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Comparison of Real-Time Instruments Used To Monitor Airborne Particulate Matter

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ABSTRACT

Measurements collected using five real-time continuous airborne particle monitors were compared to measurements made using reference filter-based samplers at Bakersfield, CA, between December 2, 1998, and January 31, 1999. The purpose of this analysis was to evaluate the suitability of each instrument for use in a real-time continuous monitoring network designed to measure the mass of airborne particles with an aerodynamic diam less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) under wintertime conditions in the southern San Joaquin Valley. Measurements of airborne particulate mass made with a beta attenuation monitor (BAM), an integrating nephelometer, and a continuous aerosol mass monitor (CAMM) were found to correlate well with reference measurements made with a filter-based sampler. A Dusttrak aerosol sampler overestimated airborne particle concentrations by a factor of ~ 3 throughout the study. Measurements of airborne particulate matter

made with a tapered element oscillating microbalance (TEOM) were found to be lower than the reference filter-based measurements by an amount approximately equal to the concentration of NH_4NO_3 observed to be present in the airborne particles. The performance of the Dusttrak sampler and the integrating nephelometer was affected by the size distribution of airborne particulate matter. The performance of the BAM, the integrating nephelometer, the CAMM, the Dusttrak sampler, and the TEOM was not strongly affected by temperature, relative humidity, wind speed, or wind direction within the range of conditions encountered in the current study. Based on instrument performance, the BAM, the integrating nephelometer, and the CAMM appear to be suitable candidates for deployment in a real-time continuous $\text{PM}_{2.5}$ monitoring network in central California for the range of winter conditions and aerosol composition encountered during the study.

IMPLICATIONS

Regulatory agencies need instruments that can monitor the concentration of $\text{PM}_{2.5}$ in real time so that public health advisories can be issued during severe pollution events. Three types of continuous, real-time instruments have been identified that can function in a routine $\text{PM}_{2.5}$ monitoring network during winter conditions encountered in central California: the BAM, the integrating nephelometer, and the CAMM. Each instrument performed well within a broad $\text{PM}_{2.5}$ concentration range composed of both volatile and semi-volatile particulate matter.

INTRODUCTION

Over the past decade, mounting evidence has suggested that exposure to elevated concentrations of airborne particles with an aerodynamic diam less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) may pose a significant human health risk.¹⁻⁵ In response to this information, regulatory agencies with a mandate to protect public health must now consider how to implement monitoring networks that will allow them to measure $\text{PM}_{2.5}$ concentrations. Ideally, these monitoring networks will allow regulatory agencies to issue advisories and to implement appropriate restrictions in target geographical locations when $\text{PM}_{2.5}$ concentrations increase to unhealthy levels.

Traditional monitoring networks for airborne particulate matter have employed filter-based samplers. While filter-based instruments have proven to be robust and accurate for the study of the detailed nature of airborne particles during intensive experiments, they have several drawbacks when used in a routine monitoring network for regulatory purposes. The chief disadvantage associated with filter-based samplers for $PM_{2.5}$ is the fact that they do not provide information in real time. Often weeks or even months pass between the time when samples are collected and when $PM_{2.5}$ data become available. This time lag makes it impossible for regulatory agencies to react quickly to changing air quality.

A second drawback related to filter-based techniques is that they require integrated sample times of hours to days to collect sufficient particulate matter mass for accurate analysis. Long sampling times result in the practice of averaging periods of high and low $PM_{2.5}$ concentrations, making it difficult to identify the concentration spikes of short duration that may be responsible for some of the health effects that are observed to be associated with increased concentrations of airborne particulate matter. A third potential drawback when using filter-based sampling methods is the possibility of sample contamination. Great care must be exercised when using filter-based methods to measure certain chemical components of airborne particles that are prone to sampling artifacts. In addition to the technical difficulties listed above, filter-based sampling techniques are labor-intensive and relatively expensive when detailed analysis is performed.

Because of the many challenges associated with the use of filter-based samplers, implementation of filter-based sampling techniques in a routine monitoring network is a difficult task. Some of the problems associated with routine monitoring for $PM_{2.5}$ could be avoided by the use of a real-time continuous instrument capable of measuring $PM_{2.5}$ concentrations. The time resolution provided by real-time $PM_{2.5}$ monitors is a function of the instrument used, but typically is on the order of minutes. With this detailed time resolution, it would be possible for regulatory agencies to monitor peak concentration events that could then be correlated to health effects data. In addition to these technical advantages, continuous real-time $PM_{2.5}$ monitors are relatively labor-free, and so they are capable of providing much more data at a reduced price relative to filter-based techniques when employed in a routine monitoring network.

Before continuous real-time $PM_{2.5}$ monitors are widely used in routine monitoring networks, confidence must be established that these instruments are capable of accurately measuring $PM_{2.5}$ concentrations under the wide variety of conditions typically encountered in the ambient

atmosphere. The purpose of this paper is to describe the results of an experiment conducted to compare the response of several real-time continuous $PM_{2.5}$ monitoring instruments to measurements made using standard filter-based sampling techniques. In the following sections, the location and design of the intercomparison experiment are given, a brief description of the operation of each instrument is provided, and the continuous airborne particle mass measurements made by different instruments are discussed.

SITE DESCRIPTION

The continuous monitoring instrument intercomparison study described in this paper was conducted at Bakersfield, CA, between December 2, 1998, and January 31, 1999. Bakersfield is a city with a population of ~300,000 located in the southern part of California's San Joaquin Valley. During the winter season, the temperature inversion in the atmosphere at Bakersfield is typically quite strong and much lower than in the surrounding mountains. This atmospheric condition leads to a stable surface layer where air pollutant concentrations quickly build up to extremely high levels. The region around Bakersfield includes notable sources of air pollutants such as agricultural operations, oil production, and vehicular emissions from traffic on the major highways that connect northern and southern California along the valley floor (CA Highway 99 and Interstate 5).

Meteorological conditions during the intercomparison experiment varied greatly. The lowest temperature, relative humidity, and wind speed recorded during the study were $-0.7^{\circ}C$, 21%, and 0 m/sec, respectively, while the highest temperature, relative humidity, and wind speed were $22^{\circ}C$, 99%, and 16 m/sec, respectively. Hourly $PM_{2.5}$ mass concentrations varied from 5 to $130 \mu g/m^3$, while hourly PM_{10} concentrations varied from 10 to $150 \mu g/m^3$. The broad range of meteorological conditions and particulate matter concentrations recorded at Bakersfield allowed for an evaluation of instrument performance under the wide variety of atmospheric conditions that can be encountered when operating a routine monitoring network in California.

INSTRUMENT DESCRIPTION

The continuous real-time airborne particle monitors evaluated in the current study included a beta attenuation monitor (BAM 1020, Met One Instruments), two integrating nephelometers (Optec NGN-2 and Optec NGN-3, Air Resource Specialists), a continuous aerosol mass monitor (CAMM, Andersen Instruments), a Dusttrak sampler (Dusttrak 8520, TSI Inc.), and a tapered element oscillating microbalance (TEOM 1400, R&P Inc.). Each instrument was equipped with either a $PM_{2.5}$ inlet

or a PM_{10} inlet to allow for sampling of a target size range of airborne particles. Those instruments equipped with PM_{10} inlets were considered to be "candidate" monitors that could be adapted to measure $PM_{2.5}$ concentrations by changing the inlet configuration. Each of the continuous instruments was operated for the maximum possible time during the study period subject to logistical and maintenance constraints. The recorded values from each instrument were then summarized into daily average concentrations that could be compared to the reference sampler measurements.

The baseline against which all continuous, real-time $PM_{2.5}$ instruments were compared in the current study is a Federal Reference Method (FRM) sampler for $PM_{2.5}$ concentrations (RAAS 2.5-300, Andersen Instruments). Instruments that were configured to measure PM_{10} were compared to a size-selective inlet high-volume sampler (SSI) (Sierra-Andersen, 1200). The FRM and SSI samplers are filter-based instruments that are approved by the U.S. Environmental Protection Agency (EPA) for the measurement of $PM_{2.5}$ and PM_{10} concentrations. In the present work, duplicate FRM and SSI samplers were collocated at the Bakersfield site to ensure that the baseline results were reproducible. The measurement principles and the details of operation for each of the instruments used in the intercomparison study are described in the next sections.

Federal Method Reference Sampler. The FRM sampler consists of a well impactor ninety-six (WINS impactor) followed by a Teflon filter. Particles in the sample stream with an aerodynamic diam greater than $2.5 \mu\text{m}$ are captured in the WINS impactor, while smaller particles are collected on the downstream 47-mm Teflon filter. The concentration of airborne particulate matter is determined by pre- and post-weighing the Teflon and then dividing the accumulated mass by the amount of air that was sampled. Protocols for the preparation and handling of filters during sampling events followed the EPA $PM_{2.5}$ guidelines referenced in the Code of Federal Regulations (40 CFR, Part 50, Appendix L). Filters were pre-weighed no earlier than 2 weeks before sampling and loaded into the FRM sampler no earlier than 3 days before sampling. The temperature of each filter was monitored while installed in the FRM sampler and did not exceed the ambient temperature by more than 5°C . Filters were recovered from the FRM sampler within 96 hr after sampling and were maintained at a temperature of 4°C during transportation and storage. After arriving in the lab, filters were allowed to equilibrate with ambient air at a temperature of $20\text{--}23^\circ\text{C}$ and a relative humidity of $30\text{--}40\%$ for 24 hr prior to post-weighing. Data from the FRM-WINS sampler used in the current study were collected from January 6 to January 31, 1999, using samplers located on the roof of the study site.

Size Selective Inlet Sampler. The SSI uses a size-selective inlet to remove PM_{10} from the sample stream. PM_{10} is collected on an $8 \times 10\text{-in.}$ quartz filter that offers high collection efficiencies and is resistant to absorbing artifacts related to the collection of sulfates and nitrates. In the present study, the sampler operated at a flow rate of 40 cfm (1133 L/min) to collect a large amount of particulate matter for precise analysis. The SSI sampler used in the current study was operated on the roof of the sampling site between December 2, 1998, and January 31, 1999.

Beta Attenuation Monitor. The automatic BAM consists of a size-selective inlet, a filter tape, a beta radiation source, and a beta radiation detector. Particles smaller than the cut-diameter of the size-selective inlet are collected at a single point on a length of filter tape. The difference in the transmission of beta radiation through the filter tape before and after a particulate sample has been collected is measured and used to determine the mass of collected particulate matter. The mass absorption coefficient for beta radiation is determined through the measurement of a series of known standards that bracket the mass range of interest.⁶ Continuous operation is achieved by an automatic mechanism that advances the filter tape between sampling events. Since the baseline attenuation signal is measured before each sampling event, significant drift in the baseline signal does not occur. In the current study, each of the beta attenuation instruments was operated with hourly time resolution.

Typical operation protocols for the BAM specify heating of the inlet line to a temperature of $\sim 30^\circ\text{C}$ to reduce relative humidity to below 60%. This methodology minimizes particle-bound water, but it may also bias the particulate measurements when large amounts of volatile particulate matter are present. Other potential sources of measurement error associated with BAMs include a slight sensitivity to hydrogen ion concentration present in airborne particles,⁶ and the fluctuations of the sample flow rate due to pressure, relative humidity, and temperature variations.⁷ Each of these sources of error are relatively minor, and studies have shown that BAMs can measure airborne particulate matter with accuracy similar to that achieved by filter-based gravimetric methods.^{6,8,9}

It should be noted that beta radiation sources used in BAMs may be subject to safety and environmental regulations that restrict operation and disposal of the instrument. Each BAM used in the current experiment was equipped with a low-activity Carbon 14 beta isotope source with a strength less than $60 \mu\text{C}$. The half-life of this beta particle source is over 5000 years, while the expected lifetime of the other sampler components is only 12–15 years; when a BAM is retired, the beta source can be recycled for re-use in another unit.

Two automatic BAMs equipped with different inlets were evaluated during the intercomparison study at Bakersfield. The first BAM was operated with a WINS PM_{2.5} impactor inlet for the entire study period. The second BAM was equipped with a PM₁₀ inlet between December 15, 1998, and January 6, 1999. After January 6, the second BAM was retrofitted with a sharp cut cyclone (SCC 16.7, BGI Inc.) calibrated to measure PM_{2.5}. Both BAMs were located inside a sheltered environment and obtained samples of ambient air through sample lines ~2.5 m in length.

Integrating Nephelometer. The integrating nephelometers used in the current study measured particle concentrations by intersecting an aerosol sample with light at several wavelengths in the visible range (0.55 μm effective center wavelength). The amount of laser light scattered at angles between 5 and 175° by particles suspended in the sample flow was measured and used to estimate a particle-scattering coefficient. This scattering coefficient was then assumed to be proportional to the mass of airborne particulate matter. The proportionality constant used to calculate airborne particle concentrations during the study period was calculated from historical data taken by the Interagency Monitoring of Protected Visual Environments (IMPROVE) sampling network throughout the United States. It should be noted that the greatest problem associated with the use of nephelometers in routine PM_{2.5} monitoring networks is the variability of light scattering by particles with different sizes and compositions. The uncertainty associated with nephelometer measurements increases when a wide distribution of particle sizes is sampled,¹⁰⁻¹² and the proportionality constant used to convert nephelometer scattering data to airborne particle mass concentrations may need to be adjusted when aerosol size distributions and composition differ significantly from the size and composition of the calibration aerosol.

Two integrating nephelometers with different inlet configurations were operated on the roof of the sampling site in the current study. The first nephelometer (Optec NGN-2) employed a direct measurement of the airborne particle-scattering coefficient with no selection to differentiate between particles with different diameters. The second nephelometer (Optec NGN-3) used a two-stage impactor inlet (Airmetrics Co.) to remove particles with an aerodynamic diam greater than 2.5 μm from the sample stream. The sample chamber of both nephelometers was maintained at a temperature ~10 °C above ambient to reduce relative humidity to less than 60%. This methodology minimizes interference in the technique associated with airborne water vapor and reduces the amount of particle-bound water, but it may bias the particulate measurements when large amounts of volatile particulate matter are present.

The response time of the integrating nephelometer can be adjusted to measure particle concentrations every 2 min, making it an attractive choice for real-time monitoring in situations where short time resolution is required. In the present study, the measurements taken by the Optec NGN-2 nephelometer were averaged over 1-hr intervals and then summarized for comparison with the filter-based reference measurements taken at Bakersfield during the period of December 17, 1998, to January 31, 1999. Measurements from the Optec NGN-3 nephelometer were only available from December 17, 18, 23, and 24, 1998, so only a limited analysis of this instrument is possible.

Continuous Aerosol Mass Monitor. The CAMM measures airborne particulate matter based on the relative difference in pressure drop between a reference airstream channel and an airstream channel where particulate matter is collected on a filter tape. This pressure difference is then correlated to the airborne particulate matter concentration. The instrument advances the filter tape in the sampling channel to get continuous measurements with a time resolution between 30 and 60 min. An impactor with a cut size of 2.5- μm aerodynamic particle diam was operated upstream of the CAMM, and a diffusion dryer was employed in the sample stream to reduce any particle-bound water. Past studies have shown good correlation between the CAMM and conventional impactor samplers.¹³ In the current study, the CAMM sampler was operated on the roof of the sampling site from January 12 to January 28, 1999.

Dusttrak. The Dusttrak sampler is a compact commercial instrument that includes an impaction inlet, laser diode, focusing optics, photodetector, vacuum pump, and control electronics. The instrument draws a continuous aerosol stream through the impaction inlet where particles with aerodynamic diam greater than 10 μm are removed (impaction inlets with 1- and 2.5- μm cuts are also available). The sample stream then passes through a sensing chamber where it is intersected by light (0.78- μm wavelength) emitted from the laser diode. Particles in the sample stream scatter light in all directions; the amount of light measured by the photodetector oriented at an angle of 90° to both the laser and the sample stream is converted to a proportional mass concentration by internal electronics. The proportionality constant used by the Dusttrak sampler is determined by calibration against a gravimetric measurement of the International Organization for Standardization (ISO) 12103-1, A1 test dust (Arizona Test Dust). The Dusttrak cannot detect particles with diam smaller than 0.1 μm , and the amount of light scattered by particles with diam smaller than 0.25 μm is proportional to particle diameter raised to the sixth power (D_p^6). These effects can cause the Dusttrak measurements

to differ from gravimetric measurements of airborne particulate matter when the size distribution of the airborne particles differs significantly from the size distribution of the test aerosol. The Dusttrak has a minimum time resolution of 1 min; in the present study, measurements were averaged to an hourly resolution. Dusttrak measurements were taken on the roof of the sampling site between January 10 and January 28, 1999.

Tapered Element Oscillating Microbalance. The TEOM measures suspended particulate matter concentrations by passing sample air and particles through a hollowed tapered channel where the particles are collected on a filter. The tapered inlet tube oscillates at a frequency that is inversely proportional to the amount of sample deposited on the collection substrate. The sample area is maintained at 50 °C to minimize thermal expansion of the tapered channel that may affect the oscillation frequency and to reduce the amount of particle-bound water. The minimum time resolution that can be measured with the TEOM is 10 min.¹⁴ In the present study, hourly average TEOM measurements were recorded.

The TEOM provides a direct measurement of airborne particle mass and it is relatively easy to calibrate, making it attractive for monitoring purposes. The principle disadvantage associated with the TEOM is the potential for volatilization of collected material when heating the sample to 50 °C. Previous studies have shown that semi-volatile particle components such as NO₃⁻ and secondary organic compounds may be lost from the sample when it is heated, leading to an underestimation of airborne particle concentrations.¹⁵⁻¹⁷ Other studies have shown that in locations where the concentration of volatile particulate matter is low, the TEOM does not underestimate particulate matter concentrations.¹⁸

A single TEOM equipped with a Sierra-Andersen PM₁₀ dichot head was used at the Bakersfield site to measure airborne particle concentrations from December 2, 1998, to January 31, 1999. The TEOM was operated inside a sheltered environment and obtained samples of ambient air through a sample line with a length of ~2.5 m. This instrument has been included in the present analysis because it can easily be converted to a PM_{2.5} configuration and because TEOMs are commonly used for routine monitoring purposes.

RESULTS

The regression statistics comparing the response of collocated airborne particle sampling instruments are summarized in Table 1. The first two rows of Table 1 show that measurements made by collocated FRM samplers (operated between January 6 and January 31, 1999) and collocated SSIs (operated between December 2, 1998, and January 31, 1999) are highly reproducible, with each

collocated instrument pair exhibiting a regression slope and correlation coefficient very close to 1.00. These results demonstrate that the baseline FRM and SSI filter measurements provide a stable data set for the evaluation of the continuous instruments described in this paper. Two of the candidate continuous aerosol measurement devices evaluated in the current study also operated with collocated pairs during portions of the experiment. A BAM equipped with a WINS impactor inlet (BAM-WINS) was operated alongside a BAM equipped with an SCC inlet (BAM-SCC) between January 6 and January 31, 1999. Collocated integrating nephelometers (Optec NGN-2 and Optec NGN-3) also were operated on December 17, 18, 23, and 24, 1998. The regression statistics summarized in the lower two rows of Table 1 indicate that on days when data were available, the responses of the collocated BAMs and integrating nephelometers were virtually identical, with regression slopes and correlation coefficients very close to 1.00. The CAMM, the TEOM, and the Dusttrak operated independently without the implementation of a collocated unit.

In the present study, the FRM filter-based PM_{2.5} measurements were used as the baseline for the evaluation of the continuous real-time PM_{2.5} instruments. The continuous measurements from the BAM, the nephelometer, and the CAMM were summarized to 24-hr average PM_{2.5} concentrations that were then compared to the FRM measurements. Figure 1 shows the response of the BAM, the nephelometer, and the CAMM along with the FRM measurements between January 6 and January 31, 1999, at Bakersfield. Both the nephelometer and the BAM tracked the response of the FRM PM_{2.5} measurements in early January when PM_{2.5} concentrations reached a peak daily value of 117 µg/m³. CAMM measurements were lower than the PM_{2.5} reference measurements during the early part of January. Measurements made by the BAM and the CAMM tracked the reference FRM readings during late January when PM_{2.5} concentrations fell to 3.5 µg/m³. Nephelometer measurements for PM_{2.5} were generally lower than the reference FRM PM_{2.5} measurements during periods of low concentrations, but fell within the bounds of error reported in previous studies.⁹

Table 1. Regression statistics for collocated airborne particle sampling instruments.

	Regression Slope	Correlation Coefficient	Intercept (µg/m ³)
FRM/FRM	0.98	1.00	0.83
SSI/SSI	1.00	1.00	0.01
BAM-WINS/SCC	1.06	0.99	2.92
NEPH NGN-2/NGN-3	1.01	0.99	-1.64

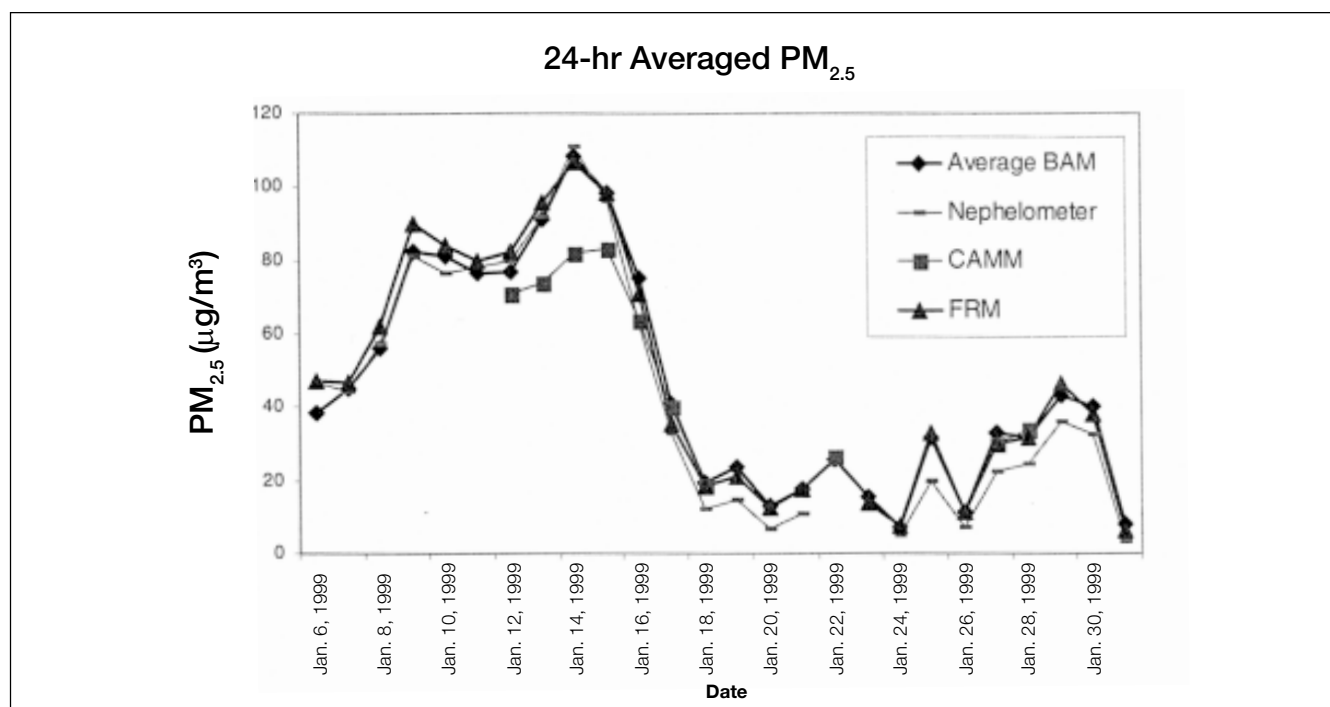


Figure 1. Time series of PM_{2.5} measurements made with a BAM, an integrating nephelometer, a CAMM, and an FRM sampler at Bakersfield between January 6 and January 31, 1999. Measurements from each real-time instrument were averaged to 24-hr periods to match the resolution of the reference FRM sampler.

Figure 2 illustrates the results of a regression calculation comparing the 24-hr averaged BAM, nephelometer, and CAMM data to the reference FRM measurements. The upper panel of Figure 2 shows that the BAM tracked the FRM measurements well with a linear regression slope of 0.95, an intercept of 1.36 µg/m³, and a correlation coefficient of 0.99. The nephelometer measurements also compared favorably to the FRM measurements, with a regression slope of 1.03, an intercept of -6.41 µg/m³, and a correlation coefficient of 0.99. The lower panel of Figure 2 shows that a comparison between the CAMM measurements and the FRM measurements yields a regression with a slope of 0.74, an intercept of 10.85 µg/m³, and a correlation coefficient of 0.96. A more thorough analysis of the time series and regressions are presented in the analysis section.

For practical considerations, several candidate PM_{2.5} continuous monitors used in the current study were equipped with PM₁₀ inlets. These instruments are included in the present analysis because they can easily be converted to measure PM_{2.5}. The ability of each continuous monitor to measure airborne particle concentrations can be evaluated independently of the inlet configuration by comparing the averaged continuous results to the SSI PM₁₀ reference filter sampler. Figure 3 shows the time series of PM₁₀ measurements recorded by the SSI, the BAM, the TEOM, and the Dusttrak from December 2, 1998, to January 31, 1999, at Bakersfield. Measurements of PM₁₀ recorded

by the BAM were only available between December 15, 1998, and January 6, 1999, since this instrument was equipped with a PM_{2.5} inlet during other portions of the experiment. Measurements of PM₁₀ from the Dusttrak are only available from January 9 to January 28, 1999, due to maintenance difficulties. Agreement between the PM₁₀ measurements taken by the different instruments is generally less favorable than the corresponding PM_{2.5} measurements, but Figure 3 clearly shows that the limited BAM measurements track the response of the filter-based reference method better than measurements taken with the TEOM and the Dusttrak.

The linear regression of the TEOM measurements plotted against the SSI reference measurements is shown in the upper panel of Figure 4. The TEOM measurements correlated well with the reference filter-based measurements (correlation coefficient = 0.95), but the linear regression slope of 0.37 indicates that the TEOM consistently underestimated PM₁₀ concentrations throughout the entire study period. The middle panel of Figure 4 shows the regression obtained between the BAM PM₁₀ and the reference SSI data. Good agreement is observed between these two sets of measurements with a linear regression slope of 1.01, an intercept of 1.85 µg/m³, and a correlation coefficient of 0.99. Good agreement between PM₁₀ BAM and SSI measurements is consistent with the results of previous experiments.⁸ The lower panel of Figure 4 shows that PM₁₀ measurements made using the Dusttrak sampler were

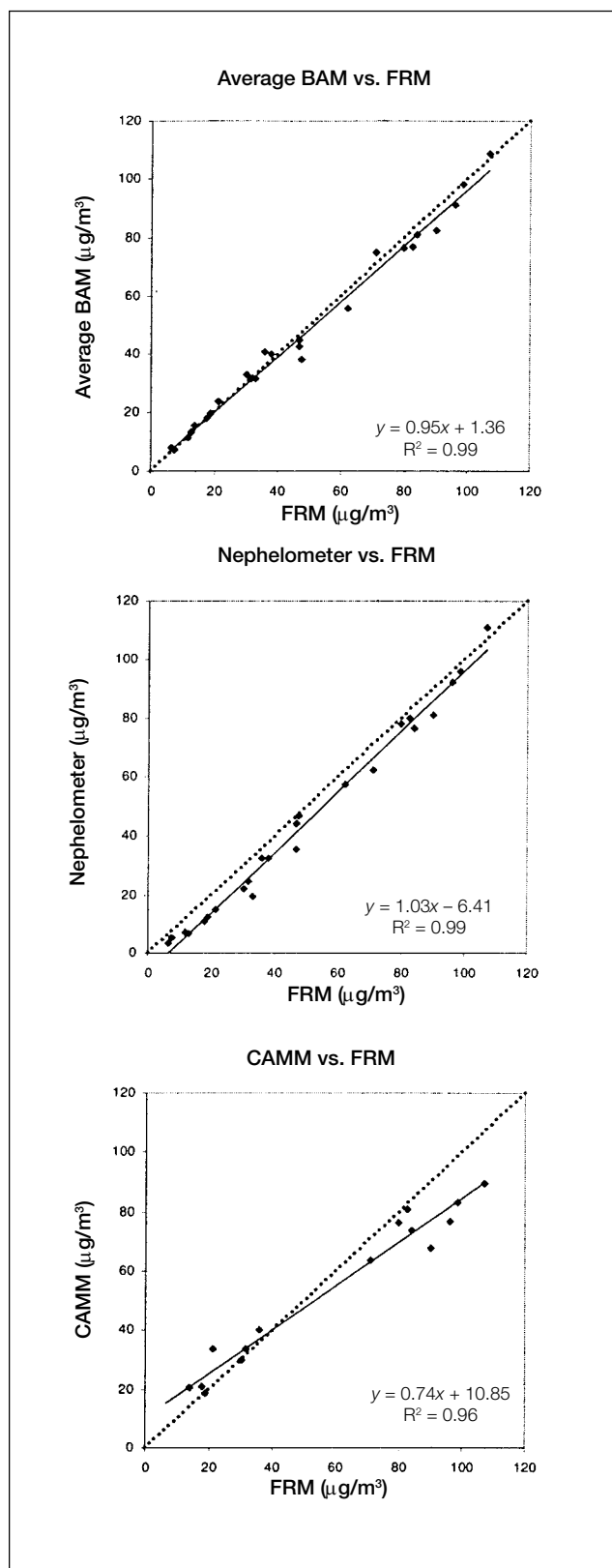


Figure 2. Comparisons of $\text{PM}_{2.5}$ measurements made by real-time instruments and a reference FRM sampler at Bakersfield. The upper panel shows the performance of the BAM between January 6 and January 31, 1999. The center panel shows the performance of the integrating nephelometer (Optec NGN-2) between December 17, 1998, and January 31, 1999. The lower panel shows the performance of the CAMM between January 12 and January 28, 1999.

highly correlated with the reference measurements, but the Dusttrak consistently overestimated PM_{10} concentrations in the current study.

ANALYSIS

The EPA defines $\text{PM}_{2.5}$ as the mass of airborne particles with aerodynamic diam less than $2.5 \mu\text{m}$ as measured by the FRM. The ability of a continuous monitor to make $\text{PM}_{2.5}$ measurements that are equivalent to FRM measurements can be gauged by the absolute instrument error (defined as the difference between the instrument reading and the corresponding FRM measurement) and the relative instrument error (defined as the absolute instrument error divided by FRM measurement). A strong correlation between a meteorological variable and the instrument error indicates that the continuous $\text{PM}_{2.5}$ monitor in question may be incapable of making measurements that are equivalent to FRM measurements under certain atmospheric conditions. Likewise, a strong correlation between instrument error and particle composition indicates that the continuous $\text{PM}_{2.5}$ monitor in question may not be able to properly measure the mass of certain aerosol components.

In the current study, the absolute and relative error for each of the continuous aerosol monitors were correlated with measurements of ambient temperature, relative humidity, wind speed, wind direction, and the concentration of particulate NO_3^- , NH_4^+ , SO_4^{2-} , total carbon (TC), organic carbon (OC), and elemental carbon (EC). The concentrations of airborne particulate matter components used in this analysis were determined from samples collected using the spiral ambient speciation sampler (SASS, Met One Instruments). It has been determined that the spiral inlet used by the original SASS design to remove particles larger than $2.5 \mu\text{m}$ from the sample stream does not provide a sharp cut at the design flow rate of $7 \text{ L}/\text{min}$.¹⁹ While this issue does not affect the accuracy of the chemical analysis performed on the samples after collection, it does suggest that under certain atmospheric conditions, the original version of the SASS collected particles larger than $2.5 \mu\text{m}$. A statistical comparison between the $\text{PM}_{2.5}$ measurements taken with the SASS and the FRM samplers used in the current study yielded a correlation slope of 1.00, a correlation coefficient of 0.98, and an intercept of $1.16 \mu\text{g}/\text{m}^3$. These results compare favorably to the variability shown between the collocated FRM samplers themselves (see Table 1), indicating that the SASS correctly sampled the $\text{PM}_{2.5}$ concentrations under the atmospheric conditions experienced in the current study. The chemical composition measurements made by the SASS compared favorably with other measurement techniques,²⁰ once again demonstrating that SASS measurements were not biased.

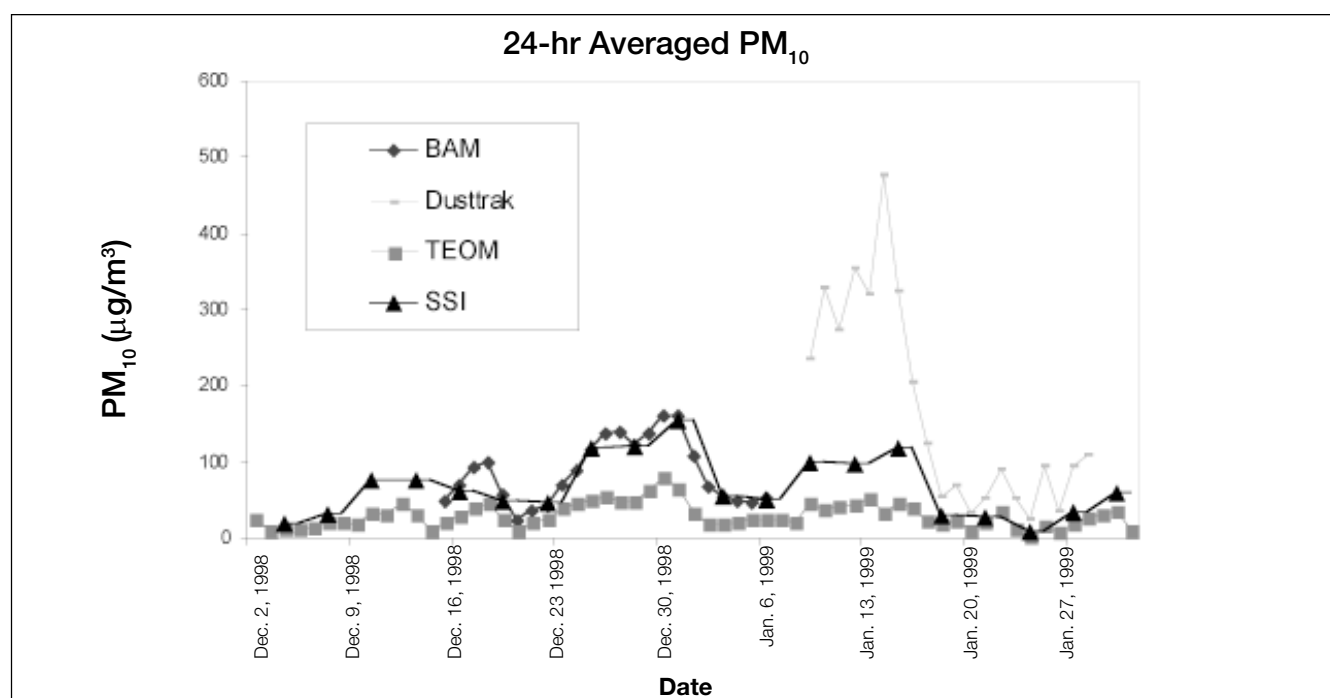


Figure 3. Time series of PM₁₀ measurements made by a TEOM, a BAM, a Dusttrak sampler, and an SSI at Bakersfield between December 2, 1998, and January 31, 1999. Measurements from each real-time instrument were averaged to 24-hr periods to match the resolution of the reference SSI.

Before performing a detailed analysis of instrument error, we must first consider possible collinearity between the independent meteorological and particle composition variables. Table 2 summarizes the correlation coefficients (R^2) between average daily ambient temperature, relative humidity, wind speed, wind direction, and the difference between the maximum and minimum daily values for temperature and relative humidity. Also included in Table 2 are the correlation coefficients between the concentrations of major aerosol chemical components including

NO_3^- , SO_4^{2-} , NH_4^+ , TC, OC, and EC. The results shown in Table 2 indicate that a high degree of collinearity exists between the concentrations of particulate NO_3^- , NH_4^+ , and SO_4^{2-} . This dependency may result from the fact that SO_4^{2-} formed in fog droplets persists in the particle phase after a fog event ends. The equilibrium vapor pressure of NH_3 and HNO_3 above SO_4^{2-} particles is significantly lower than the equilibrium vapor pressure of these components over a pure NH_4NO_3 particle.²¹ As a result, airborne SO_4^{2-} particles tend to accumulate more NH_4NO_3 than particles

Table 2. Correlation coefficients (R^2) for linear regression between meteorological variables and airborne particle composition at Bakersfield between December 2, 1998, and January 31, 1999.

	Temperature	Relative Humidity	Wind Speed	Wind Direction	Δ Temperature	Δ Relative Humidity	NO_3^-	NH_4^+	SO_4^{2-}	TC	OC	EC
Temperature	1.000	0.199	0.064	0.049	0.104	0.195	0.009	0.007	0.119	0.011	0.009	0.016
Relative Humidity		1.000	0.011	0.087	0.063	0.658	0.119	0.102	0.023	0.243	0.227	0.261
Wind Speed			1.000	0.222	0.006	0.021	0.007	0.015	0.035	0.032	0.026	0.048
Wind Direction				1.000	0.005	0.018	0.001	0.000	0.035	0.000	0.001	0.001
Δ Temperature					1.000	0.029	0.298	0.287	0.278	0.468	0.466	0.424
Δ Relative Humidity						1.000	0.085	0.086	0.048	0.304	0.300	0.285
NO_3^-							1.000	0.992 ^a	0.773 ^a	0.334	0.324	0.324
NH_4^+								1.000	0.826 ^a	0.308	0.306	0.280
SO_4^{2-}									1.000	0.285	0.317	0.189
TC										1.000	0.988 ^a	0.931 ^a
OC											1.000	0.867 ^a
EC												1.000

^aStatistically significant pairwise correlation.

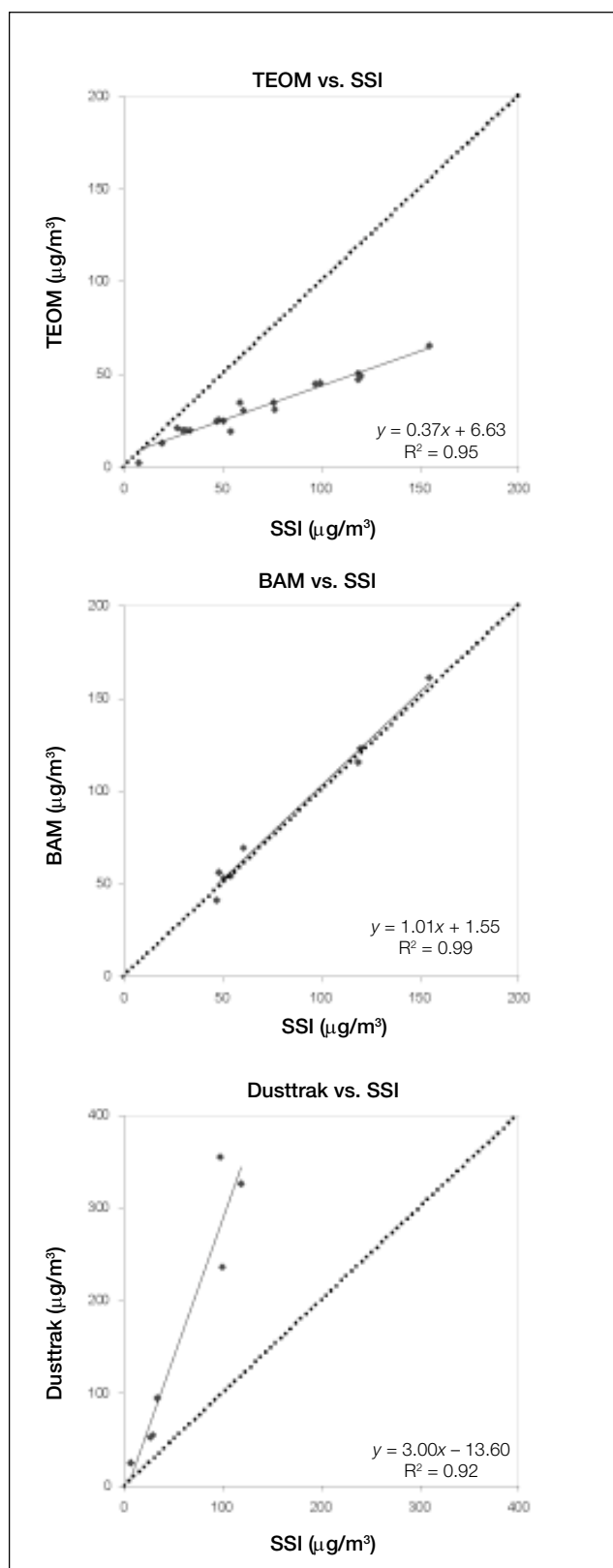


Figure 4. Comparison between PM_{10} measurements made by real-time instruments and a reference SSI at Bakersfield. The upper panel shows the performance of the TEOM between December 2, 1998, and January 31, 1999. The center panel shows the performance of the BAM between December 15, 1998, and January 6, 1999. The lower panel shows the performance of the Dusttrak sampler between January 9 and January 28, 1999.

containing large amounts of hydrophobic material during the same event.

The results summarized in Table 2 also show that concentrations of particulate TC, OC, and EC are all highly correlated. TC is the sum of OC and EC. Under typical atmospheric conditions, EC concentrations are relatively low, resulting in a large correlation between TC and OC. The significant correlation between TC and EC could result from one large source of carbonaceous aerosol in the study region or from relatively constant emissions from numerous smaller sources of carbonaceous aerosol.

Table 3 summarizes the correlation between the absolute and relative error of each of the continuous particle sampling instruments and the independent sets of variables shown in Table 2. All available sample pairings were used in this analysis to provide the most robust statistical analysis possible from the data set. Consequently, each entry in Table 3 represents a different number of sample points with a different level for statistical significance. The results shown in Table 3 indicate that there is no statistically significant correlation between the instrument error (absolute or relative) and the meteorological conditions encountered in the current study. A statistically significant correlation was found between the absolute error of the Dusttrak and TEOM and the concentration of particulate NO_3^- . A statistically significant relationship also was observed between the relative error of the integrating nephelometer and the concentration of particle NO_3^- .

Figure 5 summarizes the statistically significant interactions between instrument error and particulate NO_3^- concentrations that were identified in Table 3. The upper panel of Figure 5 shows that the Dusttrak absolute error is positively correlated with the aerosol NO_3^- concentration. Impactor data collected during the study period show that on days when aerosol NO_3^- concentrations were large, the mass distribution of ambient aerosol peaked strongly at $\sim 0.7\text{-}\mu\text{m}$ aerodynamic particle diam.²¹ Since the Dusttrak sampler is calibrated using a test aerosol that is composed of dust particles that have an aerodynamic diam greater than $1.0\ \mu\text{m}$, it is not surprising that the error of the Dusttrak sampler is correlated with particulate NO_3^- concentrations, because this instrument was not calibrated to measure submicron particles.

The center panel of Figure 5 shows that the relative error of the integrating nephelometer was negatively correlated with the concentration of particulate NO_3^- measured during the study period. As described above, impactor data collected during the study period show that on days when aerosol NO_3^- concentrations were low, the ambient aerosol size distribution was dominated by particles with an aerodynamic diam greater than $1.0\ \mu\text{m}$.²¹ The integrating nephelometer measurements were converted

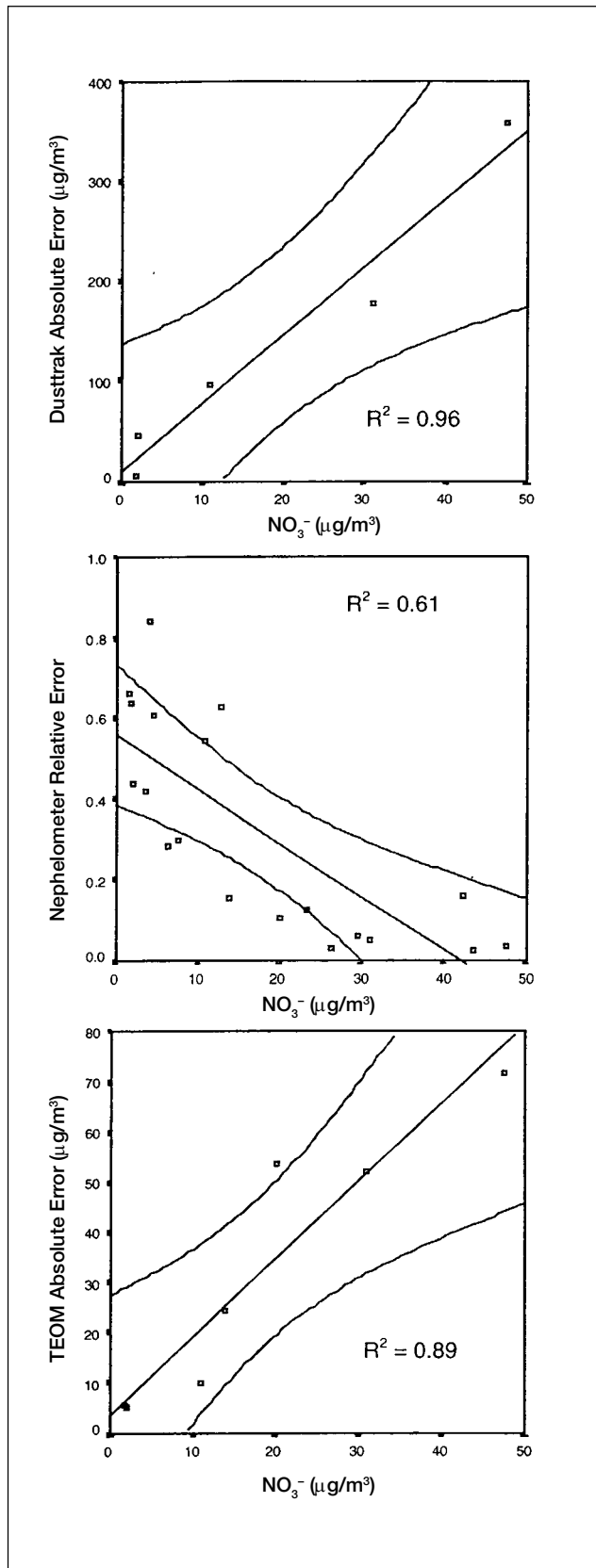


Figure 5. Correlation between the Dusttrak (upper panel), nephelometer (center panel), and TEOM (lower panel) instrument error and the concentrations of particulate NO_3^- at Bakersfield during the study period. The error bars shown correspond to a confidence interval of 99%.

to $\text{PM}_{2.5}$ concentrations using a calibration coefficient calculated based on data collected from the IMPROVE $\text{PM}_{2.5}$ sampling network. A single coefficient value cannot transform the response of the integrating nephelometer to $\text{PM}_{2.5}$ concentrations when the shape of the aerosol size distribution changes drastically. Based on the results of the current analysis, it appears that the nephelometer calibration coefficient used in the present study accurately transforms the light-scattering signal from particles smaller than $1.0\text{-}\mu\text{m}$ aerodynamic diam to $\text{PM}_{2.5}$ concentrations. The absolute error of the integrating nephelometer was small during the study period because $\text{PM}_{2.5}$ concentrations were lower when the airborne particle size distribution was dominated by particles with aerodynamic diam greater than $1.0\text{ }\mu\text{m}$. Under conditions when $\text{PM}_{2.5}$ concentrations are large and the airborne particle size distribution is dominated by particles greater than $1.0\text{-}\mu\text{m}$ aerodynamic diam, the absolute error of the integrating nephelometer would likely be greater.

The lower panel of Figure 5 shows that the absolute error of the TEOM was positively correlated with the concentration of particulate NO_3^- . Data acquired during the study period indicate that the atmospheric aerosol at Bakersfield contained more than $65\text{ }\mu\text{g}/\text{m}^3$ of particulate NH_4NO_3 during the second week of January, representing over half of the measured $\text{PM}_{2.5}$ mass at that time. The TEOM heats the captured particle sample to a greater extent than the other instruments used in the current study do, and so it is reasonable to expect that losses of volatile aerosol components such as NH_4NO_3 would be greater in the TEOM. To investigate the performance of the TEOM in the current study, the amount of particulate NH_4NO_3 contained in particles less than $2.5\text{ }\mu\text{m}$ in aerodynamic diam (measured using the SASS) was added to the raw TEOM measurements to produce a “corrected” set of TEOM measurements. This method assumes that the majority of NH_4NO_3 was present in particles with an aerodynamic diam less than $2.5\text{ }\mu\text{m}$, a result that is consistent with cascade impactor measurements made at Bakersfield during the study period.²¹

Figure 6 shows the time series of corrected TEOM PM_{10} measurements along with the SSI and BAM measurements between January 7 and January 31, 1999. By comparison to Figure 3, it can be seen that the corrected TEOM measurements in Figure 6 track the response of the SSI reference measurements much more closely than the response of the uncorrected TEOM measurements. A linear regression analysis between the corrected TEOM measurements and the reference SSI measurements reveals a correlation slope of 0.85 and a correlation coefficient of 0.98. The improved agreement between the corrected TEOM data and the reference measurements suggests that the error observed in the TEOM measurements is consistent with

Table 3. Correlation coefficients (R^2) for linear regression between instrument error and independent sets of meteorological variables and particle composition variables at Bakersfield between December 2, 1998, and January 31, 1999. NO_3^- and TC are used as representative variables in collinear independent variable sets.

	Absolute Error							Relative Error						
	BAM- WINS	BAM- SCC	BAM	NEPH NGN-2	CAMM	Dustrak	TEOM	BAM- WINS	BAM- SCC	BAM	NEPH	CAMM	Dustrak	TEOM
	($\text{PM}_{2.5}$)	($\text{PM}_{2.5}$)	(PM_{10})	($\text{PM}_{2.5}$)	($\text{PM}_{2.5}$)	(PM_{10})	(PM_{10})	($\text{PM}_{2.5}$)	($\text{PM}_{2.5}$)	(PM_{10})	($\text{PM}_{2.5}$)	($\text{PM}_{2.5}$)	(PM_{10})	(PM_{10})
Temperature	0.097	0.057	0.353	0.000	0.036	0.001	0.004	0.000	0.107	0.008	0.156	0.088	0.000	0.038
Relative Humidity	0.002	0.036	0.204	0.002	0.000	0.393	0.093	0.010	0.276	0.032	0.031	0.088	0.009	0.091
Wind Speed	0.193	0.040	0.315	0.216	0.039	0.165	0.191	0.018	0.000	0.050	0.066	0.035	0.108	0.004
Wind Direction	0.000	0.072	0.052	0.091	0.018	0.677	0.257	0.003	0.036	0.360	0.023	0.000	0.065	0.004
Δ Temperature	0.045	0.023	0.067	0.002	0.006	0.723	0.315	0.001	0.001	0.048	0.234	0.111	0.388	0.032
Δ Relative Humidity	0.003	0.032	0.155	0.035	0.003	0.346	0.062	0.004	0.027	0.003	0.063	0.116	0.021	0.065
$\text{NO}_3^-/\text{NH}_4^+/\text{SO}_4^{2-}$	0.016	0.019		0.073	0.020	0.956 ^a	0.885 ^a	0.092	0.116		0.610 ^a	0.269	0.090	0.078
TC/OC/EC	0.016	0.085		0.217	0.034	0.672	0.145	0.168	0.137		0.301	0.263	0.181	0.012

^aStatistically significant pairwise correlations.

the concentration of particulate NH_4NO_3 . The remaining difference between the adjusted TEOM data and the reference measurements may be due to the loss of other semi-volatile aerosol components such as organic compounds.

CONCLUSIONS

$\text{PM}_{2.5}$ measurements made using a BAM, an integrating nephelometer, and a CAMM correlated well with FRM filter-based $\text{PM}_{2.5}$ measurements taken between January 6

and January 31, 1999, at Bakersfield. Measurements from a Dustrak aerosol monitor overestimated PM_{10} by about a factor of 3 throughout the study. Measurements of PM_{10} made using a TEOM were lower than the reference filter-based PM_{10} measurements by an amount approximately equal to the measured concentration of particulate NH_4NO_3 . The performances of the Dustrak and integrating nephelometer aerosol monitors were affected by the size distribution of the airborne particulate matter. The

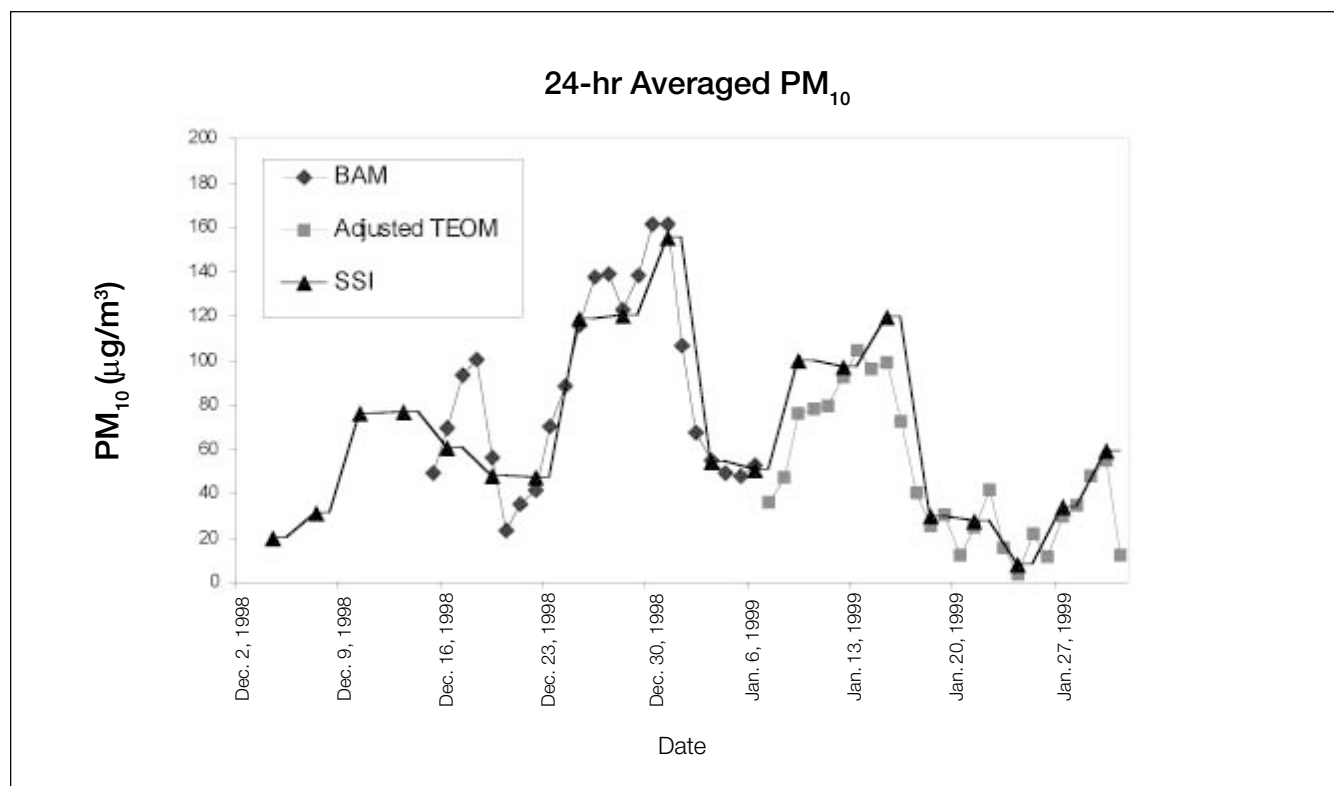


Figure 6. Time series of corrected PM_{10} measurements made by the TEOM at Bakersfield between December 2, 1998, and January 31, 1999. Raw TEOM measurements are corrected by adding the amount of NH_4NO_3 (measured using a filter-based sampler) to the base TEOM reading.

performances of the BAM and the CAMM were not strongly affected by particle composition or meteorological conditions. The BAM, the integrating nephelometer, and the CAMM appear to be suitable candidates for deployment in a real-time continuous PM_{2.5} monitoring network in central California for the range of winter conditions and aerosol composition encountered during the study.

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DISCLAIMER

The statements and conclusions in this paper are those of the authors and not necessarily those of the California Air Resources Board, the San Joaquin Valleywide Air Pollution Study Agency, or its Policy Committee, their employees, or their members. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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