Issues with the Organic and Elemental Carbon Fractions in Recent U.S. Chemical Speciation Network Data

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ABSTRACT

The carbon fractions of organic (OC1, OC2, OC3, OC4, OP) and elemental (EC1, EC2, and EC3) carbon obtained from IMPROVE (Interagency Monitoring of PROtected Visual Environments) thermal/optical carbon analysis of quartz-fiber filters have been implemented to help distinguish spark-ignition engine exhaust particulate matter (PM) contributions from those of heavy-duty diesel exhaust. The Positive Matrix Factorization (PMF) source factor containing the optical pyrolysis correction (OP) typically includes significant contributions to sulfate and/or nitrate. This factor is associated with aged secondary organic and inorganic species. The U.S. EPA changed the sampling and analytical protocols for its Chemical Speciation Network (CSN) in the 2007–2009 period to provide these well separated individual peaks in the thermogram for aerosol characterization, source apportionment, visibility, and health studies. However, after October 1, 2018, there was a change in the laboratory and instruments used to implement the IMPROVE_A protocol for CSN samples. Although this switch resulted in similar total organic and elemental carbon (OC and EC) values, the protocol changes resulted in large shifts in the OC4, OP, and EC2 fractions, resulting in a swap in the resolved contributions from gasoline and diesel engine exhaust apportionments of PM2.5 mass concentration. It also affected the OP factor contributions. As a result, using the most recent CSN carbon fractions for source apportionments to separate gasoline from diesel vehicles will not result in correct results. The only current recourse is to reanalyze remnants of those samples using the original and temporally consistent IMPROVE_A protocol.

Keywords: Carbon fractions, Source apportionment, Gas/diesel separation, Thermal/optical analysis, IMPROVE_A protocol

BACKGROUND

The IMPROVE (Interagency Monitoring of PROtected Visual Environments) thermal/optical reflectance protocol (Chow et al., 1993) has been applied from 1986 to 2004 to quantify organic and elemental carbon (OC and EC) concentrations in ambient and source samples from the United States and other countries. The method is based on the observations of Huntzicker et al. (1982) that found darkening of the quartz-fiber filter sample during heating owing to charring of its OC content. They measured reflectance from the filter particle deposit to evaluate this charring in order to quantify the EC in the sampled aerosol. They also found that charring was minimized by applying increment steps in the temperature used to volatize OC in an inert helium (He) atmosphere and subsequently combust EC in an oxidizing environment.

The IMPROVE_A protocol (Chow et al., 2007, 2015); that has been used since January 1, 2005, modified this approach by redefining the four temperature plateaus in the inert He environment (OC1, OC2, OC3, and OC4 evolving at 140, 280, 480, and 580°C, respectively) and three EC plateaus
in an O\textsubscript{2}/He carrier gas (EC1, EC2, and EC3 at 580, 740, and 840°C, respectively). The analysis temperature stays constant until each fraction is fully realized as indicated by detection of the evolved carbon gases returning to baseline. An optical pyrolysis fraction (OP) is also quantified as the carbon evolved after oxidation is introduced into the analysis environment until the reflectance returns to its initial value, and this is included in the OC fraction, not in the EC fraction. Both reflectance and transmittance have been measured since 2005, and OC/EC splits are routinely reported for both, with EC usually being smaller for the transmittance correction. This difference has been attributed to charring of organic vapors adsorbed by the quartz-fiber filter that affect the transmittance more than the reflectance that is dominated by the surface aerosol deposit (Chow et al., 2004a).

Although the thermal fractions were originally intended to reduce the OP correction, early source characterization studies (e.g., Chow et al., 2003; Chow et al., 2004b; Watson et al., 1994) found that their abundances could be indicative of different source types, such as engine exhaust, vegetative burning, and fugitive dust. As a result, these fractions were added to the OC and EC reporting on ambient and source characterization studies and efforts were made to assure their comparability across changes in instruments and procedures over the past four decades. Once reported, researchers throughout the world began using them in aerosol characterization and source apportionment studies (e.g., Begum and Hopke, 2013; Chang and Lee, 2019; Lim et al., 2012; Shibata et al., 2019; Tham et al., 2019; Zhang et al., 2020; Zhu et al., 2014, 2010). Early work (Kim and Hopke, 2004a, 2004b, 2004c; Kim et al., 2004a, 2005, 2004b) demonstrated the added value of the carbon fractions for distinguishing among PM\textsubscript{2.5} contributions using receptor models. A bibliography of published work using carbon fractions in source apportionments is provided in the supplemental material file. As illustrated in Fig. 1, the carbon fractions allowed separation of vehicular emissions into two profiles that could be assigned to gasoline and diesel exhaust. At the time of these and other contemporaneous studies, the thermal carbon fractions were only available from the IMPROVE data base (CIRA, 2023), where the samples were mostly from non-urban settings, with a few measurements in cities such as Washington DC as shown in Fig. 1.

**THE PROBLEM**

Recognizing the need for chemical speciation in urban areas similar to that obtained from the IMPROVE network, the U.S. EPA (2023) established the Chemical Speciation Network (CSN) in 2000 and adopted sampling and analysis methods that differed from the IMPROVE protocols (Solomon et al., 2014). Between 2007 and 2009, the U.S. EPA revised the sampling and analysis procedures for carbonaceous materials. New samplers were deployed and the analysis protocol...
changed from the National Institute of Occupational Safety and Health (NIOSH) thermal/optical transmittance method (Birch and Cary, 1996) to the IMPROVE_A protocol (Chow et al., 2007) that included thermal carbon fractions consistent with those measures in samples from the IMPROVE network. The resulting data provided increased source resolution of PM$_{2.5}$ from the CSN urban sites. For example, Squizzato et al. (2018) analyzed the compositional data from eight CSN sites in New York state from 2005 to 2016. In these analyses, they worked around the change in OC/EC protocols and a change in carbon instruments in 2008. The resulting data were used in a series of epidemiological studies of short-term associations between source-specific PM$_{2.5}$ exposures and cardiovascular distress (Rich et al., 2019), respiratory diseases (Hopke et al., 2020), and respiratory infections (Croft et al., 2020). In these studies, gasoline and diesel exhaust contributions were found to be associated with a number of adverse health outcomes. Thus, there was interest in extending these studies beyond 2016.

When CSN data for the New York sites from 2017 to 2019 were acquired and added to the earlier data, inconsistencies were found in the OC4 and EC2 data as shown in Fig. 2 that illustrates data from the New York State Department of Environmental Conservation site at Queens College in New York City. There were major shifts in the OC4, EC2, and EC3 concentrations and OP after October 1, 2018. EC3 was not normally detected in recent samples, and OP has generally been associated with a separate secondary aerosol factor that now was lost.

Although not documented other than in the 2018 annual data quality report (UCD, 2018), EPA’s contractor for the CSN analyses, the University of California at Davis, chose to change the analytical approach in October, 2018 by performing carbon measurements in-house rather than in cooperation with the laboratory analyzing the IMPROVE network samples. The instrumentation and procedures were not the same as applied by the prior laboratory, insufficient intercomparisons were conducted to ensure consistency of the results, and thus, the historical record of year-by-year consistency in the carbon fraction data was broken. All that is noted in the report is that there was a “slightly elevated” change in the EC to OC ratio (UCD, 2018). As a result, the key indicators of gasoline and diesel exhaust were invalidated as indicated by the obvious shift in the time series of gasoline and diesel contributions (Fig. 3) resolved by applying positive matrix factorization to the data with EPA-PMF software. GAS drops sharply and DIE rises sharply analogous to the drop in OC4 and the rise in EC2. These results are discordant with the prior time series of values since OC4 and EC2 are key tracers of gasoline and diesel exhaust, respectively.

**THE SOLUTION**

In order to have consistent data to support the source apportionment and related studies, it was necessary to have portions of the filters collected between October 1, 2018 and December 31, 2019 reanalyzed in the previously used laboratory using the instrument designed to implement the IMPROVE_A protocol. This approach resulted in the revised contributions shown in Fig. 4.
CONCLUSIONS

Currently, it is not possible to use CSN OC/EC fraction data after October 1, 2018 for the full source apportionment that will resolve gasoline from diesel vehicles since the results will be distorted relative to results based on the earlier IMPROVE_A analyses. The separation of the two vehicular fractions and the OP source depends on having the full and consistent output of the OC/EC fraction analysis and these values are not provided by the instruments currently in use by the CSN laboratory. It appears that the only alternative is to have the samples reanalyzed by a laboratory that fully implements the IMPROVE_A protocol.

ACKNOWLEDGMENT

This work was supported by the New York State Energy Research and Development Authority under contracts #125993 and #156226 and the Health Effects Institute (4986-FRA20-1A/21-9). Research described in this article was conducted in part under contract to the Health Effects Institute (HEI), an organization jointly funded by the United States Environmental Protection Agency (EPA) (Assistance Award No. CR-83998101) and certain motor vehicle and engine manufacturers. The contents of this article do not necessarily reflect the views of HEI, or its sponsors, nor do they...
necessarily reflect the views and policies of the EPA or motor vehicle and engine manufacturers. We thank the New York State Department for Environmental Conservation for permission to reanalyze their samples and staff at OAQPS-USEPA for their assistance in arranging for the release of the samples to the laboratory for analysis.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.230041

REFERENCES


