

**Evaluation of Fine Particulate Samplers (PM_{2.5})
in an Area of Volatile Constituents**

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Evaluation of Fine Particulate Samplers (PM_{2.5}) in an Area of Volatile Constituents

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ABSTRACT

A National Ambient Air Quality Standard (NAAQS) for particulate matter equal to or less than 2.5 microns in diameter is being considered by the United States Environmental Protection Agency (U.S. EPA). Particulate matter of this size is commonly referred to as PM_{2.5} or, more generally, "fine" particulate matter. PM_{2.5} matter found in California can be volatile and water soluble, complicating sampling techniques. In order to investigate potential sampling methodologies for fine particulate, the U.S. EPA funded a field study conducted by the California Air Resources Board (ARB) between November 1994 and March 1995 in Bakersfield, California.

Wintertime atmospheric conditions in Bakersfield include persistent fog, temperatures in the near-freezing range, PM₁₀ concentrations ranging up to 300 micrograms/m³ and predominant concentrations of volatile compounds, such as ammonium nitrate and carbon in the total PM₁₀ mass measurements.

This paper presents the initial results of the 1994-95 Bakerfield winter particulate matter field study. A total of 16 samplers representing a variety of existing, modified, and newly designated equivalent samplers, were sited in parallel and results for both PM₁₀ and PM_{2.5} measurements were compared. We found that losses from evaporation and other mechanisms can lead to significant particulate matter mass loss during and after sampling. Understanding and addressing these losses is critical to achieving a consistent measurement of PM_{2.5}. These factors must be addressed as the U.S. EPA proceeds to identify reference or equivalent samplers for a possible fine particle NAAQS.

INTRODUCTION

The United States Environmental Protection Agency (U.S. EPA) is currently involved in an accelerated review of the National Ambient Air Quality Standard (NAAQS) for particulate matter (PM). Many individuals within the U.S. EPA expect the aerometric diameter of PM will be supplemented with a new fine particle indicator of 2.5μ ($PM_{2.5}$) or smaller cut size. Revising the standard will require the U.S. EPA to identify and approve new samplers on an expedited schedule. They will face a considerable challenge in approving reliable samplers in time to meet new deadlines that would be triggered by adoption of a new PM NAAQS.

The U.S. EPA will also need to address problems with the reference and equivalent sampler identification procedures that have led to recurring discrepancies among some approved PM_{10} samplers. Central to the issue is the manner in which different samplers treat volatile PM constituents. Testing of new reference and equivalent samplers must be conducted with the knowledge that fine particles volatilize on filter-based samplers to one degree or another. The degree to which candidate samplers capture and retain these compounds should be fundamental to specifying requirements for approved samplers.

A fine particle NAAQS will require state and local agencies to phase-in new PM samplers into their networks. Unfortunately, little fine particulate data are available from which to base siting decisions. Survey or "screening" samplers are needed to help managers select sites. In the absence of air monitoring data, site selection will be based on analyses of emerging emission inventories, on assumptions of particle size distributions, and estimates of secondary particulate formation. Therefore, one goal of this study was to provide a preliminary comparison of different samplers that could be deployed early and assist agencies in selecting new PM sites.

The Bakersfield Winter PM study was conducted November 1994 through March 1995. The results shed light on the comparability of fine particle samplers that operated in the challenging environment found in the winter in the San Joaquin Valley (the Valley) of California. This paper contains an initial assessment of sampler performance with respect to each other for the period November 15, 1994 through January 1995. It addresses specific questions about sampling at times of high particulate concentrations when ambient temperatures are often below the dew point.

Study Location

Bakersfield is a growing community in an urbanized area with a population of approximately 190,000. It is located in the southern end of the Valley. Oil and gas production, petroleum refining, and agriculture are the principal industries in the region. Substantial emissions are also generated by commercial enterprise and residential activity. The Valley comprises the southern two-thirds of the California's Central Valley. It extends from a point south of Sacramento to the base of the Tehachipi Mountains. The Valley is flat although it gradually increases in elevation toward its southern boundary. The Valley is surrounded by the Sierra Nevada Mountains on the east, the Tehachipi Mountains on the south and the Coast Range to the west. Except for the periodic dust storms in the summer, the highest, and most persistent PM levels in the Valley occur in the late fall and winter. In December and January, the Valley commonly experiences prolonged periods of stable meteorology that lead to dense fog and high PM levels. Freezing temperatures occur periodically during early morning and late evening hours.

Ammonium nitrate and carbon comprise a significant percentage of PM_{10} in the winter in the Valley. For example, these two constituents alone represented 51% of the total $154\mu\text{g}/\text{m}^3$ PM_{10} mass measured on November 24, 1994 in Bakersfield. Typically the fine particulate fraction ($0-2.5\mu$) dominates the PM_{10} mass in the late fall and winter months, and coarse particles ($2.5-10\mu$) represent a majority at other times of the year. Figure 1 depicts seasonal (using specific days in 1992 and 1993) distributions of fine and coarse particulates from California's 17 dichotomous samplers. The highest 24-hour PM_{10} concentrations measured during the

winters of 1990/91 through 1993/94 were 287, 313, 183, and 190 $\mu\text{g}/\text{m}^3$ respectively. Sampling was conducted every sixth day using reference samplers. The seasonal pattern of fine PM using the dichotomous sampler is shown on Figure 2 for the years 1991-1993.

The site selected for this study is the new air monitoring station operated by the California Air Resources Board (ARB) which is located at 5558 California Avenue, Bakersfield, California (ARB#-1500255, AIRS#-060290014). The Bakersfield-California Avenue station began operation in March 1994, and is the replacement site for the Bakersfield-Chester Avenue station (ARB#-1500203, AIRS#-060290004). The Bakersfield-California station produces some of the highest daily PM values in the Valley. Data from this station are generally representative of the Valley in the composition of PM and the magnitude of the concentrations.

METHODS

Field Sampling

The principal objective of the Bakersfield Winter PM Study was to examine the performance of a variety of reference and non-reference PM_{10} samplers and several $\text{PM}_{2.5}$ samplers in an environment and during a season that would challenge any sampler. In addition to a meteorological system, 12 manual particulate samplers and four continuous particulate monitors were operated in the study. Manual sampling was performed every three days. A complete list of the instruments, and the measurement parameters of the study is provided in Tables 1 and 2. A description of the instruments is included below.

Size Segregated Inlet (SSI) Samplers (2): The SSIs used in the study were U.S. EPA reference high volume samplers (Sierra-Anderson Model 1200). The primary and collocated samplers were equipped with volumetric flow controllers, elapsed time meters, and Dickson chart recorders. Each sampler was also fitted with a magnehelic gauge to measure pre and post sample pressure drop and to verify the flow rates. Flows were verified monthly by a fixed orifice. Both samplers were calibrated before the study. Standard 8X10 inch quartz microfiber filters were used in this study. As a reference method for PM_{10} , these samplers were used to establish a basis to compare the performance of other instruments.

Tapered Element Oscillating Microbalance: The TEOM-50 and TEOM-30 monitors used in the study were Rupprecht & Patashnick (R&P) TEOM Series 1400a operated at standard flow rates, but at different temperatures. The TEOM is recognized by the U.S. EPA as an equivalent PM_{10} monitor. Both samplers were retrofitted with a 2.5μ cyclone inlet manufactured by University Research Glass (URG) rather than the standard 10μ head. The temperature of the enclosure that houses the microbalance was maintained at 50°C for the TEOM-50 and at 30°C for the TEOM-30. The different temperatures were selected to evaluate their effect on the mass readings. Flow rates were set at 16.7 liters per minute (LPM) at the inlet and 3.0 LPM through the microbalance filter. The monitors were calibrated before and once during the study period. Flow checks were performed biweekly.

Dichotomous: Two dichotomous samplers were used in the study. The first was the U.S. EPA reference sampler (Sierra-Anderson Model 241) equipped with a Dickson chart recorder to monitor flows. Flow rates were adjusted with rotameter needle valves and controlled by a pressure regulator. A second dichotomous sampler, referred to as the "dichot-mass flow controller," used the mass flow controllers (MFCs) and the pump component of a microprocessor controlled Xontech 920 sampler instead of the vendor-supplied pump and rotameters. The samplers used 37 mm Teflon filters in standard holders. Flows were continuously monitored by mass flow meters (MFMs) and were recorded on an Environmental Systems Corporation (ESC) Model 8800 data logger. Both units were calibrated at the beginning of the study. Leak and flow checks were performed monthly.

Monocot/920: The Monocot/920 is a single-stage sampler fabricated by ARB staff from a standard Dichotomous sampler. The dichotomous sampler's inertial separation stage was removed and one channel was

capped. A Teflon sleeve was used to join the upper and lower stages thus providing a straight path for particles to travel from the inlet to the filter. A 2.5 μ URG inlet replaced the conventional 10 μ head. The Xontech 920 pump and mass flow meter replaced the standard pump and rotameter to more closely monitor and control flows. The flow rate was set at 16.7 LPM as recommended by the inlet manufacturer. A 37 mm Teflon filter in a standard holder was used in sample collection. Hourly flows were also recorded on an ESC data logger. The sampler was calibrated before the study and leak checks were performed monthly.

AirMetrics: Two pairs of collocated AirMetrics Model 4.1 samplers were used in the study. One pair (primary and collocated) was configured for PM₁₀, and the second pair was adapted for PM_{2.5}. The basic units were identical except that different impactor inlets were used to obtain the desired size cut. The required inlet flow rate of five LPM was obtained by a voltage adjustment and was monitored by a built-in rotameter. Samples were initially collected on 47 mm Teflon filters, however periodic torn and wrinkled filters prompted a change to 37 mm Teflon filters in standard holders part way through the study. The samplers were calibrated at the beginning of study, and flow rates were checked monthly. Sample inlets were cleaned after every other run and reinstalled on the same sampler.

Partisol: The R&P Partisol Model 200H is the newest U.S. EPA approved reference sampler for PM₁₀. It used 47 mm Teflon filters in cartridges. The sampler was supplied by the manufacturer with a 2.5 μ URG inlet. A flow rate of 16.7 LPM was controlled by the Partisol's MFC and microprocessor. The flow rate was continually monitored by a MFM and recorded on an ESC data logger. The sampler was calibrated at the beginning of the study period and flow checks are performed monthly. The inlets were cleaned biweekly.

Xontech 920: The Xontech 920 is a multi-channel, microprocessor-controlled sampler that obtains samples using a variety of collection media. The Sampler used 37 mm Teflon filters in standard holders. Approximately, 22 Xontech 920s have been operating in California since the late 1980s as part of ARB's ambient toxic monitoring program. In this study, one of the eight independent channels was modified to accept the AirMetrics 2.5 μ impactor inlet. Flows were set using the Xontech 920 MFC to 5.0 LPM. The AirMetrics inlet was cleaned after every other run and flow checks were conducted. The sampler was calibrated at the beginning of the study.

Dry Deposition: The dry deposition sampler used in the study was the fine particle (0-2.5 μ), medium-volume portion of a sampler designed for the ARB's dry acid deposition monitoring program. The complete dry deposition sampler includes a fine and coarse element. The fine particle component is capable of obtaining as many as eight samples at a time on a 12 or 24-hour basis. The 2.5 μ sampler uses 47mm Teflon filters as the primary collection media and a back-up nylon filter to collect nitric acid and volatilized ammonium nitrate. The sampler's total flow rate through the inlet head was 113 LPM with 20 LPM passing through the 2.5 μ filter. The sampler was calibrated at the beginning of the study and flow checks were performed monthly.

Nephelometer: The nephelometer used was a Meteorology Research Incorporated Model 1550B with its sample inlet tube heated to approximately 17°C. Data were recorded as light scatter (b_{scat}) caused by suspended particles in ambient air. The unit was calibrated several times throughout the study.

AISI Tape Sampler: The American Iron and Steel Institute (AISI) tape sampler was manufactured by Research Appliance Corporation and operated at a flow rate of 6.25 LPM. The sampler collects 2-hour ambient air particle samples on a continuous reel of filter material. Light transmittance through each two-hour spot on the tape is measured by a sensor. The units of concentration are expressed as Coefficient of Haze (COH).

Meteorology Sensors: Wind speed, wind direction, temperature and relative humidity were monitored by a Met One Model 120 system. The sensors were calibrated prior to and during the study.

Laboratory

Mass: Samples collected on the PM₁₀ SSI samplers were measured on preweighed quartz fiber filters using a Sartorius Analytical balance (sensitivity to 0.0001g); all other samples were measured on preweighed Teflon filters using a Sartorius Microbalance (sensitivity to 0.001 mg). All filters were equilibrated for 24 hours at 23 ± 3°C and 40 ± 5% relative humidity before pre and postweighing.

Total Carbon: Total carbon content of PM₁₀ SSI samples was measured using a Dohrmann DC-85A TOC Analyzer (LOD (limit of detection) = 1.0 µg/m³C). Round punches from the filters were pyrolyzed at 800°C in an O₂ flow over a CO catalyst. The resultant CO₂ was measured using an NDIR detector.

Ions: All Teflon filters were treated with 50 µL absolute ethanol then extracted with 20 mL of deionized water by sonicating them for one hour. This was followed by shaking the filters for one hour at room temperature. Samples were refrigerated overnight. Extracts were analyzed for NO₃⁻, Cl⁻, and SO₄²⁻ by ion chromatography using a Dionex 4000i IC with an AG4A guard column and AS4A anion column (LOD = 0.1µg/m³).

Each PM₁₀ SSI quartz fiber filter was cut into quarters. One of these filter quarter was then extracted in 100 mL of deionized water by shaking for one hour at room temperature. The extracts were filtered and analyzed for NO₃⁻, Cl⁻, SO₄²⁻, NH₄⁺, and K⁺ by ion chromatography using a Dionex 4000i IC with an AG4A guard column and AS4A column for anions and a CS12 column for cations (LOD = 0.3µg/m³).

The nylon filters from the dry deposition sampler were extracted into 10 mL of deionized water by sonicating for one hour followed by shaking for one hour. Samples were refrigerated overnight. The filters were removed and the extracts analyzed for NO₃⁻ by automated colorimetry using a Lachat Quikchem AE (LOD = 0.05µg/m³).

Quality Assessment

Sampler audits consisted of flow rate checks. The flow audits were conducted according to the U.S. EPA's 40 CFR Part 58, Appendix A. The PM₁₀ SSI audits were conducted with a BGI variable orifice and a differential pressure gauge. The audit devices were certified against a National Institute of Standards and Technology (NIST) traceable roots meter. The Dichotomous sampler, the modified Xontech, TEOM, and the portable AirMetrics samplers flow audits were conducted using mass flow meters. The mass flow meters were certified against primary Sierra and Brooks flow standards. The absolute accuracy of the PM samplers was not determined.

The meteorological sensors were also audited. The wind speed sensor was audited using an R.M. Young variable drive controller. The wind direction audit was conducted with a compass and degree fixture. The wind sensor's starting threshold audits employed a torque disk and weights certified against NIST traceable standards. The ambient temperature audit was conducted with a Cole-Parmer digital thermistor certified against a NIST traceable thermometer. The dew-point and percent relative humidity audit was conducted with a Rotronics GTL hygrometer.

Laboratory analyses were consistent with the published Quality Control Manual and Standard Operating Procedures (SOP) for mass and ion determinations. No laboratory performance audits occurred during the study period, however ARB's inorganic laboratory regularly participates in the NO₃⁻ and SO₄²⁻ audits conducted by the U.S. EPA under the auspices of the National Performance Audit Program. Performance audits are done annually on mass determinations by ARB's Quality Assurance Section.

Data Management

Aerometric data from the field were collected by an ESC data logger and submitted to a central data manager. Laboratory data were compiled on a Laboratory Information Management System (LIMS) and submitted to the Program Evaluation and Standards Section. All data are stored in Microsoft ACCESS. Valid data were converted into a VOYAGER software format for final review and analysis.

RESULTS

Sampler Comparisons

Sampler performance was summarized by calculating estimates of variability among all samplers of similar size cut. Precision estimates were also calculated for the data from the collocated SSI (PM₁₀) samplers and the four AirMetrics units (PM₁₀ and PM_{2.5}). Variability estimates for the remaining samplers included nearly identical instruments (e.g., Dichot-standard configuration v. Dichot-mass flow controller) and others that were quite different (e.g., TEOM-50 v. dry deposition). Hourly TEOM data were converted into 24-hour values for comparison provided at least 75% of the hourly values in each 8-hour block of the day (i.e., 0000-0800hrs, 0800-1600hrs, 1600-2400hrs) were present. In no case was a 24-hour average calculated if more than two consecutive hours were missing during a day. This convention is the same as that used by the ARB when calculating 24-hour average NO₂ values from hourly data for comparison to the state ambient air quality standard for NO₂.

Variability and precision estimates are represented as the average of the variability of each pair of samplers.

$$\{ |a-b|/a+b/2 \} *100$$

where

a = mass of sampler a in $\mu\text{g}/\text{m}^3$

b = mass from sampler b in $\mu\text{g}/\text{m}^3$

The absolute value of the difference is used in this assessment to better understand total variability among the instruments. The absolute value method yielded estimates of variability larger than a conventional precision estimate; however, the estimates are consistent and the overall variability between samplers could be compared. Sample pairs were evaluated if both of the PM values exceeded $10\mu\text{g}/\text{m}^3$. The AirMetrics PM₁₀ and its collocated sampler showed precision of approximately 8%, and the SSI samplers reported 7% precision. The variability for the AirMetrics PM_{2.5} was 13%.

The variability among nonidentical PM_{2.5} samplers was calculated in the same manner. The results demonstrated that one group of samplers were in particularly good agreement. The six “fixed site” gravimetric samplers, i.e., the dichot-standard configuration fine (DC-SCf), dichot-mass flow controller fine (DC-MFCf), Xontech 920/Airmetric PM_{2.5} (X920-f), R&P Partisol (Psol-f), Monocot/920 (MC-f), and the dry deposition sampler (DD-f) reported variability among the data pairs of $\leq 20\%$. Six of the 15 possible combinations among the “fixed site” sampler pairs mentioned above, reported precision estimates $\leq 10\%$ (See Table 3, i.e., DC-MFCf versus Psol-f at 7%). The portable AirMetrics PM_{2.5} samplers demonstrated slightly increased variability when compared with “fixed site” PM_{2.5} samplers. Estimates were between 20% and 30%, and no pairs were $\leq 10\%$. The variability of the automated TEOM to other PM_{2.5} samplers was 40% to 75%.

The bias (slope) and correlation (r) among the PM_{2.5} samplers also suggested a strong agreement among some “fixed site” samplers. The best and most consistent correlations with other samplers were with the DC-SCf. The correlation between the DC-SCf and other samplers exceeded 0.90, and improved to 0.96 or

better when compared with the DC-MFCf, the X920-f, the DD-f, and the Psol-f samplers. Bias in each of the later case was less than 10%. The bias estimates are shown on Table 4 with those $\leq 10\%$ indicated in the shaded boxes. The dichotomous sampler showed good agreement to a variety of other samplers that operated within a wide range of inlet flow rates and filter face velocities. The results supported the dichotomous sampler as a suitable basis for comparison with other $PM_{2.5}$ samplers. We note that while in-use comparisons tend to support the ability of the dichotomous sampler to segregate particles into the 0-2.5 μ size, the sampler's federal reference designation is for PM_{10} .

The most pronounced difference among the sampler groups occurred between the gravimetric samplers and the two TEOM samplers, and between the two TEOM samplers that were operated at different temperatures. The 24-hour TEOM-30 mass accounted for approximately two-thirds of the $PM_{2.5}$ mass collected by the DC-SCf (See Figure 3). Unfortunately, only about ten data pairs were available for comparison at this point in the study. The relationship among the other "fixed site" samplers to the TEOM-30 was generally lower than its relationship to the dichotomous sampler. The TEOM-50 $PM_{2.5}$ mass levels represented about 35% of the DC-SCf mass. Although it was expected that the absolute accuracy of the PM samplers was not determined, measured mass concentrations would be lower than those measured by "fixed site" samplers, the degree of difference between the TEOM-30 $PM_{2.5}$ measurements and the "fixed site" measurements was surprising.

Data from the AISI ($COH \times 10$) and nephelometer ($b_{scat} \times 10$) were tabulated as 24-hour averages and compared with other daily measurements. The COH and nephelometer values correlated quite well to the $PM_{2.5}$ "fixed site" samplers ($r = 0.82 - 0.91$ for COH; and $r = 0.91 - 0.98$ for b_{scat}).

Sampler Operation

The Xontech 920's microprocessor contains a built-in printer that provided the start, stop, and average flow rates during 24-hour sampling runs. On high PM days early in the study, reviewers observed the flows from the fine channel (0-2.5 μ) of the DC-MFCf and the MC-f dropped from 15.03 and 16.7 LPM respectively, to less than four LPM at the end of the run. The problem was unexpected given the sampler operated with a larger pump capability and an enhanced flow controller when compared to the DC-SCf sampler. Since the Xontech 920 printout only provided information on the actual start, stop and average flows during the sample run, continuous monitoring was incorporated into the unit and stored on a data logger. This information, when related to other factors such as the mass loading, relative humidity and temperature, could possibly help define the cause of the problem with the filter plugging up. By incorporating the ability to monitor an entire sample run, flow excursions could be more closely monitored. During this study the flows of the DC-MFCf, MC-f, Psol-f and the DC-SCf samplers eventually included hourly flow as well.

An example of the flow problem discussed above, the flow data were plotted for the MC-f and the DC-MFCf for December 31, 1994 (Figure 4). The flow rate for the DC-SCf dropped to 10 LPM during the last hour of sampling, but the flow rates of the other two samplers dropped to less than 2 LPM during the last five hours of sampling. It has been hypothesized that the heavy particulate loading, in combination with high humidity, and low temperatures may have created a "slurry" on the filter surfaces thus severely restricting the sampler flow rate at the end of the sampling period. This intermittent problem, still not well understood, has illustrated the need for hourly flow rate monitoring for units deployed to the field in the future.

The AirMetrics samplers were fitted with 47 mm Teflon filters at the outset of the study. It became apparent after removing the exposed filters, however, that the filters would not always seat properly on the holder surface. Small tears and wrinkles appeared on the filters and a decision was made to change to a 37 mm Teflon filter encased in a secure holder. The smaller filters and new holders remedied the problem.

Audits

The results showed that all the meteorological sensors and PM samplers were operating within ARB's $\pm 10\%$ control limits. The TEOM-50, TEOM-30, Psol-f sampler, and the DD-f sampler flows were outside ARB's $\pm 7\%$ warning limits but within control limits at the time of the audit.

Ambient Data Comparison

Record amounts of rain fell throughout much of California during parts of January and March 1995 resulting in lower than normal PM concentrations. Winter PM_{10} concentration peaks are very often twice the measured PM_{10} ($97\mu\text{g}/\text{m}^3$) reached during this study period. Ambient temperatures ranged from -1°C to 16°C for December 1994, with an average of 7°C . The average temperature for January was 12°C with temperatures ranging from 1°C to 21°C . Relative humidity remained high for the first half of the study period with many days reporting levels of 90% or higher. The average relative humidity was 77%.

As was shown on Figure 1, fine particles form the majority of the PM in the late fall and winter, and coarse particles dominate the particle composition in the spring and summer. The distribution observed during this study was consistent with past years with the fine portion comprising approximately 75% of the total PM_{10} mass. An example of the distribution is illustrated in Figure 5, where the fine fraction was found to be $59\mu\text{g}/\text{m}^3$ out of a total mass of $81\mu\text{g}/\text{m}^3$.

The ion and constituent data from the PM_{10} samples indicated the the volatile components of PM (nitrate and carbon) made up a significant portion of the PM mass. The sulfate ion (SO_4^{2-}) concentrations comprised the least amount of the sample analytes (about 3% of both the $PM_{2.5}$ and PM_{10} mass in this study. The nitrate ion (NO_3^-) concentrations, however, reached $23\mu\text{g}/\text{m}^3$ (see Figure 6) and contributed an average of 28% to the $PM_{2.5}$ mass. From Figure 7, it is evident that the nitrate ions were found almost entirely (97%) in the $PM_{2.5}$ size range of particles.

Total carbon values in Bakersfield represented the single largest average component of the PM_{10} mass during the study. Peak concentrations were highest of the analytes with levels reaching $28\mu\text{g}/\text{m}^3$ on several occasions. The measurements of total carbon were limited somewhat by the analytical technique, but provided useful information about the composition of fine particles. The total carbon measurements were made in terms of carbon only and probably underestimated the actual contribution of carbonaceous material to PM_{10} . The analytical technique for carbon was also limited to analyses of samples that were collected on quartz fiber filters. Consequently, no total carbon data were obtained from the study for fine particulates. However, based on the high concentration of carbon found in the PM_{10} measurements, and the knowledge that combustion products are sub-micron in size, we expect to find significant levels of carbon particulates in the $PM_{2.5}$ fraction.

CONCLUSIONS

This study attempts to assess the potential for different $PM_{2.5}$ sampler configurations to measure PM on an equal basis; a must for attainment/nonattainment sampling. Furthermore, the study was to obtain and compare $PM_{2.5}$ measurements from a variety of samplers that were operated under complex environmental conditions that have been found in California. Specifically, the presence of high volatile constituents, low temperature, and high relative humidity have been shown to coincide with discrepancies among some samplers. All of these conditions occurred at times during the study.

The moist, cold air experienced in the San Joaquin Valley this winter may have contributed to the dramatic and undetected flow decreases in some samplers. If site operators retrieve filters and verify flow rates in a normal manner, i.e., during hours when temperatures may have warmed, flow reductions would not have been discovered. Continuous flow monitoring should be considered for all reference and equivalent samplers.

The experience in Bakersfield underscores the need that ambient testing be conducted to evaluate

potential reference and equivalent samplers at times of high particulate loading when volatile species are present. Testing should be conducted at times that consider low ambient temperature and high humidity. Attempts to perform equivalency testing for PM_{2.5} that do not consider these conditions will likely result in the continuation of discrepancies that exist among currently approved samplers.

A summary of the study conclusions is listed below.

- The data for the “fixed site” PM_{2.5} samplers, i.e., the two dichotomous samplers, the dry deposition sampler, the Partisol, and the Xontech 920/AirMetrics were in good agreement. The data pairs for these samplers agreed within 10% of one another. The variability among the samplers was less than 15%. It appears these instruments will yield comparable PM_{2.5} results under the conditions present in this study.
- The AirMetrics PM₁₀ and AirMetrics PM_{2.5} units agreed well between themselves with precision reported of 8% and 13% respectively. Neither sampler yielded good statistical agreement with other samplers of the same size cut. The AirMetrics PM₁₀ agreed well with the SSI in the range of 20-60µg/m³, but over the full range of particulate concentrations the sampler demonstrated a positive bias. The AirMetrics PM_{2.5} agreed well with the Dichotomous sampler data within the mid-range (20-50µg/m³) of particulate concentration. However, an overall bias, influenced by large differences between several data pairs was noted. Additional comparisons with the Dichotomous sampler are warranted.
- The TEOM PM_{2.5} devices (TEOM-30 and TEOM-50) reported data that were substantially lower than other samplers. Although the negative bias was less with the TEOM-30, both produced lower measurements suggesting losses at 30°C and a standard 3 LPM flow rate.
- The TEOM, the AISI and nephelometer at times correlated quite well to other samplers. If the relationships to other samplers are strong and consistent over time, these instruments can be valuable adjuncts to other sampling and should not be overlooked.

ACKNOWLEDGMENTS

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Seasonal Fine and Coarse PM Distribution in California

(Using specific days in 1992 and 1993)

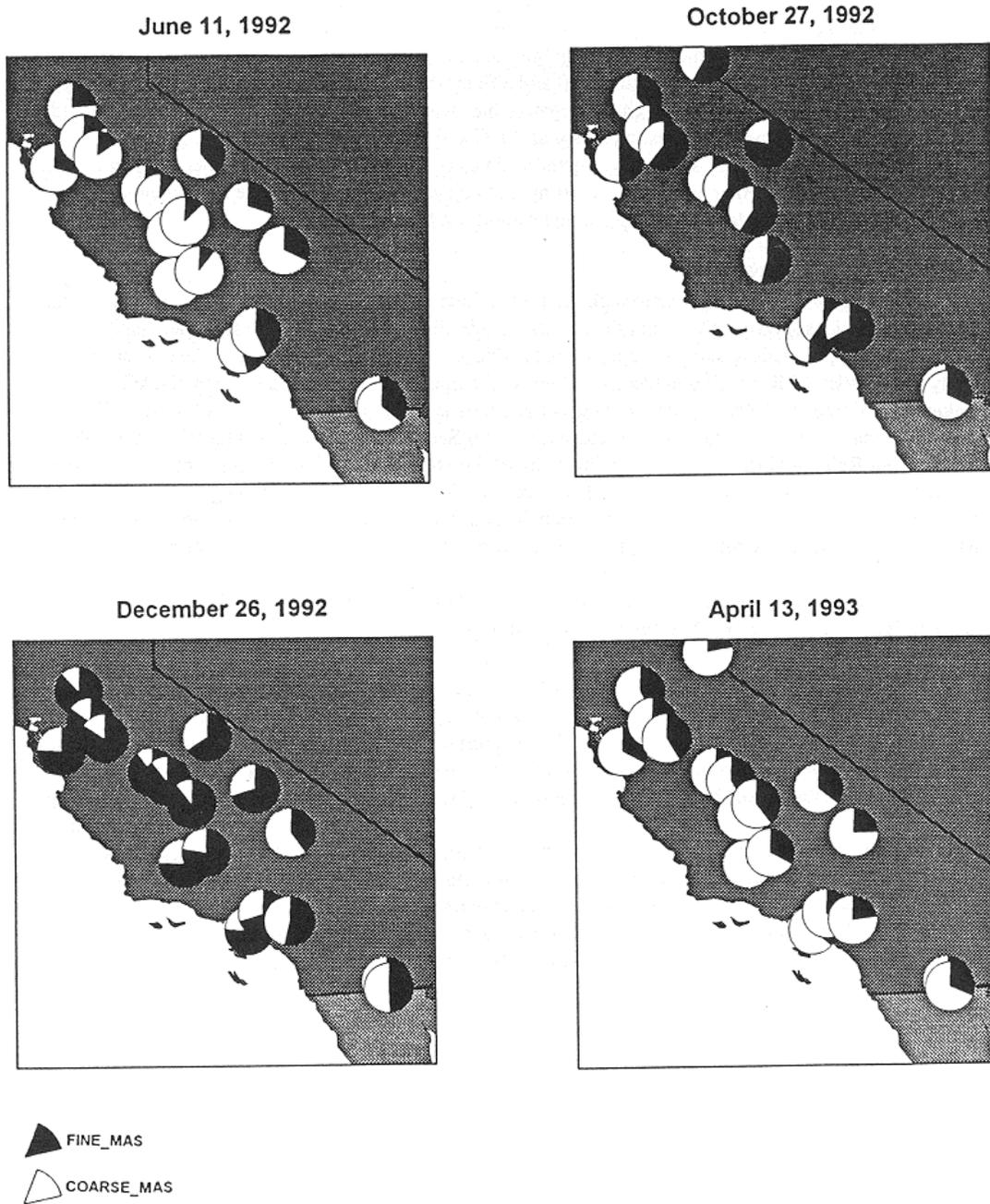


Figure 1

San Joaquin Valley, California

Fine Particulate (PM2.5) Concentrations (ug/m3)

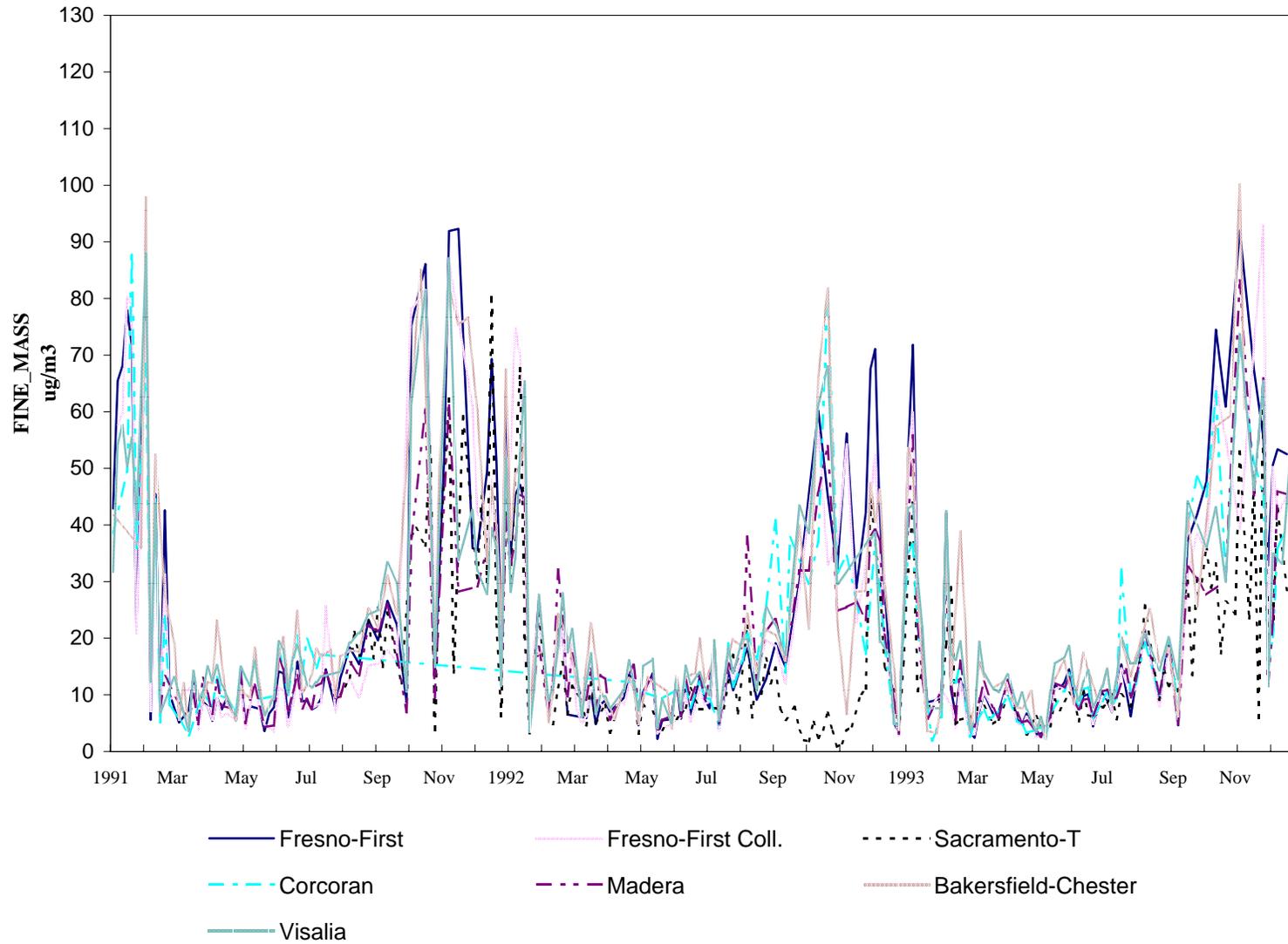


Figure 2

Bakersfield Winter PM Study 1994/95
Instrument Inventory

Instrument Type	Inlet Size	Analyte	Schedule	Sample Duration
SSI	10 μ	mass, ions*	1 in 3	24-hr; 0000-2400
SSI-collocated	10 μ	mass; ions*	1 in 3	24-hr; 0000-2400
TEOM-50	2.5 μ @ 50 deg	mass	continuous	1-hour average
TEOM-30	2.5 μ @ 30 deg	mass	continuous	1-hour average
Dichot-Std (SC)	0-2.5 μ ; 2.5-10 μ	mass, ions**	1in 3	24-hr; 0000-2400
Dichot-MFC	0-2.5 μ ; 2.5-10 μ	mass, ions**	1in 3	24-hr; 0000-2400
Monocot-MFC	2.5 μ	mass, ions**	1in 3	24-hr; 0000-2400
AirMetrics 10	10 μ	mass	1in 3	24-hr; 0000-2400
AirMetrics 10-collocated	10 μ	mass	1in 3	24-hr; 0000-2400
AirMetrics 2.5	2.5 μ	mass	1in 3	24-hr; 0000-2400
AirMetrics 2.5-collocated	2.5 μ	mass	1in 3	24-hr; 0000-2400
R&P Partisol	2.5 μ	mass	1in 3	24-hr; 0000-2400
XonTech 920/AirMetrics	2.5 μ	mass	1in 3	24-hr; 0000-2400
Dry Dep	2.5 μ	mass, ions***	1in 3	24-hr; 0000-2400
Nephelometer	TSP	bscat	continuous	1-hr
AISI	TSP	COH	continuous	2-hr
Met: WS, WD, RH, temp			continuous	1-hr

* SSI ions: nitrate, sulfate, ammonium, chloride, potassium, and total carbon.

** Dichot (2.5 μ) and monocot ions: nitrate, chloride, and sulfate.

*** Dry Dep ions: nitrate (nylon), nitrate, sulfate, and chloride and ammonium (teflon).

TEOMs will be operated in the same configuration for one day each month of the study to determine if operational characteristics are the same between like units.

Table 1

Sampler	Mass	Filter Analyses Performed					K ⁺	total carbon	Parameter Dictionary		
		NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺						
SSI	PM10	10µm	10µm	10µm	10µm	10µm	10µm	10µm	TEOM-30	Tap-Elem-Osc-Mic-30C Hourly Ave	µg/m ³
SSI-col	PM10								TEOM30Av	Tap-Elem-Osc-Mic-30C Daily Ave	µg/m ³
AirMetrics	PM10								TEOM-50	Tap-Elem-Osc-Mic-50C Hourly Ave	µg/m ³
AirMetrics-col	PM10								TEOM50Av	Tap-Elem-Osc-Mic-50C Daily Ave	µg/m ³
Dichot-SC	fine coarse PM10	fine	fine	fine	fine				NEPH	Nephelometer-Hourly Ave	Bscatx10
									Neph-Ave	Nephelometer-Daily Ave	Bscatx10
									AISI	Amer-Iron-Steel-Ind Hourly Ave	COH10
									AISI-Ave	Amer-Iron-Steel-Ind Daily Ave	COH10
									WS	Wind Speed	knts
									WD	Wind Direction	deg
Dichot-MFC	fine coarse PM10	fine	fine	fine	fine				RH	Relative Humidity	%RH
									Temp	Temperature	degC
									DC-MFCf	Dichot-fine (with MFC)	µg/m ³
									DC-MFCc	Dichot-course (with MFC)	µg/m ³
									DC-MFCs	Dichot-sum (with MFC)	µg/m ³
Monochot	fine	fine	fine	fine	fine				SSI	Size Selective Inlet-Mass	µg/m ³
Partisol	fine								Sat-f	Fine Saturation Sampler (AirMetrics)	µg/m ³
									Sat-t	Total Saturation Sampler (AirMetrics)	µg/m ³
Dry Deposition	fine	fine-t fine-n	fine	fine	fine				X920-f	XonTech 920-Fine Mass	µg/m ³
									DD-f	Dry Dep-Mass	µg/m ³
									MC-f	Monochot-Mass	µg/m ³
X920-AirMetrics	fine								Psol-f	Partisol-Fine	µg/m ³
									Ddn-NO3f	Dry Dep-Nitrate (Nylon)	µg/m ³
AirMetrics	fine								Ddt-NO3f	Dry Dep-Nitrate (Teflon)	µg/m ³
AirMetrics-col	fine								Ddt-SO4f	Dry Dep-Sulfate (Teflon)	µg/m ³
									Ddt-Cl-f	Dry Dep-Chloride (Teflon)	µg/m ³
TEOM-30	fine								Ddt-NH4f	Dry Dep-Ammonium (Teflon)	µg/m ³
TEOM-50	fine								MC-NO3-f	Monochot-Nitrate	µg/m ³
									MC-SO4-f	Monochot-Sulfate	µg/m ³
AISI	total								MC-Cl-f	Monochot-Chloride	µg/m ³
									DC-NO3-f	Dichot-Nitrate (with MFC)	µg/m ³
									DC-SO4-f	Dichot-Sulfate (with MFC)	µg/m ³
									DC-Cl-f	Dichot-Chloride (with MFC)	µg/m ³
									SSI-NO3	SSI-Nitrate	µg/m ³
									SSI-SO4	SSI-Sulfate	µg/m ³
									SSI-Cl	SSI-Chloride	µg/m ³
									SSI-K	SSI-Potassium	µg/m ³
									SSI-TC	SSI-TotalCarbon	µg/m ³
									SSI-NH4	SSI-Ammonium	µg/m ³
									DC-SCf	Dichot-fine (Std Config)	µg/m ³
									DC-SCc	Dichots-coarse (Std Config)	µg/m ³
									DC-SCs	Dichot-sum	µg/m ³
									DC-NO3SC	Dichot-Nitrate (Std Config)	µg/m ³
									DC-SO4SC	Dichot Sulfate (Std Config)	µg/m ³
									DC-ClSC	Dichot-Chloride (Std Config)	µg/m ³

Table 2

PM2.5 v. PM2.5

for pairs with correlation coefficient (r) ≥ 0.90

1 Dichot-SC

	correlation	prec(%)
Dichot-MFC	0.99	15
X920-AirMet	0.97	14
Dry Dep	0.97	10
Partisol	0.97	14
Monocot	0.91	13
TEOM-30	0.90	36
TEOM-50	0.93	52
AirMet	0.93	28

2 Dichot-MFC

	correlation	prec(%)
Dichot-SC	0.99	15
X920-AirMet	0.99	7
Dry Dep	0.98	8
Partisol	0.98	7
Monocot	0.90	15
TEOM-30		
TEOM-50		
AirMet		

3 X920/AirMET

	correlation	prec(%)
Dichot-SC	0.97	14
Dichot-MFC	0.99	7
Dry Dep	0.99	11
Partisol	0.96	8
Monocot		
TEOM-30		
TEOM-50	0.94	66
AirMet	0.90	23

4 Dry Dep

	correlation	prec(%)
Dichot-SC	0.97	10
Dichot-MFC	0.98	8
X920-AirMet	0.99	11
Partisol	0.99	10
Monocot	0.92	16
TEOM-30		
TEOM-50	0.91	58
AirMet		

5 Partisol

	correlation	prec(%)
Dichot-SC	0.97	14
Dichot-MFC	0.99	7
X920-AirMet	0.96	8
Dry Dep	0.99	10
Monocot		
TEOM-30	0.90	43
TEOM-50	0.92	65
AirMet		

6 Monocot

	correlation	prec(%)
Dichot-SC	0.91	13
Dichot-MFC	0.90	15
X920-AirMet		
Dry Dep	0.92	18
Partisol		
TEOM-30		
TEOM-50		
AirMet		

7 TEOM-30

	correlation	prec(%)
Dichot-SC	0.90	36
Dichot-MFC		
X920-AirMet		
Dry Dep		
Partisol	0.90	43
Monocot		
TEOM-50		
AirMet	0.91	58

8 TEOM-50

	correlation	prec(%)
Dichot-SC	0.93	52
Dichot-MFC		
X920-AirMet	0.94	66
Dry Dep	0.91	58
Partisol	0.92	65
Monocot		
TEOM-30		
AirMet	0.93	78

9 AirMetrics

	correlation	prec(%)
Dichot-SC	0.94	28
Dichot-MFC		
X920-AirMet	0.90	23
Dry Dep		
Partisol		
Monocot		
TEOM-30	0.91	58
TEOM-50	0.93	78

1. precision (%) = $[(a-b)/(a+b)/2] * 100$

2. precision estimates based on both values $10\mu\text{g}/\text{m}^3$

3. precision ≤ 20% shown in bold

Table 3

PM2.5 Sampler Comparison
Slope And Intercept

Sampler B

	Sat-f	Sat-f(col)	DC-SCf	DC-MFCf	X920-f	DD-f	Psol-f	MC	TEOM-30	TEOM-50	
S a m p l e r A	Sat-f	0.76 4.75	0.56 5.47	0.67 5.55	0.63 7.17	0.50 8.04	0.64 6.92	0.52 6.16	0.38 5.66	0.27 5.89	
	Sat-f(col)	1.20 -3.39		0.69 2.43	0.70 4.63	0.80 2.79	0.65 4.41	0.80 2.97	0.62 5.18	0.49 2.28	
	DC-SCf	1.57 -4.30	1.20 2.66		1.09 1.12	1.00 4.12	0.86 4.47	0.96 4.52	0.84 4.35	0.63 1.69	
	DC-MFCf	1.10 0.91	1.12 0.15	0.89 -0.36		1.09 -1.23	0.95 0.11	1.09 -1.24	0.72 3.13	0.49 3.92	
	X920-f	1.29 -3.33	1.10 0.54	0.94 -1.95	0.90 1.77		0.85 1.25	1.00 0.85	0.60 5.55	0.56 1.35	
	DD-f	1.56 -5.63	1.31 -1.45	1.10 -3.18	1.02 0.69	1.16 -1.03		1.10 -0.40	0.88 0.64	0.47 4.92	
	Psol-f	1.25 -2.43	1.06 0.98	0.98 -2.52	0.89 1.81	0.93 1.77	0.88 1.18		0.62 5.78	0.55 1.77	
	MC	1.42 -2.22	1.40 -4.21	0.98 -0.24	1.13 0.86	1.14 1.79	0.96 3.33	1.06 2.41		0.25 12.04	0.31 7.17
	TEOM-30	2.20 -5.63	1.61 4.46	1.28 3.02	1.29 5.24	1.35 6.99	1.23 9.10	1.47 3.66	1.19 5.81		0.67 4.11
	TEOM-50	3.23 -14.10	2.55 -7.15	2.47 -11.52	2.17 -4.42	2.36 -5.19	2.23 -5.89	2.58 -8.42	2.17 -6.48	1.03 2.76	

Slope	Shaded	Box, slope is ≤ 10%
Intercept		

Sampler A x [Slope] + Intercept = Sampler B

Table 4

Bakersfield Winter PM Study 1994/95
Dichot_SCf and TEOM_30AV

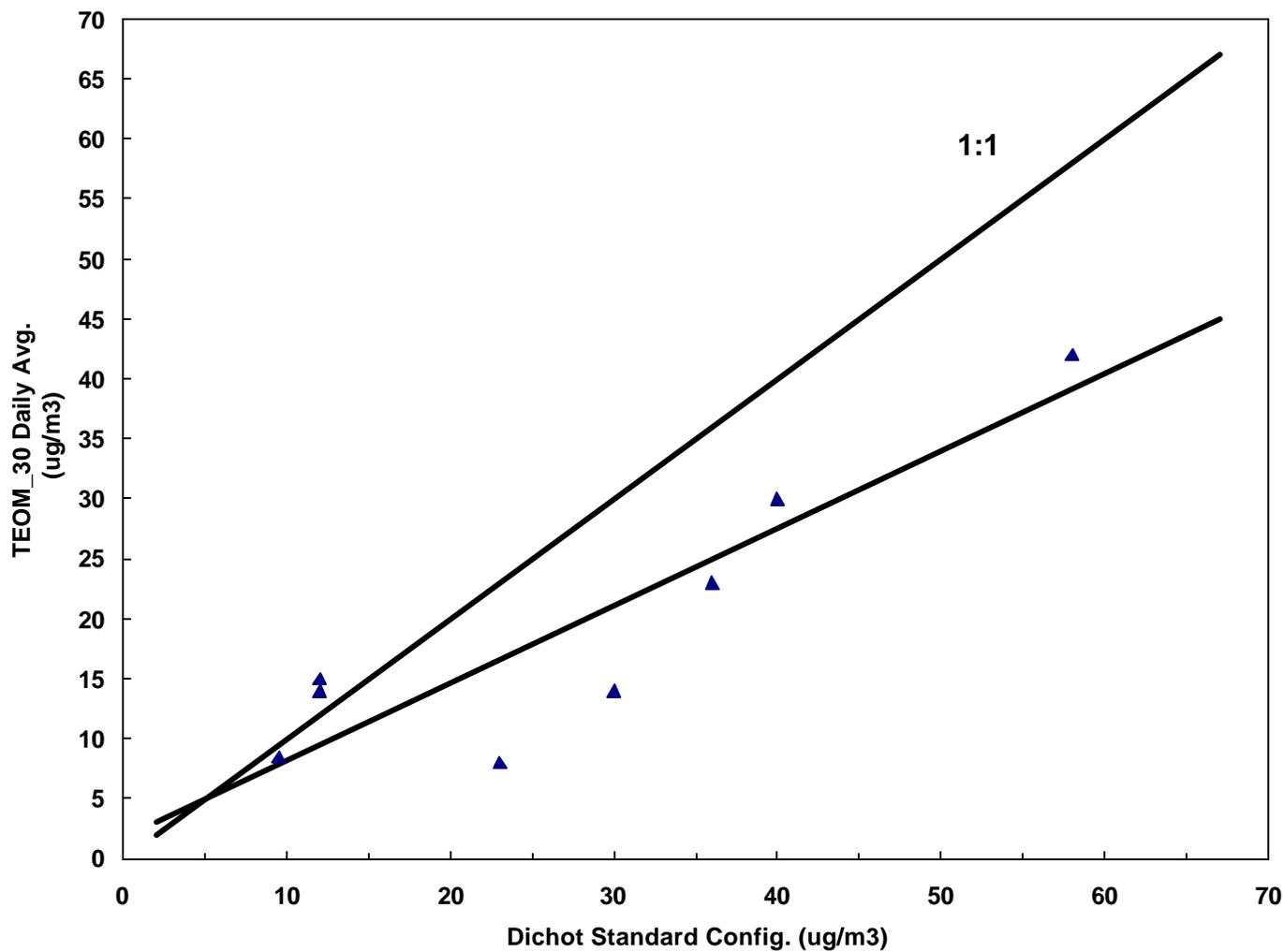


Figure 3

BAKERSFIELD PM2.5 STUDY
DECEMBER 31, 1994

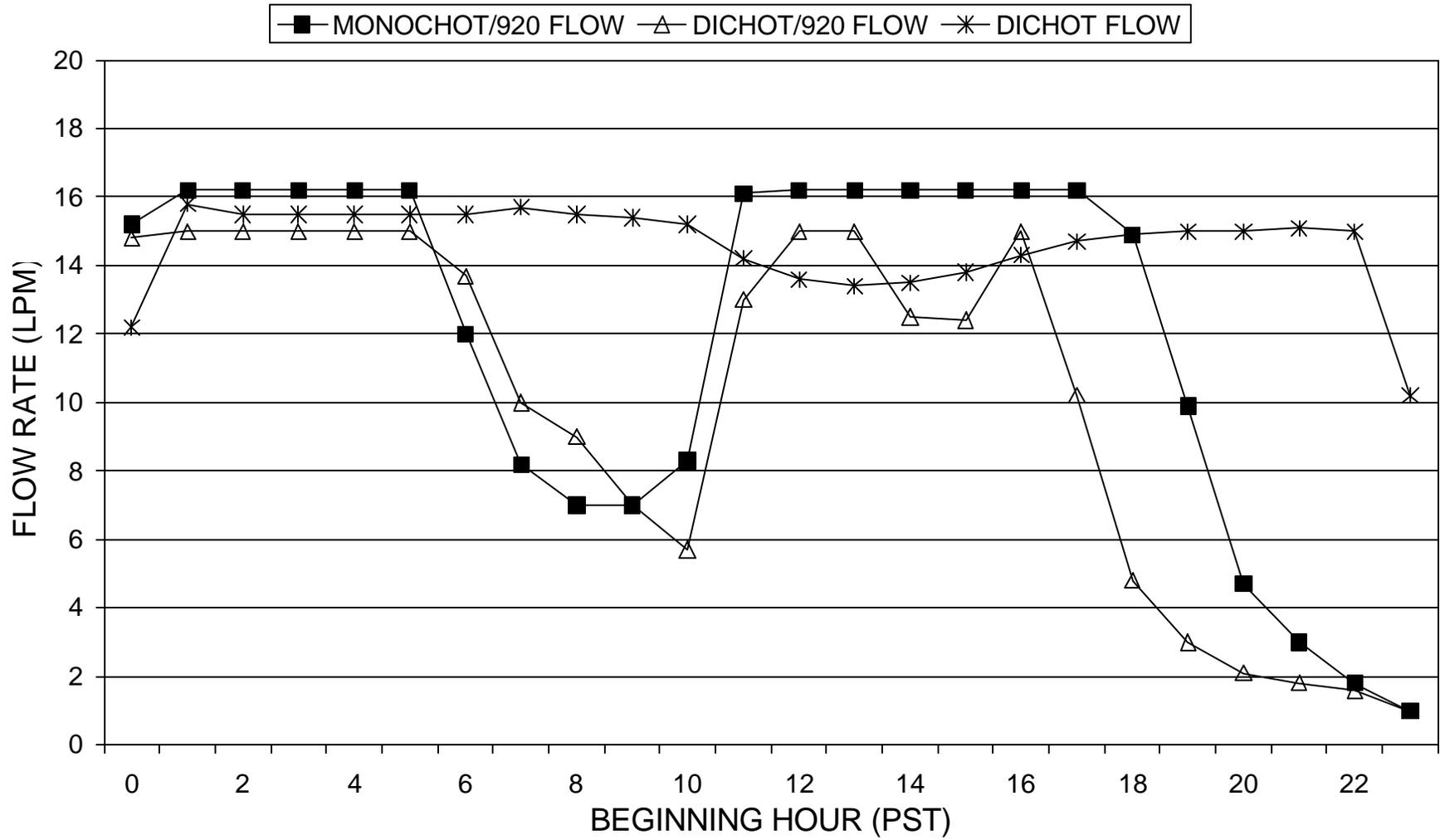


Figure 4

Bakersfield Winter PM Study 1994/95

Fine Particle Distribution December 31, 1994

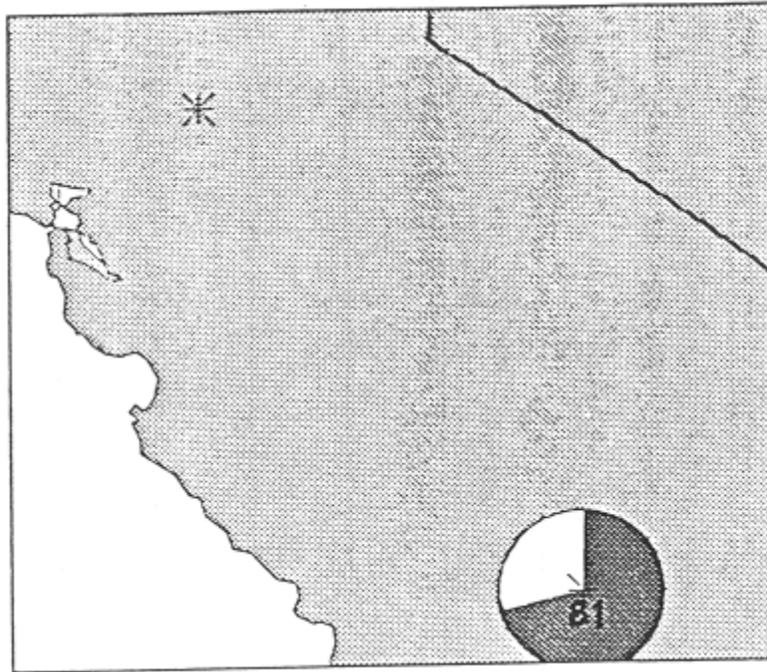


Figure 5

Bakerfield Winter PM Study 1994/95
Total Carbon (10u) - Nitrate (10u) - Temperature (deg C)

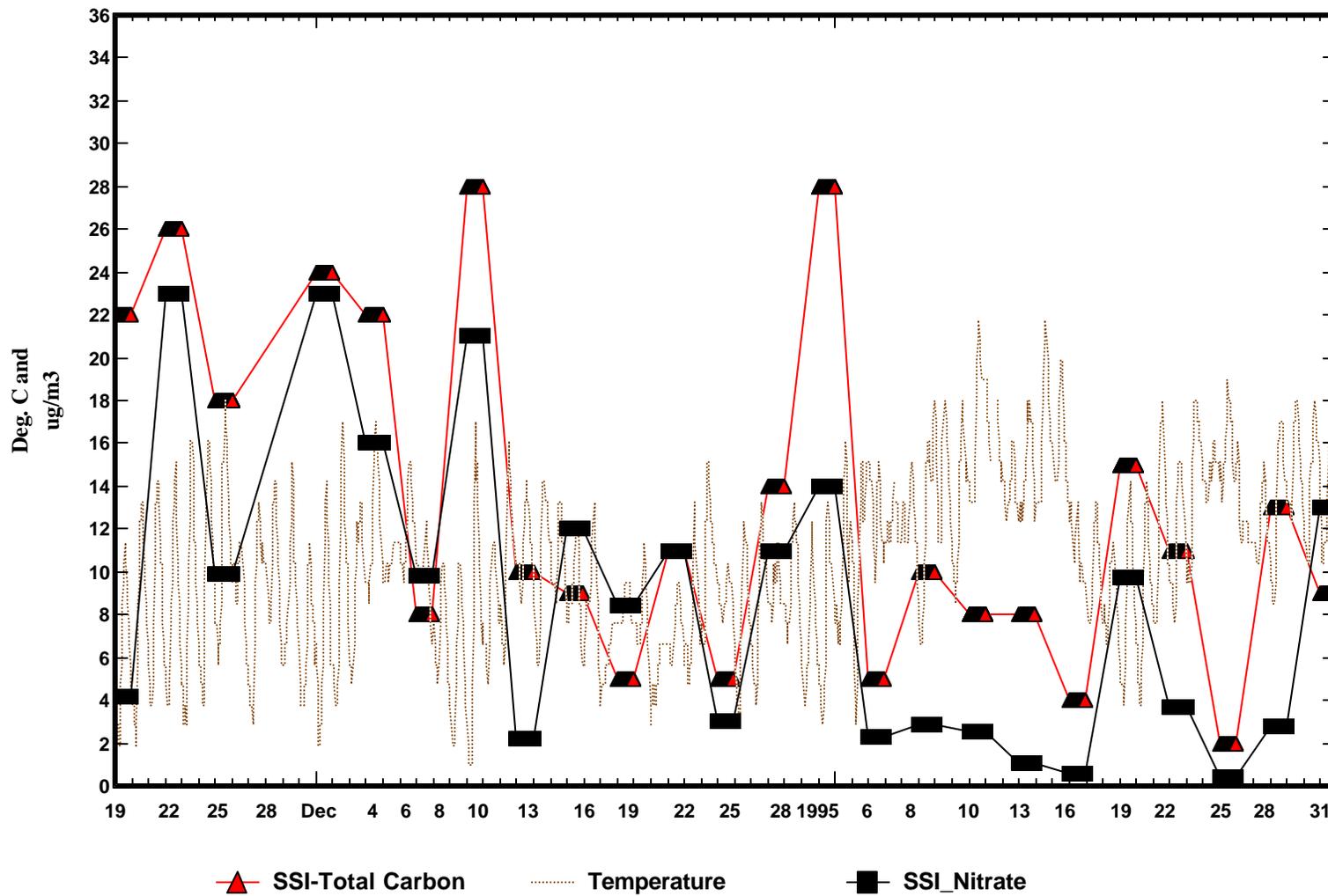


Figure 6

Bakersfield Winter PM Study 1994/95
Size-Fractionated Mass and Nitrate

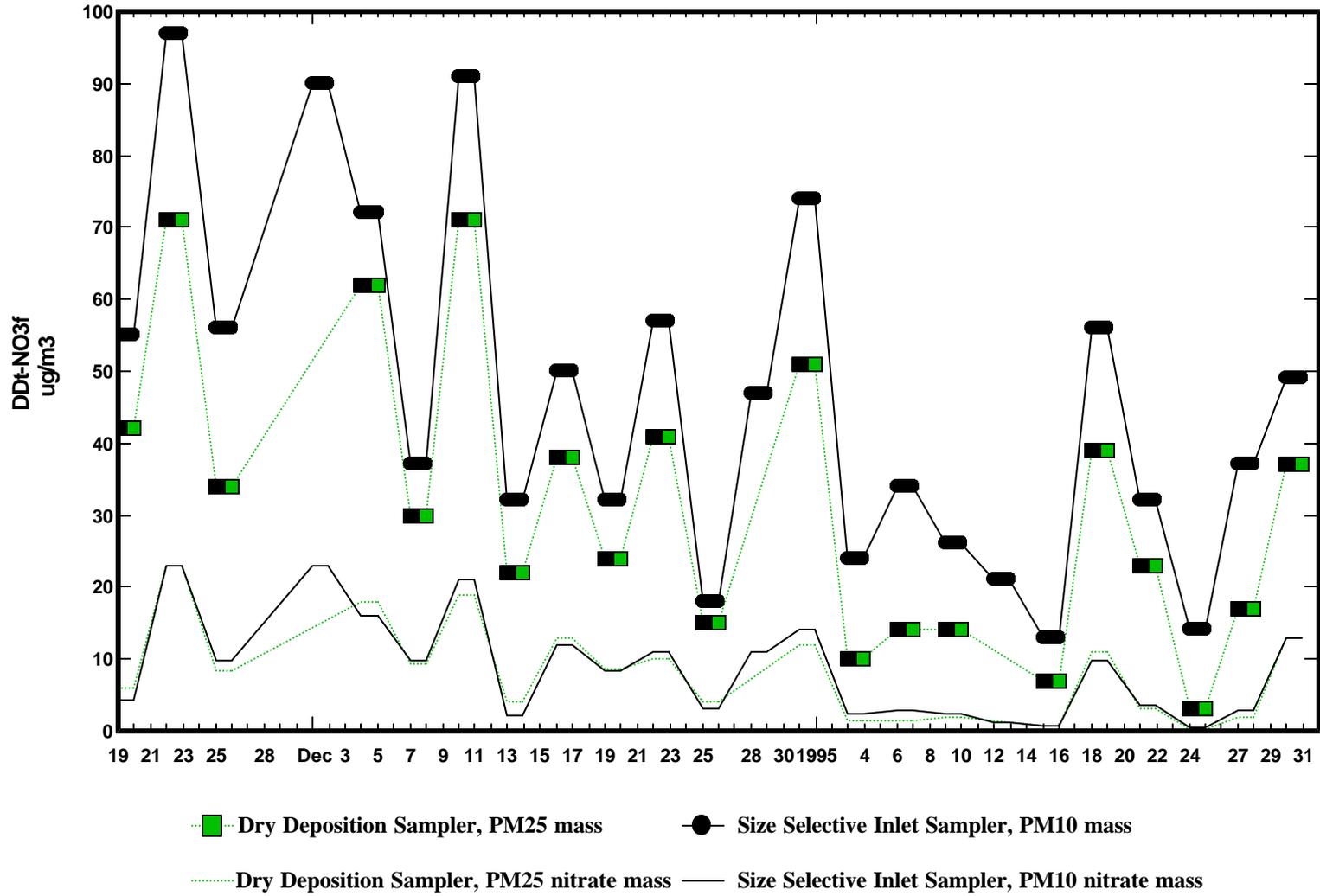


Figure 7