IMPROVE filters are not refrigerated during shipping or while in the field and are shipped into the field in three-week batches. Dillner et al. (2009) found that post-sampling latency and temperature effects significantly decreased OC and TC concentrations by volatilization of vapor adsorbed during sampling. The sample handling differences may result in greater retention of post-sampling semi-volatile carbonaceous species on the CSN filters and account for the remaining offset.

Inter-network comparisons of both blank subtracted and non-subtracted collocated pairs were further explored with Theil Sen regression analysis (Sen, 1968) using the *mblm* software package in the *R* environment (Komsta, 2013; R Core Team, 2017). This method of bivariate regression is non-parametric and robust to outliers in both ordinates. Regression was performed over the entire dataset for each

parameter as well as by site for both blank subtracted and non-blank subtracted, while the discussion focuses on blank subtracted IMPROVE data as reported to AQS. The overall results are summarized in Figure 4 as well as Table 4. It should be noted that calculated uncertainties for the slope and intercept parameters were very low, owing to the large number of sample pairs used in the assessment. Therefore, to provide a more useful measure of the variability, we report the range of slopes estimated from regressions based on each of the individual collocated sites.

From Figure 4, it is immediately evident that the EC, OC, and TC measurements are in better agreement after the instrument and analytical changes based on slopes approaching unity and intercepts approaching zero. Consistent with previous studies (Chow et al., 2001; Malm et al., 2011; Rattigan et al., 2011), the differing analytical allocation of OC and EC along with the different filter face velocities resulted in a multiplicative bias between the networks for both EC and OC, as observed in the differences in slope before and after the change. Post-change slopes for EC ranged from 0.72 to 1.08 for the individual sites with an overall median of 0.98; similarly, OC slopes ranged from 0.79 to 1.12 for the individual sites with an overall slope of 1.04. The lower bounds were much closer to unity when the Birmingham site was excluded; 0.94 and 1.03 for EC and OC, respectively. Rattigan et al. (2011) found similar slopes for EC and OC using bivariate linear regression (0.99 ± 0.25 and 1.05 ± 0.13 , respectively). The TC regressions consistently mirrored the OC regression results. The better agreement of post-change measurements supports greater potential for inter-comparison of rural and urban assessments.

The CSN additive excesses (intercepts of CSN regressions on IMPROVE) between pre- and post-change EC measurements decreased from 0.08 to 0.02 $\mu\text{g m}^{-3}$. The additive differences between pre- and post-change OC measurements decreased more significantly from 1.21 to 0.20 $\mu\text{g m}^{-3}$; the OC intercepts varied greatly from site-to-site with ranges of 0.49 to 2.04 and 0.14 to 0.30 $\mu\text{g m}^{-3}$ for pre-change and post-change, respectively. The intercepts were not affected by removal of the Birmingham site. The relatively large reduction in OC additive difference may largely be due to the well-documented artifacts associated with carbon sampling on quartz filters (Chow et al., 2010; Kirchstetter et al., 2001; McDow and Huntzicker, 1990; Turpin et al., 1994). The greater air face velocity of the URG and IMPROVE samplers compared to the replaced instruments in CSN results in lower retention of semi-volatile organic compounds during sampling, ergo lower mass concentrations of OC. Also, the smaller filter area and higher flow rate used in the URG 3000N and IMPROVE samplers results in the retention of less total organic carbon mass because the retention is strongly related to the filter face velocity. The lower areal density loadings of the pre-change CSN filters enhanced the effect of this artifact. The relatively small blank subtraction performed by IMPROVE and recently implemented in CSN (November 20, 2015) is expressed in Figure 5. By increasing the filter face velocity on smaller filters like IMPROVE, the inter-network regression intercept was reduced by 83%.

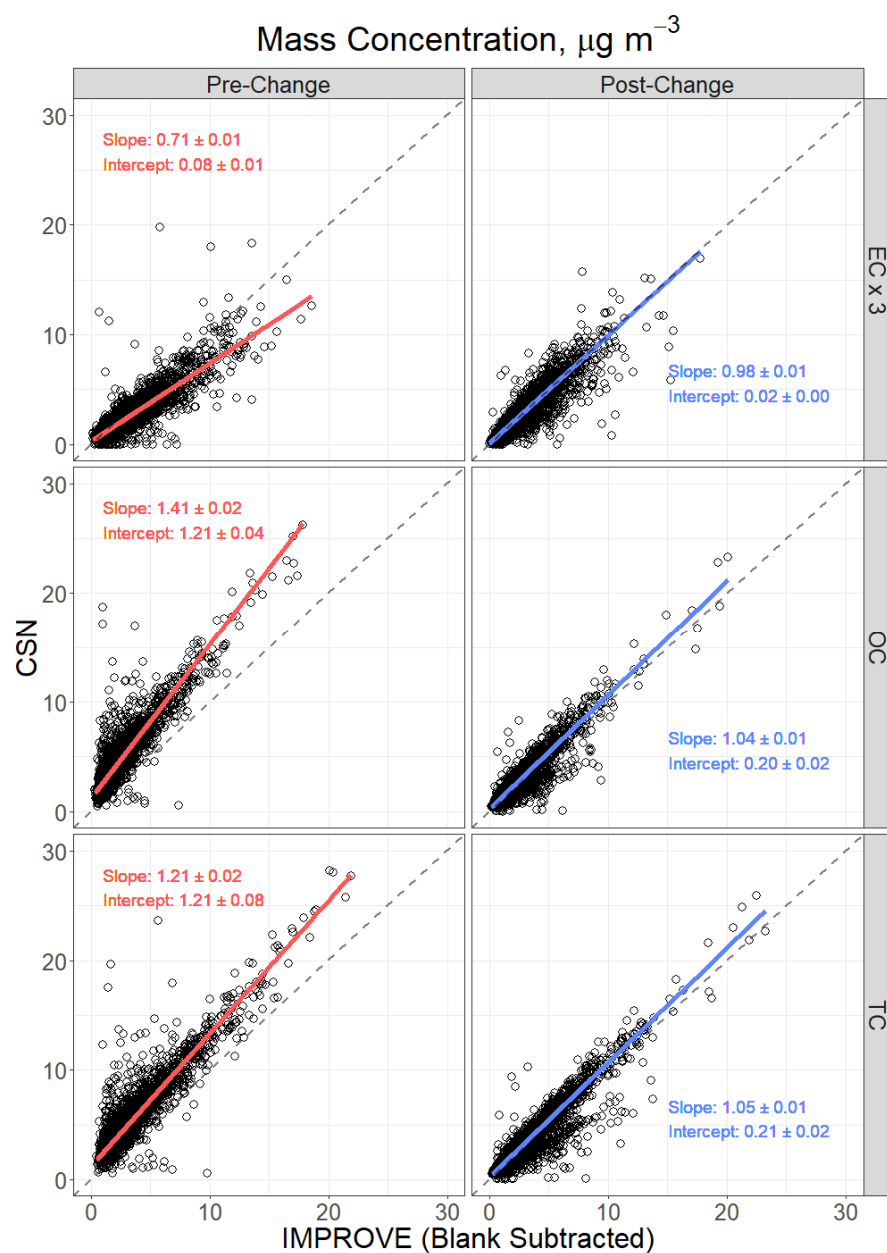


Figure 4. Theil-Sen regression of carbon measurements for CSN and IMPROVE. The CSN data is not blank subtracted. Note that the EC point values were multiplied by three to facilitate plotting with OC and TC. The EC slope and intercept values shown in text are unaltered.

		EC	OC	TC
Slope	(Pre-Change)	0.57 – 0.79	1.07 – 1.54	0.92 – 1.32
	(Post-Change)	0.72 – 1.08	0.79 – 1.12	0.76 – 1.12
Intercept	(Pre-Change)	-0.01 – 0.16	0.49 – 2.04	0.53 – 2.20
	(Post-Change)	-0.02 – 0.05	0.14 – 0.30	0.15 – 0.31

Table 4. The ranges of Theil-Sen regression slopes and intercepts for individual sites. The median values from each site were computed and the minimum and maximum of these are reported below.

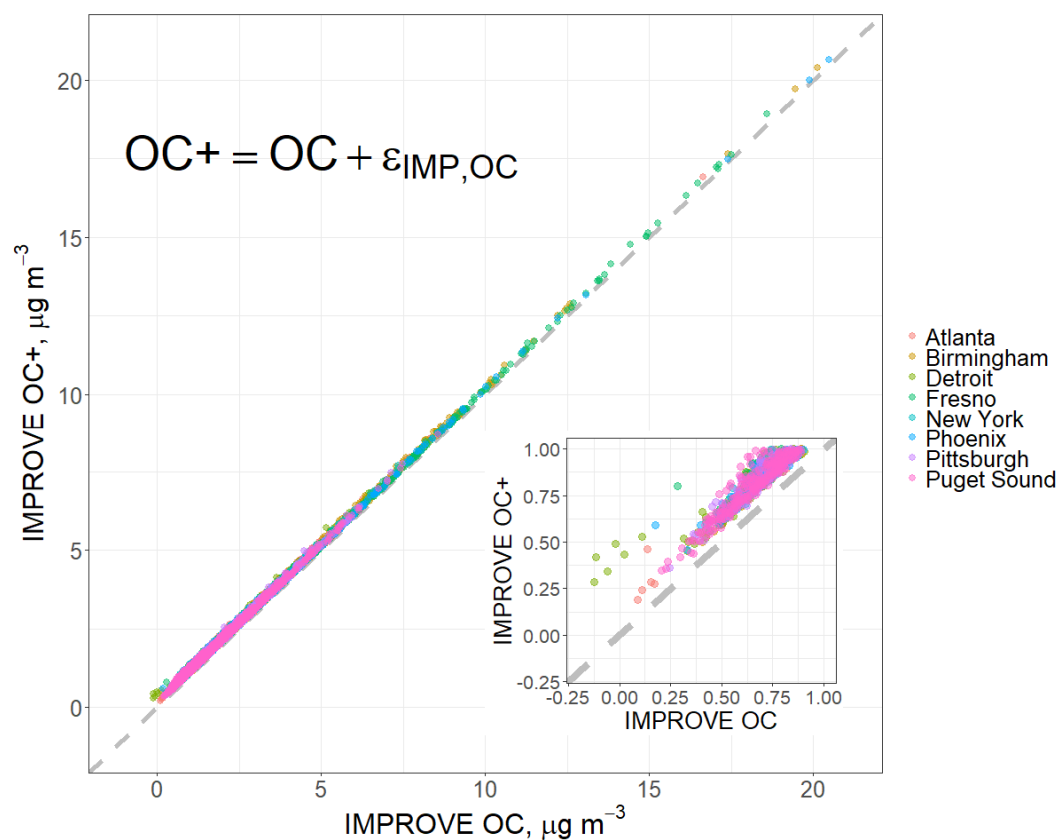


Figure 5. Comparison of blank-subtracted to non-subtracted IMPROVE OC measurements. Note all IMPROVE data is from sites with colocated CSN samplers. The $\epsilon_{\text{IMP,OC}}$ term represents the sum of the field blank filter concentrations. Negative sampling artifacts are not accounted for when in IMPROVE or CSN.

4. Conclusions

Carbonaceous compounds are an important component of atmospheric aerosols; however, the measurement results are strongly influenced by the sampling and analysis methodologies employed. Carbon measurements from the IMPROVE and CSN networks from 2005 through March 2016 were analyzed to determine inter-network comparability. Inter-network and intra-network comparability was quantified using percentile imprecision estimates, which is the current method for estimating analytical uncertainty in both networks. Changes in comparability were further evaluated using Theil-Sen regression.

As expected, better imprecision was observed for the years following sampling and analytical changes in CSN. Inter-network imprecision improved from 17% pre-change to 14% post-change for EC, 17 to 12% for OC, and 16 to 10% for TC. Similarly, the accompanying biases between networks approached zero post-changes: specifically, 0.22 to $-0.02 \mu\text{g m}^{-3}$ for EC, -2.15 to $-0.26 \mu\text{g m}^{-3}$ for OC, and -1.94 to $-0.29 \mu\text{g m}^{-3}$ for TC. Regression analysis underscored the improved comparability with slopes approaching unity (0.98 ± 0.01 , 1.04 ± 0.01 , and 1.05 ± 0.01) while the ordinate intercepts approached zero (0.02 ± 0.00 , 0.20 ± 0.02 , and 0.21 ± 0.02) for post-changes EC, OC, and TC, respectively. The results of this analysis show that the sampling and analytical changes made in CSN has brought the two

networks closer in terms of aerosol chemical characterization, thus enabling a more useful combined dataset for geospatial and temporal analyses.

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Highlights

- Collocated carbon aerosol measurements were compared between US networks
- Systematic network bias was greatly reduced by analytical and instrumental changes
- Inter-network precision estimates approached intra-network precision for all species

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