



Short communication

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.

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., 2001, 2007; 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 h 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

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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-3000 N 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 2 300 (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-3000 N is nearly identical to the IMPROVE carbon sampler with the addition of active flow control. The URG-3000 N 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. Fig. 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 (ϵ) is implemented corresponding to the analytical detection limits quoted by the laboratory, found in the IMPROVE SOP 351 Tables 3a and b (Cheng,

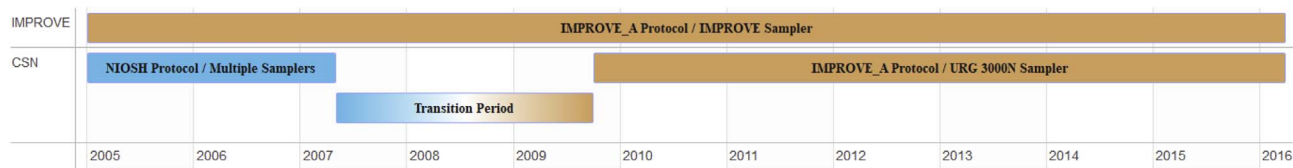


Fig. 1. Timeline of instrumental and analytical methods.

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