Obtaining More Information from Existing Filter Samples in PM Speciation Networks

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A closer look at fine particulate matter data samples taken from long-term speciation networks.
The United States has operated the long-term non-urban Interagency Monitoring of PROtected Visual Environments (IMPROVE) network since 1987 and the urban Chemical Speciation Network (CSN) since 2000. The 2017 Annual A&WMA Critical Review and Discussion papers describe these networks and provide references for greater detail. Solomon et al. summarizes similarities and differences for these networks and changes in methodology that occurred during their long-term operation. A limited number of analyses are routinely performed on these samples, although modern laboratory technology now permits more specific speciation to determine source contribution and evaluate adverse environmental effects.

Fine particulate matter (PM$_{2.5}$; particles with diameters 2.5 micrometers and smaller), is collected on Teflon-membrane, quartz-fiber, and nylon-membrane filters to quantify mass concentrations by gravimetry, elements by x-ray fluorescence (XRF), carbon fractions (including organic and elemental carbon [OC and EC]) by thermal/optical reflectance (TOR) analysis, and water-soluble ions by ion chromatography (IC), as illustrated in the sidebar on the following page, Collecting, Analyzing, and Storing PM Samples. The 2017 Critical Review Discussion Paper noted the need for long-term consistency of these methods to detect trends that indicate the effectiveness of emission reduction strategies, as illustrated in Figure 1. In addition to these trends, the data from these networks have been used to: 1) identify and quantify source contributions using receptor models; 2) improve emission inventories; 3) validate urban- and regional-scale source models; and 4) elucidate atmospheric processes. PM$_{2.5}$ speciation data can be downloaded in comma-delimited formats for any or all of these uses.

The Critical Review also indicated complementary analyses that can be applied to the archived filters or water extracts to better address these goals:

- IC with pulsed amperometric and conductimetric detection can examine the water extract residual for bioaerosol,
Collecting, Analyzing, and Storing PM Samples

**Gravimetric analysis** is non-destructive and weighs the Teflon-membrane filter before and after sampling in a controlled environment to determine PM$_{2.5}$ mass concentration.

**X-ray fluorescence** is non-destructive and bombards the Teflon-membrane filter with high energy x-ray electromagnetic radiation that removes an inner shell electron, thereby emitting a lower energy photon when outer shell electrons replace the missing inner-shell electron. The wavelength of this energy indicates the element and the number of photons is proportional to the elemental concentration.

**Ion chromatography** acts on the destruction of the nylon-membrane filter by extracting it in ultrapure distilled-deionized water. This extract then passes through an ion exchange column that separates the anions or cations in time for detection of their electrical conductivity. The retention time identifies the ion and the level of conductivity determines the concentration.

**Thermal/optical reflectance carbon analysis** submits a small punch from the quartz-fiber filter to step-wise heating in inert (He), then oxidizing (98% He, 2% O$_2$) environments to determine OC, EC, and thermal carbon fractions that are indicative of sources. Laser light reflectance and transmittance are monitored to determine and correct for OC charring. Since 2016, these optical measurements have been made at seven wavelengths ranging from 405 nm to 980 nm, permitting estimation of brown carbon (BrC), commonly found in the smoldering phase of biomass combustion. A different method was used in the CSN prior to 2009.

**Sample Storage** is in sealed Petri slides in a refrigerated environment to preserve sample integrity. Although stored at the analysis facilities, these Teflon-membrane and quartz-fiber filter remnants are the property of the state agencies participating in the CSN and can be retrieved for more complex analyses when a request is made to EPA.
biomass burning, and secondary organic aerosol markers. The procedures are the same as those for the inorganic ions with different columns, detectors, and calibrations.

- Thermal desorption-gas chromatography/mass spectrometry extracts organic species through heating of a small quartz-fiber filter section and directs ions with a mass spectrometer. These spectra yield concentrations of polycyclic aromatic hydrocarbons (PAH) and other markers for fossil fuel and biomass combustion sources.

- Inductively coupled plasma-mass spectrometry (ICP-MS) complements, rather than replaces, XRF by detecting rare-earth elements and lead isotopes that may differentiate among fugitive dust source contributions. This method is applied to a strong acid extract of the Teflon-membrane filter that leave the sample unavailable for other analyses.

- Ultraviolet/Visible spectrometer measures light transmission through the Teflon-membrane filter that illustrate different wavelength-specific absorption characteristics among fossil fuel combustion, biomass burning, and fugitive dust sources.

Related to the last technique is the multiwavelength thermal/optical analysis that has been applied in IMPROVE and CSN since January 2016. This is a minor modification to the method applied previously that does not affect the long-term OC and EC quantification. However, with the same procedures and analysis times used before, the method provides a spectrum of absorption properties for the aerosol deposit, as illustrated in Figure 2.

Biomass burning produces light absorbing OC, termed “brown carbon” (BrC) in their aggregate, that are indicative of their contributions. Per unit of black carbon, which is present to some extent in all combustion samples, the smoldering peat and burning pine needles in Figure 2 absorb light more strongly at shorter wavelengths than do the particle emissions from diesel-engine exhaust. This difference permits identification of the biomass burning contribution. While smoke from residential wood combustion is a long-established wintertime PM$_{2.5}$ contributor in many areas, and is being effectively controlled through stove design, fuel specifications, and burning bans, non-winter contributions from ever increasing wildfires are more difficult to identify with currently available data. These contributions are important when defining natural visibility conditions related to the Clean Air Visibility Rule, formerly the Regional Haze Rule, and in exempting exceptional events from compliance determination.

Figure 3 shows an example of black carbon (BC) and BrC contributions during a Northern California wildfire that adversely affected air quality across the region. Lava Beds National Monument (NM) is located in far northeastern California, close to the Oregon border. The Carr fire started on July 23, 2018 approximately 150 km southwest of Lava Beds NM and burned over 90,000 hectares before containment occurred on August 30, 2018. Elevated OC and EC concentrations were sustained from July 24 to August 24 with a total carbon (TC = OC + EC) concentration reaching 50 µg/m$^3$. For much of this time period the Carr Fire was active, but little or no growth of the Carr fire area was occurring toward the end of August. Averaged over the summer, BC and BrC absorption contributed about 12 Mm$^{-1}$ and 10 Mm$^{-1}$ to total absorption at Lava Beds NM, respectively. On five days (July 4, 25, and 31 and August 24 and 30), all light absorption was attributed to BrC, indicative of the biomass contribution.

![Figure 2](image-url)
While these contributions are currently expressed as contributions to light absorption, work is underway to develop source-specific mass absorption efficiencies for fires that will translate these into PM$_{2.5}$ source contributions. There is growing evidence that secondary organic aerosol contains a substantial BrC component that could also be determined with these data.

As the obvious PM$_{2.5}$ emission sources become more completely controlled, it will be necessary to develop more specific markers for the remaining sources that cause exceedances of National Ambient Air Quality Standards. Filter samples from the national PM speciation networks have a high potential to assist in determining these contributions.

**Figure 3.** Organic and elemental carbon (OC and EC) concentrations, as well as brown carbon (BrC) contributions at Lava Beds National Monument during the 2018 northern California Carr Fire that destroyed large parts of the city of Redding, CA. Besides the Carr Fire, the Klondike Fire, about 200 km west northwest of Lava Beds NM in Southwestern Oregon from mid-July to November 2018, also impacted the area.

**Acknowledgment:**
This work was jointly supported by National Science Foundation grants AGS-1464501 and CHE-1214163, and the National Park Service IMPROVE Carbon Analysis Contract (P16PC0029). Thanks to Megan Johnson, now at North Carolina State University, for acquiring the data illustrated in Figure 2.

**References**

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