**Title**

# Evaluating Past And Improving Present And Future Measurements Of Black Carbon Particles In The Atmosphere



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Arnold Schwarzenegger
*Governor*

# EVALUATING PAST AND IMPROVING PRESENT AND FUTURE MEASUREMENTS OF BLACK CARBON PARTICLES IN THE ATMOSPHERE

**PIER FINAL PROJECT REPORT**

*Prepared For:*

**California Energy Commission**
Public Interest Energy Research Program

*Prepared By:*
Lawrence Berkeley National Laboratory

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# Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Energy Commission), conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

The PIER Program strives to conduct the most promising public interest energy research by partnering with RD&D entities, including individuals, businesses, utilities, and public or private research institutions.

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*Evaluating Past and Improving Present and Future Measurements of Black Carbon Particles in the Atmosphere* is the final report for the Evaluating Past and Improving Present and Future Measurements of Black Carbon Particles in the Atmosphere project (contract number 500-02-004) conducted by Lawrence Berkeley National Laboratory. The information from this project contributes to PIER's Energy-Related Environmental Research Program.

For more information about the PIER Program, please visit the Energy Commission's website at www.energy.ca.gov/pier or contact the Energy Commission at 916□654□5164.

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# Abstract

Soot produced from the combustion of fossil fuel is a public health concern. The strongly light-absorbing black carbon (BC) core of soot contributes to global warming and regional climate change. This research evaluates the accuracy of BC measurements and estimates trends in ambient BC concentrations and BC emission factors from diesel vehicles in California. The aethalometer is a widely used instrument for measuring BC concentrations. Laboratory and field measurements show that temporally resolved BC measurements are subject to error because the response of the aethalometer diminishes as its sampling filter becomes increasingly darkened with black particles. The magnitude of the error depends on the relative amounts of light-absorbing BC and light-scattering particles sampled. A retrospective analysis of ambient BC concentrations is performed, based on archived measurements of coefficient of haze (COH). It is shown that COH levels can be converted to BC concentrations. Estimated annual BC concentrations for the San Francisco Bay Area, where diesel vehicle are the dominant BC source, decreased by a factor of ~3 from the late 1960s to the early 2000s despite a factor of ~6 increase in diesel fuel consumption. Derived diesel BC emission factors (expressed as mass of BC emitted per mass of diesel fuel consumed) decreased from ~13 to <1 g $kg^{-1}$ over this period. The decreases in ambient concentrations and emission factors are attributed to pollutant abatement policies in California. Further evaluation of BC measurement methods and analysis of BC trends at other locations in California is recommended.



Keywords: Black carbon (BC), aethalometer, coefficient of haze (COH), air quality, climate change, aerosol light-absorption, particulate matter, diesel vehicle, emission factor, pollution abatement

# Executive Summary

## Introduction

Fine particulate matter air pollution levels persistently exceed air quality standards in 12 counties in California. Fine particles, including soot produced from the combustion of diesel fuel, are a public health concern because they are small enough to deposit directly in the lungs. Additionally, the strongly light-absorbing black core of the soot, known as black carbon (BC), contributes to global warming and regional climate change.

Although emissions from power plants represent a small source of BC soot in California, the trend toward distributed energy resources in California will likely continue. Distributed energy resource equipment includes microturbines, conventional combustion turbine generators, and reciprocating engines, all of which may run on diesel fuel. Also, a portion of the backup utility generators used during power outages in California are diesel fueled.

An accurate method for measuring BC concentrations is requisite to understanding the effects of BC in the environment. It is widely recognized, however, that measurements of BC are highly uncertain. Moreover, BC measurements have been made only recently, so retrospective analyses of BC air pollution must rely on proxy historical data that can be related to modern BC measurements.

The aethalometer is a widely used instrument for measuring BC concentrations. The aethalometer filters particles from the air and periodically estimates the amount of BC in the particles by measuring the amount of light absorbed by the filtered particles. However, a growing body of evidence suggests that the calibration of the aethalometer is overly simplified, resulting in inaccurate measurements of temporally resolved BC concentrations.

The measurement of BC is similar to the measurement of coefficient of haze (COH), the index of particulate air pollution that was routinely monitored throughout California from the late 1960s to the early 2000s. The relationship between BC measured with the aethalometer and COH in California has not been explored. However, given the similarity in their measurement methods, the archived COH record may be useful for estimating and evaluating the history of BC concentrations in California.

## Purpose

This purpose of this project is to (1) improve the accuracy of BC measurements by evaluating the performance of the aethalometer in the laboratory and in the field, and (2) analyze the past history of BC in the atmosphere, including its relationship to air pollution abatement policies and emission sources, by establishing the relationship between modern BC measurements and archived measurements of COH in California.

## Project Objectives

The research team established the following project objectives.

- Evaluate the accuracy of temporally resolved measurements of BC made with the aethalometer through laboratory experiments using a specialized combustion apparatus–an inverted diffusion flame–developed at Lawrence Berkeley National Laboratory.
- Evaluate the performance of the aethalometer when sampling aerosols in the field, and compare with laboratory experiments.
- Determine the relationship between measured contemporary BC and historical COH through new measurements and analysis of existing data.
- Estimate the trend in ambient BC concentration in California from the late 1960s to the present using archived records of COH and reconcile with implemented pollution abatement policies and fuel consumption trends.

## Project Outcomes

Laboratory experiments, field sampling, and analysis of archived data sets were conducted to achieve the objectives of the project. The research produced the following outcomes.

- BC concentrations measured by the aethalometer diminish by a factor of approximately two throughout the aethalometer's measurement cycle–beginning with a pristine and ending with a particle-laden filter–when sampling freshly emitted BC soot.
- The filter-induced aethalometer sampling artifact was characterized in the laboratory and confirmed by field measurements of diesel emissions, including in a roadway tunnel.
- The aethalometer responds to light-scattering particles in addition to light-absorbing BC particles. Particle light-scattering may reduce the filter-induced sampling error in time-resolved BC concentrations, depending on the relative amounts of scattering and absorbing aerosols sampled.
- A modified aethalometer calibration is derived and recommended for time-resolved BC measurements when sampling highly light-absorbing aerosols, as in roadway tunnels. Away from the direct influence of BC sources, time-resolved aethalometer data are not significantly affected by the filter-induced measurement artifact.
- Time-resolved measurements of COH are subject to the same filter-induced measurement artifact as aethalometer measurements of BC. However, time-averaged measurements of BC and COH are not influenced by this sampling artifact.
- Collocated BC and COH measurements are linearly correlated, so historical COH measurements can be used to estimate past BC concentrations. The history of BC concentrations in the San Francisco Bay Area was estimated in this research.
- Ambient BC concentrations in the San Francisco Bay Area and, as a consequence, the population's exposure to BC is up to five times greater in winter than summer. This seasonality is caused by meteorologically driven changes in pollutant dispersion.

- BC concentrations are significantly lower on weekends than weekdays, which is consistent with decreased diesel traffic volume on weekends. The weekly cycle suggests that, in the Bay Area, diesel vehicle emissions are the dominant source of BC aerosol.
- Annual Bay Area average BC concentrations decreased by a factor of approximately three from the late 1960s to the early 2000s despite the six fold increase in diesel fuel consumption in California.
- Derived diesel BC emission factors (expressed as mass of BC emitted per mass of fuel burned) decreased from 13 g $kg^{-1}$ in the late 1960s to <1 g $kg^{-1}$ after 2000. The decrease is attributed to pollutant abatement policies, which led to improvements in engine technology and emission controls and to changes in diesel fuel composition.

## Conclusions

Time-resolved BC concentrations measured with the aethalometer are subject to error due to a filter-induced sampling artifact: a reduction in instrumental response as the sampling filter becomes increasingly particle-laden. A modified aethalometer calibration is derived and recommended for time-resolved BC measurements when sampling highly light-absorbing aerosols, as in roadway tunnels. Away from the direct influence of BC sources, time-resolved BC concentrations are not significantly affected by this measurement artifact. Time-averaged BC concentrations are generally unaffected by this sampling artifact.

Historical records of COH can be used to estimate the history of ambient BC concentrations. This research estimated the trend in BC emissions in the San Francisco Bay Area, where diesel vehicles are the main BC source. Despite a six fold increase in diesel fuel consumption from the late 1960s to the present, a three fold decrease in ambient BC concentrations occurred. This is because the BC emission factor for diesel vehicles decreased by an order of magnitude over this period. Successful emission control measures are credited with the reduced BC emission factors and ambient BC concentrations.

## Recommendations

The following are recommended areas for additional research.

- Evaluation of new methods of measuring light-absorbing BC aerosol, including the single particle soot photometer and cavity-ring down technique, using the approach developed in this research.
- Application of the laboratory BC generation method developed in this research to understand how mixing BC with other aerosol species (e.g., sulfates, organics) affects climate relevant aerosol properties: light absorption coefficient and aerosol single scattering albedo (the fraction of incident sunlight that is scattered instead of absorbed).
- Further evaluation of time-resolved aethalometer BC concentrations using a variety of atmospherically relevant aerosol mixtures.
- Evaluation of COH records and BC concentration trends, and reconciliation with trends in energy consumption and pollution controls, in other air basins in California.
- Additional collocated measurements of COH and BC at several monitoring sites in California to strengthen the needed for converting archived COH data to BC concentrations.

## Benefits to California

This project offers several benefits and meets the following PIER program objectives.

- **Providing safe energy.** Improving the accuracy of measured BC concentrations will aid epidemiologists and climate change scientists in understanding how BC soot affects public health and the environment.
- **Providing environmentally sound energy.** In addition to the direct effects of BC on climate and air quality, light extinction by BC impacts the chemistry that leads to the formation of other air pollutants, including ground-level ozone. Ozone is both a pervasive urban air pollutant and a potent greenhouse gas. Temporally and spatially resolved BC concentrations in California will be useful for examining how air quality and aerosol climate forcing have been influenced by past changes in energy technology, fuel consumption, and emission control strategies in California. Such information will provide regulators and other decision makers with a better foundation for planning the state's future energy supply.

# 1.0 Introduction

In California, air pollution levels for fine particulate matter persistently exceed air quality standards in 12 counties reaching from the central to the southern part of the state. Fine particles in the air are a public health concern because they are small enough to be inhaled and deposited directly in the lungs, where they can cause asthma and other health problems. One common type of fine particulate material, the soot produced from the combustion of diesel fuel, is considered a toxic air contaminant [CARB 1998] and a suspected carcinogen [Cal EPA 2005] in California. Black carbon (BC) is a major component of the soot produced during the combustion diesel fuel and has been used as an indicator of exposure to diesel soot [e.g., Fruin et al. 2004].

The BC in soot is the primary sunlight-absorbing particulate matter species. The absorption of sunlight by BC contributes to visibility degradation in polluted atmospheres [Horvath 1993] and to human-induced climate forcing in several ways [Houghton et al. 2001]. The heating of the atmosphere due to absorption of sunlight by BC exerts a direct global warming forcing that may be comparable to the forcing of the greenhouse gas methane [Jacobson 2001]. It has also been suggested that BC light absorption alters precipitation patterns and cloud lifetime [Menon et al. 2002; Ackerman et al. 2000], and decreases the reflectivity and increases the melting of snow and ice [Hansen and Nazarenko 2003].

Although emissions from power plants represent a small source of BC soot in California, the trend toward distributed energy resources in California will likely continue. Distributed energy resource equipment includes microturbines, conventional combustion turbine generators, and reciprocating engines, all of which may run on diesel fuel. Also, a portion of the backup utility generators used during power outages in California are diesel fueled.

Concern about the public health and climate effects of BC soot has prompted scientists and regulatory agencies to develop emission inventories, determine emission trends, and better understand the atmospheric chemistry and physics of BC. Many of these efforts require a method for measuring BC concentrations accurately. Moreover, BC measurements have been made only recently, so a retrospective analysis of BC air pollution must rely on historical proxy data that can be related to modern BC measurements.

## 1.1. Uncertainty in Measured BC Concentrations

Despite the importance of BC in the environment, quantifying BC has long been and remains an uncertain practice. BC concentrations are most commonly measured by analysis of quartz filter samples using thermal-optical analysis (TOA) methods or with the aethalometer. The aethalometer was developed in the mid 1980s [Hansen et al. 1984] and has since become the most widely used instrument for measuring temporally resolved BC concentrations. It has been used to measure BC in hundreds of studies, including at EPA Particulate Matter Speciation Network and California Regional Particulate Air Quality Study monitoring locations. Its widespread use can be attributed to the fact that it operates autonomously and provides highly time-resolved data. The concentration of BC in the atmosphere varies spatially and temporally, and is dependent on combustion sources, atmospheric transformations, and meteorology. As a result, the temporally resolved measurements provided by the aethalometer are desirable, for example in exposure assessment studies [Fruin et al. 2004]

In the aethalometer, the amount of light transmitted through a quartz filter is periodically measured while particles are collected, and the mass of BC on the filter (μg $cm^{-2}$) is calculated with Equation 1:

$$\mathbf{BC} = \frac{\mathbf{ATN}}{\boldsymbol{\sigma}} \qquad (1).$$

Light attenuation is calculated from the measurements of transmitted light intensity: ATN = $100 \cdot \ln(I_o/I)$, where intensities $I_o$ and I correspond to initial and subsequent filter conditions, respectively (e.g., blank and particle-laden). Use of a constant proportionality constant, □, also known as the attenuation coefficient, implies a linear relationship between the BC content and ATN of the particle-laden filter. The aethalometer estimates BC concentrations from intensity measurements using infrared light (880 nm) assuming an attenuation coefficient of 16.6 $m^2$ $g^{-1}$, which was derived partly from the work of Gundel et al. [1984]. The attenuation coefficient is not a property of the BC particles only; rather it is a property of the particle-laden filter. Sadler et al. [1981] demonstrated that the amount of light absorbed by BC particles is enhanced when they are collected in highly scattering quartz fibers.

A growing body of evidence suggests that the calibration of the aethalometer is overly simplified, which results in inaccurate measurements of temporally resolved BC concentrations. One uncertainty pertains to the assumption that the attenuation coefficient, □ in Equation 1, is constant as the filter darkens during the collection of light-absorbing particles. Using the aethalometer to measure the aerosol absorption coefficient (the product of the absorbing aerosol mass concentration and its mass absorption efficiency), Arnott et al. [2005] found that the extent to which particle light-absorption is enhanced diminishes as the aethalometer's filter darkens and, thus, becomes less highly scattering. This filter loading effect reported by Arnott et al. is consistent with the results of similar studies on the measurement of aerosol absorption coefficient with the aethalometer [Weingartner et al. 2003], other light transmission instruments [Petzold et al. 2005] and measurements with the particle soot absorption photometer (PSAP) [Virkulla et al. 2005; Bond et al. 1999]. These laboratory based results are supported by field observations indicating the tendency of BC concentrations to increase following the switching of the aethalometer's particle-laden filter with a pristine filter [LaRosa et al. 2002].

A related uncertainty pertains to the influence of particle light-scattering. By virtue of the scattering of light by the filter fibers in which the particles become collected, the light transmission measurement is sensitive primarily to the fraction of particle light extinction that is absorption rather than scattering. In calculating BC concentrations with Equation 1, the aethalometer neglects any influence of particle light-scattering. However, others have reported that the particle scattering of light away from the aethalometer's detector is not negligible and is erroneously interpreted as particle light absorption [Arnott et al. 2005] or acts to minimize the particle loading effect discussed above [Weingartner et al. 2003]. These reports are generally consistent with evaluations of other light transmission methods [Bond et al. 1999; Virkulla et al. 2005; Horvath et al. 1997], which indicate that the influence of particle light-scattering increases as the BC mass fraction decreases.

Strictly speaking, none of the studies cited above relate directly to the influence of filter loading and particle light-scattering on aethalometer measurements of BC. These studies evaluated measurements of aerosol absorption coefficient, not BC, using the aethalometer and similar instruments. However, BC is the primary light-absorbing aerosol species and, therefore, these studies provide a strong indication that aethalometer measurements of BC are subject to the same sources of error as measurements of absorption coefficient.

It is quite telling that the aethalometer has been evaluated for measuring absorption coefficient [Weingartner et al. 2003, Arnott et al. 2005], but a similarly rigorous evaluation of the aethalometer for measuring BC has not been presented. The most obvious reason for this is the existence of a reference measurement of absorption coefficient (i.e., a measurement that is accepted as being reliable, e.g., the difference of in-situ extinction and scattering coefficients) but the absence of an accepted reference measurement of BC concentration. One of the objectives of this research project is to overcome this barrier by using a specialized combustion apparatus, which facilitates a reference measurement of BC concentration that can be used to judge the accuracy of the aethalometer's measurement of BC.

## 1.2. Trends in BC Concentrations

Coal and diesel are the primary BC-producing fossil fuels. BC emissions depend on the combustion technology in addition to the amount and type of consumed fuels. BC sources (i.e., the combustion technologies) in the United States and other industrialized countries have changed markedly over time [Novakov et al. 2003]. In the past, inefficient coal combustion in the domestic and industrial sectors generated most of the anthropogenic BC emissions. In the second half of the past century, however, petroleum-based fuels replaced coal as the principal BC source in the United States.

Presently, diesel engines in the transportation sector are the main sources of BC in urban regions in the United States, and are thus responsible for much of the environmental impacts of BC. It is clear that diesel fuel consumption has increased in the United States over the past 30+ years [Cal BOE 2007]; and over this period air pollution abatement policies have resulted in changes to diesel technology. However, trends in ambient BC concentrations and diesel emission factors–which specify the mass of BC emitted for a given amount of fuel burned–are not well known. Thus, it is difficult to say how changing diesel technology has influenced ambient BC concentrations. Trends in ambient BC concentrations are not known because most BC measurements, such as those made with the aethalometer, lack long-term and regional coverage. BC emission factors could be combined with available diesel fuel consumption data to estimate diesel BC emissions. Published emission factors, however, differ by about a factor of ten [Cooke et al. 1999; Bond et al. 2004; Ito and Penner 2005]. Therefore, significant uncertainty accompanies estimates of ambient concentration trends based on published emission factors and fuel consumption data.

In lieu of direct measurements of BC, a retrospective analysis of BC air pollution could rely on proxy data, such as archived measurements of coefficient of haze (COH). COH was one of the earliest measures of particulate matter air pollution adopted by regulatory agencies. COH levels were monitored throughout California beginning in the late 1960s. Most, if not all, COH instruments have now been retired.

Like the modern measurement of BC made with the aethalometer, the COH measurement involved drawing a known volume of air through a white filter and periodically measuring the light (from an incandescent bulb) transmitted through the particle-laden filter to determine the aerosol optical density [Hemeon et al.,1953]. Whereas the aethalometer measures the mass concentration of BC ($\mu$g $m^{-3}$), the COH unit was defined as the amount of aerosol that produced an optical density of 0.01. COH values express aerosol concentrations in terms of COH per 1000 linear feet of sampled air. As the optical density of urban aerosols is largely due to light-absorbing black carbon, especially in the visible and near infrared wavelengths used to measure COH, COH values are highly correlated with BC concentrations simultaneously measured using filter-based optical methods [Cass et al. 1984; Allen et al. 1999]. The archived COH database could, therefore, be useful for estimating and evaluating the long term trend in BC concentrations in California.

## 1.3. Project Objectives

The goals of this research are to improve the accuracy of BC measurements by evaluating the accuracy of aethalometer measurements in the laboratory and in the field, and analyze the past history of BC in the atmosphere, including its relationship to air pollution abatement policies and emission sources, by establishing the relationship between modern BC measurements and archived measurements of COH in California. The research team established the following project objectives.

- Evaluate the accuracy of temporally resolved measurements of BC made with the aethalometer through laboratory experiments using a specialized combustion apparatus–an inverted diffusion flame–developed at Lawrence Berkeley National Laboratory.
- Evaluate the performance of the aethalometer when sampling aerosols in the field, and compare with outcomes of the laboratory experiments.
- Determine the relationship between measured contemporary BC and historical COH through new measurements and analysis of existing data.
- Estimate the trend in ambient BC concentrations in California from the late 1960s to the present using archived records of COH, and establish the relationship between ambient concentrations, source emissions, and implemented pollutant abatement policies.

# 2.0 Project Approach (Methods)

The project objectives were accomplished via laboratory experiments (tasks 1 and 2), field measurements outside of the research team's laboratory (task 3), and analysis of archived data (task 4).

- Task 1: Evaluation of temporally resolved aethalometer measurements when exposed to BC generated with a specialized laboratory flame.
- Task 2: Evaluation of temporally resolved aethalometer measurements when exposed to light-absorbing BC mixed light-scattering aerosol.
- Task 3: Assessment of the aethalometer in the field, exposed to typical combustion sources of soot
- Task 4: Determination and analysis of historical trends in BC concentration in California based on archived COH data.

## 2.1. Laboratory Experiments

### *2.1.1. Diffusion Flame*

A diffusion flame of methane and air in an inverted flow reactor was used to generate BC aerosols. The inverted flame used in this research is a slight modification of that developed by Stipe et al. [2005]. This flame has two remarkable features that made it ideally suited for evaluating the accuracy of aethalometer BC measurements. The first is its stability. There is no flickering or rotation a few seconds after ignition. Consequently, the particle generation rate and the concentration of particles produced are very stable, as illustrated below. The concentration of particles produced is readily varied by altering the fuel flow rate or the flow rate of particle-free dry air used to dilute the flame effluent. Whereas premixed methane/air flames are largely soot free, diffusion flames can be prolific sources of soot. As in a diesel engine, soot is produced due to a fuel rich environment in the diffusion flame. The second remarkable feature is the composition of the generated soot particles: they are composed of only light-absorbing BC, free of organic compounds. This, as discussed in section 3, allowed for unambiguous quantification of the BC concentration exposed to the aethalometer.

Two transmission electron microscope images obtained at different levels of magnification are shown in Figure 1. These illustrate that the particulate matter emitted from the diffusion flame consists of aggregated primary spherules of approximately 20 to 30 nm in diameter, with an onion-shell nanostructure typical of diesel soot [Hays and VanderWal 2006; Wentzel et al. 2003]. The diffusion flame produces particle sizes in the range of those generated by modern engines, which makes it a good source of particles for air quality studies [Stipe et al. 2005]. The generated particle size distribution is unimodal and approximately log normal with a peak mobility diameter of 130 nm [Kirchstetter and Novakov 2007].

Climate-relevant characteristics of the BC particles with the diffusion flame are described in Kirchstetter and Novakov [2007], including the aerosol single scattering albedo (SSA, the fraction of incident radiation that is scattered instead of absorbed) and mass absorption efficiency. Bond and Bergstrom [2006] noted that measurements of combustion aerosol SSA range from 0.15 to 0.28, including 0.17 for diesel soot. The SSA of the diffusion flame BC (0.15 @ 530 nm) is at the low end of this range, and close to the value for diesel soot. The mass absorption efficiency of the BC from the flame (8.5 $m^2$ $g^{-1}$ @ 530 nm) is consistent with most values reported for freshly emitted light-absorbing carbon (7.5 ± 1.2 $m^2$ $g^{-1}$) [Bond and Bergstrom 2006].

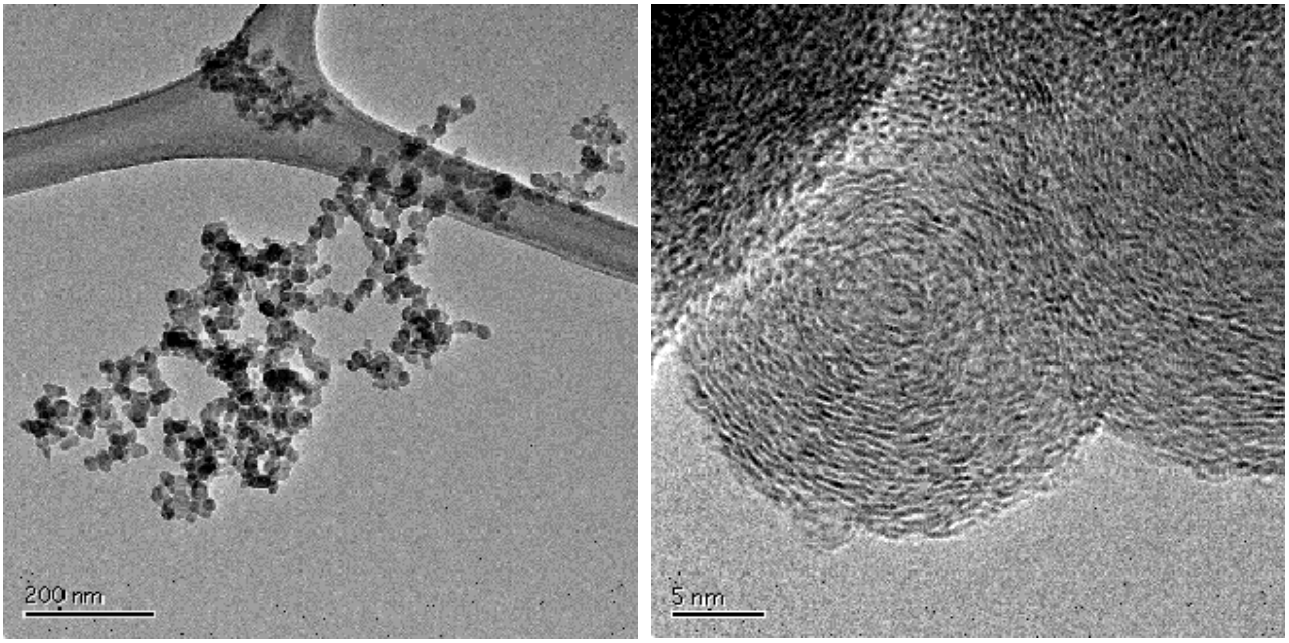



**Figure 1. Transmission electron microscope images of particulate matter generated with the diffusion flame and deposited on lacey carbon coated grids, provided courtesy of Randy VanderWal's group at NASA's Glenn Research Center**

### *2.1.2. Particle Sampling*

BC particles in the diluted effluent of the flame were drawn into an anodized aluminum manifold that accommodated sampling with several instruments. In experiments to evaluate the response of the aethalometer to mixed composition aerosols, BC from the flame was mixed with sodium chloride (NaCl), which is a purely light-scattering material. The NaCl aerosol was produced by atomizing water solutions of NaCl with a Collison nebulizer (BGI Inc, model CN24). The atomized NaCl was injected into the air that diluted the diffusion flame effluent, which dried (to a relative humidity of 22%) the atomized spray and created external mixtures of BC and salt without altering the production of BC from the flame.

Particle light absorption and scattering coefficients, respectively, were measured with a three wavelength particle soot absorption photometer (PSAP. a modification of the Radiance Research PSAP operating at 467, 530 and 660 nm, as described by Virkulla et al. [2005]) and a single wavelength integrating nephelometer (Radiance Research, 530 nm, model M903). The aethalometer (Magee Scientific) was used to measure BC concentrations; BC concentrations presented in this manuscript are based on measurements using the standard 880 nm aethalometer channel. A COH monitor [Hemeon et al. 1953] was included for comparison of BC and COH measurements. The nephelometer was calibrated using zero air and Freon-22. The calibration of the PSAP in this research is discussed in Kirchstetter and Novakov [2007].

Particle samples were collected with quartz fiber filters (Pallflex 2500 QAT-UP) for subsequent determination of BC content and quantification of the BC concentration exposed to the aethalometer. Quartz filters were baked at 800ºC for six hours prior to use to remove carbonaceous impurities.

### 2.1.3. Analysis of Particle Samples

The carbon content of quartz filter samples was measured using a variation of the TOA method originally described by Novakov [1981]. Filter samples were heated at a constant rate of 40°C $min^{-1}$ from 50 to 700°C in a pure oxygen atmosphere. The evolved carbon was fully oxidized over a platinum coated ceramic catalyst maintained at 800°C, and the resultant carbon dioxide was measured with a nondispersive infrared analyzer (LI-COR, model 7000). The intensity of light transmitted through the sample was continuously monitored during analysis. The light source was a white light emitting diode and the detector was a spectrometer (Ocean Optics, model S2000). The recovery of the TOA instrument was determined to be 100% ± 5% by analysis of prepared samples of potassium hydrogen phthalate and glucose.

Selected samples of particulate matter were deposited onto lacey carbon coated grids and analyzed with a high resolution transmission electron microscope at NASA's Glenn Research Center [VanderWal et al. 2004].

## 2.2. Field Measurements

The accuracy of temporally resolved BC measurements was evaluated in two settings outside of the research team's laboratory. This purpose of these additional evaluations was to determine if the outcomes of the laboratory experiments were consistent with observations when sampling aerosols from combustion sources that are atmospherically relevant, most notably diesel engines.

### 2.2.1. Diesel Engine Emissions in a Chamber

The accuracy of BC concentrations measured with the aethalometer when exposed to diesel soot was evaluated in a 116 $m^3$ experimental chamber equipped with a diesel engine. The chamber was operated by the Department of Environmental and Occupational Health Sciences at the University of Washington. Diesel soot was emitted into the chamber from a turbocharged direct-injection 5.9-liter Cummins B-series Diesel engine (6BT5.9G6, Cummins, Inc., Columbus, IN), which is comparable to engines used in delivery trucks and school buses. The engine drove a 100 kW generator connected to an electric load bank (Simplex, Springfield, IL), and the load applied to the running engine was set to 75 kW. The engine fuel was highway grade diesel No 2 un-dyed, which is commonly used in delivery vehicles. The particle mass concentration inside the chamber (55±1 $\mu g\ m^{-3}$) was controlled during the experiments. Additional details of the experimental setup are provided by Jimenez et al. [2006].

### 2.2.2. Diesel Vehicle Emissions in a Roadway Tunnel

Aethalometer measurements were also evaluated when sampling motor vehicle exhaust in the Caldecott tunnel. Located east of San Francisco Bay on state highway 24, the Caldecott tunnel connects Oakland, Berkeley and San Francisco with Contra Costa County. It is comprised of three traffic bores, each about 1100 m long, and has a roadway grade of 4.2%. Additional details of the tunnel are available elsewhere [Kirchstetter et al. 1999a].

The research team located two aethalometers in the ventilation duct of southernmost bore of the tunnel, which carries both light-duty gasoline and heavy-duty diesel vehicles. Measurements were made weekdays between 1200 and 1800 h, when vehicles traveled uphill (i.e., under load) toward Contra Costa County. Previous apportionment calculations indicate that diesel vehicles contribute significantly to BC concentrations in the tunnel despite comprising a small fraction of the vehicle population [Kirchstetter et al. 1999a].

## 2.3. Analysis of Archived COH Data

The research team analyzed archived measurements of COH dating from 1967 to 2003. COH data collected at approximately 100 sites throughout California are available from the California Air Resources Board [CARB 2006]. This project considered measurements at 11 sites in the San Francisco air basin with daily average COH records most (65 to 96%) of the days in this 37 year period: Concord, Fremont, Livermore, Napa, Pittsburg, Redwood City, Richmond, San Jose, San Rafael, Santa Rosa, and Vallejo. COH data from other sites in this air basin with limited coverage during this period (4 to 34% of daily averages available) was excluded from the analysis.

# 3.0 Project Outcomes (Results)

## 3.1. Laboratory Evaluation of the Aethalometer

### *3.1.1. Chemical Composition of the Diffusion Flame Soot*

Carbon and optical thermograms are presented in Figure 2 for a sample of particles from the diffusion flame. These show rates of evolved carbon and optical attenuation, respectively, as the sample temperature is increased (i.e., dC/dT and dATN/dT) during TOA. For the purpose of this illustration, ATN was computed such that a peak in the optical thermogram indicates the removal of light-absorbing material. A single peak in the carbon thermogram at high temperatures indicates that all of the carbon in the sample is refractory. The complete overlap of the carbon and optical thermograms indicates that the carbon is entirely light-absorbing and, thus, is composed entirely of BC and free of organic compounds. There is additional evidence that the flame-generated particles do not contain significant amounts of organic compounds. The optical thermogram does not drop below the baseline (i.e., ATN ≥ 0) because light-absorbing char was not formed during the analysis. Char is often the product of the pyrolysis of organic compounds if they are present in the sample [Watson et al. 2005]. Furthermore, no carbon evolves and charring does not occur when the sample is heated in an inert helium atmosphere (not shown). These observations demonstrating that the soot emitted from the flame is composed entirely of BC are consistent with the results of Stipe et al [2005], who reported that the flame-produced particles do not have measurable $C_2$ or CH emission peaks (common to organic compounds) when analyzed using laser fragmentation-fluorescence spectroscopy.

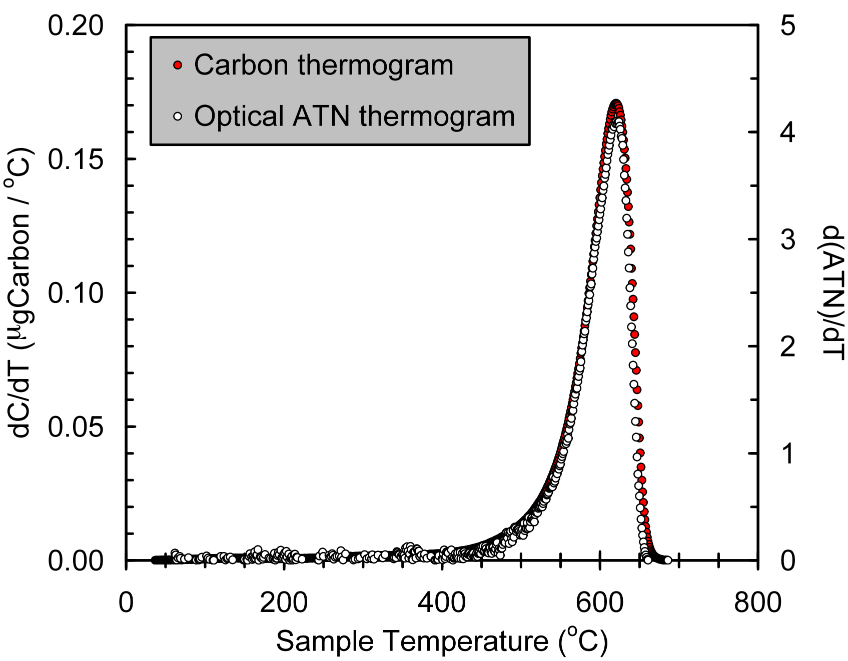



**Figure 2. Carbon, dC/dT, and optical, d(ATN)/dT, thermograms from the thermal-optical analysis of diffusion flame particles**

The absence of organic compounds in the flame particles is significant because organic compounds complicate the quantification of BC. In atmospheric particles, organic compounds are almost always present with BC, which generally leads to large uncertainties in the TOA determination of BC [Watson et al. 2005]. In contrast, the quantification of BC is straightforward if the particles do not contain organic compounds–the mass of BC in the sample is equal to the total carbon in the sample. In the case of the inverted flame particles represented in Figure 2, the BC content is obtained by integrating the entire carbon thermogram. Therefore, in this research project, TOA provides the reference measurement of BC, which is used to determine the accuracy of BC measurements made with the aethalometer.

### *3.1.2. Exposure to BC Aerosol*

BC concentrations measured by the aethalometer when sampling a constant concentration of BC from the diffusion flame are presented in Figures 3a and b. The constant BC concentration during this 6 hr experiment is indicated by the stable BC concentrations measured by TOA and the constant values of scattering coefficient and SSA. The repeating trend of decreasing BC concentrations erroneously reported by the aethalometer indicates a measurement artifact. The BC concentration reported by the aethalometer at the start of its measurement cycle is 1.8 times larger than it is at the end of its measurement cycle (i.e., when $ATN_{880nm}$ ~ 75 or transmission ~ 0.47).

The aethalometer reported decreasing BC concentrations not because the concentration or the mass absorption efficiency of the BC changed during the experiment, but because the attenuation coefficient of the collected BC decreased as the aethalometer's filter became increasingly darkened with these light-absorbing particles. One explanation of this effect is that as the filter becomes darker, the internal reflection of light diminishes and, thus, the extent of the enhancement in the amount of light absorbed by the collected BC particles diminishes. Arnott et al. [2005] reported the same phenomenon in similar terms. Weingartner et al. [2003] described the particle loading effect somewhat differently, namely as a particle shadowing effect, which is interpreted as meaning that some particles physically block light from reaching other particles. Note that when aethalometer measurements were extended beyond the default maximum $ATN_{880nm}$ of 75, reported BC concentrations decreased only marginally more than is shown in Figure 3a before leveling off. For example, when the measurement cycle was extended to $ATN_{880nm}$ = 150, the BC concentration at the start of the cycle was 2.2 times larger than the concentration at the end of the cycle. This factor of 2.2 is comparable to factor of 2.14, which is amount that aethalometer's filter enhances particle light absorption [Weingartner et al. 2003], which gives credence to the phenomenological explanation of Arnott et al.

This particle loading effect is not specific to aethalometer's measurement; rather it is common to all light transmission measurements using highly scattering filters. The same particle loading effect was observed in the collocated COH measurements in these experiments (not shown). Additionally, measurements with the PSAP and the more recently developed multi-angle absorption photometer have been calibrated to account for a nonlinear instrumental response to particle loading [Bond et al. 1999; Virkulla et al. 2005; Petzold et al. 2005].

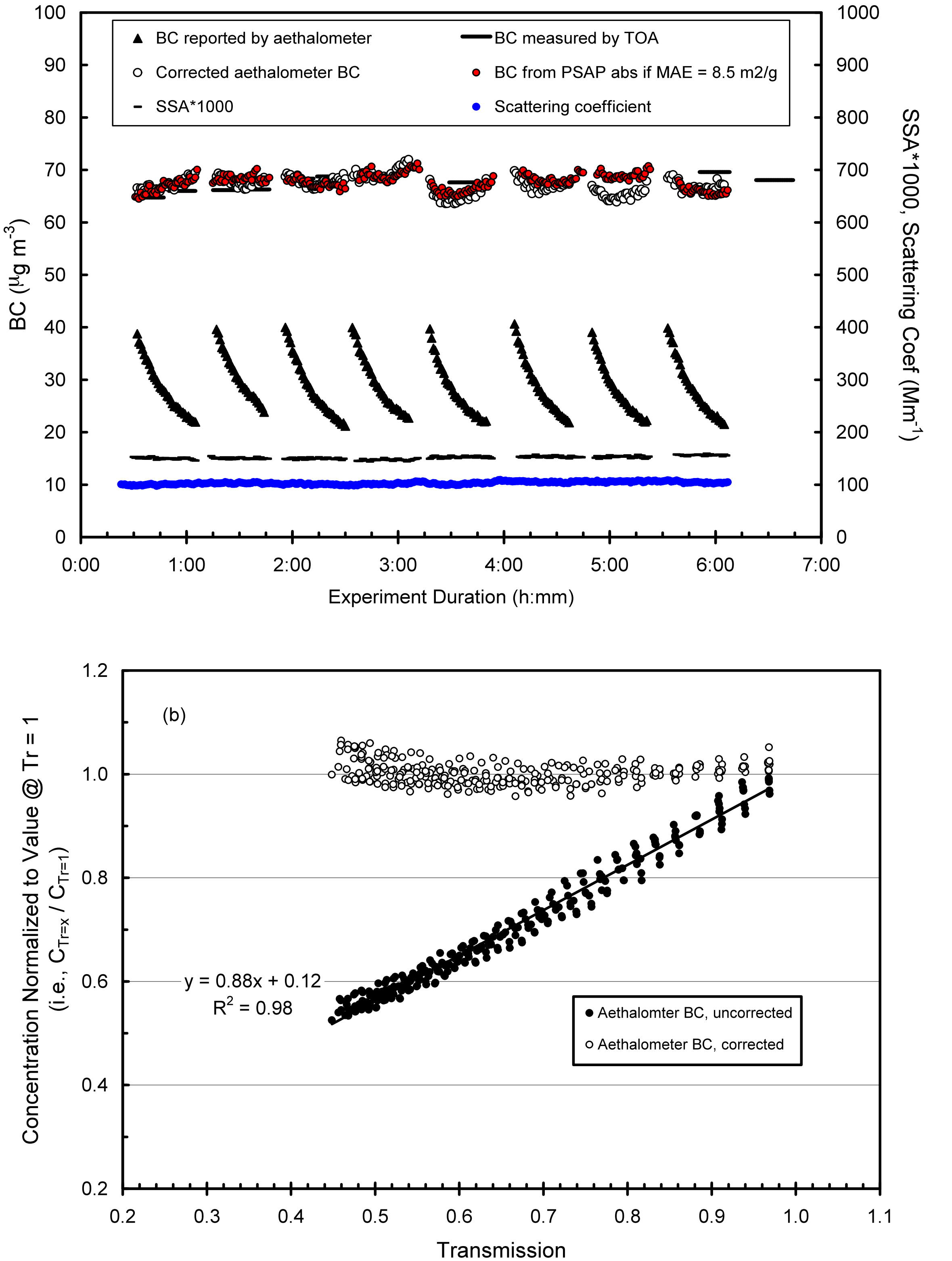



**Figure 3. (a) Measured aerosol properties during a 6 hr experiment to evaluate the accuracy of time-resolved BC concentrations measured with the**

**aethalometer (b) Normalized BC concentrations before and after correction for the aethalometer's measurement artifact**

As shown in Figure 3b, the BC concentrations reported by the aethalometer decreased linearly with decreasing filter transmission. This suggests a simple means of correcting reported concentrations, namely using Equation 2:

$$BC = \frac{BC_o}{0.60(0.88Tr + 0.12)} = \frac{ATN}{10(0.88Tr + 0.12)} \quad (2).$$

In Equation 2, BC and $BC_o$ are the corrected and uncorrected BC concentrations (on the filter, in $\mu g\ cm^{-2}$), Tr is the measured filter transmission, and the constants 0.88 and 0.12 are the slope and intercept of the regression line shown in Figure 6b. (The factor 0.60 reduces the manufacturer's attenuation coefficient ($\square_{880nm}$) from 16.6 to 10 $m^2\ g^{-1}$, as discussed below.) Transmission can be computed directly from the ATN measured by the aethalometer: Tr = exp(-ATN/100). As the aethalometer's filter collects BC and Tr decreases from unity, the denominator of Equation 2 decreases, which accounts for the decreasing attenuation coefficient. Applying Equation 2 to the BC concentrations reported by the aethalometer (i.e., to $BC_o$) largely eliminated the influence of particle loading on the attenuation coefficient, as evidenced by the nearly constant corrected BC concentrations shown in Figures 3a and b.

Note that at the start of a new aethalometer cycle when Tr = 1, Equation 2 reduces to BC = $BC_o$/0.60. The factor 0.60 reduces the manufacturer's attenuation coefficient ($\square_{880nm}$) from 16.6 to 10 $m^2\ g^{-1}$ and was applied in order to increase the aethalometer BC concentrations to equal those determined by TOA, as shown in Figure 3a. The difference between the manufacturer's □ (16 $m^2\ g^{-1}$) and the value derived in this research (10 $m^2\ g^{-1}$) is at least partly due to the collection of BC when the aethalometer initializes its filter between measurement cycles. During this period of several minutes, the aethalometer continues to draw sample air through its filter. In experiments like those conducted in this research, a significant loading of the filter occurs in this period of time, which begins to reduce the enhancement of particle light absorption before the aethalometer reports any measurements. To demonstrate this effect, in this research the sample air was occasionally filtered to remove all particles during the period of filter initialization in the aethalometer. In these cases, measured BC concentrations were 20 to 40% higher, depending on the BC concentration established during the experiment, compared to BC concentrations measured after initialization without particle filtering. Similarly, when comparing sampling events in highly polluted (particle-laden laboratory experiments) and relatively clean (ambient) air, Arnott et al. [2005] concluded that the pre-loading of the aethalometer's filter during its initialization period affects measured absorption coefficients.

### *3.1.3. Exposure to Mixed Composition Aerosol*

The observations discussed above suggest that aethalometer data is subject to a significant measurement artifact when the aerosol SSA is low, as it is for the BC from the diffusion flame. This is relevant when close to combustion sources such as diesel-fueled motor vehicles (as illustrated in section 3.2), however, the BC mass fraction is much smaller, and thus the SSA is much higher, for ambient aerosols than the diffusion flame BC. The SSA of ambient aerosols is generally in the range 0.80-0.95.

Experiments with mixed composition aerosol were conducted to evaluate the aethalometer's response to aerosol mixtures characterized by increasing SSA (i.e., increasing light-scattering material relative to light-absorbing BC). Results summarized in Figure 4 indicate that the aethalometer exhibits the greatest particle loading effect when sampling aerosols with the lowest SSA (between 0.15 and 0.62), and exhibits an insignificant particle loading effect when sampling aerosols with SSA as high as 0.86. These results indicate that the aethalometer responds to light-scattering aerosol in addition to light-absorbing BC aerosol, and that the response to particle light-scattering minimizes the particle loading effect. Moreover, it suggests that in many ambient environments, the particle loading effect may not be an issue. Similar to these results, Sheridan et al. [2005] demonstrated that the particle loading effect on the PSAP is less pronounced at higher SSA. Likewise, Turner et al. [2005] reported that the particle loading effect is not always evident in ambient data sets.

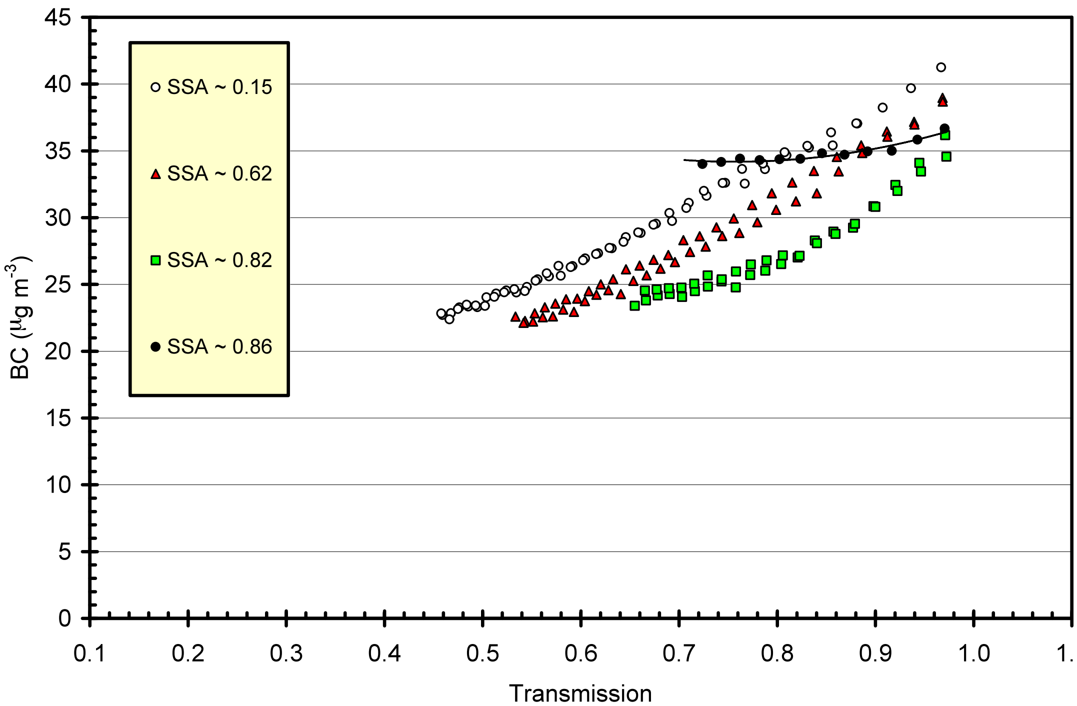



**Figure 4. Reported BC concentrations versus the loading of the filter (expressed as transmission) in the aethalometer when sampling aerosols of constant BC concentration and increasing SSA**

The research team concludes that the modified aethalometer calibration presented above (i.e., Equation 2) should be applied only in situations where the aerosol SSA is known to be below about 0.6, such as near BC emission sources. At the other end of the spectrum, when it can be verified that the aerosol SSA is greater than about 0.85, time-resolved aethalometer need no correction for the particle loading effect. This conclusion is not ideal because the measurements of light scattering and absorption coefficients needed to estimate the aerosol SSA are not always available when the aethalometer is in use. The authors recommend additional research to more closely examine the transitional response of the aethalometer as the aerosol SSA is increased incrementally from very low (e.g., 0.15) to very high (e.g., 0.98) values.

## 3.2. Field Evaluation of the Aethalometer

Linear regression of the time-resolved aethalometer measurements during exposure to diesel engine exhaust in the experimental chamber yielded the same relationship derived in the laboratory experiments discussed above (i.e., the same line in Figure 3b). While the aerosol SSA of the diesel exhaust was not quantified during the chamber measurements, it is likely that the aerosol SSA was very low (within the range 0.15 to 0.28 [Bond and Bergstrom 2006]).

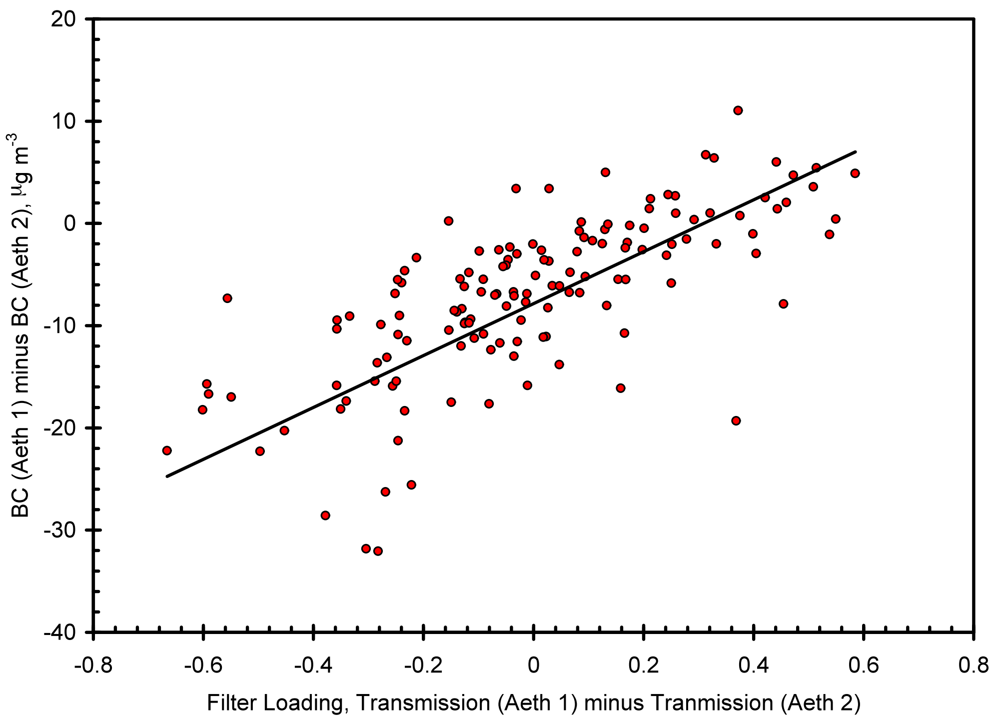



**Figure 5. Comparison of BC concentrations measured by two collocated aethalometers inside the Caldecott roadway tunnel**

Whereas in the chamber and laboratory experiments the BC concentration was held constant, the BC concentration inside the Caldecott tunnel was highly variable. This is because of the variation in vehicle pollutant emission rates and air mixing (i.e., pollutant dilution) inside the tunnel. As a consequence, time-resolved data from the aethalometer varied more because of real variation in BC concentration then because of the effect of particle loading on the aethalometer's response. Therefore, the research team deployed two aethalometers side-by-side in the tunnel to evaluate if there was discernable particle loading effect. In this case, differences between the BC concentrations measured with each aethalometer and the extent to which the sampling filters were particle-laden in each aethalometer were compared. This comparison is shown in Figure 5, which clearly illustrates that the measured BC concentrations differed most when the difference in filter loading was greatest (i.e., when the difference in light transmission through the sampling filters, $Tr_1$–$Tr_2$, was greatest). The measured aerosol SSA in the tunnel, like in the chamber and laboratory experiments, was also quite low (0.20). The correction that resulted in the least discernable particle loading effect (i.e., a slope of zero in Figure 5) was 0.84Tr + 0.17, which is practically the same correction derived in the laboratory experiments (Equation 2).

The measurements of diesel engine and motor vehicle exhaust corroborate the laboratory results, meaning that the aethalometer's response to the flame-generated BC accurately reflects the aethalometer's response to "real" BC aerosols–those that are generated from the primary sources of BC to the atmosphere.

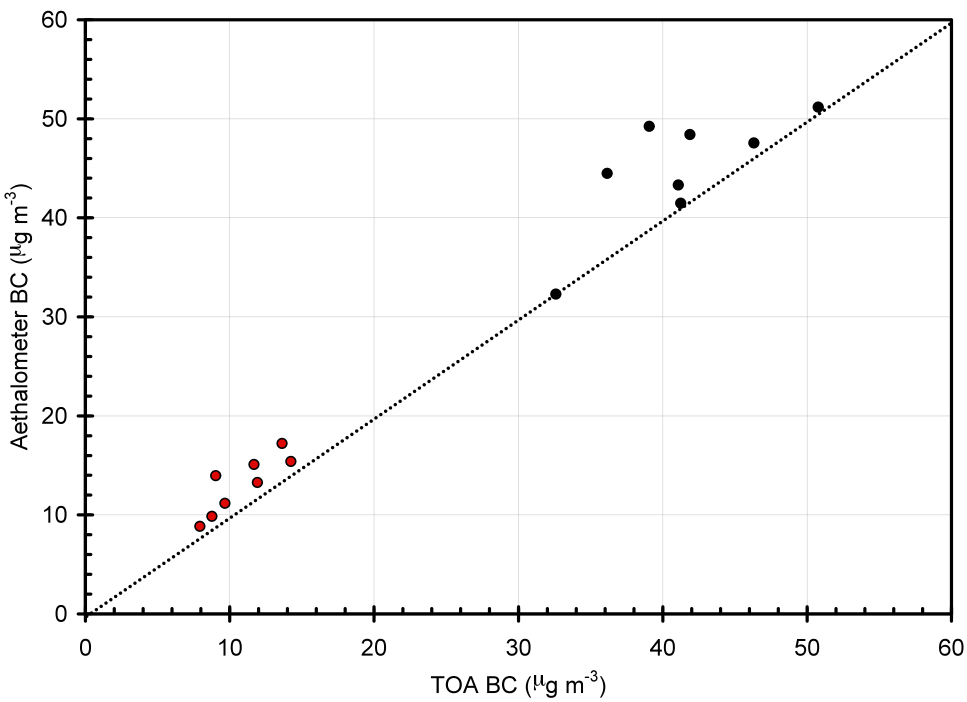



**Figure 6. Comparison of 2-hr average BC concentrations in the Caldecott tunnel measured by an aethalometer and TOA analysis of collected samples of particles**

It is worth noting that while the particle loading effect affects the accuracy of time-resolved BC concentrations, time-averaged BC concentrations are not affected by the particle loading effect. The reason is that time-averaged BC concentrations correspond to several sampling cycles of the aethalometer, and thus the particle loading effect is essentially "averaged out." The length of the averaging period depends on the frequency of sampling cycles, which depends on how quickly the filter becomes the darkened with particles and triggers a filter advance, which depends on the sampled BC concentration. In a heavily polluted environment, such as the Caldecott tunnel, the aethalometer may cycle several times in one hour. Figure 6 show relatively good agreement between 2-hr average aethalometer and TOA BC concentrations, which illustrates this point. In typical outdoor settings, cycling occurs less frequently, and therefore, a daily averaging period may be required to eliminate the particle loading effect. Certainly monthly data, as considered in section 3.3, are immune to this measurement artifact.

## 3.3. Analysis of Archived COH Data and Estimation of BC Trends

This analysis first determines the relationship between COH and BC and then discusses trends in BC concentrations over different time scales–weekly, seasonal and long term–which reveal information about predominant emission sources, the population's exposure to primary particulate matter, and the impact of technology changes on ambient concentrations and emissions.

### *3.3.1. The Relationship between COH and BC*

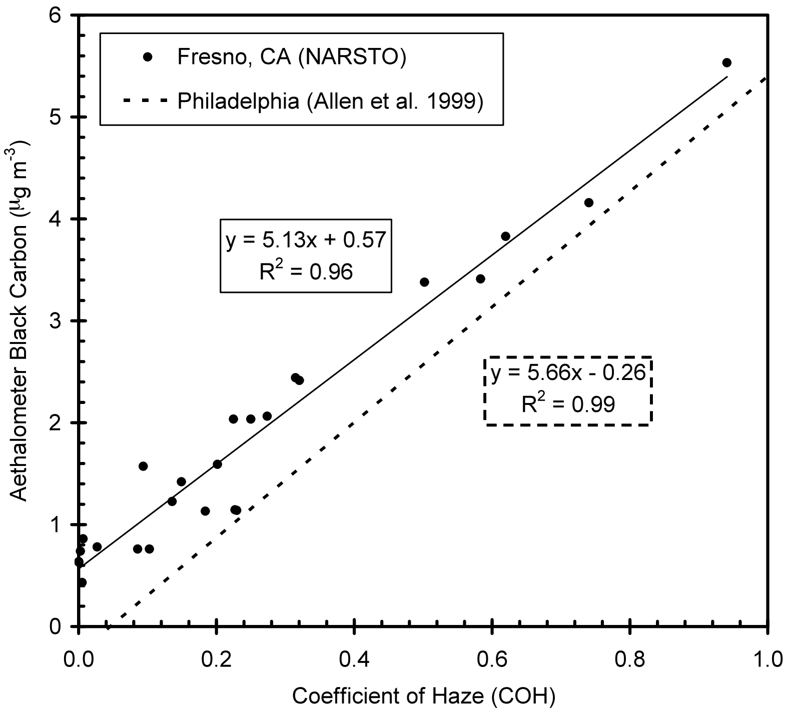



**Figure 7. Collocated measurements of BC (aethalometer) and COH in Fresno, CA during the North American Research Strategy for Tropospheric Ozone study, and the linear regression line reported by Allen et al. [1999] for measurements in Philadelphia, PA**

The basis for using COH data to estimate trends in BC stems from the similarity in the techniques used to measure both species, as noted above. Allen et al. [1999] reported a strong linear relationship between COH levels and aethalometer BC concentrations in Philadelphia during the summer of 1992: BC (□g $m^{-3}$) = 5.66·COH – 0.26 with $R^2$ = 0.99. As shown in Figure 7, COH and BC measurements recorded in Fresno, California (just south of the San Francisco air basin) during the North American Research Strategy for Tropospheric Ozone study [NARSTO, 2007] from December 1999 to August 2002 yield a similar linear relationship: BC (□g $m^{-3}$) = 5.13·COH + 0.57 with $R^2$ = 0.96. While additional collocated COH and BC measurements would strengthen the relationship, the measurements in Philadelphia and Fresno both indicate that the relationship is linear. In this research, the average slope (5.4) was used to estimate BC from measured COH, and the offset was disregarded because it was in one case slightly positive and in the other slightly negative.

### 3.3.2. Weekly Variations in BC Concentrations

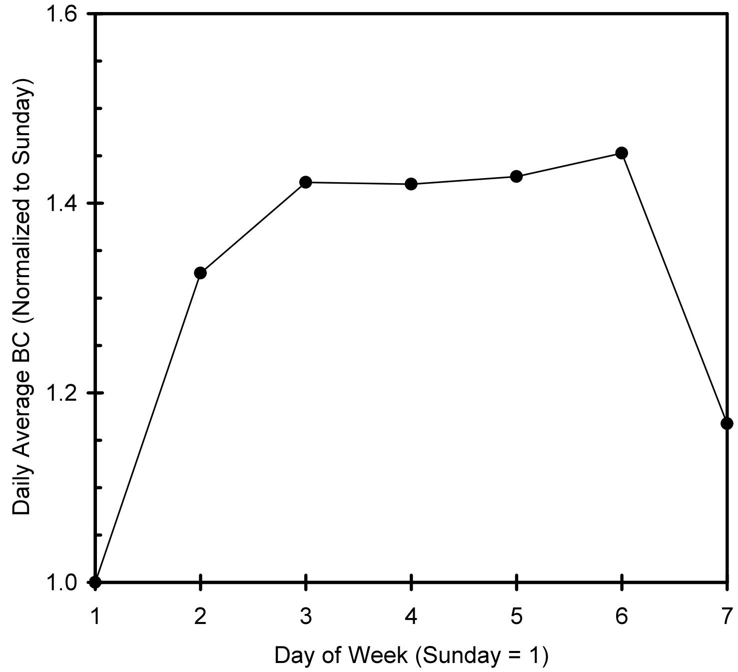
BC concentrations in the Bay Area show a pronounced weekly cycle, as illustrated in Figure 8a. On average, over the entire 37 year observation period, weekday concentrations were about 1.4 times larger than Sunday concentrations. This weekly pattern is attributed to a reduction in diesel traffic on weekends, particularly on Sundays. Dreher and Harley [1998] report a marked reduction in diesel fuel use and diesel vehicle traffic on Sundays in the San Francisco Bay Area. Thus, diesel vehicle emissions are a dominant source of BC emissions in the Bay Area.

The weekly cycle in BC concentrations is more pronounced in the summer months when BC concentrations are lowest than in the winter when BC concentrations are highest (Figure 8b). For example, in July and August the average weekday BC concentration is 1.8 times higher than it is on Sunday, while in December and January, this ratio decreases to 1.2. This seasonal difference in the weekly cycle is at least partly due to pollutant dispersion, which is discussed in more detail in section 3.3.3. In the summertime when pollutants are more effectively dispersed and the build up of pollutants in the air basin is at a minimum, the ambient BC concentration is more sensitive to the weekly cycle in emissions than it is in the wintertime, when the baseline pollution level rises due to reduced dispersion. Reduced pollutant dispersion in the wintertime also results in carryover of the previous day's emissions, as evidenced by the monatomic increase in BC concentration during weekdays in January and February (Figure 8b).

### 3.3.3. Seasonal Variations in BC Concentrations

BC concentrations in the Bay Area show pronounced maxima in winter and minima in summer, and this seasonal trend persisted throughout the 37 year period of observation, as illustrated in Figures 9a and b. Wintertime maxima are up to five times higher than summertime minima. A similar seasonal trend was observed by Cass et al. [1984] at seven locations in the Los Angeles area (1958 to mid-1981). These authors attributed the seasonality in concentration to decreased atmospheric dispersion (i.e. low inversion height) during the late fall and early winter rather than to temporal changes in the emissions from the principal BC sources, namely diesel vehicles. Diesel vehicle emissions of BC were considered to be approximately constant throughout the year. Likewise, Glen et al. [1996] demonstrated that meteorologically driven dispersion, not seasonal variation in emissions, caused the same seasonal trend in carbon monoxide concentrations in several urban centers, including the San Francisco air basin.

The similarity in the seasonal variation in Bay Area BC concentrations to the studies cited above suggests that this seasonality is also governed by changes in inversion height (i.e., pollutant mixing volume), as opposed to changes in emissions. Strong inter-site correlations among concentration time series measured at different Bay Area sites, in addition to weak seasonality


1.6
1.4
1.2
1.0
Daily Average BC (Normalized to Sunday)
1
2
3
4
5
6
7
Day of Week (Sunday = 1)

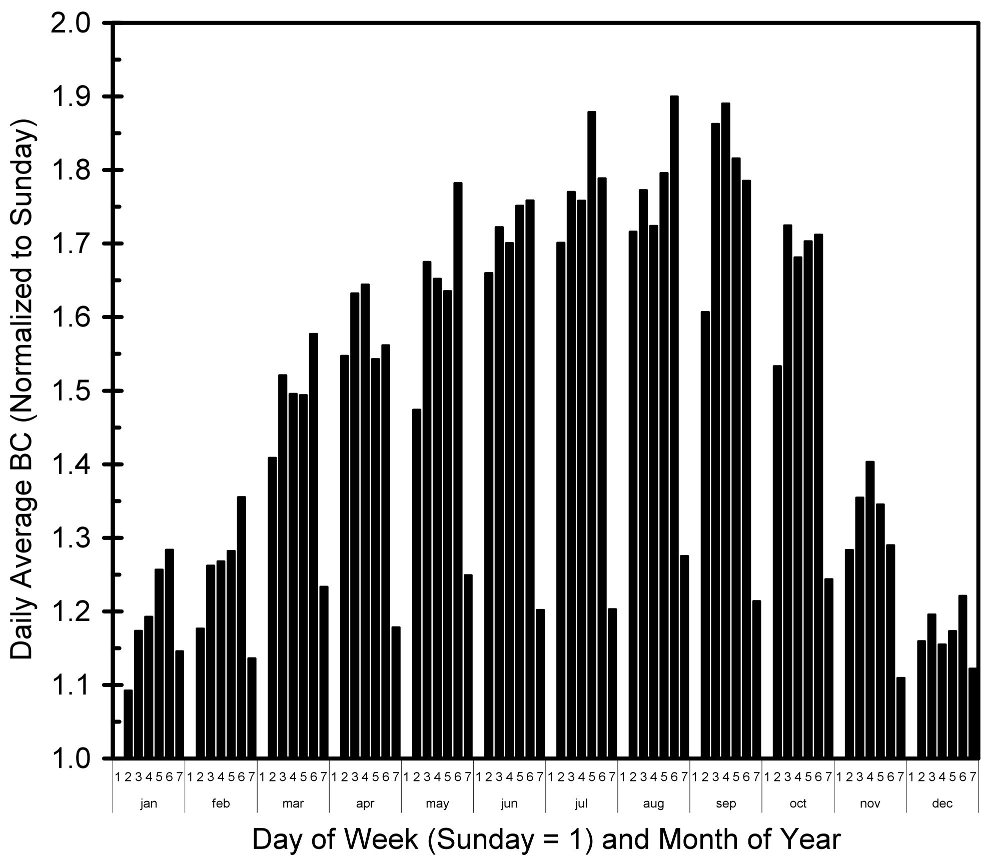
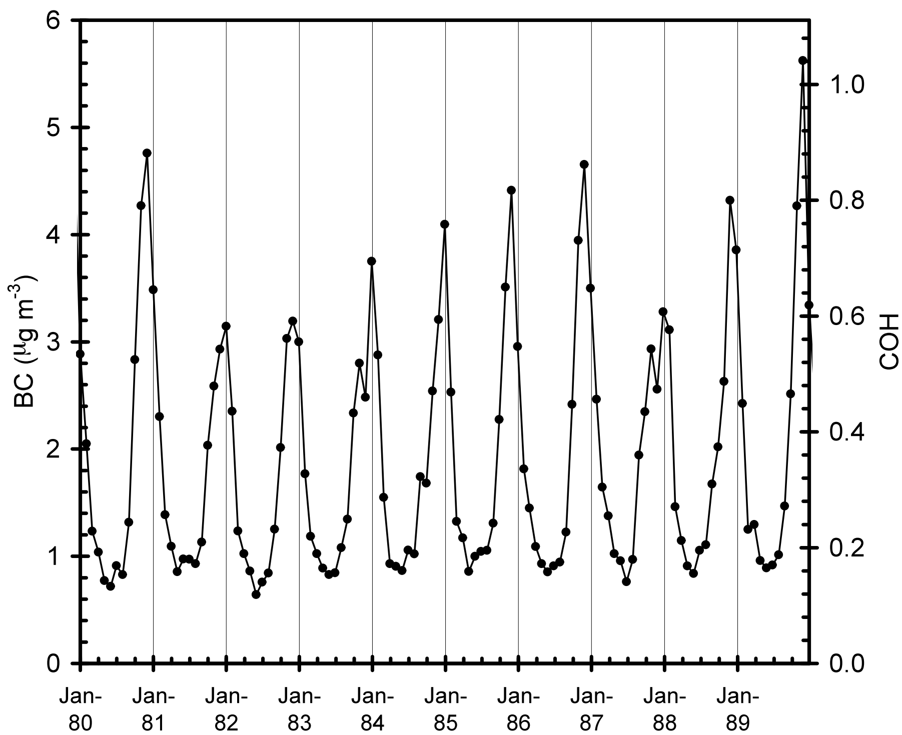

2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Daily Average BC (Normalized to Sunday)
jan
feb
mar
apr
may
jun
jul
aug
sep
oct
nov
dec
Day of Week (Sunday = 1) and Month of Year

**Figure 8. Average Bay Area BC concentrations by day of week over the period 1967 to 2003 (a) averaged over the whole year and (b) averaged for each month of the year**



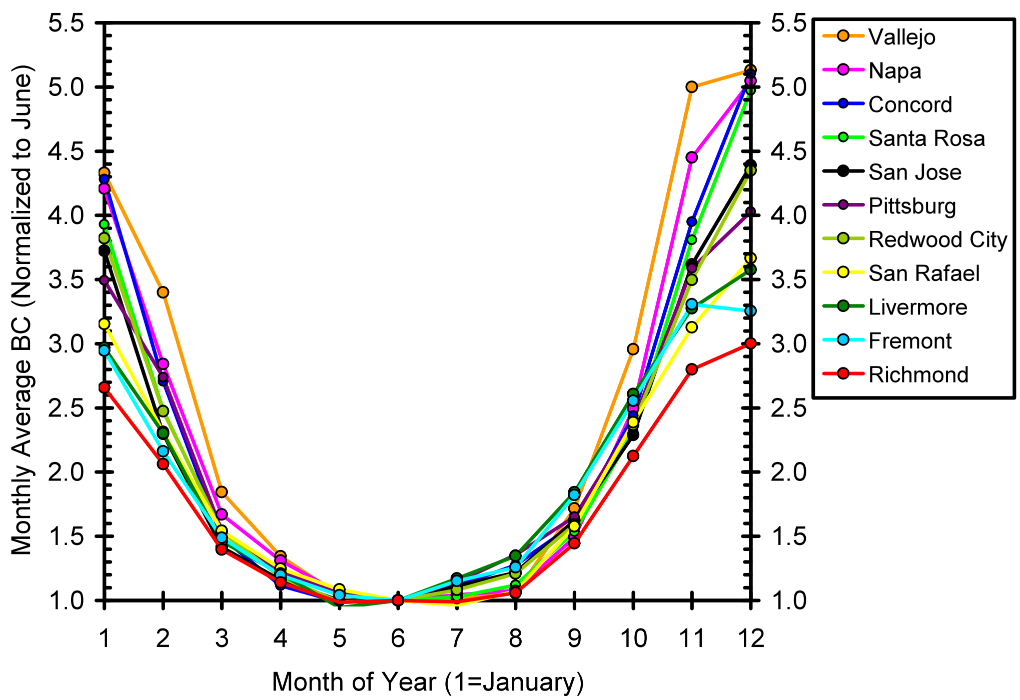



**Figure 9. (a) Monthly BC concentrations (COH also shown) averaged for 11 locations in the San Francisco Bay area from 1980 to 1990 (b) Annual trend in BC over the period 1967-2003 at each location; monthly concentrations are normalized to June**

in diesel fuel consumption [Dreher and Harley 1998], supports this conclusion. Linear correlation coefficients ($R^2$) among pairs of sites, some separated by as far as 140 km, average 0.74 and are generally between 0.65 and 0.85 (Table 1). Such high correlations indicate that changes in inversion height are area-wide and occur synchronously at these Bay Area sites.

The similarity in the seasonal variation in Bay Area BC concentrations to the studies cited above suggests that this seasonality is also governed by changes in inversion height (i.e., pollutant mixing volume), as opposed to changes in emissions. Strong inter-site correlations among concentration time series measured at different Bay Area sites, in addition to weak seasonality in diesel fuel consumption [Dreher and Harley 1998], supports this conclusion. Linear correlation coefficients ($R^2$) among pairs of sites, some separated by as far as 140 km, average 0.74 and are generally between 0.65 and 0.85 (Table 1). Such high correlations indicate that changes in inversion height are area-wide and occur synchronously at these Bay Area sites.

Note that the seasonality in BC concentrations is opposite that of photochemical air pollutants, most notably ozone. In the summertime, increased solar insolation (and thus photochemistry) and higher temperatures lead to peak ozone concentrations. While the population's health risk due to ozone exposure is at a maximum in the summertime [Tager et al. 2005 and references therein], its exposure-related risk to (toxic and carcinogenic) diesel emissions, as indicated by increased BC concentrations, is at a maximum in the wintertime, primarily because of the meteorology of this region. Increased residential wood burning in the winter months [Fairley 2006] also contributes BC emissions to the air basin, though this source tends to be a much greater emitter of organic carbon than BC [Bond et al. 2004].

| | Redwood City | Livermore | Richmond | San Jose | San Rafael | Pittsburg | Fremont | Santa Rosa | Napa | Vallejo | Concord |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Redw.Citty | X | | | | | | | | | | |
| Livermore | 0.62 | X | | | | | | | | | |
| Richmond | 0.64 | 0.64 | X | | | | | | | | |
| San Jose | 0.84 | 0.66 | 0.67 | X | | | | | | | |
| S. Raf. | 0.66 | 0.52 | 0.63 | 0.69 | X | | | | | | |
| Pittsburg | 0.69 | 0.68 | 0.73 | 0.72 | 0.67 | X | | | | | |
| Fremont | 0.75 | 0.70 | 0.74 | 0.78 | 0.68 | 0.78 | X | | | | |
| S. Rosa | 0.73 | 0.57 | 0.73 | 0.81 | 0.68 | 0.70 | 0.75 | X | | | |
| Napa | 0.82 | 0.66 | 0.77 | 0.86 | 0.74 | 0.80 | 0.78 | 0.87 | X | | |
| Vallejo | 0.69 | 0.68 | 0.78 | 0.77 | 0.71 | 0.73 | 0.77 | 0.74 | 0.79 | X | |
| Concord | 0.84 | 0.73 | 0.80 | 0.89 | 0.77 | 0.81 | 0.81 | 0.85 | 0.86 | 0.85 | X |

**Table 1. Regression coefficients ($R^2$) among monthly BC concentrations at locations throughout the San Francisco air basin (1967-2003)**

### *3.3.4. Historical Trends in BC Concentrations and Diesel Vehicle Emission Factors*

Annual average BC concentrations in the Bay Area over the 1967 to 2003 period are shown in Figure 10a. Annual motor vehicle diesel fuel sales for California [Cal BOE 2007] are also shown for comparison. While diesel fuel use, the main source of BC emissions increased by a factor of ~6, BC concentrations decreased by a factor of ~3 over the same period. (The estimated BC concentration in 1967 is likely biased high because COH data were available only for winter months at many of the active sampling locations that year.) The contrast in the trends in BC concentration and diesel fuel use is striking, especially beginning in the early 1990s when BC concentrations began markedly decreasing despite sharply rising diesel fuel consumption. This contrast illustrates that technology changes that reduce BC emission factors–the amount of BC emitted per mass of diesel consumed–have been successful.

Estimated diesel vehicle BC emission factors for the period 1968–2003 are reported in Figure 10b. These are based on the ratio of the time series of BC mass concentration to fuel consumption (Figure 10a). These ratios are a relative measure of the diesel BC emission factors, assuming that ambient concentrations are proportional to BC emissions from this source. The absolute emission factors in each year, *i*, are derived by normalizing to the ratio for 1997 and the BC emission factor of 1.3 g BC per kg of diesel fuel consumed, which was measured in a Bay Area roadway tunnel [Kirchstetter et al. 1999a], using the following equation:

$$\mathrm{BC\,(g\,kg^{-1})}_i = \left(\frac{\text{BC conentration}}{\text{Diesel Consuption}}\right)_i \cdot \left(\frac{\text{Diesel Consumption}}{\text{BC conentration}}\right)_{1997} \cdot 1.3\,\mathrm{g\,kg^{-1}} \qquad (3).$$

Application of Equation 3 assumes that only diesel vehicles contribute to ambient BC concentrations. While the weekly cycle in BC concentration described above points to diesels as the dominant BC emitter, other sources likely contribute non-negligibly. Gasoline engines are most likely the next largest source of BC. While the BC emission factor from diesel engines is approximately 40 times larger than from gasoline engines, roughly six times more gasoline than diesel fuel is sold in California [Kirchstetter et al. 1999a]. Based on BC emission factors, fuel use and fuel properties reported in Kirchstetter et al., gasoline engines contribute about 14% of on-road BC emissions, which are neglected in this analysis. Additionally, it is assumed that the fuel consumption trend for the San Francisco Bay Area is the same as the statewide trend because the fuel data are not available for separate regions of the state. While these assumptions add uncertainty to the diesel BC emission factors (Figure 10b), they provide an estimate of the emission factor trend that is otherwise unavailable.

Estimated BC emission factors decreased by an order of magnitude, from about 13 g $kg^{-1}$ in 1968 to less than 1 g $kg^{-1}$ in 2003. The continued decrease beyond the BC emission factor measured in 1997 is in agreement with more recent emission factor measurements in the Bay Area [Ban-Weiss et al. 2007]. These emission factors can be compared with other values often cited in

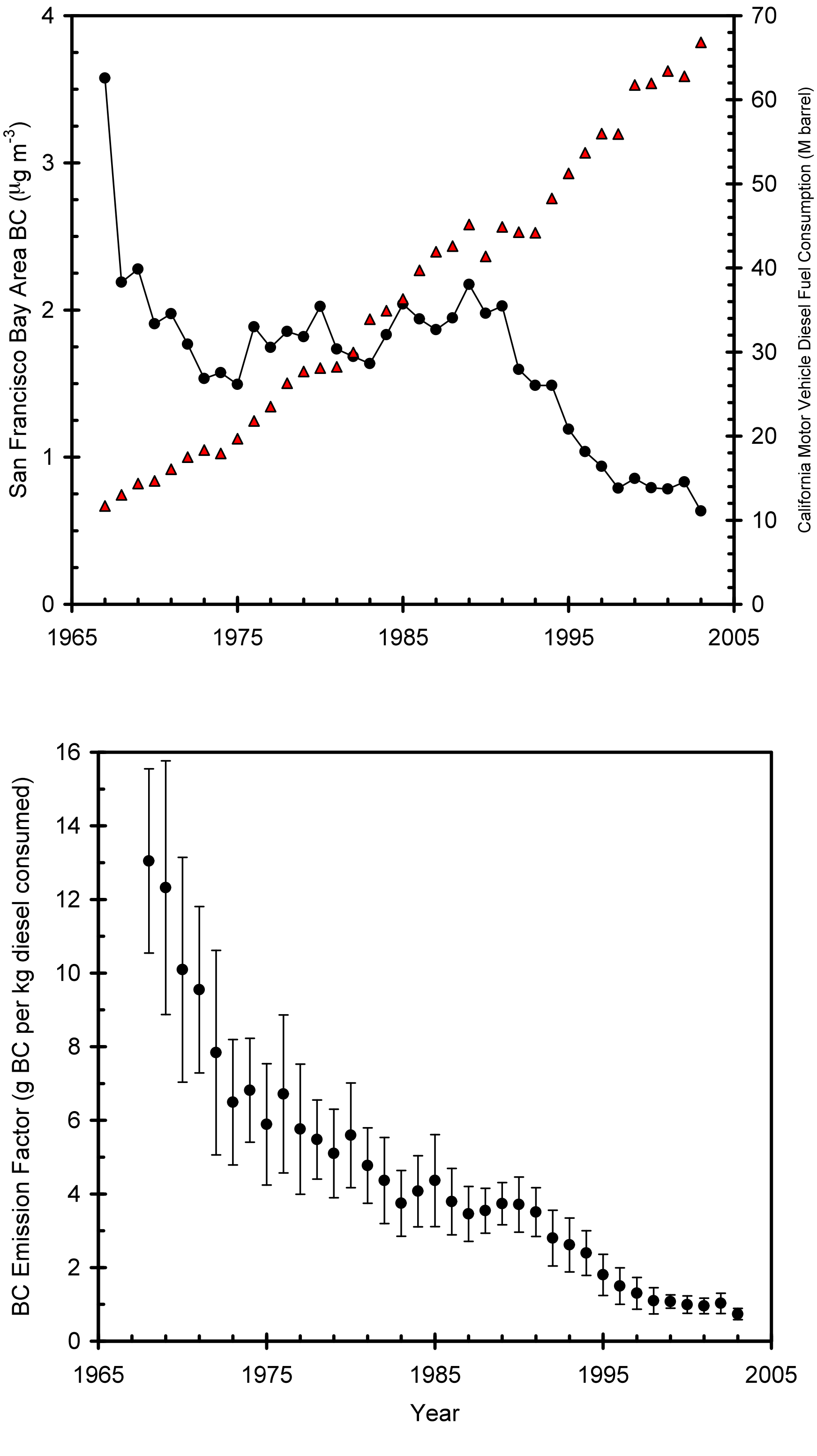



**Fig 10. Annual trends in (a) San Francisco air basin annual BC concentrations (•) and California vehicular diesel fuel sales (Δ) and (b) estimated diesel BC emission factor. The error bars reflect the**

**standard deviation over sampling sites in the annual average BC concentration.**

emission inventories. Cooke et al. [1999] and Ito and Penner [2005] derived diesel BC emission factors of 2 and 1.15 g $kg^{-1}$, respectively, for diesel technology in developed regions of the world. Bond et al. [2004] reported BC emission factors ranging from 1.3 to 3.6 g $kg^{-1}$ for diesels in the contemporary transportation sector. These values agree best with our estimates for the period from 1990 to 1995.

The data in Figure 10 provide an estimate of how BC emission factors and ambient concentrations changed from 1967 to 2003. Three periods are evident these time series: (i) pre 1975 when a marked decrease in emission factor and ambient concentration occurred, (ii) 1975–1990, a period with a gradual decrease in emission factor and approximately level ambient BC concentration, and (iii) post 1990 when the emission factor and ambient concentration again decreased markedly. These three time segments qualitatively correspond to the following major milestones in emission control policy described by Lloyd and Cackette [2001]. The first diesel emission controls were directed to visible smoke reduction. Federal smoke emission standards were introduced in 1970. Diesel fuel composition, including sulfur content reduction, changed concurrently with smoke controls. These changes roughly correspond to the pre-1975 decreases in ambient BC concentrations and emission factors. Diesel particulate matter emissions, of which BC is the majority, were subsequently controlled mostly through improvements of the engine design. On road heavy-duty diesel particulate matter emission standards were first implemented in California in 1973. Statewide diesel particulate matter emissions were reduced as the new vehicles replaced older more polluting vehicles. These developments correspond to the more gradual decreasing trend in BC emission factor between 1975 and 1990.

Several factors may have contributed to the significant BC concentration and emission factor decrease after 1990. In the 1990s, many urban transit buses were retrofitted with oxidation catalysts to reduce PM and, consequently, BC emissions. In 1993, California limited the sulfur content in diesel fuel to 500 ppm compared to a pre-regulation average of 2500 ppm and limited aromatic hydrocarbon content to 10%. The data in Figure 10 clearly indicate that BC concentrations and emission factors were significantly reduced following the 1993 regulations. Reducing the aromatic fuel content is expected to reduce BC emissions. The reduction in fuel sulfur may also have reduced BC emissions because high fuel sulfur promotes soot formation. Sulfur oxides produced in combustion catalyze the recombination of O and OH radicals, reduce the degree of acetylene oxidation and thus enhance the formation of soot precursors (see for example [Smith, 1981] and references therein). McKenzie et al. [2005] showed that lowering the fuel sulfur content from 500 ppm to 50 ppm greatly reduced emissions of polycyclic aromatic hydrocarbons (PAH) from heavy-duty diesel buses. Although BC emissions were not measured in that study, similar reduction of BC is expected because PAH and BC are both products of incomplete combustion and are highly correlated [Westerdahl et al. 2005].

It is relevant to note that, similar to the observations discussed above, a combination of vehicle emission control technology and fuel reformulation resulted in significant reductions in gas-phase emissions of nitrogen oxides, volatile organic compounds and carbon monoxide from gasoline vehicles in California [Kirchstetter et al. 1999b]. Lastly, analysis of COH levels in New Jersey from 1971 to 2001 [NJ DEP, 2007] indicate a decrease in BC emissions comparable to the decrease observed in this study, suggesting that air quality in other urban regions of the country has also improved due to air quality regulations.

# 4.0 Conclusions and Recommendations

The accuracy of temporally resolved BC concentrations measured with the aethalometer was evaluated in laboratory experiments and field measurements. The following conclusions were drawn.

- BC concentrations measured by the aethalometer diminish by a factor of approximately two throughout the aethalometer's measurement cycle–beginning with a pristine and ending with a particle-laden filter–when sampling freshly emitted BC soot.
- The filter-induced aethalometer sampling artifact was characterized with a specialized combustion apparatus in the laboratory and corroborated by field measurements in a roadway tunnel dominated by strongly light-absorbing particulate matter from motor vehicles, and by measurements of particulate matter from a diesel engine in an experimental chamber.
- The aethalometer responds to light-scattering particles in addition to light-absorbing BC particles. Particle light-scattering may reduce the filter-induced sampling error in time-resolved BC concentrations, depending on the relative amounts of scattering and absorbing aerosols sampled.
- A modified aethalometer calibration is derived and recommended for time-resolved BC measurements when sampling highly light-absorbing aerosols (SSA $< 0.60$). Away from the direct influence of BC sources (SSA $> 0.85$), time-resolved BC concentrations are not significantly affected by the filter-induced measurement artifact.
- Time-resolved measurements of COH are subject to the same filter-induced measurement artifact as aethalometer measurements of BC. However, time-averaged measurements of BC and COH are not influenced by this sampling artifact.

The research team recommends the following areas of related research.

- A closer examination of the transitional response of the aethalometer as the aerosol SSA is increased incrementally from very low (e.g., 0.15) to very high (e.g., 0.98) values using a variety of atmospherically relevant aerosol mixtures.
- An evaluation of new methods of measuring light-absorbing BC aerosol, including the single particle soot photometer and cavity-ring down technique. These methods are being adopted by the scientific community, particularly in climate change research, without prior extensive calibration.
- The application of the laboratory BC generation method employed in this research to understand how mixing BC with other aerosol species (e.g., sulfates, organics) affects climate relevant aerosol properties: light absorption coefficient and aerosol SSA

Trends in BC concentrations in the San Francisco Bay Area were estimated and BC emission factors for diesel vehicles were derived from an analysis of archived COH data covering the period from 1967 to 2003. The following conclusions were drawn.

- Collocated BC and COH measurements are linearly correlated, and historical COH measurements can be used to estimate past BC concentrations.

- Ambient BC concentrations in the San Francisco Bay Area and, as a consequence, the population's exposure to BC is up to five times greater in winter than summer. This seasonality is caused by meteorologically driven changes in pollutant dispersion.
- Weekend BC concentrations are significantly lower than weekday BC concentrations, consistent with decreased diesel traffic volume on weekends. The weekly cycle suggests that, in the Bay Area, diesel vehicle emissions are the dominant source of BC aerosol.
- Annual Bay Area average BC concentrations decreased by a factor of approximately three from the late 1960s to the early 2000s despite the factor of six fold increase in diesel fuel consumption in California.
- Derived diesel BC emission factors (expressed as mass of BC emitted per mass of fuel burned) decreased from approximately 13 g $kg^{-1}$ in the late 1960s to <1 g $kg^{-1}$ after 2000. This decrease is attributed to the success of pollutant abatement policies that led to improvements in engine technology and emission controls and changes in diesel fuel composition.

The research team recommends the following areas of related research.

- Evaluation of COH records and BC concentration trends, and reconciliation with trends in energy consumption and pollution controls, in other air basins in California.
- Additional collocated measurements of COH and BC at several monitoring sites in California to strengthen the relationship needed for converting archived COH data to BC concentrations.

## 4.1. Benefits to California

This project offers several benefits and meets the following PIER program objectives.

- **Providing safe energy.** Improving the accuracy of measured BC concentrations will aid epidemiologists and climate change scientists in understanding how BC soot affects public health and the environment.
- **Providing environmentally sound energy.** In addition to the direct effects of BC on climate and air quality, light extinction by BC impacts the chemistry that leads to the formation of other air pollutants, including ground-level ozone. Ozone is both a pervasive urban air pollutant and a potent greenhouse gas. Temporally and spatially resolved BC concentrations in California will be useful for examining how air quality and aerosol climate forcing have been influenced by past changes in energy technology, fuel consumption, and emission control strategies in California. Such information will provide regulators and other decision makers with a better foundation for planning the state's future energy supply.

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# 6.0 Glossary

| | |
|---|---|
| ATN | attenuation: a measure of amount of light passing through the aethalometer's sampling filter, proportional to the logarithm of the amount of transmitted light |
| BC | black carbon: the primary light-absorbing aerosol species that contributes to global warming and regional climate change |
| COH | coefficient of haze: a measure of the amount of particulate air pollution, used extensively in California beginning in the late 1960s until the early 2000s, measured with a filter-based optical technique similar to that used in the contemporary aethalometer |
| MAE | mass absorption efficiency: a measure of how much light is absorbed per unit mass of an aerosol material; dividing the aerosol absorption coefficient by the MAE gives the mass concentration of the absorbing aerosol (see, e.g., Figure 3a) |
| NaCl | sodium chloride: salt; a light-scattering aerosol material used in this research |
| NARSTO | North American Research Strategy for Tropospheric Ozone study, a source of collocated BC and COH measurements used in this research |
| PSAP | particle soot absorption photometer: a filter-based instrument that operates much like the aethalometer but measures the aerosol absorption coefficient instead of the black carbon concentration |
| SSA | single scattering albedo: the fraction of incident sunlight that is scattered instead of absorbed, a parameter that determines whether an aerosol is climate-warming or climate-cooling |
| TOA | thermal-optical analysis: a method of measuring the carbon content of atmospheric particulate matter collected on quartz filters |