Attachment 2

Multi-Site Evaluations of Candidate Methodologies for Determining Coarse Particulate Matter ($PM_{10-2.5}$) Concentrations: August 2005 Updated Report Regarding Second-Generation and New $PM_{10-2.5}$ Samplers

by

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ABSTRACT

Comprehensive field studies were conducted to evaluate the performance of sampling methods for measuring the coarse fraction of PM_{10} in ambient air. In the first stage of this evaluation (2003 and 2004), five separate sampling approaches were evaluated at each of three sampling sites. As the primary basis of comparison, a discrete difference method was used which employs two designated FRM samplers, one to measure $PM_{2.5}$ and the other to measure PM_{10}. The numerical difference of these reference method concentrations (PM_{10}-$PM_{2.5}$) represented an estimate of $PM_{10\text{-}2.5.}$ A second sampling approach involved a sequential dichotomous sampler, which provided both $PM_{2.5}$ and $PM_{10\text{-}2.5}$ measurements. In both of these filter-based, time-integrated measurement approaches, the collected aerosol mass was analyzed gravimetrically in the laboratory under controlled conditions. Three continuous coarse particle samplers that measure $PM_{10\text{-}2.5}$ directly with a time resolution of one hour or less were also evaluated. One such sampler was a commercially available system based on beta attenuation, the second was based on TEOM technology. Both of these measurement approaches used dichotomous virtual impactors for separating fine and coarse particles. The third real-time sampler evaluated was an aerodynamic particle sizer (APS) that measures the aerodynamic diameter of individual particles, calculates the mass of the particle based on an assumed particle density, then sums the mass within the size range of interest to estimate the $PM_{10\text{-}2.5}$ mass concentration.

Sampling sites and timing of the studies were selected to provide diverse challenges to the samplers with respect to aerosol concentration, aerosol particle size distribution, and aerosol composition. Results from performance evaluations of the candidate $PM_{10\text{-}2.5}$ samplers at Gary, IN, Phoenix, AZ, and Riverside, CA during 2003 and 2004 are presented.

Once the instrument manufacturers were provided the results of these studies, EPA encouraged the manufacturers to revise their $PM_{10\text{-}2.5}$ samplers in an effort to address the measurement uncertainties identified during the 2003 and 2004 field campaigns. Following a one year time period, EPA conducted a follow-on field study of these second-generation samplers in Phoenix, AZ during April and May, 2005. In addition to evaluating the measurement performance of these modified samplers, the field study also evaluated four new prototype samplers designed to measure ambient $PM_{10\text{-}2.5}$ aerosols. Two of these newer samplers were time-integrated, filter-based designs, and two were designed to measure $PM_{10\text{-}2.5}$ aerosols on a continuous basis. Despite operational problems encountered with some of the instruments during this phase of the testing, overall measurement results were encouraging and the instrument manufacturers are continuing efforts towards development of reliable coarse mode samplers possessing minimal measurement uncertainty.

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1.0 INTRODUCTION

In response to increasing evidence of the adverse health effects associated with exposure to ambient fine particles, the United States Environmental Protection Agency (EPA) promulgated in 1997 a national ambient air quality standard (NAAQS) for $PM_{2.5}$[1]. Accompanying the standard were strict design and performance requirements which candidate $PM_{2.5}$ samplers must meet in order to be approved by EPA for use in making compliance measurements[2]. The 1997 regulations retained the existing annual PM_{10} standard and made only slight modifications to the statistical basis upon which to assess compliance with the 24-hour PM_{10} standard.

Based on subsequent litigation, the U.S. Court of Appeals for the District of Columbia reviewed the 1997 regulations and upheld EPA's promulgation of the $PM_{2.5}$ standard. While acknowledging the need to regulate coarse particles, the Court vacated the 1997 PM_{10} standard after concluding that PM_{10} is a "poorly matched indicator for coarse particulate pollution" because PM_{10} includes the $PM_{2.5}$ fraction. EPA did not appeal this ruling and now intends to promulgate a new NAAQS for $PM_{10-2.5}$ (i.e. the coarse fraction of PM_{10}).

Inherent to any new NAAQS is the need for sampling and analysis methods capable of measuring the new indicator with known quality. In support of this goal, the purpose of these field studies was to conduct a survey of available instrumentation designed to measure the coarse fraction of PM_{10}, and to conduct a multi-site performance evaluation of these instruments. Sampling sites were selected in order to evaluate the instruments under a wide variety of environmental conditions, particle concentrations, particle size distributions, and particle compositions. At three separate cities (Gary, IN, Phoenix, AZ, and Riverside, CA) thirty daily, 22-hour tests were conducted. Following the Riverside study, an additional fifteen days of 22-hour tests were conducted at the Phoenix, AZ sampling site. In addition to filter-based samplers which provide integrated test results, near real-time $PM_{10-2.5}$ monitors were evaluated which possess time resolutions of one hour or less. Multiple monitors of each type were used in order to determine the inherent precision of each sampler's design.

A July 2004 report provided a description of the instruments evaluated in the 2003 and the 2004 field studies, outlined the sampling and analysis procedures used to conduct the performance evaluations, described the characteristics of each of the three sampling sites, and provided a summary of test results. Since the time that report was prepared, additional validation of the data has been conducted, and this August 2005 report provides an updated presentation of those results. In addition, shape factors have been incorporated into the data obtained with the TSI aerodynamic particle sizer which appreciably improved its agreement with the collocated FRM samplers.

Following the completion of the 2003 and 2004 field tests, EPA has been working with the instrument manufacturers to improve the measurement performance of their respective

$PM_{10-2.5}$ samplers. This report details the modifications that were made to each of the samplers as a result of that collaborative effort. In April and May, 2005, these "second generation" samplers were evaluated during a 30-day field tests in Phoenix, AZ. In addition to these samplers, the field tests incorporated four new $PM_{10-2.5}$ samplers designs. Two of these designs were integrated, filter-based units (BGI Incorporated frmOmni saturation sampler and the Rupprecht & Patashnick (R&P) single-event dichotomous sampler) and two of the designs (Grimm EnviroCheck Model 1.107 and the R&P dichotomous TEOM sampler) were designed to provide $PM_{2.5}$ and $PM_{10-2.5}$ measurements on a near real-time basis. This report describes these samplers in detail and presents a summary of the 2005 Phoenix field test results for all samplers involved in the study.

To challenge the same suite of candidate samplers to different aerosol size distributions, aerosol composition, and environmental conditions, preparations are currently underway to conduct an additional sampler evaluation study in Birmingham, AL during fall 2005.

2.0 DESCRIPTION OF $PM_{10-2.5}$ SAMPLERS

Selection of the samplers to be involved in the field comparison study was based on the following criteria. First, all samplers had to be designed to provide a measurement of the mass concentration of $PM_{10-2.5}$ aerosols based on aerodynamic diameter. Selected filter-based samplers had to be capable of providing integrated samples at least every 24 hours and use the $PM_{2.5}$ FRM's standard cassette and Teflon afterfilter. Selected continuous and semi-continuous instruments had to be capable of providing $PM_{10-2.5}$ mass measurements at least every one hour. All samplers had to be capable of automated operation over a period of 24 hours, with active control of flow rates. Last, all selected samplers had to be either commercially available or in the final prototype stage of their design.

Based on these criteria, five separate $PM_{10-2.5}$ measurement approaches were selected for evaluation in the 2003 and 2004 field studies. Table 1 lists each sampler used in this study, its manufacturer, its inlet type, its inlet flow rate in actual liters per minute (alpm), and the number of replicate samplers used at each sampling site. For the filter-based samplers, the filter composition is listed along with the species to be determined during the filter's post-sampling gravimetric and/or chemical analysis. Due to funding constraints, not all the collected filters could be chemically analyzed. Instead, a representative subset of archived filters from each site was selected for chemical analysis based on the review of the comparative mass concentration results.

The voluntary participation and involvement of the $PM_{10-2.5}$ sampler manufacturers during these field studies was a critical component of studies' success. With the exception of the $PM_{2.5}$ and PM_{10} FRM samplers which were supplied by EPA, all field samplers in this study were supplied by their respective manufacturers. The supplied samplers all represented the latest models of each design and were equipped with the most current hardware, firmware, and

software. All manufacturers supervised installation and calibration of their respective samplers during the initial shakedown tests conducted in Research Triangle Park (RTP), NC and provided technical reviews of SOPs written for the instrument's setup, calibration, and operation. Each manufacturer was also provided the opportunity to visit each field site during site setup in order to verify the working condition of their samplers. At the completion of sampling at each field site, each manufacturer was supplied their respective field data in order to ensure that their sampler data was being properly retrieved from the instrument, correctly analyzed, and correctly interpreted.

2.1 Collocated $PM_{2.5}$ and PM_{10} FRM Samplers

In the first $PM_{10-2.5}$ measurement approach, commonly referred to as the "difference method," a designated $PM_{2.5}$ FRM sampler is collocated with a designated PM_{10} FRM sampler. For accurate determination of $PM_{10-2.5}$ concentrations, the PM_{10} sampler is simply a designated $PM_{2.5}$ FRM with its WINS fractionator replaced by a straight downtube (Figure 1). Both samplers are installed, calibrated, operated, and analyzed using standard $PM_{2.5}$ protocols. The two samplers thus have identical inlet aspiration characteristics, produce identical PM_{10} fractions, and collect aerosol at the same face velocity through the same filter media. At the completion of concurrent sampling periods, the $PM_{10-2.5}$ concentration is calculated as the numerical difference between the measured PM_{10} concentration and the measured $PM_{2.5}$ concentration. Due to its fundamental measurement principle, the difference method was used as the basis of comparison upon which to evaluate the performance of the other $PM_{10-2.5}$ samplers in the study. For purposes of this report, data collected using this method is termed "$PM_{10-2.5}$ FRM" data.

In this study, a designated PM_{10}-$PM_{2.5}$ FRM pair was used from each of three separate sampler manufacturers: Thermo-Andersen (AND), BGI, and Rupprecht and Patashnick (R&P). Each of these six FRM samplers were operated with preweighed Teflon filters for subsequent gravimetric and ion chromatography (IC) or x-ray fluorescence (XRF) analysis. A fourth set of $PM_{2.5}$ and PM_{10} FRM samplers was used and both samplers were equipped with a quartz filter to enable subsequent thermal optical measurement of the aerosol's elemental carbon (EC) and organic carbon (OC) constituents. In this study, the prefired quartz filters were not analyzed gravimetrically but were archived under cold conditions for subsequent EC/OC analysis.

2.2 R&P Model 2025 Sequential Dichotomous Sampler

The Model 2025 dichot was designed to provide integrated measurement of both fine and coarse fractions of a PM_{10} aerosol. As depicted in Figure 2a, the sampler actively provides volumetric flow control through a standard 16.7 alpm PM_{10} inlet. Following the aspirated

aerosol's fractionation in the inlet's internal fractionator, the resulting PM_{10} aerosol enters a virtual impactor where the aerosol is then split into major and minor flow streams. Ideally, the major flow (maintained at 15 lpm) is intended to collect only the $PM_{2.5}$ fraction of the PM_{10} aerosol while the minor flow (maintained at 1.7 alpm) is intended to collect only the $PM_{10-2.5}$ fraction of the PM_{10} aerosol. In practice, however, this size fractionation is never ideal, and 10% of the $PM_{2.5}$ mass theoretically deposits onto the $PM_{10-2.5}$ filter. The presence of these fine particles is numerically accounted for during subsequent calculation of the $PM_{10-2.5}$ concentration. Assuming that particle losses within the instrument are negligible, the sum of the measured $PM_{2.5}$ and $PM_{10-2.5}$ concentrations provide a measure of the ambient aerosol's PM_{10} concentration.

The Model 2025 sequential dichot allows unattended, multi-day operation through the use of a filter exchange mechanism (Figure 2b) for transferring filter cassettes from a supply tube to the sampling position, then conducting a post-sampling transfer of the cassettes to a storage tube. During this study, however, the multi-day capability of the Model 2025 was not utilized; supply magazines were manually loaded with only one cassette shortly before each test, and the post-sampling cassette was manually retrieved from the storage magazine shortly after each test. Procedures for gravimetric and chemical analysis of the Model 2025's filters were identical to those of the FRM's filters.

Four separate R&P sequential dichotomous samplers were used during the 2003 and 2004 field tests, three of which were equipped with Teflon filters while the fourth was equipped with prefired quartz filters to enable determination of elemental and organic carbon components of the ambient aerosol.

2.3 Kimoto Electric, Model SPM-613D Dichotomous Beta Gauge

Manufactured by Kimoto Electric Co., LTD., the Kimoto SPM-613D dichotomous beta gauge (Figure 3) is designed to provide near real-time measurement of both the fine and coarse fractions of the PM_{10} aerosol. Similar to the R&P Model 2025 dichot, the SPM-613D aspirates the ambient aerosol through a standard 16.7 lpm inlet and introduces the fractionated PM_{10} aerosol into a custom-designed virtual impactor. The virtual impactor in the SPM-613D has different dimensions than that of the R&P design and operates its major and minor flow rates at slightly different flow rates, 15.4 lpm and 1.3 lpm, respectively. Flow control in the two SPM-613D channels is monitored using separate mass flow sensors. The system's flow control system, however, is designed to maintain the calibrated mass flow rate and thus does not maintain true volumetric flow rates through the inlet at actual ambient temperature and pressure conditions. By conducting flow rate calibrations at the sampler's inlet under actual temperature and pressure conditions, however, the effect of this lack of volumetric flow control is minimal if ambient conditions do not differ substantially from those existing during the flow calibration.

Downstream of the SPM-613D's virtual impactor (Figure 4), the separate fine and coarse flow streams are continuously collected on a paper roll composed of low hygroscopicity polyfon. Following each hour of aerosol collection, the attenuation of ^{147}Pm beta rays by each channel's aerosol deposit is quantified using two separate sets of beta sources and detectors. Based on previous span calibrations performed by the user, the theoretical relationship between beta attenuation and collected aerosol mass is used to estimate the mass of each separate aerosol deposit. Because beta rays are also attenuated by condensed water, an external heater is located downstream of the sampler's inlet and maintains the temperature of the aspirated airstream above 25 °C. As in the R&P 2025 dichot, numerical corrections must be made to account for the theoretical mass of fine particulates contained within the SPM-613D's coarse channel filter. In the Kimoto design, these mathematical corrections are made within the system's software.

Three identical SPM-613D beta gauges were used during the course of the study at all three sampling sites.

2.4 R&P Continuous Coarse TEOM Monitor

As designed by Misra, et al.[3] and licensed to R&P, the coarse TEOM (Figure 5) was designed to provide a near real-time measurement of $PM_{10-2.5}$ concentrations. The instrument aspirates ambient aerosol at 50 lpm through a custom size-selective inlet, which was made by modifying a standard 16.7 alpm size-selective PM_{10} inlet by adjusting the internal dimensions in an effort to provide a 10 μm cutpoint at 50 lpm. Downstream of the inlet, the PM_{10} fraction then enters a custom virtual impactor whose major and minor flow rates are 48 lpm and 2 lpm, respectively. In this design, the fine fraction (major flow) is collected in a replaceable total filter and the collected fine aerosol mass is not subsequently quantified. Downstream of the virtual impactor, coarse aerosols in the minor flow stream are first heated to 50 °C to minimize interferences from particle bound water and are then deposited in a standard R&P 1400a Tapered Element Oscillating Microbalance (TEOM). The mass of the deposited aerosol is then estimated based on the observed change in vibrational frequency of the TEOM filter during the collection period. Due to the high flow rate ratio between the total and minor flows (25 to 1), no correction is made for the mass of fine particles on the coarse filter in this design. The $PM_{10-2.5}$ mass concentration is then calculated as the measured coarse mass divided by the volume of ambient air aspirated during the sampling event. Three replicate R&P coarse TEOMs were used during this field study in order to determine the inherent measurement precision of the samplers.

2.5 TSI Inc. Model 3321 Aerodynamic Particle Sizer (APS)

The final measurement approach used in the 2003 and 2004 field studies involved the TSI

Inc. Model 3321 APS (Figure 6a) to estimate the mass of ambient coarse particles based on their aerodynamic properties in an accelerating flow stream. To adapt the 5 lpm APS to field use, a standard 16.7 lpm PM_{10} inlet was used in conjunction with a custom designed flow splitter located downstream of the inlet. In the splitter, a sharp-edged, isokinetic nozzle extracts a representative sample of the PM_{10} aerosol for measurement in the APS. The remaining 11.7 lpm portion of the PM_{10} aerosol was drawn through a total filter using a volumetrically controlled vacuum source. The mass of the aerosol collected on the total filter was not quantified.

The 5 lpm representative aerosol sample is introduced into the APS, and the aerodynamic diameter of individual particles is estimated using time of flight technology, as depicted in Figure 6b. The mass of each particle is then calculated based on its measured aerodynamic diameter and a particle density specified by the user. For purposes of this field study, a particle density of 2 g/cm^3 was assumed as representative for the coarse fraction of PM_{10} aerosols. The mass concentration of $PM_{10-2.5}$ aerosols is then calculated as the sum of the mass of all particles penetrating the PM_{10} inlet whose aerodynamic diameters were greater than 2.5 micrometers. Because the APS is only capable of resolving particles larger than approximately 0.7 micrometers aerodynamic diameter, the system is not applicable for measurement of either $PM_{2.5}$ or PM_{10} ambient concentrations because particulate mass less than 0.7 micrometers is not quantified.

It should be noted that the primary purpose of incorporating the two APS units into the field study was to provide ambient aerosol size distribution information at each site. However, because the APS's measurement method has legitimate potential for providing continuous $PM_{10-2.5}$ concentration measurements, it was evaluated in this study in the same manner as the other $PM_{10-2.5}$ samplers.

2.6 R&P Single-Event Dichotomous Sampler

In terms of aerosol aspiration, fractionation, and aerosol collection, the R&P single-event dichot sampler is identical in design and fractionation performance to that of the Model 2025 sequential sampler. Designed in 2004 (Figure 7), the single-event sampler was developed as a smaller, lower-cost unit for users who do not require unattended, multi-day sampling capabilities. As in the case of the sequential dichot, the ambient aerosol is aspirated through a standard PM_{10} low-vol inlet at a volumetric flow rate of 16.7 lpm. The PM_{10} aerosol which exits the inlet is then separated into fine and coarse mode fractions in a virtual impactor at flow rates of 15 lpm and 1.7 lpm, respectively. Samples are collected on standard 47 mm filter cassettes and are retrieved manually following each sampling event. Unlike the design of the Model 2025 sampler where post-sampling cassettes are transported to a storage canister for subsequent retrieval by the user, the cassettes in the single-event sampler remain stationary. The potential for post-sampling loss of large particles, therefore, is thus minimized in the single-event dichot design.

Because the single-event dichot was developed in 2004, the design was not evaluated until the 2005 Phoenix field tests. For evaluation purposes, the manufacturer provided EPA with two prototype single-event dichot units.

2.7 Sierra-Andersen Model 241 Dichotomous Sampler

At the request of the State of Arizona Department of Environmental Regulations, limited tests were conducted with two Sierra-Andersen Model 241 dichotomous samplers during the January 2004 Phoenix field tests. Being the first designated PM_{10} sampler, the Model 241 (Figure 8) has been widely deployed for routine monitoring of both $PM_{2.5}$ and $PM_{10-2.5}$. In addition, the size selective performance of the sampler's 246b inlet has been fully wind tunnel evaluated and served as the basis for the 1997 $PM_{2.5}$ FRM's inlet design. The 246b inlet was designed to efficiently aspirate ambient aerosols and to provide an internal cutpoint of 10 micrometers aerodynamic diameter at a volumetric flow rate of 16.7 alpm. In the 241 dichot, PM_{10} aerosols exiting the inlet are then size fractionated in a virtual impactor whose design was based on research conducted by Loo and Cork[4]. The separate fine and coarse aerosols (at flow rates of 15 alpm and 1.7 lpm, respectively) are then collected on separate 37 mm filters for subsequent retrieval and analysis. Because the Model 241 does not provide active volumetric flow control, the flow rate of each unit was measured and recorded at the end of each test. If necessary, adjustments were made immediately prior to the next test to provide the correct channel flow rates at actual sampling conditions. The 37 mm teflon filters used in the Model 241 were equilibrated, handled, and analyzed using the same procedures as the 47 mm filters used during these tests.

2.8 BGI frmOMNI Ambient Air Sampler (Filter Reference Method)

The BGI Omni sampler was designed for monitoring agencies interested in conducting short-term, saturation sampling at a relatively low cost. To allow flexible setup and operation, the Omni system was designed to operate continuously on AC power or through use of a solar power supply. In conjunction with the low power requirements of the sampling pump, the 5 lpm flow rate enables operation up to 48 hours using its built-in storage battery. A constant volumetric flow rate of 5 lpm is maintained at the system's inlet using calibrated ambient temperature sensors, ambient pressure sensors, and flow sensors.

A photograph of the Omni unit is shown in Figure 9. Its inlet was designed by geometrically scaling down the PM_{10} FRM's 16.7 lpm inlet, and its aspiration performance has been evaluated in the laboratory at wind speeds up to 11 km/hr. Unlike the design of the $PM_{2.5}$ FRM's inlet, which has a fixed internal cutpoint of 10 micrometers, the cutpoint of the Omni inlet

was designed to be user-selectable at 1, 2.5, or 10 micrometers. This is accomplished through the use of interchangeable, single-jet impaction nozzles whose jet diameters were designed to provide the desired cutpoints. An ungreased impaction plate is designed to remove particles above the stage's cutpoint. Particles penetrating the impaction stage collect on a standard 47 mm filter for subsequent gravimetric and/or chemical analysis. To provide a measure of an airshed's TSP (total suspended particulate matter), the system may also be configured without an internal impaction jet.

Prototype Omni units became available for evaluation only after the 2004 Phoenix tests. For the 2005 Phoenix tests, the manufacturer provided EPA with a total of four Omni units - two which were configured as PM_{10} samplers and two configured as $PM_{2.5}$ samplers. Because preliminary tests showed that excessive bounce of large particles could occur from the ungreased $PM_{2.5}$ impaction plate, the plate of the $PM_{2.5}$ Omni units was greased daily during the 2005 Phoenix tests using a high vacuum silicone grease.

2.9 Grimm EnviroCheck Model 1.107 Sampler

The Grimm EnviroCheck Model 1.107 sampler was designed to measure the size distribution of airborne particles in ambient air or in occupational settings. The system aspirates the surrounding aerosols at 1.2 lpm through a small, omni-directional inlet (Model 170M) equipped with a bug screen. The aspirated aerosol is not heated and thus is designed to retain the aerosol's volatile and semi-volatile components. In the instrument's sensing region, individual particles pass through a flat laser beam, and the scattered signal is detected at an angle of 90 degrees. Based on the intensity of the scattered signal, each particle is classified into one of 31 different size channels. Using signal to mass concentration algorithms developed by the manufacturer, the system can report ambient aerosol concentrations as $PM_{1.0}$, $PM_{2.5}$, $PM_{10-2.5}$, or PM_{10}. All analyzed particles are collected on a PTFE filter, which can be subsequently removed and analyzed gravimetrically or chemically.

All sensitive components of the Grimm 1.107 are housed within a weatherproof housing (Figure 10) whose internal temperature is maintained at 22 °C. The Grimm 1.107 units first became available to EPA for the 2005 Phoenix tests and represented the only continuous instruments which were mounted directly on the roof of the motor home. All other continuous samplers involved in the field campaigns were not inherently weatherproof and thus had to be mounted inside the motor home.

2.10 R&P Dichotomous TEOM Sampler

The dichotomous TEOM sampler (Figure 11) was developed by R&P to determine near

real-time mass concentrations of both fine mode and coarse mode fractions of PM_{10}. In the dichot TEOM, the ambient aerosol is continuously aspirated through a standard PM_{10} FRM inlet at 16.7 lpm. The PM_{10} aerosol which exits the inlet is then fractionated into fine and coarse fractions in a virtual impactor whose design and channel flow rates are identical to those of the R&P Model 2025 dichot. Unlike the integrated, filter-based dichots (both manual and sequential) which collect the two aerosol fractions on teflon filters for subsequent gravimetric analysis, aerosol fractions in the dichot TEOM are designed to be quantified in near real-time using filter-dynamics measurement system (FDMS) TEOM technology. In the dichot TEOM design, two separate FDMS systems are functionally integrated to provide short-term measurements of both the coarse and fine fractions of PM_{10}.

As first marketed in the R&P Model 8500, the FDMS design goal is to measure both the non-volatile and volatile components of ambient aerosol. Every six minutes, the aerosol of interest is collected by a standard TEOM mass sensing unit and the mass concentration quantified. Because loss of volatile and semi-volatile aerosol components is inherent to the TEOM's use of a heater to remove particle-bound water, this estimated mass concentration often underestimates the actual concentration of the aerosol. To correct for this inadvertent loss of aerosol mass, a switching valve in the FDMS unit periodically diverts the aerosol flow stream into a purge filter conditioning section, which purges the airstream at a regulated temperature of 4 ^{o}C. The resulting purged airstream then passes through the TEOM mass sensor, and the change in mass is noted during the 6 minute time period. Any decrease in mass concentration measured during this time period is numerically added to that mass concentration measured for the non-purged aerosol sample. In the dichotomous TEOM, two separate TEOM sensing units are used to quantify both the fine particle concentration and the coarse particle concentration. As in the case of the sequential dichot and the manual dichot, the theoretical presence of fine aerosols within the coarse aerosol fraction must be numerically accounted for during calculation of $PM_{2.5}$ and $PM_{10-2.5}$ concentrations.

Two prototype dichot TEOM units were made available to EPA by R&P for the Phoenix 2005 tests. Similar to the coarse TEOM units, the dichot TEOM units were installed inside the motor home with their downtubes extending through the roof up to their external sampling inlets.

3.0 SITE SETUP AND OPERATING PROCEDURES

All field and laboratory activities associated with this study were conducted by RTI International under EPA contract 68-D-00-206. Prior to conducting the study, RTI International developed a Quality Assurance Project Plan (QAPP) which encompassed all aspects of the study's field and laboratory activities. The QAPP was subsequently reviewed and approved by QA personnel within EPA's Office of Research and Development (ORD) prior to initiation of the

study. All field and laboratory operations of the study were also reviewed and approved during a comprehensive Systems Audit conducted by ORD QA personnel prior to the field tests.

The multi-site performance evaluations of the 20 separate field samplers involved in the 2003 and 2004 studies presented a unique logistical challenge. With the exception of the FRM samplers and the R&P dichots, none of the other samplers have weather enclosures and must thus be protected from the elements during sampling. To enable efficient transportation of all field equipment and to house the field samplers, a 25 foot long motor home was adapted for use in this study. The twelve FRM and R&P dichot samplers were installed either on the roof of the motor home or on a 10' by 10' auxiliary platform positioned immediately adjacent to the motor home. The remaining eight $PM_{10-2.5}$ samplers were installed inside the motor home with their downtubes extending through the roof of the motor home and attached to their respective inlets. Within ± 0.2 m, all inlets were at the same 5 m elevation above ground level.

The motor home's environmental controls maintained the interior temperature at 23 ºC ± 3 ºC during all field tests. Per compliance testing requirements, the inlets of all samplers were installed 2 m above the sampling platform, and all samplers were spaced horizontally at least 1 m apart from each other. At each site, the motor home and auxiliary platform were free of nearby obstructions which might adversely influence the spatial uniformity of $PM_{10-2.5}$ concentrations. Figure 12 is a photograph of the sampling setup at the Gary, IN sampling site.

Prior to each field test, all samplers were cleaned and leak-checked. Each sampler was then calibrated for volumetric flow rate, ambient temperature, and ambient pressure measurement using a calibrated transfer standard (BGI DeltaCal). For calibration of the 50 lpm flow rate of the R&P coarse TEOM, a BGI TriCal was equipped with a 55 lpm capacity flow module which had been specifically designed and fabricated for this purpose. Following the calibration of each instrument, a performance audit was conducted using a separate audit device, and any necessary adjustments were made to the instruments. In addition to the initial audit conducted at each field site, performance audits were also conducted following Run 15 and Run 30. Field blank tests of the filter-based samplers were conducted at the same frequency as that of the performance audits. Field blank values were not used to correct the measured PM concentrations but served as an indicator of filter mass changes during all phases of filter handling and transport. Per the field study's QAPP, the occurrence of excessive field blank values would have triggered a systems audit and appropriate corrective actions would have been taken.

At each sampling site, 30 daily, 22-hour tests were conducted from 11 am (local time) to 9 am of the following morning. The two hour interval between successive tests enabled the site operator sufficient time for sample changeover, data recording, and minor maintenance while still allowing for daily sampling. Typically, a 45 day test period was required to complete site setup, 30 days of sampling, and site shutdown.

Gravimetric analysis of the filter-based samplers' teflon filters was conducted both in the

EPA weighing facility in RTP, NC and at each sampling site. At each site, one room of a two-room hotel suite was set up and used for all filter conditioning, weighing, and handling operations. The proper temperature and relative humidity within the room was maintained through appropriate use of the room's AC unit in conjunction with use of in-room humidifier and dehumidifier systems. In RTP, presampling filters were equilibrated and preweighed in an environmentally controlled chamber whose temperature and relative humidity setpoints were 22 °C and 35%, respectively. All filter weighings were conducted using a Cahn C-44 microbalance which had a readability of 1 μg and a capacity of 5 g. The analytical balance was tared and calibrated prior to each weighing session, and Class 1 calibration weights were used during each session to verify the balance's internal calibration. In order to increase the confidence in the gravimetric analysis, 100% replicate weighings (with a 5 μg reweigh threshold) were used for each filter during all preweighing and postweighing operations. Quality control also included the use of three laboratory blank filters during each weighing session. At the completion of the preweighing in RTP, the filters were loaded in sampling cassettes and the cassettes were sealed with metal endcaps, and the sealed cassettes placed in Thermo-Andersen cassette canisters (Figure 13). The canisters were then shipped to the field site in coolers designed to maintain post-sampling filters at temperatures below 2 °C.

Upon receipt of the preweighed filters from RTP, field personnel would then unpack and equilibrate the filters in the weighing facility setup within the hotel room. Through careful adjustment of the room's environmental controls, site personnel were able to maintain the room's weighing conditions within allowable temperature and relative humidity limits. Presampling and postsampling site weighings were conducted using a Sartorius MC5 microbalance with the same capability as the Cahn microbalance used for the RTP weighings. Identical weighing protocols were used at all field sites and at the RTP weighing facility. Once postsampling filters were weighed at the site, they would be shipped to RTP under cold conditions for final postweighing and subsequent archiving. Conducting filter weighing at the field site enabled faster determination of test results than could be obtained if samples were shipped back to RTP. Conducting filter weighing at the site and at RTP also enabled measurement of particle losses which might occur during shipping. Lastly, site weighing provided valid test results in the event that a cooler might be inadvertently damaged or lost during its shipment back to the RTP weighing facility. As will be presented, properly observing sampling handling, shipping, and analysis protocols typically resulted in excellent agreement between gravimetric results obtained at each field site's weighing laboratory versus results obtained at the RTP weighing laboratory.

4.0 SITE CHARACTERISTICS

Following the initial installation and evaluation of the $PM_{10-2.5}$ samplers in RTP, NC to

verify the proper operating condition of the samplers and to finalize operating protocols, successive field tests were conducted in Gary, IN (2003), Phoenix, AZ (2003, 2004, and 2005), and Riverside, CA (2003). The following section will provide a description of these three sites along with the meteorological conditions and aerosol characteristics encountered during each site's field tests.

4.1 Gary, IN (March - April, 2003)

The Gary, IN site was selected as representing a midwest industrial city where primary $PM_{10-2.5}$ aerosols are predominantly generated by industrial activity rather than by wind blown soils. Selection and setup of the Gary, IN sampling site was made in cooperation with personnel from the Indiana Department of Environmental Management. This State and Local Air Monitoring site (AIRS # 18-089-0022, N41° 36.391', W87° 18.308') is located approximately 2 km south of Lake Michigan and is immediately adjacent to the property line of a steel mill. Nearby sources of emissions include the steel mill, which was located approximately 0.7 km northwest of the site, and a 0.5 km long open coal pile which was located approximately 0.5 km northeast of the site.

The 30 days of testing at the Gary site were conducted from March 6 to April 7, 2003. Weather at the site was typically cloudy, windy, and cold, and only one rain event occurred during the study period. Temperatures at the site ranged from -15.1 °C to 27.8 °C and a mean daily site temperature of 4.6 °C was recorded.

As measured by the three collocated FRM samplers, $PM_{2.5}$ concentrations measured at the Gary site during the tests ranged from 10.3 $\mu g/m^3$ to 46.9 $\mu g/m^3$, with a measured mean of 22.8 $\mu g/m^3$. Excellent inter-manufacturer agreement was observed among the filter-based $PM_{2.5}$ FRM samplers, as expressed by the coefficient of variation (CV) of 1.5%. It should be noted that the inter-manufacturer precision calculated for all FRM data throughout this report is data representing three different manufacturer's reference method samplers. Because each manufacturer has different fabrication facilities, uses different components, and uses different flow control strategies, it is reasonable to expect that intra-manufacturer precision of the reference method samplers may be even better than the reported inter-manufacturer precision for the $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} metrics.

As expressed by a coefficient of variation of 2.4%, excellent inter-manufacturer agreement was also observed for the PM_{10} FRM measurements. PM_{10} concentrations measured during the tests ranged from 22.6 $\mu g/m^3$ to 85.0 $\mu g/m^3$, with a measured mean of 42.6 $\mu g/m^3$. $PM_{10-2.5}$ concentrations (expressed as the numerical difference between collocated PM_{10} and $PM_{2.5}$ FRM measurements), ranged from 4.5 $\mu g/m^3$ to 58.1 $\mu g/m^3$ with a measured mean of 19.9 $\mu g/m^3$. Inter-manufacturer precision of $PM_{10-2.5}$ concentrations was determined to be 5.7% CV. As indicated by a mean $PM_{2.5}$ /PM_{10} ratio of 0.55 during the 30 sampling events, slightly more than one-half of the

site's PM_{10} aerosol was associated with $PM_{2.5}$ aerosols. $PM_{2.5}$ /PM_{10} ratios ranged from 0.32 to 0.83 during the 30 days of testing, indicating that the size distribution of ambient aerosols was quite variable during the month-long field tests. Predominant winds from the direction of the nearby steel mill typically contributed to $PM_{2.5}$ concentrations at the site, while winds predominating from the direction of the open coal piles resulted in measurement of high $PM_{10-2.5}$ site concentrations.

Filter weighing at the Gary site began with Run 5 filters. As indicated in Figure 14, excellent agreement was observed between $PM_{10-2.5}$ concentrations based on the site weighings versus the RTP weighings during Runs 5 through 30. The filter shipping and handling protocols designed for the study, therefore, appeared to result in negligible $PM_{2.5}$ or PM_{10} particle loss from the FRM filters during their transport from the field site to the RTP weighing facility.

4.2 Phoenix, AZ (May - June, 2003)

The first set of tests conducted in Phoenix, AZ occurred during early summer of 2003. Phoenix represents a large arid southwestern urban area with natural and anthropogenic sources of particulate pollution. Phoenix is a city of approximately 1.3 million people, with a total population of 3.3 million in the greater metropolitan area. The sampling site was selected primarily to challenge the coarse particle samplers with high concentrations of dry, wind blown crustal materials. Through cooperation with personnel at the Air Quality Division of the Maricopa County Environmental Services Department, the county-operated Durango Complex sampling site (AIRS # 04-013-9812, N33° 25.589', W112° 7.085') in the southwestern portion of Phoenix was selected as an appropriate field site. The site is located at a county facility complex, which includes a prison, offices, and general storage. The site location is impacted by commercial districts to the north and two main interstate highways located to the east and northeast of the site. With the predominant wind direction being from the west and southwest, however, the site is primarily impacted by large windblown soils originating from non-vegetated, open fields and from earthmoving activities during nearby commercial construction.

The month-long field tests at the Phoenix sampling site were conducted from May 14 to June 15, 2003. Weather at the site was typically clear, windy, and very hot, and no rain events occurred during the 30-day study period. Temperatures at the sampling site ranged from 17.1 °C to 43.5 °C and a mean daily site temperature of 32.3 °C was recorded.

$PM_{2.5}$ concentrations measured during the 2003 Phoenix tests ranged from 6.4 $\mu g/m^3$ to 22.0 $\mu g/m^3$, with a measured mean of 11.0 $\mu g/m^3$. As observed during the Gary tests, excellent inter-manufacturer agreement was achieved among the filter-based FRM samplers. As expressed by the coefficient of variation, mean inter-manufacturer precision for $PM_{2.5}$ was determined to be 3.4%. As expressed by a coefficient of variation of 3.1%, excellent inter-manufacturer agreement

was also observed for the PM_{10} FRM measurements. PM_{10} concentrations measured during the tests ranged from 37.1 $\mu g/m^3$ to 230.9 $\mu g/m^3$ with a measured mean of 66.7 $\mu g/m^3$. $PM_{10-2.5}$ concentrations (expressed as the numerical difference between collocated PM_{10} and $PM_{2.5}$ FRM measurements), ranged from 26.5 $\mu g/m^3$ to 209.0 $\mu g/m^3$, with a measured mean of 55.7 $\mu g/m^3$. Inter-manufacturer precision of $PM_{10-2.5}$ concentrations measured by the three FRM pairs was determined to be 3.3% CV. As indicated by the mean $PM_{2.5}/PM_{10}$ ratio of 0.18 during the 30 sampling events, a large fraction of the site's PM_{10} concentration was associated with $PM_{10-2.5}$ aerosols. $PM_{2.5}/PM_{10}$ ratios ranged from 0.10 to 0.28, which indicated that coarse particle mass dominated the PM_{10} concentrations during each day of the Phoenix tests. Figure 15 depicts the daily dominance of the coarse particles in the Phoenix area and also shows the strong agreement observed between the FRM filter weighings conducted at the sampling site versus those conducted at the RTP weighing facility.

4.3 Riverside, CA (July - August, 2003)

The Riverside, CA sampling site was selected as a West Coast site where significant secondary fine mode aerosols might be present in conjunction with primary coarse aerosols. Riverside is a city of approximately 260,000 people, and industrial, agricultural, transportation, soil, and marine sources all contribute to airborne particulates. Selection and setup of the Riverside site was made through cooperation with the University of California-Riverside (UCR). The monitoring site is located on the edge of a 420-acre Agricultural Operations Center of UCR and is operated by the South Coast Air Quality Management District (California Air Resources Board Site # 33162, N33° 57.679', W117° 20.017'). The agricultural test facility contains large areas of citrus trees and is adjacent to interstate highway I-215, approximately 60 km northeast of the Pacific Ocean. Local sources of ambient aerosols include photochemical pollution from mobile sources, resuspended road dust, dairy and agricultural farms, wind-blown soils, and sea salt particles from the ocean.

Field tests were conducted at the Riverside sampling site from July 23 to August 24, 2003. Weather at the sampling site during the 30 daily tests was typically warm with clear or partly cloudy skies. No rain events occurred during the Riverside field tests although morning fog was occasionally observed at the site. Temperatures at the site ranged from 15.4 °C to 40.4 °C, and a mean daily site temperature of 25.9 °C was recorded.

As had been experienced during the Gary and Phoenix sites, excellent inter-manufacturer agreement was observed among the filter-based FRM samplers. As expressed by the coefficient of variation, mean inter-manufacturer precision for $PM_{2.5}$ was determined to be 3.1%. Daily $PM_{2.5}$ concentrations measured during the tests ranged from 9.9 $\mu g/m^3$ to 32.7 $\mu g/m^3$, with a measured mean of 17.7 $\mu g/m^3$. As expressed by a coefficient of variation of 2.9%, excellent inter-

manufacturer agreement was also observed for the PM_{10} FRM samplers. PM_{10} concentrations measured during the tests ranged from 27.0 $\mu g/m^3$ to 69.3 $\mu g/m^3$, with a measured mean of 48.0 $\mu g/m^3$. $PM_{10-2.5}$ concentrations (expressed as the numerical difference between collocated PM_{10} and $PM_{2.5}$ FRM measurements), ranged from 16.2 $\mu g/m^3$ to 46.1 $\mu g/m^3$ with a measured mean of 30.4 $\mu g/m^3$. Inter-manufacturer precision of $PM_{10-2.5}$ FRM measurements was determined to be 4.1% CV. As indicated by the mean $PM_{2.5}/PM_{10}$ ratio of 0.37 during the 30 sampling events, approximately two-thirds of the site's PM_{10} concentration was associated with $PM_{10-2.5}$ aerosols. $PM_{2.5}/PM_{10}$ ratios ranged from 0.25 to 0.50 during the 30 days of testing at the Riverside site, indicating that coarse particles dominated the PM_{10} aerosol during all tests.

4.4 Phoenix, AZ (January 2004)

Following the completion of the Riverside, CA field tests, a second set of tests was conducted at the Phoenix, AZ sampling site in order to investigate issues raised during the prior Phoenix field tests. In particular, tests were conducted to investigate potential loss of large particles within the R&P sequential dichotomous samplers. Tests were also conducted with a prototype coarse TEOM constructed by USC to compare its performance versus two commercial coarse TEOM units manufactured by R&P.

These follow-up field tests in Phoenix were conducted from January 10 to January 25, 2004. $PM_{2.5}$ concentrations measured during the 2004 Phoenix tests ranged from 6.0 $\mu g/m^3$ to 22.4 $\mu g/m^3$, with a measured mean of 13.2 $\mu g/m^3$. As observed during the previous field campaigns, strong inter-manufacturer agreement was achieved among the filter-based FRM samplers. As expressed by the coefficient of variation, mean inter-manufacturer precision for $PM_{2.5}$ measurements was determined to be 2.2%. As expressed by a coefficient of variation of 3.6%, excellent inter-manufacturer agreement was also observed for the PM_{10} FRM measurements. PM_{10} concentrations measured during the tests ranged from 14.8 $\mu g/m^3$ to 177.5 $\mu g/m^3$ with a measured mean of 52.8 $\mu g/m^3$. $PM_{10-2.5}$ concentrations (expressed as the numerical difference between collocated PM_{10} and $PM_{2.5}$ FRM measurements), ranged from 7.7 $\mu g/m^3$ to 95.1 $\mu g/m^3$ with a measured mean of 39.5 $\mu g/m^3$. Inter-manufacturer precision of $PM_{10-2.5}$ concentrations measured by the three FRM pairs was determined to be 4.8% CV. As indicated by the mean $PM_{2.5}/PM_{10}$ ratio of 0.30 during the 30 sampling events, a large fraction of the site's PM_{10} concentration was associated with $PM_{10-2.5}$ aerosols. $PM_{2.5}/PM_{10}$ ratios ranged from 0.13 to 0.57, which indicated that coarse particle mass dominated the PM_{10} concentrations during each day of the Phoenix tests. .

Weather at the site during the first 10 days of testing was typically warm with clear or partly cloudy skies. Movement of a cold front into the Phoenix area during Runs 10-11 dramatically altered the weather and the nature of the aerosol at the sampling site. Prior to this

time, the weather at the sampling site was warm and the relative humidity was typically in the 30% to 40% range. During Runs 12-15, however, rain events were common and the relative humidity at the site was typically in excess of 60%. These rain events resulted in significantly lower $PM_{10-2.5}$ concentrations. As measured by the FRM pairs, the mean $PM_{10-2.5}$ concentration during Runs 1-11 was approximately 50 μg/m³, while the $PM_{10-2.5}$ concentration during Runs 12-15 was only 10 μg/m³. The size distribution of the ambient aerosol was also appreciably different during these two time periods. For Runs 1-11, the $PM_{2.5}/PM_{10}$ ratio averaged only 0.24 (with a low of 0.13) but averaged 0.49 (with a high of 0.57) during Runs 12-15.

As was observed during previous field tests, the gravimetric samplers ($PM_{2.5}$ FRMs, PM_{10} FRMs, and R&P dichots) all provided precise test results as evidenced by coefficient of variations typically on the order of a few percent. The overall data capture rate of the filter based samplers during the 15 day Phoenix study was 98%.

4.5 Phoenix, AZ (April - May, 2005)

Following design modifications to the $PM_{10-2.5}$ samplers evaluated in the 2003 and 2004 field campaigns, another series of tests was conducted at the Phoenix sampling site. The purpose of these tests was to evaluate the effectiveness of the design modifications to the samplers since the time of the January 2004 Phoenix tests and to evaluate four newly available $PM_{10-2.5}$ sampler designs. Addition of these new samplers increased the total sampler count to 28 units. Table 2 provides a description of the various samplers used during the 2005 Phoenix field tests.

Tests were conducted at the Phoenix site from April 27 to May 28, 2005. All site setup, operating procedures, and analysis protocols were identical to the 2003 and 2004 field campaigns. During the 30 daily sampling events, $PM_{2.5}$ concentrations (as measured by the R&P, BGI, and Andersen FRMs) at the site averaged 9.9 μg/m³ and ranged from 4.9 μg/m³ to 16.6 μg/m³. $PM_{10-2.5}$ concentrations averaged 46.2 μg/m³ and ranged from 23.4 μg/m³ to 122.8 μg/m³. PM_{10} concentrations averaged 56.0 μg/m³ and ranged from 30.1 μg/m³ to 134.6 μg/m³. Similar to FRM results obtained during previous field campaigns, the inter-manufacturer precision for the $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} metrics was strong, as indicated by calculated coefficient of variations of 2.8%, 2.4%, and 1.9%, respectively. The mean $PM_{2.5}/PM_{10}$ concentration ratio for the study was 0.18, indicating that a large percentage of the PM_{10} aerosol was associated with coarse mode aerosols. Incidentally, this mean ratio of 0.18 is identical to that observed during the 2003 Phoenix tests conducted during a similar time of year. The lowest $PM_{2.5}/PM_{10}$ ratio occurred on the final testing day during which the $PM_{10-2.5}$ concentration was measured to 134.6 μg/m³. Thus, over 90% of the PM_{10} mass concentration was associated with $PM_{10-2.5}$ aerosols during this particular sampling event. Weather during the study was generally hot and no rain events were recorded during the 30 days of sampling. In many respects, the ambient aerosol and sampling conditions

during this recent study were similar to those of the May 2003 Phoenix study.

5.0 TEST RESULTS

5.1 Collocated $PM_{2.5}$ and PM_{10} FRM Samplers

5.1.1 Year 2003, 2004, and 2005 Test Results

As previously described, field tests involved the use of four sets of $PM_{2.5}$ and PM_{10} samplers from BGI, Andersen, and R&P. Because there exist no absolute standards for ambient particulate matter, the absolute accuracy of these devices cannot be determined from these tests. However, the performance of the three separate manufacturers' samplers with respect to each other can be calculated. As summarized in Table 3, the inter-manufacturer precision of the FRM samplers was considered to be excellent for all three metrics ($PM_{2.5}$, $PM_{10-2.5}$, and PM_{10}) at all three sampling sites. Calculating the $PM_{10-2.5}$ concentration as the numerical difference between collocated designated PM_{10} and $PM_{2.5}$ FRMs did not produce any zero or negative $PM_{10-2.5}$ concentrations during the 135 sampling events conducted during the field studies. Because three separate manufacturer's samplers were used during these events, this represents a total of 405 separate difference method measurements during the five separate field campaigns.

With the exception of a pump failure and a faulty ambient temperature sensor connection, few functional problems were experienced with the eight FRM samplers despite the wide range of environmental conditions experienced during the study. The three performance audits conducted at each sampling site revealed that the FRMs generally maintained their flow rate, temperature, and pressure calibrations within the required specifications. Overall data capture rate for the FRM samplers during the three site, five field campaign studies was determined to be 99%.

5.2 R&P Model 2025 Dichotomous Samplers

5.2.1. Year 2003 and 2004 Test Results

Only two operational problems were experienced with the four R&P Model 2025 sequential dichotomous samplers during the 2003 and 2004 field studies. In Gary, a faulty cassette seal in one of the dichot's coarse channels caused the majority of the coarse aerosol to bypass the collection filter. As a result, the coarse particle mass concentration measured by this instrument was significantly less than that measured by the other collocated dichots. The data for this sampler's coarse channel was thus invalidated. The second problem experienced with the Model 2025 dichots occurred towards the latter half of the Phoenix tests, where significantly low $PM_{2.5}$

and PM_{10} measurements were obtained by one of the dichots. At the completion of the Phoenix tests, this behavior was explained by the discovery of a dense spider web in the dichot's size selective inlet. The $PM_{2.5}$ and PM_{10} measurements for this instrument were thus invalidated for 17 of the 30 sampling events. At all sites, invalid data were not used to calculate daily aerosol mass concentrations nor used to estimate intra-sampler precision. Discounting the invalid data obtained due to the presence of the spider web, overall data capture rate of the dichots during the study was 98%. Performance audits of the Model 2025 dichots indicated that they maintained their flow rate, temperature, and pressure calibrations within the required specifications.

Table 4 summarizes the field performance of the Model 2025 dichots at all three Year 2003 sites in comparison to the collocated FRM samplers. As the table indicates, excellent intra-sampler precision was observed for the R&P dichots at all three sites for all three metrics. As an example, the precision (expressed as the coefficient of variation) in Gary for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} concentrations was determined to be 3.8%, 3.2%, and 1.7%, respectively. The largest coefficient of variation (4.1%) was observed in Phoenix (May - June, 2003) for measurement of $PM_{10-2.5}$ aerosols.

As Table 4 indicates, the $PM_{2.5}$ concentrations measured by the R&P dichots in Gary and Riverside agreed almost exactly with concentrations measured by the collocated FRM samplers. For $PM_{2.5}$ measurements in Gary, Figure 16 depicts the strong agreement and high correlation between the R&P sequential dichotomous samplers and the collocated $PM_{2.5}$ FRMs.

In Phoenix, however, the dichots consistently over-predicted the $PM_{2.5}$ concentration by about 8%. This over-measurement is hypothesized to be due to the inadvertent intrusion of coarse mode aerosols into the fine channel, which has been known to occur in virtual impactors[4].

The Model 2025 dichots consistently under-measured $PM_{10-2.5}$ concentrations at all three sites although results were highly correlated (mean R^2 equaled 0.977). A high coefficient of determination at a site indicates that the sampler's performance, with respect to the collocated FRMs, was very consistent during the 30 days of testing. For $PM_{10-2.5}$, mean sampler to FRM ratios at Gary, Phoenix, and Riverside were determined to be 0.90, 0.80, and 0.96, respectively. Summing the dichots' measured $PM_{2.5}$ and $PM_{10-2.5}$ concentrations to estimate the PM_{10} concentrations, it was observed that mean sampler to FRM ratios for PM_{10} in Gary, Phoenix, and Riverside were 0.94, 0.85, and 0.97, respectively. For Phoenix, therefore, 15% of the aspirated PM_{10} aerosol mass cannot be accounted for when compared to the collocated PM_{10} FRM samplers. The consistency of this behavior in Phoenix is illustrated in Figure 17. Because collected aerosol deposits in the R&P dichots are analyzed gravimetrically using the same procedure as that of the FRM samplers, it was hypothesized that the noted PM_{10} mass balance problem in the R&P dichots was either due to internal particle losses or loss of particles prior to their gravimetric analysis. In particular, the question was raised whether large particles were being lost during the mechanical transport of the $PM_{10-2.5}$ filter cassette from its sampling position to its post-sampling position in

the storage magazine. To address this issue, R&P modified two of the four dichotomous samplers from automatic sequential operation to manual operation. The sample cassettes in the manual samplers, therefore, do not undergo the pre-sampling or post-sampling transport operations associated with the sequential design. These modified units were evaluated in Phoenix, AZ in January 2004 during 15 days of testing.

Results from these tests of the R&P dichotomous samplers are presented in Table 5. While the nature of the aerosol during these January 2004 tests did not produce PM_{10} measurement discrepancies as experienced during the May - June, 2003 tests, 8% of the aspirated PM_{10} aerosol was still being unaccounted for in the sequential dichotomous samplers. Mean dichot to FRM ratios for $PM_{10-2.5}$ and PM_{10} were determined to be 0.89 and 0.92, respectively. When the R&P samplers were operated in manual mode, however, the ratio of the samplers to the collocated FRMs was 0.99 and 1.00 for $PM_{10-2.5}$ and PM_{10}, respectively. Results for the dichot performance versus that of the FRMs for these two metrics were extremely highly correlated as indicated by R^2 values of 0.998 and 0.999, respectively.

Due to the lack of active flow control in the Sierra-Andersen dichot samplers, less confidence can be placed in the results of these limited field tests. Overall, however, it appears that the Sierra-Andersen dichot behaves somewhat similarly to the R&P manual dichot. Mean Sierra-Andersen dichot to FRM ratios for $PM_{10-2.5}$ and PM_{10} were determined to be 0.95 and 0.97, respectively. Similar to the virtual impactor in the R&P model, it also appears that some intrusion of coarse particles into the fine channel occurs in the Sierra-Andersen's virtual impactor. It may be the nature of virtual impactor technology, therefore, that some contamination of the fine particle mass by coarse particles is unavoidable. Because the resulting bias in measured $PM_{2.5}$ concentrations is dependent upon the size distribution of the PM_{10} aerosol, significant measurement biases will occur only if the coarse fraction of PM_{10} appreciably exceeds the $PM_{2.5}$ fraction.

As a result of these follow-up tests in Phoenix, it was concluded that large particles were not being lost in the R&P 2025 dichot during collection nor during post-sampling transport but lost during their automated transport to the storage container. Since the time that these field tests were conducted, R&P has conducted additional tests of the samplers in Phoenix, AZ and concluded that the majority of the particle loss is associated with the cassette's post-sampling horizontal movement rather than its subsequent vertical placement within the storage canister.

5.2.2 Sampler Design Modifications

As described in the previous section, the results of the Phoenix 2004 dichot tests, as well as subsequent laboratory testing by R&P, indicated that loss of large particles was occurring in the sequential dichot during the post-sampling transfer of the cassette into its storage canister. To address this issue, the cassette exchange mechanism of the sequential dichot was redesigned by

R&P to provide a much slower acceleration of the cassette during its post-sampling movement. The effectiveness of this design change was subsequently evaluated in the Phoenix tests conducted in 2005. No other design changes to the sequential dichot sampler were considered necessary at this time.

5.2.3 Year 2005 Phoenix Test Results

The 2005 Phoenix tests involved the use of two R&P sequential dichots (with redesigned cassette exchange mechanisms) in conjunction with two single-event samplers. For both $PM_{2.5}$ and $PM_{10-2.5}$, Figure 18 indicates that good agreement was generally observed between both dichotomous samplers designs and the collocated FRM samplers. As observed during previous Phoenix field campaigns, the timeline indicates that the $PM_{2.5}$ concentrations during the 30-day study were relatively constant but that wide variations in $PM_{10-2.5}$ typically occurred. The respective results obtained with the single-event dichot and sequential dichot will be discussed separately.

Single-Event, Manual Dichotomous Sampler

Table 6 provides a summary of the results obtained with the dichots versus the collocated FRM samplers. On average, the manual dichots tended to over-measure $PM_{2.5}$ concentrations by approximately 10% when compared to the three collocated $PM_{2.5}$ FRMs. This performance is quite consistent with the results obtained during the previous two Phoenix campaigns and is again hypothesized to result from the inadvertent intrusion of a small fraction of coarse particles into the fine channel of the virtual impactor. At these $PM_{2.5}$ concentrations, however, the over-sampling results in an over-measurement of only approximately 1 $\mu g/m^3$. $PM_{2.5}$ measurement results for the two manual dichots versus the collocated FRMs were highly correlated as evidenced by the calculated R squared value of 0.983. Intra-sampler $PM_{2.5}$ measurement precision for the single-event dichots was strong as indicated by the CV of 1.9%.

For the manual dichot's $PM_{10-2.5}$ and PM_{10} measurements, mean Dichot/FRM concentration ratios were calculated to be 0.99 and 1.01, respectively. Correlation coefficients for these two metrics were calculated to be 0.995 and 0.995, respectively, indicating extremely consistent measurement performance independent of concentration. From an aerosol mass balance perspective, the mean Dichot/FRM PM_{10} concentration ratios indicated that the aspirated aerosol is being transported and collected efficiently within the single-event sampler and that a negligible amount of particle loss occurs during filter retrieval. These results are quite consistent with the January 2004 Phoenix tests when the R&P sequential dichotomous sampler was modified to operate in manual, single-event mode.

The only operational problem experienced with the manual dichot was a periodic leak check failure, which was diagnosed as being associated with the virtual impactor assembly. In particular, the clips on the impactor's housing could not be adjusted to provide sufficient compression between the upper and lower housing. Greasing of the virtual impactor's o-rings reduced the leak rate but did not eliminate it entirely. Based on the magnitude of the leak, however, it was judged that the presence of the leak did not adversely affect the performance of the virtual impactor nor degrade the quality of the measured data. Since the end of the Phoenix study, R&P has addressed the leak issue by replacing the virtual impactor's assembly clips with multiple set screws.

Multi-Event, Sequential Dichotomous Sampler

Similar to results obtained with the manual dichot, inspection of Table 6 reveals that the sequential dichot also tended to overestimate $PM_{2.5}$ concentrations by approximately 10%. Again, this behavior is consistent with the 2003 and 2004 field studies and reflects the inherent behavior of the virtual impactor rather than any particular aspect of the sequential design. Results of the $PM_{2.5}$ measurements were highly correlated as evidenced by the R squared value of 0.978. For the $PM_{10-2.5}$ channel, the Dichot/FRM concentration ratio is 0.93 indicating that 7% of the aspirated coarse mode mass is being lost; probably in the post-sampling phase of the sequence. This percentage loss, however, is substantially reduced from the over 20% $PM_{10-2.5}$ mass loss measured during a similar time of year in 2003. From a mass balance perspective, the PM_{10} loss within the sequential dichot was only 4% during these recent tests versus the 15% loss observed in 2003. It appears, therefore, that the redesigned exchange mechanism in the sequential sampler is more effective in preventing large particle loss than that of the original design. It should also be noted that the ambient conditions in Phoenix coupled with the aerosol's size distribution and morphology would tend to maximize any large particle loss. For most sampling locations, one might expect virtually identical mass loss between the manual dichot and a sequential dichot equipped with the new exchange mechanism. Correlations for the sequential sampler's $PM_{10-2.5}$ and PM_{10} measurements were quite high, as indicated by the R squared values of 0.997 and 0.998, respectively.

Overall, the sequential dichot sampler (with modified exchange mechanism) provided results similar to those of the single-event dichot design. For $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} metrics, the mean of daily sequential/single-event ratios was determined to be 1.00, 0.96, and 0.97, respectively.

There was one operational issue which occurred regarding the sequential dichot's modified exchange mechanism. On quite a number of occasions during the 30 day study, the sample cassettes would tend to bind within the new mechanism. This problem occurred during both pre-

sampling exchange operations as well as post-sampling exchange operations. Fortunately, the site operator was present during these events and could manually move the cassette into the correct position. As a result, the data capture rate with the sequential sampler was high. However, for most routine sampling situations where the operator would not be present during sample exchange operations, a large percentage of the data would have been lost. Following the study, these samplers were returned to the manufacturer, and R&P has purportedly identified and addressed the cassette transfer problem.

5.3 R&P Coarse TEOM Samplers

5.3.1 Year 2003 and 2004 Test Results

Few operational problems were experienced with the three R&P coarse TEOM monitors during the three site study. The exception occurred during the Riverside testing, where the third coarse TEOM monitor consistently measured about 17% higher than the other two coarse TEOM units, which agreed extremely well with each other. The exact reason for the consistent difference between the third unit and the other two units is not known but may have been an operational problem associated with the TEOM control unit itself. In two successive tests, exchanging the inlets and virtual impactors between units three and two did not appear to correct the noted discrepancy.

Table 7 summarizes the field performance of the R&P coarse TEOM monitors at all three sampling sites in comparison to the collocated FRM samplers. Considering that these are automated samplers which provide both sampling and mass analysis, strong intra-manufacturer precision was observed for the three coarse TEOM monitors during all four field campaigns, as indicated by measured CVs of 4.4%, 6.6%, 9.4%, and 2.7%, respectively. The higher CV value for the Riverside data is indicative of the problem mentioned in the previous paragraph.

At the Gary, Riverside, and Phoenix (2004) field sites, the coarse TEOMs produced $PM_{10-2.5}$ values which were consistently lower than those measured by the collocated FRMs. On average, the coarse TEOMs provided $PM_{10-2.5}$ measurements that were 31%, 24%, and 21% lower than the FRMs in Gary, Riverside, Phoenix (2004), respectively. This underestimation may be partly due to the fact that the sampler's inlet reportedly provides an internal cutpoint closer to 9 μm than its 10 μm design cutpoint[5]. Note from the table that the data is strongly correlated for Gary and Phoenix (2004) and that near zero intercepts were observed for regressions of the coarse TEOMs versus the collocated FRMs during all field campaigns but Phoenix (2003). The Gary, IN timeline presented in Figure 19 illustrates that the coarse TEOM monitors track the FRMs well but consistently provide an under-measurement of $PM_{10-2.5}$ concentrations. Based on the high coefficient of determination in Gary of 0.983, this behavior was very consistent as a function of

concentration during the 30 day test period.

Better agreement between the coarse TEOMs and the FRM was observed during the May to June 2003 tests conducted in Phoenix. For these tests, the coarse TEOMs provided $PM_{10-2.5}$ concentrations that averaged 5% higher than those measured by the collocated FRM samplers. As depicted in Table 7, however, the slope and intercept for the TEOM versus FRM regression deviated significantly from one and zero, respectively.

The January 2004 Phoenix tests were designed to compare the performance of the prototype coarse TEOM (constructed by USC) versus two of the coarse TEOM units manufactured by R&P. The purpose of these tests was to ensure that the R&P manufactured units met all the USC prototype design specifications. If differences in performance between the USC coarse TEOM and the R&P coarse TEOMs was observed, the field tests provided a potential opportunity to identify and correct any noted problems.

Results showed that the two R&P coarse TEOM samplers agreed well with each other during Runs 1-11 as evidenced by a mean CV of 2.0%. During the rain event days (Runs 12-15), however, CVs averaged approximately 10%. For the entire 15 day study, coarse R&P TEOM 1 measured an average $PM_{10-2.5}$ concentration of 31.5 $\mu g/m^3$ while R&P TEOM 2 measured an average $PM_{10-2.5}$ concentration of 31.0 $\mu g/m^3$. During this same time period, the USC coarse TEOM measured an average $PM_{10-2.5}$ of 30.2 $\mu g/m^3$. For the 15 day study, the R&P coarse TEOMs provided $PM_{10-2.5}$ concentrations which averaged 21% less than the collocated FRM pairs. Similarly, the USC coarse TEOM produced $PM_{10-2.5}$ concentrations which averaged 22% less than the collocated FRM pairs. This behavior was fairly consistent throughout the 15 days of testing and did not change during Runs 12-15. Based on the strong agreement between the USC coarse TEOM and the two collocated R&P coarse TEOMs, it was concluded that the R&P coarse TEOMs had been accurately manufactured by R&P per the USC design specifications.

5.3.2 Sampler Design Modifications

Subsequent to the 2003 and 2004 field tests, three design and operating changes were made to the R&P coarse TEOM sampler. As was discussed in the previous section, the inlet's 9 μm cutpoint was suspected to be responsible for a significant portion of the systematic negative bias observed during the 2003 and 2004 field tests. Analysis of the APS size distribution data collected during the two years of field tests revealed that, depending upon the size distribution of the aspirated aerosol, approximately 10% of the $PM_{10-2.5}$ negative measurement bias could be attributed to the inlet's lower cutpoint. Based on conventional impactor theory, the diameter of the inlet's internal nozzle was thus increased from 1.7 cm to 1.9 cm. The effect of the dimensional change on the inlet's internal cutpoint was then evaluated by USC in the laboratory using polydisperse calibration aerosols. Through use of an APS to measure the aerosol's size

distribution before and after the inlet, it was concluded that the cutpoint of the modified inlet was approximately 10 μm aerodynamic diameter.

To further validate the inlet's cutpoint, a coarse TEOM was fitted with the new inlet design and the system was collocated outdoors with a $PM_{2.5}$ MetOne BAM and an R&P PM_{10} FRM. During each of five separate tests, the reference ambient $PM_{10-2.5}$ concentration was estimated by subtracting the $PM_{2.5}$ concentration measured by the BAM from the PM_{10} concentration measured by the PM_{10} FRM sampler. Over $PM_{10-2.5}$ concentrations ranging from approximately 10 $\mu g/m^3$ to 33 $\mu g/m^3$, the coarse TEOM to reference $PM_{10-2.5}$ concentration ratios for the five days were 0.99, 0.91, 1.10, 0.95, and 0.92; and averaged 0.97. Plotting the coarse TEOM's response versus the reference $PM_{10-2.5}$ concentration resulted in a slope of 0.93, an intercept of 0.80 $\mu g/m^3$, and an R^2 value of 0.95. In conjunction with the laboratory test results, these results were used to conclude that the modified inlet exhibited acceptable size selective performance.

In addition to this physical design change, two operational changes were made to the coarse TEOM's design. In the prototype coarse TEOMs, measured coarse mass on the TEOM element had been divided by 25 to account for the 25:1 ratio between the inlet's flow rate of 50 lpm versus the 2 lpm used by the TEOM sensing unit. To account for theoretical particle losses within the virtual impactor and associated transport tubing, the designers decided to modify the conversion factor from 25:1 to 23:1. This operational modification results in measured $PM_{10-2.5}$ concentrations approximately 9% higher than in the prototype TEOMs. The final operational modification made to the coarse TEOM was a reduction in the TEOM's operating temperature from 50 ºC to 40 ºC. Although coarse mode aerosols were not considered to be hygroscopic, concern was expressed that a fraction of any volatile or semi-volatile $PM_{10-2.5}$ components might be inadvertently lost at the higher operating temperature, thus accounting for a portion of the negative measurement bias observed during the 2003 and 2004 field tests.

All three coarse TEOM units evaluated in the 2005 Phoenix tests used the modified inlet, were operated at 40 ºC, and used a 23:1 factor in estimating ambient $PM_{10-2.5}$ concentrations.

5.3.3 Year 2005 Phoenix Test Results

No operational problems were noted with the three coarse TEOM samplers during the entire 30-day study conducted in 2005. Pre-study, mid-study, and post-study performance audits indicated that all three units were operating within the required specifications for total flow rate, ambient temperature measurement, ambient pressure measurement, and leak rate. During all three audits, total flow rates were typically within 2-3% of their 50 lpm design flow rate and primary flows were typically within 2-3% of their design flow rate of 2.0 lpm. Per the SOPs for operation of the coarse TEOM, the tapered element filters on each unit were replaced after 15 days of sampling even though filter capacity during this test series had only reached approximately 40%.

The data capture rate for the coarse TEOMs during the 30-day study was 100%. Hourly concentrations from each TEOM sampler were averaged over the same 22 hour period during which the integrated FRM filter sampling was conducted.

During the 30 days of testing, the mean $PM_{10-2.5}$ concentrations reported by the three coarse TEOM samplers were 47.4 $\mu g/m^3$, 48.1 $\mu g/m^3$, and 50.0 $\mu g/m^3$, respectively. The TEOM-3 unit typically measured a higher $PM_{10-2.5}$ concentration than the other two units, although the difference was typically less than 1.0 $\mu g/m^3$ (with the exception of Day 20). In general, the level of agreement among the three coarse TEOM samplers was generally excellent during each of the 30 test days. On average, the coefficient of variation for the three coarse TEOM samplers was determined to be 3.6%. By comparison, the intra-manufacturer precision of the three $PM_{2.5}$ FRM samplers was determined to be 2.4% CV.

A regression of TEOM $PM_{10-2.5}$ concentrations versus those of the collocated $PM_{10-2.5}$ FRMs is presented in Figure 20. Using the daily TEOM/FRM $PM_{10-2.5}$ ratio as a measure of accuracy, the minimum ratio measured was 0.94 (Day 5) and the maximum ratio was 1.17 (Day 19). On average, the mean daily TEOM/FRM $PM_{10-2.5}$ ratio during these tests was determined to be 1.04.

It is worth noting that this 1.04 value compares very closely to the mean ratio of 1.05 observed in May 2003, which was prior to the design modifications. During the 2003 Phoenix tests, however, values of the slope, intercept, and coefficient of determination for the coarse TEOM units were determined to be 0.79, 12.8 $\mu g/m^3$, and 0.95, respectively. Values of the slope and intercept during the 2003 Phoenix tests, therefore, deviated appreciably from one and zero, respectively. As indicated by the regression presented in Figure 20, the values of the slope, intercept, and coefficient of determination during the 2005 Phoenix tests were 1.09, -1.9 $\mu g/m^3$, and 0.982, respectively.

The response of the three coarse TEOMs during the 2005 Phoenix tests thus shows a improvement over results obtained during the 2003 field campaign during times in which the nature of the aerosol is expected to be similar. Considering that the aerosol during the upcoming Birmingham tests is expected to be more variable in composition and might contain a higher volatile content than the Phoenix aerosol, it will be interesting to compare the Birmingham results to those of the recent Phoenix tests.

5.4 Kimoto SPM-613D Dichotomous Beta Gauge Monitors

5.4.1 Year 2003 and 2004 Test Results

No significant operational problems were encountered during field operation of the Kimoto SPM-613D dichotomous beta gauge samplers at the three sampling sites. Overall data capture

rate during 2003 and 2004 was nearly 100% at all three sites.

Table 8 summarizes the performance of the three Kimoto units in comparison with the collocated FRM samplers. Inspection of the table reveals that precision of the samplers was generally good for all three metrics at all three sampling sites. In general, higher intra-sampler CV values (i.e. less precision) were observed for measurements of $PM_{10-2.5}$ concentrations than for measurement of $PM_{2.5}$ concentrations.

At all three sites, the Kimoto SPM-613D units tended to significantly over-estimate the $PM_{2.5}$ concentrations when compared to the collocated $PM_{2.5}$ samplers. For $PM_{2.5}$ measurements, the mean sampler to FRM ratio at Gary, Phoenix (2003), Riverside, and Phoenix (2004) were calculated as 1.26, 1.70, and 1.65, and 1.43, respectively. As illustrated in Figure 21 for Phoenix (2003), this over-estimation by the Kimoto units was quite consistent versus those of the collocated $PM_{2.5}$ FRM samplers. The consistency of the Kimoto's performance at each sampling site was high as evidenced by R squared values of 0.949, 0.947, 0.904, and 0.939, respectively. As was the case for the R&P dichot, it is hypothesized that this over-estimation might be due, in part, to the inadvertent intrusion of coarse mode particles into the sampler's fine mode channel. This hypothesis is supported by the fact that larger overestimations occur at sites with the lowest mean $PM_{2.5}/PM_{10}$ ratios. The fact that the Kimoto sampler typically provides PM_{10} concentrations higher than the collocated PM_{10} FRM samplers, however, may indicate that other measurement uncertainties may be responsible for the observed $PM_{2.5}$ measurement bias.

The Kimoto SPM-613D units provide more accurate measurements of ambient $PM_{10-2.5}$ concentrations than $PM_{2.5}$ concentrations. For $PM_{10-2.5}$ measurements, the mean sampler to FRM ratio at Gary, Phoenix (2003), Riverside, and Phoenix (2004) was calculated as 0.91, 1.04, 1.08, and 1.05, respectively. Consistency of this performance during the month-long sampling at each site is demonstrated by the high coefficient of determination (0.978, 0.995, 0.957, and 0.994, respectively) obtained in sampler versus FRM $PM_{10-2.5}$ regressions.

5.4.2 Sampler Design Modifications

Following the Phoenix 2004 tests, several design modifications were made to the Kimoto SPM 613-D dichotomous beta gauge in an attempt to improve its overall performance. First, design changes were made to reduce the size of the $PM_{10-2.5}$ aerosol deposit on the paper tape roll. Reducing the diameter from 11 mm to 8 mm effectively reduced the deposition area by approximately one-half, thus essentially doubling the $PM_{10-2.5}$ measurement sensitivity. This modification also made it easier for the user to visually recognize the $PM_{2.5}$ deposit from the $PM_{10-2.5}$ deposit on the beta tape in the event that post-sampling chemical analysis of the collected aerosol was desired.

Modifications to the Kimoto design were also made to convert the flow control algorithm

from mass flow control to volumetric flow control. Although the 1.3 lpm coarse flow rate is still controlled using a critical orifice, an in-line mass flow sensor (in conjunction with the measured ambient temperature and pressure) allows calculation of the actual coarse channel flow rate. A separate flow control unit continuously adjusts the total sampling flow rate to 16.7 lpm at the inlet's ambient conditions. The measured channel flow rates, ambient temperature, and ambient pressure are continuously recorded and available to the user following each sampling event. Reported $PM_{2.5}$ and $PM_{10-2.5}$ concentrations are now reported at actual conditions.

Results from the previous four field campaigns indicated that the SPM 613-D typically measured $PM_{10-2.5}$ concentrations accurately but produced $PM_{2.5}$ measurements which were 26% to 70% higher than measured by the collocated $PM_{2.5}$ FRM samplers. Because the size selective performance of the Kimoto's custom designed virtual impactor has not been rigorously determined in the laboratory, uncertainties existed regarding the cutpoint and slope of its fractionation curve. To address this uncertainty, a new virtual impactor was constructed based on the Loo and Cork design. Because this design requires coarse and fine channel flow rates to be maintained at 1.7 lpm and 15.0 lpm, respectively, a 1.7 lpm critical orifice was designed to replace the 1.3 lpm orifice.

During the first 15 sampling events of the Phoenix 2005 tests, both Kimoto units were configured with the custom virtual impactor used during the previous four field campaigns. For Runs 16 through 30, the virtual impactor in one of the units was replaced with the Loo and Cork design and system flow rates were adjusted accordingly.

The influence of these design changes were evaluated during the 2005 Phoenix field tests.

5.4.3 Year 2005 Phoenix Test Results

Runs 1 - 15

As mentioned, the two Kimoto units were identically configured during the first 15 sampling events in terms of their virtual impactors and channel flow rates. During these 15 days of testing, the mean $PM_{2.5}$ concentrations reported by the two samplers were 12.6 $\mu g/m^3$ and 11.9 $\mu g/m^3$, respectively. The Kimoto-1 unit usually reported $PM_{2.5}$ concentrations higher than those reported by the Kimoto-2 unit. On average, the Kimoto-1 to Kimoto-2 $PM_{2.5}$ concentration ratio was 1.06 for the 15 combined tests. Precision between the two Kimoto samplers was fairly good during each of the 15 test days and the maximum CV measured was 13.8%. On average, the coefficient of variation for the 15 discrete $PM_{2.5}$ measurements was 5.0%. By comparison, the intra-manufacturer precision of the three $PM_{2.5}$ FRM samplers was determined to be 2.8% CV.

Both Kimoto units provided $PM_{2.5}$ mean measurement responses which exceeded the collocated $PM_{2.5}$ FRM samplers' mean measurement of 7.7 µg/m3. For details, the timeline of Kimoto and FRM $PM_{2.5}$ concentrations is presented in Figure 22. The extent of the over-

estimation (as calculated by the mean Kimoto to FRM concentration ratio) was variable and ranged from a minimum of 1.29 on Day 12 to a maximum of 2.03 on Day 2. For the two Kimoto units during the 15 sampling events, the mean $PM_{2.5}$ overestimation averaged 1.61 (i.e., 61% higher than the collocated $PM_{2.5}$ FRMs). The mean Kimoto/FRM ratios during these 15 tests were calculated to be 1.66 and 1.57 for Kimoto-1 and Kimoto-2, respectively. The slope, intercept, and coefficient of determination for the Kimoto-1 unit during these tests were determined to be 1.42, 1.7 $\mu g/m^3$, and 0.74, respectively. For the Kimoto-2 unit, these values were determined to be 1.29, 2.0 $\mu g/m^3$, and 0.73, respectively.

For $PM_{10-2.5}$ measurements, both Kimoto units provided concentration measurements similar to each other, with the exception of Run 9. For the first 15 days, the mean Kimoto-1/Kimoto-2 ratio was 1.04. If one chooses to treat Day 9 as a potential outlier, then the Kimoto-1/Kimoto-2 ratio reduces to 1.03. An inspection of the Runs 1-15 $PM_{10-2.5}$ timelines in Figure 23 reveals that the two Kimoto units tracked the FRMs with the exception of Day 4. On average, the extent of the Kimoto's $PM_{10-2.5}$ estimation averaged 1.11 and 1.13 for Kimoto-1 and Kimoto-2, respectively. If Run 4 is considered an outlier, however, the concentration ratios reduce to 1.10 and 1.05, respectively. As in the case of the $PM_{2.5}$ measurement, the reason for the bias between the Kimoto units and the FRM units for Run 4 is not clear and needs to be investigated for potential influences of meteorology and aerosol chemistry.

Runs 16 - 30

Following Run 15, the manufacturer's virtual impactor was removed from the Kimoto-2 unit and replaced with one based on the Loo and Cork design. The flow control system within in the Kimoto-2 unit was modified to provide 15 lpm and 1.67 lpm to the impactor's fine and coarse channels, respectively. Runs 16 through 30 were then conducted with the Kimoto-2 unit in this configuration. No physical or operational changes were made in the Kimoto-1 unit.

If one compares the $PM_{2.5}$ timelines in Figure 22, it appears that the Kimoto-2 data moves somewhat towards the FRM data following the virtual impactor modification. The extent of the improvement is far from complete, however. The mean $PM_{2.5}$ concentrations measured by the Kimoto units during Runs 16-30 were 16.6 $\mu g/m^3$ and 14.9 $\mu g/m^3$, respectively, and exceed the FRMs' mean of 12.0 $\mu g/m^3$. For these 15 tests, the mean bias ratio of the Kimoto-1 and Kimoto-2 units was 1.39 and 1.24, respectively. Note that the Kimoto-1's overestimation of 1.39 during these tests is noticeably lower than the 1.66 value observed during Runs 1-15 even though its configuration has not changed. Again, this is hypothesized to be due to the improved response of the Kimoto units to high $PM_{2.5}$ concentrations versus lower $PM_{2.5}$ concentrations. The slope, intercept, and coefficient of determination for the Kimoto-1 unit during these tests was determined to be 1.10, 3.4 $\mu g/m^3$, and 0.88, respectively. For the Kimoto-2 unit, these values were

determined to be 1.15, 1.1 μg/m^3, and 0.83, respectively. Compared to the Run 1-15 data, these values generally indicate better agreement with the FRMs during Runs 16-30 than was observed during Runs 1-15.

Figure 24 provides a comparison of the Kimoto-2 data regression for Runs 16-29 versus Runs 16-30. As noted on the figure, inclusion of the Run 30 data results in a slope, intercept, and coefficient of determination of 0.80, 11.7 μg/m^3, and 0.976, respectively. For Runs 16-30, the mean Kimoto-2 to FRM $PM_{10-2.5}$ ratio was calculated to be 1.08. If one eliminates the Run 30 data from the regression, the slope, intercept, and coefficient of determination improve to values of 1.03, 0.2 μg/m^3, and 0.993, respectively. For Runs 16-29, the mean Kimoto-2 to FRM $PM_{10-2.5}$ ratio was calculated to be 1.09. This comparison illustrates that one data point can dramatically affect the values of the regression coefficients even though the mean sampler to FRM ratio may not change appreciably.

5.5 TSI Inc. Model 3321 APS

5.5.1 Year 2003 and 2004 Test Results

Few problems were experienced with the two TSI Model 3321 APS units during the course of the 2003 and 2004 field tests. The exception occurred approximately halfway through the field sampling in Phoenix (2003) when the response of APS Unit 2 began to deviate substantially from that of Unit 1. During the units' subsequent return to the manufacturer for cleaning, a circuit board within Unit 2 was diagnosed as faulty and was replaced. Data from this unit during the second half of the Phoenix tests, therefore, were not used in comparing the performance of the APS units to that of the collocated FRM samplers. Overall data capture rate for the APS units during the three city study was 85%.

In the August 2004 report, it was noted that the APS units tended to track the FRM's fairly well but tended to under-predict the $PM_{10-2.5}$ concentration by about a factor of two when compared to measurements provided by the FRM samplers. Mean sampler to FRM $PM_{10-2.5}$ ratios for Gary, Phoenix (2003), Riverside, and Phoenix (2004) were calculated in 2004 to be 0.42, 0.55, 0.58, 0.62, respectively. Since that time, however, it has been recognized that the APS does not properly account for a non-spherical particle's shape factor when estimating mass concentration as a function of size. Because coarse mode particles are typically generated by mechanical means and are not as hygroscopic as fine mode aerosols, they tend to be non-spherical in nature. As a result, mass concentrations of coarse aerosols reported by the APS tend to be negatively biased.

Proper conversion of APS response to $PM_{10-2.5}$ concentration requires an estimate of an aerosol's specific gravity and shape factor. Based on a review of the literature [8, 9, 10], a specific gravity of 2.0 and a shape factor of 1.4 was adopted for all APS calculations. Table 9 summarizes

the influence of incorporating the shape factor of 1.4 into all APS field data. As opposed to the data reported in the August 2004 report, mean APS to FRM $PM_{10-2.5}$ ratios for the four field campaigns are now calculated to be 0.76, 0.94, 1.00, and 1.02. In comparing regression results to those reported in the August 2004, it is observed that the primary influence of the shape factor's use is movement of regression slopes significantly closer to unity. Values of the regression's intercepts and coefficients of determinations did not appreciably change. Figure 25 provides a timeline of the APS's $PM_{10-2.5}$ responses versus those of the collocated FRMs during the Phoenix 2004 field campaign. Figure 26 provides APS versus FRM $PM_{10-2.5}$ (PMc) regressions for data collected during the 2003 and 2004 field campaigns. Noted regression coefficients provided in the figure differ slightly from those in Table 9 due to differences in treatment of apparent outliers.

5.5.2 Sampler Design Modifications

An inspection of Table 9 reveals that $PM_{10-2.5}$ concentrations estimated by the APS tended to agree well at the 2003 Riverside site and the 2003 and 2004 Phoenix sites but less agreement was observed in Gary, IN. Although there naturally existed differences is particle size distribution and composition among these sites, the primary difference was that sampling conditions in Gary were considerably cooler and more humid than during the other field campaigns. These conditions in Gary could result in particle growth due to the uptake of water vapor. While the effect of hygroscopic growth on APS measurement is far from certain, one hypothesis is that these larger, wetter particles may become more difficult to transport efficiently to the APS's sensing zone and are thus not quantified. Laboratory tests conducted by Volckens and Peters[11] showed that counting efficiencies of the Model 3321 were high for large, solid particles but that efficiencies progressively declined from 75% for 0.8 micrometer particles to only 25% for 10 micrometer liquid droplets. If this hypothesis is correct, then drying of the aerosol prior to its introduction into the APS may be one approach towards improving the $PM_{10-2.5}$ measurement performance of the APS.

To test this hypothesis, one of the two APS units was modified to include a smart heater upstream of the APS inlet. The heating element consisted of a silicone resistance heater tape wrapped around the downtube's 1.25" external diameter. The moisture content of the aspirated aerosol was continuously measured and the heater activated if the flow stream's relative humidity exceeded 45%. This design modification was made immediately prior to the 2005 tests conducted in Phoenix, AZ. As was expected for the Phoenix site at that time of year, however, the aerosol heater was activated on only a few occasions during the 30-day test period.

5.5.3 Year 2005 Phoenix Test Results

Pre-study, mid-study, and post-study performance audits of the two Model 3321 APS units indicated that they were both operating within the required specifications for total sampling flow rate. Audits of each system's 11.7 lpm auxiliary flow control system also revealed that they were also routinely performing within specification. Unlike the previous four field campaigns, however, functionality problems with the two APS units occurred during the 2005 Phoenix study. Periodic inspection of the APS's real-time response often revealed that the two units were not providing the same measurement results. In particular, one of the APS units sometimes indicated PM concentrations orders of magnitude higher than the other unit. The frequency and magnitude of the measurement problem was quite variable but affected both APS units. During the few days when both APS units appeared to provide valid measurement results, the precision between the two units was good, as indicated by a coefficient of variation of 7.0%.

For comparing the performance of the two APS units to the collocated FRM samplers, it was first necessary to eliminate data which represents apparent outliers, then apply an assumed particle shape factor and particle density to the remaining data. Following an inspection of all the raw data provided by the two units, data were eliminated for 14 of the 30 sampling days. For the remaining 16 sampling events, a shape factor of 1.4 and a particle specific gravity of 2.0 were used to estimate the mass concentration of $PM_{10-2.5}$ aerosols. For this limited data, the two APS units typically under-measured $PM_{10-2.5}$ concentration by approximately 14%. A regression of the resulting APS versus FRM data reveals a slope of 0.84, an intercept of 0.55 $\mu g/m^3$, and a coefficient of determination of 0.942. The valid data are thus highly correlated and have a low intercept but a slope significantly lower than unity. Because of the overall functionality issues experienced with both APS units during the 2005 Phoenix tests, however, observations and conclusions made regarding these limited test results should be considered with caution.

Since the conclusion of the Phoenix tests, TSI has been actively investigating the field data and conducting laboratory tests with both APS units in an effort to identify and resolve the source of the functionality problem. While the results of these efforts are preliminary, it appears that incorrect voltage settings were made to both APS units during their factory calibration immediately prior to the Phoenix 2005 field tests. As a result, the counting response of all size channels significantly exceeded calibrated values when high ambient aerosol concentrations were encountered. It is expected that the functionality problems with the two units, however, will be identified and resolved in time for the fall 2005 tests in Birmingham, AL. Unlike the situation in Phoenix, the Birmingham tests should provide an opportunity to evaluate the effect of drying of the aspirated aerosol on the response of the APS.

5.6 BGI frmOMNI Ambient Air Sampler (Filter Reference Method)

5.6.1 Year 2005 Phoenix Test Results

The Phoenix 2005 study design called for the use of two Omni units configured to measure $PM_{2.5}$ and two Omni units configured to measure PM_{10}. However, only three Omni units were initially available for evaluation due to delivery delays of the fourth unit. Functionality problems were encountered with the Omni control units, which reduced the data capture rate. As a result, the two $PM_{2.5}$ Omni units were both concurrently operated on only 12 of the 30 sampling events, and the two PM_{10} Omni units were concurrently operated on only 12 of the 30 sampling events. Because $PM_{10-2.5}$ precision calculations require that both $PM_{2.5}$ Omni units and both PM_{10} Omni units be functional at the same time, precision of Omni $PM_{10-2.5}$ measurements could be calculated on only 6 of the 30 sampling events.

As mentioned earlier, the $PM_{2.5}$ impaction plates of the Omni were cleaned and then greased on a daily basis. None of the Omni's PM_{10} stages were greased during the study.

For the 30 days of sampling, the Omni units on average tended to over-measure $PM_{2.5}$ concentrations by approximately 7% when compared to the three collocated $PM_{2.5}$ FRMs. At these $PM_{2.5}$ concentrations, however, the overmeasurement represents only approximately 1 $\mu g/m^3$. The Omni's $PM_{2.5}$ measurements versus those of the collocated $PM_{2.5}$ FRMs are plotted in Figure 27. The plotted data are somewhat scattered, as indicated by the coefficient of determination of 0.808. Slope of the regression line is 0.92 and the intercept is 1.46 µg/m3. Excluding Day 30 (during which very high $PM_{10-2.5}$ concentrations were measured) did not change the correlation appreciably.

The scatter of the data may be a reflection of the relatively low mass collected by the Omni filters versus the FRM filters. Due to the Omni's 5 lpm flow rate, it can be expected that the Omni's $PM_{2.5}$ mass gain would be only approximately one third that of the 16.7 lpm FRM sampler. At these relatively low concentrations, uncertainties in gravimetric analysis could result in greater concentration measurement uncertainty for the $PM_{2.5}$ Omni than that of the $PM_{2.5}$ FRM. For example, if one assumes a gravimetric measurement uncertainty of 10 micrograms, this equates to a concentration measurement uncertainty of only 0.5 $\mu g/m^3$ for the FRM sampler in a 22 hour sampling period. For the same measurement uncertainty, however, this results in a 1.5 $\mu g/m^3$ uncertainty in $PM_{2.5}$ concentrations measured by the Omni units. As will be discussed, much higher correlations and better precisions were observed with the $PM_{2.5}$ Omni units where appreciably higher mass gains occurred.

Precision (as expressed by the coefficient of variation) between the two collocated Omni $PM_{2.5}$ samplers was measured to be 8.8% for the 12 days during which both $PM_{2.5}$ Omni units were operating. This value is higher than the 3.2% precision of the three FRMs during the same 12

sampling events and may be another indication that low mass gains on the Omni filters can result in greater measurement uncertainty. This conjecture is supported by the fact that the PM_{10} precision for the Omni units was 3.3% for the 12 days that both PM_{10} Omni units were operating. This precision compares favorably with the FRM's precision of 2.2% during the same 12 sampling events.

For all 30 sampling events, the PM_{10} Omni units provided PM_{10} concentrations lower than the three collocated FRM samplers. On average, the Omni's PM_{10} concentrations were 11% lower than the FRM samplers. The greatest difference (19%) occurred during Run 30 in which the FRM PM_{10} concentration was measured to be 134.7 µg/m3. The slope, intercept, and R squared values of the PM_{10} Omni versus the PM_{10} FRM were determined to be 0.83, 3.59 $\mu g/m^3$, and 0.97, respectively. If one excludes Run 30 from the regression, then the slope, intercept, and R squared values are 0.93, -1.79 $\mu g/m^3$, and 0.969, respectively. The Run 30 data point, therefore, strongly influences the slope and intercept of the PM_{10} regression curve.

Systematic biases in measured PM_{10} concentrations could be attributed to incomplete aspiration of large particles by the low flow rate Omni inlet. Since large particle aspiration efficiency typically decreases with increasing wind speed, correlating Omni PM_{10} concentrations with site meteorological data may be of value. Systematic biases in measured PM_{10} concentrations could also be caused by differences in the Omni's collection efficiency curve versus that of the FRM's internal PM_{10} fractionator. In particular, a cutpoint less than 10 micrometers and/or a sharper efficiency curve in the Omni unit would tend to reduce penetration of large particles to the Omni's afterfilter. Whatever the cause of the bias, the magnitude of the undermeasurement is accentuated by the large particle distribution inherent to the Phoenix airshed.

Because the $PM_{10-2.5}$ aerosol comprises such a large percentage of the PM_{10} aerosol in the Phoenix area, the Omni units consistently underestimated the $PM_{10-2.5}$ concentrations. On average, the Omni units under-measured $PM_{10-2.5}$ concentrations by approximately 15% when compared to the collocated FRMs. The slope, intercept, and R squared values of the $PM_{10-2.5}$ Omni versus the $PM_{10-2.5}$ FRM were determined to be 0.81, 1.17 $\mu g/m^3$, and 0.949, respectively. If one excludes the Run 30 data from the regression, then the slope, intercept, and R squared values are 0.95, - 4.16 $\mu g/m^3$, and 0.932, respectively. The Run 30 data point, therefore, strongly influences the slope and intercept of the $PM_{10-2.5}$ regression curve similar to its influence on the PM_{10} regression curve.

CV's for the Omni $PM_{10-2.5}$ measurements averaged 5.0%, which compared favorably to the FRM's $PM_{10-2.5}$ CV of 3.5% measured during the same test days. It should be reiterated, however, that precision calculations can be based on only the 6 days in which all four Omni units were operating during the 30 day study.

Since the completion of the 2005 Phoenix tests, BGI has identified that faulty relative humidity circuitry in the Omni units was responsible for the periodic functionality problems

encountered in Phoenix. This problem has subsequently been addressed and no further problems have been encountered with repaired units. In addition, the single-stage $PM_{2.5}$ impactor of the prototype Omni units has been replaced with a 5 lpm version of BGI's sharp-cut cyclone design. This modification will thus not require the user to clean and prepare the $PM_{2.5}$ impaction surface daily as was previously required.

5.7 Grimm EnviroCheck Model 1.107

5.7.1 Year 2005 Phoenix Test Results

During the 30 days of testing, the three Grimm Model 1.107 samplers measured average $PM_{2.5}$ concentrations of 13.0, 12.8, and 13.2 $\mu g/m^3$, respectively. Precision among the three Grimm samplers was excellent during each of the 30 test days and the maximum CV measured was only 2.2%. On average, the coefficient of variation for the $PM_{2.5}$ measurements was 1.5%. By comparison, the intra-manufacturer precision of the three $PM_{2.5}$ FRM samplers was determined to be 2.8% CV.

A timeline of measured Grimm versus FRM $PM_{2.5}$ concentrations is provided in Figure 29. Inspection of the timeline indicates that the Grimm samplers tracked the FRMs well but overestimated $PM_{2.5}$ concentrations on each of the 30 test days. The extent of the overestimation (as calculated by the Grimm to FRM concentration ratio) was variable and ranged from a minimum of 1.12 on Day 21 to a maximum of 1.86 on Day 10. For the 30 sampling events, the Grimm's $PM_{2.5}$ over-estimation averaged 1.37 (i.e., 37% higher than the collocated $PM_{2.5}$ FRMs).

Regression of the Grimm's $PM_{2.5}$ measurement response versus those of the $PM_{2.5}$ FRMs indicated that results were well correlated (R squared = 0.908) but that the slope was 0.83 and the intercept was 4.80 $\mu g/m^3$. The influence of the large intercept on the $PM_{2.5}$ response is particularly important considering that the mean $PM_{2.5}$ concentration during these tests was less than 10 $\mu g/m^3$. The upcoming tests in Birmingham should provide an opportunity to evaluate the Grimm's response at higher $PM_{2.5}$ concentrations than were encountered at the Phoenix sampling site.

During the 30 days of testing, the three Grimm samplers measured average $PM_{10-2.5}$ concentrations of 70.0, 73.2, and 68.3 $\mu g/m^3$, respectively. With the exception of a few sampling events, daily precision among the three Grimm samplers was excellent and averaged 4.1% CV during the 30 day study. By comparison, the intra-manufacturer precision of the three $PM_{10-2.5}$ FRM samplers was determined to be 2.4% CV.

Inspection of the timeline (Figure 30) of Grimm and FRM $PM_{10-2.5}$ responses indicates that the Grimms again tracked the FRM fairly well but overestimated $PM_{10-2.5}$ concentrations on each of the 30 test days. The extent of the measurement bias was variable and ranged from a minimum of 1.08 on Day 13 to a maximum of 1.84 on Day 4. For the 30 sampling events, the Grimm's $PM_{10-2.5}$

overestimation averaged 1.53 (i.e., 53% higher than the collocated $PM_{10-2.5}$ FRMs). A regression of the Grimm versus FRM $PM_{10-2.5}$ concentrations resulted in slope, intercept, and R squared values of 1.35, 8.4 $\mu g/m^3$, and 0.847, respectively. Unlike the response of the Grimm to $PM_{2.5}$ aerosols, the $PM_{10-2.5}$ measurement bias is associated more with the regression's slope than its intercept. Inspection of the Grimm's responses to $PM_{10-2.5}$ concentrations showed no real trend in instrument bias versus $PM_{10-2.5}$ concentration.

The highest measured $PM_{10-2.5}$ concentration during the 2005 Phoenix study occurred during Day 30. For this sampling event, the three Grimm units reported concentrations of 133.4, 177.6, and 139.2 $\mu g/m^3$, respectively. The response of Unit 2 for this sampling event is thus significantly higher than that of the other two Grimm units, although no operational problems were noted by the site operator. If one chooses to exclude all data from this sampling event, then the correlation between the Grimms and the FRMs improves somewhat but results in dramatically different slopes and intercepts than if the Day 30 data is included. Specifically, using only Run 1-29 data results in slope, intercept, and R squared values of 1.87, -13.7 $\mu g/m^3$, and 0.887, respectively. As had been illustrated in Figure 24 for the Kimoto-2 unit, excluding the Day 30 data point from the 2005 Phoenix data has a dramatic influence on the regression coefficients.

Because the Phoenix PM_{10} aerosol is heavily dominated by coarse mode particles, one would expect that the Grimm's PM_{10} response would be more similar to its $PM_{10-2.5}$ response than its $PM_{2.5}$ response. Inspection of the Grimm's actual data reveals that this hypothesis is correct. During the 30 days of testing, the three Grimm samplers measured mean PM_{10} concentrations of 83.0, 86.0, and 83.5 $\mu g/m^3$, respectively. As in the case of the $PM_{10-2.5}$ measurements, precision of the Grimm samplers for PM_{10} measurement was excellent, as evidenced by the calculated CV of 3.4%.

Inspection of the Grimm PM_{10} data indicated that the Grimms tracked the FRM well but over-estimated PM_{10} concentrations on each of the 30 test days. The extent of the measurement bias was variable and ranged from a minimum of 1.18 on Day 13 to a maximum of 1.71 on Day 4. For the 30 sampling events, the Grimm's PM_{105} over-estimation averaged 1.49 (i.e., 49% higher than the collocated PM_{10} FRMs). A regression of the Grimm versus FRM PM_{10} concentrations resulted in slope, intercept, and R squared values of 1.37, 6.9 $\mu g/m^3$, and 0.900, respectively. As is in the case of the $PM_{10-2.5}$ data analysis, removing the Day 30 data from the regression resulted in dramatically different correlation coefficients.

Similar to observations of the $PM_{10-2.5}$ data, inspection of the Grimm's response to PM_{10} aerosols shows no real trend in instrument bias versus PM_{10} concentration.

5.8 R&P Dichotomous TEOM Sampler

5.8.1 Year 2005 Phoenix Test Results

No operational problems were noted with the two dichot TEOM samplers during the entire 30-day study. Pre-study, mid-study, and post-study performance audits indicated that both units were operating within the required specifications for channel flow rates, ambient temperature measurement, and ambient pressure measurement. Per our SOPs for operation of the dichot TEOM, the tapered element filters on each unit's channels were replaced after 15 days of sampling even though only moderate increases in filter capacity readings were noted during this time period. At the completion of the first 15 days of testing, filter capacities of the units' fine and coarse channels averaged only 38% and 21%, respectively. At the completion of the subsequent two weeks of sampling (i.e., following Run 30), filter capacities of the units' fine and coarse channels averaged 44% and 28%, respectively. Data was captured for all sampling events with the exception of tests conducted on May 15th (Run 18). During this test, data collected by dichot TEOM-1 could not be recovered. Data capture rate for the dichot TEOMs during the 30-day study was thus calculated to be 98%.

A timeline of the two dichot TEOMs' responses versus mean FRM $PM_{2.5}$ is provided in Figure 31. Inspection of the timeline indicates that the two dichot TEOMs generally tracked the $PM_{2.5}$ FRMs during the 30 day study. The notable exception was during Runs 1-3 for dichot TEOM-2, during which times daily $PM_{2.5}$ concentrations measurements were -7.1, -24.2, and -7.5 $\mu g/m^3$, respectively. Similar measurement problems were noted with the dichot TEOM-1 during Runs 1-3 although the magnitude of the under-measurement was not as great as that of dichot TEOM-2.

Inspection of the data from the two dichot TEOMs revealed that a large percentage of the reported hourly $PM_{2.5}$ concentrations were less than zero. For the dichot TEOM-1 and dichot TEOM-2, the percentages of negative $PM_{2.5}$ concentrations were 20% and 38%, respectively. There appeared to be no discernable pattern (e.g. time of day) during which negative $PM_{2.5}$ concentration values were reported. As can be expected, however, the preponderance of these negative values adversely influences the level of agreement between the dichot TEOMs and the collocated $PM_{2.5}$ FRM samplers. If one chooses to use all 30 days of data, then the mean $PM_{2.5}$ concentrations measured by the two dichot TEOMs were 7.9 and 3.5 $\mu g/m^3$, respectively, compared to the FRMs' mean $PM_{2.5}$ concentration of 9.9 $\mu g/m^3$. Mean dichot TEOM to FRM ratios for the two units were 0.80 and 0.63, respectively. A regression of mean dichot TEOM response versus mean $PM_{2.5}$ FRM response results in slope, intercept, and correlation coefficient values of 1.9, -13.1 $\mu g/m^3$, and 0.765, respectively. On average, the dichot TEOM-1/TEOM-2 ratio was 2.23 for the 30 sampling events.

If one chooses to treat the Day 1-3 data as outliers, then the level of agreement between the dichot TEOMs and the collocated $PM_{2.5}$ FRMs improves somewhat. For the Run 4-30 data, the mean $PM_{2.5}$ concentrations measured by the two dichot TEOMs were 8.7 $\mu g/m^3$ and 5.4 $\mu g/m^3$, respectively, compared to the FRMs' mean $PM_{2.5}$ concentration of 10.2 $\mu g/m^3$. Mean

dichot TEOM to FRM ratios for the two units were 0.85 and 0.42, respectively. A regression of mean dichot TEOM responses versus mean $PM_{2.5}$ FRM responses results in slope, intercept, and correlation coefficient values of 1.58, -9.2 $\mu g/m^3$, and 0.770, respectively. On average, the dichot TEOM-1/TEOM-2 ratio was 1.58 for the Run 4-30 sampling events.

As opposed to the $PM_{2.5}$ measurement, where a large percentage of the measured concentrations were negative, negative $PM_{10-2.5}$ concentrations were reported for only 9 hourly sampling events during the 30 days of testing. As depicted in Figure 32, there also appeared to be better $PM_{10-2.5}$ agreement between the dichot TEOMs and the FRMs than was observed for the $PM_{2.5}$ measurements. The mean $PM_{10-2.5}$ concentrations reported by dichot TEOM-1 and TEOM-2 were determined to be 38.1 $\mu g/m^3$ and 41.1 $\mu g/m^3$, respectively, compared to the FRMs' mean $PM_{10-2.5}$ concentration of 46.2 $\mu g/m^3$. Mean dichot TEOM to FRM ratios for the two units were 0.85 and 0.89, respectively. Expressed as the coefficient of variation, the level of precision between the two dichot TEOMs was determined to be 5.4% for $PM_{10-2.5}$ measurements. On average, the dichot TEOM-1/TEOM-2 ratio was 0.95 for the 30 $PM_{10-2.5}$ sampling events.

A comparison between the dichot TEOMs' mean response versus the collocated FRMs indicated that results were very highly correlated ($R^2 = 0.992$) with a low intercept (0.73 $\mu g/m^3$) but that the slope was only 0.85. Inspection of the data showed that this measurement response was highly consistent with time and was virtually independent of ambient $PM_{10-2.5}$ concentration. Elimination of the Run 1-3 data from the regression did not significantly alter the calculated slope, intercept, or R^2 values. For the Run 4-30 data, the precision between the two dichot TEOMs was 5.2% and the mean TEOM-1/TEOM-2 ratio was 0.98.

For the dichot TEOMs, PM_{10} concentrations can be calculated as the numerical sum of measured $PM_{2.5}$ and $PM_{10-2.5}$ concentrations. The mean PM_{10} concentrations reported by the dichot TEOM-1 and TEOM-2 were determined to be 47.0 $\mu g/m^3$ and 44.6 $\mu g/m^3$, respectively, compared to the FRMs' mean PM_{10} concentration of 56.0 $\mu g/m^3$. Mean dichot TEOM to FRM ratios for the two units were 0.84 and 0.80, respectively. Expressed as the coefficient of variation, the level of precision between the two dichot TEOMs was determined to be 9.7% for PM_{10} measurements. On average, the dichot TEOM-1/TEOM-2 ratio was 1.05 for the 30 PM_{10} sampling events.

A comparison between the dichot TEOMs' mean PM_{10} response versus the collocated PM_{10} FRMs indicated that results were very highly correlated as indicated by the R^2 value of 0.950. Unlike the TEOM's $PM_{10-2.5}$ response, however, the regression between the TEOMs and the collocated FRMs resulted in a slope close to unity (0.972) but the intercept was -8.7 $\mu g/m^3$. On average the dichot TEOMs' calculated PM_{10} concentration was 82% of the value measured by the PM_{10} FRMs. Elimination of the Run 1-3 data from the regression only slightly altered the calculated slope, intercept, and R^2 values. For the Run 4-30 data, the precision between the two dichot TEOMs was 6.2% and the mean TEOM-1/TEOM-2 ratio was 1.03.

6.0 SUMMARY

1. Through coordination with state and local air monitoring agencies, the Gary, IN, Phoenix, AZ, and Riverside, CA sampling sites met the study's siting objectives well and challenged the candidate samplers with a wide range of aerosol size distributions, aerosol concentrations, and meteorological conditions. Relatively few operational problems were experienced with the sampling equipment and the overall data capture rate during the five separate field campaigns exceeded 95%. Prestudy, midstudy, and poststudy performance audits conducted at each sampling site revealed that the samplers typically held their calibrations well during the month-long field tests. The involvement and cooperation of the various sampler manufacturers was a key factor in the study's ability to successfully determine the inherent performance of the samplers.

2. The filter-based, integrated samplers involved in the study provided precise test results at all three sampling sites during the five field campaigns and their overall data capture rate was approximately 99%. For the FRM samplers, the mean inter-manufacturer coefficients of variation for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} were 2.7%, 4.1%, and 2.8%, respectively. As an example, for three samplers which provide a mean concentration of 25 $\mu g/m^3$, a 4% CV would equate to readings of 24, 25, and 26 $\mu g/m^3$. Effective shipping protocols resulted in negligible particle loss during transport of collected aerosol samples from each sampling site to the RTP weighing facility. Concentrations calculated using site weighing data versus the use of RTP weighing data typically agreed within 1% of each other.

3. Independent of design (i.e., R&P sequential, R&P single-event, or Sierra-Andersen single-event), the intra-manufacturer precisions of the filter-based dichotomous samplers were excellent for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} measurements. For example, the coefficient of variations for the three R&P Model 2025 dichotomous samplers during all five field campaigns for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} measurements averaged 3.0%, 3.1%, and 2.3%, respectively.

4. At the Gary, IN and the Riverside, CA sampling sites, the $PM_{2.5}$ concentrations measured by the R&P dichotomous samplers agreed almost exactly with those measured by the collocated $PM_{2.5}$ FRM samplers. During all three field campaigns in Phoenix, however, the dichots typically measured $PM_{2.5}$ concentrations which were approximately 10% higher than those of the $PM_{2.5}$ FRMs. It is hypothesized that this $PM_{2.5}$ measurement bias resulted from the inadvertent contamination of the fine particle fraction with a small percentage of coarse mode particles. Because this behavior was independent of dichot sampler design

(i.e., R&P sequential, R&P sequential converted to manual mode, R&P single-event, or Sierra-Andersen single-event), this contamination may be inherent to virtual impactor size fractionation technology. However, because the resulting bias in measured $PM_{2.5}$ concentrations depends upon the size distribution of the PM_{10} aerosol, significant measurement biases will occur only if the coarse fraction of PM_{10} appreciably exceeds the $PM_{2.5}$ fraction.

5. During the Year 2003 field tests, the R&P dichotomous samplers underestimated $PM_{10-2.5}$ concentrations at all sampling sites, and under-measured $PM_{10-2.5}$ by 20% at the Phoenix site. Mass balance calculations revealed that 15% of the aspirated PM_{10} mass during the Phoenix tests was not accounted for during subsequent gravimetric measurement of fine and coarse channel filters. During the 2004 follow-up tests in Phoenix and during subsequent laboratory tests by the manufacturer, the loss of coarse mode aerosols during the samplers' automated, post-sampling movement of the coarse particle cassette to the sample storage position was identified as the source of the measurement bias. As demonstrated during the 2005 Phoenix field tests, a redesigned cassette exchange mechanism effectively reduced this coarse particle loss from 20% to 7%. Because the dry, bouncy nature of windblown coarse particles tends to maximize the extent of the particle loss, it is expected that this modified exchange mechanism will result in minimal coarse particle loss in most sampling locations. In R&P's new single-event dichotomous sampler, the sampling cassettes remaining stationary during all phases of sampler operation. As a result, dichot to FRM ratios for $PM_{10-2.5}$ concentrations and PM_{10} concentrations were measured to be 0.99 and 1.01, respectively, during the 2005 Phoenix tests.

6. With the exception of the problem noted during the Riverside tests, excellent inter-manufacturer precision of the R&P coarse TEOM samplers was observed at all three sampling sites, and no operational problems were encountered with the samplers. During the January 2004 Phoenix tests, very close agreement was observed between the USC prototype coarse TEOM versus the two coarse TEOMs manufactured by R&P, indicating that the USC prototype's basic design had been faithfully duplicated by R&P. However, with the exception of the 2003 Phoenix tests, the coarse TEOM tended to underestimate the $PM_{10-2.5}$ concentration by as much as 30%. The high correlation between the coarse TEOMs' response versus the collocated FRMs indicated that this performance was very consistent from one sampling event to another. Following the 2004 Phoenix tests, modifications were made to the coarse TEOM design including increasing the inlet's cutpoint to approximately 10 μm aerodynamic diameter. The 2005 Phoenix follow-up tests showed excellent intra-sampler precision (CV = 2.4%) and improved correlation

coefficients when compared to those obtained during the 2003 Phoenix field tests. However, because the mean coarse TEOM to $PM_{10-2.5}$ FRM ratio of 1.05 was identical during the 2003 and 2005 Phoenix tests, it is not yet certain if the 30% under-measurement bias (observed at the Gary and Riverside sites) has been properly addressed by the coarse TEOM's design modifications. The fall 2005 sampler evaluation tests in Birmingham, AL should provide an additional opportunity to assess the effectiveness of these design changes.

7. During the 2003 and 2004 field tests, the Kimoto SPM-613D samplers provided precise, highly correlated test results at all three sites for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} measurements. Although performance varied by site, the Kimoto units generally provided $PM_{10-2.5}$ measurements within 10% of those of the collocated FRM samplers. However, the SPM-613D units consistently provided $PM_{2.5}$ concentrations significantly higher than the collocated $PM_{2.5}$ FRM samplers. As an example, the mean over-estimation in $PM_{2.5}$ concentrations at the Phoenix site was 70%. The magnitude of the Kimoto's $PM_{2.5}$ bias suggested that possible intrusion of coarse mode particles into the fine channel only partly accounted for the bias. The fact that the sampler produced PM_{10} concentrations higher than the collocated PM_{10} FRM samplers also suggested that the problems were associated with the aerosol's analysis, rather than with regard to aerosol sampling and transport. Following the 2004 tests, modifications were made to the Kimoto's design which included reduction of the $PM_{2.5}$ deposition area to increase measurement sensitivity, and change in mass flow control to volumetric flow. In addition, a Loo and Cork virtual impactor design was evaluated as a replacement to the system's custom virtual impactor. However, as indicated by the 2005 Phoenix results presented in section 5.4.3, is appears that these design modifications did not adequately address the Kimoto's $PM_{2.5}$ measurement bias. Based on a review of the data, it is recommended that future instrument development initiatives focus on accurate calibration of the fine channel's beta gauge at low $PM_{2.5}$ concentrations. It also recommended that the system's software be validated to ensure that the measured $PM_{2.5}$ aerosol mass during a sampling event is being accurately converted to $PM_{2.5}$ concentration.

8. With the exception of a single electronics failure, the two TSI Model 3321 units appeared to function well and provided acceptable levels of precision during the 2003 and 2004 field tests. Following a review of the literature, a coarse aerosol specific gravity and shape factor of 2.0 and 1.4, respectively, were used to convert the APS' response to $PM_{10-2.5}$ mass concentration. For the Riverside, 2003 Phoenix, and 2004 Phoenix field campaigns, results were highly correlated with the collocated FRM samplers and provided similar

$PM_{10-2.5}$ concentrations. For the Gary, IN data, however, the APS results were less correlated and under-measured $PM_{10-2.5}$ by approximately 30%. Based on the hypothesis that the negative $PM_{10-2.5}$ measurement bias might be attributable to transport losses of large, hygroscopic particles in the humid Gary sampling environment, a smart heater was designed and constructed to heat the incoming aerosol if the ambient relative humidity exceeded 45%. Unfortunately, the environmental conditions during the 2005 Phoenix tests did not enable this modification to be evaluated. In addition, operational problems were encountered with both APS units during the 2005 Phoenix tests which invalidated a large percentage of the collected data. While the source of the operational problem is still under investigation, it is believed to be associated with a calibration error which occurred during the factory servicing of the two APS units immediately prior to the 2005 Phoenix tests. The manufacturer has indicated that this problem can be properly identified and addressed prior to the start of the fall 2005 field tests in Birmingham.

9. The battery-operated, 5 lpm BGI Omni samplers were designed to provide a low-cost means of conducting saturation monitoring studies. Four prototype Omni monitors first became available for evaluation during the 2005 Phoenix tests. Two of these units were configured to operate as $PM_{2.5}$ samplers while two were configured to operate as PM_{10} samplers. While functional problems with the Omni's relative humidity sensor limited the overall data capture rate, the samplers were generally able to maintain their flow rate, ambient temperature measurement, and ambient pressure measurement calibrations. The Omni's intra-sampler precision for $PM_{2.5}$ was determined to be 8.8% . On average, the Omni units provided $PM_{2.5}$ concentrations which exceeded the $PM_{2.5}$ FRMs by approximately 7%. The relatively large scatter of the Omni $PM_{2.5}$ data versus the collocated $PM_{2.5}$ FRMs may be due to uncertainties in gravimetric measurements associated with the relatively small amount of mass collected at the sampler's 5 lpm flow rate. The Omni's PM_{10} CV of 3.3% compares favorably with the FRM's $PM_{2.5}$ CV of 2.2% during the same sampling events. On average, the Omni's PM_{10} concentrations were 11% lower than those of the collocated PM_{10} FRM samplers. Systematic biases in PM_{10} measurements may reflect inadequate aspiration of large particles and/or a PM_{10} fractionation curve which does not sufficiently match that of the PM_{10} FRM inlet.

10. No operational problems were encountered with the three Grimm EnviroTrack Model 1.107 samplers during the 30-day 2005 Phoenix study and the units tended to hold their calibrations well. Intra-sampler precision among the three units was excellent as evidenced by CVs of 2.2%, 4.1%, and 3.4% for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} measurements, respectively. In comparison to the collocated FRMs, the Grimm units over-measured

$PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} concentrations during all 30 sampling events. On average, the Grimm units over-predicted $PM_{2.5}$ concentrations by 37% when compared to the collocated $PM_{2.5}$ FRMs. Results were well correlated (R^2 = 908) for $PM_{2.5}$ but the slopes and intercepts were 0.83 and 4.8 $\mu g/m^3$, respectively. $PM_{10-2.5}$ results were also well correlated (R^2 = 0.847) but slopes and intercepts were 1.35 and 8.4 $\mu g/m^3$, respectively. As for all samplers which became available only in time for the Phoenix 2005 field tests, these limited tests results are insufficient to make strong conclusions regarding the Grimm's measurement capabilities. The upcoming field tests in Birmingham will provide additional comparative data upon which to make more reliable observations and conclusions.

11. No functional problems were apparent with the two prototype dichotomous TEOM samplers during the 2005 Phoenix tests. Upon examination of the collected field data, however, it became apparent that some operational problems existed with the units during the 30-days of testing. In particular, negative $PM_{2.5}$ concentrations were reported at a frequency of 20% and 38% for the two TEOM units, respectively. Although results are preliminary, the manufacturer reports that flow leaks have been discovered in the purge filter conditioning section of the prototype units. Leaks in this component would tend to occur during the instrument's purge cycle and introduce ambient aerosol into the flow stream where it would be subsequently collected and analyzed. Since this measured concentration is subsequently subtracted from the concentration measured during the instrument's normal sampling cycle, these component leaks would tend to produce negative $PM_{2.5}$ calculations. The manufacturer indicates that this problem can be adequately addressed prior to start of the fall 2005 field tests in Birmingham. As compared to the $PM_{2.5}$ measurements, negative $PM_{10-2.5}$ concentrations were reported by the dichotomous TEOM during only 9 hourly events. Mean dichot to FRM $PM_{10-2.5}$ ratios for the two units were determined to be 0.85 and 0.89, respectively. The mean $PM_{10-2.5}$ response of the two units was very highly correlated with the collocated FRMs as evidenced by a mean correlation coefficient of 0.992.

7.0 REFERENCES

1. U.S. EPA (1997). Part 50 - National Primary and Secondary Ambient Air Quality Standards, *Federal Register*, Vol. 62, No. 138, p38711. July 18, 1997.

2. Noble, C.A.; Vanderpool, R.W.; Peters, T.M.; McElroy, F.F.; Gemmill, D.B.; Wiener, R.W. "Federal Reference and Equivalent Methods for Measuring Fine Particulate Matter." *Aerosol Sci. Technol.* **2001**, 34, 457-464.

3. Misra, C.; Geller, M.; Shah, P.; Sioutas, C., Solomon, P. *J. of Air Waste Manage. Assoc.* **2001**, 51, 1309-1317.

4. Loo, B.; Cork, C. "Development of High Efficiency Virtual Impactors." *Aerosol Sci. Technol.* **1988**, 9, 167-176.

5. L. Kenny, et al. "Aspiration and Sampling Efficiencies of the TSP and Louvered Particulate Matter Inlets", *J. Environ. Monitoring*, **2005**, 7 481-487.

6. Allen, G.A.; Oh, J.A.; Koutrakis, P.; Sioutas, C. *J. of Air Waste Manage. Assoc*. **1999**, 49, 133-141.

7. Misra, C.; Geller, M.; Sioutas, C.; Solomon, P. *Aerosol Sci. Technol* **2003,** 37, 271-281.

8. Stein, F.; Esmen, N.A.; Corn, M., "The Shape of Atmospheric Particles in Pittsburgh Air." *Atmospheric Environment* **1988**, 22, 1461-1468.

9. Noll, K.E.; Fang, K.Y.P.; Watkins, L.A., "Characterization of the Deposition of Particles from the Atmosphere to a Flat Plate." *Atmospheric Environment* **1988**, 22, 1461-1468.

10. Lin, J.; Noll, K.E.; Holsen, T.M., "Dry Deposition Velocities as a Function of Particle Size in the Ambient Atmosphere." *Aerosol Sci. Technol.* **1994**, 20, 239-252.

11. Volckens, J.; Peters, T.M., "Counting and Particle Transmission Efficiency of the Aerodynamic Particle Sizer." *J. Aerosol Sci.* **in press**.

Table 1. Inventory of samplers used in the 2003 and 2004 multi-site performance evaluations.

Measurement Method	PM Metric	Sampler Manufacturer(s)	Inlet Type	Inlet Flow Rate (alpm)	# Used	Filter Composition	Species Analyzed
Integrated FRM	PM_{10}	BGI, R&P, AND	Std. PM_{10}	16.7	3	Teflon	Mass, sulfate, nitrate, metals
Integrated FRM	PM_{10}	BGI	Std. PM_{10}	16.7	1	Quartz	EC, OC
Integrated FRM	$PM_{2.5}$	BGI, R&P, AND	Std. PM_{10}	16.7	3	Teflon	Mass, sulfate, nitrate, metals
Integrated FRM	$PM_{2.5}$	AND	Std. PM_{10}	16.7	1	Quartz	EC, OC
Integrated Dichot, sequential	$PM_{2.5}$, $PM_{10-2.5}$	R&P	Std. PM_{10}	16.7	3	Teflon	Mass, sulfate, nitrate, metals
Integrated Dichot, manual (Phoenix 2004 only)	$PM_{2.5}$, $PM_{10-2.5}$	Sierra-Andersen	Std. PM_{10} (non-louvered)	16.7	2	Teflon	Mass, sulfate, nitrate, metals
Integrated Dichot, sequential	$PM_{2.5}$, $PM_{10-2.5}$	R&P	Std. PM_{10}	16.7	1	Quartz	EC, OC
Coarse TEOM	$PM_{10-2.5}$	R&P	Std. PM_{10} (modified for 50 lpm)	50.0	3	Glass fiber	none
Beta Attenuation	$PM_{2.5}$, $PM_{10-2.5}$	Kimoto	Std. PM_{10}	16.7	3	Polyfon	none
Time of Flight (APS)	$PM_{10-2.5}$	TSI	Std. PM_{10}	16.7	2	none	none
					Total = 22		

Table 2. Inventory of samplers used in the 2005 Phoenix performance evaluation.

Measurement Method	PM Metric	Sampler Manufacturer(s)	Inlet Type	Inlet Flow Rate (alpm)	# Used	Filter Composition	Species Analyzed
Integrated FRM	PM_{10}	BGI, R&P, AND	Std. PM_{10}	16.7	3	Teflon	Mass, sulfate, nitrate, metals
Integrated FRM	PM_{10}	BGI	Std. PM_{10}	16.7	1	Quartz	EC, OC
Integrated FRM	$PM_{2.5}$	BGI, R&P, AND	Std. PM_{10}	16.7	3	Teflon	Mass, sulfate, nitrate, metals
Integrated FRM	$PM_{2.5}$	AND	Std. PM_{10}	16.7	1	Quartz	EC, OC
Integrated Dichot, sequential	$PM_{2.5}$, $PM_{10-2.5}$	R&P	Std. PM_{10}	16.7	2	Teflon	Mass, sulfate, nitrate, metals
Integrated Dichot, single-event	$PM_{2.5}$, $PM_{10-2.5}$	R&P	Std. PM_{10} (non-louvered)	16.7	2	Teflon	Mass, sulfate, nitrate, metals
Integrated Saturation Monitor	$PM_{2.5}$, $PM_{10-2.5}$	BGI	Custom "Total"	5.0	4	Quartz	EC, OC
Coarse TEOM	$PM_{10-2.5}$	R&P	Std. PM_{10} (modified for 50 lpm)	50.0	3	Glass fiber	none
Beta Attenuation	$PM_{2.5}$, $PM_{10-2.5}$	Kimoto	Std. PM_{10}	16.7	2	Polyfon	none
Time of Flight (APS)	$PM_{10-2.5}$	TSI	Std. PM_{10}	16.7	2	none	none
Dichotomous TEOM	$PM_{2.5}$, $PM_{10-2.5}$	R&P	Std. PM_{10}	16.7	2	Glass fiber	none
Light Scattering at 90°		Grimm	Custom "Total"	1.2	3	Teflon	none
					Total = 28		

Table 3. Inter-manufacturer precision of the collocated FRM samplers as a function of sampling site.

Metric	Gary, IN	Phoenix, AZ (May - June, 2003)	Riverside, CA	Phoenix, AZ (January 2004)	Phoenix, AZ (April - May, 2005)
$PM_{2.5}$	1.5%	3.4%	3.1%	2.6%	2.8%
$PM_{10-2.5}$	5.7%	3.6%	4.1%	4.7%	2.4%
PM_{10}	2.4%	3.3%	2.9%	3.6%	1.9%

Table 4. Performance of the R&P 2025 Sequential Dichot versus the FRM during 2003.

Metric	Performance Criteria	Gary, IN	Phoenix, AZ (May - June, 2003)	Riverside, CA
$PM_{2.5}$	Dichot CV	3.8%	2.3%	1.3%
	Regression Equation (Dichot vs. FRM)	Dichot = 1.01*FRM - 0.10	Dichot = 1.24*FRM - 1.6	Dichot = 1.00*FRM + 0.0
	Coefficient of determination (R^2)	0.991	0.974	0.995
	Mean Dichot/FRM Ratio	1.00	1.08	1.00
$PM_{10-2.5}$	Dichot CV	3.2%	4.1%	1.6%
	Regression Equation (Dichot vs. FRM)	Dichot = 0.87*FRM + 0.39	Dichot = 0.71*FRM + 4.8	Dichot = 0.95*FRM + 0.21
	Coefficient of determination (R^2)	0.968	0.982	0.982
	Mean Dichot/FRM Ratio	0.90	0.80	0.96
PM_{10}	Dichot CV	1.7%	2.9%	1.2%
	Regression Equation (Dichot vs. FRM)	Dichot = 0.95*FRM - 0.33	Dichot = 0.76*FRM + 5.7	Dichot = 1.00*FRM - 1.21
	Coefficient of determination (R^2)	0.982	0.982	0.992
	Mean Dichot/FRM Ratio	0.94	0.85	0.97

Table 5. Comparison of sequential versus manual operation of the R&P 2025 dichots and Sierra-Andersen dichot in Phoenix, AZ (2004 tests).

Metric	R&P Sequential Dichot	R&P Sequential Dichot (Manual Mode)	Sierra-Andersen Dichot
$PM_{2.5}$	Slope = 1.10 Intercept = -0.64 R^2 = 0.991 CV = 2.3% Mean Dichot/FRM ratio = 1.05	Slope = 1.07 Intercept = -0.39 R^2 = 0.990 CV = 3.4% Mean Dichot/FRM ratio = 1.04	Slope = 1.13 Intercept = -1.17 R^2 = 0.988 CV = 1.6% Mean Dichot/FRM ratio = 1.03
$PM_{10-2.5}$	Slope = 0.81 Intercept = 2.04 R^2 = 0.979 CV = 3.5% Mean Dichot/FRM ratio = 0.89	Slope = 0.96 Intercept = 0.75 R^2 = 0.998 CV = 1.2% Mean Dichot/FRM ratio = 0.99	Slope = 0.91 Intercept = 1.45 R^2 = 0.995 CV = 1.8% Mean Dichot/FRM ratio = 0.95
PM_{10}	Slope = 0.86 Intercept = 2.35 R^2 = 0.981 CV = 2.9% Mean Dichot/FRM ratio = 0.92	Slope = 0.99 Intercept = 0.53 R^2 = 0.999 CV = 1.0% Mean Dichot/FRM ratio = 1.00	Slope = 0.95 Intercept = 0.90 R^2 = 0.996 CV = 1.0% Mean Dichot/FRM ratio = 0.97

Table 6. Performance of the R&P sequential dichots and single-event dichots versus the FRMs during the 2005 Phoenix tests.

	$PM_{2.5}$	$PM_{10-2.5}$	PM_{10}
FRM (3 each)	9.8 μg/m^3	46.1 μg/m^3	56.0 μg/m^3
Precision (CV)	2.8%	2.4%	1.9%
Single-Event Dichot (2 each)	10.9 μg/m^3	45.5 μg/m^3	56.6 μg/m^3
Precision (CV)	1.9%	2.4%	2.4%
Mean Ratio to FRM	1.11	0.99	1.01
Slope	1.07	1.01	1.02
Intercept	0.21	-1.40	-0.79
R^2	0.983	0.995	0.995
Sequential Dichot (2 each)	10.7 μg/m^3	42.7 μg/m^3	53.5 μg/m^3
Precision (CV)	5.4%	3.0%	2.6%
Mean Ratio to FRM	1.09	0.93	0.96
Slope	1.01	0.90	0.92
Intercept	0.74	1.10	1.97
R^2	0.978	0.997	0.998
Mean Sequential/Single-Event Concentration Ratio	1.00	0.96	0.97

Table 7. Performance of the R&P Coarse TEOM versus the FRM.

Metric	Gary, IN	Phoenix, AZ (May - June, 2003)	Riverside, CA	Phoenix, AZ (January 2004)
$PM_{10-2.5}$	Slope = 0.68 Intercept = +0.18 R^2 = 0.983 CV = 4.4% Mean TEOM/FRM ratio = 0.69	Slope = 0.79 Intercept = +12.6 R^2 = 0.953 CV = 6.6% Mean TEOM/FRM ratio = 1.05	Slope = 0.77 Intercept = -0.50 R^2 = 0.926 CV = 9.4% Mean TEOM/FRM ratio = 0.76	Slope = 0.77 Intercept = +0.70 R^2 = 0.999 CV = 2.7% Mean TEOM/FRM ratio = 0.79

Table 8. Performance of the Kimoto SPM-613D Beta Gauge Dichot versus the FRM.

Metric	Gary, IN	Phoenix, AZ (May - June, 2003)	Riverside, CA	Phoenix, AZ (January 2004)
$PM_{2.5}$	Slope = 1.17 Intercept = +0.16 R^2 = 0.949 CV = 7.1% Mean Kimoto/FRM ratio = 1.26	Slope = 2.03 Intercept = -3.4 R^2 = 0.947 CV = 5.9% Mean Kimoto/FRM ratio = 1.70	Slope = 2.07 Intercept = -6.9 R^2 = 0.904 CV = 4.1% Mean Kimoto/FRM ratio = 1.65	Slope = 1.43 Intercept = -0.11 R^2 = 0.939 CV = 5.2% Mean Kimoto/FRM ratio = 1.43
$PM_{10-2.5}$	Slope = 0.885 Intercept = +0.34 R^2 = 0.978 CV = 10.5% Mean Kimoto/FRM ratio = 0.91	Slope = 0.920 Intercept = +5.9 R^2 = 0.995 CV = 9.5% Mean Kimoto/FRM ratio = 1.04	Slope = 1.17 Intercept = -2.7 R^2 = 0.957 CV = 5.8% Mean Kimoto/FRM ratio = 1.08	Slope = 0.99 Intercept = +1.66 R^2 = 0.994 CV = 9.9% Mean Kimoto/FRM ratio = 1.05
PM_{10}	Slope = 1.02 Intercept = +2.5 R^2 = 0.987 CV = 4.3% Mean Kimoto/FRM ratio = 1.09	Slope = 1.02 Intercept = +7.8 R^2 = 0.996 CV = 7.4% Mean Kimoto/FRM ratio = 1.16	Slope = 1.53 Intercept = -10.6 R^2 = 0.880 CV = 3.5% Mean Kimoto/FRM ratio = 1.29	Slope = 1.07 Intercept = +2.9 R^2 = 0.998 CV = 7.3% Mean Kimoto/FRM ratio = 1.14

Table 9. Performance of the TSI APS Model 3321 versus the FRM.

Metric	Gary, IN	Phoenix, AZ (May - June, 2003)	Riverside, CA	Phoenix, AZ (January 2004)
$PM_{10-2.5}$	Slope = 0.68 Intercept = 1.7 R^2 = 0.53 Mean APS/FRM ratio = 0.76	Slope = 0.92 Intercept = 0.97 R^2 = 0.98 Mean APS/FRM ratio = 0.94	Slope = 1.05 Intercept = -2.6 R^2 = 0.84 Mean APS/FRM ratio = 1.00	Slope = 1.00 Intercept = 0.27 R^2 = 0.99 Mean APS/FRM ratio = 1.02

Figure 1. Schematic diagram of the FRM samplers used in the $PM_{10-2.5}$ difference method.

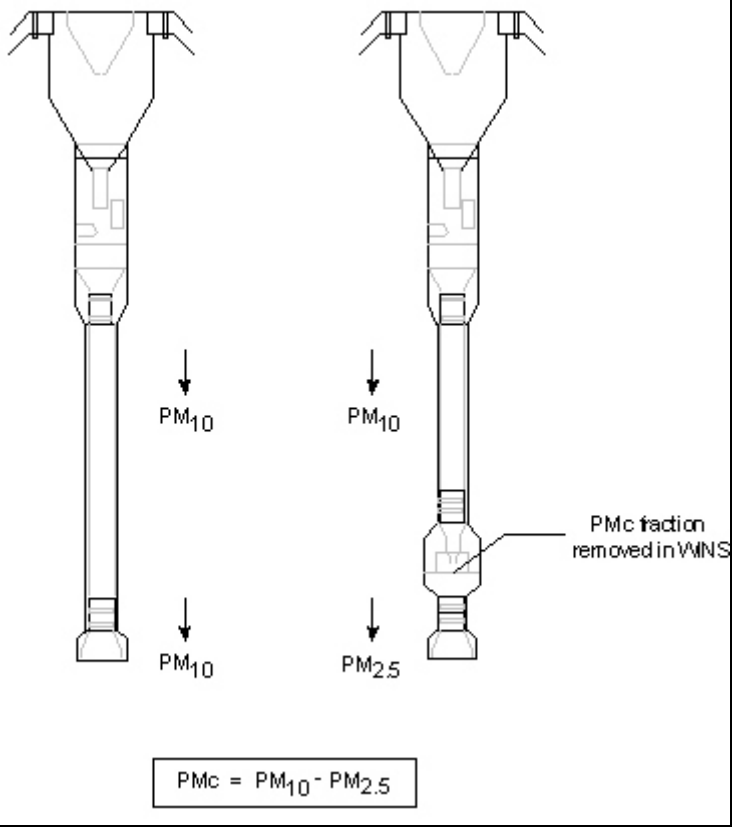


Figure 2. Schematic diagram of flow system (a) and sample exchange mechanism (b) of the R&P Model 2025 sequential dichotomous sampler.

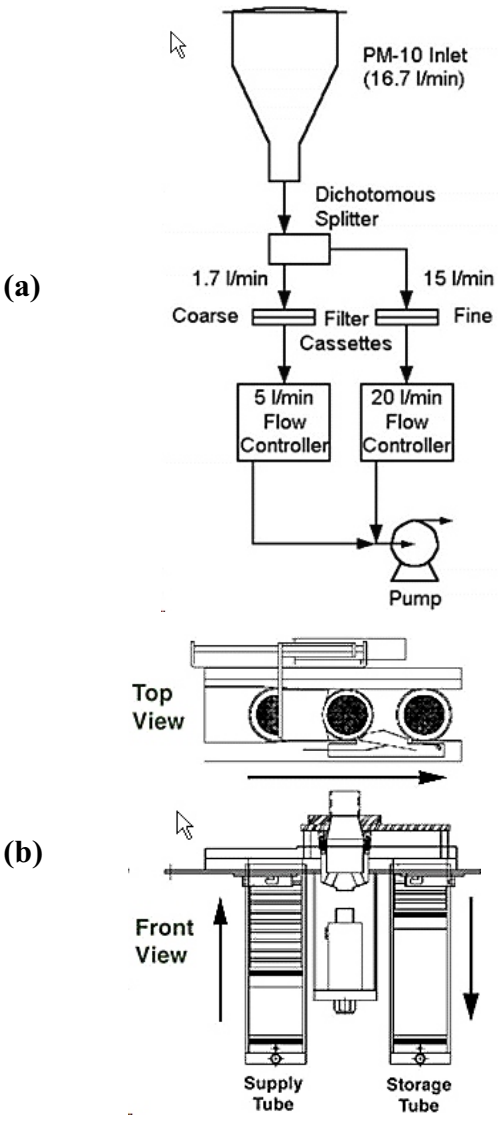


Figure 3. Photograph of the Kimoto Model SPM-613D Beta Gauge

Figure 4. Schematic diagram of the Kimoto Model SPM-613D Beta Gauge

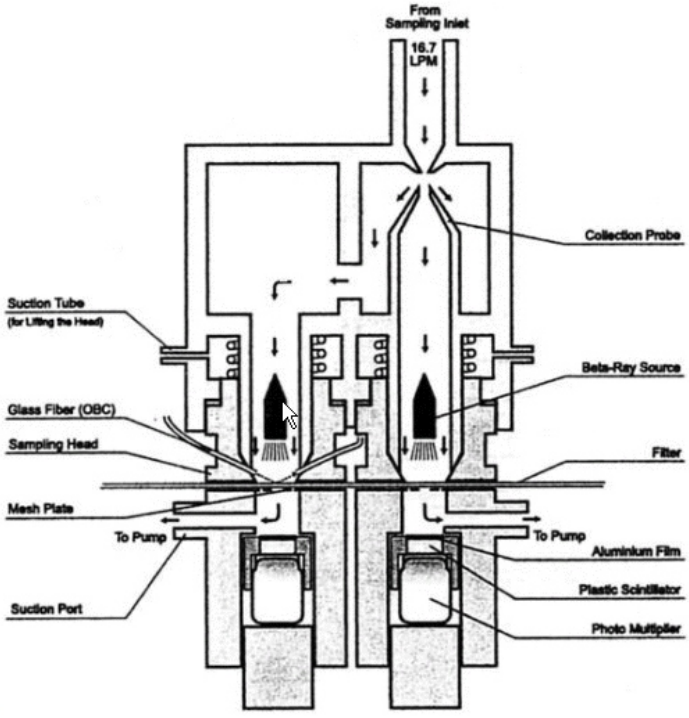


Figure 5. Photograph of the R&P $PM_{10-2.5}$ TEOM.

Figure 6. Photograph (a) and measurement principle schematic (b) of the TSI Aerodynamic Particle Sizer

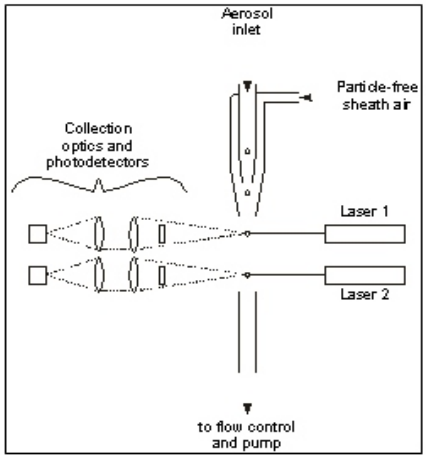


Figure 7. Photograph of the R&P single event dichotomous sampler.

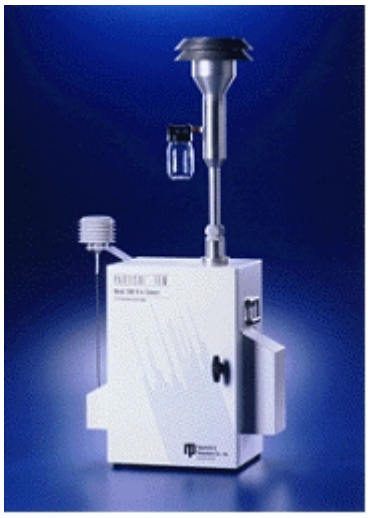


Figure 8. Photograph of the Sierra-Andersen Model 241 dichotomous sampler.

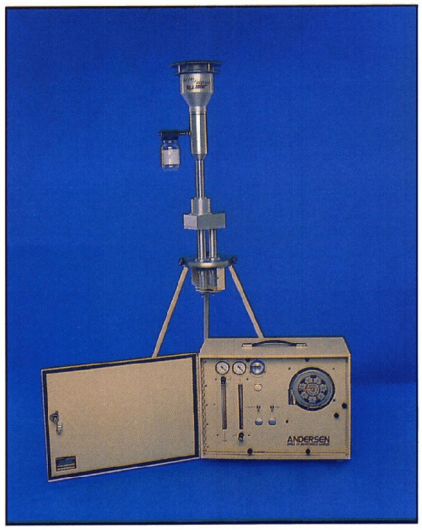


Figure 9. Photograph of BGI Omni saturation sampler.

Figure 10. Photograph of the Grimm Model 1.107

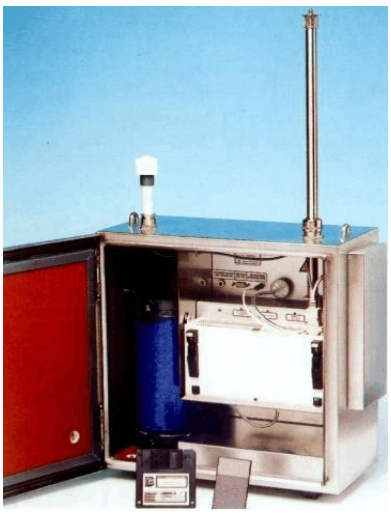


Figure 11. Diagram of the R&P dichotomous TEOM sampler.

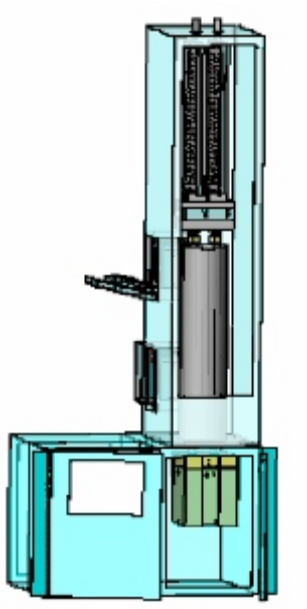
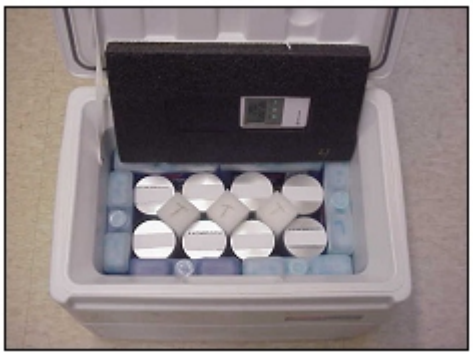


Figure 12. Photograph of the $PM_{10-2.5}$ sampler evaluation platform at the Gary, IN site.

Figure 13. Photographs of shipping canisters and temperature-controlled coolers.



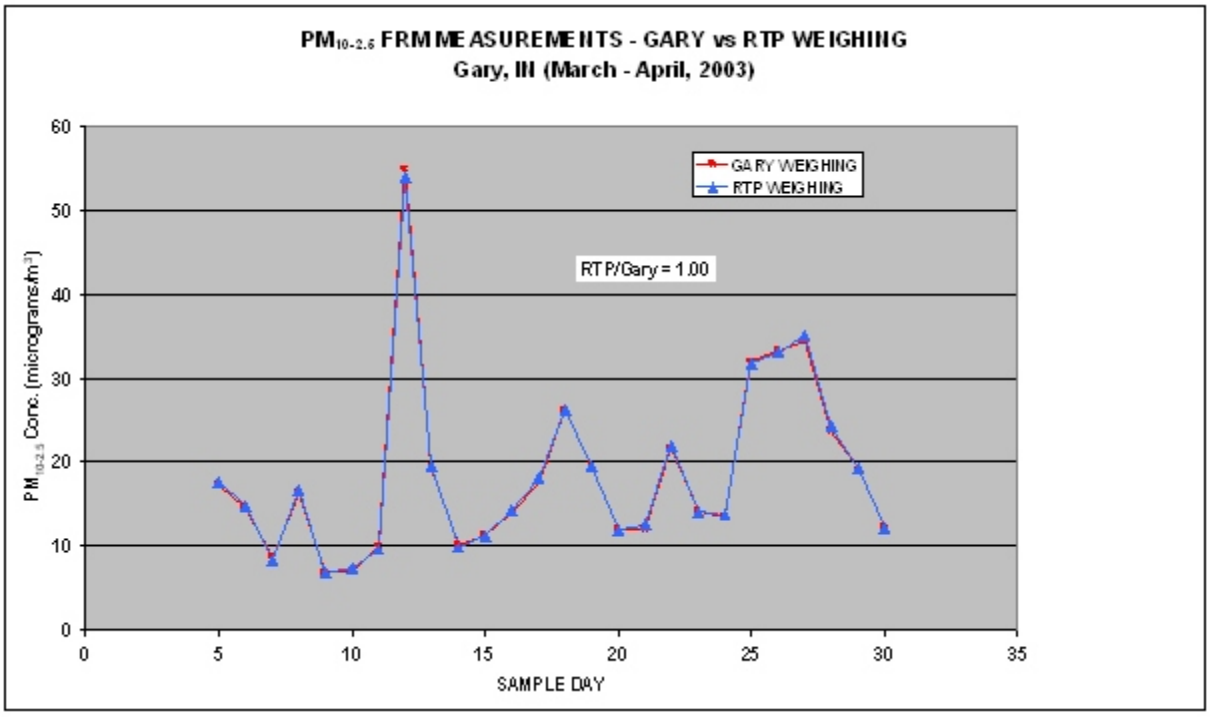


Figure 14. Timeline of Gary, IN $PM_{10-2.5}$ concentration showing level of agreement between site weighing and RTP, NC weighings.

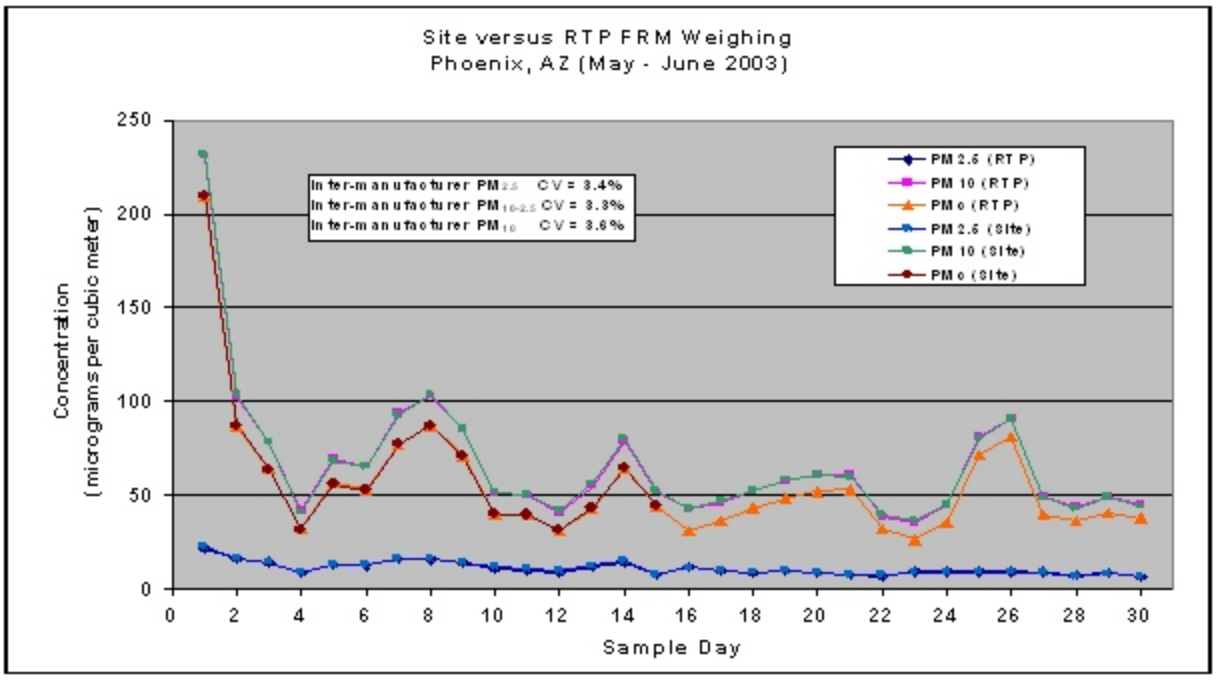


Figure 15. Site versus RTP, NC weighing of $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} concentrations at the 2003 Phoenix, AZ site.

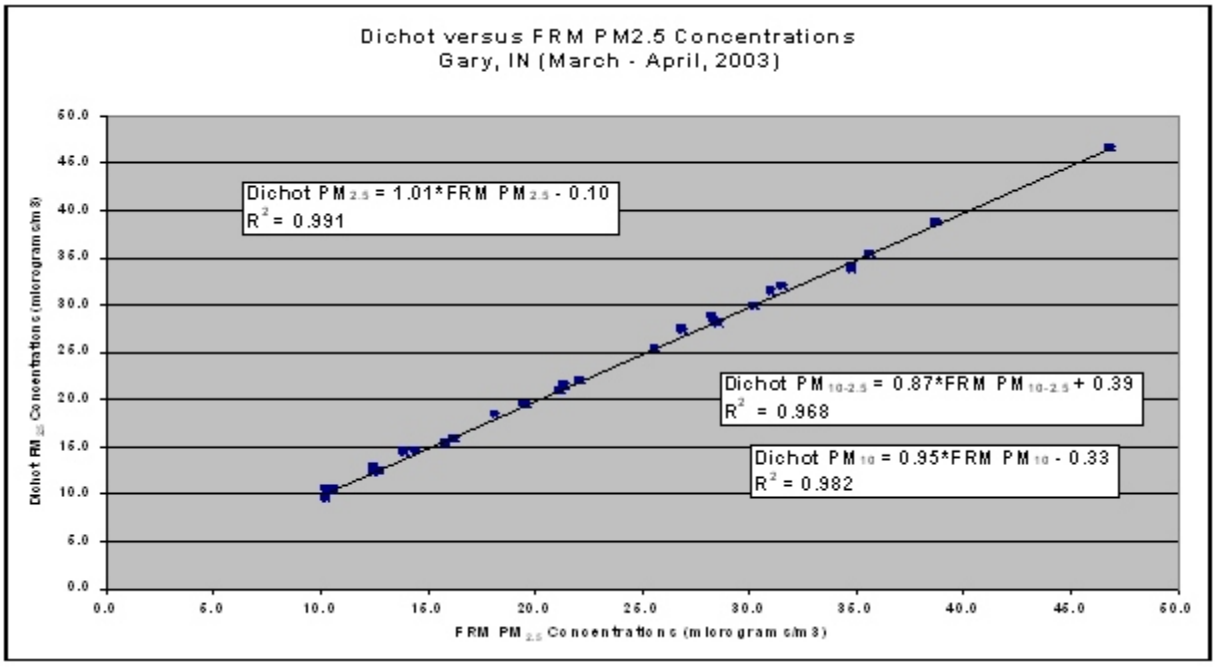


Figure 16. Performance of the R&P dichotomous samplers in Gary, IN versus the collocated FRM samplers.

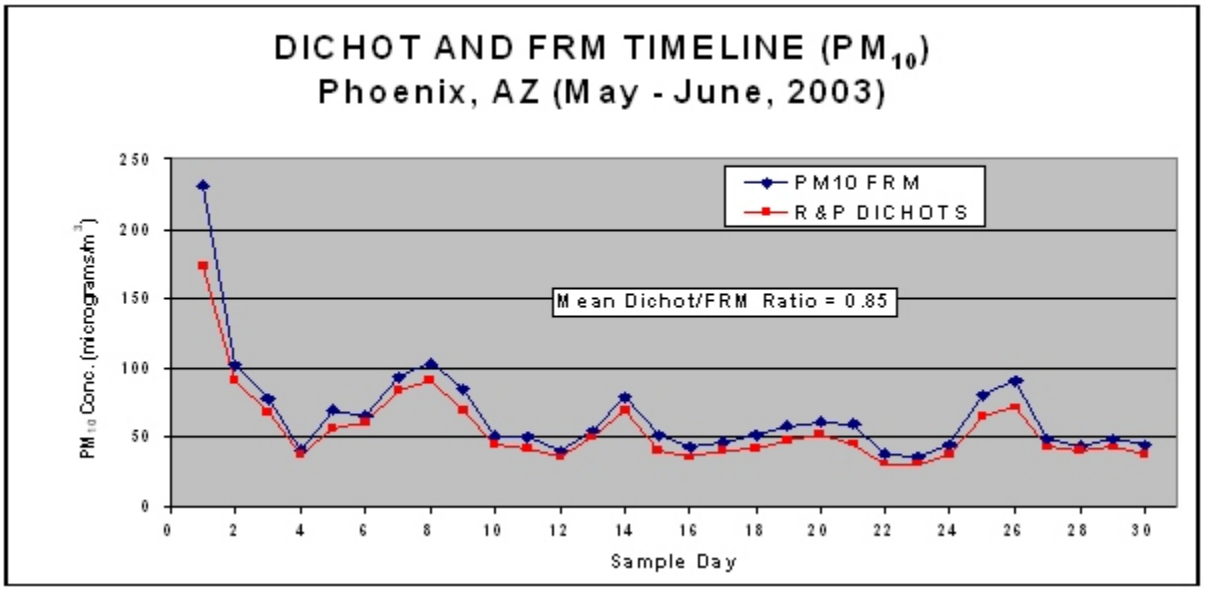


Figure 17. Timeline of R&P sequential dichot versus FRM PM_{10} concentrations in Phoenix, AZ

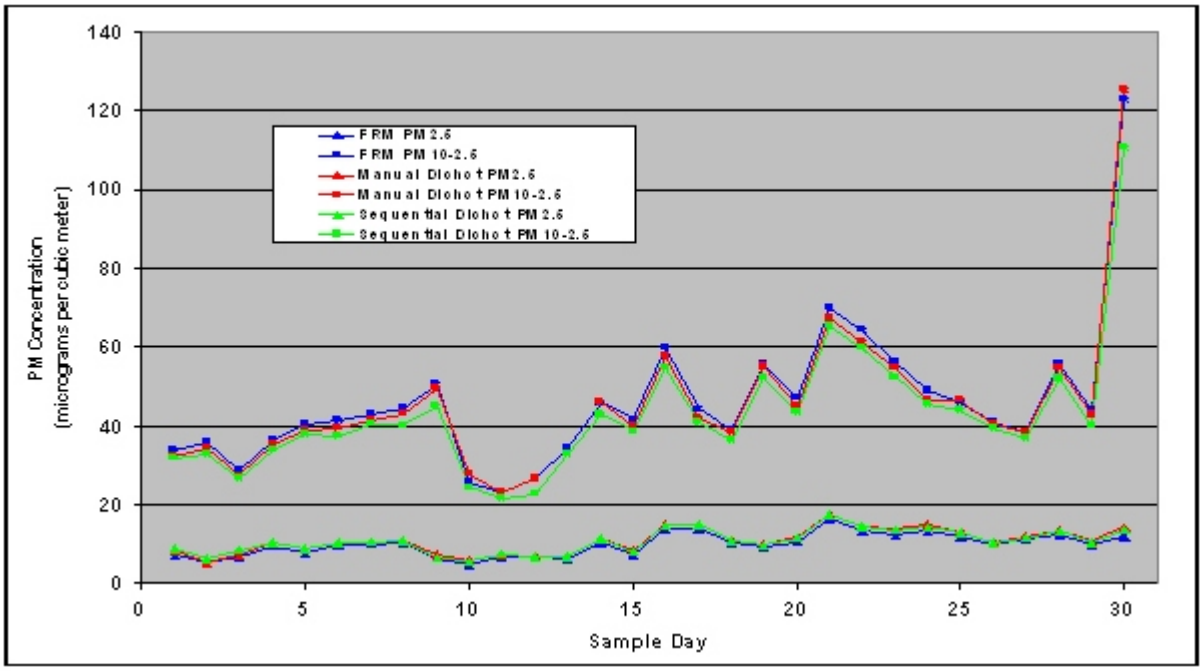


Figure 18. Timeline of R&P sequential and single-event dichots versus collocated FRMs in Phoenix, AZ (2005).

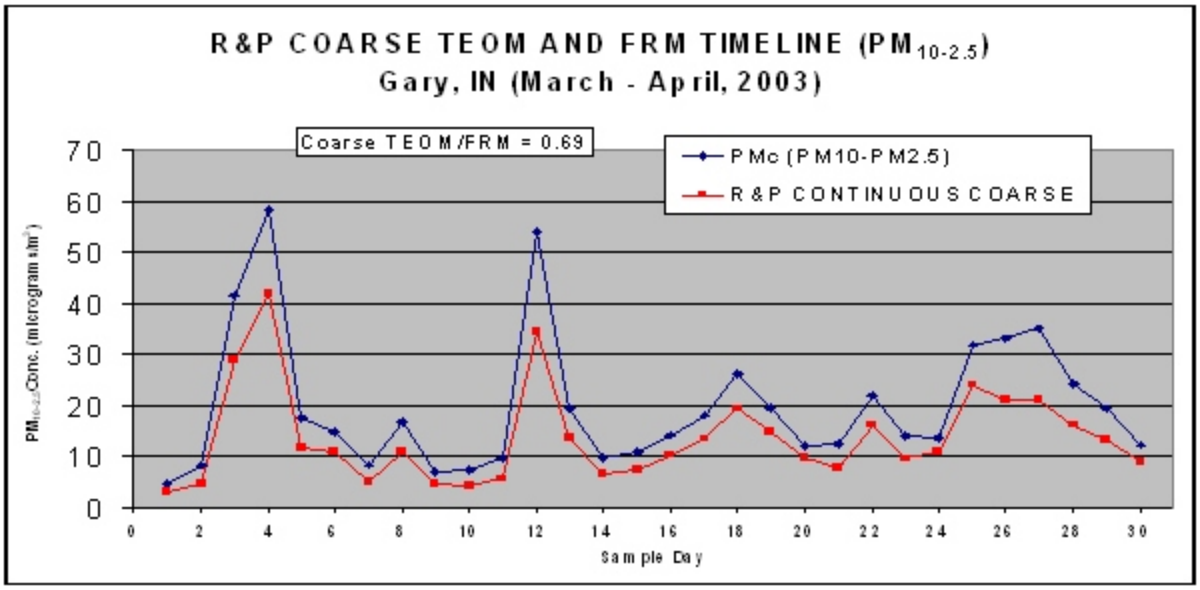


Figure 19. R&P coarse TEOM versus FRM $PM_{10-2.5}$ concentrations in Gary, IN.

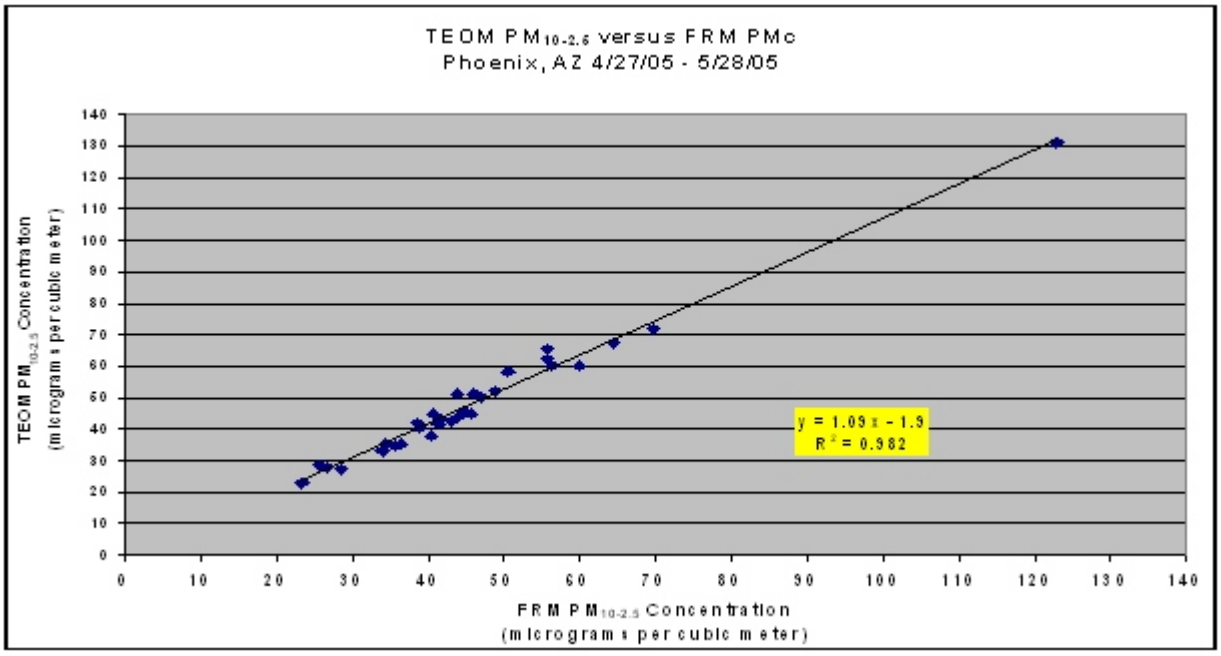


Figure 20. Regression of coarse TEOM versus $PM_{10-2.5}$ FRMs during the 2005 Phoenix tests.

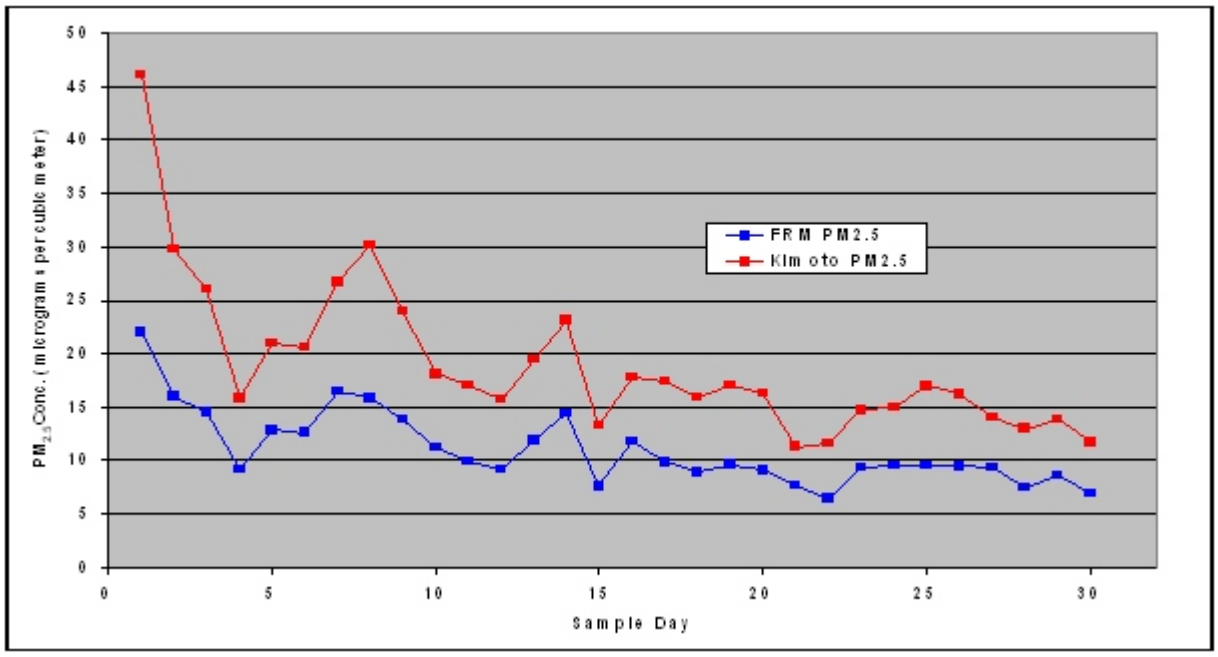


Figure 21. Timeline of Kimoto SPM-613D versus FRM $PM_{2.5}$ concentrations in Phoenix, AZ (2003).

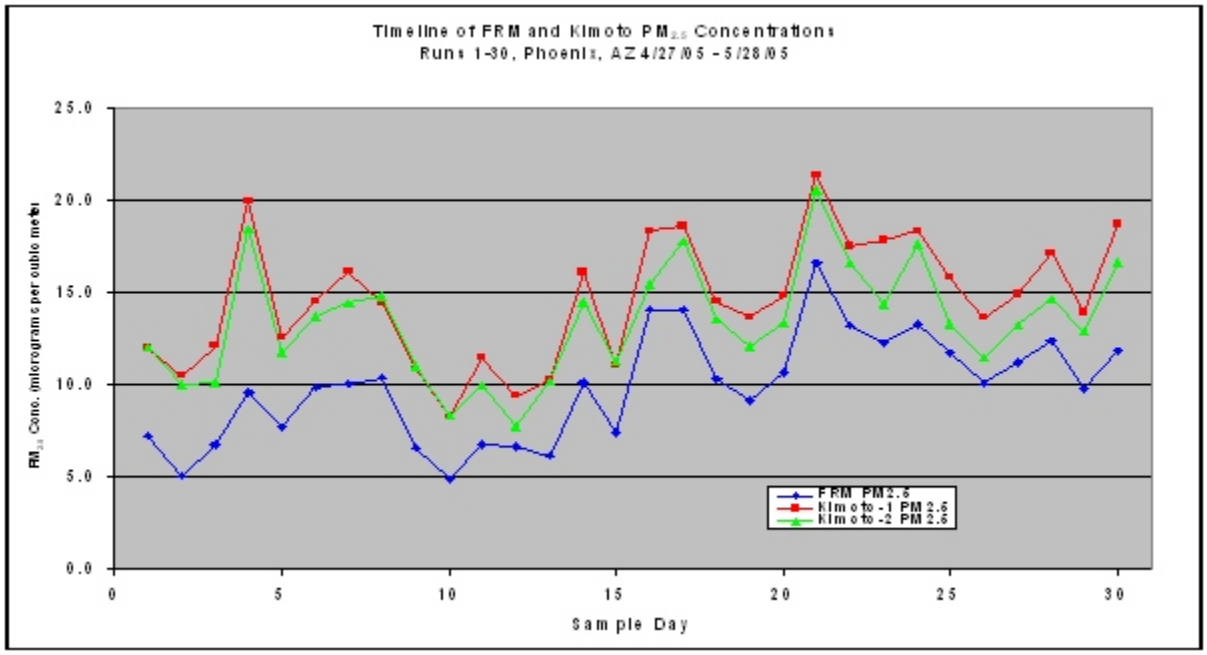


Figure 22. Timeline of FRM and Kimoto $PM_{2.5}$ concentrations during the 2005 Phoenix tests. The virtual impactor of Kimoto-2 was replaced following Day 15.

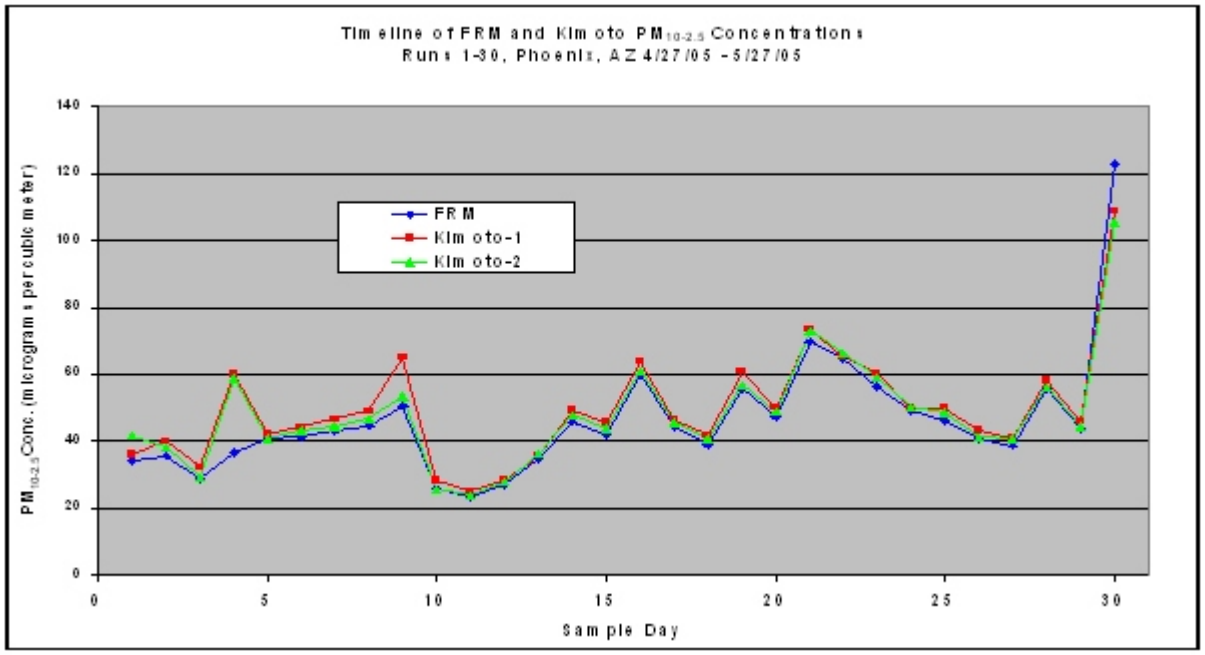


Figure 23. Timeline of FRM and Kimoto $PM_{10-2.5}$ concentrations during the 2005 Phoenix field tests. The virtual impactor in the Kimoto-2 unit was replaced following Day 15.

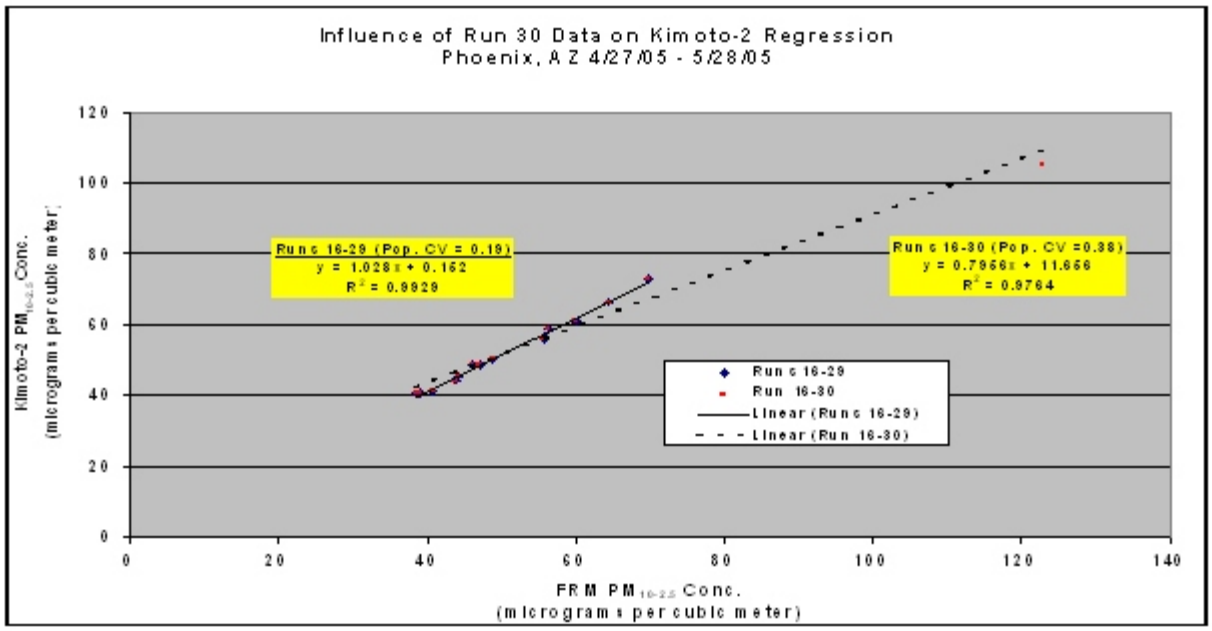


Figure 24. Regression of Kimoto-2 versus the FRM showing the influence of the Run 30 data on the regression outcome.

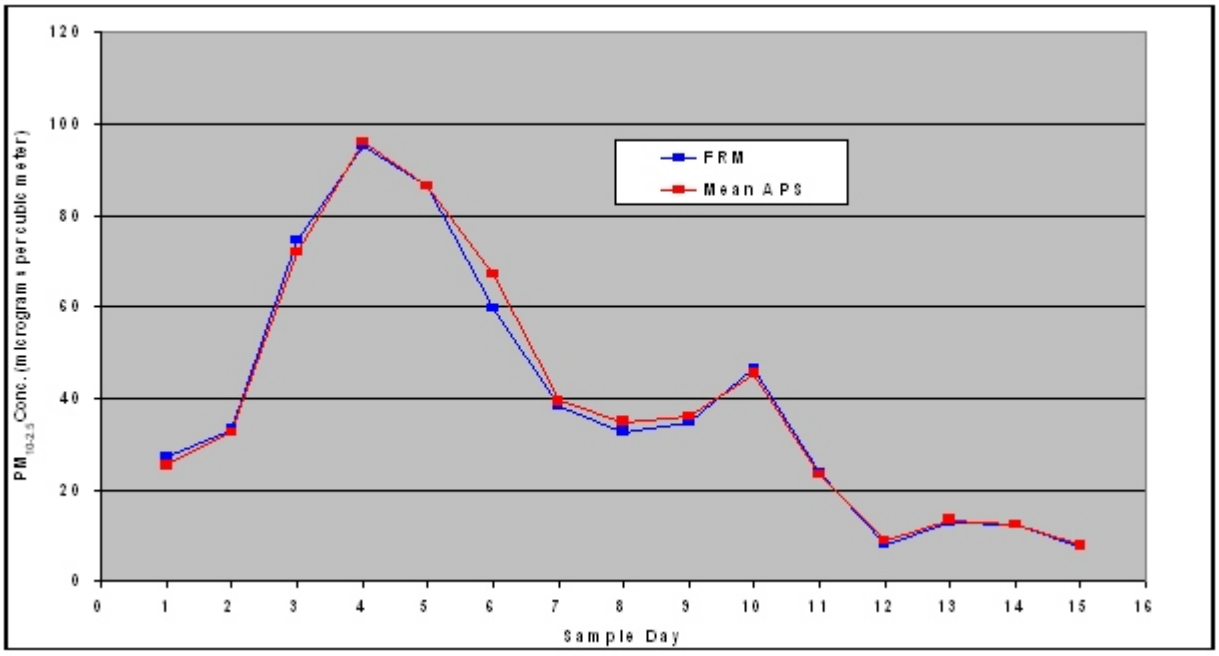


Figure 25. Timeline of mean APS and FRM $PM_{10-2.5}$ concentrations during the 15-day Phoenix 2004 field tests.

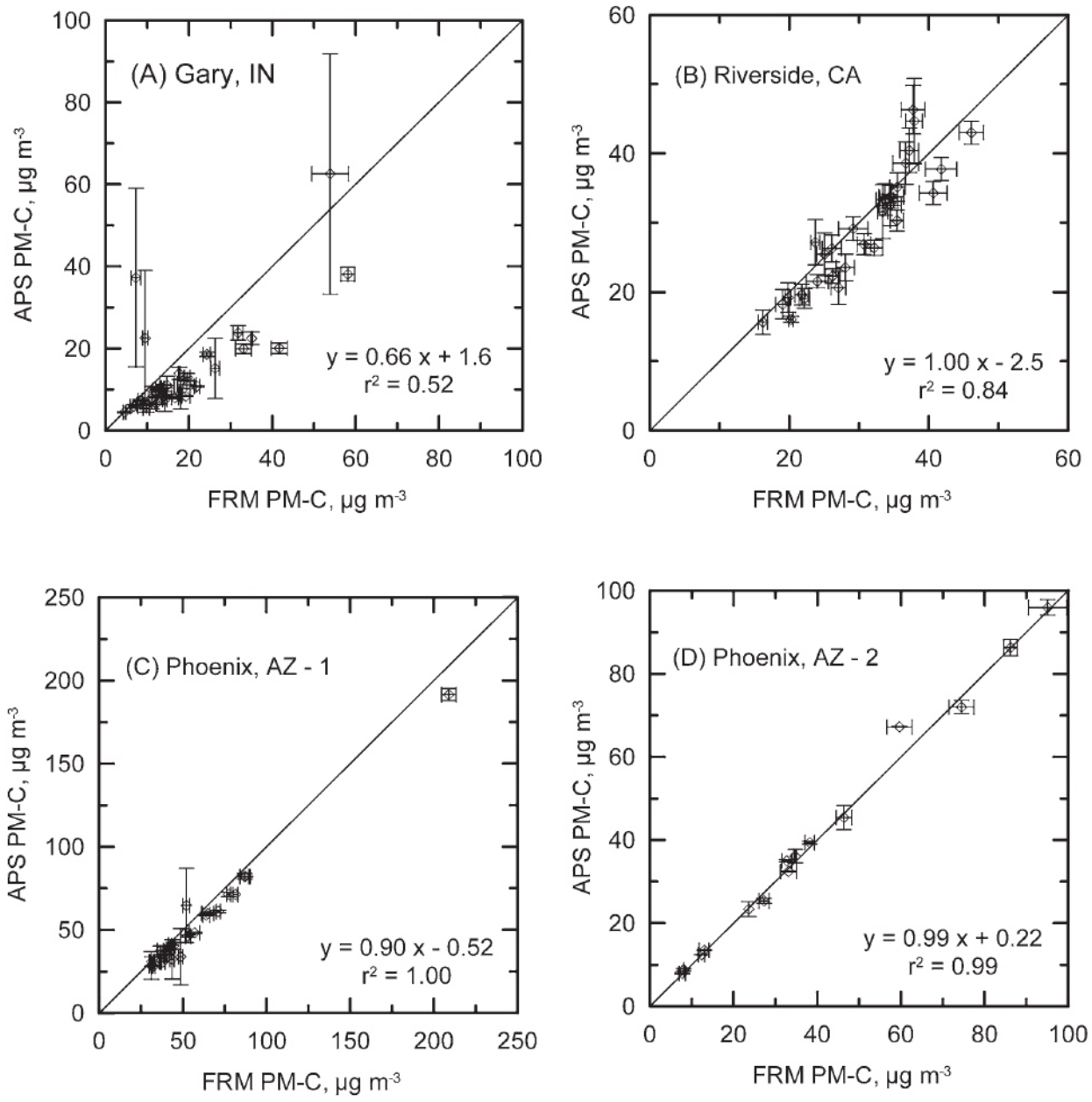


Figure 26. Regressions of $PM_{10-2.5}$ concentrations estimated by the Model 3321 APS versus those measured by the collocated FRM samplers. The Phoenix, AZ-1 and Phoenix, AZ-2 designations refer to data collected in Phoenix during 2003 and 2004, respectively.

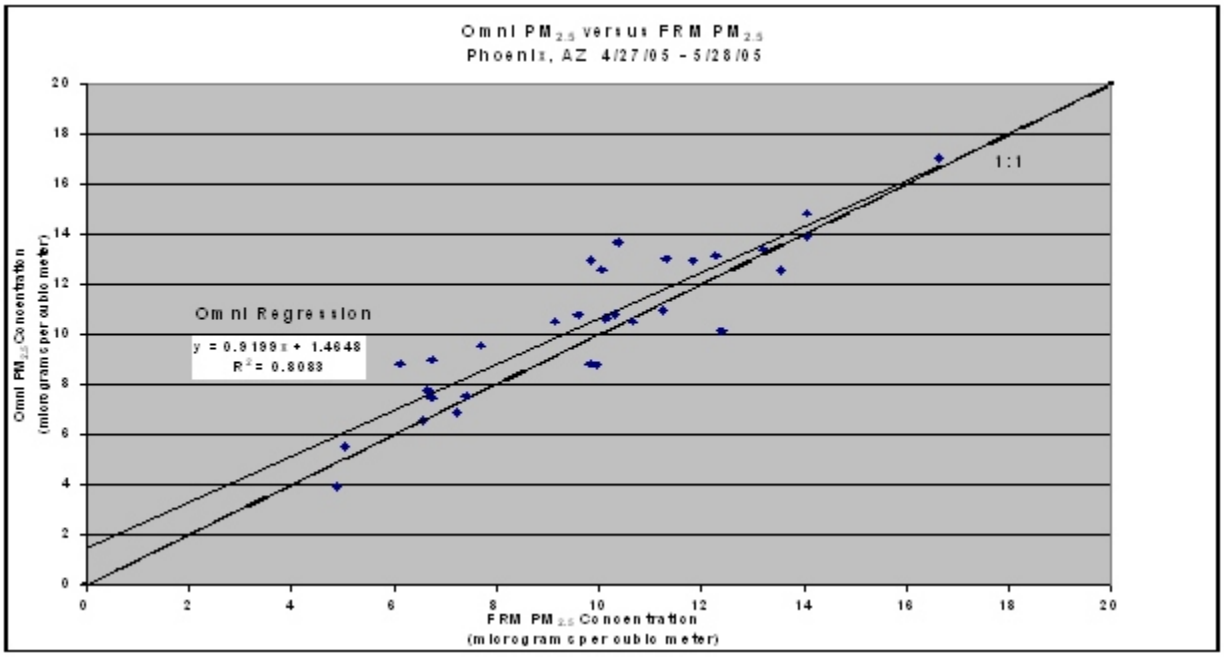


Figure 27. Regression of the BGI Omni $PM_{2.5}$ concentrations versus those of the collocated $PM_{2.5}$ FRM samplers.

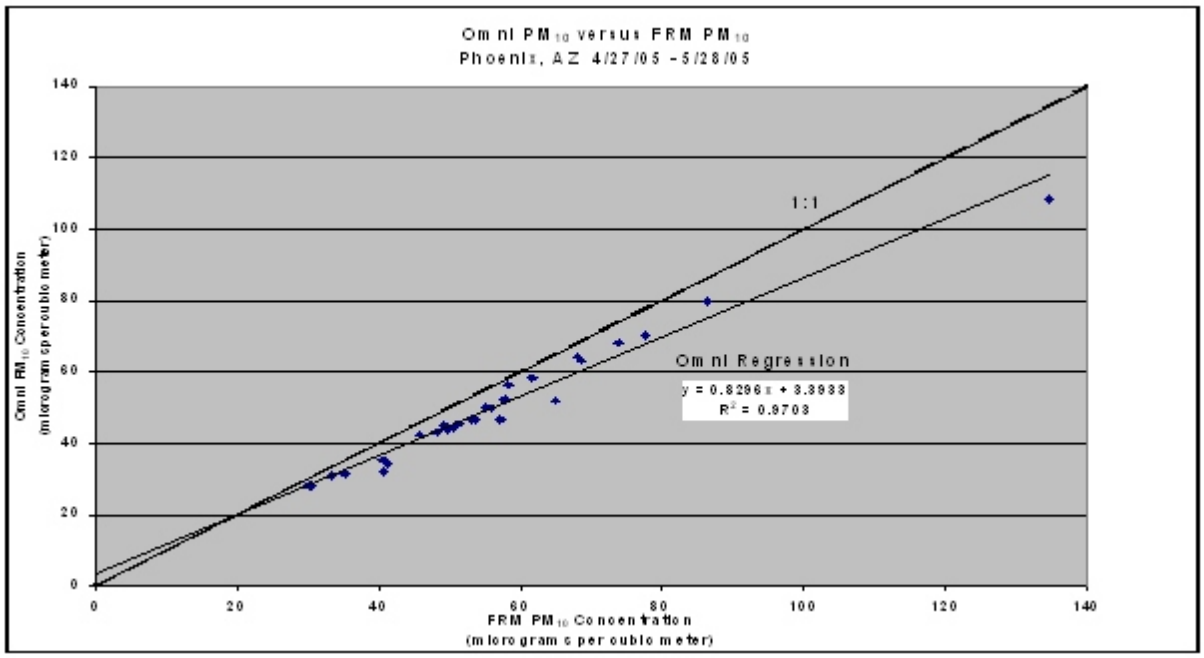


Figure 28. Regression of Omni PM_{10} concentrations versus those of the collocated PM_{10} FRM samplers.

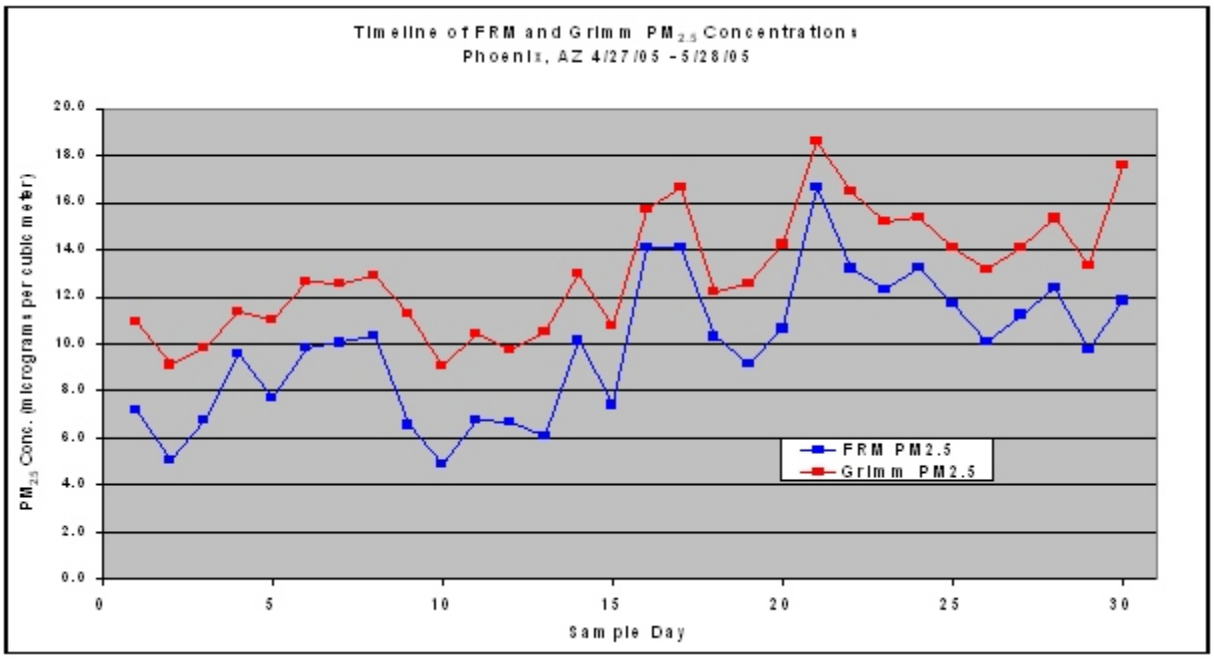


Figure 29. Timeline of Grimm Model 1.107 $PM_{2.5}$ concentrations versus those of the collocated $PM_{2.5}$ FRMs.

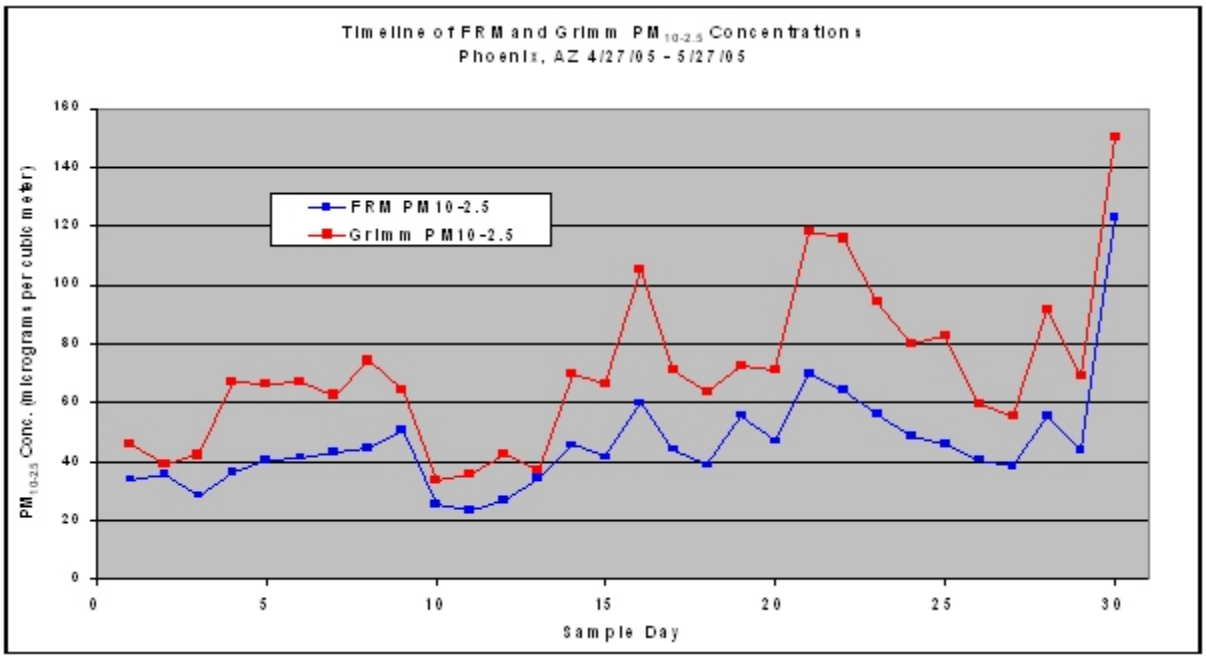


Figure 30. Timeline of Grimm Model 1.107 $PM_{10-2.5}$ concentrations versus those of the collocated FRMs.

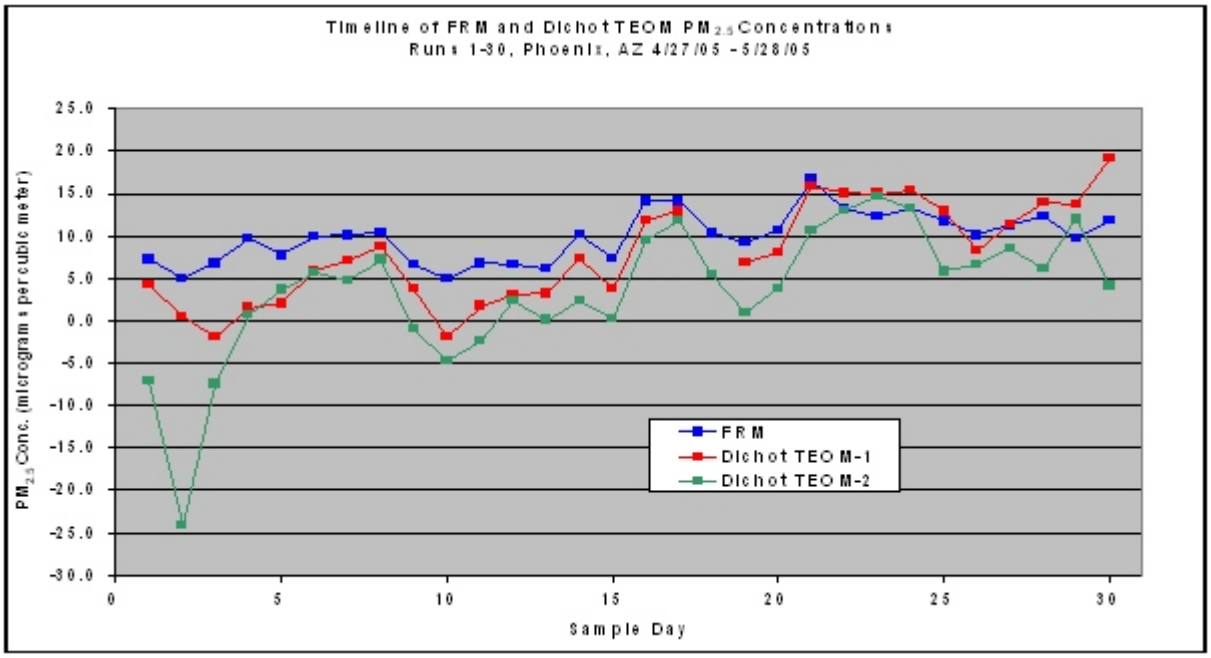


Figure 31. Timeline of R&P dichotomous TEOM $PM_{2.5}$ concentrations versus those of the collocated $PM_{2.5}$ FRMs.

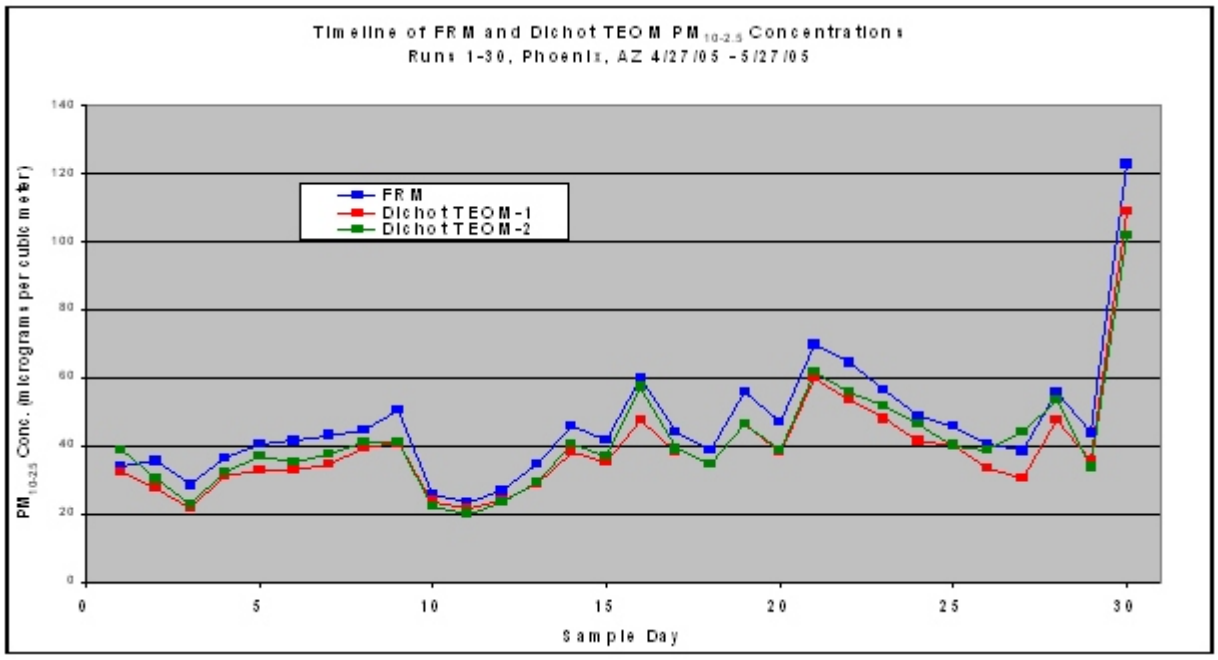


Figure 32. Timeline of R&P dichotomous TEOM $PM_{10-2.5}$ concentrations versus those of the collocated FRMs