4. Measurement Evaluation

This section evaluates the measurements taken during the study and determines the degree of confidence that is associated with each one. Most of the measurements were characterized in terms of their completeness, precision, lower quantifiable limit, and accuracy. The specific approaches for determining these parameters for each measurement are described in the following subsections. Generally, however, they can be defined as follows:

Completeness reflects the percentage of valid Level-1 data obtained, as compared to the maximum amount that could have been obtained. Level 1 (univariate) validation involves checking the data for outliers, unrealistic rates of change, and proper indication of time and location of data.

Precision is a measure of mutual agreement among individual measurements of the same observable under similar prescribed conditions. Precision is estimated by repeated measurements with the same monitor and calibration system.

The lower quantifiable limit (LQL) is the lowest value that can be distinguished in the ambient atmosphere. Sources of variability that influence the LQL can include instrument noise and variability.

Accuracy represents the extent to which a measurement differs from its true value. Accuracy is evaluated by the deviation of a measurement from a reference value which is provided by known or standard reference materials.

4.1 Optical Data Quality

Visual air quality was monitored during Project MOHAVE using integrating nephelometers to measure light scattering and transmissometers to measure total light extinction. The details of these measurements were described in Section 3.4.

4.1.1 Nephelometers

Optec, Inc. NGN nephelometers were used for the light scattering measurements. The quality of the nephelometer data is summarized below.

4.1.1.1 Completeness

Data completeness for the nephelometer is defined as the percent of hours each instrument was collecting valid Level-1 data throughout its complete period of operation. Data completeness exceeded 90% for all sites during the winter intensive and for four of the six sites during the summer. The sites falling below 90% completeness during the summer were Meadview (81.3%) and Cajon Pass (60.3%). Data recovery exceeded 95% during both intensives for all of the ambient temperature and relative humidity sensors that were collocated with the nephelometers.

4.1.1.2 Precision and Lower Quantifiable Limit

The precision of the NGN nephelometers was determined from the drift of the slope of the calibration line based on multiple manual zero air checks and span checks using Freon-22. The estimated precisions during the winter intensive were all within ±20%, determined at 95% confidence from the standard deviation of repeated calibrations. Nephelometer performance during the summer intensive was variable. For three instruments (Joshua Tree, Cajon Pass, and Meadview), precision was within ±15%. Two other instruments suffered poorer precision, Meadview #1 at 25.5% and Kelso (an NGN-1 nephelometer) at 41.1%. For the remaining three instruments (El Centro, Tehachapi, and Cajon Pass #1), only two calibration checks were conducted during the course of the study, so insufficient data were available for statistical analysis.

For the NGN nephelometer, the LQL is ±1 count, the maximum resolution of the electronics of the instrument, which represents approximately ±1 Mm^{-1}.

4.1.1.3 Accuracy

The NGN nephelometer accuracy was judged against instrument response to a separate supply of Freon-22 gas, supplied by an independent auditor. Audits were conducted at three sites during the summer intensive (Cajon Pass, Joshua Tree, and Meadview). The accuracy of all instruments was judged to be within ±4% at the Freon-22 calibration level of approximately 80 Mm^{-1}.

4.1.1.3.1 Sampling Bias

The NGN nephelometer was designed to minimize sampling biases, compared to older model nephelometers. Still, some small biases remain which would cause the measured scattering to underestimate ambient scattering. First, a perfect nephelometer would measure scattering throughout the entire field of view of the instrument, from 0 to 180°. The integration angles for the NGN are 5 to 175°. For small particles ($PM_{2.5}$), this truncation error is less than 10%.

Next, the measured scattering corresponds to a nominal wavelength of 550 nm for the NGN nephelometer. The actual spectral response of the instrument’s light detector can cause an error of less than 2%, again determined for fine particles.

Finally, heating of the air sample in the nephelometer chamber can cause volatile aerosol components such as water to be lost, thereby reducing the measured scattering. However, the open-air design of the NGN nephelometer reduces chamber heating to less than 1°C in most cases. At the low relative humidities common in Project MOHAVE, the effects of such heating are minimal, well within the precision of the measurement.

4.1.2 Transmissometers

Total light extinction was determined using transmissometers, which measure the average irradiance of a light source of known intensity over the path length of the instrument. The quality of the transmissometer data is summarized below.

4.1.2.1 Completeness

Data completeness for the transmissometer is defined as the percent of hours each instrument was collecting valid Level-1 data throughout its complete period of operation. Data completeness exceeded 95% for most sites and 85% for all sites during the winter intensive, the summer intensive, and the interim period between intensives. Data completeness for the transmissometer is also reported in terms of the number of valid 1-hour averages obtained during periods not influenced by meteorological events such as fog, rain, and blowing dust. Weather-modified completeness exceeded 70% for many sites and exceeded 50% for most sites, with the exception of Big Bend (45%), Canyonlands (35%), Chiricahua (41%), and Petrified Forest (23%) during the winter intensive, and Chiricahua (37%) during the summer intensive. These lower values reflect adverse weather events and are not necessarily indicative of poor instrument performance.

4.1.2.2 Precision and Lower Quantifiable Limit

For the transmissometers, the precision of the light extinction measurements, determined from the variability of light extinction within a single hour, varied from ±2% without optical interference to ±20% with optical interference, such as clouds passing through the sight path.

For transmissometer measurements, the LQL represents the resolution of the instrument, or the smallest change in extinction that can be distinguished. The LQL for the instrument is approximately 0.3% transmittance, which corresponds to an extinction change of $\pm 1.5\ \mathrm{Mm}^{-1}$ under clear conditions of around $10\ \mathrm{Mm}^{-1}$. At the other end of the range, the ability of the instrument to quantify hazy conditions is determined by values at low transmittance (i.e., high extinction, or low visibility). For every transmissometer sight path, a maximum usable b_{ext} was calculated that corresponds to a 5% transmittance for the path. All sight paths were selected such that, based on historical visibility data, extinction greater than this maximum b_{ext} occurs less than 1% of the time. When the measured b_{ext} was greater than this maximum value, it was assumed that meteorological or optical interferences, not ambient aerosols, were causing the high extinction. All measurements greater than the calculated site-specific maximum threshold are flagged in the data file.

4.1.2.3 Accuracy

The accuracy of the transmissometer measurements was determined through pre- and post-study lamp calibrations and through routine field checks which verified instrument alignment and cleanliness. Accuracy of ±3% transmittance was met throughout the study. Independent system audits of several transmissometers revealed no problems with instrument alignment or settings.

4.1.2.3.1 Measurement Bias

During validation, all transmissometer data were subjected to checks to identify meteorological or optical interferences. The intensity of the light in the sight path can be modified not only by the intervening aerosol, but also by:

- The presence of condensed water vapor in the form of fog, clouds, and precipitation.

- Condensation, frost, snow, or ice on the shelter windows.

- Reduction in light intensity by insects, birds, animals, or vegetation along the sight path, or on the optical surfaces of the instrumentation or shelter windows.

- Fluctuations in light intensity due to optical turbulence, beam wander, atmospheric lensing, and miraging caused by variations in the atmospheric index of refraction, and by the known drift in lamp intensity.

Validation checks based on expected minimum and maximum values and rates of change were applied to identify these anomalous conditions. Data failing the checks are flagged with identifier codes in the data base.

Large diurnal fluctuations in the transmissometer values at Meadview were observed during the winter intensive. It was determined that a cold air drainage flow in the sight path was apparently broadening the beam at nighttime due to density discontinuities in the atmosphere. The transmissometer sight path was changed prior to the summer intensive in order to alleviate this problem.

4.1.3 Light Absorption

Light absorption (b_{abs}) measurements in Project MOHAVE were conducted using the Laser Integrating Plate Method (LIPM) on the IMPROVE sampler Teflon filters collected for gravimetric mass and elemental analysis. Data quality for these measurements is described in detail in Section 4.2, which covers the filter-based measurements, and will be summarized here.

The overall sample recovery rate was 94% during the winter intensive and 92% during the summer intensive. Sites that did not achieve at least 80% recovery are listed in Section 4.2.

The mean relative precision for the b_{abs} measurements was 13% for the winter intensive and 15% for the summer intensive. In the winter intensive, 98% of samples registered b_{abs} values above the LQL, compared with 100% of samples in the summer.

The LIPM used for b_{abs} measurements was subjected to a calibration check after every fifth sample, using a set of ten control filters. The average standard deviation of these calibration checks during Project MOHAVE was 1.5%.

Differing interpretations of the light absorption measurement (b_{abs}) can lead to a discrepancy of a factor of two in the reported b_{abs} values. In reporting b_{abs} for IMPROVE and Project MOHAVE, UC Davis (UCD) applies a correction factor to account for shadowing of absorbing particles by other particles captured on the filter (UC Davis, 1994). This shadowing correction typically increases the reported b_{abs} value by about a factor of two over the LIPM measurement. Other groups, such as DRI, apply no correction to the measured b_{abs}, and still others (Weiss, 1989; Waggoner, 1995) argue that the measured b_{abs} should be decreased by up to a factor of two to account for filter matrix effects. Heintzenberg et al. (1997) conclude that the b_{abs} methods used in IMPROVE appear to yield values that are high, perhaps by large amounts. This conclusion is supported by laboratory experiments conducted by Horvath (1993). To date, the b_{abs} correction discrepancy has not been resolved, so the numbers reported in the Project MOHAVE data base can be considered to be an upper bound to the possible range of values.

4.2 Aerosol Data Quality

The aerosol measurement methods were described in Section 3.1.1. Most of the filter sampling measurements were conducted using the IMPROVE aerosol sampler and various samplers operated by BYU. Additional, specialized aerosol measurements were also conducted by the University of Minnesota and Aerosol Dynamics, Inc.

4.2.1 UCD IMPROVE Samplers

Aerosol sampling at most sites was conducted using the IMPROVE sampler. The quality of the IMPROVE aerosol data is summarized below.

4.2.1.1 Completeness

Sample recovery rates and observed ranges for flow rate and particle cut point are summarized below. The recovery rate is based on the number of samples in the final database with valid analysis of the Teflon A filters. The flow rate and particle cut point are for the A modules. There were 33 sampling days in winter and 53 in summer.

The overall recovery rate during the winter intensive was 94%. Three of the 33 samplers had less than 80% recovery. The Indian Gardens 12-hour sampler had a defective relay that caused the loss of every third sample at times, so recovery was 77%. Fortunately, the 24-hour Teflon A sampler at Indian Gardens had a 97% recovery rate. The Overton Beach site was vandalized twice, so only 70% recovery was achieved. A week of samples at New Harmony was lost when water collected in the cyclone, resulting in 79% recovery.

The overall recovery rate during the summer intensive was 92%. Six of the 34 samplers had less than 80% recovery. The low recoveries at four of these sites (Petrified Forest: 74%, Wickenburg: 75%, Cibola: 60%, and New Harmony: 75%) appear to have been associated with summer electrical storms and related high winds, power outages, and power surges. Six clocks were damaged by power surges at these sites and two samplers were blown over. Overton Beach again had vandalism, losing the last two weeks and achieving 72% recovery overall. Operator problems at El Centro resulted in 70% recovery.

The IMPROVE sampler is designed such that a 50% capture particle size cutpoint of 2.5 μm is achieved at a flow rate of approximately 22.8 lpm (actual volume, not corrected to STP). The equation used to calculate the D_{50} cut point of the sampler is

$$D_{50} = 2.5 - 0.334(Q - 22.8) \qquad (4\text{-}1)$$

where Q is the flow rate in lpm. At most sites the mean flow rate over each intensive period was between 21.1 and 24.1 lpm, yielding cutpoints between 3.0 and 2.0 μm, respectively. The exceptions during the winter were Joshua Tree (21.0 lpm, 3.1 μm), Hualapai Mountain (20.9 lpm, 3.1 μm), Jacob Lake (21.0 lpm, 3.1 μm), Las Vegas Wash (19.2 lpm, 3.7 μm), Mountain

Springs (18.2 lpm, 4.0 µm), New Harmony (20.7 lpm, 3.2 µm), and Wickenburg (27.3 lpm, 1.0 µm). The exceptions during the summer were Baker (20.8 lpm, 3.1 µm), Cottonwood Cove (20.9 lpm, 3.1 µm), and Mountain Springs (20.8, 3.1 µm). In all but one of these cases, the flow deviation resulted in a cutpoint exceeding the design value, which would allow somewhat more coarse material to pass but, for most aerosols, would not alter the measured concentration of secondary particles appreciably. At Wickenburg in the wintertime, however, the 1.0 µm cutpoint might cause some of the secondary material to be missed.

4.2.1.2 Precision

The concentrations for gravimetric mass, carbon, and ions were calculated from the measured mass of the component, M, the mean field blank value, B, and the sampled volume, V, using the equation:

$$C = \frac{M - B}{V} \tag{4-2}$$

For gravimetric analysis, M is the difference between the mass measurements before and after sampling. Similarly for light absorption (b_{abs}) measurements, M represents the difference between light transmittance through the filter before and after sampling. For carbon and ions, M is the amount of the component measured on the filter.

The equations for PIXE, PESA, and XRF differ from those above for two reasons. First, the analytical methods measure areal density in ng/cm^2, so that the collection area, A, enters into the equation for concentration. Second, a blank filter is used during analysis to estimate spectral background, which is subtracted before the instrumental values are reported, so no field blank values are subtracted for any variable. The concentrations are calculated using:

$$C = \frac{A}{V}\left(\text{areal density}\right) \tag{4-3}$$

The precision in the concentration will thus depend on the fractional precision of the analysis associated with calibration (f_{cal}), the fractional precision in volume (f_V, typically around 5%), and for all but the elements, the standard deviation of the field blanks (σ_{fb}). The constant analytical precision drops out because it is included in σ_{fb}. The equation for carbon and ions is:

$$\sigma^2(\mathrm{C}) = \left(\frac{\sigma_{fb}}{V}\right)^2 + \left(\frac{2B}{V}\right) f_{cal}^2\, C + \left(f_{cal}^2 + f_v^2\right) C^2 \tag{4-4}$$

The equation for mass and b_{abs} is:

$$\sigma^2(\mathrm{C}) = \left(\frac{\sigma_{fb}}{V}\right)^2 + \left(f_v\, C\right)^2 \tag{4-5}$$

The calibration term (f_{cal}) is not included because both mass and b_{abs} are determined from small differences between two measured values.

For PIXE, PESA, and XRF, there are two sources of uncertainty: the fractional calibration error (f_{cal}), and the statistical precision determined from the number of counts in the peak and background (f_s), based on standard Poisson statistics. The calibration uncertainty is the same for every element. It is monitored every analytical session from the precision for sulfur, hydrogen, and iron for a group of around 25 reanalyzed samples. The statistical precision is determined for every variable from the actual spectrum. The equation for precision for elemental measurements is:

$$\sigma^2(\mathrm{C}) = \left(f_s^{\,2} + f_{cal}^{\,2} + f_v^{\,2} \right) C^2 \qquad (4\text{-}6)$$

For small concentrations, below around 10 times the minimum detectable limit (mdl), the precision is generally a constant µg/m^3, with a value of one-half the mdl. For large concentrations, above 10 mdl, the uncertainty due to counting statistics becomes unimportant, and the precision is generally a constant fraction of the concentration. This fraction is the quadratic sum of the volume and calibration precisions; for most variables, this is around 5%.

The mean relative precision was reported for each season, determined as the mean precision divided by the mean concentration for the season. These values are listed in Table 4-1 and Table 4-2. The variables beginning with OC and EC represent various fractions of organic and elemental carbon from TOR analysis. OCLT (organic carbon low temperature) is operationally defined as carbon evolved from filters at temperatures < 140 deg C in the absence of oxygen. OCHT (organic carbon high temperature) is carbon evolved from filters at temperatures between 140 and 550 deg C in the absence of oxygen plus pyrolyzed carbon. OC tot is the sum of OCLT and OCHT. ECLT (elemental carbon low temperature) is the non-pyrolyzed carbon evolved from filters at temperatures of 550 deg C in the presence of 2% oxygen. ECHT (elemental carbon high temperature) is the carbon evolved from filters at temperatures of 550 – 800 deg C in the presence of 2% oxygen. LAC (light absorbing carbon) is the sum of ECLT and ECHT.

Relative precision was generally under about 20% for gravimetric mass, light absorption (b_{abs}), most of the ions, and about half of the elements. Precision generally exceeded 20% for organic and elemental carbon, largelly due to high blank variability, and for elements with small concentrations. Precision was worse for 12-hour samples than for 24-hour samples because less material was collected on the filters.

Precision was also quantified at a few sites from collocated sampling using identical measurement systems. Precision determined in this manner accounts for all aspects of uncertainty, both in the field and in the laboratory.

A special study was conducted at Meadview in November 1991, just prior to the winter intensive, which included 14 fine IMPROVE modules with Teflon filters. Some modules had denuders and some did not, but it was assumed that the denuders would have no effect on the concentrations of elements on Teflon. The standard deviations of the collocated measurements were approximately equal to the propagated precisions for S, H, Zn, and b_{abs}, indicating that the propagated values accounted for all of the principal aspects of precision for these observables. However, the standard deviations of the soil elements (Si, K, Ca, Fe) exceeded the propagated precisions by over a factor of two. This difference may be attributable to a combination of particles near the cutpoint of the cyclone (recall the dependence of cutpoint on flow rate) and possible inhomogeneities in the ambient concentrations, neither of which are incorporated into the propagated precision.

During the winter intensive sampling period collocated modules with Teflon filters were operated at Joshua Tree. During the summer intensive sampling period collocated modules with Teflon filters and carbonate impregnated afterfilters were operated at Cajon Summit and Spirit Mountain. Here, again, collocated precision for the soil elements, especially Fe, exceeded the propagated precisions, as did precisions for SO_2 determined on the impregnated filters, presumably due to the variability of loss of SO_2 in the sampler inlet.

Table 4-1 Mean relative precisions for variables measured by PIXE, PESA, XRF, and LIPM on the Teflon A filter.

Variable	**Winter**	**Summer**	**Variable**	**Winter**	**Summer**
H	7%	12%	Fe	5%	5%
Na	35%	46%	Ni	65%	38%
Si	6%	6%	Cu	8%	8%
S	5%	5%	Zn	7%	7%
Cl	79%	21%	As	44%	50%
K	7%	7%	Se	11%	11%
Ca	6%	6%	Br	7%	7%
Ti	12%	17%	Sr	17%	12%
V	71%	79%	Zr	54%	54%
Cr	64%	79%	Pb	11%	12%
Mn	24%	60%	b_{abs}	13%	15%

4.2.1.3 Lower Quantifiable Limit

For particulate matter measurements, the LQL is defined as the concentration equal to twice the precision. It is considered to be the lowest concentration that can be measured reliably. For low concentrations (at or near the LQL), the precision is dominated by the counting uncertainty for elemental analyses and by the blank variability for all other analyses. The other components of precision, flow rate and analytical calibration uncertainty, contribute little at low concentrations.

Table 4-2 Mean relative precisions for mass, carbon, ion, and SO_2

Variable	substrate	winter 24-hour	summer 24-hour	winter 12-hour	summer 12-hour
Mass	Teflon	6%	4%	17%	7%
OCLT	quartz	>100%	46%	>100%	>100%
OCHT	quartz	23%	12%	39%	43%
OC tot	quartz	24%	12%	39%	44%
ECLT	quartz	55%	13%	>100%	59%
ECHT	quartz	36%	25%	58%	49%
LAC (EC tot)	quartz	31%	13%	65%	38%
SO_4^{2-}	nylon	5%	5%	5%	7%
NO_3^-	nylon	5%	5%	11%	8%
Cl^-	nylon	57%	89%	>100%	>100%
SO_4^{2-}	Teflon	NA	NA	5%	5%
NO_3^-	Teflon	NA	NA	93%	9%
NH_4^+	Teflon	NA	NA	9%	8%
NH_3	citric acid	NA	NA	13%	35%
SO_2	carbonate	10%	7%	24%	7%

The chemical components whose concentrations fell above the LQL for more than 90% of the samples were, for the most part, those whose mean relative precisions fell below 10% (see Table 4-1 and Table 4-2). Thus, for example, elemental sulfur was detected in all samples, whereas organic and elemental carbon were detected in only about half of the samples.

4.2.1.4 Accuracy

Two components of the measurement are critical in assessing the accuracy of aerosol concentrations determined on filters: the accuracy of the flow measurement in the field and the accuracy of the analytical measurement in the laboratory.

Flow measurement accuracy is determined through flow checks using a metering device independent of that used for routine flow measurements. In Project MOHAVE, these checks were conducted during independent performance audits, which were conducted during each of the two intensives. Flow audits were performed on 28 IMPROVE modules at seven sites during the winter intensive, and on 37 modules at ten sites during the summer.

IMPROVE sampler flow rates were measured accurately during both intensives. During the winter, all but two of the 28 sampler flow rates agreed with the audit flow rate within 5%, and all but one agreed within 10%, the exception being the 24-hour A module at Indian Gardens, which read high by 11.6%. During the summer, all but five of the 37 sampler flow rates agreed with the audit flow rate within 5%, and all but two agreed within 10%, the exceptions being the two D modules at Joshua Tree, one of which read high by 18.8% and the other low by 20.6%.

Analytical accuracy is determined through regular (typically daily) instrument checks using independent standards. Standards are analyzed after each batch of filters, and the filters in that batch are reanalyzed if the response to the standards deviates from the accuracy goal, which is typically ±10%. Thus, analytical accuracy was maintained within ±10% for all analytical values.

4.2.1.4.1 Sampling Bias

Beyond these readily quantifiable components of accuracy, some measurements are subject to biases due to the design of the sampling device or assumptions applied to the data. Several of these biases, and their implications to measurement accuracy, are described here.

Sulfur Dioxide: The IMPROVE sampler was designed originally to collect particulate matter only, so the materials in the flow system were not selected to minimize losses of gases. Before reaching the impregnated filter, the sample stream passes through an aluminum inlet, a metal cyclone, and the particulate-matter filter.

Tests by UCD have shown that the metallic surfaces of the inlet and cyclone adsorb some of the SO_2 in the sample. UCD concluded that approximately 20 percent of the SO_2 is lost in the fine inlet and 40 percent in the PM_{10} inlet, but losses but can be substantially greater or smaller for any individual sample. Ambient relative humidity has also been shown to influence the deposition of SO_2 in the sampler inlet. The actual loss for any given sample could often range from 0 to 50 percent, with an even wider margin for some samples. As a further complication in the Project MOHAVE network, SO_2 was determined using a PM_{10} head at the full IMPROVE sites (such as Meadview) but using a $PM_{2.5}$ head at the outlying sites.

Although these tests have provided evidence for the loss of SO_2 in the IMPROVE sampler inlet, these losses have not yet been precisely quantified, and the physical conditions which lead to losses have not been fully characterized. Thus, the magnitude of the loss cannot be predicted or quantified for a specified sampling period, and individual concentration values cannot be reliably adjusted to account for inlet losses. Because the SO_2 inlet losses cannot be predicted reliably for a given sample, the IMPROVE SO_2 data have been used as they exist for data analysis, acknowledging that SO_2 concentrations may have been underestimated.

The implications of this SO_2 bias on the study conclusions are varied. Table 8-2 indicates which techniques used ambient SO_2 concentrations as part of the analysis. Only methods that rely on the IMPROVE SO_2 data would be affected (i.e. Exploratory Data Analysis (Mirabella and Farber, 1998), Tracer Mass Balance Regression (Ames and Malm, 1998), and Differential Mass Balance Regression (Ames and Malm, 1998)). Note, the Modified CMB analysis used SO_2 data collected by researchers from BYU and not the IMPROVE SO_2.

Sulfate: The other potentially significant bias in the measurement of sulfur compounds involves adsorption of gaseous SO_2 by particles already collected on the filter, which would result in a loss of SO_2 and a concomitant gain in particulate sulfate on the filter. Such a conversion mechanism has been presented as a hypothesis by BYU to explain their observations that particulate sulfate concentrations determined following an annular denuder (to remove SO_2) are smaller than sulfate concentrations measured with no denuder for about 25% of samples collected in the desert Southwest. The observed artifact can approach 0.4 $\mu g/m^3$ for the collection of particles <3.5 µm. However, for collection of <2.5 µm particles, the observed difference is smaller, typically less than 0.1 $\mu g\ /m^3$, and, for all samples, averaging close to 0.02 $\mu g\ /m^3$ (Eatough et al., 1997b, 1995, Lewis et al., 1991).

Measurements using the IMPROVE sampler, however, provide no evidence for this sampling bias. As part of the routine IMPROVE network, UC Davis has collected thousands of parallel $PM_{2.5}$ samples on completely independent Teflon and nylon filters. Particles are collected on a Teflon filter with no denuder and on a parallel nylon filter following a carbonate denuder which is believed to remove SO_2, but whose efficiency has not been established. The Teflon filters are analyzed for sulfur using PIXE and the nylon filters are analyzed for sulfate by ion chromatography. Their data show good agreement between 3xS on Teflon (PIXE) and sulfate on Nylon (IC), suggesting that removing SO_2 prior to the filter does not alter the measured particulate sulfur concentration.

In the Project MOHAVE data analyses, the measured IMPROVE sulfate concentrations have not been modified to account for the sampling artifact that BYU has proposed, although a possible sulfate oversampling of 0.1 to 0.4 $\mu g/m^3$ was considered by analysts when interpreting the data. Interpretation of the data with and without accounting for this effect would represent the upper and lower bounds of sulfate measurement uncertainty. Although BYU's findings are intriguing and suggest that further research is warranted to better understand the sampling differences, their data are not sufficient to quantify the artifact nor to demonstrate conclusively that it exists. BYU's findings suggest that there is an artifact, but we do not yet understand why it occurs and we cannot predict it or quantify it reliably.

Volatile Organic Carbon: Filter collection of particulate organic carbon is complicated by adsorption and volatilization of organic material. Compounds which exist as gases in the atmosphere can be adsorbed on the quartz filter, resulting in oversampling of organic carbon. Conversely, semi-volatile particulate material on the filter can be lost due to volatilization during sampling, resulting in undersampling.

Organic carbon in Project MOHAVE was determined using quartz filters in the IMPROVE sampler, followed by analysis using the Thermal Optical Reflectance (TOR) method. Quartz filters were collected in tandem in a filter pack, with the afterfilter designed to capture volatile organic material. In calculating ambient concentrations, it was assumed that volatilization of the particulate matter on the front filter was minimal, so that the material on the afterfilter was due only to the collection of atmospheric organic gases. Thus, the afterfilter values were subtracted from the front filter values to determine ambient concentrations.

During the summer, a single average afterfilter value was used to represent the entire network. During the winter, separate afterfilter values were used to represent the average for each of the three field laboratories where filters were loaded and distributed.

Approximately 20 percent of the Project MOHAVE afterfilters were analyzed, and the average values were subtracted from the front filter values to determine ambient concentrations. For the summer period, the average afterfilter loading of 13 μg/filter represented approximately 0.8 $\mu g/m^3$ for 12-hour samples and 0.4 $\mu g/m^3$ for 24-hour samples. Similar values were observed at most sites during the winter, with a separate value used for each of the monitoring sites.

By comparison, reported ambient organic carbon concentrations typically ranged from about 0.5 to 4 $\mu g/m^3$. Thus, the afterfilter correction ranged from around 100 percent at small concentrations to around 10 percent or less at higher concentrations

Other studies in the desert Southwest, principally by BYU, have provided evidence that the collection of gas-phase organic compounds by a quartz filter may produce a small positive artifact, but that a much larger negative error results from the loss of 20-80 percent of the particulate-phase organic material during sampling (Eatough *et al.*, 1993; Cui *et al.*, 1997). Tests conducted using a sampling system employing diffusion denuders, quartz filters, and sorbent filters have indicated that concentrations of particulate-phase organic compounds in the southwestern U.S. have been underestimated by collection of particles with only quartz filters.

The magnitude and chemical nature of particulate volatilization have not been fully characterized, nor has its variability. But, there is good evidence that volatilization exists, and that particulate carbon may be underestimated by up to about a factor of two if it is not considered. Consequently, it is likely that the IMPROVE sampler values represent a lower bound on particulate carbon concentration. If the organic carbon values are biased low, some likely ramifications include:

- For mass balance calculations, carbon is probably underrepresented. However, the same volatilization losses would occur in the measurement of gravimetric mass on Teflon filters, so the mass balance may appear complete.

- For Mie calculations, the extinction contribution of organic carbon is probably underestimated, unless typical volatilization losses are accounted for.

- For light extinction budgets (LEB) based on Multiple Linear Regression (MLR), the regression slope for carbon (i.e., the apparent extinction efficiency) will probably be underestimated and the intercept will be over estimated. These biases occur because the loss of semi-volitile particulate organic material is variable, with the uncertainty in the values driven by variations in temperature and particle concentration.

Elemental Carbon and Light Absorption: Uncertainty in the IMPROVE sampler carbon measurements can arise from the apportionment of organic carbon (OC) versus elemental carbon (EC) by the Thermal Optical Reflectance (TOR) analysis method. Huffman (1996) conducted a statistical comparison of the organic and elemental carbon data with light absorption data from the Teflon filters in the IMPROVE network, assuming a light absorption efficiency of 10 m^2/g for EC. He suggested that the TOR assignment overestimates organic and underestimates elemental carbon. Huffman's statistical model indicated that a portion of the TOR organic carbon should be in the elemental category, typically decreasing the reported total organic carbon by around 20% and doubling the total elemental carbon.

Horvath (1996) offers an alternate explanation for the discrepancy between measured elemental carbon and light absorbtion. Using laboratory generated aerosol, he found that non absorbing aerosols could interfere with and positively bias the LIPM measurement.

Differing interpretations of the light absorption measurement (b_{abs}) can also lead to a discrepancy of a factor of two in the reported b_{abs} values, as described in Section 4.1.3. To date, neither the OC/EC discrepancy nor the b_{abs} correction discrepancy has been resolved. Hence, there is no clear consensus to guide the Project MOHAVE data analysis. The bounds of disagreement in the measurement of EC and b_{abs} can be summarized as follows:

- EC (or, more accurately, light absorbing carbon, LAC) can differ by about a factor of two, depending on the interpretation of the TOR thermograms. EC as reported by DRI includes only the EC peaks. Huffman and others have suggested that a portion of the OC is light absorbing (perhaps even chemically elemental), so that the LAC should be larger than that reported by DRI, by about a factor of two.

- The integrating plate method as applied by UCD (with the shading adjustment) yields higher b_{abs} values than does densitometry as applied by DRI. The difference depends on the filter loading correction, but on average is about a factor of two. In comparison tests UCD and DRI uncorrected b_{abs} values agree very well, so any differences lie in the interpretation (i.e., adjustment) of the data.

In practice, two combinations of these interpretations of EC and b_{abs} are used:

- IMPROVE and Project MOHAVE have used UCD's b_{abs} (with the shadowing correction) and TOR EC. This combination results in an absorption efficiency of 20 m^2/g. However, there is some support among the IMPROVE community for interpreting LAC as EC plus a portion of the (presumably) light absorbing OC, which would yield an effective efficiency of 10 m^2/g.

The Grand Canyon Visibility Transport Commission (GCVTC) elected to use b_{abs} with no shadowing or matrix correction, along with TOR EC. This combination has also been used by DRI and others in many other studies such as the Phoenix, Tucson, and Dallas urban haze studies. This approach is consistent with an absorption efficiency of 10 m^2/g, which agrees with theoretical estimates based on Mie theory.

The questions surrounding the interpretation of EC and b_{abs} measurements have yet to be resolved. Therefore, the bounds on the Project MOHAVE conclusions are defined by the combinations of interpretations that could be used. The base case for Project MOHAVE, as described above, uses UCD's b_{abs} and TOR EC. The uncertainty bounds can be summarized as follows:

- Modifying the base case by assigning a portion of the OC to the EC fraction would typically decrease OC by about 20% and double the EC concentration. b_{abs} would be unchanged.

- Using the GCVTC approach would decrease b_{abs} by about a factor of two. OC and EC would be unchanged.

One combination that has not been used in practice is DRI b_{abs} (uncorrected) combined with LAC increased by adding a portion of the OC. This combination would result in an absorption efficiency of 5 m^2/g, which is too low to meet theoretical expectations. Thus, it need not be considered in assessing the bounds of the Project MOHAVE conclusions.

One complicating factor related to this topic is that some soil oxides also absorb light. The contribution of such crustal fine material should be considered when comparing b_{abs} with EC.

4.2.1.4.2 Method Intercomparisons

Several method intercomparisons were conducted during data validation. These intercomparisons employed two different measurements which should be expected to yield the same quantity, which can provide an indication of sampling bias. Intercomparisons were conducted during Project MOHAVE for sulfate versus three times elemental sulfur, for organic carbon versus carbon estimated from concentrations of H and S (OMH), for gravimetric versus calculated mass (CALMAH), and for PIXE versus XRF. These intercomparisons and their findings are summarized below.

Sulfate: The sulfate collected on the nylon filter and analyzed by ion chromatography should be 3.0 times the sulfur collected on the Teflon filter and analyzed by PIXE, based on the stoichiometric ratio. This assumes that all particulate sulfur is in the form of sulfate. Figure 4-1 compares these two values for data from the sites with multiple IMPROVE modules in winter and summer. Because the B module includes a carbonate denuder, which is intended to remove SO_2, the close agreement suggests that any effects such as interaction of SO_2 with soil particles already on the filter are negligible.

Organic Mass: The total organic carbon (OMC) collected on the quartz filter is the sum of the two measured organic carbon concentrations (OCLT and OCHT). They are included in the sum as determined, even if negative. The total organic concentration is obtained by multiplying the sum by 1.4 to include the noncarbon components of the organic particle.

The organic mass can also be calculated from the concentrations of H and S measured on the Teflon filter (Cahill et al., 1989). The total hydrogen on a sample comes from organics, sulfate, nitrate and water. Assuming that all the sulfur is present as fully neutralized ammonium sulfate, that the Teflon filter has negligible hydrogen from nitrate compared to that from sulfate, and that any water volatilizes from the filter during the exposure to vacuum, then the difference between the measured hydrogen and the hydrogen in sulfate is organic hydrogen. The mass of organic material, OMH, can be estimated by multiplying the organic hydrogen by 11 which is consistent with a hydrogen/carbon molar ratio of 1.53.

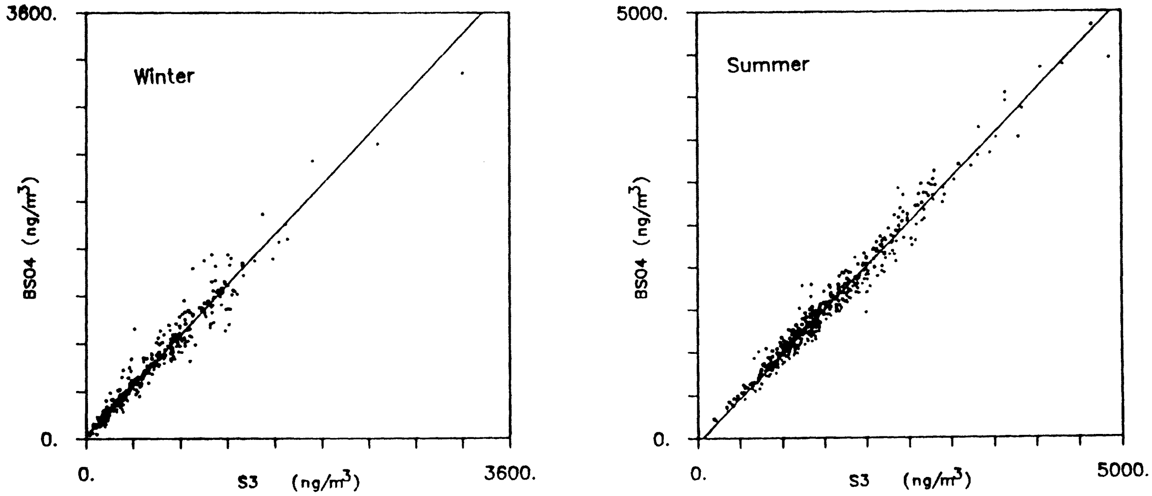

Figure 4-1 Comparison of sulfur collected on Teflon A and measured by PIXE with sulfate collected on nylon B and measured by ion chromatography for 12-hour and 24-hour samples at the IMPROVE sites during both intensives. The sulfur is multiplied by 3.0 to account for the oxide. The left plot is for winter and the right plot is for summer. The slopes are 1.06 (winter) and 1.04 (summer). The correlation coefficients (r^2) are 0.95 (winter) and 0.97 (summer). The number of data pairs are 342 (winter) and 289 (summer).

Figure 4-2 illustrates comparisons of OMC and OMH at the IMPROVE sites within the Project MOHAVE network. The spread of the points and the deviations of the slopes from unity reflect the imprecision and sampling biases inherent in both methods.

In general, the precision for organic mass by either method is not as good as for the other major species, such as sulfate, soil, and nitrate. The precision for OMC is associated primarily with the variation of the afterfilters. The mean relative precision for OMC was 23% for the 24-hour winter samples, 12% for 24-hour summer samples, 39% for 12-hour winter samples and 44% for 12-hour summer samples.

The form of the precision for OMH is somewhat more complicated. Both S and H separately have good precision (5% for S, 7% for H in winter and 12% for H in summer), but when the difference of H-S/4 is small relative to S, then the precision can become large. The key variable to the precision is the ratio of sulfur to organic material. Whenever the ammonium sulfate is greater than 4.5 times OMH, then the precision will exceed 50%. During winter, the mean ammonium sulfate was only slightly larger than OMH (840 vs. 600 ng/m^3), and the mean precision for OMH was 13% for both 12-hour and 24-hour data. Less than 1% of the samples had a relative precision exceeding 50%. During summer, however, the mean ammonium sulfate was 3 times the organic mass. As a result the overall precision for summer rose to 38%, which is higher than the OMC precision at 24-hour IMPROVE sites. Figure 4-3 gives the ratio of the mean ammonium sulfate to the mean OMH at each site. Note that at any given site, the ratio of sulfate to organic will vary widely from sample to sample, so that the mean ratio does not indicate the precision for each sample.

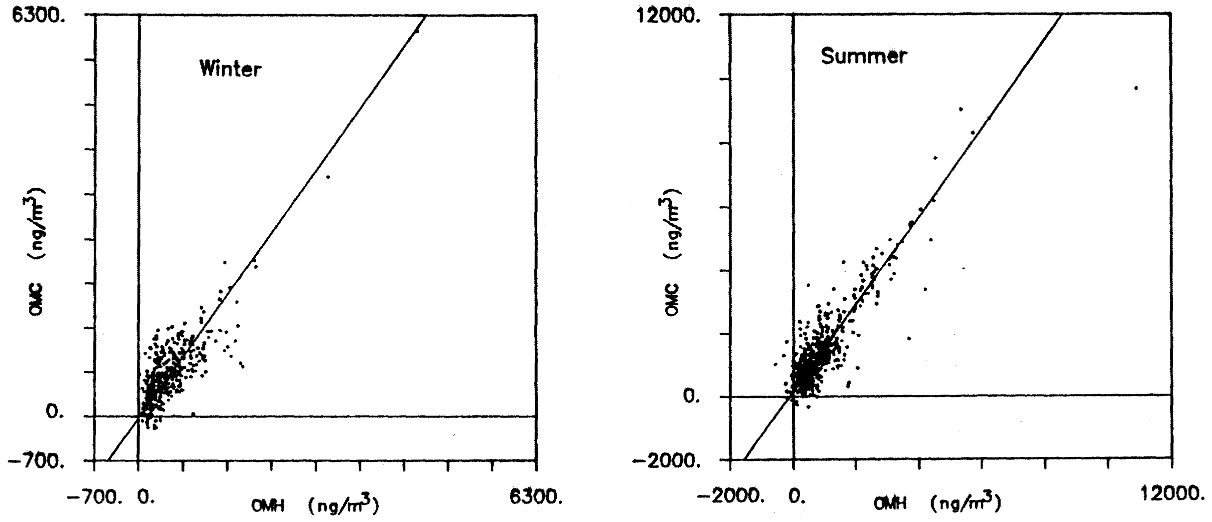

Figure 4-2 Comparison of two organic measurements, OMC and OMH, collected at the nine IMPROVE sites. The left plot is for winter and the right plot is for summer. The slopes are 1.39 (winter) and 1.38 (summer). The correlation coefficients (r^2) are 0.64 (winter) and 0.78 (summer). The r^2 during winter is improved to 0.80 by excluding the 12 hour data. The number of data pairs are 351 (winter) and 286 (summer).

Two possible corrections to the assumptions underlying OMH are (1) for ammonium nitrate on the Teflon filter, and (2) for partially acidic sulfate. If a nitrate correction were applied, it would decrease OMH. The nitrate concentration on the Teflon filter is known only at one site, Meadview, where the simultaneous measurement of NO_3 on nylon and Teflon provides a rough estimate of the nitrate levels on the Teflon filter. The ratio of Teflon mean / nylon mean was 0.25 in winter and 0.50 in summer. Thus, 75% of the nitrates in winter were volatilized during sampling. Because OMH and NO_3 are uncorrelated the effect is to decrease OMH by a constant value of 20 to 70 ng/m^3, based on the ratios of 0.25 and 0.50.

If some of the sulfate were present as sulfuric acid, OMH would be underestimated, with the amount depending on the concentration of sulfuric acid. For example, if 5% of the sulfur were present as sulfuric acid, then OMH would be underestimated by 10 to 30 ng/m^3 in winter and 40 to 80 ng/m^3 in summer at most sites.

Gravimetric and Calculated Mass: Two forms of the calculated mass can be determined from the measured data. The first is based only on the variables measured on the Teflon filter, and will be labeled CALMAH. This form can be used for samples from the background sites as well as from the IMPROVE sites. The second form uses the carbon concentrations from the quartz C filter, and will be labeled CALMAC. This can be used only for data from the nine IMPROVE sites.

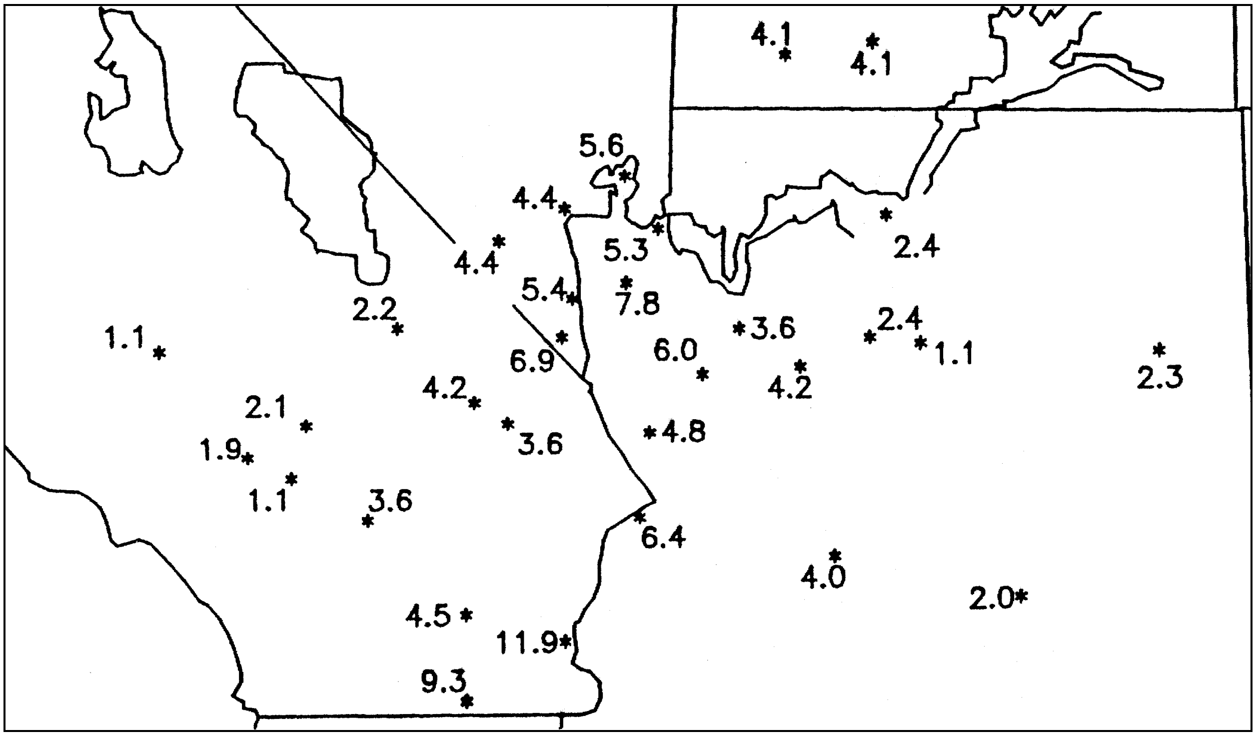

Figure 4-3 Map of ratio of mean ammonium sulfate to mean organic by hydrogen for the summer intensive based on data from the IMPROVE samplers. The ratio for a given sample will vary widely from the overall site ratio.

The calculated mass from the Teflon filter (CALMAH), is the sum of ammonium sulfate, soil, nonsulfate potassium, salt, elemental carbon, and organic carbon. The ammonium sulfate is calculated from the sulfur measured by PIXE. The soil component consists of the sum of the predominantly soil elements measured by PIXE, plus oxygen for the normal oxides, plus a factor of 1.16 for unmeasured compounds. Potassium is treated separately because fine potassium can be derived from both soil and smoke. Salt is calculated from the sodium concentration, as 2.5*Na. Elemental carbon (soot) is estimated from b_{abs}, and organic carbonis represented by OMH. The only components not included in calculated mass are water and nitrate.

Comparison of CALMAH and gravimetric mass at all sites for both intensives are shown in Figure 4-4. Part of the difference between gravimetric and calculated mass is the ammonium nitrate on the Teflon filter, estimated to constitute between 1% and 3% of the calculated mass at most sites. At San Gorgonio, the site with the most nitrate, the ratio rises to 6%. The conclusion is that nitrate generally does not constitute the major part of the missing mass. Since the samples were weighed at a relative humidity of 41 ± 6%, considerable water should be present.

The second form of calculated mass, CALMAC, uses the carbon components from the quartz filter and the other components from the Teflon filter. As in CALMAH, the sum does not include water and nitrates. Comparisons of CALMAC and gravimetric mass for the IMPROVE sites are shown in Figure 4-5. As with CALMAH, approximately 25% of the measured mass was not reconciled.

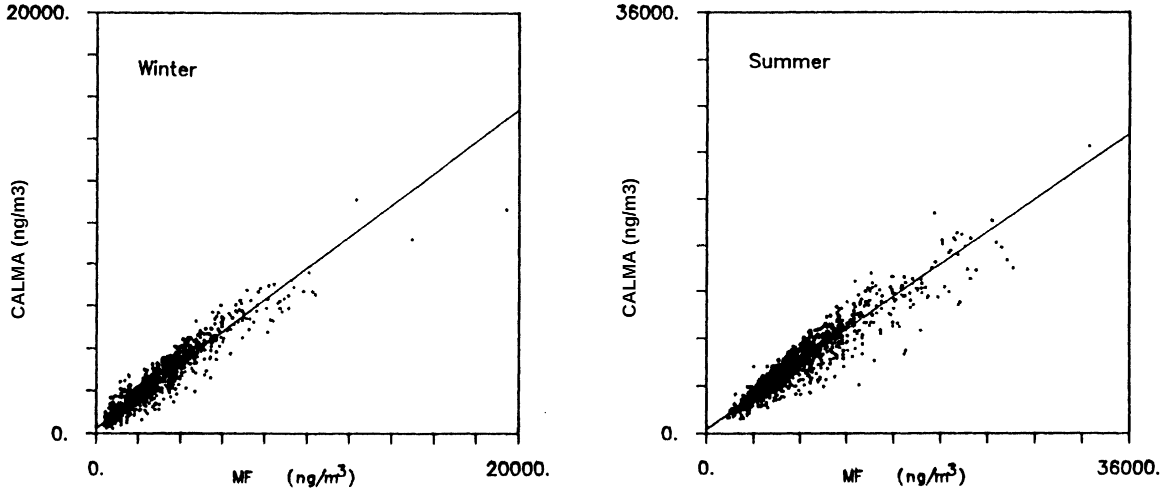

Figure 4-4 Comparison of gravimetric mass (MF) and calculated mass (CALMAH) at all Project MOHAVE IMPROVE sites. The left plot is for winter and the right plot is for summer. The slopes are 0.76 (winter) and 0.70 (summer). The correlation coefficients (r^2) are 0.89 (winter) and 0.89 (summer). The number of data pairs are 1102 (winter) and 1533 (summer).

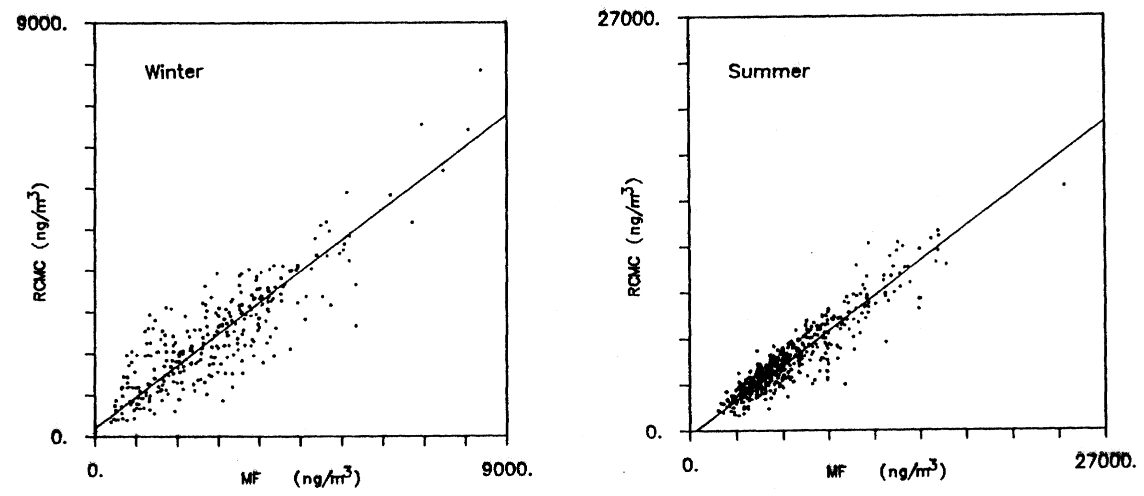

Figure 4-5 Comparison of gravimetric mass (MF) and calculated mass (CALMAC) at all Project MOHAVE IMPROVE sites. The left plot is for winter and the right plot is for summer. The slopes are 0.76 for both intensives. The correlation coefficient (r^2) are 0.75 (winter) and 0.85 (summer). The number of data pairs are 341 (winter) and 285 (summer).

PIXE and XRF: All of the Teflon A filters were analyzed by both XRF and PIXE. The measured concentrations for overlapping elements were compared by scatter plots. Figure 4-6 shows the comparison for the summer intensive for iron and zinc, the two elements with the best overlap. The iron comparison gave a slope of 0.99 ± 0.01 and a regression coefficient (r^2) of

0.99. For the winter intensive the slope was 1.01 ± 0.01 and the regression coefficient was again 0.99.

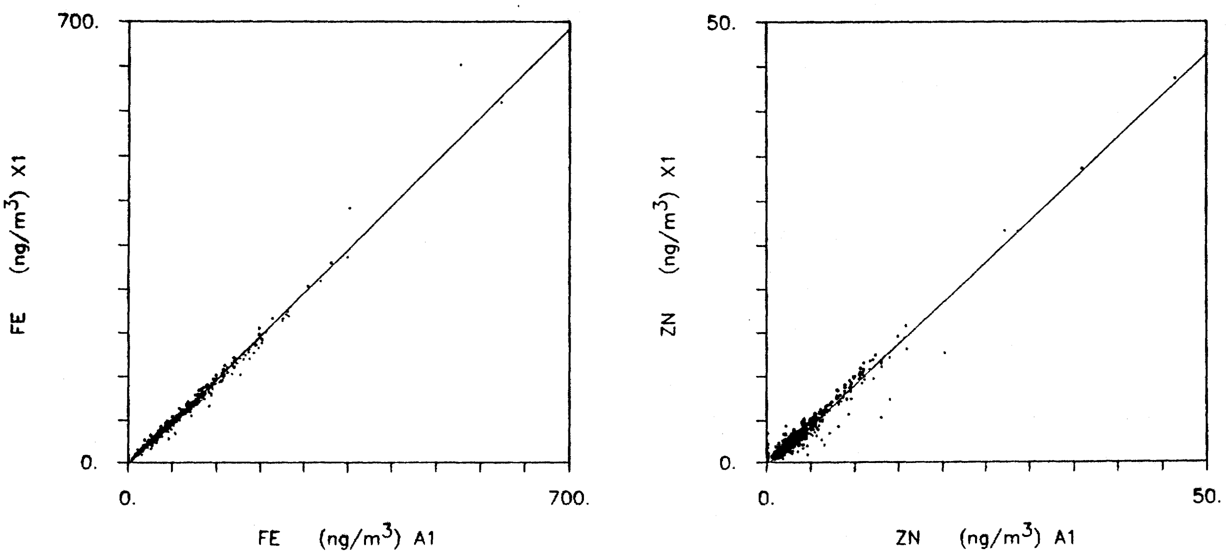

Figure 4-6 Comparison of XRF and PIXE for all Project MOHAVE IMPROVE summer samples for iron and zinc. The PIXE values are on the x-axis and the XRF values are on the y-axis. The slopes are 0.99 (Fe) and 0.93 (Zn). The correlation coefficients (r^2) are 0.99 (Fe) and 0.95 (Zn). The number of data pairs are 1556 for both Fe and Zn.

4.2.2 BYU Aerosol Sampling

The BYU aerosol sampling program during Project MOHAVE used two methods for the collection and determination of SO_2(g), HF(g), spherical aluminosilicate (SAS) particles, and particulate sulfate, nitrate and fluoride during both the winter and summer studies; high-volume cascade impactor and annular diffusion denuder sampling systems. In addition, particulate organic material was determined during the summer at Meadview only using a diffusion denuder sampler. The quality of the BYU aerosol data is summarized below.

4.2.2.1 Completeness

Annular denuder and high volume cascade impactor samples were collected on a twelve-hour basis at Indian Garden, Hopi Point and Meadview from 14 January through 12 February during the Winter Intensive. However, only the 27 January through 9 February time period was selected for the analysis of all components for Chemical Mass Balance (CMB) analysis. Annular denuder and high volume cascade impactor samples were collected on a twelve-hour basis at Hopi Point and Meadview from 12 July through 30 August during the summer intensive sampling period. All available samples were selected for the analysis of all components for CMB analysis. BOSS samples were only collected at Meadview from 15 July through 28 August during the summer intensive sampling period to provide data for attribution of visibility. Table 4-3 lists the completeness of sample collection for the periods during which full analysis was performed.

4.2.2.2 Precision and Lower Quantifiable Limit

The precision of BYU's aerosol measurements was estimated from collocated replicate samples at selected sites during Project MOHAVE and from similar tests using the same instruments during other studies (Eatough, et al., 1997; Cui, et al., 1997). The precision was defined as the standard deviation of the replicate differences:

$$\sigma = \sqrt{\frac{1}{2N}\sum_{i=1}^{N}(C_{1,i} - C_{2,i})^2 - (\overline{C}_1 - \overline{C}_2)^2} \qquad (4\text{-}7)$$

where N is the total number of replicate pairs, $C_{1,\mathrm{i}}$ and $C_{2.\mathrm{i}}$ are the concentrations of the chemical species of interest in the two replicate data sets, and $\overline{C_1}$ and $\overline{C_2}$ are the average of each collocated set. The $(\overline{C_1} - \overline{C_2})^2$ term corrects the standard deviation for bias between the two replicate data sets. The collocated standard deviation, σ, is also considered to be the lower quantifiable limit (LQL), or the smallest concentration that can be distinguished in an ambient sample.

Table 4-3 BYU Completeness of sample collection and analysis during project MOHAVE winter and summer intensive studies.

	Winter		Summer		
Sampling Site	Denuder	High Vol	Denuder	High Vol	BOSS
Meadview	100	96	75	83	84
Hopi Point	100	89	94	95	-
Indian Garden	100	82	-	-	-

The percent precision for the replicate sets is calculated as:

$$\sigma_{\%} = \frac{\sigma}{\frac{1}{2}(\overline{C}_1 + \overline{C}_2)} \times 100 \qquad (4\text{-}8)$$

The results from this statistical analysis of the various collocated data sets are given in Table 4-4. The table provides the number of replicates analyzed, the number rejected, the precision (σ), and the percent precision ($\sigma_{\%}$). For each measured species, statistics are provided for the comparisons performed during Project MOHAVE and for all comparisons performed during all BYU studies, including Project MOHAVE. Collocated low-volume filter packs were not sampled during Project MOHAVE, so the value from other BYU tests is shown. The results listed for particulate organic carbon were obtained exclusively during Project MOHAVE. Detailed statistics for all of the comparisons are provided by Eatough, et al. (1997) for the inorganic species and by Cui, et al. (1997) for organic carbon.

In these calculations, BYU rejected all sample sets on the basis of Taylor's test, which essentially eliminates collocated pairs with a difference greater than three times the standard deviation of the entire data set. Doing so caused them typically to reject about 5 to 10% of the points, which is much higher than one would expect for a Gaussian distribution, for which about 0.3% of points would be expected to lie beyond 3σ. This high rejection rate indicates that the samples fell into two populations: those for which data quality was controlled and quantified (i.e., those falling within 3σ), and those compromised by measurement errors which could not be explained based on physical evidence (i.e., quality control test data). Thus, the reported precision (σ) represents the variability in the majority of samples that were under control. Because samples were rejected based on statistics and not based on known sampling problems (torn filters, samples dropped in the dirt, etc.), the proportion of rejected sample sets (5 to 10%) represents the probability that any given sample in the data base is highly inaccurate for unknown reasons.

Table 4-4 Summary of BYU Aerosol Measurement Precision

Network/Analyte	No. of Replicate Samples	No. of Replicates Rejected	Sigma (LQL), µg/m^3	% Precision
ANNULAR DIFFUSION DENUDERS				
Particulate Sulfate				
Project MOHAVE, Hopi Point	56	0	0.28	37.0
Project MOHAVE, Meadview	32	2	0.24	12.4
All BYU Samples	114	2	0.24	40.5
SO_2 (g)				
Project MOHAVE, Hopi Point	52	1	0.12	26.7
Project MOHAVE, Meadview	31	4	0.22	19.4
All BYU Samples	109	12	0.12	17.9
F_{Total}				
Project MOHAVE, Hopi Point	39	3	0.006	54.0
All BYU Samples	48	3	0.006	50.4
LOW-VOLUME FILTER PACKS				
Particulate Sulfate				
All BYU Samples	43	2	0.12	25.2
HIVOL SAMPLERS				
SAS Particles				
Project MOHAVE, Hopi Point	11	0	105 (sphere/m^3)	11.2
All BYU Samples	27	2	170 (sphere/m^3)	17.7
Particulate Sulfate				
Project MOHAVE, Hopi Point	9	0	0.19	16.6
All BYU Samples	29	2	0.20	21.9
SO_2 (g)				
Project MOHAVE, Hopi Point	11	1	0.031	32.3
All BYU Samples	31	8	0.019	32.1
F_{Total}				
Project MOHAVE, Hopi Point	15	1	0.005	78.4
All BYU Samples	19	2	0.003	30.1
BYU ORGANIC SAMPLING SYSTEM (BOSS)				
Particulate Organic Carbon				
BOSS #1: Qtz. filter (denuder)	18	0	0.20 µgC/m^3	14.4
BOSS #2: Qtz. filter (filter/denuder)	19	0	0.21 µgC/m^3	18.9
BOSS Charcoal Impregnated Filter	7	0	0.27 µgC/m^3	37.5

The percent precision of the annular denuder particulate sulfate measurements was poor overall (40.5%), largely because the average sulfate concentration in most of the studies was only about three times the σ value for sulfate. The exception among the collocated sites was Meadview, for which ambient sulfate concentrations were generally higher and the percent precision was lower.

The low volume filter pack sulfate precision was around 25% in all tests performed. The precision of determination of particulate sulfate collected by the high-volume cascade impactor was better than the corresponding precision for the annular denuder. Conversely, the annular denuder provided better precision for SO_2 than did the hivol sampler.

The precision for SAS particles was better in Project MOHAVE than it was overall, but in all cases it was better than 20%. The precision in the annular denuder total fluoride (F_{total}) measurement was poorer for Project MOHAVE than it was overall because concentrations were lower during Project MOHAVE. The precision of the Project MOHAVE hivol F_{Total} measurement was poor due to poor agreement in the replicate HF(g) results. Because the HF(g) data were not reliable, the hivol F_{Total} data were not used in subsequent interpretation of the Project MOHAVE data.

Collocated comparisons were conducted for the BYU organic sampling system (BOSS). The sampling configuration included a charcoal denuder followed by a quartz filter and a charcoal absorbent filter. In addition, collocated data were obtained where a filter pack preceded the denuder to determine the efficiency of the denuder for the removal of gas phase organic material for each sample. The average percent precision (for both configurations) for sampling on the quartz filters was around ±17%. The percent precision on the charcoal impregnated filter was greater, largely due to lower concentrations.

4.2.2.3 Accuracy

As with the IMPROVE sampler data discussed previously, two components of the measurement are critical in assessing the accuracy of aerosol concentrations determined on filters: the accuracy of the flow measurement in the field and the accuracy of the analytical measurement in the laboratory.

Flow measurement accuracy is determined through flow checks using a metering device independent of that used for routine flow measurements. In Project MOHAVE, these checks were conducted during independent performance audits, which were conducted during each of the two intensives. The annular denuder and filter pack samplers were audited during both intensives, the hivol samplers only during the summer intensive.

Flow rates in both the annular denuder and filter pack samplers were found to be significantly compromised during the first part of the winter intensive. For about half of the samplers, the flow readings exceeded the audit values by a factor of two or more. After the audits, BYU discovered that dirt had gotten into many of the mass flow controllers and caused them to malfunction, leading to the erroneously high readings. This problem was corrected in the field by cleaning the flow controllers and adding protective filters. Subsequent audits during the summer intensive found six samplers agreeing with audit values within 10%, another three within 20%. Deviation exceeded 20% for only one filter pack, but water was in that filter pack at the time of the audit.

The high-volume cascade impactors were audited during the summer intensive only. Flows from eight of the nine samplers agreed with the audit values to within 10%, and the ninth fell within 20%.

Annular denuder flow data from the first half of the winter intensive were adjusted by comparing total SO_x (the sum of particulate sulfate and SO_2) measured with the annular denuder to that measured with the high volume sampler, which had demonstrated more reliable flow measurements. SO_x values from the two systems were expected to agree within about ±0.25 $\mu g/m^3$ based on prior studies, so substantial differences could be attributed to flow inaccuracy. The denuder data were adjusted based on the SO_x ratio and the hivol flows, and these adjusted values were reported to the data base.

The BOSS system for organic sampling was not audited during Project MOHAVE. However, a flow audit of the same sampling system was conducted in Azusa, California, in June 1992, just prior to the summer intensive. This audit showed the BOSS flow rates to be within 5% of the audit flow rates.

Analytical accuracy is typically determined through regular instrument checks using independent standards. However, a system audit of the BYU laboratory conducted in April 1992 (between the winter and summer intensives) revealed that rigorous, multi-point calibrations were not being performed, although they were instituted following the audit. To follow up, performance audit samples for sulfate and nitrate were submitted to the BYU laboratory in June 1992. Both aqueous solutions and spiked filters were used in the audit.

BYU's reported values were within 20% of the audit values for all of the aqueous solutions and for spiked $NaHCO_3$-impregnated filters (for sulfate) and spiked nylon filters (for nitrate). The differences for sulfate on two of three spiked quartz filters exceeded 25% of the audit values, with BYU's reported levels below the spiked amounts. Since sulfate results were substantially closer for the other samples, these errors were likely caused by incomplete extraction or by improperly prepared standard filters. Subsequent chamber experiments on the collection of SO_2 by several techniques and studies on consecutive extractions indicated that the BYU single extraction protocol did result in complete extraction of collected SO_2 on BYU prepared carbonate saturated filters. Consequently, the BYU protocols were not changed.

4.2.3 Harvard HEADS Sampler

Harvard University conducted aerosol sampling at Meadview, AZ from July 15 through August 30, 1992. The quality of the HEADS aerosol data is summarized below.

4.2.3.1 Completeness

The number of twice-daily samples possible during the 47-day period was 94. A total of 92 samples (98% of the number possible) was collected and analyzed successfully. However, three of these samples had sampling durations shorter than the 4.5-hour acceptance criterion, and one additional sample had a flow rate reading outside of acceptance criteria. Thus, 88 samples (94% of the number possible) met all acceptance criteria.

4.2.3.2 Precision

The precision of Harvard's aerosol measurements was estimated from 10 collocated replicate samples collected at Meadview on August 24 and on August 27 through August 30. The precision was defined as the standard deviation of the replicate differences as was done for the BYU aerosol samples as described in Section 4.2.2.2. However, none of the HEADS collocated pairs was excluded from the calculations. Table 4-5 lists the precisions, average measured concentrations, and precisions expressed as percentages of the average measured concentrations for the Harvard measurements. Note that the listed average concentrations include the reported values for concentrations below the lower quantifiable limit. The precisions of all of the species except nitrous acid and ammonia were less than about 15% of the average measured concentrations.

Table 4-5 Precisions and Average Measured Concentrations from Harvard HEADS Measurements

Species	Precision	Average Concentration	Percent Precision
Total strong acidity	1.2 ng/m^3	6.9 ng/m^3	17%
Particulate sulfate	180 ng/m^3	1,704 ng/m^3	11%
Particulate nitrate	18 ng/m^3	131 ng/m^3	14%
Particulate ammonium	46 ng/m^3	419 ng/m^3	11%
Sulfur dioxide	0.023 ppb	0.41 ppb	6%
Nitrous acid	0.14 ppb	0.026 ppb	538%
Nitric acid	0.049 ppb	0.92 ppb	5%
Ammonia	0.35 ppb	0.75 ppb	47%

4.2.3.3 Lower Quantifiable Limit

Harvard estimated the limits of detection (assumed to be the lower quantifiable limits) from previous studies that utilized the HEADS sampler. Alternatively, the lower quantifiable limit can be defined as a multiple of the precision determined from the collocated sampling. Table 4-6 lists the limits of detection estimated by Harvard along with lower quantifiable limits defined as twice the precisions of the measurements. With the exceptions of nitrous acid and ammonia, the lower quantifiable limits estimated from the precisions from the collocated measurements are substantially smaller than the values that Harvard estimated for the limits of detection. This suggests that the precision of the measurements at Meadview was much better than in the previous studies.

4.2.3.4 Accuracy

As with the other aerosol samplers, two components of the measurement are critical in assessing the accuracy of aerosol concentrations determined on filters and denuders: the accuracy of the flow measurement in the field and the accuracy of the analytical measurement in the laboratory.

A performance audit of the flow rate measurement was conducted at Meadview on July 21, 1992, which was the seventh day of sampling. The audit flow rate was 38.0 liters per minute (LPM), which was approximately twice the intended flow rate of 20 LPM. This difference was caused by incorrect instructions to the personnel who operated the sampler. It was corrected, and flow rates for subsequent samples were set correctly. However, additional flow rate audits were not conducted, so the accuracy of the flow rate measurements was not evaluated independently.

Table 4-6 Estimates of Lower Quantifiable Limits of Harvard HEADS Measurements

Species	Limit of Detection Estimated by Harvard	Lower Quantifiable Limit Defined as Two Times the Precision
Total strong acidity	8.2 ng/m^3	2.4 ng/m^3
Particulate sulfate	1,180 ng/m^3	360 ng/m^3
Particulate nitrate	130 ng/m^3	36 ng/m^3
Particulate ammonium	297 ng/m^3	92 ng/m^3
Sulfur dioxide	0.41 ppb	0.046 ppb
Nitrous acid	0.21 ppb	0.28 ppb
Nitric acid	0.41 ppb	0.098 ppb
Ammonia	0.62 ppb	0.70 ppb

These high flow rates for the first seven sampling days reduced the estimated collection efficiencies of the annular denuders for sulfur dioxide, nitrous acid, nitric acid and ammonia from 97.7%, 98.6% 96.6% and 99.8%, respectively, to 86%, 90%, 83%, and 97%. Additionally, the elevated flow rates reduced the cut-point for the impactor from 2.5 μm to 1.8 μm.

Independent audits of the sample analysis were not conducted, so the accuracy of the Harvard measurements can not be evaluated from independent performance audits. However, Turpin et al. (1997) compared data from the Harvard measurements with results from concurrent IMPROVE sampler measurements at Meadview. Since the accuracy of the IMPROVE sampler measurements has been evaluated (see Section 4.2.1.4), these comparisons provide a limited indirect evaluation of the Harvard measurement accuracy. Turpin et al. (1997) report a value of 0.91 for the average sulfate concentration from the IMPROVE nylon filter divided by the average sulfate concentration from the HEADS sampler. The R^2 value for a regression between the two measurements was 0.88 for the 31 sample pairs that were used. These results suggest that the accuracy of the Harvard particulate sulfate measurements is probably within 10%.

4.3 Aerosol Size Distribution Measurements

Aerosol Dynamics Inc. (ADI) measured ambient particle size distributions, and the University of Minnesota (UM) measured particle chemical composition as a function of size. UM also measured particle growth characteristics as a function of relative humidity.

4.3.1 ADI Size Distribution Measurements

ADI developed the Differential Mobility and Optical Particle Size Spectrometer (DMOPSS) to measure ambient particle size distributions in the range from 0.1 to 1.0 μm diameter. This instrument was first used at Meadview from July 14 through August 30, 1992.

Independent standards do not exist to evaluate the accuracy of the instrument, and appropriate data were not available to estimate precision. However, ADI analyzed the results from the measurements to estimate various characteristics of the aerosol that could be compared with other measurements of the same characteristics. These comparisons, described below, suggest that the results of the measurements are reasonable.

Measured total particle volume was strongly correlated with measurements of the light scattering coefficient made by ADI using a nephelometer equipped with a 2.5 μm cut-point inlet (R^2 = 0.79), with a mean scattering-to-volume ratio of 5 m^2/cm^3. ADI also estimated the average particle density to be 1.69 g/cm^3. Dividing the mean scattering-to-volume ratio by this density gives an estimate of 3 m^2/g for the particle light scattering efficiency, which is consistent with other estimates in this report.

The particle scattering coefficient calculated from the size distributions were also well correlated with the nephelometer measurements (r^2 = 0.79), but the mean calculated scattering coefficient was about 20% lower than the mean measured value. ADI suggested that this discrepancy might be accounted for by scattering by particles between 1 and 2.5 μm diameter, which were not measured by the DMOPSS.

ADI also estimated the volume median particle diameter from the DMOPSS data and compared it with the mass median diameter calculated from measurements made concurrently by UM with Micro Orifice Uniform Deposit Impactors (MOUDIs) (see Section 4.3.2). The two diameter estimates were highly correlated and the ratio of the average values was 1.03.

4.3.2 UM MOUDI Measurements

The University of Minnesota measured the size distribution of particulate matter constituents from July 15 through August 30, 1992, at Meadview, AZ, using three Micro Orifice Uniform Deposit Impactors (MOUDIs). Samples were collected once each day from 7:00 am to 7:00 pm MST. The quality of the UM MOUDI data is summarized below.

4.3.2.1 Completeness

Valid data were obtained from all stages and the after filters of all three MOUDIs on 42 of the 47 sampling days (89%). Complete valid sample sets from the individual MOUDIs included 43 days for ions (91%), 44 days for chemical elements (94%) and 43 days for carbon (91%).

4.3.2.2 Precision and Lower Quantifiable Limits

For ion and carbon measurements, UM defines the precision of the MOUDI measurements as the larger of three times the standard deviation of the field blank value divided by the sample volume or the pooled standard deviation of replicate sample analyses, divided by the sample volume. The precisions and LQL’s for the MOUDI chemical measurements are summarized in Table 4-7. Replicate ion analyses were performed for 9.5%-12.1% of the samples, and replicate carbon analyses were performed for 13.9% of the stages and 9.1% of the after filters. The precisions of elemental analyses by x-ray fluorescence and PIXE were estimated from counting statistics during sample analyses and results of replicate analyses of archived samples.

The LQLs for ion and carbon analyses were defined as three times the standard deviation of the blank samples, and the LQLs for elemental analyses were defined as 3.3 times the uncertainty in the x-ray counting statistics.

Table 4-7 Precisions and Lower Quantifiable Limits for MOUDI Ion and Carbon Measurements

Species	Precision (ng/m^3)	Lower Quantifiable Limit (ng/m^3)
Chloride	74	24
Nitrite	190	190
Bromide	45	19
Nitrate	56	56
Sulfate	41	22
Ammonium	28	25
Organic Carbon (impactor stage)	79	79
Organic Carbon (after filter)	42	42
Elemental Carbon (impactor stage)	15	15
Elemental Carbon (after filter)	12	12

Sulfate and ammonium were above the LQL in most samples, while the other ions were almost always below the LQL. The precisions of sulfate and ammonium concentrations were typically 10% or less.

The chemical elements that were usually detected on one or more impactor stages in each sample were sulfur, iron, nickel and bromine. For sulfur and iron, the precision was generally 10% or less of the concentration on the stage with the highest average concentration. Precisions for nickel, zinc and bromine were generally less than about 20% of the concentration on the stage with the highest average.

Organic carbon was usually above the LQL on the impactor stages and after filters with precisions typically being about 25-40% of the concentrations. Elemental carbon was usually detected on one to three impactor stages in each sample with precisions of 25-75% of the concentrations.

4.3.2.3 Accuracy

As with the other aerosol samplers, two components of the measurement are critical in assessing the accuracy of aerosol concentrations determined on filters and denuders: the accuracy of the flow measurement in the field and the accuracy of the analytical measurement in the laboratory.

An independent performance audit of the MOUDI flow rates was conducted at Meadview on July 17, 1992. All audit flow rates were within 4% of the nominal 30 LPM sampler flow rate.

The ion and elemental analyses of the MOUDI samples were performed by the same laboratories that performed these analyses on samples from the IMPROVE samplers. The accuracies of those laboratories' analyses were discussed in Section 4.2.1.4.

The accuracy of the carbon analyses was not audited. Turpin, et al. (1997) compared total carbon (sum of organic and elemental carbon) measured concurrently by the IMPROVE and MOUDI samplers at Meadview. The average MOUDI total carbon concentration was 88% higher than the average IMPROVE concentration, and the values were uncorrelated. Turpin et al. (1997) suggested that the poor agreement and the bias may have been caused by the use of an average backup filter organic carbon concentration to correct the IMPROVE front filter organic carbon for adsorption artifacts.

4.3.3 University of Minnesota Particle Growth Measurements

Scientists from the University of Minnesota measured particle growth characteristics as a function of relative humidity at Meadview between July 15 and August 30, 1992. Data were not available to characterize the precision, lower quantifiable limits or accuracy of these non-routine measurements.

4.4 Precision of Tracer Measurements

Several experiments that were performed to quantify the precision of the PFT measurements are described below. The accuracy of these measurements was not characterized.

Use of collocated samplers was a key component of the quality assurance evaluation for Project MOHAVE tracer data. A previous perfluorocarbon tracer study performed by organizations not involved with Project MOHAVE had collocated tracer measurement results showing uncertainties in the tracer measurements larger than the highest concentration at the Grand Canyon receptor sites (Richards, *et al* 1991); thus, demonstration of good precision using collocated samplers was critical for credibility of the Project MOHAVE tracer data. For both the winter and summer intensive periods, two locations (Meadview, at the west edge of Grand Canyon National Park, and Hopi Point, near Grand Canyon Village) were chosen to have 3 tracer samplers each. Not only did this arrangement allow for calculation of collocated precision, it also provided for insurance at these key Grand Canyon monitoring sites in case of sampler failure. In addition to the collocated BATS samplers, the 15 minute real-time sampler at Meadview allows for comparison with the BATS at Meadview for a portion of the summer period. The Environmental Monitoring Laboratory (EML) of the U.S. Department of Energy also made PFT measurements at one site (Dolan Springs); this data allows comparison of the Brookhaven concentrations to a completely independent measurement. The EML study also had duplicate samplers, allowing for calculation of collocated precision for their measurements. Brookhaven National Laboratory was blinded to the locations of samplers, except by site number, as well as to which site number corresponded to collocated measurements.

Some problems were experienced in the collection of samples due to sampler malfunction and, in the summer, incorrect instructions given to site operators. In addition, a small percentage of the samples could not be indisputably assigned sampling times or locations.

Regression statistics (r^2, slope, intercept, standard errors of slope, intercept, and y-estimate) were computed for each pairing of samplers, for each tracer compound, summer and winter. Root-mean-square errors for winter and summer collocated PFT measurements at Meadview and Hopi Point are shown in Table 4-8. Figure 4-7 and Figure 4-8 show regression plots of PMCP and ocPDCH concentrations (above mean background) at the three collocated monitoring sites at Meadview during the winter study. The plots show good agreement (r^2=0.87-0.88 for ocPDCH, 0.97-0.98 for PMCP). Concentrations of ocPDCH at most sites, including the collocated sites were low during the winter study, as winds were predominantly from the north, carrying the MPP emissions and ocPDCH to the south, away from Grand Canyon National Park. Conversely PMCP, which was released to the northeast of the Grand Canyon was frequently observed at elevated concentrations at the Grand Canyon sites during the winter. The spatial concentration patterns for winter and summer will be described in more detail in Section 5.

Figure 4-9 shows scatterplots for collocated summer measurements of released tracers (ocPDCH, PMCP, PMCH, and PTCH) at Meadview. There is good precision for ocPDCH (r^2=0.997); this is especially important because the ocPDCH was used to tag the MPP emissions, the main source of interest for this study. The other tracers concentrations had a higher noise level.

Collocated precision gives a measure of uncertainty in PFT concentrations over the range of concentrations experienced for two or more samplers at a given site. However, there may be additional uncertainty in the concentration of *released* PFTs due to variation in apparent background caused by a combination of actual variation in background and measurement error.

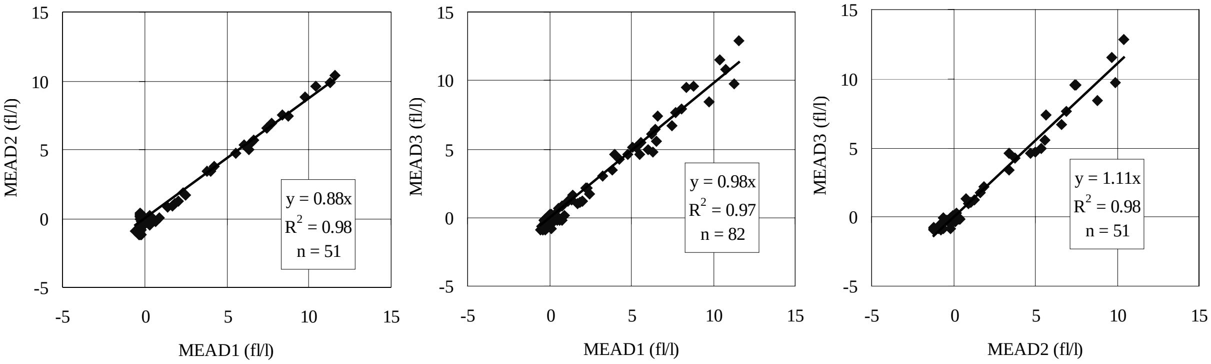

Figure 4-7 Regression of collocated PMCP tracer measurements at Meadview during the winter intensive period.

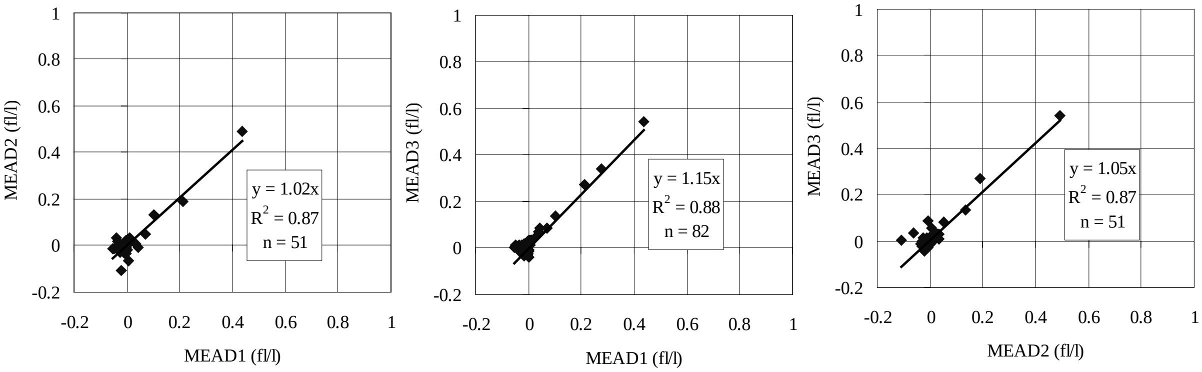

Figure 4-8 Regression of collocated ocPDCH measurements at Meadview during the winter intensive period.

Because the average network-wide background PFT concentration was subtracted for each site, backgrounds that are constant at each site, but varying between sites would result in constant additive biases (systematic error) for each site. Background concentrations varying in time at each site, but averaging the same at all sites would appear as random errors. For determination of PFT concentrations due to the release, the background variation calculation is preferred to collocated precision (especially at near background levels) because it includes both measurement error and actual variation background. At high concentrations of released tracer, collocated precision measurements more appropriately demonstrate multiplicative errors (e.g. slopes of regression analyses significantly different from one). When considering the amount of SO_2 associated with a given amount of ocPDCH released from MPP, the variation in the SO_2/ocPDCH emission rate must also be considered.

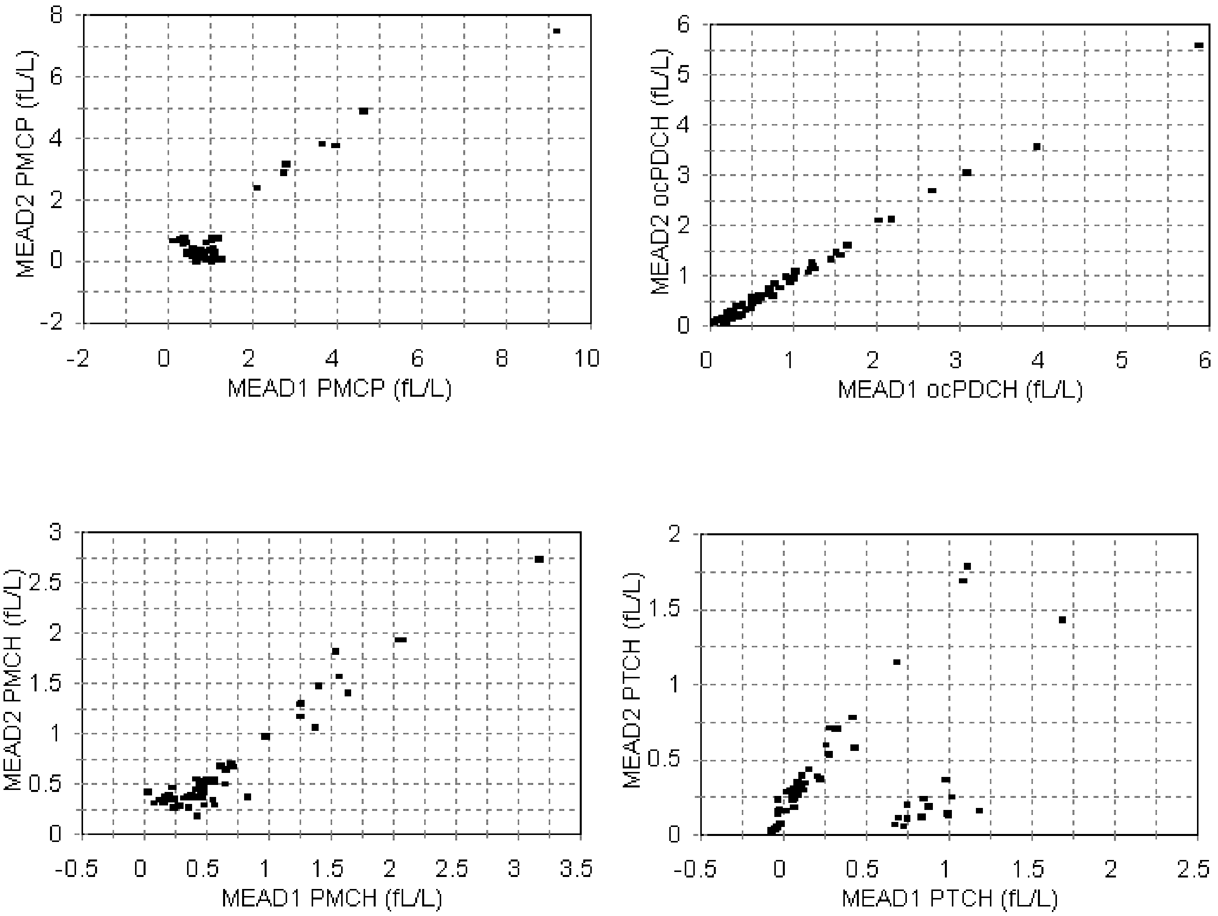

Figure 4-9 Scatter plots of collocated tracer measurements at Meadview, summer intensive period.

Table 4-8 Root-mean-square error (fL/L) for collocated sites.

	Winter		Summer	
	rmse	n	rmse	n
ocPDCH	0.021	(279)	0.059	(246)
PMCP	0.421	(279)	0.43	(246)
PMCH	0.108	(41)	0.28	(246)
PTCH			0.16	(237)

Standard deviations of the PFT compounds (pooled over all sites) during the winter and summer pre-release periods and the interim period between the winter and summer studies are shown in Table 4-9. The ocPDCH background uncertainties of 0.05 fL/L for winter and 0.06 fL/L for summer are similar to our goal of 0.06 fL/L determined to be the lowest concentration change associated with one estimate of perceptible visibility impact due to MPP. If we consider concentrations of 2 standard deviations above background to be "significantly" above background, then these values of 0.10 fL/L for winter and 0.12 fL/L would exceed this design value. However, because of the conservative nature of the assumptions made in deriving this value, it is unlikely that perceptible visibility impacts would occur unless measured ocPDCH concentrations were greater than 2 standard deviations above mean background.

From July 28, 1992 through August 14, 1992 a gas chromatograph analyzed PFT concentrations for 15 minute sampling periods at Meadview. Although numerous power outages affected the overall data collection, a sufficient number of samples were collected to determine diurnal patterns of tracer concentrations, as well as peak 15 minute to 12 hour average ratios, in particular for ocPDCH emitted from the MPP stack. For each 12-hour averaging period the average of the 15 minute samples from the dual trap analyzer (DTA) were compared to concentrations from the Meadview 12-hour average sample from the BATS. There were usually fewer than 48 valid 15-minute samples for comparison, so the actual sampling periods varied somewhat between the DTA and BATS. The squared correlation coefficient (r^2) between the DTA and BATS (with somewhat different sampling periods) was 0.79 (n=30).

Table 4-9 Standard deviation (fL/L) of pre-release and interim PFT concentrations.

	Winter		Summer		Interim	
	standard deviation	n	standard deviation	n	standard deviation	n
ocPDCH	0.05	(105)	0.061	(155)	0.037	(83)
PMCP	0.84	(105)	0.59	(156)	0.63	(83)
PMCH	0.43	(42)	0.3	(156)	0.48	(46)
PTCH			0.62	(151)		

The Department of Energy's Environmental Monitoring Laboratory (DOE-EML) measured PFTs using the BATS samplers for 2 hour periods at Dolan Springs for the period July 11- July 31, 1992. Dolan Springs is approximately 50 km north-northeast of MPP and was expected to often be in the transport path of MPP emissions during summer late-morning through afternoon periods. Table 4-10 shows collocated RMS error and r^2 for released tracers.

Table 4-10 RMS error and r^2 for DOE-EML collocated tracer measurements at Dolan Springs.

	RMS error (fL/L)	r^2
ocPDCH	0.16	0.98
PMCP	0.28	0.75
PMCH	0.23	0.89
PTCH	0.07	0.99

There were 14 days for which the EML PFT measurements could be compared to the Brookhaven PFT measurements at Dolan Springs. The 2 hour measurements from EML were averaged over 24 hour periods to compare with the BNL measurements. Most days had either 10 or 12 two-hour samples; several days were missing the 1600 and 1800 samples from EML.

Time series plots comparing Brookhaven and DOE-EML concentrations are shown in Figure 4-10. Temporal patterns between Brookhaven and DOE-EML concentrations are similar for all PFTs (r^2=0.99 both ocPDCH and PTCH, 0.90 for PMCP, and 0.77 for PMCH). However, offsets are apparent for ocPDCH and PTCH; for PMCP and PMCH, the values from the two laboratories differ by scaling factors. The offsets indicate differences in apparent background and do not affect concentrations due to the release; thus the ocPDCH from MPP would not be affected by the offsets. The scaling factors would affect concentrations due to the releases at Tehachapi Pass; for this study, this is not important because the tracers from Tehachapi Pass were intended only for use as markers for flow through the pass.

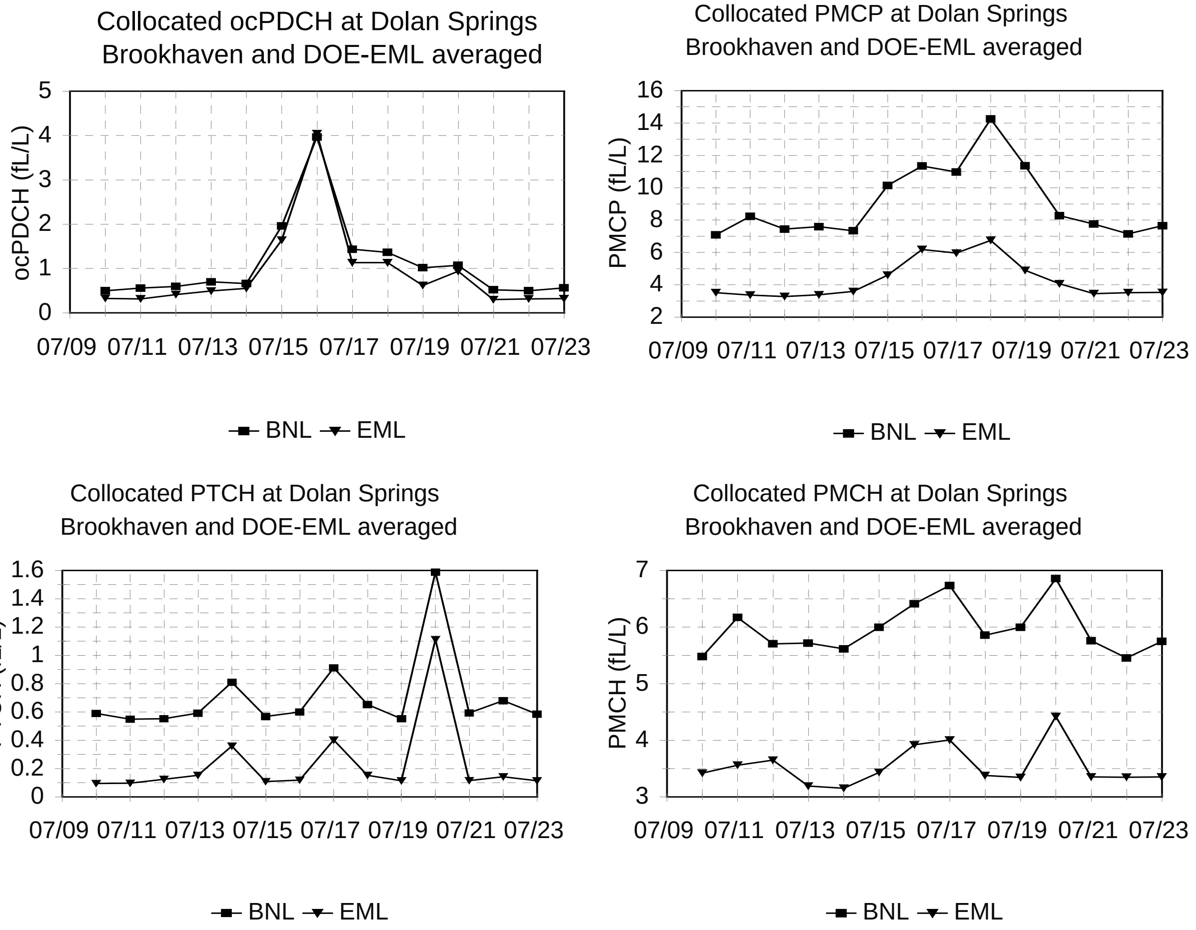

Figure 4-10 Time series of collocated BNL and DOE-EML tracer measurements at Dolan Springs, summer intensive period.

4.5 Meteorological data quality.

This section describes the data quality of the meteorological observations collected during Project MOHAVE.

4.5.1 Upper-Air Wind Speed and Direction

Determination of the accuracy of the wind measurements is problematic because the “true” values are not known. However, comparisons of various measurement methods (e.g. rawinsondes, sodars, tall towers, radar wind profilers) and collocated precision calculations of a given method allow for a general level of uncertainty to be estimated. A review of routine field audits of radar wind profilers using rawinsondes, Doppler sodars, tethered-sonde systems, and pilot balloon tracking showed consistency of wind profiler measurements to within about 1-2 m s^{-1} in speed and 10 to 20 degrees in direction (Neff, 1994). Comparison of radar wind profiler observations to aircraft and tall tower measured winds indicated RMS differences of 1 m s^{-1} and 10 degrees (Angevine & MacPherson, 1996; Angevine et al., 1998). Guidelines for quality assurance of upper air meteorological data prepared for the USEPA give “expected” performance characteristics for radar wind profilers and rawinsondes (Lindsey et al., 1995). These guidelines give expected comparability for radar wind profilers of 2 m s^{-1} in speed and 30 degrees in direction, with systematic differences of 1 m s^{-1} and 10 degrees. The corresponding values for rawinsondes are 5-18 degrees in direction and 3.1 m s^{-1} in speed for comparability, based upon collocated precision, with systematic differences of 0.5-1 m s^{-1} for each component.

During about the first two weeks of the winter intensive study, a radar wind profiler (RWP) was located at MPP and rawinsondes were released nearby in the “Riviera” section of Bullhead City, Arizona, about 4 km southwest of the RWP location. The heights of the MPP RWP site and Bullhead City rawinsonde site were 213 m MSL and 167 m MSL, respectively. Although the instruments were nearby, they were not collocated, the reported measurement heights differed somewhat, and the RWP data were hourly averages while the rawinsonde data were nearly instantaneous. Nonetheless, comparison of the data from the two systems can give an upper limit on the measurement uncertainty of these instruments. Both the RWP and rawinsonde gave wind direction and speed approximately every 100 meters in height. For heights of about 400 m to 2700 m MSL, measurements from both systems were available for comparison. In order to compare values at the same height, the observations were linearly interpolated to the nearest 100 m.

Figure 4-11 and Figure 4-12 compare wind direction and wind speed at the RWP and rawinsonde sites. Because wind directions may vary considerably during light wind speed conditions, the wind direction comparisons are shown only for periods with wind speeds at least 3 m s^{-1}. Table 4-8 shows the percent of wind speed and direction measurements meeting specified criteria. There was a bias of 5 degrees between the Bullhead City rawinsonde resultant wind direction and the MPP radar wind profiler resultant wind direction.

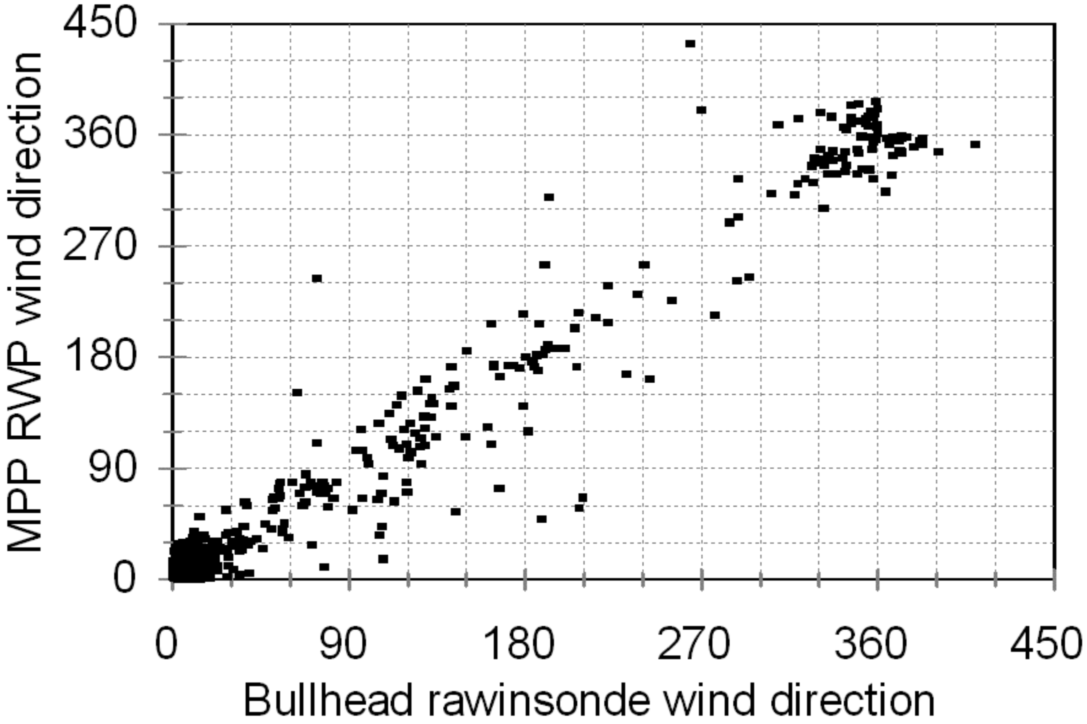

Figure 4-11 Comparison of direction measured by the MPP radar wind profiler and Bullhead City-Riviera rawinsonde during the second half of January 1992.

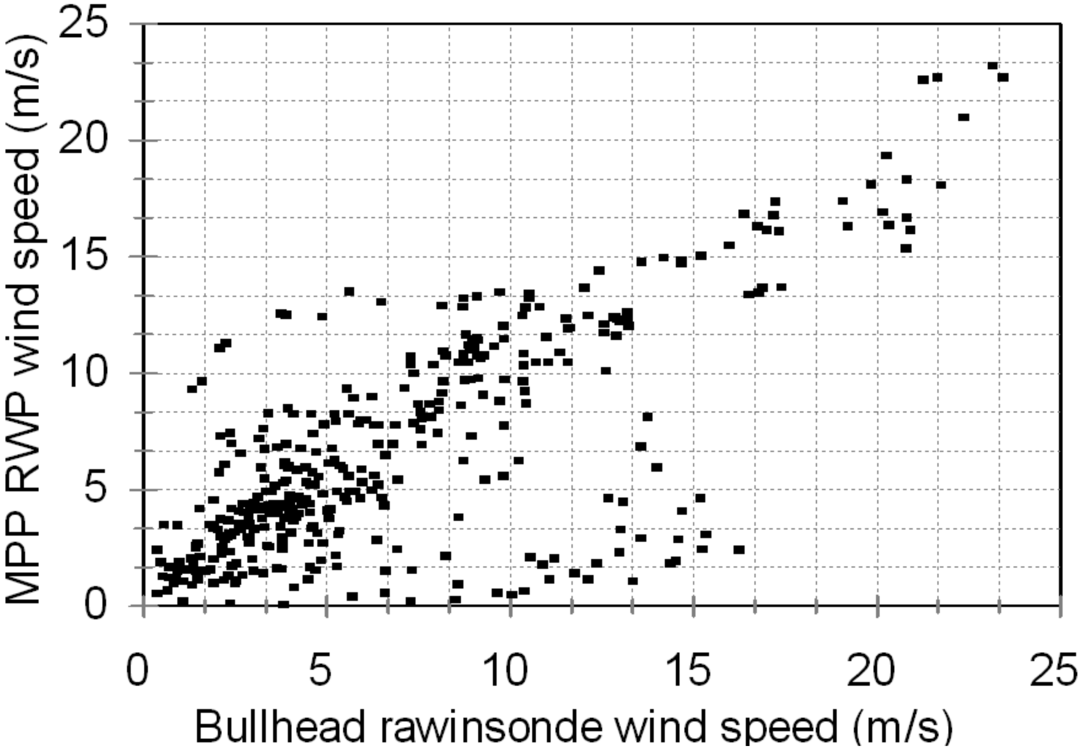

Figure 4-12 Comparison of wind speed measured by the MPP radar wind profiler and Bullhead City-Riviera rawinsonde during the second half of January 1992.

Table 4-11 Comparison of winds from rawinsonde and radar wind profiler.

Wind direction: Percent within given direction difference	
10 degrees	50%
20 degrees	78%
30 degrees	94%

Wind speed: Percent within given speed difference	
1 m s^{-1}	41%
2 m s^{-1}	63%
4 m s^{-1}	84%

Combined wind speed and direction: Percent meeting both speed and direction criteria	
2 ms^{-1} and 20 degrees	52%
4 m s^{-1} and 30 degrees	83%