

United States National PM_{2.5} Chemical Speciation Monitoring Networks – CSN and IMPROVE: Description of Networks

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ABSTRACT

The U.S. EPA initiated the national PM_{2.5} Chemical Speciation Monitoring Network (CSN) in 2000 to support evaluation of long-term trends and to better quantify source impacts of particulate matter (PM) in the size range below 2.5 μm aerodynamic diameter (PM_{2.5}; fine particles). The network peaked at over 260 sites in 2005. In response to the 1999 Regional Haze Rule and the need to better understand the regional transport of PM, EPA also augmented the long existing Interagency Monitoring of Protected Visual Environments (IMPROVE) visibility monitoring network in 2000, adding nearly 100 additional IMPROVE sites in rural Class 1 Areas across the country. Both networks measure the major chemical components of PM_{2.5} using historically accepted filter-based methods. Components measured by both networks include

major anions, carbonaceous material, and a series of trace elements. CSN also measures ammonium and other cations directly whereas IMPROVE estimates ammonium assuming complete neutralization of the measured sulfate and nitrate. IMPROVE also measures chloride and nitrite. In general, the field and laboratory approaches used in the two networks are similar; however, there are numerous, often subtle differences in sampling and chemical analysis methods, shipping, and quality control practices. These could potentially impact merging the two datasets when used to better understand source impacts and the regional nature and long-range transport of PM_{2.5}. This paper describes, for the first time in the peer-reviewed literature, these networks as they have existed since 2000, outlines differences in field and laboratory approaches, provides a summary of the analytical parameters that address data uncertainty, and summarizes major network changes over the years. Additional papers are in preparation that will directly compare results from colocated measurements at three urban and three rural sites and examines if there are practical differences when using the same datasets in the same receptor modeling application.

KEY WORDS

Fine particles; long-term trends; visibility; NAAQS support; chemical composition; sulfate; nitrate; elemental carbon; organic carbon; trace elements; sampling and analysis methods; TOA, thermal optical analysis, EDXRF

INTRODUCTION

Particulate matter (PM) is emitted into the air from a wide variety of anthropogenic and biogenic sources. Particles can be emitted directly into the air (primary particles) or formed in the atmosphere (secondary particles) from gaseous precursor emissions that nucleate to form new particles or condense on existing particles (Seinfeld and Pandis 1998). The resulting chemical composition of ambient particles is complex due to the many different sources of primary particles and precursor gases and their subsequent chemical reactions and physical interactions in air. Understanding the sources of ambient PM is important because PM has been shown to have adverse effects on human health, degrade visibility, increase the acidity of lakes and streams, damage materials and crops, and impact global climate (U.S. EPA 2009a). Linking sources to ambient PM concentrations and ultimately to health effects and visibility degradation is

achieved, in part, by understanding the chemical composition of atmospheric PM and how it varies temporally and spatially (Hopke 1991; Schauer et al. 1996; Hopke 2003; Brook et al. 2004; Watson et al. 2008; Solomon et al. 2008; Solomon and Hopke 2008; Solomon et al. 2012). However, near the end of the 20th century detailed information on particle composition was lacking for many locations around the country. To fill this gap, the U.S. Environmental Protection Agency (EPA) and the National Park Service (NPS) established or expanded national chemical speciation monitoring networks to collect atmospheric particulate matter at urban sites (EPA) with a focus on linking sources to health effects (Federal Register 1997) and at rural to pristine sites (Class I areas; NPS) with a focus on linking sources to visibility degradation (Federal Register 1999). Of interest here are the networks related to collecting particles with aerodynamic diameters (AD) less than 2.5 μm (fine or PM_{2.5}) as particles in this size range have been associated with adverse health effects and visibility degradation (U.S. EPA 2009a; Harrison and Yin 2000; McClellan et al. 2004; Kampa and Castanas 2008; Solomon et al. 2012).

The two monitoring programs are referred to as EPA's PM_{2.5} National Chemical Speciation Network (CSN) (U.S. EPA 1999a) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (IMPROVE 2012a). These programs were designed to obtain information about the spatial and temporal chemical composition of ambient fine particles. Due to the regional nature of fine particles and the impact of regional PM on urban PM levels (and vice versa), EPA realized the need to have a combined dataset that includes both CSN (urban) and IMPROVE (rural) data. This combined dataset has been used to develop effective emissions control strategies for fine particles in urban areas, including the impacts of short- and long-range transport. While similar in design, the science and policy objectives of the individual programs impacted their specific sampling and analysis approaches.

Variations in design and operation between these networks have resulted in potential differences in the measured values. Understanding these differences is critical to using the combined dataset and comparing results among sites in these two networks.

Data from these networks have been used in State Implementation Plans for over a decade. Shortly EPA and the states will begin the PM_{2.5} designation and SIP process for 2018 attainment (McCarthy, 2013) and the information presented here should be useful for the

analyses needed to support relevant policy objectives. The specific objectives of this paper are to 1) describe the ambient measurement and laboratory chemical analysis methods employed in these networks since 2000; 2) describe the related quality assurance procedures employed; 3) report observed quality assurance results (e.g., blanks, minimum detection limits [MDLs], and uncertainty); and 4) summarize changes in the networks that have occurred over the years.

NETWORK DESCRIPTIONS

EPA's CSN Program was established through promulgation of the 1997 PM_{2.5} National Ambient Air Quality Standards (NAAQS) (Federal Register 1997). The CSN began as a small pilot network of 13 sites operating from February through July 2000. As the program grew, some sites were specified as part of the National Air Monitoring Stations (NAMS) network designed to track long-term trends in PM_{2.5} mass and composition to validate the efficacy of emission reductions strategies and support implementation of the NAAQS (State Implementation Plans – SIPS). These sites were initially referred to as Speciation Trends Network (STN) sites. Other sites were specified as part of the State and Local Air Monitoring Stations (SLAMS) network established primarily to support NAAQS implementation, with states and air quality agencies determining the need for length of operation. Note NAMS or STN is a subset of SLAMS. Both the STN and SLAMS chemical speciation sites are now referred to as the Chemical Speciation Network designed to support the additional objectives of health and exposure research studies and programs aimed at improving environmental welfare (e.g., visibility degradation).

In the fall of 2000, CSN began a network expansion from its original 13 sites and by October 2005 there were 54 STN, 181 SLAMS and Tribal sites, and 28 SLAMS that had IMPROVE monitors (IMPROVE Protocol Sites, defined below) (U.S. EPA 2005a). All STN sites are located in urban areas, but a few of the SLAMS sites are in non-urban areas. In early 2005, EPA began reducing the number of speciation monitors in the CSN network due to Congressional budget reductions at EPA. In April 2006, the network consisted of 54 STN, 159 SLAMS sites, 28 SLAMS IMPROVE protocol sites, and three tribal sites (U.S. EPA 2006). In 2012, there were 51 STN, 127 SLAMS sites, and, 28 SLAMS IMPROVE protocol sites (U.S. EPA 2013). Figure 1a indicates the CSN site locations as of 2006 and Figure 1b as of 2012.

The IMPROVE monitoring program was established in 1985 to aid in the development of Federal and State implementation plans for the protection of visibility in Class I areas as stipulated in the 1977 amendments to the Clean Air Act. The network began collecting samples in 1988 with 20 sites (Eldred et al., 1990). At that time, IMPROVE had a long-term goal of monitoring for regional haze in all visibility-protected Federal Class I areas as stipulated in the 1999 Regional Haze Rules (Federal Register 1999). By 1999, the IMPROVE network had increased to 30 IMPROVE sites in Class I areas and 40 IMPROVE Protocol sites, that is, sites that are part of the IMPROVE database, but are funded separately by a Federal Land Manager, state agency, or other entity. IMPROVE sites and IMPROVE Protocol sites are operationally identical in every respect, the only differences being their source of funding and, in some cases, their proximity to Class I areas. With implementation of the Regional Haze Rule and EPA's desire to combine CSN and IMPROVE data the IMPROVE network was expanded by spring 2004 to 110 IMPROVE sites in Class I areas and 57 Protocol sites. All but a few IMPROVE sites are located in Class I Areas where aerosol concentrations are typically much lower than urban levels. Twenty-eight of the IMPROVE Protocol sites are operated at state SLAMS sites, as noted above, and these SLAMS data are also included in EPA's Air Quality System (AQS) (U.S. EPA 2012a). The number of IMPROVE sites has remained roughly the same since 2004. Figure 1a indicates the IMPROVE site locations as of 2006 and Figure 1b as of 2012.

Similar time-integrated, filter-based approaches and laboratory analytical methods are used in both networks; each measuring $PM_{2.5}$ mass and its major components including sulfate, nitrate, ammonium (CSN only), organic carbon and elemental carbon (OC, and EC, respectively), and a number of elements found in crustal and industrial sources including, but not limited to Mg, Al, Si, S, Ca, Ti, V, Fe, and Zn. However, due to the different policy objectives of the two networks, differences, sometimes subtle in nature, exist between the sampling and analytical procedures employed (IMPROVE 2012a; Koutrakis 1998; Koutrakis, 1999; U.S. EPA 1999a). Choices in specific measurement and analytical methods also were made based on funding, available technology, and the desire for long-term monitoring (Koutrakis 1998; Koutrakis, 1999; U.S. EPA 1999). Current information relating to CSN and IMPROVE measurements is provided at their respective websites (IMPROVE 2012a; U.S. EPA 2012b).

Tables 1-7 present various aspects of the two measurement programs showing the subtle and not so subtle differences among the methods employed. Despite these many differences, results from the two networks typically agree well for high-concentration and non-labile species such as sulfate.

- Table 1 provides design specifications for IMPROVE and the three STN samplers. See Figures 2 and 3 for sampler schematics.
- Table 2 summarizes analytical laboratory methods by filter type and chemical component.
- Table 3 summarizes filter media, acceptance tests, and sample preparation procedures.
- Table 4 lists the original CSN and current CSN and IMPROVE operating conditions for the OC/EC analysis protocols.
- Table 5 describes denuders used to remove acidic gases in the channel that contains the nylon filter. See Figures 2 and 3.
- Table 6 provides a summary of sample handling, shipping conditions, holding times, and laboratory storage requirements.
- Table 7 describes the filter characteristics, flow rates, and face velocities for both networks.

Sampling Methods

CSN and IMPROVE samplers both employ filter -based time-integrated (24-hr average) sampling approaches that can provide a nearly complete mass balance via subsequent laboratory chemical analysis of the collected PM. For the collection of nitrate, both networks use denuders and reactive nylon filters to minimize sampling artifacts caused by nitrate volatilization (Hering et al. 1988; Hering and Cass 1999). Carbon artifacts are accounted for by using various blank correction approaches (Kim et al. 2005; Chow et al. 2008; Watson et al. 2009; Chow et al. 2010; Maimone et al. 2011), as discussed below. Therefore, these samplers are designed to minimize sampling artifacts for nitrate while allowing flexibility for estimating organic carbon artifacts.

Additional details regarding CSN and IMPROVE samplers are given in Table 1 and in standard operating procedures (RTI 2013; IMPROVE 2012b).

CSN. Three prototype and commercially available chemical speciation samplers were initially evaluated for use in the CSN (Solomon et al. 2000; Solomon et al. 2003) and results are summarized briefly below. The prototype samplers were the MetOne SASS (Spiral Ambient Speciation Sampler), the URG MASS (University Research Glassware Mass Aerosol Speciation Sampler), and the Thermo Anderson RAAS (Reference Ambient Air Sampler). Photographs and schematics of the three samplers can be found in the literature (Solomon et al. 2000) and on the EPA's Technology Transfer Network web site (U.S. EPA 2012c). All three samplers, one at each of the three sites, also were included in the 2001 – 2003 CSN-IMPROVE comparison, which will be the focus of a subsequent paper. R&P samplers (Model 2300; Rupprecht & Patashnick, Co., now Thermo-Scientific) were not available at the time of initial testing, and therefore were not included in the CSN-IMPROVE comparison study. In addition, few CSN sites used R&P samplers (7 % in 2006, none in 2012) and they will not be discussed in this paper.

Figure 2 shows a schematic drawing of the MetOne sampler, which, as of January 2007 was used at 84% of the CSN sites. Given the high percentage of MetOne samplers at this time, EPA made a decision to convert the entire network to MetOne samplers for collecting PM on the Teflon and nylon filters. This conversion was completed by mid-2009. The original MetOne sampler consisted of five sampling channels. A second version (Super SASS) was developed with 8 channels to allow for sequential sampling, which as of the beginning of 2014 has not been implemented. In both the SASS and the Super SASS, each channel operates at a flow rate of 6.7 L/min and each has its own sampling module designed for 47 mm diameter filters. In the SASS, three channels (SuperSASS, six channels - two sets used for sequential sampling) are normally used for CSN sampling, one each for Teflon, nylon, and quartz-fiber filters (QFFs). In both samplers, only three channels employ mass flow controllers allowing flow control to within 1% or better although corrections need to be made for variations in temperature and pressure to obtain volumetric flow. The additional channels in both samplers employ critical flow orifices for flow control (Baker and Pouchot 1983; Hinds 1999) and are available for replicate sampling or other uses. Each sampling module uses a sharp cut cyclone (SCC 2.141) that has similar performance characteristics to the EPA Well Impact Ninety-Six (WINS) impactor used in the

PM_{2.5} FRM (Peters et al. 2001). Sampling modules consisting of the filter cassettes and denuders are shipped to and from the laboratory with each sample.

The Anderson RAAS has four available flow channels, two each under two identical cyclone/manifold sets. The total flow rate through the inlet is 48 L/min and through each manifold is 24 L/min. Like the SASS, three channels are used for CSN sampling. The fourth channel is available for other needs, such as collecting a replicate sample. One channel under each manifold operates at 16.7 L/min and each includes a Teflon filter, one used for mass and elemental analysis, the other for replicate measurements. The second channel under each manifold operates at 7.3 L/min. One channel includes the nylon filter, which is preceded by an MgO coated annular denuder to remove acidic gases and the other includes a QFF. All channels employ mass flow control and each use 47 mm diameter filters. Sampling modules consisting of the filter cassettes and denuders are shipped to and from the laboratory with each sample.

The URG MASS 400/450 sampling system uses two standalone samplers operating at 16.7 L/min, each with mass flow control. Each sampler includes a filter holder for 47 mm diameter filters and both samplers employ the WINS impactor identical to that used in the PM_{2.5} FRM program. The MASS 450 contains a single QFF for OC and EC analysis. The MASS 400 includes a sodium carbonate coated annular denuder upstream of the Teflon – nylon sequential filter pack. Nitrate that can volatilize from the front Teflon filter during sampling is captured and measured on the backup nylon filter (Hering and Cass 1999; Solomon et al. 2000). Therefore, for this sampler only, nitrate is the sum of nitrate measured on the Teflon front and nylon backup filter. Mass, trace elements, and then ions in that sequence are measured on the Teflon filter. As a result, lower nitrate values are observed on the URG relative to the other samplers, since nitrate can volatilize off the Teflon filter during analysis by energy-dispersive x-ray fluorescence (EDXRF), which occurs prior to analysis for ions (Solomon et al. 2000; Solomon et al. 2003, Yu et al. 2006).

Starting in February 2007, CSN started transitioning sampling on QFF for carbonaceous components to the URG 3000N sampler (U.S. EPA 2007b; U.S. EPA 2012e). This sampler is virtually identical to the sampler used by IMPROVE for collecting OC and EC, except the critical orifice was replaced with a mass-flow controller and how filters are shipped between the

laboratory and field as described later. QFF collected by the URG 3000N are analyzed by the IMPROVE_A method. This transition was completed by late 2009 and all carbon analyses are now done using the URG 3000N/IMPROVE_A protocols.

CSN samplers are operated by state, local, and tribal agency personnel. Research Triangle Institute International (RTI, Research Triangle Park, NC) is currently the laboratory responsible for filter preparation, shipping, chemical analysis, and database management for all STN sites. Primarily RTI, but others also are responsible for these tasks at SLAMS sites. These include state laboratories in California, Oregon, Nevada, the two former for California and Oregon sites and the latter for SLAMS sites in the State of Texas. Samples are collected once every three days at STN sites and once every three or six days at SLAMS sites, the latter schedule is defined by the state, local, or tribal agency responsible for the sampling site. Samples collected by CSN can remain on the sampler for up to 3 days (U.S. EPA 2012d). All CSN filters remain in their sampling modules or filter holders, which are sealed at both ends, placed in sealed anti-static Ziploc plastic bags, and shipped in coolers with blue ice by overnight carrier service. The temperature target at receipt is not to exceed 4° C, although this has been frequently exceeded by a few degrees, particularly in the summer months. A flag is noted in the database for samples arriving at greater than 4° C. Before and after sampling filters remain in clear polystyrene Petri dishes (Millipore PetriSlides™ or equivalent) that are stored at reduced temperatures (< 0° C). Petri slides are used as they come from the manufacturer, without further cleaning but are visually inspected for debris or deformities. Petri slides are not reused in CSN. Additional details about the CSN sampling and analysis protocols can be found at the AMTIC web site (U.S. EPA 2012b) .

IMPROVE. All IMPROVE and IMPROVE Protocol sites use the same sampler design as shown in Figure 3 and summarized in Table 1. The sampler consists of three separate modules for PM_{2.5} and a fourth module for PM₁₀. Each module uses a critical orifice to control flow, and contains 4 solenoid valves and corresponding filter holders to allow for a blank sample to be collected and/or for sequential operation. One of the PM_{2.5} modules uses a 25 mm diameter Teflon filter for mass, light absorption, and trace elements, a second uses a 37 mm nylon filter for ions, which is preceded by a sodium carbonate coated Al annular denuder; and a third uses a

25 mm QFF for organic and elemental carbon. Finally, a 25 mm Teflon filter is used in the PM₁₀ module for PM₁₀ mass.

IMPROVE samplers are operated by local operators at each site, often National Park Service (NPS) personnel or state agency personnel. Currently, IMPROVE samples are collected once every three days, to be consistent with CSN, whereas prior to 2000 they were collected only on every Wednesday and Saturday. Filters are allowed to be left on the sampler for up to 7 days after collection (IMPROVE 2012c). IMPROVE filters are prepared at UC Davis with the exception of QFF filters that are pre-fired at the Desert Research Institute (DRI) and shipped to UC Davis prior to sampling. Filters are sent between the field sites and UC Davis in their sampling cassettes sealed in Ziploc plastic bags at ambient temperature. Shipping is by UPS or by standard U.S. mail in plastic containers designed for durability but not thermal stability. Following sampling, QFF filters for organic carbon analysis are shipped between UC Davis and DRI at reduced temperatures, where the QFF are stored below 0° C and analyzed. Nylon filters are shipped in Petri dishes at ambient temperatures by US mail to RTI for analysis of ions. Petri dishes are used initially as they come from the manufacturer, without further cleaning but are visually inspected for debris or deformities. Used Petri slides for nylon filters are washed in ethanol and reused with no contamination observed. Other Petri slides are not reused. Additional details are given in the IMPROVE Quality Assurance Project Plan (Flocchini et al. 2002) and in IMPROVE standard operating procedures (IMPROVE 2012b).

Analytical Methods

Similar analytical methods are employed by the CSN and IMPROVE monitoring programs, as summarized in Table 2. PM_{2.5} mass is measured gravimetrically by weighing conditioned filters before and after sampling. Water soluble ionic species are extracted from the nylon filter (the Teflon filter in the case of the URG MASS samplers) and determined by ion chromatography (IC). Organic and elemental carbon are determined by thermal optical analysis (TOA) from QFF and up to 48 trace elements have been measured by EDXRF from the Teflon filter used first for mass determination. Organic species are not measured routinely in either network. Numerous subtle and not so subtle differences exist between the methods employed in

the two networks with regards to the analytical methods, preparation procedures, sample storage, shipping, and methods for determining and correcting for blanks and interferences.

Additional details for the CSN analytical methods are given in Solomon et al. (2001) and U.S. EPA (1998) and in specific laboratory standard operating procedures (SOPs) for mass and chemical speciation (RTI 2008; RTI 2009a-f, RTI 2011)

IMPROVE mass and chemical analyses are conducted at UC Davis, RTI, and DRI. Mass, elemental, and light absorption analyses are conducted at UC Davis, ions are analyzed at RTI, and OC/EC analysis is at DRI. Additional details for IMPROVE analytical procedures are given in the IMPROVE Quality Assurance Project Plan (Flocchini et al. 2002) and standard operating procedures (IMPROVE 2012b).

The remainder of this section gives brief summaries of the methods employed by both programs and addresses some of the differences.

Acceptance Testing. Acceptance testing of new filter lots is conducted to ensure filter quality and consistency over time. Acceptance tests and sample preparation procedures are summarized in Table 3 for both networks (DRI 2005; RTI 2011, IMPROVE 2012d). Differences between acceptance testing protocols exist but likely make little difference in the measurements since quality assurance procedures require the collection and analysis of blanks throughout the sample and analysis process.

For CSN, Teflon filters are visually inspected and a subset analyzed for trace elements. If the average blank level ($\mu\text{g}/\text{cm}^2$) for any element is greater than three times the variability (3σ) of the MDL, then an intercept is included in the EDXRF calibration equation for that element. The same intercepts are used until a new batch of filters is received; the 10 filters do not constitute a fixed percentage of filters.

CSN nylon filters received from the manufacturer are washed for 24-hr in several changes of DI water (RTI 2009b). The washing solution for 2 out of every 100 filters is analyzed for ionic species to ensure they are below acceptance levels as given in Table 3 (U.S. EPA 2000)

CSN QFF are heat treated to remove OC associated with new filters from the manufacturer (Table 3). This process lowers the blank level to below the MDL. However, while heat treating removes the initial OC artifact, QFF medium continues to sorb organic gases until reaching pseudo-equilibrium. The overall artifact is both passive and active and depends on the sampled volume and several other factors and can reach the equivalent of $4 \mu\text{g}/\text{m}^3$ for CSN filters sampled with the MetOne sampler (McDow and Huntzicker 1990; U.S. EPA 1998; Solomon et al. 2000; Turpin et al. 1994; Turpin et al. 2000; Maimone et al. 2011).

All Teflon filters used in IMPROVE are visually inspected for imperfections. For each new lot, the pressure drop at 22.8 L/min is checked in the laboratory using a manometer and a subset (10) filters are weighed to verify the correct weight range of each new batch of filters. Finally, selected filters are analyzed by EDXRF, Proton Elastic Scattering Analysis (PESA, discontinued January 2011), and Hybrid Integrating Plate/Sphere analysis (HIPS) to check for contamination.

New lots of IMPROVE nylon filters also are visual inspected and the pressure drop measured similar to the Teflon filters. A subset of filters is analyzed for sulfate, nitrate, nitrite, and chloride contamination to ensure they are below acceptance levels as given in Table 3

IMPROVE QFF filters are visually inspected and heat treated to reduce initial blank levels similar to CSN. However, while filters in both networks are heated at the same temperature the time is slightly different as well as how the filters are treated and stored after heating (Table 3). A subset of filters is selected after the initial cleaning and analyzed for OC and EC to ensure blank values are within acceptable levels.

Mass. Gravimetric analysis is used in both networks to obtain $\text{PM}_{2.5}$ mass (Table 2). IMPROVE also measures PM_{10} mass by this method. An estimate of coarse particle mass (particles in the size range between 2.5 and 10 μm AD) can be obtained by difference between simultaneously measured PM_{10} and $\text{PM}_{2.5}$ mass concentrations. Collection of PM_{10} also provides a quality control check on the $\text{PM}_{2.5}$ mass since $\text{PM}_{2.5}$ mass must always be less than the PM_{10} mass. CSN Teflon filters used to obtain PM mass are equilibrated for 24-hr before and after weighing to minimize mass variation due to particle bound water (Table 2). CSN adheres to the FRM $\text{PM}_{2.5}$ mass analysis protocol to obtain concentrations in units of $\mu\text{g}/\text{m}^3$ (Federal Register

1997; U.S. EPA 1998; RTI 2008). IMPROVE equilibrates Teflon filters for mass at a slightly different temperature and RH range but only for several minutes (Table 2). Unpublished laboratory tests of exposed Teflon filters at UC Davis as well as EPA audits have demonstrated that filters collected at rural and remote monitoring sites appear to equilibrate to laboratory conditions within a few minutes (IMPROVE 2012d).

Ions. Ion chromatography is used to determine concentrations of major water soluble ions from the PM collected on the nylon filter in both networks (Table 2). Ions also were measured on the Teflon front filter collected by the URG MASS. In this case, total nitrate equaled the sum of nitrate measured on the Teflon front filter and nylon backup filter. Both networks measure sulfate, and nitrate. CSN also measures ammonium, sodium, and potassium ions whereas IMPROVE also measures, chloride and nitrite ions and estimates ammonium based on fully neutralized sulfate ($(\text{NH}_4)_2\text{SO}_4$) and nitrate (NH_4NO_3). RTI analyzes filters for ions for both networks (RTI 2009c, RTI 2009d; IMPROVE 2005). The same IC conditions are used in both networks and both networks extract nylon filters in DI water, except for the CSN URG nylon backup filter, which is extracted in IC eluent. Slightly different extraction conditions are used between the networks. IMPROVE extracts at room temperature, whereas CSN extracts at reduced temperatures to stabilize semi-volatile species, such as nitrate and ammonium. However, high extraction efficiencies have been demonstrated for both programs (Clark 2002a). Differences in ion analysis approaches are summarized in Table 2. Use of nylon as the collection medium results in a potential negative artifact for ammonium (Solomon et al. 2000; Yu et al. 2006).

Carbon. Thermal optical analysis is used to determine concentrations of organic and elemental carbon in both networks (Table 2). The two programs initially used different temperature protocols and optical approaches, the latter to correct for OC charring. The different temperature protocols are shown in Table 4. The different optical approaches occur during the He temperature steps (Chow et al. 1993; Chow et al. 2001; Chow et al. 2004; Chow et al. 2005a; Chow et al. 2007; Peterson and Richards, 2002; Watson et al. 2005; RTI 2009e). Beginning in 2008 and finishing in 2009, CSN transitioned to the IMPROVE_A analysis protocol to obtain consistency between the networks. Prior to 2009, CSN used thermal optical transmittance (TOT) (Peterson and Richards, 2002), whereas IMPROVE used thermal optical

reflectance (TOR) (Chow et al. 1993). Differences due to use of TOT versus TOR have been observed (Chow et al. 2004). Beginning with samples collected in January 2005, IMPROVE provides both TOR and TOT results (DRI 2005; Chow et al. 2007). Several studies have been conducted comparing the IMPROVE, CSN, and in some cases other protocols for OC and EC (Chow et al. 2001; Schmid et al. 2001; Conny et al. 2003; Chow et al. 2004; Watson et al. 2005; Cheng et al., 2011).

The variation between the two approaches for OC measured on typical urban and rural samples ranges from about 10-30%; for EC the difference can be up to a factor of 2 or more for the different analytical protocols used in the comparison studies (Solomon et al. 2000; Chow et al. 2001; Schmid et al. 2001; Solomon et al. 2003; Chow et al. 2004; Watson et al. 2005; Chow et al. 2008; Cheng et al. 2011). Total carbon (TC), equal to the sum of OC and EC, usually agrees to within 10-15%. Agreement for TC indicates that differences in the analytical approaches for OC and EC are likely due to how the two protocols determine the split between OC and EC and/or correct for OC charring (i.e., TOT vs. TOR).

IMPROVE also analyzes the PM_{2.5} Teflon filters for optical absorbance (1/m) of the particles collected on the filters by HIPS (Bond et al. 1999). Optical Absorbance is not measured in CSN. Absorbance by the collected particles is important for estimating light extinction, a critical parameter for quantifying visibility and IMPROVE's primary policy objective. The absorbance is divided by an empirically determined absorptivity coefficient (m²/μg) to convert it to black carbon (BC) in concentration units of μg/m³ although a range of values exist for this conversion (Bond and Bergstrom 2006). BC measured optically is similar to but not the same as EC measured thermally (Fehsenfeld et al. 2004). In HIPS, the filters are exposed to light at 633 nm wavelength from a He (Ne) laser and the light transmitted through the sample is collected with a photodiode detection system. This measurement provides a quality control check on the absorptivity coefficient and/or elemental carbon measurements, the latter since elemental carbon is typically the predominant light absorbing particulate species in the atmosphere.

Trace Elements. Energy dispersive X-ray fluorescence is used by both programs to quantify trace elements (Na – Pb) in PM_{2.5} collected on Teflon filters (Table 2) (RTI 2009f; IMPROVE 2012e). IMPROVE has also used PESA to measure hydrogen (IMPROVE 2012f),

but this analysis was discontinued in 2011 for budgetary reasons. The CSN program initially reported 48 elements (reduced to 33 elements in 2009), while IMPROVE reports 25, focusing only on those that are reliably measured above the MDL of the instrument. As noted in Table 2, prior to December 2001, IMPROVE used Proton Induced X-ray Emission (PIXE) for Na-Mn and EDXRF for Fe-Pb (IMPROVE 2006). The switch to only EDXRF provides lower MDLs for most elements of interest, as well as ensures better sample preservation for reanalysis (PIXE can damage filters). Still, EDXRF is not sufficiently sensitive for many of the elements measured by both networks, so typically only about 10-15 elements are reported above their detection limit for the primarily urban CSN and about 15-20 elements for the primarily rural IMPROVE network. The higher filter loading (volume sampled/area of filter, m^3/cm^2) combined with differences in analytical parameters result in better ambient MDLs for IMPROVE, which allows more species to be measured above their detection limits.

Different EDXRF instruments are used by the two programs. In addition, to obtain sample throughput, CSN uses two EDXRF instruments and laboratories, one operated by RTI and the other by Chester LabNet (Portland, OR).

The RTI EDXRF and Chester LabNet laboratories analyze filters from the long-term trend networks (STN and NCORE; U.S. EPA 2005c; Scheffe et al. 2009). Filters collected by California, Oregon, and Texas are analyzed by state and local district laboratories (California Air Resources Board, DRI, and Oregon Dept. of Environmental Quality, South Coast Air Quality Management District) (Smiley 2013). RTI uses Thermo Scientific QuantX EDXRF analyzers, each equipped with a high flux rhodium anode X-ray tubes and an electronically cooled lithium-drifted silicon detector (RTI 2009f). Elements are analyzed using one of five different excitation conditions defined by different anode operating conditions and X-ray filters. Chester LabNet uses similar anodes and detector systems, though there are slight differences in the excitation conditions relative to the CSN laboratory (Chester 2009). While each instrument is calibrated to meet QC criteria individually, between-instrument and between-laboratory variations can introduce additional uncertainty in the CSN EDXRF results (Smiley 2013).

Prior to 2011 IMPROVE used a Cu anode EDXRF system to quantify elements with atomic weights from Na through Fe, and a Mo anode for elements with atomic weights from Ni

through Pb. Prior to 2005 the Cu anode system utilized a helium purge to remove air around the sample thus minimizing interferences due to the argon spectral peak. Beginning with samples collected in January 2005, a vacuum system was introduced because He diffused through the Be window of the SiLi detector, changing the calibration and eventually destroying the detector. A second (nominally identical) vacuum-based EDXRF system was introduced in October 2005 to increase laboratory capacity. In 2011 the aging Cu and Mo anode systems were replaced by PANalytical Epsilon 5 EDXRF instruments. With the Epsilon 5 system elements are analyzed using one of seven different excitation conditions defined by different exposure times and secondary X-ray targets. Data advisories addressing the impacts of changes in EDXRF hardware and procedures are available from IMPROVE (IMPROVE 2012g). CSN has similar information available in annual data reports (<http://www.epa.gov/ttn/amtic/specdat.html>), special study reports (TTN 2012a), and CSN the newsletters (2004 – 2009; <http://www.epa.gov/ttn/amtic/spenews.html>).

Self-absorption corrections for particle size and filter loading were applied by both networks but a detailed description of the approaches employed are beyond the scope of this paper. Self-absorption corrections for IMPROVE were applied to the legacy EDXRF data prior to 2011 (Dzubay and Nelson 1975; IMPROVE 1997). A homogeneously distributed sample deposit on the filter is assumed as well as incorporating particle-size and mass loading effects. Self-absorption is strongest for the lightest elements such as Na and Al decreases substantially for heavier elements. The correction was discontinued with the introduction of the new PANalytical Epsilon 5 instruments, which provide much improved sensitivity for the lighter elements where self-absorption is greatest.

Similar to the IMPROVE methodology, the CSN self-absorption assumes a homogeneous and uniformly distributed sample and incorporates particle-size and mass loading effects. The CSN self-absorption procedure is a modification of the protocol used by EPA with the Thermo Scientific QuantX spectrometers (Dzubay and Wilson 1974; U.S. EPA 1999c). The procedure corrects for signal loss due to scattering and absorption by calculating an absorption correction factor that compensates for measured intensities in a homogeneous sample relative to a thin-film standard. Self-absorption corrections vary by sample composition, but in general are similar to those in the IMPROVE network.

EDXRF round-robin performance evaluations of CSN and IMPROVE laboratories were conducted by EPA (Smiley 2013). Comparability between laboratories for many high concentration elements (e.g., elements, Fe, Ca, K, Zn) was considered acceptable. The poorest agreement was for Al and Na. This is expected, since low molecular weight elements have a relatively poor instrument response and typically require correction for self-absorptions, both of which can lead to higher uncertainty for these elements. Furthermore, the two networks use different approaches to correct for self-absorption as noted above, though the uncertainties seem to agree reasonably well (U.S. EPA 2011).

MEASUREMENT UNCERTAINTY

As in all measurement programs, measurement uncertainty in CSN and IMPROVE includes both random and systematic errors. Precision is a measure of random errors, which is usually determined for the combined field and laboratory operations by collecting colocated replicate samples or by propagating individual instrument errors through all components of the measurement process. Accuracy provides a measure of systematic error, which is a measure of the difference between a ‘true value’ and the estimate of the true value based on the measurement. Overall measurement accuracy is not possible for most PM measurements since traceable standards applied in the field are not available (Fehsenfeld et al. 2004). However, analytical laboratory measurement accuracy is reported and general values are provided in Fehsenfeld et al. (2004). Factors affecting overall uncertainty include the coupled effects of measurement precision, interferences, measurement and analysis artifacts, and MDL. Estimating these parameters is critical to understanding the validity of a measurement.

A number of studies have been conducted to better understand uncertainty and factors influencing uncertainty in CSN and IMPROVE measurements. A selection of papers published since about 2000, i.e., most relevant to the current networks, are cited herein and provide information about uncertainties associated with measuring the chemical components of PM; however, a comprehensive review and evaluation of results published is beyond the scope of this manuscript. Studies examined uncertainty issues in only one network or the other; whereas others examined it between networks. These studies include the initial CSN intercomparisons (Solomon et al. 2000; Coutant and Stetzer 2001; Solomon et al. 2003), estimating the overall

measurement uncertainty for mass or one or more chemical components for CSN and IMPROVE (Solomon et al. 2000; Chow et al. 2001; Solomon et al. 2003; Ashbaugh et al. 2004a-b; Chow et al. 2004; Watson et al. 2005; White et al. 2005; Yu et al. 2006; Smiley 2013; Hyslop and White 2008b), and estimating different uncertainty components (blanks, MDL, sampling artifacts) for OC, mass, ions, and elements by EDXRF (Iyer et al. 2000; Gutknecht et al. 2001; Kim et al. 2001; Lewtas et al. 2001; Fehsenfeld et al. 2004; Subramanian et al. 2004; Gego et al. 2005; Kim et al. 2005; Gutknecht et al. 2006; Zhao et al. 2006; Chow et al. 2008; Hyslop and White 2008a; Watson et al. 2009; Chow et al. 2010; Gutknecht et al. 2010; Cheng et al. 2011; Maimone et al. 2011; Malm et al. 2011). Several special EPA Office of Air Quality Planning and Standards (OAQPS) studies also were conducted to examine sampling artifacts associated with QFF medium caused by a specific filter cassette (Clark 2002b); the effect of QFF filter type (manufacturer) for collection and analysis of OC and EC (Peterson et al. 2007), the extraction efficiency of ions from nylon filters using water rather than a basic solution, the latter as used historically (Clark 2002a; Clark 2003); examining the efficacy and capacity of different diffusion denuder coatings for the removal of acid gases (Fitz 2002); and the reanalysis of existing filters for independent inter-laboratory comparisons and sample storage stability testing (Coutant and Stetzer 2001; TTN 2012b). Approaches used to estimate uncertainty for the CSN and IMPROVE networks based on CSN and IMPROVE measurements are summarized in the next few sections, including estimates for sampling artifacts, blank estimates, and MDL. Data completeness, an important parameter with regards to data validity also is summarized for both networks.

CSN AND IMPROVE QUALITY ASSURANCE PROGRAMS

A rigorous quality assurance program (U.S. EPA 1998; Flocchini et al. 2002; U.S. EPA 2012d; U.S. EPA 2012f; Smiley 2013), as conducted by EPA for CSN and IMPROVE, helps to ensure the delivery of high quality data with known uncertainty to data users, such as state and local agencies, the NPS, and other stakeholders. These groups use these data to develop strategies to protect public health and welfare from the adverse effects of air pollution. Quality assurance helps to identify factors that can increase uncertainty, and once minimized, ensures those uncertainty levels are maintained by establishing a set of performance criteria or data quality objectives (DQOs) (U.S. EPA 1999b; White et al. 2005). For historical purposes, Table 8

lists the performance criteria recommended for the CSN and IMPROVE networks in developing the joint networks (Koutrakis 1999; Solomon et al. 2000, Solomon et al. 2003).

QA Field and Laboratory Programs

EPA conducts system and performance audits for field and laboratory measurements in accordance with EPA's Quality Assurance Project Plans for CSN and IMPROVE (U.S. EPA 2000; Flocchini et al. 2002; U.S. EPA 2012f). Field and laboratory audits include both system and performance audits. Laboratory audit results are available at U.S. EPA (2011). Field audit results are not currently posted for public access although RTI is beta testing an input to EPA's Air Quality System (AQS) for field audit results. AQS is EPA's repository of ambient air quality data.

Field Audits. Quality Assurance Project Plans (QAPP) for CSN (U.S. EPA 2000) and IMPROVE (Flocchini et al. 2002) field sampling operations provide guidance and detailed direction on field audits and procedures. The updated CSN QAPP (U.S. EPA 2012f) and IMPROVE QAPP (IMPROVE 2002) are currently the overarching quality assurance documents for CSN and IMPROVE's external EPA field audits. Additional individual guidance documents are available for CSN (U.S. EPA 2012b) and IMPROVE (IMPROVE 2012e). A limited number of independent field audits were conducted by EPA's Office of Radiation and Indoor Air (ORIA), Radiation and Indoor Environments National Laboratory (R&IENL), Las Vegas, NV (western sites) and by EPA's Office of Air Quality Planning and Standards (OAQPS; eastern sites). Based on guidance in the CSN QAPP (U.S. EPA 2000), comprehensive field audits were to occur on approximately 25% of the CSN sites annually. This percentage was never realized due to reductions in 2001 in EPA's travel budget so EPA began to aggressively train State, Local, and Tribal (SLT) agency and NPS personnel to conduct the field audits. SLT and NPS audits are conducted by groups within these organizations that are independent of field sampling operations. Audits by EPA personnel were eliminated by 2010. , which

Field systems audits consist of six parts; 1) identifying organization and responsibilities for site operations, 2) evaluating safety, 3) validating that site location and samplers meet 40 CFR Part 58, Appendices A and E siting criteria, 4) confirming that the monitoring area and logbooks are maintained, 5) validating proper sample handling and chain of custody, and 6)

ensuring that proper procedures are being followed for onsite storage and shipping. Performance audits, conducted simultaneously with systems audits, consist of validating MQOs (Table 9; U.S. EPA 2012f) against traceable reference standards.

Laboratory Audits. EPA's Office of Radiation and Indoor Air (ORIA), National Analytical Radiation Environmental Laboratory (NAREL) provides annual performance evaluation (PE) samples to laboratories that analyze CSN and IMPROVE filters. These samples consist of filters and solutions with known quantities of the analyte spiked onto the filters using NAREL laboratory analysis results as the reference (U.S. EPA 2012b). NAREL also collects colocated ambient filters using the SuperSASS, which are then distributed with blank filters for analysis of mass (Teflon filters), ions (nylon and Teflon filters), carbon (QFF), and trace elements (Teflon filters). Separate anion and cation solutions of known concentrations and uncertainty also are provided for IC analysis. NAREL also sends performance audit (PA) samples to the analytical laboratories. These include NIST traceable metal weights for gravimetric analysis and sucrose spiked QFF for TOA analysis. For trace elements, Teflon filters with ambient PM are circulated that have been independently analyzed by the EPA's National Exposure Research Laboratory's (NERL) EDXRF facility. Once the audited laboratories have analyzed the filters, they are returned to NERL for reanalysis to ensure that the concentrations of elements on the filters have not changed due to handling and shipping. On-site laboratory technical systems audits (TSA) also are conducted by NAREL personnel. Results from system and performance laboratory audits are available (U.S. EPA 2011).

Artifact and Blank Corrections

A blank is a relatively constant error affecting the measurement value and can be evaluated with a control sample in which all steps of the analysis are performed in the absence of the actual sample. The blank value is then applied as a correction (subtraction) to the measurement. Three types of blank filters have been collected for these programs: laboratory, trip, and field. Each type helps to identify potential areas of contamination and is part of the standard EPA quality assurance/quality control programs.

Artifacts can be positive or negative and are variable errors that affect the measurement and may not always be properly evaluated with a blank. When sampling atmospheric particles,

artifacts are typically due to collection of gases on a sampling substrate or volatilization of sample already collected. Determining the impact of an artifact on the measurement may be complicated as noted below (e.g., Chow 1995; Hering and Cass 1999; Solomon et al. 2000; Turpin et al. 2000; Kim et al. 2001; Pang et al. 2002; Ashbaugh et al. 2004a-b; Subramanian et al. 2004; Chow et al. 2005a-b; Kim et al. 2005; White et al. 2005; Yu et al. 2006; Watson et al. 2009; Chow et al. 2010; Maimone et al. 2011). For example, issues associated with sampling OC on QFFs include adsorption and absorption on both collected particles and quartz-fiber filter material (positive sampling artifacts) and may occur passively during storage, transport, and handling or actively during sampling. Conversely, volatilization of semi-volatile organic compounds (SVOC) from collected particles (negative sampling artifacts) can occur during sampling with a likely dependence on flow rate or pressure drop, temperature, and RH (McDow and Huntzicker 1990). Negative artifact also can occur throughout the transport and storage processes after collection. Both positive and negative OC sampling artifacts are further influenced by VOC and SVOC ambient concentrations and species, by filter lot, filter preparation (thermal cleaning temperature and duration), filter holder material, and other variables. Loss of semi-volatile ammonium nitrate also has been well documented (e.g., Hering and Cass; 1999; Clark 2002b; Pang et al. 2002; Ashbaugh et al. 2004a; White et al. 2005; Yu et al. 2006; Solomon et al. 2008 and references within).

Ammonium nitrate artifact (loss), related to nitrate only, is minimized in these networks by the use of a denuder-reactive filter (nylon) pair (Table 5; Solomon et al. 1992, Solomon et al. 2003; Hering et al. 2004; Chow et al. 2005b). The denuder removes the gas phase interferences, primarily nitric acid and the nylon filter captures any nitrate volatilized (HNO_3) from the particles during sampling (Solomon et al. 1992, Solomon et al. 2003; Hering et al. 2004; Chow et al. 2005b).

Several alternative techniques have been suggested to estimate the OC artifact, including use of a single QFF back-up filter behind the primary QFF, such as IMPROVE uses or use of a QFF behind a Teflon filter; use of a denuder (e.g., activated carbon impregnated strips or XAD coated glass annular denuder) in front of a reactive back-up filter (e.g., carbon or XAD impregnated glass-fiber filter) behind the primary QFF, and application of a linear regression method where OC (y-axis) is plotted versus $\text{PM}_{2.5}$ mass as obtained on a Teflon filter (Peters et

al. 2000; Turpin et al. 2000; Solomon et al. 2000; Lewtas et al. 2001; Tolocka et al. 2001; Subramanian et al. 2004; Kim et al. 2005; Watson et al. 2009; Chow et al. 2010; Maimone et al. 2011). Other statistical methods also have been investigated for CSN (Kim et al. 2001).

The CSN and IMPROVE programs use different strategies to account for blanks and artifacts associated with the filter material, filter handling, transport, storage, and laboratory contamination with the greatest difference associated with OC. These different strategies for OC were part of the reason for CSN switching to IMPROVE protocols for sampling and analysis of organic and elemental carbon as noted above. Below we describe the analytical protocols and highlight the differences providing data for 2006 and 2012 in Tables 10-13.

CSN: Field and trip blanks have been collected at a rate of 10% and 3%, respectively. This resulted in greater than 1000 trip and field blanks per year for each species. Approaches for collecting trip and field blanks in CSN are similar (U.S. EPA 2000). Trip blanks are not removed from their containers in the field, while cartridges containing field blanks are installed in the sampler for a few minutes, sealed, and then stored in the sampler housing until the samples are retrieved. Based on CSN field and trip blank data collected since 2000, there is no statistical difference between these two types of blanks for the major species, so these data sets are merged to estimate blank or artifact values for each component by sampler type (Tables 10 and 12). For this and for budgetary reasons, CSN stopped collecting and analyzing trip blanks in 2013. Field and trip blank values, along with various other operational and QC data are summarized in the CSN semiannual and annual data reports posted on AMTIC (TTN 2012a).

CSN concentration data available in AQS are not corrected for measured blank or artifact values. This allows data user's flexibility to calculate and apply corrections to meet their own data analysis and policy objectives. CSN semi-annual and annual data summary reports show low blank values for ionic species (sulfate, nitrate, ammonium, sodium, and potassium) as measured on nylon filters (Table 10), below MDL (Table 11) for EC as measured on QFF, and most trace elements as measured by EDXRF on Teflon filters, the latter since late 2002 and early 2003 when filter contamination issues for a few specific element were resolved. Gravimetric mass, on the other hand, is subject to relatively frequent outliers above the MDL, probably due to contamination during sampling and handling. Blank values for organic carbon (including

subfractions) are almost always above the MDL of the analysis method due to sorption of gas-phase carbon compounds on to the quartz-fiber filter medium as well as on previously collected particles ("organic artifact") as discussed earlier. High blank values also can occur episodically for virtually any species. For example, during 2001 and 2002, sodium ion blanks were unusually high due to high sodium levels in the nylon filters as received from the manufacturer. This situation was addressed by modifying the SOP to include washing new nylon filters prior to use as described in the modified SOP (RTI 2009b). Another episode of high blank values for gravimetric mass was apparently caused by Teflon filters contaminated with excessive manufacturing debris. This was addressed by flagging suspicious data and increasing the rate of laboratory QC. This QC included increased duplicate weighings: all filters were weighed in duplicate prior to being used for field sampling; after field sampling, replicates were performed at a rate of 30%. No further filter batch problems were detected after several years, so the rate of QC replicates was reduced to the baseline of 10%.

Average OC artifact values (average of trip and field samples) for CSN by sampler type for 2006 and 2012 and seasonal averages for each year are presented in Table 12 . However, it should be noted that trip and field blanks may not be good estimates of the true OC artifact, since blanks only experience passive sorption and active positive and negative sampling artifacts are not reflected in the blank data (e.g., Maimone et al. 2011). Also not considered are positive and negative artifacts due to the filters remaining in the samplers for up to three days after collection. Since the artifact equilibrium changes due to a variety of physical (e.g., pressure drop across the filter) and environmental conditions (e.g., T, RH, SVOC concentration) (Turpin et al. 2000), the OC artifact associated with QFF field blanks vary not only by sampler type, but by season and from year-to-year with MetOne and Anderson having similar levels but both higher than URG and IMPROVE.

When EPA changed from using the MetOne sampler for collecting PM on QFF to the URG 3000N, CSN started collecting dynamic blanks that could be used for blank correction. The new approach as described below employed a QFF filter behind the front QFF filter with the assumption that the same artifact would be observed on both filters (Subramanian et al. 2004; Watson et al. 2009; Maimone et al. 2011). CSN results are reported without the dynamic OC blank correction, although the dynamic blank results are posted to AQS and could be used to

make the correction, if desired. Table 12 lists typical OC artifact corrections for each of the carbon components reported by CSN in ng/m^3 . Collection of dynamic blanks for OC also is collected at all sites rather than at 6 to 12 sites (depending on the year) as done for IMPROVE. To achieve this within budget the number of field blanks collected in the rest of the network was reduced from 10% to 5% (U.S. EPA 2007c). Because no difference was seen between trip and field blanks and due to budget reductions, trip blanks were discontinued in 2013. *IMPROVE*: The IMPROVE program collects field blanks at a rate of approximately 1% for Teflon filters and 2 to 5% for nylon and QFFs. IMPROVE field blanks are installed in the sampler in an unused sampling port or sampling port in a separate module. Filters are left in the port the entire sampling period as opposed to CSN where they are installed in the sampler for only a few minutes.

The IMPROVE program applies blank and artifact corrections to data prior to calculating atmospheric concentrations (i.e., at the $\mu\text{g}/\text{filter}$ level). Thus, data available on the IMPROVE web site have been blank corrected. Blank values for mass and elements as measured on Teflon filters are typically below detection limits so no correction is applied. Sulfate, chloride, nitrite, and nitrate as measured on nylon filters are corrected using data obtained from field blanks. OC/EC artifacts are estimated using the dynamic blank, an active rather than a passive approach, as described below. Seasonal (e.g., March, April, May) median artifact correction values were applied to the concentration data for IMPROVE prior to June 2002. Since then, monthly artifact correction values are applied to the concentration data.

Table 10 lists typical average blank values for 2006 and 2012 and seasonal averages for each year for ionic species reported by IMPROVE. While IMPROVE applies these corrections prior to calculating ambient concentrations, the values in Table 10 have been divided by 33 m^3 , the nominal volume collected by an IMPROVE sampler (i.e., 22.8 L/min, 24-hr duration) to allow for direct comparison to CSN results.

Carbon artifact in IMPROVE is estimated from a backup QFF placed immediately downstream of the primary QFF, thus a dynamic blank rather than the static blank used in CSN (Turpin et al. 2000; Subramanian et al. 2004; Maimone et al. 2011). Prior to 2008, a backup QFF was collected with each sample at only 6 geographically dispersed sites. Beginning in

2008, the number of sites was expanded to 12. As described above, it is assumed that the second QFF collects the same fraction of gas phase quartz adsorbable SVOC and VOC as the front filter, and therefore, provides an estimate of the front QFF OC artifact (Subramanian et al. 2004; Watson et al. 2009; Maimone et al. 2011). Table 12 lists typical OC artifact corrections for each of the carbon components reported by IMPROVE, adjusted for sample volume as described above for ions. EC artifact corrections are applied but they are typically near zero and are not listed here.

On a sample-by-sample basis, the median backup QFF should provide a reasonable estimate of the OC artifact on the primary QFF if both filters reach equilibrium, which is often the situation in urban atmospheres (Subramanian et al. 2004), although studies need to be conducted to ensure this is true in more remote areas where IMPROVE sites are located. However, averaging across multiple sites located in different parts of the country where the OC artifact also can vary significantly by season may bias the correction for samples that are not close to the average (Maimone et al. 2011).

Minimum Detectable Limits (MDL)

CSN and IMPROVE use slightly different approaches to calculate MDLs as summarized in Table 13 and below. Hyslop and White (2008a) examined the variability in MLD values between the two networks from colocated measurements for six trace elements by EDXRF. Analytical MDL values (ng/cm^2) were similar indicating that the analytical methods have similar sensitivities, at least for species described and before IMPROVE changed to the PANalytical EDXRF instrument. Similar analytical sensitivities (ng/cm^2) are observed for ion chromatography since the same laboratory analyzes samples from both networks. Since CSN switched to the IMPROVE protocol by the end of 2009 for TOA the analytical MDL values are the same for OC and EC. As described below, differences are observed between the networks when MDL values are given in concentration units. -

CSN: Between the start of the program in 2000 and June 2003, a single set of MDL values ($\mu\text{g}/\text{m}^3$) were reported for each species and sampler type. These MDL values are given in the CSN data summary reports (TTN 2012a) and were provided in response to data users' inquiries. The original MDL estimates were established in several ways: for OC/EC, the

instrument manufacturer's published detection limit was used; for gravimetric mass, the balance resolution was taken as the limit of detection; for ions, the standard deviation of 7 to 10 low-level replicate measurements multiplied by the appropriate Student's t factor was used for the MDL (Federal Register 2014); and for EDXRF, MDL values were determined by Chester LabNet according to Method IO 3.3 (with a multiplier of 2) (U.S. EPA 1999c).

After June 2003, MDL are determined for each analyzer separately and data records in AQS report instrument -specific MDL values with each concentration, and thus, can sometimes vary significantly from filter-to-filter.. Individual MDL values are based on three times the standard deviation of a large set of laboratory blanks, low-level samples, or equivalent (Federal Register 2013, Federal Register 2014; U.S. EPA 1999c). MDL values are re-evaluated and updated annually or when an instrument has undergone major maintenance that could affect its performance. AQS does not include a data field to identify the instrument used to analyze each sample.

CSN zero and below-detection limit data are maintained in AQS as reported without flagging, setting to zero, or other substitute options such as MDL/2. The only exception is negative concentration values that are automatically set to zero when uploaded to AQS. By not censoring data, users have flexibility regarding use of the reported data.

A summary of average MDL values (ng/m^3) for the CSN SASS sampler for 2006 and 2012 is provided in Table 11 and results for all years since 2004 at TTN (2012a). Method detection limits for OC, EC, and carbon fractions changed for CSN during this period, as shown in Table 11, due to the change from the CSN OC/EC method to the IMPROVE OC/EC method.

IMPROVE: Individual MDL are provided with each concentration value in the IMPROVE database. A concentration is determined to be significantly different from zero only if it is greater than the MDL. For IC and TOR OC/EC analyses the MDL corresponds to twice the standard deviation of the field blanks or backup QFF filters, respectively. For mass and light absorption, the MDL corresponds to twice the analytical precision determined by laboratory blanks (mass) or low-absorbing controls (light absorption). Prior to 2011, the MDL for each element for PESA and EDXRF (the latter using the Cu and Mo anode XRF systems described previously) was based on system blanks and specifically 3.29 times the square root of the

background counts under the region that would have been occupied if the element was present in the sample (IMPROVE 1997). Beginning in 2011, the MDL for EDXRF (using the PANalytical Epsilon 5) is determined as the 95th percentile of the intensity measured on a set of typically 50 to 100 field blanks (IMPROVE 2014a).

Lower MDL values reported in ambient concentrations ($\mu\text{g}/\text{m}^3$) are observed for IMPROVE relative to CSN because of the higher mass loading used in IMPROVE relative to the MetOne SASS (Table 1; Hyslop and White 2008a). This relates to a factor of almost 6 potential improvement in sensitivity (m^3/cm^2 of filter) often needed by IMPROVE due to the lower ambient PM concentrations in pristine areas. Larger filter areas and lower flow rates were employed in CSN to avoid filter clogging due to the higher PM concentrations observed in urban locations. The effect of this theoretical advantage in sensitivity between the networks is an important issue that will be investigated in a later paper. The ability to detect and quantify low levels of elements in remote areas used as tracer species for certain sources (e.g., V, Se for oil and coal combustion) could significantly impact the ability of receptor models to apportion ambient PM to its sources (Flanagan et al. 2014).

Data Completeness

Completeness describes the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained if all samples were collected successfully. It is an important quality assurance indicator and provides a measure of data validity. For example, when determining compliance for PM_{10} , a minimum of 75 percent of the scheduled PM_{10} samples per quarter are required for compliance calculations (Federal Register 2006, Part 50). Table 14 provides percent data completeness for major PM components for both CSN and IMPROVE for two representative years, 2006 and 2012. Data completeness for both networks was in the range of 90-100%.

Precision Based On Colocated Data

Whole-system precision estimates based on colocated sampling are obtained for both networks according to the procedure described in the Federal Register (2006, Part 58, App. A, section 4.3)..

Colocated CSN samplers have been operated at six STN sites since the beginning of the program, accounting for between 3% and 5% of the entire network or roughly 12% of the STN sites. The full network percentage has increased slightly as network reductions have taken place. Colocated samplers at a given site are operated by the same operator and use filters prepared and shipped at the same time, but shipped in separate containers. No effort is made to randomize the filter pairs between laboratory instruments. Precision estimates for CSN based on colocated sampling results are calculated annually and are summarized for the major species in the CSN annual data summary reports (U.S. EPA 2012g). At each of the six colocated CSN sites, the primary sampler operates on a 1-in-3 day schedule, while most of the colocated samplers operate on a 1-in-6 day schedule.

Precision results as percent average relative difference are presented in Table 15 for 2006 and 2012 for components that are typically 3 times above their MDL. Other elements are not quantified so they are not included in the table. Precision results for CSN mass, ionic species (by IC), and carbon components are around $20\% \pm 5\%$. Trace elements by EDXRF are mostly in the range from 25% to 40%. Light elements analyzed by EDXRF such as sodium and aluminum show relatively poor precision compared with heavier elements due to self-absorption as described previously (see for example, Dzubay and Nelson 1975; Berry et al. 1969)

The IMPROVE sampler includes four filter holders per module (either A, B, C, or D; see Figure 3) that have separate solenoid valves to allow for sequential sampling over multiple sampling days. Prior to 2003, one of the four filter sets was used to obtain a colocated sample for the specific filter type assigned to that module. Beginning in 2003, IMPROVE installed single colocated modules (either A, B, C, or D) at different sites. Phoenix has all four modules colocated. There are seven duplicate modules of each type (A, B, C, and D), which is equivalent to having colocated samplers at 4% of the ~170 IMPROVE sites.

For major components, precision estimates in IMPROVE range from 3% for sulfate to 130% for the third elemental carbon fraction. Table 15 presents colocated precision estimates as percent average relative difference determined from IMPROVE samples collected in 2006 and 2012. Colocated precision tends to improve with increasing data completeness, is typically better

when the analysis is performed on the whole filter instead of a fraction of the filter, and is better for species that are predominantly in the fine size fractions (Hyslop and White 2008b).

CSN AND IMPROVE PROGRAM HISTORIES

Changes to network field sampling and analytical procedures can cause a step change in reported data. Therefore, it is important to identify when these changes took place. Several network changes took place in IMPROVE before 2000 and these are noted in the IMPROVE newsletters (IMPROVE 2014b). Table 16 provides a brief history of the networks since 2000, summarizes field and laboratory changes in both networks, and indicates the reason for the change. Major changes are highlighted below with possible implications of that change to long-term network results.

Between 2005 and 2006 CSN underwent a reduction in the number of monitoring locations due to reduced funding. Most of the reductions occurred at SLAM sites and at locations where PM concentrations no longer exceeded the PM NAAQS. However, the most significant change to CSN began in early 2007 with replacement of the CSN carbon measurement approach with the IMPROVE carbon measurement approach, albeit with minor exceptions as described earlier (U.S. EPA 2007a-b; U.S. EPA 2009b; U.S. EPA 2012e). The replacement was completed in October 2009 (U.S. EPA 2009b). Starting in 2008, CSN started transitioning to the IMPROVE_A analysis method for carbon, which was completed by 2009. These changes were implemented to obtain consistency between the two networks for carbon. A reduction in the collection of network field blanks was applied to offset the increased cost of analyzing the additional backup QFF used to estimate OC artifact.

It is anticipated that as sites were changed from the CSN OC/EC approach to the IMPROVE approach a step change is likely to be observed, potentially with slightly lower OC and higher EC; total carbon will likely change little (Chow et al. 2001, 2004; Schmid et al. 2001; Conny et al. 2003; Watson et al. 2005; Cheng et al. 2011). This change also resulted in better precision and lower MDL values for OC, EC, and OC fractions as seen in Table 11 in comparison of 2006 to 2012. Since changing from the CSN to IMPROVE approach for OC and EC took place over about 2.5 years, with a few sites at a time, the Carbon Conversion Site Lists (U.S. EPA 2012e) will need to be reviewed on a site-by-site basis when examining long-term

trends for OC and EC during the period mid-2007 through near the end of 2009. However, the consistency achieved between the networks for understanding regional impacts of carbon in urban areas and vice versa was deemed sufficient reason for the change.

Several small changes have taken place since 2000, including switching to a smaller shipping container and reducing the number of trace elements determined by EDXRF from 48 to 33 (see Table 11) since many of the elements removed were below their MDL. Both of these were implemented to reduce cost but should have no long-term impact on the results. In 2009 CSN also adjusted the attenuation factor used for four low molecular weight elements. This resulted in a small step change to the reported concentrations of these elements.

IMPROVE has had several changes since 2000, although most with only minor and typically positive impacts on results. At the end of 2001, the analysis method for elements from Na to Mn was changed from PIXE to EDXRF by Cu anode and at the end of 2002 EDXRF run times were standardized at 1000 s. These changes resulted in improved and more consistent detection limits for elements of interest. At the beginning of 2005 the carbon analysis instrument was replaced with a new model resulting in a small change to the IMPROVE analysis approach (IMPROVE_A) and details of this change can be found in Chow et al. (2007). In 2008 the number of sites with QFF backup filters was increased from six to twelve providing better spatial coverage and geographic diversity of the data used to correct for potential positive and negative OC sampling artifacts. In 2011 the EDXRF was replaced with a new instrument (PANalytical Epsilon 5); the list of elements reported remained unchanged. Also in 2011 the PESA analysis for hydrogen was discontinued due to budget limitations. The hydrogen data from PESA were used almost exclusively for quality control checks so eliminating the measurement had no effect on most data analysis projects. Better precision and lower MDL values were realized for a number of elements due to the switch to the PANalytical XRF systems. Improvements were observed for sulfur and the soil-related elements required by the Regional Haze Rule as well as improvements for the lighter elements such as sodium, aluminum, and silicon. There is degradation of the precision and MDL values for some trace elements such as zinc and selenium.

SUMMARY AND CONCLUSIONS

This paper describes the CSN and IMPROVE networks in detail through 2012 with minor updates through the beginning of 2014. It outlines the differences in the field and laboratory approaches and summarizes the analytical parameters that affect data quality.

In general, the field and laboratory approaches used in the CSN and IMPROVE networks are similar; yet there are many detailed and subtle differences in the sampling and analysis methods employed, as well as shipping, blank/artifact estimation and correction approaches, and estimation of uncertainties. These differences may be more or less important depending on the application of the results and related policy objectives of the study using these data. Several changes in measurement and analytical protocol also occurred since 2000. While some of these changes may result in step changes in the long-term database they have been identified and in general will have minimal impact on use of these data.

A recent assessment of the CSN network (Landis 2014) examined a range of parameters that would suggest which sites to remove from the CSN network beginning in early 2015 due to reduced budgets. The assessment considered, for example, the number of sites within a geographic area, how PM correlated among those sites, and if the sites were within an attainment area. Fifty-three sites were recommended for defunding. Other recommended network reductions include eliminating the CSN mass measurement at the 119 sites beginning in July 2014 where mass is measured by the FRM; reduce sampling frequency to 1 in 6 days at all but NCORE sites (U.S. EPA 2005c; Scheffe et al. 2009) and STN sites; reduce carbon blanks from 10% – 5% and eliminate carbon dynamic blanks currently at 5%. Implementation of recommendations is scheduled for early 2015 if approved and after all stakeholders have input. While not final, the impact of these potential reductions will not be known for several years.

Future papers will directly compare results from colocated measurements at three urban and three rural sites, each site having one of the three CSN samplers and an IMPROVE sampler and examines if there are practical differences when using the same datasets in the same receptor modeling application.

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LIST OF FIGURE CAPTIONS

Figure 1. a) CSN and b) IMPROVE site locations as of 2006 and 2012. Colocated – sites where a network had side-by-side samplers to estimate precision. Carbon backup filter – IMPROVE sites (6 in 2006 and 12 in 2012) that had a QFF backup filter to estimate the OC artifact (see text for details). All CSN sites had backup QFF for OC artifact once the IMPROVE methods (URG 3000N sampler and IMPROVE_A analysis protocol) were implemented, between 2007 and 2009; prior to implementation of the URG 3000N no sites included backup QFF. An interactive IMPROVE map with a complete site list can be found at <http://views.cira.colostate.edu/fed/Tools/SiteBrowser.aspx>. CSN site listing can be found at U.S. EPA (2013).

Figure 2. CSN MetOne SASS sampler schematic. RAAS and MASS schematics available at Solomon et al. (2000) and pictures, including SASS, at U.S. EPA (2012c).

Figure 3. IMPROVE sampler schematic. Pictures available at U.S. EPA (2012c).

Table 1. Design specifications for IMPROVE and CSN samplers, the latter employed in EPA’s Speciation Trends Network.

| | IMPROVE | | CSN | | |
|--|--|--|---|---|---|
| Sampler Name; Model | IMPROVE | Spiral Ambient Speciation Sampler; SASS TM or SuperSASS TM | Reference Ambient Air Sampler (RAAS TM); RAAS 2.5-400 | Mass Aerosol Speciation Sampler; MASS 400 and 450 | URG 3000N Speciation Sampler ^b ; 3000N |
| Manufacturer | URG | MetOne ^a | Andersen | URG | URG |
| Sampler schematic and picture. | http://vista.cira.colostate.edu/improve/Overview/IMPROVEProgram_files/v3_document.htm . (see Figure 3, IMPROVE schematic) | | http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25pict.pdf (includes IMPROVE sampler). (see Figure 2, MetOne schematic) | | |
| External exposure. | Samplers inside or under open shelter, no AC. | | Samplers outside, standalone units. | | |
| Sampling inlet height, agl (m). | 2 to 15 with most between 3 and 4. | | 2 and 15. | | |
| Sampling inlet. | PM _{2.5} modules – weather cap. PM ₁₀ – Wedding or Sierra-Andersen PM ₁₀ inlet. All Wedding inlets replaced by Sierra-Andersen in 2009. | Sharp-cut cyclone with downward facing inlet nozzle; solar/weather shield. | FRM PM ₁₀ inlet, modified to 48 L/min. | FRM PM ₁₀ inlet. | Identical to IMPROVE. |
| Inlet cutpoint (µm); slope ^c . (Watson and Chow 2011) | PM _{2.5} module inlet head not characterized. PM ₁₀ – 10; NA. | 2.5; 1.1. (Kenny et al. 2000) | 10; NA. | 10; NA. (Tolocka et al. 2001; Kenny et al. 2005) | Identical to IMPROVE. |
| Inlet material; coating | Anodized aluminum. | Anodized aluminum. | Teflon-coated aluminum. | Anodized aluminum; Teflon® coating optional. | Identical to IMPROVE. |
| Length of inlet tube (m); material, coating. | 1.83; Anodized aluminum. | Cyclone inlet tube – 0.34; Anodized aluminum. | 0.3 m; Anodized aluminum. | 0.3 m; Anodized aluminum. | Identical to IMPROVE. |

| | IMPROVE | | CSN | | |
|---|--|--|---|---|---|
| Sampler Name; Model | IMPROVE | Spiral Ambient Speciation Sampler; SASS TM or SuperSASS TM | Reference Ambient Air Sampler (RAAS TM); RAAS 2.5-400 | Mass Aerosol Speciation Sampler; MASS 400 and 450 | URG 3000N Speciation Sampler ^b ; 3000N |
| Manufacturer | URG | MetOne ^a | Andersen | URG | URG |
| PM _{2.5} fractionator; cutpoint (µm) (50% collection efficiency) at flow rate (L/min); slope ^c . (Watson and Chow 2011) | AIHL-type cyclone; Cutpoint = 52.5*Q ^{-0.99} Q in L/min; 1.16 (slope at 24 L/min); NA (John and Reischl, 1980). | Sharp-cut cyclone ^a ; 2.5 at 6.7; 1.2. | AIHL-type PM _{2.5} cyclone; 2.7 at 24; 1.16 | WINS Impactor 2.5 at 16.67; 1.18. | Identical to IMPROVE. |
| Fractionator – material; coating. | Anodized aluminum. | Anodized aluminum. | Anodized aluminum; Teflon. | Anodized aluminum; Teflon (optional). | Identical to IMPROVE. |
| Sampler configuration – number of channels. | 4 individual sampling modules, each with 4 filter cassettes that can rotate. | 1 instrument with 5 or 8 channels, one filter canister per channel; 3 channels for CSN sampling. | 1 instrument with 4 channels, one filter canister per channel, 3 channels for CSN sampling. | Two units with single channel, one filter canister per channel. | Identical to IMPROVE. |
| Flow splitter; split flow rates (L/min). | None. | None. | Inlet at 48; split 24 into two cyclones and manifold; 16.7 and 7.3 from manifold. | None. | None. |
| Flow control and measurement. | Orifice; pressure transducers. | Mass flow controller (CSN); critical orifice (others). | Mass flow controller. | Mass flow controller; dry gas meter. | Mass flow controller. |
| Volume, temperature, & pressure reported in . | Actual conditions. | Actual conditions. | Actual conditions. | Actual conditions. | Actual conditions. |
| # of pumps; vacuum manifold. | 1; NA. | 1; all channels. | 1; all channels. | 1; NA. | 1; NA. |

^a. Spiral inlet replaced with sharp-cut cyclone (Kenny et al., 2000; Kenny and Gussman 2000) after EPA's chemical speciation evaluation study (Solomon et al. 2000) due to large particle penetration through Spiral inlet.

^b. For organic and elemental carbon measurements only using QFF. MetOne OC/EC carbon measurements using QFF replaced between mid-2007 and 2009.

^c. Slope = square root of particle diameter ratios for inlet penetration at 16% and 84%.

Table 2. Analytical procedures by filter type and component. All measured species are listed in Table 11.

| PTFE/Teflon® | IMPROVE | CSN |
|--|---|---|
| Mass | Gravimetric. Equilibrated several minutes, RH = 30-50 %, T = 20-25° C. | Gravimetric. Equilibrated 24-hr, RH = 30-40 % ± 5 %, T = 20-23° C ± 2° C, per FRM protocol. |
| Filter transmittance | Hybrid integrating plate/sphere. | N/A ^a |
| Hydrogen | Proton elastic scattering analysis, discontinued January 2011. | N/A |
| Elemental analysis | Proton induced X-ray emission (PIXE) – Na-Mn, Energy dispersive X-ray fluorescence (EDXRF) – Fe-Pb through November 2001. EDXRF – Na-Pb beginning December 2001. | N/A EDXRF for Na - Pb. |
| Anions and Cations | N/A | Ion Chromatography. URG MASS: Teflon front filter DI water extract, 4° C, shaken overnight, analyzed for NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , NH ₄ ⁺ , and K ⁺ . |
| Nylon | | |
| Anions and Cations | Ion Chromatography. DI water extract, room temperature overnight, second day at 4° C, analyzed for NO ₃ ⁻ , NO ₂ ⁻ , Cl ⁻ , and SO ₄ ²⁻ . | Ion Chromatography. DI water extract, 4° C, sonicate 1-hr, shaken overnight, analyzed for NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , and K ⁺ . URG MASS: nylon backup filter, IC eluent extract, 4° C, shaken overnight, analyzed for NO ₃ ⁻ . |
| Differences between IMPROVE and CSN ionic analysis methods (both performed by the RTI Laboratory). | | |
| | <u>IMPROVE</u> | <u>CSN</u> |
| Extraction solution. | DI H ₂ O | DI H ₂ O; IC eluent ^c – URG nylon backup |
| Extraction volume ^b (mL). | 20 | 25 |
| Sonication (min). | 30 | 60 |
| Mechanical shaking. | None | Overnight 4° C |
| Additional extraction time. | Second day at 4° C, | None |
| Quartz | | |
| OC, EC, and OC and EC fractions | DRI Thermal Optical Reflectance (TOR) until 2005, modified to IMPROVE_A with TOR and TOT (Chow et al. 2007). OC and EC fractions reported in 8 temperature steps (Chow et al. 2001, Chow et al. 2008), analysis by DRI. Details in Table 4. | Sunset Thermal Optical Transmittance (TOT), modified NIOSH Method 5040 (RTI 2009e). OC reported in 5 temperature steps. Details in Table 4. By late 2009 CSN switched to IMPROVE_A method, analysis by RTI. |

^{a.} N/A - not applicable.

^{b.} Based upon filter size (37 mm for IMPROVE; 47 mm for STN)

^{c.} IC eluent is 0.3 mM NaHCO₃/2.7 mM Na₂CO₃

Table 3. Filter medium, acceptance tests, and sample preparation^a.

| Filter Type | IMPROVE | CSN |
|--------------|---|---|
| | Manufacturer (Model) // Acceptance Tests // Preparation. | |
| PTFE/Teflon® | Pall Corporation (Teflo®) // All filters visually inspected for holes, deformities; ~24 filters per new lot checked for pressure drop, trace element blank levels by EDXRF ^b , light absorption by HIPS // Filter equilibrated at constant T and RH as noted in Table 2. | Whatman (Part 7592-304) // All filters visually inspected for holes, deformities; selected filters checked for weight loss or gain over time; ten filters per new lot analyzed for trace elements by EDXRF // Filter equilibrated at constant T and RH as noted in Table 2. |
| Nylon | Pall Corporation (Nylasorb®) (changed from Osmonics in 2004) // All filters visually inspected for holes, deformities; ~24 filters per new lot checked for pressure drop and ion blank levels by IC // Nylon filters not washed, used as received. | Whatman (Part 7410-004) // All filters visually inspected for holes, deformities, washed in deionized (DI) water, filter extract analyzed by IC, if extract ion concentrations exceed 0.1 µg/mL (K ⁺ , 0.02 µg/mL) wash repeated // All filters washed in DI water, dried in dedicated drying oven; 2 percent analyzed and must be less than 1% of any measured species for acceptance.. |
| QFF | Pall Corporation Pallflex® (Tissuquartz) // All filters visually inspected for holes, deformities; filters heat-treated and 24 filters analyzed for OC and EC by TOT and TOR // Pre-fired at 900° C for 4-hr. | Whatman 47 mm (Part 18561-047) or Pall Corporation 25 mm (Tissuquartz 2500 QAT-UP-25MM) // All filters visually inspected for holes or other deformities; filters heat-treated, selected filters analyzed for OC and EC by TOR. // Pre-fired at 900°C for ≥ 3 hrs, cooled under N ₂ . |

^a. Shipping conditions, holding times, and laboratory storage requirements described in Table 6.

^b. PESA discontinued November 2001.

Table 4. Operating conditions for the original CSN and the current CSN and IMPROVE OC/EC analysis protocols.

| Atmosphere/ Fraction | CSN/TOT ^a | | IMPROVE_A/TOR-TOT ^b | |
|--------------------------------|----------------------|---------------------|--------------------------------|---------------------|
| | Analyte Name | Maximum Temperature | Analyte Name | Maximum Temperature |
| He/1st OC Peak | Pk1_OC | 310°C | OC1 | 140°C |
| He/2nd OC Peak | Pk2_OC | 480°C | OC2 | 280°C |
| He/3rd OC Peak | Pk3_OC | 615°C | OC3 | 480°C |
| He/4th OC Peak | Pk4_OC | 900°C | OC4 | 580°C |
| He-O ₂ /PCT | Pyrol_C | Varies | OPT | 580°C |
| He-O ₂ /PCR | Not Calculated* | N/A | OPR | 580°C |
| He&He-O ₂ /OCT | OC ^c | 900°C | OCT | 580°C |
| He&He-O ₂ /OCR | Not Calculated* | N/A | OCR | 580°C |
| He-O ₂ /1st EC Peak | Not Reported | 675°C | EC1 | 580°C |
| He-O ₂ /2nd EC Peak | Not Reported | 750°C | EC2 | 740°C |
| He-O ₂ /3rd EC Peak | Not Reported | 825°C | EC3 | 840°C |
| He-O ₂ /4th EC Peak | Not Reported | 920°C | N/A | N/A |
| He-O ₂ /ECT | EC | 920°C | ECT | 840°C |
| He-O ₂ /ECR | Not Calculated* | N/A | ECR | 840°C |

^a CSN/TOT adopted by EPA in 2000 (Peterson and Richards, 2002). Switched to IMPROVE_A protocol at all sites by late 2009. Pk# refers to peak number in the thermogram since temperature step time varies.

^b IMPROVE adopted IMPROVE_A in 2005 (Chow et al. 2007); OC and EC reported using TOR and TOT. OC# and EC# refers to the OC and EC peak number in the thermogram since the temperature steps are fixed in time.

*Not Calculated – CSN method did not include laser reflectance values.

*Not Reported – CSN temperature profile included the step indicated, but the data were not reported to AQS.

Table 5. Denuder characteristics by sampler type. Nylon channel in all samplers, see Figures 2 and 3.

| Sampler | IMPROVE | | CSN | | |
|---|--|---|---|--|--|
| | IMPROVE | SASS™ | RAAS | MASS | URG 3000N |
| Denuder type; material; active surface coating; length (m). | Annular; aluminum; Na ₂ CO ₃ ; 0.6. | Honeycomb; Al/Mg alloy; MgO; 0.025. | Annular (6 surfaces); glass; MgO; 0.22. | Annular (7 surfaces); glass; Na ₂ CO ₃ ; 0.25. | NA |
| Denuder location. | Before cyclone. | After cyclone before filter. | After cyclone. | Before WINS impactor. | NA |
| Denuder change Frequency. | Annually. | 3 months ^a | Quarterly. | Each exposure. | NA |
| Filter cassette material; support screen material. | Delrin; stainless steel screen ^b (McDade et al. 2009) | Nylon & QFF: Delrin; stainless steel ^c Teflon: hard plastic rings; stainless steel ^d | Delrin; stainless steel ^d . | Delrin; stainless steel (integrated into sample module). | Delrin; stainless steel ^e . |

- ^{a.} Six sets of denuders issued per site to accommodate rotation of MetOne canisters between laboratory and field. Each denuder replaced every 18 months, sampling 1/6 of days in that period.
- ^{b.} Screen holes are larger than those in PM_{2.5} FRM filter holder.
- ^{c.} Same as FRM sampler.
- ^{d.} Alternate material adopted when Delrin contamination observed with early lot of MetOne filter cassettes (Clark, 2002b; Gutknecht et al., 2001).

Table 6. Sampling handling, shipping conditions, holding times, and laboratory storage requirements.

| | IMPROVE | CSN (MetOne) |
|--|--|--|
| Packing filters into cassettes. | Filters loaded into filter cassettes in laboratory; cassettes capped and cartridge with up to four cassettes stored in sealed Ziploc [®] bag. | Filters loaded into filter cassettes with powder-free gloves in laboratory; filter canisters sealed with end caps at inlet and outlet. |
| Pre-sampling storage temperature (° C) | | |
| Teflon | Ambient | 4 until assembly, then ambient until sampling |
| Nylon | Ambient | 4 until assembly, then ambient until sampling |
| QFF | Ambient | -15 until assembly, then ambient until sampling |
| Pre-sampling holding time in sampler (hr). | 24-144. | 12-36. |
| Post-sampling holding time (hr) in sampler. | 24-144. | 1-in-3 day sampling schedule: 24 maximum; 1-in-6 day sampling schedule: 48 maximum. |
| Post sample shipping conditions. | Ambient temperature; no temperature control, shipped in special mailer, UPS or USPS. | 4° C or less; shipped in special container with blue ice; overnight express shipping. |
| Laboratory storage Temperature (° C); analysis location. | | |
| Teflon | Room temperature; UC Davis. | 4; RTI. |
| Nylon ^a | 4; RTI | 4; RTI. |
| QFF ^b | -20; DRI. | -20; RTI. |
| Time in laboratory storage before analysis (days). | 1-2 – gravimetric analysis, variable other analyses. | Teflon – If shipping < 4° C, ≤ 30 days to post-weigh; 10 business days once removed from 4° C storage. QFF – ≤ 20 days upon receipt from field. Nylon – ≤ 20 days upon receipt from field. |

^a. Nylon filters shipped to RTI at ambient temperature.

^b. IMPROVE QFF filters sent from field to UC Davis at ambient temperature and shipped to DRI with blue ice.

Table 7. Filter characteristics, flow rates, and face velocities.

| Characteristic | IMPROVE | | CSN | | |
|---|---|---------------------------|--|----------------------|-----------|
| | IMPROVE | SASS™ | RAAS | MASS | URG 3000N |
| Flow rate through filter (L/min) (nominal). | 22.8 @ 20° C. | 6.7 per channel (module). | 16.67 for Teflon channel; 7.3 for QFF and nylon channel. | 16.67 per channel. | 22.8 |
| Filter size (outside diameter) (mm). | 25 for Teflon (PM _{2.5} and PM ₁₀) and QFF, 37 for nylon. | 46.2 | 46.2 | 46.2 | 25 |
| Exposed filter area Teflon ^a (cm ²). | 3.53 for most sites; masked to 2.20 at certain western sites with low loadings. Masks removed from all sites by 2008. | 11.3 [Note 1] | 11.3 [Note 1] | 11.3 [Notes 1 and 2] | |
| Nylon ^b (cm ²). | 9.08 | 11.76 | 11.76 | 11.76 | NA |
| QFF ^c (cm ²). | 3.53 | 11.76 | 11.76 | 11.76 | 3.38 |
| Calculated face velocity; Teflon (cm/sec). | 108.6; 174.2 (masked) | 9.5 | 24.5 | 24.5 | NA |
| Nylon (cm/sec). | 43.2 | 9.5 | 10.4 | 24.5 | NA |
| QFF (cm/sec). | 108.6 | 9.5 | 10.4 | 24.5 | 108.6 |

^a Used to convert EDXRF analytical results from mass per unit area to mass per filter

^b Nylon filter area not required for calculations.

^c - Used to convert OC/EC analytical results from mass per unit area to mass per filter

Note 1: 11.3 cm² area for the Teflon filter is consistent with a nominal diameter of 3.8 cm for the sampled filter diameter and used to convert EDXRF data from mass/area to mass/filter since beginning of the CSN program. 11.76 cm² value used for QFF determined in RTI's OC/EC laboratory by repeat measurements of the inside diameters of filter cassette rings and the perforated area of the metal support screens. QFF are thicker than Teflon, so there can be significant "feathering" around the edge where the filter meets the cassette ring, which might justify using a slightly larger effective area for QFF relative to Teflon. There is approximately a 2% uncertainty in the accuracy of deposit diameter, which propagates to 4% in area.

Note 2: Cassette rings for QFF, nylon, and Teflon filters approximately identical in size for the Andersen and MetOne. URG cassette rings integrated into the filter module and have a slightly wider inside diameter than the Andersen and MetOne cassette rings. The metal support screens identical for the three CSN samplers.

Table 8. Recommended performance criteria used to develop data quality objectives for CSN.

Performance criteria recommended by EPA's Expert Chemical Speciation Panel (Koutrakis 1998; Koutrakis 1999)^a, observed in the 4-City Study (Solomon et al. 2000)^b, and the Atlanta Supersites Integrated Comparison Study (Solomon et al. 2003)^b

| Species | Expert Panel | 4-City Study | Atlanta ^c | Expert Panel (R ²) | 4-City Study (R ²) | Atlanta ^d (r) |
|------------------------------------|--------------|-----------------|----------------------|-----------------------------------|-----------------------------------|-----------------------------|
| | Ratio 1 ± X% | | | Regression Coefficient | | |
| Mass | 10 | 10 | 20 | ≥0.9 | ≥0.9 | ≥0.9 |
| SO ₄ ²⁻ or S | 5 | 10 | 10 | ≥0.95 | ≥0.95 | ≥0.95 |
| NO ₃ ⁻ | 10 | 15 | 35 ^e | ≥0.9 | ≥0.9 | ≥0.20 |
| NH ₄ ⁺ | 10 | 10 | 15 | ≥0.9 | ≥0.9 | ≥0.95 |
| OC | | 15 ^f | 20 ^g | | ≥0.9 | ≥0.9 |
| EC | | 15 ^f | 20 ^h | | ≥0.85 | ≥0.85 |
| Trace Elements | 15 | 30 | 30% | ≥0.85 | ≥0.85 ⁱ | ≥0.85 ^j |

^a Expert Panel did not provide criteria for OC and EC.

^b Criteria is ratio of test sampler to relative reference value and regression coefficient (R² for expert panel and 4-City Study; r for Atlanta), the latter is the test sampler regressed against the relative reference or FRM depending on the study.

^c Twelve samplers including CSN in comparison. Values likely represent an outer bound for uncertainty between two sampler types.

^d Regression coefficient for Atlanta only considers CSN sampler results relative to results obtained by the FRM or for OC to the Versatile Air Pollution Sampler using a denuder.

^e Average nitrate values during the study were approximately 0.5 µg/m³, approaching the limit of detection for the method of about 0.2 µg/m³; therefore, results for nitrate likely have considerably more variability than in locations where nitrate concentrations are well above the limit of detection for the method. Compared to the relative reference value, r ≥ 0.9 could be expected.

^f Greater than 15% may be a more realistic expectation.

^g Both samplers either with or without denuders; uncertainty increases to 35-45% if one sampler is using a denuders and the other is not.

^h When comparing between results using the same TOA analytical method, uncertainty increases up to 200% if comparing between different TOA methods.

^j For elements (S, Si, Ca, Fe, Zn, K) measured on samples collected using the Anderson RASS as compared to elements measured on a Teflon filter collected using a PM_{2.5} FRM sampler, with some exceptions. The MetOne sample in the 4-City study employed the spiral inlet, which had poor collection efficiency, was biased high for crustal related elements, and had a correspondingly lower regression coefficients. Sulfur R² > 0.97.

ⁱ For higher concentration elements (S, Si, K, Ca, Fe, Zn, Pb, Cu) and r = 0.7 for Mn and 0.46 for As, all to the relative reference as defined in Solomon et al. (2003), only these 10 reported.

Table 9. Measurement quality objectives for the CSN and IMPROVE networks^a.

| Measurement ^b | IMPROVE | CSN |
|--------------------------|------------------|--|
| | Acceptable Range | |
| Flow (L/min) | 22.8 ± 10% | design flow (varies by sampler type) ± 10% |
| Ambient temp (° C) | ± 10 | ± 2 |
| Ambient pressure (mm Hg) | ± 10 | ± 10 |
| Sample duration (min) | ± 5 | ± 5 |
| Leaks (mL/min) | < 100 | < 100 |

^a IMPROVE system audits from 2000-2006 included comparison of the reference measurement to the reported value, but not the design value. Beginning in 2007, the flow rate was checked against the design value to identify cases in which the flow rate may have been measured properly but had drifted from the design value. The flow was adjusted to the design value. This revision was for all parameters listed.

^b Temperature and pressure as measured using instruments in samplers.

Table 10. Trip^a and field-filter blank values for ionic species by year and sampler.

| Sampler Type ^b | Averaging Period | Ionic Species / Filter Type / Average Concentration ± Standard Deviation (ng/m3) | | | | | |
|---------------------------|------------------|--|---------------------------------------|---------------------------------------|---|---|---|
| | | NH ₄ ⁺ Teflon ^c (front) | K ⁺ Teflon (front) | Na ⁺ Teflon (front) | SO ₄ ⁼ Teflon (front) | NO ₃ ⁻ Teflon (front) | NO ₃ ⁻ Nylon (after) ^c |
| MASS | 2006 Annual | 0±3 | 0±0 | 5±8 | 6±11 | 30±30 | 28±38 |
| MASS | 2006 Winter | 0±1 | 0±0 | 2±3 | 4±6 | 25±19 | 25±15 |
| MASS | 2006 Spring | 1±3 | 0±0 | 3±5 | 3±5 | 27±17 | 24±13 |
| MASS | 2006 Summer | 0±0 | 0±0 | 8±8 | 11±13 | 26±12 | 44±71 |
| MASS | 2006 Fall | 1±5 | 0±0 | 9±11 | 7±15 | 45±57 | 20±13 |
| | | NH ₄ ⁺ Nylon | K ⁺ Nylon | Na ⁺ Nylon ^d | SO ₄ ⁼ Nylon | NO ₃ ⁻ Nylon | |
| RAAS | 2006 Annual | 1±4 | 1±6 | 7±16 | 26±23 | 21±34 | |
| RAAS | 2006 Winter | 0±2 | 0±0 | 5±11 | 21±22 | 25±40 | |
| RAAS | 2006 Spring | 1±5 | 2±8 | 4±11 | 33±30 | 24±46 | |
| RAAS | 2006 Summer | 1±7 | 0±0 | 10±20 | 32±18 | 19±25 | |
| RAAS | 2006 Fall | 0±0 | 2±10 | 7±20 | 17±21 | 14±25 | |
| | | NH ₄ ⁺ Nylon | K ⁺ Nylon | Na ⁺ Nylon | SO ₄ ⁼ Nylon | NO ₃ ⁻ Nylon | |
| SASS | 2006 Annual | 4±27 | 1±10 | 13±158 | 22±71 | 21±36 | |
| SASS | 2006 Winter | 3±21 | 1±11 | 19±280 | 23±114 | 22±34 | |
| SASS | 2006 Spring | 2±12 | 1±10 | 6±22 | 24±30 | 17±41 | |
| SASS | 2006 Summer | 7±41 | 1±10 | 12±39 | 24±34 | 24±34 | |
| SASS | 2006 Fall | 2±20 | 1±6 | 13±49 | 14±54 | 20±35 | |
| SASS | 2012 Annual | 2±7 | 1±5 | 9±22 | 34±22 | 15±33 | |
| SASS | 2012 Winter | 2±5 | 1±6 | 8±19 | 13±27 | 5±17 | |
| SASS | 2012 Spring | 2±11 | 0±3 | 5±18 | 42±43 | 16±48 | |
| SASS | 2012 Summer | 1±2 | 1±2 | 12±26 | 48±29 | 11±19 | |
| SASS | 2012 Fall | 3±4 | 2±7 | 13±25 | 31±17 | 13±25 | |
| | | Cl ⁻ Nylon | NO ₂ ⁻ Nylon | SO ₄ ⁼ Nylon | NO ₃ ⁻ Nylon | | |
| IMPROVE | 2006 Annual | 11±8 | 16±3 | 0±4 | 12±4 | | |
| IMPROVE | 2006 Winter | 27±1 | 18±1 | 7±6 | 15±1 | | |
| IMPROVE | 2006 Spring | 8±1 | 16±4 | 0±4 | 9±3 | | |
| IMPROVE | 2006 Summer | 11±1 | 14±2 | 0±0 | 7±4 | | |
| IMPROVE | 2006 Fall | 12±1 | 16±1 | 0±4 | 12±2 | | |

| | | | | | |
|---------|-------------|------|------|-------|-------|
| IMPROVE | 2012 Annual | 9±1 | 13±8 | 17±5 | 18±4 |
| IMPROVE | 2012 Winter | 10±1 | 18±4 | 18±4 | 20±1 |
| IMPROVE | 2012 Spring | 9±1 | 0±8 | 15±3 | 22±21 |
| IMPROVE | 2012 Summer | 9±1 | 0±7 | 16±2 | 15±1 |
| IMPROVE | 2012 Fall | 8±1 | 17±3 | 18±10 | 13±2 |

^a CSN Field and trip blanks were indistinguishable so they were averaged and the overall average reported here. CSN trip blanks were discontinued in 2013.

^b Only CSN SASS samplers employed in the network in 2012.

^c Nylon after filter was only used with the MASS sampler.

^d Nylon filter washing began in early 2003.

Table 11. Minimum detection limits for CSN and IMPROVE mass and species for 2006 and 2012.

For CSN, concentrations are based on the MetOne flow rate of 6.7 L/min and for IMPROVE at 22.8 L/min, both assuming 24-hr sampling period. MDL calculations are given in Table 13.

| Species ^b | MDL (ng/m ³) ^a | | | |
|------------------------|---------------------------------------|----------|-----------------|-----------------|
| | Average | | IMPROVE 2006 | IMPROVE 2012 |
| | CSN 2006 | CSN 2012 | | |
| Gravimetric | | | | |
| PM _{2.5} mass | 810 | 840 | 308 | 307 |
| IC | | | | |
| Sulfate | 13 | 18 | 16 | 22 |
| Nitrate | 8.8 | 23 | 12 | 13 |
| Nitrite | NA | NA | 25 | 34 |
| Chloride | NA | NA | 11 | 6.5 |
| Ammonium | 27 | 26 | NA | NA |
| Sodium Ion | 33 | 32 | NA | NA |
| Potassium Ion | 25 | 25 | NA | NA |
| TOT | | | | |
| Organic carbon | 320 | NA | | |
| Pk1_OC | 320 | NA | | |
| Pk2_OC | 320 | NA | | |
| Pk3_OC | 320 | NA | | |
| Pk4_OC | 320 | NA | | |
| PyroIC | 320 | NA | | |
| Elemental carbon | 320 | NA | | |
| TOR | | | | |
| OC1 | NA | 65 | 46 | 48 |
| OC2 | NA | 65 | 65 | 90 |
| OC3 | NA | 97 | 95 | 92 |
| OC4 | NA | 97 | 47 | 38 |
| OP | NA | NA | 23 | 8.4 |
| EC1 | NA | 97 | 23 | 15 |
| EC2 | NA | 65 | 20 | 11 |
| EC3 | NA | 65 | 24 | 0.5 |
| EDXRF | | | | |
| Hydrogen | NA | NA | 6.0 | NA |
| Sodium | 220 | 57 | 17 | 3.7 |
| Magnesium | 65 | 19 | 7.8 | 2.7 |
| Aluminum | 25 | 27 | 3.0 | 1.9 |
| Silicon | 19 | 19 | 1.3 | 2.8 |

| Species ^b | MDL (ng/m ³) ^a | | | |
|-------------------------|---------------------------------------|----------|---------|---------|
| | Average | | IMPROVE | IMPROVE |
| | CSN 2006 | CSN 2012 | 2006 | 2012 |
| Phosphorus | 17 | 18 | 0.93 | 0.23 |
| Sulfur | 11 | 11 | 0.60 | 0.26 |
| Chlorine | 15 | 11 | 0.36 | 0.26 |
| Potassium | 11 | 11 | 0.20 | 1.1 |
| Calcium | 8.2 | 8.3 | 0.10 | 2.0 |
| Scandium ^b | 40 | NA | NA | NA |
| Titanium | 5.8 | 5.8 | 0.05 | 0.30 |
| Vanadium | 4.2 | 4.2 | 0.03 | 0.10 |
| Chromium | 2.8 | 2.8 | 0.03 | 0.12 |
| Manganese | 3.6 | 2.9 | 0.03 | 0.25 |
| Iron | 3.4 | 3.4 | 0.04 | 1.4 |
| Cobalt | 2.2 | 2.0 | NA | NA |
| Nickel | 1.9 | 1.9 | 0.06 | 0.10 |
| Copper | 2.6 | 2.6 | 0.04 | 0.21 |
| Zinc | 3.8 | 8.8 | 0.04 | 0.25 |
| Gallium ^b | 5.3 | NA | NA | NA |
| Arsenic | 3.8 | 2.8 | 0.09 | 0.19 |
| Selenium | 3.3 | 2.7 | 0.03 | 0.21 |
| Bromine | 3.1 | 2.5 | 0.03 | 0.20 |
| Rubidium | 3.4 | 2.8 | 0.05 | 0.28 |
| Strontium | 3.9 | 3.8 | 0.08 | 0.24 |
| Yttrium | 4.7 | NA | NA | NA |
| Zirconium ^b | 5.6 | 25 | 0.13 | 1.2 |
| Niobium ^b | 6.5 | NA | NA | NA |
| Molybdenum ^b | 9.7 | NA | NA | NA |
| Silver | 16 | 40 | NA | NA |
| Cadmium | 20 | 24 | NA | NA |
| Indium | 24 | 35 | NA | NA |
| Tin | 34 | 39 | NA | NA |
| Antimony | 45 | 56 | NA | NA |
| Cesium | 57 | 47 | NA | NA |
| Barium | 92 | 60 | NA | NA |
| Lanthanum ^b | 110 | NA | NA | NA |
| Cerium ^b | 130 | NA | NA | NA |
| Samarium ^b | 10 | NA | NA | NA |
| Europium ^b | 18 | NA | NA | NA |
| Terbium ^b | 12 | NA | NA | NA |

| Species ^b | MDL (ng/m ³) ^a | | | |
|-----------------------|---------------------------------------|----------|---------|---------|
| | Average | | IMPROVE | IMPROVE |
| | CSN 2006 | CSN 2012 | 2006 | 2012 |
| Hafnium ^b | 41 | NA | NA | NA |
| Tantalum ^b | 30 | NA | NA | NA |
| Tungsten ^b | 21 | NA | NA | NA |
| Iridium ^b | 9.2 | NA | NA | NA |
| Gold ^b | 8.3 | NA | NA | NA |
| Mercury ^b | 10 | NA | NA | NA |
| Lead | 8.5 | 6.4 | 0.05 | 0.62 |

^a. MDLs are given in ambient concentration (ng/m³); however, since the RAAS and MASS operated at higher flow rates, the effective MDLs will be proportionately lower than for the SASS.

^b. The number of elements analyzed by EDXRF for CSN was reduced from 48 to 33, elements labeled were no longer reported.

Table 12. Carbon artifact concentrations based on a nominal flow rates for CSN and IMPROVE and assuming a 24-hr sample.
For CSN average of trip and field blank samples. For IMPROVE median of QFF after filter values.

| Sampler Type | | Average Concentration (ng/m ³) ^a | | | | | |
|--------------|-------------|---|----|-----|-----|-----|-----|
| | | OC | EC | OC1 | OC2 | OC3 | OC4 |
| MASS | 2006 Annual | 346 | 3 | 91 | 144 | 85 | 22 |
| MASS | 2006 Winter | 376 | 4 | 85 | 155 | 109 | 25 |
| MASS | 2006 Spring | 280 | 0 | 51 | 88 | 52 | 16 |
| MASS | 2006 Summer | 425 | 3 | 106 | 186 | 99 | 28 |
| MASS | 2006 Fall | 360 | 3 | 126 | 144 | 69 | 20 |
| RAAS | 2006 Annual | 920 | 7 | 283 | 352 | 217 | 63 |
| RAAS | 2006 Winter | 917 | 3 | 300 | 321 | 227 | 60 |
| RAAS | 2006 Spring | 771 | 3 | 230 | 332 | 170 | 36 |
| RAAS | 2006 Summer | 1032 | 17 | 278 | 385 | 273 | 91 |
| RAAS | 2006 Fall | 906 | 6 | 310 | 367 | 171 | 54 |
| SASS | 2006 Annual | 1035 | 8 | 289 | 421 | 250 | 70 |
| SASS | 2006 Winter | 970 | 4 | 300 | 376 | 229 | 62 |
| SASS | 2006 Spring | 864 | 3 | 212 | 371 | 214 | 63 |
| SASS | 2006 Summer | 1188 | 8 | 294 | 470 | 329 | 89 |
| SASS | 2006 Fall | 1078 | 18 | 342 | 467 | 202 | 62 |
| URG 3000N | 2012 Annual | 130 | 3 | 14 | 43 | 65 | 8 |
| URG 3000N | 2012 Winter | 122 | 3 | 14 | 38 | 63 | 7 |
| URG 3000N | 2012 Spring | 139 | 3 | 12 | 48 | 70 | 9 |
| URG 3000N | 2012 Summer | 132 | 2 | 14 | 46 | 63 | 8 |
| URG 3000N | 2012 Fall | 130 | 3 | 14 | 42 | 65 | 9 |
| IMPROVE | 2006 Annual | NR | NR | 53 | 77 | 93 | 20 |
| IMPROVE | 2006 Winter | NR | NR | 51 | 63 | 72 | 9 |
| IMPROVE | 2006 Spring | NR | NR | 59 | 77 | 103 | 21 |
| IMPROVE | 2006 Summer | NR | NR | 58 | 101 | 158 | 40 |
| IMPROVE | 2006 Fall | NR | NR | 43 | 69 | 84 | 18 |
| IMPROVE | 2012 Annual | NR | NR | 17 | 64 | 91 | 19 |
| IMPROVE | 2012 Winter | NR | NR | 22 | 56 | 67 | 12 |
| IMPROVE | 2012 Spring | NR | NR | 17 | 72 | 98 | 21 |
| IMPROVE | 2012 Summer | NR | NR | 17 | 89 | 120 | 32 |
| IMPROVE | 2012 Fall | NR | NR | 20 | 53 | 70 | 13 |

NR: Not Reported.

^a Zero indicates the reported average is below the MDL.

Table 13. Overview of MDL calculations for CSN^a and IMPROVE.

| Analysis Method | CSN | IMPROVE |
|--------------------------|---|--|
| Gravimetry | Three times the standard deviation of ~ 50 filters per lot received and acceptance tested, typically annually or more often. | Twice the analytical uncertainty. A constant analytical uncertainty is applied, determined previously from laboratory weighing controls. |
| Ion Chromatography | Three times the standard deviation of ionic species concentrations measured on ~7 laboratory blanks. Instrumental MDLs are determined annually. | Two times the standard deviation of ionic species concentrations measured on 45 field blanks collected each month. |
| Thermal Optical Analysis | Three times the standard deviation of the instrument MDL provided by the manufacturer based on analysis of a large number of filters. | Two times the standard deviation of OC and EC concentrations measured on 60 secondary filters collected each month. |
| EDXRF | Three times the average instrument counting uncertainty for each element based on the analysis of ten new lot blanks. Determined with each new filter lot of Teflon filters | Prior to 2011, MDL was 3.29 times the square root of the background counts under the region that would have been occupied by a peak of normal width (IMPROVE 1997). This is expressed as ng/cm ² . Beginning in 2011, with the change to the PANalytical instrument, MDL was 95th percentile of the intensity measured on a set of 50 to 100 field blank (IMPROVE 2014a). |

^a Employed since June 2003. See text for prior to June 2003.

Table 14. Data completeness estimates for CSN and IMPROVE from 2006 and 2012 by year and analytical method.

| <i>Analysis Method</i> | <i>IMPROVE</i> | | <i>CSN</i> | |
|---|----------------|-------------|-------------|-------------|
| | <i>2006</i> | <i>2012</i> | <i>2006</i> | <i>2012</i> |
| <i>Mass</i> | 92 | 94 | 94 | 96 |
| <i>Anions (all species)</i> | 92 | 94 | 95 | 96 |
| <i>Cations - NH₄⁺</i> | N/A | N/A | 95 | 96 |
| <i>Cations - Na⁺ and K⁺</i> | N/A | N/A | 95 | 96 |
| <i>OC/EC (all fractions)</i> | 94 | 94 | 95 | 94 |
| <i>EDXRF (all elements)</i> | 92 | 94 | 95 | 96 |

N/A – Not measured.

Table 15. Precision estimates for major components as Percent Average Relative Difference between colocated samplers.

| | CSN ^a (2006) (%) | CSN ^a (2012) (%) | IMPROVE (2006) (%) | IMPROVE (2012) (%) | Comments |
|------------------|-----------------------------|-----------------------------|--------------------|--------------------|--|
| Mass | 20 | 13 | 11 | 7 | |
| Sulfate | 18 | 7 | 7 | 3 | |
| Nitrate | 20 | 8 | 8 | 7 | |
| Ammonium | 16 | 11 | N/A | N/A | |
| Sodium | 40 (ion) | 20 (ion) | N/A | N/A | |
| Potassium | 31 (elemental) | 19 (elemental) | 61 | 35 | |
| | 19 (ion) | 22 (ion) | N/A | N/A | |
| | 20 (elemental) | 13 (elemental) | N/A | N/A | |
| Organic Carbon | 24 | 6 | 14 | 9 | |
| OC1 | N/A | N/A | 42 | 48 | OC and EC fractions not reported in CSN |
| OC2 | N/A | N/A | 21 | 16 | |
| OC3 | N/A | N/A | 17 | 15 | |
| OC4 | N/A | N/A | 18 | 18 | |
| OCP | N/A | N/A | 29 | 30 | |
| Elemental Carbon | 17 | 9 | 1424 | 13 | |
| EC1 | N/A | N/A | ** | 21 | |
| EC2 | N/A | N/A | ** | 130 | |
| EC3 | N/A | N/A | | ** | |
| Fe | 30 | 18 | 18 | 14 | |
| Ca | 31 | 23 | 19 | 16 | |
| Si | 31 | 22 | 32 | 17 | |
| Al | 41 | 27 | 44 | 18 | |
| Ti | 28 | 28 | 26 | 20 | |
| V | 22 | 19 | 30 | 25 | |
| Ni | 30 | 28 | 29 | 30 | |
| Pb | 25 | 20 | 23 | 27 | |
| Zn | 33 | 16 | 22 | 16 | |
| Cd | ** | ** | N/A | N/A | |

^a Precision estimates are given for species where the ambient concentrations were greater than 3 times their MDL.

**Less than 10 valid sample pairs; average not calculated.

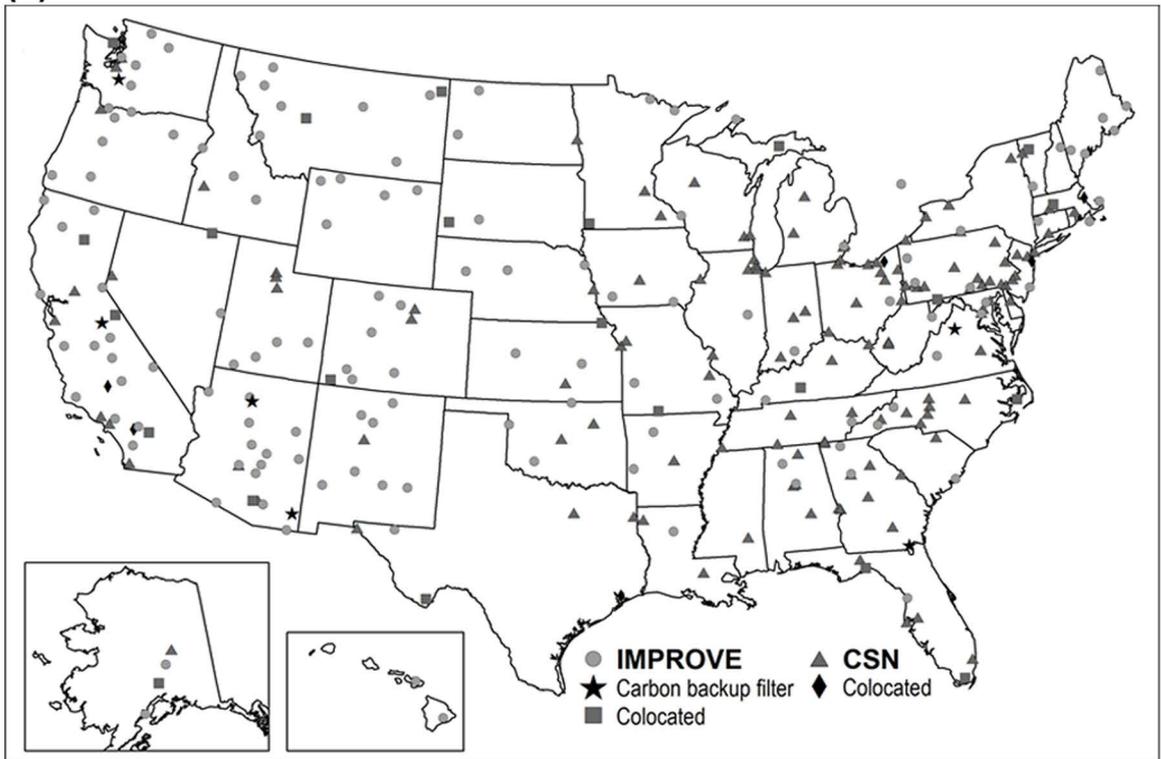
N/A - Not measured.

Table 16. Start-up history and summary of changes in field and laboratory network operations since 2000 when CSN began initial operations.

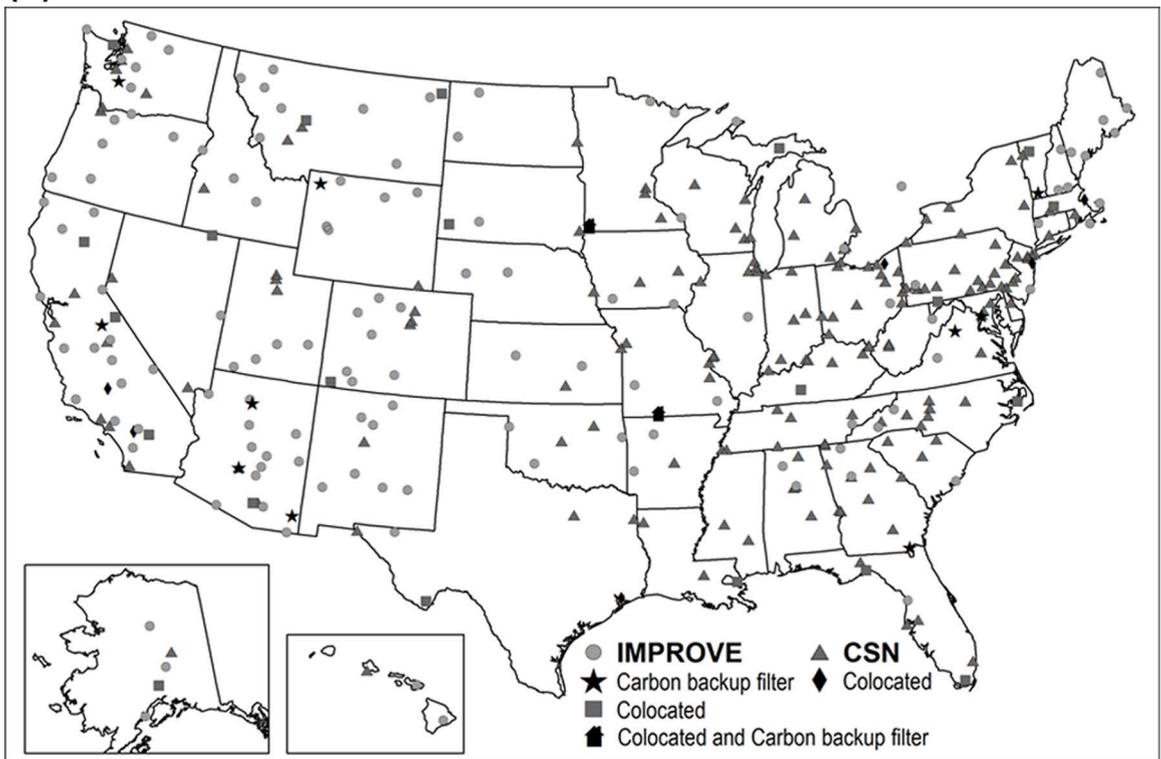
| Date (Year/Month) | Change in Network Operations | Reason for Change |
|------------------------|--|---|
| IMPROVE 1988 | 20 sites established in Class 1 Areas. | |
| 1999 | Network increased to 30 IMPROVE and 40 IMPROVE Protocol sites. | |
| 2000-2002 | Network increased to 110 IMPROVE sites in Class I areas and 57 Protocol sites with funding from EPA. | The network was expanded to meet the needs of the Regional Haze Rule and in support of CSN objectives |
| 2000/10 | Nylon filters extracted using IC anion eluent (0.3 mM NaHCO ₃ /2.7 mM Na ₂ CO ₃) at all sites except GRSM1, SHEN1, and DOSO1 where filters were extracted with DI water. Previously nylon filters extracted some years in eluent, some years in water. | |
| 2001/04 | Nylon filters extracted using DI water at all sites. | To reduce blank levels and allow for the measurement of ammonium ion if desired. |
| 2001/12 | Analysis of elements from Na to Mn was changed from PIXE to EDXRF by Cu anode. | Improved detection limits for most elements of interest, plus better sample preservation for reanalysis. |
| 2002/06 | Changed from quarterly to monthly medians to estimate OC artifact corrections from field blanks and QFF backup filters. | To obtain an improved estimate of the OC artifact since the artifact varied by season and within season. |
| 2002/10 | Standardized EDXRF run times changed from variable times to a standard 1000 seconds. | A single standardized exposure time was selected, providing acceptable detection limits for all elements of interest. |
| 2004/01 | Changed nylon filter supplier from Osmonics to Pall Corporation. | Field blank concentrations were decreased substantially, especially for chloride. |
| 2005/01 | Changed carbon analysis instrument from DRI/OGC to Model 2001 Thermal/Optical Carbon Analyzer (Desert Research Institute). Changed analysis protocol from IMPROVE to IMPROVE A. | To replace obsolete equipment. New equipment provided better temperature control and more stable analysis environment. (Chow et al. 2007) |
| 2005/01 | Changed from He flush to vacuum on Cu anode XRF system | He diffused through the Be window of the SiLi detector, changing the calibration and eventually destroying the detector. |
| 2008/08 | Number of samplers with carbon backup filters increased from 6 to 12. Used to determine carbon artifact corrections. | To obtain an improved estimate of the OC artifact since artifact varied by region due to differences in ambient conditions |
| 2011/01 | EDXRF analysis switched from custom-built legacy systems to PANalytical Epsilon 5. | MDLs improved for many elements, x-ray self-absorption correction no longer applied, several spectral interferences eliminated. |
| 2011/01 | PESA analysis discontinued, used to quantify hydrogen. | Due to reduced funding. |
| CSN | | |

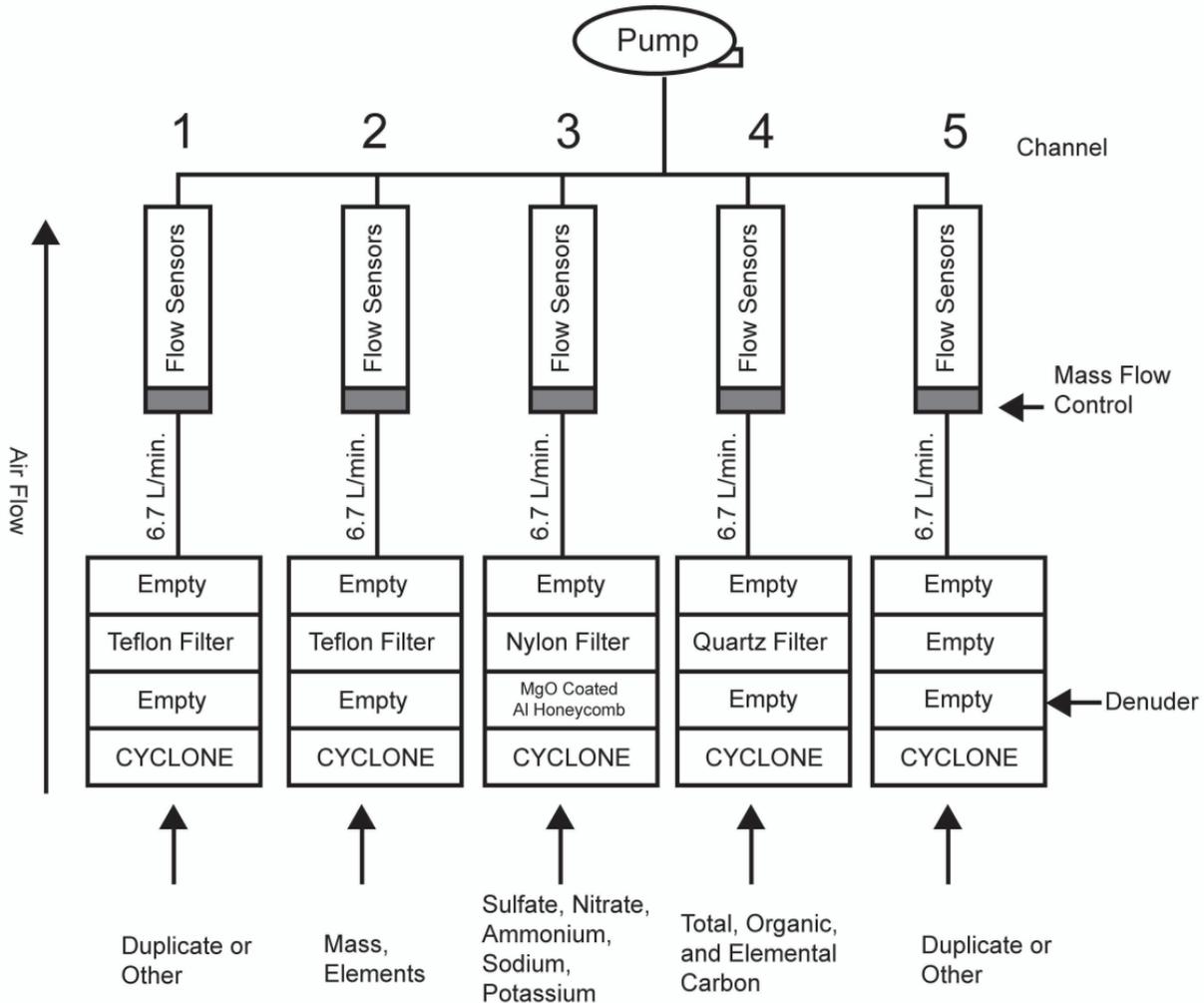
| | | |
|---------------|--|--|
| 2000 | Pilot study of 13 sites established and operated through July 2000. | |
| 2000 | Network increased January 2001 through October 2005 to 54 STN and 181 SLAMS and Tribal sites, with 28 SLAMS IMPROVE protocol sites. | |
| 2002/02 | Improved nylon filter washing procedures. | Higher levels of sodium and nitrate seen in filters as supplied from manufacturer. |
| 2003 | Implemented improved OC/EC thermogram software that reduced background noise and improved blank levels. Samples reported before this date were reprocessed using the new software and resubmitted to AQS (reprocessing and reposting done in 2007) | Software was upgraded by vendor and implemented on RTI's analyzers as part of normal system upgrades. |
| 2003/6 | Prior to June 2003, a single set of MDL values (ng/m ³) for each species and sampler type was reported in AQS for CSN. After June 2003, MDL values were reported with each concentration value in AQS | Changed to be more consistent with IMPROVE reporting of MDL values. |
| 2006/01* | Lighter weight shipping containers integrated into CSN network (*Fully implemented by March 2006.). Initially composed of reinforced corrugated cardboard; changed after a short period to corrugated plastic boxes with longer lifetimes and about the same weight. | Filter temperatures were maintained at 4° C or better because of the new shipping containers. Shipping costs were reduced. |
| 2006/04 | Network reductions began in 2005; CSN reduced to 54 STN and 159 SLAMS, 28 IMPROVE Protocol, 3 Tribal sites. | Due to reduced funding. |
| 2007/3-2009/9 | Transition to URG 3000N sampler and IMPROVE_A method for carbon analysis on QFF. | Requested by EPA to remove differences observed between the two networks for OC and EC. |
| 2009 | Last MASS and RASS Samplers replaced by SASS samplers (2009/02 for last MASS, 2009/04 for last RASS) | Improved uniformity across network and reduction in costs associated with multiple sampler types. |
| 2009 | Number of elements analyzed by XRF reduced from 48 to 33 (See Table 12). | Elements removed were seldom seen in field measurements |
| 2009 | XRF attenuation correction implemented for Na, Mg, Al, P, and Si. (see text for details) | EPA added XRF attenuation corrections to the new CSN analytical contract. |
| 2013/1 | Trip blanks discontinued | Due to reduced funding. Trip blanks were statistically similar to field blanks (the latter continued). |

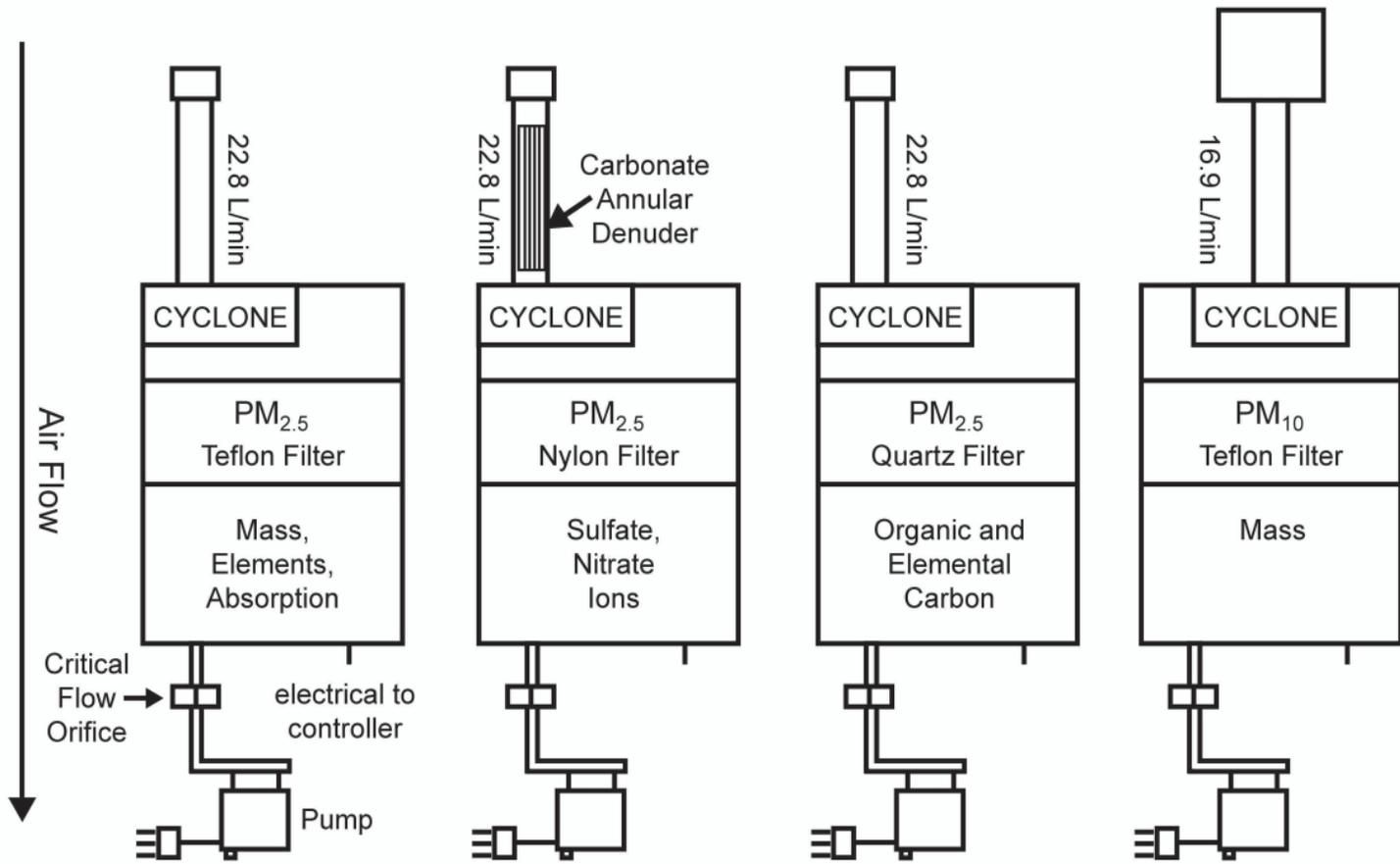
(a)



(b)







Module A

Module B

Module C

Module D