Appendix 1

Ambient and Emissions Measurement of Black Carbon

A1.1 Introduction

Measurements of BC and other PM constituents are critical to understanding the climate impacts of these substances, as well as evaluating human health and environmental effects. These measurements serve as important inputs to air quality forecasting and climate models, source apportionment models, and emissions inventories. Deposition measurements are also needed to judge impacts on snow and ice.

Observational data for BC comes from two main sources: ambient measurements and source-based emissions measurements. These measurements involve both sample collection and sample analysis procedures, with each step having important impacts on reported measurements. Most estimates of BC are based on thermal-optical and filter-based optical techniques, which classify the measured quantity as apparent elemental carbon (ECa) and apparent black carbon (BCa). While the terms "black carbon" and "elemental carbon" are frequently used as labels for quantities produced, the addition of the term "apparent" clarifies that these are considered to be estimates of BC concentrations. This appendix describes the most common sample analysis methods (thermal-optical and optical), the types of instruments that can be used for these methods, and key limitations in current measurement methods, approaches, and instruments. This appendix also describes the key sources of ECa and BCa measurement data in the United States, in terms of the types of ambient data collected and the information gathered from testing of both stationary and mobile sources. Next, this appendix describes key applications of source-testing data, particularly for constructing U.S. emissions inventories. Data from other countries is reported where available and applicable.

A1.2 Ambient Black Carbon Measurements

BC mass concentration estimates are routinely measured at ground-level in the ambient air or in deposited materials, but can also be taken in aircraft and on remote sampling platforms. Globally, a significant amount of ambient data has been compiled from the following types of measurements:

- *Ground-based ambient air measurements* are taken in near real time using field analyzers or obtained in a laboratory following collection of PM onto a filter. This is by far the largest source of observational data on BCa and ECa. Details on some of the key ambient air monitoring networks producing these data are described in Table A1-1.

- *Ice core measurements* of BCa and ECa have been conducted in glaciers around the world, providing a historical record of BC concentrations.

- *Surface snow measurements* have been conducted to quantify recent BC in snow based on BCa and ECa concentrations in locations around the world. Snow data is much more limited in spatial and temporal coverage in comparison to ambient monitoring.

The concentration of carbon in PM is regularly measured using methods based on the chemical, physical, and light absorption properties of the particles. The chemical and physical properties of carbonaceous PM vary in terms of both refractivity (the inertness of the carbon at high temperatures) and light absorption. Each carbon measurement technique provides unique information about these properties. All current analysis methods are operationally defined, meaning that there is no universally accepted standard measurement. When developing these methods and operational criteria, some scientists use PM's optical properties or light-absorbing characteristics (optical or light absorption methods), some use its thermal and chemical stability (thermal-optical methods), while others use its morphology or microstructure or nanostructure (microscopy methods). One major class of methods, thermal or thermal-optical techniques, distinguishes refractory and non-refractory carbon as ECa and OCa, respectively (Figure A1-1). The second major class of methods, optical methods, quantifies the light absorbing component of particles as BCa,

Table A1-1. Global Monitoring Activities. (Source: U.S. EPA)

Network	Worldwide Air Monitoring Networks[a, b] for Black Carbon					
	Country/ Agency	Years of Data	BC – Indicator	Number of Sites	Measurement Method	Location of Information and/ or Data
ESRL/GMD Aerosol Network Baseline Stations Regional Stations Mobile/Cooperative Platforms	United States / NOAA	1957–Present	BCa and/ or Aerosol optical properties	4 Rural 3 Rural 15 Rural	Aerosol Monitoring System – Aethalometers, Particle Soot/ Absorption Photometers, Nephelometers, etc.	http://www.esrl.noaa.gov/gmd/aero/index.html
World Data Centre for Aerosols	Global Atmospheric Watch	1974–Present	BCa and/or Aerosol optical properties	~16 Rural	Aerosols – Light Absorption/ EBC, AOD, Light scattering & back scattering, Size distribution	http://wdca.jrc.it/ http://gaw.tropos.de/gaw_program.html
Nepal Climate Observatory-Pyramid (NCO-P)	Nepal	2006–2008	BCa	1 Rural	MAAP	http://www.atmos-chem-phys-discuss.net/10/8379/2010/acpd-10-8379-2010.pdf
CSN/STN—PM$_{2.5}$ Speciation Trends Network[c]	United States / EPA	1999–Present	ECa	~200 urban	Thermal Optical Transmittance	http://www.epa.gov/ttnamti1/specgen.html
IMPROVE—Interagency Monitoring of Protected Visual Environments	United States / NPS	1988–Present	ECa	110 rural (plus ~67 protocol sites)	Thermal Optical Reflectance	http://vista.cira.colostate.edu/IMPROVE/
ARIES / SEARCH—Aerosol Research Inhalation Epidemiology Study / SouthEastern Aerosol Research and Characterization Study experiment	United States / EPRI / SC	1992–Present	ECa	5 Urban 3 Rural	Thermal Optical Reflectance	http://www.atmospheric-research.com/studies/SEARCH/index.html
NAPS—National Air Pollution Surveillance Network	Canada	2003–Present	ECa	4 rural 13 urban	R&P Partisol-Plus 2025 R&P Partisol Model 2300	http://www...gc.ca/rnspa-naps/Default.asp?lang=En&n=5C0D33CF-1
CAPMoN—Canadian Air and Precipitation Monitoring Network	Canada	2002–Present	ECa	29 Rural	R&P Partisol Model 2300 PM$_{2.5}$ Speciation Sampler	http://www.msc.ec.gc.ca/capmon/particulate_general_e.cfm
European Monitoring and Evaluation Program (EMEP)	Norwegian Institute for Air Research	2002–2003	ECa	2 Urban 12 Rural	Thermal Optical Tranmittance – Sunset Lab	http://www.atmos-chem-phys.net/7/5711/2007/acp-7-5711-2007.pdf
European Supersites for Atmospheric Aerosol Research (EUSAAR)	European Union	2006–Present	BCa / ECa	20 Rural	Aerosol properties including – absorption, scattering, AOD Aethalometer / Sunset Lab	http://www.eusaar.net/files/overview/infrastructures.cfm
China Atmosphere Watch Network (CAWNET)	Chinese Meteorological Administration	1999–Present	ECa	6 Urban 12 Rural	Thermal Optical Reflectance	http://www.agu.org/journals/jd/jd0814/2007JD009525/2007JD009525.pdf

	Worldwide Air Monitoring Networks[a,b] for Black Carbon					
Network	**Country/ Agency**	**Years of Data**	**BC - Indicator**	**Number of Sites**	**Measurement Method**	**Location of Information and/ or Data**
Multiple Independent Sites –two groups by pollutant (BC & ECa) by Vignati et al. (2010)	Multiple Agencies	Various periods 1976–2002	BCa ECa	11 Rural 7 Rural	Various	*http://www.atmos-chem-phys. net/10/2595/2010/acp-10-2595-2010. pdf*

a The emphasis is on surface-based continuous air monitoring networks. Some networks listed separately may also serve as subcomponents of other larger listed networks; as a result, some double counting of the number of individual monitors is likely.

b The information on some networks is sketchy. It is frequently unclear (1) when the network actually started up and whether all monitors were operating at that time (or were added over time), (2) whether the pollutant measured is measured as BCa, ECa or some other surrogate for BC, (3) what the definition of urban/rural is for a given network and the exact numbers of urban/rural monitors, and (4) what the exact nature of the measurement method is and whether it applies to all or just some sites.

c Collocated at CSN sites for the period 2009 to present, there are ~40 Aethalometers for measuring BC and 5 Sunset Laboratory Carbon Aerosol monitors for ECa.
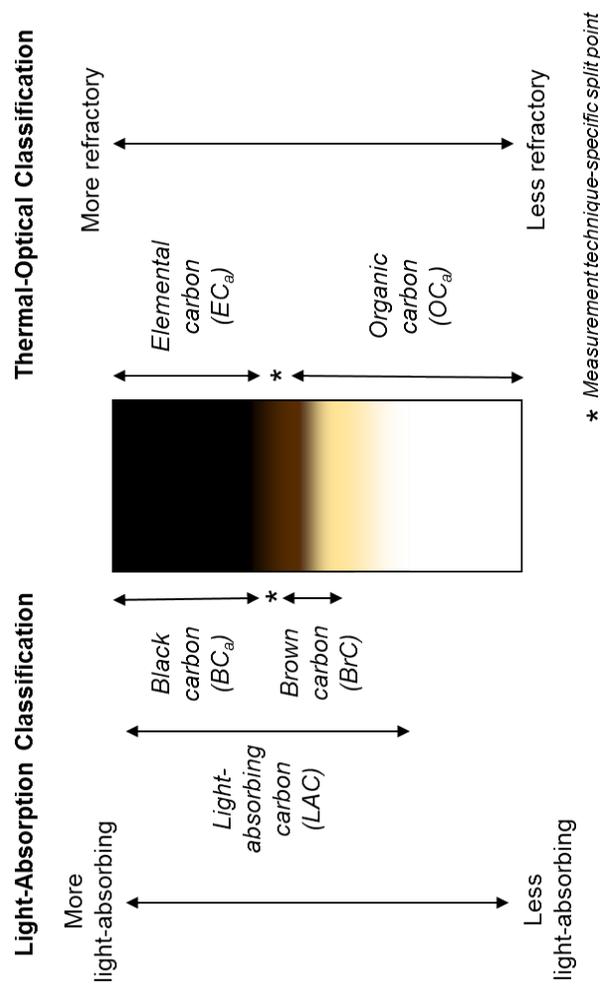
Figure A1-1. Measurement of the Carbonaceous Components of Particles. Black carbon and other types of light-absorbing materials can be characterized by measuring their specific light-absorption properties, as seen on the left side of the figure (BCa/BrC/LAC). This contrasts with other approaches to characterizing particles based on measurements of the refractory nature of the material (inertness at high temperatures), as seen on the right-hand side of the figure (ECa and OCa). (This figure is also as shown as Figure 5-1.) (Source: U.S. EPA)

which can be used to estimate BC concentrations and can also indicate the existence of components that absorb in the near-UV (i.e., brown carbon, BrC). Light absorbing carbon (LAC) is a term used for light absorbing substances in the atmosphere, which includes soot and its components, BC and BrC. There is a lack of consensus and standardization regarding the operational criteria used, calibration materials used, and defining characteristics or properties of the BC measured. The methods used to measure ECa and BCa require standardization and re-evaluation for climate and regulatory uses.

A1.2.1 Thermal-Optical Methods, ECa

As noted in Chapter 5, thermal-optical methods are by far the most commonly used. Since 1982, thermal-optical analysis methods have been applied to measure the ECa and OCa component of ambient and source aerosols (Huntzicker et al., 1982; NIOSH, 1999; Birch and Cary, 1996; Chow et al., 1993; Peterson and Richards, 2002; Chow et al., 2007). PM collected on a filter is heated to isolate the refractory and non-refractory carbon. Laser correction measurements help prevent charred organic materials from being misinterpreted as ECa. Thermal optical-reflectance (TOR) methods use reflectance for char correction and separation of ECa from OCa, while thermal-optical transmittance (TOT) uses transmittance. Long-standing reliance on these methods—which measure ECa, rather than BC—has resulted in an extensive observational record based on ECa and OCa splits, and the frequent substitution of ECa data for BCa data, since availability of the latter is limited. In addition to laboratory-based thermal-optical methods for ECa, semi-continuous or near real-time thermal-optical methods for ECa and OCa are commercially available. The semi-continuous analyzer provides hourly in-field measurements of ECa and OCa. This semi-continuous analyzer also provides a measure of light absorbing or optical BCa.

A1.2.2 Light-Absorption Measurements, BCa

Currently, light-absorption or "optical" measurements of BCa are not consistently deployed in routine monitoring programs in the United States. The one program area in which light-absorption methods are used is in assessing visibility impairment in national parks and wilderness areas via the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. To date, optical methods have not been widely used in urban monitoring networks. However, such approaches are commercially available and could be more widely deployed. These approaches fall into two general categories—

optically absorbing and incandescent (thermal emission of light) measurement. Relative to the incandescence techniques, optical techniques for BCa are in wider use. A listing of a variety of commercially available instruments used for monitoring ambient or source concentrations of BCa and the wavelength selected for measurement is provided in the Table A1-2.

Modern light-absorbing techniques rely on passing a laser beam at a specific wavelength through a particle sample, either in an air volume or deposited onto a filter, and observing how much light is absorbed by the particles. BCa is typically measured over the green to infrared wavelengths, where it absorbs more strongly than other LAC. BrC may also absorb light at shorter wavelengths (near-UV and UV). Many BCa instruments can measure at multiple wavelengths, sometimes simultaneously depending on the exact instrument configuration. This provides information about components that absorb light over different parts of the UV/Visible spectrum. Thus, these instruments may be used to distinguish between BCa and BrC; however, in many cases researchers have not been careful to distinguish how much of the measured light-absorbing carbon falls into each category. In order to convert light absorption to a BC mass concentration, a mass absorption coefficient or similar conversion factor is used. The conversion factor is based on experiments that simultaneously measure light absorption at a specific wavelength and BC mass (either as ECa from ambient measurements or particle mass from soot generation experiments). It is recommended that light absorption be reported in the original units of absorption along with any mass absorption coefficients or conversion factors used to convert absorption to BC mass concentration.

Incandescence is the second approach used to quantify BCa. Laser induced incandescence (LII) subjects particles in an air stream to a high-intensity laser in the infrared. Some LII techniques can measure individual particles, providing data on particle size, BCa mass concentration (based on an assumed BC density), and an indication of the mixing state of the particles. LII is currently used in limited research applications in the United States.

A1.2.3 Inter-comparisons Among Optical BCa and Thermal-Optical ECa Measurements

Given that ECa concentrations are commonly used to represent BCa, and vice versa, the relationship between BCa and ECa is important to characterize.

Table A1-2. Examples of Commercially Available Optical BCa Measurement Techniques. (Source: U.S. EPA)

Instrument (Manufacturer)[a]	Real-time (R) or Off-line (O)	Filter (F) or Air Stream (A)	Wavelengths Measured (See Chapter 2)[b]
Aethalometer (Magee Scientific)	R	F	370 nm, 880 nm standard 370, 470, 520, 590, 660, 880 and 950 optional
Particle Soot Absorption Photometer (Radiance Research)	R	F	467, 530 and 660 nm
Multi-Angle Absorption Photometer (Thermo Scientific)	R	F	670 nm
Transmissometer (Magee Scientific)	O	F	370 nm and 880 nm
Densitometer (Tobias Associates Inc.)	O	F	400 – 650 nm; peak at 575 nm
Smoke Stain Reflectometer (Diffusion Systems, Ltd.)	O	F	Monochromatic light; wavelength not specified
Hybrid Integrating Plate/Sphere	O	F	633 nm
Photoacoustic soot spectrometer (Droplet Measurement Technologies, Desert Research Institute)	R	A	405, 532, 781 nm
Single particle soot photometer (Artium Technologies, Droplet Measurement Technologies)	R	A	1064 nm
Semi-continuous Field Analyzer (Sunset Labs)	R	F	632 nm
Photoacoustic Micro Soot Sensor (AVL)	R	A	808 nm

[a] The use of commercial trade names or vendor names does not constitute an endorsement by the U.S. EPA.

[b] A variety of mass absorption coefficients (MACs) or similar conversion factors are used to convert light absorption at a particular wavelength to BC mass concentration. See the BCa:ECa comparison in Table A1-3 for the MACs used in the comparison studies referenced.

It should be noted that the two measurements are not always entirely independent, as the selected conversion factor to estimate BCa is sometimes based on experiments establishing a relationship between light absorption and ECa. A number of inter-comparison studies have examined several different BCa or ECa measurement approaches simultaneously to evaluate how well they agreed (Table A1-3). Recent studies, published in the year 2000 or later, that compare ambient BCa and ECa measurements were reviewed (Chow et al., 2009; Bae et al., 2007; Hitzenberger et al., 2006; Snyder and Schauer, 2007; Sharma et al., 2002; Sahu et al., 2009; Yang et al., 2006; Miyazaki et al., 2008; Babich et al., 2000; Ram et al., 2010; Husain et al., 2007; Jeong et al., 2004; Lim et al., 2003; Hagler et al., 2007a). In a wide variety of environments, ranging from the remote Arctic to urban cities, BCa and ECa measurements were reported to have consistently high correlation (average R = 0.86 +/- 0.11). In addition, Figure A1–2 shows that ratios of BCa/ECa are typically near 1 (BCa/ECa = 0.7-1.3, or within 30%,

for 70% of studies), however there do exist studies reporting very low BCa/ECa ratios (~0.5) and very high BCa/ECa ratios (~2).

The ratio of BCa to ECa and the consistency of the relationship may depend on the aerosol mixture and/or the specific method used. The difference in BCa and ECa concentration may also be largely influenced by the conversion factors used to change light absorption into mass concentrations for optical methods as well as corrections for measurement artifacts. The differences between BCa and ECa may also be due to a lack of consistency in the post-processing of the raw measurements among studies (Venkatachari et al., 2006; Collaud Coen et al., 2010; Park et al., 2010; Virkkula et al., 2007; Chow et al., 2009; Bond et al., 1999; Chen et al., 2004; Jimenez et al., 2007). It should be noted that these inter-comparison data are based on ambient measurements and similar data are needed for source measurements.

Table A1-3. Inter-comparison of Ambient BCa and ECa Measurements. Comparisons include (a) BCa measurements using different instruments; (b) BCa measurements using different instruments after application of correction algorithm; (c) ECa measurements using different instruments; and (d) BCa measurements compared to ECa measurements. (Source: U.S. EPA)

Table A1-3 (a) BCa–BCa comparison.

Citation	Instrument A	Instrument B	r	r²	Ratio (high/low)	Notes
Chow et al. (2009)	7-AE (660 nm)	PSAP (660 nm)	0.98		1.28	Fresno Supersite, CA
Chow et al. (2009)	7-AE (660 nm)	MAAP (670 nm)	0.99		3.52	Fresno Supersite, CA
Chow et al. (2009)	PSAP (660 nm)	MAAP (670 nm)	0.99		2.68	Fresno Supersite, CA
Chow et al. (2009)	7-AE (520 nm)	PA (532 nm)	0.96		4.68	Fresno Supersite, CA
Chow et al. (2009)	PSAP (530 nm)	PA (532 nm)	0.95		3.69	Fresno Supersite, CA
Chow et al. (2009)	MAAP (670 nm)	PA (670 nm)	0.98		1.51	Fresno Supersite, CA
Snyder and Schauer (2007)	Aethalometer	PSAP	0.93	0.86	1.41	Slope of line (intercept small)
					2.68	Overall Average Ratio

Table A1-3 (b) BCa–BCa comparison for study data with correction algorithms applied.

Citation	Instrument A	Instrument B	r	r²	Ratio (high/low)	Notes
Chow et al. (2009)	7-AE adj (660 nm)	PSAP adj (660 nm)	0.95		1.02	Fresno Supersite, CA
Chow et al. (2009)	7-AE adj (660 nm)	MAAP (670 nm)	0.97		0.9	Fresno Supersite, CA
Chow et al. (2009)	PSAP adj (660 nm)	MAAP (670 nm)	0.97		0.81	Fresno Supersite, CA
Chow et al. (2009)	7-AE adj (660 nm)	PA (532 nm)	0.95		1.24	Fresno Supersite, CA
Chow et al. (2009)	PSAP adj (530 nm)	PA (532 nm)	0.95		1.17	Fresno Supersite, CA
					1.03	Overall Average Ratio

Table A1-3 (c) ECa–ECa comparisons.

Citation	High Measurement	Low Measurement	r	n	Ratio (High/Low)	Notes
Bae et al. (2007)	NIER-EC NIOSH TOT	UT-EC NIOSH TOT	0.99	223	1.11	Semicontinuous Sunset with different temperature protocols: NIER - shortened protocols, UT: nine-step
Bae et al. (2009)	IMPROVE TOR	ACE-Asia TOT	0.79	709	2.14	St. Louis Supersite, MO
Cheng et al. (2010)	IMPROVE_A TOR	IMPROVE_A TOT	0.95	89	1.74	TOT and TOR from single DRI Model 2001 analyzer with denuder
Cheng et al. (2010)	IMPROVE_A TOR	IMPROVE_A TOT	0.95	89	1.83	TOT and TOR from single DRI Model 2001 analyzer without denuder
Cheng et al. (2011)	IMPROVE TOR	NIOSH TOT	0.97	81	1.72	Birmingham, AL urban SEARCH site
Cheng et al. (2011)	IMPROVE TOR	NIOSH TOT	0.92	97	2.78	Jefferson Street, Atlanta, GA urban SEARCH site
Cheng et al. (2011)	IMPROVE TOR	NIOSH TOT	0.85	75	3.57	Pensacola, FL coastal SEARCH site
Cheng et al. (2011)	IMPROVE TOR	NIOSH TOT	0.81	80	4.00	Centerville, AL rural SEARCH site
Chow et al. (2006)	IMPROVE_A TOR	STN NIOSH TOT		17	1.87	Fresno Hi-Vol Summer

Citation	High Measurement	Low Measurement	r	n	Ratio (High/Low)	Notes
Chow et al. (2006)	IMPROVE_A TOR	STN NIOSH TOT		8	2.86	Fresno Hi-Vol Winter
Chow et al. (2006)	IMPROVE_A TOR	STN NIOSH TOT		17	1.49	Fresno RAAS Summer
Chow et al. (2006)	IMPROVE_A TOR	STN NIOSH TOT		5	2.17	Fresno RAAS Winter
Chow et al. (2006)	IMPROVE_A TOR	STN NIOSH TOT		17	1.46	Fresno RAAS Summer with denuder
Chow et al. (2006)	IMPROVE_A TOR	STN NIOSH TOT		5	1.69	Fresno RAAS Winter with denuder
Chow et al. (2009)	IMPROVE_A_TOR_EC	IMPROVE_A_TOT EC	0.95	49	1.30	Fresno Supersite, CA
Chow et al. (2009)	STN_TOR EC	STN_TOT EC	0.9	18	1.41	Fresno Supersite, CA
Chow et al. (2009)	IMPROVE_A TOR EC	STNTOR EC	0.94	18	1.10	Fresno Supersite, CA
Chow et al. (2009)	IMPROVE_A TOR EC	French two step EC	0.9	8	1.03	Fresno Supersite, CA
Chow et al. (2009)	IMPROVE_A TOR EC	Sunset Field EC TOT	0.87	48	1.82	Fresno Supersite, CA
Fujita et al. (2007)	IMPROVE TOR	NIOSH TOT	0.94	14	1.60	Ambient (urban)
Fujita et al. (2007)	IMPROVE TOR	NIOSH TOT	0.99	21	1.20	Ambient (on-road)
Gan et al. (2010)	IMPROVE TOR	NIOSH TOT		6	1.09	Submarine diesel PM
Klouda et al. (2005)	IMPROVE TOR	STN-NIOSH TOT		99	1.66	RM 8785 suspended PM
					1.89	**Overall Average Ratio**

Table A1-3 (d) is on the following two pages.

Table A1-3 (d) BCa–ECa comparisons.

Citation	BCa Method	MAC ($m^2 g^{-1}$)	l, nm	EC Method	r	Avg BCa	Avg EC	Ratio BCa/EC	Location
Chow et al. (2009)	Aethalometer AE-31 $PM_{2.5}$	16.6	660	IMPROVE_A_TOR $PM_{2.5}$	0.89	0.94	1.01	0.93	Fresno, CA
Chow et al. (2009)	MAAP $PM_{2.5}$	6.6	670	IMPROVE_A_TOR $PM_{2.5}$	0.96	0.95	0.95	1.00	Fresno, CA
Chow et al. (2009)	Sunset Optical BC $PM_{2.5}$		660	IMPROVE_A_TOR $PM_{2.5}$	0.87	0.52	1.01	0.51	Fresno, CA
Bae et al. (2007)	Aethalometer AE-16 $PM_{2.5}$	16.6	880	Sunset $PM_{2.5}$ hourly	0.93	0.59	0.68	0.87	Gosan, Korea
Bae et al. (2007)	Aethalometer AE-16 $PM_{2.5}$	16.6	880	Sunset $PM_{2.5}$ hourly	0.92	0.59	0.74	0.80	Gosan, Korea
Bae et al. (2007)	Aethalometer AE-16 $PM_{2.5}$	16.6	880	Sunset $PM_{2.5}$ hourly	0.80	1.89	2.18	0.87	Gosan, Korea
Bae et al. (2007)	Aethalometer AE-16 $PM_{2.5}$	16.6	880	Sunset $PM_{2.5}$ hourly	0.70	1.89	2.3	0.82	Gosan, Korea
Jeong et al. (2004)	Aethalometer AE-20	16.6	880	Sunset $PM_{2.5}$ every two hrs.	0.92	0.9[a]	0.4[a]	2.25	Rochester, NY
Jeong et al. (2004)	Aethalometer AE-20	16.6	880	Sunset $PM_{2.5}$ every two hrs.	0.77	0.9	0.4[a]	2.25	Philadelphia, PA
Jeong et al. (2004)	Sunset Optical BC $PM_{2.5}$	16.6	660	Sunset $PM_{2.5}$ every two hrs.	0.97	0.3[a]	0.4[a]	0.75	Rochester, NY
Jeong et al. (2004)	Sunset Optical BC $PM_{2.5}$	16.6	660	Sunset $PM_{2.5}$ every two hrs.	0.85	0.4[a]	0.4[a]	1.00	Philadelphia, PA
Hagler et al. (2007)	PSAP	[b]	565	NIOSH TOT	0.95		7ngm^{-3}	[b]	Greenland - no BC mass
Hitzenberger (2006)	AE-9	19	830	Cachier two step 1000C in O_2	0.72			1.14	Vienna, Austria
Hitzenberger (2006)	MAAP	6.5	670	Cachier two step 1000C in O_2	0.91			1.20	Vienna, Austria
Hitzenberger (2006)	Integrating sphere	Calc[c]	550	Cachier two step 1000C in O_2	0.86			0.98	Vienna, Austria
Hitzenberger (2006)	Light transmission-white light		white	Cachier two step 1000C in O_2	0.89			1.20	Vienna, Austria
Hitzenberger (2006)	AE-9	19	830	VDI 650 C in O_2	0.66			0.95	Vienna, Austria
Hitzenberger (2006)	MAAP	6.5	670	VDI 650 C in O_2	0.88			1.05	Vienna, Austria
Hitzenberger (2006)	Integrating sphere	Calc[c]	550	VDI 650 C in O_2	0.78			0.84	Vienna, Austria
Hitzenberger (2006)	Light transmission-white light		white	VDI 650 C in O_2	0.79			1.05	Vienna, Austria
Hitzenberger (2006)	Aethalometer AE-9	19	830	TOT 800C in O_2	0.61			1.11	Vienna, Austria
Hitzenberger (2006)	MAAP	6.5	670	TOT 800C in O_2	0.88			1.11	Vienna, Austria
Hitzenberger (2006)	Integrating sphere	Calc[c]	550	TOT 800C in O_2	0.67			0.93	Vienna, Austria
Hitzenberger (2006)	Light transmission-white light		white	TOT 800C in O_2	0.83			1.13	Vienna, Austria
Snyder and Schauer (2007)	PSAP	[b]	565	Sunset $PM_{2.5}$ hourly	0.91			[b]	Riverside, CA
Snyder and Schauer (2007)	Aethalometer AE-31	[b]	880	Sunset $PM_{2.5}$ hourly	0.93			[b]	Riverside, CA
Sharma et al. (2002)	Aethalometer AE-11 $PM_{2.5}$	19	880	IMPROVE TOR $PM_{2.5}$	0.89		0.58[a]		Egbert, Canada
Sharma et al. (2002)	PSAP $PM_{2.5}$	10	565	IMPROVE TOR $PM_{2.5}$	0.99		0.58[a]		Egbert, Canada
Sharma et al. (2002)	Aethalometer AE-11 $PM_{2.5}$	19	880	IMPROVE TOR $PM_{2.5}$	0.98		1.42[a]		Downsview, Canada

Citation	BCa Method	MAC ($m^2\,g^{-1}$)	λ, nm	EC Method	r	Avg BCa	Avg EC	Ratio BCa/EC	Location
Sharma et al. (2002)	PSAP $PM_{2.5}$	10	565	IMPROVE TOR $PM_{2.5}$	0.69		1.42[a]		Downsview, Canada
Sharma et al. (2002)	Aethalometer AE-11	19	880	Cachier two step EC 1100C in O_2	0.91		0.087, 0.012[a]		Alert, Canada (Arctic)
Sharma et al. (2002)	PSAP	10	565	Cachier two step EC 1100C in O_2	0.93		0.087, 0.012[a]		Alert, Canada (Arctic)
Sharma et al. (2002)	Aethalometer AE-11 $PM_{3.5}$	19	880	NIOSH TOT $PM_{2.5}$	0.92		1.95[a]		Evans Ave, Canada
Sharma et al. (2002)	PSAP $PM_{2.5}$	10	565	NIOSH TOT $PM_{2.5}$	0.96		1.95[a]		Evans Ave, Canada
Sharma et al. (2002)	Aethalometer AE-11 $PM_{2.5}$	19	880	NIOSH TOT $PM_{2.5}$	0.89		1.82[a]		Palmerston, Canada
Sharma et al. (2002)	PSAP $PM_{2.5}$	10	565	NIOSH TOT $PM_{2.5}$	0.89		1.82[a]		Palmerston, Canada
Sharma et al. (2002)	Aethalometer AE-11 $PM_{2.5}$	19	880	NIOSH TOT $PM_{2.5}$	0.92		1.48[a]		Winchester, Canada
Sharma et al. (2002)	PSAP $PM_{2.5}$	10	565	NIOSH TOT $PM_{2.5}$	0.54		1.48[a]		Winchester, Canada
Venkatachari et al. (2006)	Aethalometer AE-20 $PM_{2.5}$	16.6	880	Sunset $PM_{2.5}$ hourly	n/a	1.01	0.85	1.2	New York City, NY
Venkatachari et al. (2006)	Aethalometer AE-20 $PM_{2.5}$	16.6	880	R&P 5400 $PM_{2.5}$ hourly	n/a	1.01	0.55	1.8	New York City, NY
Venkatachari et al. (2006)	Aethalometer AE-20 $PM_{2.5}$	16.6	880	CSN TOT $PM_{2.5}$	n/a	1.01	0.53	1.9	New York City, NY
Sahu et al. (2009)	PSAP $PM_{2.5}$	8.9	565	Sunset $PM_{2.5}$ hourly	0.98	1.18	n/a	1.0	Jeju Island, South Korea
Yang et al. (2006)	Aethalometer AE-16 $PM_{2.5}$	16.6	880	IMPROVE TOR $PM_{2.5}$	0.72	16.5	12	1.4	Xi'an, China
Miyazaki et al. (2008)	COSMOS	9.8	565	Sunset $PM_{1.0}$ hourly	0.96	n/a	n/a	n/a	Thailand
Babich et al. (2000)	Aethalometer AE-20	19	880	IMPROVE TOR $PM_{2.5}$	0.87	1.1	1.4	0.79	Bakersfield, CA
Babich et al. (2000)	Aethalometer AE-20	19	880	IMPROVE TOR $PM_{2.5}$	0.98	1.2	1.5	0.80	Chicago, IL
Babich et al. (2000)	Aethalometer AE-20	19	880	IMPROVE TOR $PM_{2.5}$	0.95	0.8	1.3	0.62	Dallas, TX
Babich et al. (2000)	Aethalometer AE-20	19	880	IMPROVE TOR $PM_{2.5}$	0.95	1.1	1.5	0.73	Philadelphia, PA
Babich et al. (2000)	Aethalometer AE-20	19	880	IMPROVE TOR $PM_{2.5}$	0.96	3.1	3.9	0.79	Phoenix, AZ
Babich et al. (2000)	Aethalometer AE-20	19	880	IMPROVE TOR $PM_{2.5}$	0.92	1.6	1.9	0.84	Riverside,CA
Ram et al. (2010)	Aethalometer	16.6	880	Sunset TOT NIOSH PM_{10}	0.79	4.45	3.84	1.2	Kanpur, India
Husain et al. (2007)	Aethalometer AE-21 $PM_{3.2}$	16.6	880	Sunset TOT NIOSH $PM_{2.5}$	0.84	n/a	n/a	1.3	Lohore, Pakistan
Lim et al. (2003)	PSAP $PM_{2.5}$	10	565	R&P 5400 $PM_{2.5}$ hourly	n/a	1.26	2.8	0.5	Atlanta, GA
Lim et al. (2003)	PSAP $PM_{2.5}$	10	565	RU/OGI TOT $PM_{2.5}$ hourly Sunset predecessor	n/a	1.26	2.33	0.5	Atlanta, GA
Lim et al. (2003)	Aethalometer AE-16 $PM_{2.5}$	12.6	880	R&P 5400 $PM_{2.5}$ hourly	n/a	2.61	2.8	0.9	Atlanta, GA
Lim et al. (2003)	Aethalometer AE-16 $PM_{2.5}$	12.6	880	RU/OGI TOT $PM_{2.5}$ hourly Sunset predecessor	n/a	2.61	2.33	1.1	Atlanta, GA

[a] Median concentration.

[b] BC data presented as absorption coefficients (Mm^{-1}). Ratio of BCa/ECa and linear regression equations not extracted for these papers, although it could be calculated.

[c] Calibration curve based on dissolved carbon black.
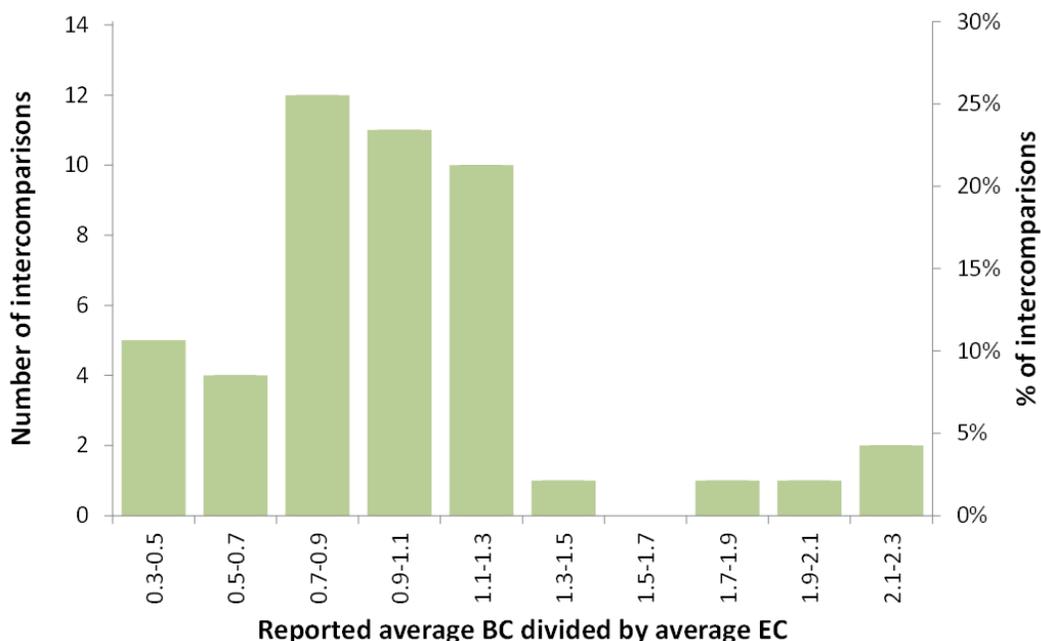
Figure A1-2. Reported BCa/ECa Ratios for a Pair of Measurement Techniques Reported in Ambient Field Studies. (Source: U.S. EPA)

Instruments measuring light absorption are often capable of measuring light absorption at additional wavelengths in the near-UV or UV, which may help indicate the presence of BrC. Such approaches are currently used to attempt separation of the influence of wood smoke aerosols, which tend to be rich in BrC, from those that are dominated by diesel emissions and other fossil fuel combustion, which are rich in BC.

The disagreement among BCa measurements may be due in part to differing instrument sensitivities and responses to other PM components (Slowik et al., 2007), filter-loading artifacts, or the use of an incorrect light-absorption-to-BC mass concentration conversion factor for studies reporting BCa in terms of their mass concentrations. Chow et al. (2009) found that applying post-processing algorithms greatly improved the agreement among different filter-based BCa techniques (Refer to Table A1-3 above). EPA and other researchers (Collaud Coen et al., 2010; Park et al., 2010; Virkkula et al., 2007; Bond et al., 1999; Chen et al., 2004; Jimenez et al., 2007) are similarly assessing whether post-processing algorithms and site-specific conversion factors may also be beneficial to better understand the differences among BCa and ECa measurements. In addition to issues with the various BCa and ECa measurement techniques mentioned above, BCa-to-

ECa ratios are likely to be affected by the presence of other light-absorbing species (e.g., BrC and dust). The specific inter-comparison circumstances (e.g., location, season, sample collection and analysis procedures, optical wavelength, data corrections, and aerosol mixture[1]) may be important to understand and reconcile reported differences. A summary of the data presented in Figure A1-2 and comparisons of BCa/BCa (with and without correction algorithms) and ECa/ECa along with the circumstances for the inter-comparison measurements is found in Table A1-3 (Inter-comparison of Ambient BCa and ECa Measurements).

A1.2.4 Inter-comparisons Among Thermal-Optical ECa Measurements

The differentiation between OCa and ECa by thermal-optical methods is highly dependent on the specific measurement method operational procedures used. Different instrument operating procedures, thermal temperature profiles, and correction for char can lead to differences in ECa. Previous method comparison studies summarized

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[1] The mixture can be important because of the relative amount of non-graphitic absorbing materials, e.g., BrC and dust, as well as internal mixtures with water, organics, and sulfates.

in Watson et al. (2005) showed differences of a factor of 2 to be common for measurements of ECa. Method differences have been found not only to depend on the operational definitions of the methods, but also to depend on the chemical composition and source of aerosol collected (i.e., location and seasons), particle loading on the filter, and uniformity of the filter deposit. Samples containing biomass smoke present more difficulties due to components (inorganic compounds) that result in an overestimation of ECa (Novakov and Corrigan, 1995a). The presence of BrC can also affect the measurement of ECa. Reisinger et al. (2008) evaluated the BrC content of samples and the impact on the comparison of thermal-optical methods and found TOT methods to be less sensitive to the presence of BrC than other thermal methods tested.

There are currently no reference materials that reflect the variety of aerosol types in the atmosphere and there is no standardized method protocol. There is one consensus-based standard reference material (SRM 8785) available from the National Institute of Standards and Technology (NIST) that has values assigned for OCa and ECa as measured by the two EPA protocols discussed below (IMPROVE TOR and NIOSH-like TOT). The ECa assigned by the two protocols (IMPROVE: NIOSH) in the NIST SRM differ by a factor of 1.7 (Klouda et al., 2005).

Results from thermal-optical ECa:ECa comparison studies that use methods similar to the two EPA protocols that are not summarized in Watson et al., (2005) and published since 2005 were reviewed and summarized in Table A1-3 (Klouda et al., 2005; Bae et al., 2007; 2009; Cheng et al., 2010; 2011; Chow et al., 2006; 2009; Fujita et al., 2007; Gan et al., 2010). The average ratio of ECa:ECa from these studies is 1.9. Chow et al. (2006) also compared ECa measurements by IMPROVE and NIOSH-like TOT methods for a variety of lab generated source samples. The IMPROVE:NIOSH-like TOT ECa range of ratios were from 1.01 to 1.04 for diesel, acetylene flame, carbon black, and graphite source samples, and 1.13 for electric arc samples. The biggest difference was found for the wood smoke source sample (ratio of 1.88).

A1.2.5 Inter-comparison of Two EPA ECa Measurement Protocols

The IMPROVE TOR and NIOSH-like TOT methods have been widely used in the EPA's national urban Chemical Speciation (CSN) and rural IMPROVE ambient monitoring networks. EPA has transitioned the urban CSN from the NIOSH-type TOT method to the IMPROVE_A TOR method. The transition began in May 2007 and was completed in October 2009 and includes a change to the sampling system as well as the analytical method. The major difference in the sampling method is the sampling flow rate (increased to ~22 LPM from ~6.7 LPM) and sample filter diameter (reduced from 46.2 mm to 25 mm), which results in an overall increase in pressure drop across the filter during sampling. The combination of these changes results in a reduction in the OC measured, which is most likely related to a change in sampling artifacts. The rationale for the transition of the urban CSN to IMPROVE-like sampling and analysis method was to institute consistency in the carbon measurements across the EPA's national particulate monitoring networks.

To understand the differences between the two carbon monitoring protocols, EPA established pairs of old and new CSN monitors at 11 sampling locations and collected parallel carbon measurements for 12 months from May 2009 to April 1010. Most other CSN sites also collected 2 months of parallel measurements when they initially transitioned between May 2007 and October 2009. In addition, lower flow rate CSN samplers whose carbon was measured with the NIOSH-type TOT method were used to collect data at 14 urban sites in the IMPROVE network.

The comparison between the previous CSN TOT data and the current CSN IMPROVE TOR data indicates that measured EC is reasonably consistent between the methods at the 11 locations that produced 2009-2010 data (Figure A1-3). These data suggest that both monitoring protocols could be interchangeably used to evaluate BC aerosols predicted by climate and air quality models, and to evaluate trends. The seasonal differences in these EC differences are modest, and may be related to the combined effect of sampling rates and analytical protocol and the resulting differences in measured OC as described above. However, when all the parallel EC measurements are considered, a different pattern emerges.

The comparison of urban EC derived with the IMPROVE TOR method to that from the CSN NIOSH-like TOT method in Figure A1-4 shows the ratio of monthly values decreasing from approximately 1.5 in 2005 to approximately 1.0 towards the end of 2009. The higher monthly ratios observed between 2005-2006 are consistent with the finding that CSN EC is on average 30% lower than IMPROVE EC (Hand et al., 2011) and the ratios shown for the last 12 months are consistent with the data presented
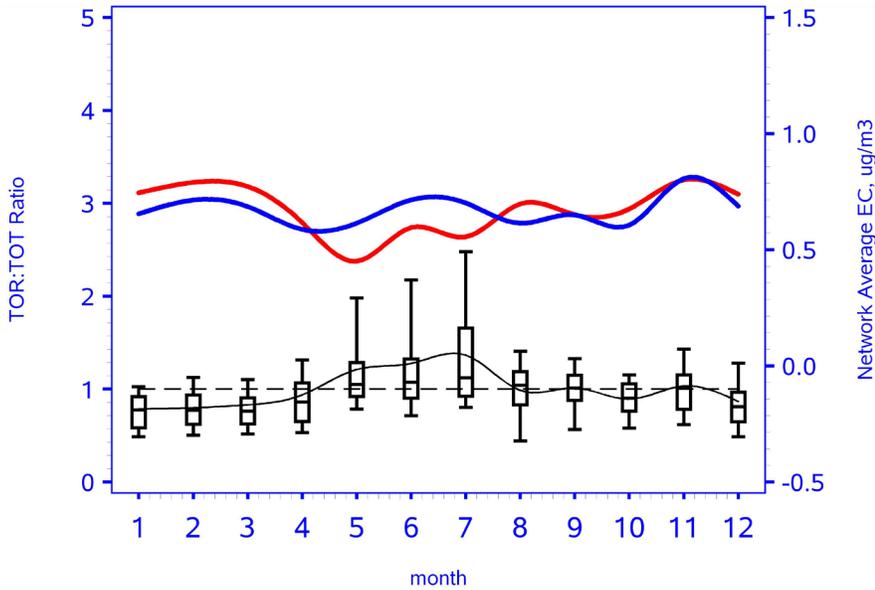
**Figure A1-3. Monthly Distribution of ECa/ECa Ratio For Two EPA methods
(TOR/TOT) From 897 Collocated Measurements Among 11 Urban CSN
Locations.** Average CSN NIOSH ECa concentration is red; IMPROVE TOR
ECa is blue; the distribution of daily ratios is presented as box plots (black).
(Source: U.S. EPA, AQS)

Because sampling artifacts are most likely to affect measurements of OCa, they may be most important for understanding OCa/ECa ratios (i.e., representing OC/BC). Figure A1-5 shows the monthly distribution of OC/BC among 897 measurements at 11 urban monitoring sites[2] that concurrently sampled with two alternative measurement protocols (NIOSH TOT and IMPROVE TOR) during 2009-2010. Though ECa can vary somewhat according to the monitoring protocol (see further discussion of NIOSH TOT and IMPROVE TOR), OCa can vary even more widely as a result of the correction used for OCa sampling artifacts. As the figure shows, the OCa/ECa ratios with the CSN NIOSH TOT method have large seasonal variation and for the 11-site group, the median value is

in Figure A1-3. Although the number of included monitors varies from month to month, the pattern from a consistent set of 5 collocated IMPROVE–CSN sites from 2005 thru 2009 reveals the same general trend. Although the ratio appears to have decreased during this five year period, the cyclical behavior suggests that relatively higher ratios often occur during the warmer months. EPA will continue to evaluate the differences between the two measurement protocols and possible connections to changes in the way the measurements were conducted as well as the potential influence of changes in other collected aerosols.

A second implication of the change from the NIOSH-like TOT to the IMPROVE TOR monitoring method along with the change in samplers, relates to measured OCa and its sampling artifacts. In some cases, sample collection procedures can lead to the inclusion of *positive artifacts*—mistakenly measuring non-PM components such as vapors as if they were in fact carbonaceous PM. Other procedures can lead to the exclusion of relevant material, producing *negative artifacts*. These artifacts are a problem particularly for measuring concentrations of OCa; sampling artifacts for EC are thought to be negligible, simply because the EC collected on the filter is more stable (non-reactive or volatile).

as high as 5. On the other hand, the CSN TOR OC/EC ratios do not display strong seasonality and have monthly median values of ~2-2.5. The latter are more consistent with average estimated direct emission OCa/ECa levels described in Chapter 5, as well as with the artifact corrected ratios described elsewhere (Novakov et al., 2005). However, they do not display the seasonal change in OCa/ECa ratios due to secondary organic aerosol (SOA) reported elsewhere. As discussed in Chapter 2 and Chapter 5, the correct characterization of OCa aerosol is critical for differentiating among reflecting vs. absorbing particles for assessment of radiative forcing, where OC is assumed to be mainly light scattering. While the IMPROVE TOR OCa is adjusted for sampling artifact with backup filters, the CSN NIOSH TOT protocol is only adjusted with nominal network value of 1 μg/m³ which may be too low (Chow et al., 2010a). On the other hand the much more suppressed seasonal behavior in the TOR carbon ratios could be related to the higher flow rate IMPROVE protocol samplers which may not fully retain semi-volatile OC particles. The latter will require further study to understand its implications for using these measurements to develop emissions

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[2] 11 site inter-comparison group includes Bronx and Queens, NY; Atlanta GA, Birmingham AL, Detroit MI, Cleveland OH; Chicago IL, Denver CO, LA (Rubidoux), CA; Sacramento CA and Seattle, WA.
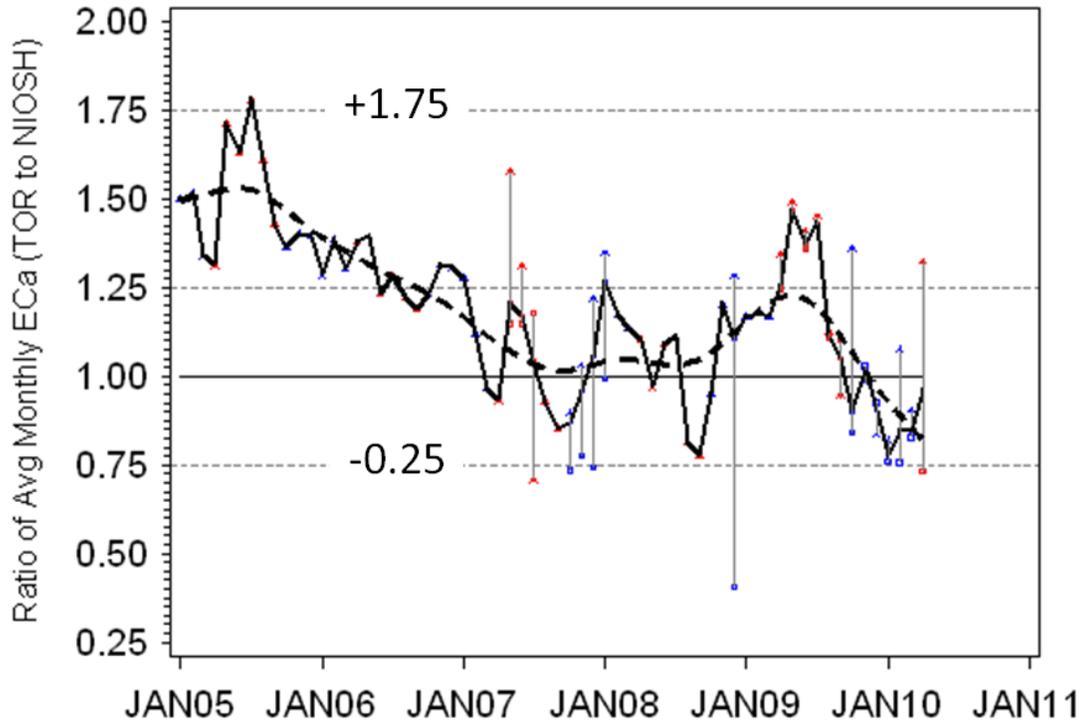
Figure A1-4. Trend in Ratio of Urban EC Derived From IMPROVE TOR and CSN NIOSH-like TOT Methods. The ratio of monthly averages derived from collocated IMPROVE (or CSN IMPROVE-like) with CSN MetOne samplers is shown, where the former measurements are produced with the IMPROVE protocol and the latter measurements are produced with the NIOSH-like TOT protocol. The results provided by ECa from the IMPROVE network samplers are shown with (*) and those from the CSN are represented by squares. Months October-March are denoted in blue and months April-September are shown in red. The dotted line is a spline fit through the monthly data. (Source: U.S. EPA, AQS)
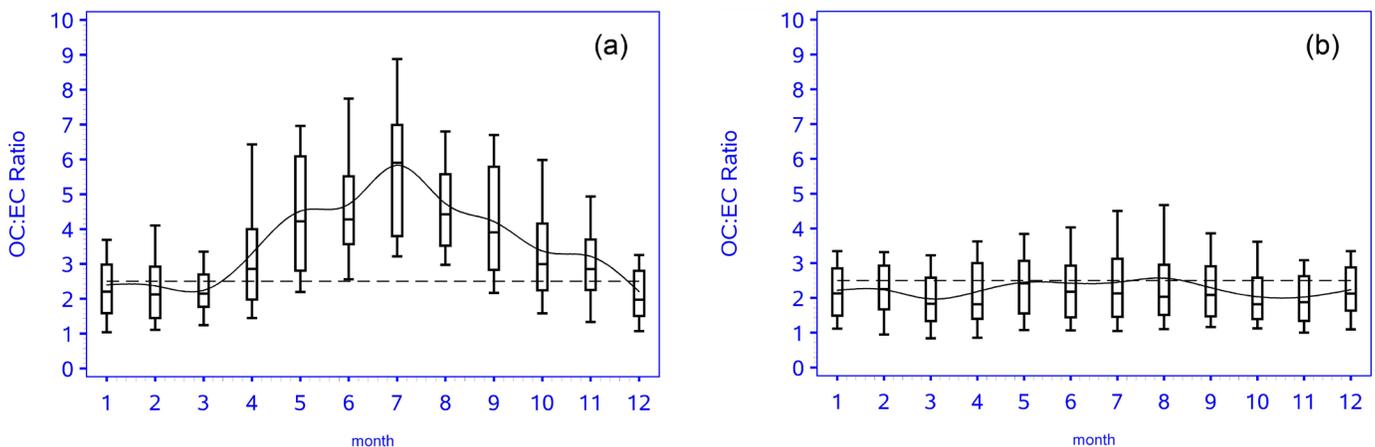
Figure A1-5. Monthly Distribution of OC/BC ratios for 11 CSN Sites Produced With (a) the NIOSH-like TOT and (b) IMPROVE_A TOR Monitoring Protocols, 2009-10. Nominal OC sampling corrections of 1 µg/m3 for CSN NIOSH type TOT have been used (Frank, 2006). The IMPROVE protocol data are adjusted with backup filters. Due in part to inability to adequately correct the CSN NIOSH OC sampling artifacts (Chow et al., 2010a), these data may in fact overstate ambient OC/BC and imply a seasonal pattern which may be an artifact of the monitoring method. (Source: U.S. EPA)
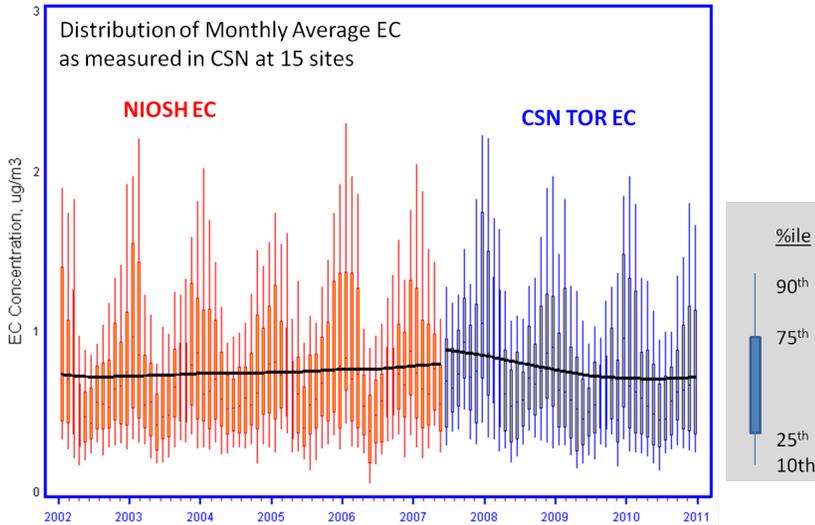
Figure A1-6. Monthly Distribution of Reported CSN EC at 15 sites From 2002 Through 2010. The ECa data produced with the CSN NIOSH-like TOT is shown in red and the ECa data produced with the IMPROVE_A TOR monitoring protocol is shown in blue. (Source: U.S. EPA, AQS)
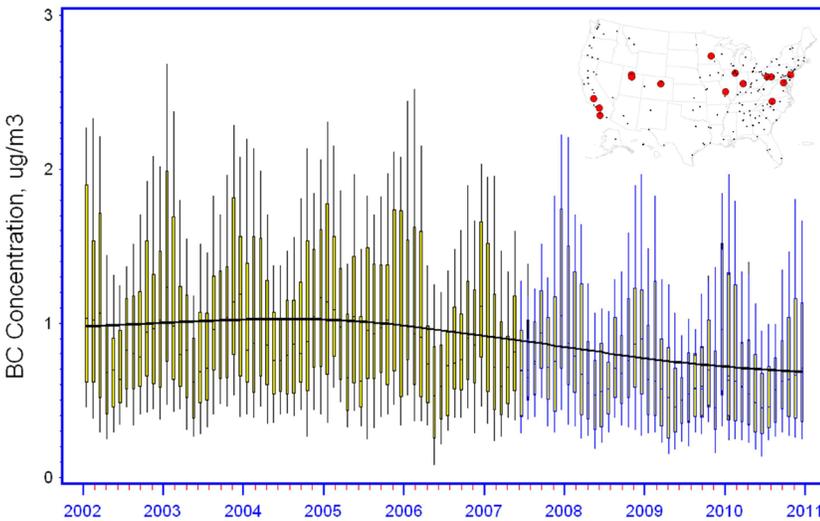
Figure A1-7. Ambient BC Trends (2002-2010), Based on Monthly Distribution of Average ECa Concentrations Among 15 CSN Monitoring Locations in the United States. The map shows the location of the 15 monitoring sites. (This figure is also as shown as Figure 5-12.) (Source: U.S. EPA)

inventories and to evaluate climate modeling data.

A1.2.6 Implications of Changes in ECa Monitoring on Estimated Concentration Trends

The urban ECa measurements as reported by the CSN in Figure A1-6 reveal a different picture than the one presented in Chapter 5, Figure 5-12. (For convenience, Figure 5-12 is also re-produced as Figure A1-7.) The reported EC data based on the NIOSH-type measurements in Figure A1-6 appear to depict a slight upward progression from 2002 thru 2006. However, when the data are adjusted using a 5-month moving average of the monthly ratios for 2005-2010 shown in Figure A1-4, together with the 2005 average ratio for earlier data, an estimated downward trend in EC is revealed.

A1.2.7 Other Measurements

Microscopy (the use of microscopes to view the structure of particles) and spectroscopy (measurement of a chemical as a function of wavelength) provide additional information about the physical and chemical structure of carbonaceous PM. An advantage of these methods is that they provide detailed information about how particles age and transform from the point of emission to the atmosphere. A variety of microscopy techniques have been applied to investigate carbon particles. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and Raman Microspectroscopy (RM) are the most widely used and have provided the most significant information about carbon aerosol composition to date. Like the thermal-optical

and light absorption measurement methods, microscopy has limitations and is subject to artifacts and interpretation issues, but these techniques do provide additional information not gathered by the thermal and optical measurement techniques.

A1.2.8 Limitations of Ambient Measurement Methods

Specific operating conditions, such as the heating temperature, time of heating, and char correction procedures, can influence thermal-optical measurement results. Chemical composition and emissions sources of the measured aerosol, filter loading, and uniformity of the filter particle deposit can also influence OCa and ECa values obtained. Studies suggest that EC measurements for some types of emissions (biomass smoke, dust) may be more strongly affected than traffic-related (e.g., diesel) samples, in part because of higher levels of inorganic components and BrC (Novakov and Corrigan, 1995b). A summary of the comparison of optical BCa to thermal ECa measurements is provided above.

Currently, there are no reference standards for assessing the accuracy of OCa or ECa measurements by thermal methods, nor is there a standardized method protocol for distinguishing between OCa and ECa. Development of standard reference materials and the consensus on standardized method protocols (including data reporting procedures) will be important in the future for the consistent measurement of OCa and ECa for climate purposes.

All optical BC measurements share a fundamental limitation in that they do not directly measure BC mass concentration. Instead, conversion factors (e.g., mass absorption efficiency or mass absorption cross-section) are necessary to generate BCa mass concentrations from the different optical measurements. In addition, the most commonly used filter-based methods are prone to artifacts during sampling. The extent of filter loading can influence particle scattering and shadowing effects which bias results (Park et al., 2010; Bond et al., 1999; Weingartner et al., 2003). While several filter-loading-based correction algorithms have been introduced (e.g., Virkkula et al., 2007), it is uncertain as to whether a correction algorithm should be universally applied as the artifacts may depend upon the particle composition and concentration. Because the aerosol absorption and derived BCa depend on wavelength, it should be noted that some reported

BC that is based on wavelengths in the visible spectrum may include other LAC.

A1.2.9 Critical Gaps and Research Needs in Ambient Measurement Methods

In light of the limitations discussed above, the following research can help improve the ambient measurement of BC and LAC in the future and reduce the uncertainty:

- Further comparisons of the predominant thermal and optical methods in use today are needed to better understand and characterize the differences and uncertainties. As comparisons are made, it is important to clearly document the operational conditions of the methods used.

- Having a consistent, well-defined "BC" reference material would help to better understand method differences and define the uncertainties in the various measurement methods.

- It is important to agree on a standardized method of operation and calibration for those methods identified as most important for measuring BC in support of climate and health.

- There is a need to develop methods capable of quantifying particulate components, referred to as BrC or (collectively with BC) as LAC, that provide additional light absorption in the near-UV and UV wavelengths.

- To ensure proper use of measurements, consistent data reporting (including metadata) of the sampling and analysis protocols and data adjustments must be provided.

- Continued research and further development is needed for continuous or real-time single particle measurements (e.g., aerosol time-of-flight mass spectrometry and single particle soot photometers) to enhance our knowledge of particle composition and mixing state.

A1.3 Black Carbon Emissions Source Measurements

Source measurements are used for a variety of purposes, including regulatory compliance. However, in the United States and elsewhere, such Measurements generally focus on total PM$_{2.5}$ mass. measurements of specific components are not required in the United States as part of regulatory

testing, and EPA does not have an official source measurement method. Instead, PM composition is measured largely for research purposes, including development of EPA's emissions models. Available source measurements are also used to develop and verify emissions inventories, refine standard measurement approaches, and assess control technologies and mitigation approaches. Due to the limited amount of source emissions data for the carbonaceous content of PM, EPA often must rely on data and methodologies for total PM mass, or substitute emissions models.

A1.3.1 Stationary Source Emissions Measurement Methods

Most current federal stationary source emission standards are focused on the regulation of filterable total PM mass. For most stationary sources in the current inventory, $PM_{2.5}$ emissions are derived from use of a scaling factor applied to collection of filterable total PM and the PM_{10} size fractions. Some local/state and site specific standards also require testing for PM_{10} and $PM_{2.5}$ mass, which sometimes includes both size fractions of filterable and condensable PM. The latter allows for inclusion of certain semi-volatile particles. EPA has recently promulgated a stationary method for $PM_{2.5}$ mass and refined the condensable stationary source

Table A1-4. Stationary Source Emissions Measurement Methods. (Source: U.S. EPA)

Method	PM Type	Filtration Temperature (°F)	Purpose	CFR Reference
EPA Method 5	Filterable	248 ± 25	General	40 CFR 60 Appendix A-3
EPA Method 5A	Filterable	108 ± 18	Asphalt Roofing	40 CFR 60 Appendix A-3
EPA Method 5B	Filterable	320 ± 25	Utility Plants	40 CFR 60 Appendix A-3
EPA Method 5D	Filterable	248 ± 25	Positive Pressure baghouses	40 CFR 60 Appendix A-3
EPA Method 5E	Filterable and Total Organic Material	248 ± 25	Wool Fiberglass	40 CFR 60 Appendix A-3
EPA Method 5F	Filterable	320 ± 25	Non sulfate Filterable PM	40 CFR 60 Appendix A-3
EPA Method 5G	Filterable and Condensable	<90	Wood Heaters - Dilution	40 CFR 60 Appendix A-3
EPA Method 5H	Filterable and Condensable	<248 and <68	Wood Heaters	40 CFR 60 Appendix A-3
EPA Method 5I	Filterable	248 ± 25	Low level general	40 CFR 60 Appendix A-3
EPA Method 17	Filterable	Stack Temperature	General	40 CFR 60 Appendix A-6
EPA Method 201	Filterable 10 µm	Stack Temperature	General – Particle Sizing	40 CFR 51 Appendix M
EPA Method 201A	Filterable 10 µm/2.5 µm	Stack Temperature	General – Particle Sizing	40 CFR 51 Appendix M
EPA Method 202	Condensable	85	General – Condensable PM	40 CFR 51 Appendix M
EPA Conditional Test Method -039	Total 10 µm/2.5 µm (Filterable and Condensable)	85	General – Dilution based PM	
Example State, VCS, and International Methods				
CARB 5	Filterable	248 ± 25		
CARB 501	Filterable, multiple aerodynamic sizes	Stack Temperature	General – Particle Size	*http://www.arb.ca.gov/ testmeth/vol1/Meth_501.pdf*
ASTM D6831 - 05a	Filterable	Stack Temperature	Continuous PM	
ISO 9096 and EN 13284	Filterable			
VDI 2066 Part. 10 method and in the Norm EN 13284-1	Filterable 10 µm/2.5 µm			

measurement protocol (U.S. EPA, 2010f); over time this will help ensure greater consistency in stationary source emissions measurements. However, stationary source data currently available for $PM_{2.5}$ inventory purposes are based on non-standardized methods and procedures for PM_{10} and total filterable PM.

Due to the complex nature and variety of sources, regulatory and other standardized source PM methods are mainly designed to provide consistent results across a certain category of sources and not necessarily the entire universe of sources (Myers, 2006). Thus, compilations of source emissions measurements for total PM mass exist such as EPA's AP-42 (compilation of EPA's emission factors) and the U.S. National Emissions Inventory (NEI). However, none of these compilations reflects routine sampling required by regulation for all sources in the inventory. Measurement of carbonaceous PM components including BC or EC are not required as part of compliance testing. Such results are generally available only in the academic literature.

There are a large variety of methods for the measurement of PM mass from stationary sources, many of which measure both the filterable and condensable fractions of $PM_{2.5}$. These methods vary due to operational differences such as filtration temperature and conditioning and treatment of the different components of PM. Table A1-4 provides a list of commonly used stationary source methods and some examples of operational differences for determining PM mass from a variety of sources.

A1.3.2 Mobile Source Emissions Measurement Methods

Mobile sources consist of a diverse group of vehicles and engines, including light-duty gasoline vehicles, heavy-duty diesel trucks, gasoline-powered nonroad engines (e.g., lawnmowers, snowmobiles, recreational boats), nonroad diesel engines (e.g., excavators, locomotives, and marine vessels), and turbine and propeller-driven aircraft. Due to their diverse technologies and applications for highway and nonroad uses, there is considerable variability in BC emissions from mobile sources.

In the United States, particles in mobile source exhaust emissions are measured for compliance with PM emission standards and are expressed on a mass per unit work (g/bhp-hr) or mass per distance traveled (g/mi) basis. For regulatory certification, diesel exhaust particle emissions are measured using procedures described in 40 CFR Part 1065, which employs an engine dynamometer paired

with a dilution sampling system collecting samples on Teflon filters at temperatures of about 125°F (which reduces water condensation, yet allows for condensation of organic compounds). The filters are then conditioned at a specific temperature and humidity[3] and weighed. This procedure is commonly used to measure PM from non-diesel mobile sources for research purposes.

Mobile source emissions of BC are almost always measured as ECa. Unlike PM measurements, however, ECa measurements are not routinely taken and EPA does not presently have an official (or even recommended) EC measurement method for mobile sources for regulatory purposes. However, EPA does measure BC in its mobile source emissions characterization programs. There, BC is measured as a particulate matter (PM) component for both gasoline vehicles such as light-duty cars/trucks and diesel vehicles such as heavy-duty diesel trucks (up to 80,000 lbs. gross vehicle weight). It is also measured to a more limited extent from nonroad diesel and even gasoline engines (both 2-stroke cycle engines which have lubricating oil mixed with the fuel) and 4-stroke cycle engines. It is also measured in PM from locomotives, commercial marine, and aircraft.

Sampling temperature has a major effect on the quantity and even the composition of PM. PM emissions are collected on a filter from diluted exhaust. The general methodology for measuring mobile source PM involves diluting the vehicle exhaust with ambient air roughly at a 10/1 dilution ratio (although the dilution ratio varies greatly depending on engine operating mode) using a stainless steel dilution tunnel. The filter temperature is about 125°F, which is high enough to prevent water condensation on the filter from the copious amounts of water vapor present in vehicle exhaust formed from fuel combustion. This temperature also allows some condensation of the organic hydrocarbon compounds present in vehicle exhaust. This general method was developed and has been in use since about 1970 for both diesel and gasoline exhaust. This methodology is also used for EPA emission standards for exhaust from diesel engines including on-road trucks and more recently nonroad diesel engines. This measurement system, known as constant volume sampling of an exhaust stream that is diluted with varying amounts of dilution air, allows for accurate mass weighting of emissions over transient driving conditions (accelerations,

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[3] Mobile source measurements are made at 45%RH, while ambient measurements and many other source tests use 35%RH.

decelerations, steady-state cruise, and idle) where exhaust volume varies. In the ambient air though, vehicle exhaust is rapidly diluted to about 1,000:1 which results in somewhat different condensation of the hydrocarbon compounds into particulate.

The PM measurement method is more developed for diesel PM than for gasoline PM. Numerous studies have been done measuring diesel PM starting with the first EPA emission standard for the 1970 model year for visible smoke from diesel engines.

A1.3.3 Use of Emissions Source Test Data

Though carbonaceous components of PM are not systematically measured across all categories, both EPA and external researchers have measured these components from some source categories. EPA has compiled all available source emissions data into a database called SPECIATE, which currently contains 3,326 raw PM profiles. Because many of these measurements are drawn from research on emissions measurements, the data comes from a variety of sampling and analytical technologies (e.g., see Chang and England, 2004). Despite the uncertainties and limited size of the testing dataset compared to the total number of sources, the SPECIATE database represents the best compiled source of data available. A subset of these data was selected to characterize the source profiles for 15 source categories reported in Chapter 4, Figure 4-1.[4] The number of individual profiles by source category can be quite limited and sometimes only a single value was used. Similar summaries are available elsewhere (Chow et al., 2010a). Note that for some sources, the sum of BC and OC is less than 100% of $PM_{2.5}$ mass. The raw data used to compile Figure 4-1 is available in Table A1-5, along with the percent of estimated non-carbon PM and the OC/BC ratios.

As discussed in Chapter 4, however, EPA does not use any of these profiles for on-road vehicles, since the mobile MOVES model directly calculates EC emissions (U.S. EPA, 2010c). Mobile sources have more variability in emissions than stationary sources, because mobile-source EC varies with driving mode, specific model mix, and other conditions. MOVES is

designed to capture this variability. Currently, EPA still uses speciation profiles for nonroad diesel.

A1.3.4 Limitations of Source Emissions Measurement Methods

To estimate EC emissions for a specific source category, EC is typically assumed to be a specific fraction of $PM_{2.5}$ and then total $PM_{2.5}$ mass is used as the starting point. Thus, the measurement and/or estimate of $PM_{2.5}$ mass is one very important source of potential uncertainty. There are inconsistencies in the way $PM_{2.5}$ is measured among source categories, including in the approach for determining filterable and condensable mass, filter equilibration conditions (including laboratory relative humidity), temperature of testing, and dilution and related procedures for semi-volatile PM. Some of these variables can also affect the measurement of carbon components. Because of the way estimates of PM components are generated, both the PM and carbon-specific measurements can affect estimates of BC and OC emissions for a given source category.

Current $PM_{2.5}$ estimation methods based on PM_{10} and total filterable PM can produce variable results, particularly the methods that include condensable PM. For certain stationary source categories, this can produce measurement artifacts that can overestimate the condensable PM emissions by an order of magnitude.[5]

The use of scaling factors applied to filterable total PM and/or PM_{10} to generate estimates of $PM_{2.5}$ introduces additional uncertainty to the estimated emission rate (National Research Council, 2004).

Finally, the representativeness of a particular source profile based on a limited number of source tests is questionable, and derived composite profiles applied to a large number of sources is another source of uncertainty. For both PM and speciation test data, there are the related representativeness issues of tests conducted with actual vs. allowable emissions from the stacks and effluents; tests conducted at facilities of varying age and with different degree and type of controls; and tests affected by other operating conditions. These factors are often not taken into account when BC profiles are applied to $PM_{2.5}$ emissions. There are also potential issues regarding $PM_{2.5}$ mass closure (including treatment of volatile components, particle

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[4] Following the procedures of Reff et al. (2009), the raw profiles in SPECIATE were modified so that all EC was adjusted to be representative of the TOR analytical method and so that the sum of the species equals the $PM_{2.5}$ mass, if the raw profile was not provided in that format. To provide a more representative median among available test data, subsets of multiple source tests were first combined into a composite profile. Some uncertainty in expressing EC as a fraction of $PM_{2.5}$ may be related to the water content of $PM_{2.5}$ mass.

[5] Example artifacts include the potential conversion of sulfur dioxide gas into sulfate particles, affecting the reported PM mass.

bound water) and comparison of BC data based on different measurement methods.

A1.3.5 Critical Gaps and Research Needs in BC Emissions Sampling and Measurement Methods

In light of the limitations discussed above, the following research can help shed light on amounts of BC and LAC emitted by various sources and lessen the uncertainty in developing an inventory of emissions:

1. For all source measurements

- Understand how the source EC values relate to source BC values based on currently available techniques.

- Develop high-quality source profiles for sources that need improved characterization for BC, including research into how to quantify the additional light-absorbing components in the near-UV or UV spectrum that are referred to as BrC or, collectively with BC, as LAC.

- Develop a standard "BC" reference material and establish a standard measurement method to report source data as BC.

2. Stationary source measurements

- Understand the effect of varying source test methods and conditions on measured $PM_{2.5}$ and BC; and standardization of PM source testing procedures for filterable and condensable PM.

- Perform uncertainty analysis of all source profiles that exist in SPECIATE and how the total mass from the SPECIATE collection methods relates to the total mass from the methods used in the emissions inventory.

- Increase the quantity and quality of meta-data available in the databases that better explain how $PM_{2.5}$ and EC fractions were derived for the various sources in EPA's inventories.

3. Mobile source measurements

- Develop standard measurement methods for BC for both on-road and nonroad engines, especially diesels but also gasoline vehicles/engines.

- Establish more routine measurement procedures for BC, including ones that can measure these quantities over short time periods (even instantaneously) as well as over an entire driving cycle.

Table A1-5. Data Used to Prepare BC and OC Source Profile Box Plots (Chapter 4, Figure 4-1). OC/BC Ratios and OC+BC as Percent of PM Are Also Included. (Source: U.S. EPA)

Stats (%ile)	Agricultural Burning	Bituminous Combustion	Charbroiling	Distillate Oil Combustion	HDDV Exhaust	LDDV Exhaust	Natural Gas Combustion	Noncatalyst Gasoline Exhaust	Onroad Gasoline Exhaust	Prescribed Burning	ProcessGas Combustion	Residential Wood Combustion: HardSoft	SubBituminous Combustion	Wildfires	Wood Fired Boiler
OC Fraction of PM$_{2.5}$															
10th	0.30	0.02	0.34	0.25	0.18	0.20	0.25	0.84	0.30	0.65	0.05	0.39	0.02	0.47	0.33
25th	0.34	0.02	0.46	0.25	0.18	0.25	0.25	0.84	0.44	0.70	0.20	0.47	0.02	0.47	0.33
50th	0.40	0.03	0.70	0.25	0.18	0.32	0.25	0.84	0.55	0.71	0.35	0.53	0.03	0.56	0.33
75th	0.44	0.07	0.84	0.25	0.18	0.39	0.25	0.84	0.67	0.79	0.46	0.58	0.04	0.64	0.33
90th	0.56	0.12	0.87	0.25	0.18	0.44	0.25	0.84	0.75	0.83	0.57	0.68	0.04	0.64	0.33
N	9	3	4	1	1	4	1	1	10	7	3	12	2	2	1
BC Fraction of PM$_{2.5}$															
10th	0.05	0.01	0.00	0.10	0.77	0.31	0.38	0.01	0.09	0.01	0.10	0.01	0.02	0.03	0.14
25th	0.08	0.01	0.01	0.10	0.77	0.38	0.38	0.01	0.14	0.01	0.13	0.04	0.02	0.03	0.14
50th	0.10	0.02	0.02	0.10	0.77	0.53	0.38	0.01	0.19	0.02	0.17	0.06	0.04	0.09	0.14
75th	0.12	0.05	0.06	0.10	0.77	0.63	0.38	0.01	0.23	0.04	0.22	0.10	0.07	0.16	0.14
90th	0.13	0.08	0.10	0.10	0.77	0.64	0.38	0.01	0.34	0.07	0.27	0.12	0.07	0.16	0.14
N	9	3	3	1	1	4	1	1	10	7	3	12	2	2	1
OC:BC Ratios															
10th	5.9	1.9		2.5	0.2	0.6	0.6	59.9	3.3	54.3	0.5	27.6	1.0	14.5	2.4
25th	4.2	1.7	41.2	2.5	0.2	0.7	0.6	59.9	3.2	49.4	1.5	12.4	1.0	14.5	2.4
50th	4.1	1.6	31.1	2.5	0.2	0.6	0.6	59.9	2.9	38.6	2.1	9.4	0.7	5.9	2.4
75th	3.6	1.5	13.5	2.5	0.2	0.6	0.6	59.9	3.0	19.3	2.1	5.9	0.7	4.1	2.4
90th	4.3	1.4	8.5	2.5	0.2	0.7	0.6	59.9	2.2	12.0	2.1	5.5	0.7	4.1	2.4
BC+OC, as % PM															
10th	36%	3%	34%	35%	95%	51%	63%	85%	39%	66%	15%	40%	4%	50%	46%
25th	43%	4%	47%	35%	95%	63%	63%	85%	57%	72%	34%	51%	4%	50%	46%
50th	49%	4%	72%	35%	95%	86%	63%	85%	74%	73%	53%	58%	7%	65%	46%
75th	57%	12%	90%	35%	95%	102%	63%	85%	90%	83%	68%	68%	11%	80%	46%
90th	69%	20%	97%	35%	95%	108%	63%	85%	109%	90%	83%	81%	11%	80%	46%