3.0 DATA BASE STRUCTURE

A flow diagram of the data base management system applied to this study is shown in Figure 3-1. Final data are stored in an Access data base, "Texas.mdb". To assemble and validate the final data files, information was merged from many data sets derived from field monitoring and laboratory analyses.

3.1 Analytical Specifications

Every measurement consists of: 1) a value; 2) a precision; 3) an accuracy; and 4) a validity (Hidy, 1985; Watson et al., 1989, 1995). The measurement methods described in this volume are used to obtain the value. Performance testing via regular submission of standards, blank analysis, and replicate analysis are used to estimate precision. The submission and evaluation of independent standards through quality audits are used to estimate accuracy. Validity applies both to the measurement method and to each measurement taken with that method. The validity of each measurement is indicated by appropriate flagging within the data base, while the validity of the methods has been evaluated in this study by tests described in Section 3.3.

3.1.1 Measurement Attributes

The precision, accuracy, and validity of the Texas $PM_{2.5}$ Sampling and Analysis Study aerosol measurements are defined as follows (Chow et al., 1993c):

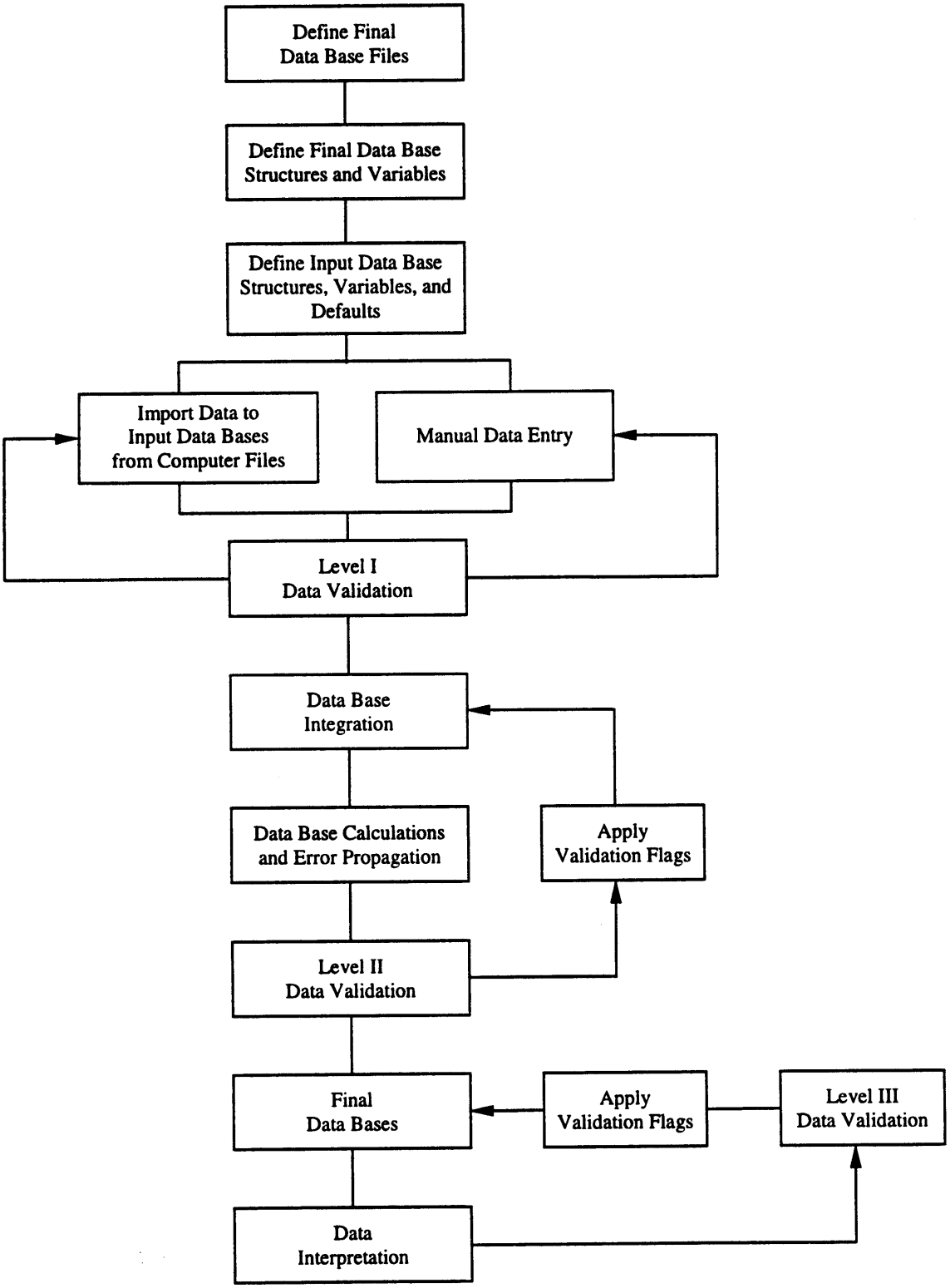
- A **measurement** is an observation at a specific time and place which possesses: 1) value – the center of the measurement interval; 2) precision – the width of the measurement interval; 3) accuracy – the difference between measured and reference values; and 4) validity – the compliance with assumptions made in the measurement method.

- A **measurement method** is the combination of equipment, reagents, and procedures that provides the value of a measurement. The full description of the measurement method requires substantial documentation. For example, two methods may use the same sampling systems and the same analysis systems. These are not identical methods, however, if one performs acceptance testing on filter media and the other does not. Seemingly minor differences between methods can result in major differences between measurement values.

- **Measurement method validity** is the identification of measurement method assumptions, the quantification of effects of deviations from those assumptions, the evaluation that deviations are within reasonable tolerances for the specific application, and the creation of procedures to quantify and minimize those deviations during a specific application.

- **Sample validation** is accomplished by procedures that identify deviations from measurement assumptions and the assignment of flags to individual measurements for potential deviations from assumptions.

Figure 3-1. Flow diagram of the data base management system.



- The **comparability and equivalence of sampling and analysis methods** are established by the comparison of values and precisions for the same measurement obtained by different measurement methods. Interlaboratory and intralaboratory comparisons are usually made to establish this comparability. Simultaneous measurements of the same observable are considered equivalent when more than 90% of the values differ by no more than the sum of two one-sigma precision intervals for each measurement.

- **Completeness** measures how many environmental measurements with specified values, precisions, accuracies, and validities were obtained out of the total number attainable. It measures the practicability of applying the selected measurement processes throughout the measurement period. Data bases which have excellent precision, accuracy, and validity may be of little use if they contain so many missing values that data interpretation is impossible.

3.1.2 Completeness

A total of 1,131 sample sets of aerosol samples were acquired during the study, these included 971 ambient samples and 160 field blanks. Of the 971 ambient samples, 847 (86.4%) were considered valid samples after data validation and final review by committee (on 09/01/98). Of these 847 validated samples, 742 were regularly scheduled samples, which represents 88.4% of the possible sampling days. Several samples were invalidated by the review committee due to $PM_{2.5}/PM_{10}$ ratios being greater than unity or for having unusually high or low ratios when compared to the other samples taken in the area. The remaining 105 samples were obtained as forecast days, representing 74.5% of the possible forecast day samples. The lower percentage of successful samples on forecast days was likely due to site operators being unable to set up the sampler for the additional sampling when given short notice. The analysis of the sample sets acquired during of the Texas $PM_{2.5}$ Sampling and Analysis Study resulted in a data base of ~30,000 data points.

3.1.3 Measurement Precision

Measurement precisions were propagated from precisions of the volumetric measurements, the chemical composition measurements, and the field blank variability using the methods of Bevington (1969) and Watson et al. (1995). The following equations calculated the precision associated with filter-based measurements:

$$C_i = (M_i - B_i)/V \quad (3\text{-}1)$$

$$V = F \times t \quad (3\text{-}2)$$

$$B_i = \frac{1}{n}\sum_{j=1}^{n} B_{ij} \quad \text{for } B_i > \sigma_{Bi} \quad (3\text{-}3)$$

$$B_i = 0 \quad \text{for } B_i \le \sigma_{Bi} \quad (3\text{-}4)$$

$$\sigma_{Bi} = STD_{Bi} = [\frac{1}{n-1}\sum_{j=1}^{n}(B_{ij} - B_i)^2]^{1/2} \quad \text{for } STD_{Bi} > SIG_{Bi} \tag{3-5}$$

$$\sigma_{Bi} = SIG_{Bi} = [\frac{1}{n}\sum_{j=1}^{n}(\sigma_{Bij})^2]^{1/2} \quad \text{for } STD_{Bi} \leq SIG_{4Bi} \tag{3-6}$$

$$\sigma_{Ci} = [\frac{\sigma_{Mi}^2 + \sigma_{Bi}^2}{V^2} + \frac{\sigma_V^2 (M_i - B_i)^2}{V^4}]^{1/2} \tag{3-7}$$

$$\sigma_{RMS_i} = (\frac{1}{n}\sum_{j=1}^{n}\sigma_{Ci}^2)^{1/2} \tag{3-8}$$

$$\sigma_V/V = 0.05 \tag{3-9}$$

where:

B_i = average amount of species i on field blanks

B_{ij} = the amount of species i found on field blank j

C_i = the ambient concentration of species i

F = flow rate throughout sampling period

M_i = amount of species i on the substrate

M_{ijf} = amount of species i on sample j from original analysis

M_{ijr} = amount of species i on sample j from replicate analysis

n = total number of samples in the sum

SIG_{Bi} = the root mean square error (RMSE), the square root of the averaged sum of the squared of σ_{Bij}.

STD_{Bi} = standard deviation of the blank

σ_{Bi} = blank precision for species i

σ_{Bij} = precision of the species i found on field blank j

σ_{Ci} = propagated precision for the concentration of species i

σ_{Mi} = precision of amount of species i on the substrate

σ_{RMS_i} = root mean square precision for species i

σ_V = precision of sample volume

t = sample duration

V = volume of air sampled

Dynamic field blanks were analyzed to estimate background concentrations. Measurement precisions associated with each chemical species are reported in the Texas data base.

3.2 Quality Assurance

Quality control (QC) and quality auditing establish the precision, accuracy, and validity of measured values. Quality assurance integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of quality assurance are data values with specified precisions, accuracies, and validities.

Quality control (QC) is intended to prevent, identify, correct, and define the consequences of difficulties that might affect the precision and accuracy, and or validity of the measurements. QC activities for the Texas measurements included: 1) modifying standard operating procedures (SOPs) followed during ambient/source sampling, chemical analysis, and data processing; and 2) quality auditing.

The quality auditing function consisted of systems and performance audits. The systems audit included a review of the operational and QC procedures to assess whether they were adequate to assure valid data that met the specified levels of accuracy and precision. It also examined all phases of the measurement activity to determine that procedures were followed and that operators were properly trained. Performance audits established whether the predetermined specifications were achieved in practice. The performance audits challenged the measurement/analysis systems with known transfer standards traceable to primary standards.

Both system and performance audits were performed in DRI's Environmental Analysis Facility on an annual basis to assure data quality. Auditors acquired and reviewed the standard operating procedures and examined all phases of measurement activities to assure that procedures were followed and that operators were properly trained.

For laboratory performance audits, both thin-film standards and laboratory-spiked filters were submitted to independent laboratories for x-ray fluorescence, ion chromatographic, automated colorimetric, and carbon analyses. The following subsections summarize the results of laboratory intercomparison conducted during the summer of 1997 and winter of 1998 to demonstrate the accuracy and validity of laboratory measurements.

3.2.1 Laboratory Intercomparisons of Polymer-Film XRF Standards

The polymer film standards consist of organo-metallic compounds in a stable polymer matrix and are not commercially available. The standards were made at the U.S. EPA's Office of Research and Development Laboratory in 1977 (Dzubay et al., 1981), and sets have been in use for more than ten years in EPA laboratories as calibration and quality control standards with excellent stability. They are thicker than commercially available thin-film standards and require attenuation corrections which should be small because of the elements selected to be incorporated into the standards. The intercomparison results of the polymer film standards analysis of three XRF analyzers between the U.S. EPA and DRI laboratories are shown in Table 3-1.

The target values of the 18 elements from the nine polymer-film standards are used as the true values to assess measurement accuracy. Agreement to within ±5% is considered to be excellent, and agreement within ±10% is within the tolerance of measurement errors. With the DRI Kevex XRF analyzer, Table 3-1 shows that over half of the elements (i.e., Ni, V, Cr, Cu, Pb, Ba, Rb, Co, Sb, Sr) reported values within ±5% of the target value; values for two other elements (i.e., Ti, Zn) fell in the range of ±5% to ±10% difference. The largest discrepancies of up to ±20% difference between the DRI laboratory and the target value were found for Mn, Fe, and As, and up to ±13% difference was found for Zr and Cd.

Similar results were found with the two EPA XRF analyzers. Table 3-1 shows that among the three XRF analyzers, deviations from the target values ranged from –12.2% (EPA LBL) to –19.9% (DRI) for Mn, +18.0% (EPA LBA) to +19.8% (EPA Kevex) for Fe, –12.7% (DRI) to +10.8% (EPA LBL) for Zr, –13.3% (DRI) to +9.0% (EPA LBL) for Cd, and –11% (EPA LBL) to –19% (DRI) for As. These discrepancies could result either from the degradation of the polymer film standards (e.g., As, Mn, Fe) or bias in instrument calibration. DRI reported Zr and Cd results with a flag indicating manual adjustment of background but there was no indication that would explain the low results for these elements. Likewise, no definitive explanation can be offered for V, Cr, and Ba results on the EPA LBL or Ba results on the EPA Kevex. In general the agreement and results are quite good. With the possible exceptions of Mn, Fe, As, Zr, and Cd, these intercomparisons show no serious bias among the three XRF instruments.

3.2.2 Laboratory Intercomparison for Carbon

A set of 12 ambient and source samples acquired near Denver, Colorado, during the Northern Front Range Air Quality Study (Chow et al., 1998; Watson et al., 1998) were submitted for laboratory intercomparison between DRI and National Institute of Standards and Technology laboratories. The filter loadings on these samples ranged from 20 to 220 µg/filter. Table 3-2 summarizes the results of these analyses. With the exception of two samples, the difference (i.e., DRI total carbon minus NIST total carbon) in measured total carbon ranged from -2.7 ± 3.9 to 2.8 ± 1.0 µg/filter with average percent differences from -6.3% to 5.3%. A side-by-side comparison is presented in Figure 3-2. Large differences were found for sample ID NWQNK026C (ambient sample) and DYDQ0700E (dynamometer sample), which reported differences of 4.9 µg/filter (19.8%) and 13.1 µg/m^3 (26.1%),

Table 3-1. Laboratory intercomparisons for polymer film XRF standards (January 1998).

Standard ID	Element	Target Value ($\mu g/cm^2$)	EPA LBL[a]	Percent[b] Difference	EPA Kevex[c]	Percent[b] Difference	DRI Kevex[d]	Percent[b] Difference
TIGE40D	Ti	2.403	2.456	2.220	2.408	0.190	2.258	-6.030
	Ge	6.064	6.093	0.480	6.246	3.000	No Data	
NIV40F	Ni	5.846	5.815	-0.540	5.658	-3.210	5.988	2.430
	V	6.873	7.774	13.110	7.162	4.200	6.755	-1.720
CRCU40G	Cr	8.642	9.497	9.900	8.573	-0.800	8.417	-2.600
	Cu	8.120	7.918	-2.480	7.688	-5.320	8.090	-0.370
MNZN42B	Mn	11.242	9.869	-12.210	9.418	-16.230	9.010	-19.850
	Zn	8.474	8.608	1.580	8.478	0.040	9.058	6.890
FEPB44A	Fe	6.645	7.839	17.980	7.959	19.780	7.939	19.470
	Pb	7.561	7.554	-0.090	7.695	1.770	7.538	-0.300
ZRCD39Y	Zr	10.767	10.776	0.090	10.553	-1.980	9.400	-12.700
	Cd	9.150	9.002	-1.620	8.686	-5.070	7.932	-13.310
BAAS41Y	Ba	4.754	4.193	-11.800	4.290	-9.770	4.810	1.180
	As	5.344	4.760	-10.930	4.609	-13.740	4.314	-19.270
RBCO35W	Rb	7.529	8.121	7.870	7.844	4.190	7.883	4.700
	Co	7.659	7.943	3.710	7.715	0.730	7.592	-0.870
SBSR35X	Sb	4.951	5.227	5.570	5.247	5.980	4.794	-3.170
	Sr	4.919	5.164	4.980	4.943	0.480	4.742	-3.600

[a] EPA Lawrence Berkeley Laboratory XRF analyzer.

[b] $\text{Percent Difference} = \frac{\text{Target Value} - \text{Measured Value}}{\text{Target Value}} \times 100\%$

[c] EPA Kevex 0770 XRF analyzer.

[d] DRI Kevex 0700/8000 XRF analyzer.

Table 3-2. Summary of DRI/NIST laboratory intercomparison results for total carbon (July 1997).

Sample ID	DRI Organic Carbon (µg/filter)	DRI Elemental Carbon (µg/filter)	DRI OC/TC	DRI Total Carbon[a] (µg/filter)	NIST Total Carbon (µg/filter)	Difference[b] (µg/filter)	Percent Difference[c]
NWQNK026 C [d]	19.4 ± 0.7 [e]	7.6 ± 0.2 [e]	0.72	27.0 ± 0.6 [e]	22.14 ± 1.78 [e]	4.86 ± -1.18 [e]	19.79 ± 0.94 [e]
NWQNK026 E [d]	20.3 ± 0.8	7.6 ± 0.2	0.73	27.9 ± 0.6	26.83 ± 1.99	1.07 ± -1.39	3.92 ± 1.04
NWQNK144 C	28.2 ± 1.0	17.4 ± 0.5	0.62	45.6 ± 0.8	46.34 ± 2.97	-0.74 ± -2.17	-1.62 ± 1.54
NWQNK144 E	28.6 ± 1.1	17.0 ± 0.5	0.63	45.6 ± 0.8	46.14 ± 2.96	-0.54 ± -2.16	-1.18 ± 1.53
NWQNK151 C	13.3 ± 0.6	6.0 ± 0.2	0.69	19.3 ± 0.4	20.55 ± 1.72	-1.25 ± -1.32	-6.25 ± 0.88
NWQNK151 E	13.9 ± 0.6	5.7 ± 0.2	0.71	19.6 ± 0.4	18.92 ± 1.65	0.68 ± -1.25	3.51 ± 0.85
DVSQ004 E	173.1 ± 7.6	43.4 ± 2.3	0.80	216.5 ± 9.0	219.17 ± 12.85	-2.67 ± -3.85	-1.23 ± 7.84
DYDQ1436 C	11.2 ± 0.5	49.5 ± 3.1	0.18	60.7 ± 2.5	61.28 ± 3.78	-0.58 ± -1.28	-0.95 ± 2.27
DYDQ1436 E	10.5 ± 0.5	49.8 ± 3.1	0.17	60.3 ± 2.4	62.12 ± 3.83	-1.82 ± -1.43	-2.98 ± 2.26
DYDQ0700 C	54.5 ± 2.1	3.2 ± 0.2	0.94	57.7 ± 2.3	56.52 ± 3.52	1.18 ± -1.22	2.06 ± 2.10
DYDQ0700 E	50.9 ± 1.9	3.1 ± 0.2	0.94	54.0 ± 2.2	51.19 ± 3.23	2.81 ± -1.03	5.34 ± 1.95
DYDQ0700 E	50.9 ± 1.9	3.1 ± 0.2	0.90	56.7 ± 2.3	43.61 ± 2.29	13.09 ± 0.01	26.09 ± 1.62

[a] Sum of organic and elemental carbon

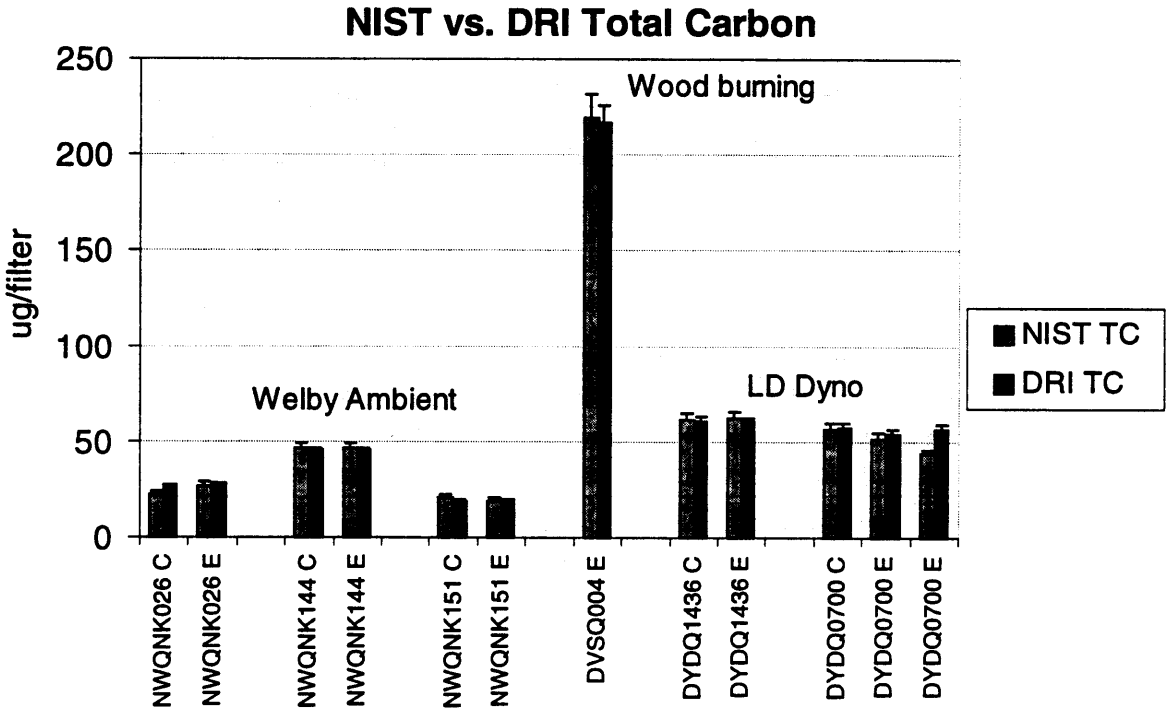
[b] Difference = DRI total carbon – NIST total carbon.

[c] Percent difference = [(DRI total carbon – NIST total carbon) ÷ [(DRI total carbon + NIST total carbon) × 0.5]] × 100%.

[d] Filter sections taken from center (C) and edge (E) of each sample.

[e] Measurement uncertainty.

Figure 3-2. Intercomparison results for DRI versus NIST total carbon.



respectively, with NIST's laboratory reporting much lower concentrations than DRI's laboratory. Either some of the carbon particles may have fallen off from the deposit during shipping, or some inhomogeneous sample deposit occurred on these two samples.

As shown in Table 3-2, two different sample punches (0.5 cm^2 each at the center and edge of each filter disc) were taken from each sample at each laboratory to assure homogeneous sample deposit. DRI analyses show that consistent results are received for all but the dynamometer sample (ID DYDQ0700). Up to 7% difference was found on this sample for sample punches taken between the center and edge of the filter deposits; NIST analyses also found 12.9 µg/filter or 25% difference on the same sample between the center and edge filter punches. In addition, NIST analyses reported 4.7 µg/filter or 5% difference on sample NWQNK026. Visual inspection on these samples confirmed inhomogeneous sample deposits on some of the dynamometer samples.

This laboratory carbon intercomparison shows that even though the carbon deposits varied by over a factor of 10, and organic-to-total-carbon ratios varied from 0.17 to 0.94, the measurement differences between the two laboratories were well within ±6%. Linear regression statistics yield excellent correlation (r = 0.997), with close to unity slope (0.975 ± 0.024) and reasonable intercept (2.7 ± 1.8 µg/filter). The analysis of variance (ANOVA) also shows that carbon measurements from these two laboratories are statistically equivalent.

3.3 Data Validation

Data acquired from the Texas $PM_{2.5}$ Sampling and Analysis Study were submitted to four levels of data validation:

- Level 0 sample validation designates data as they come off the instrument. This process ascertains that the field or laboratory instrument is functioning properly.

- Level I sample validation: 1) flags samples when significant deviations from measurement assumptions have occurred; 2) verifies computer file entries against data sheets; 3) eliminates values for measurements which are known to be invalid because of instrument malfunctions; 4) replaces data from a backup data acquisition system in the event of failure of the primary system; and 5) adjusts values for quantifiable calibration or interference biases.

- Level II sample validation takes place after data from various measurement methods have been assembled in the master data base, and it is the first data analysis task. Level II applies consistency tests to the assembled data based on known physical relationships between variables.

- Level III sample validation is part of the data interpretation process. Upon finding a measurement that is inconsistent with physical expectations, the first assumption is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified during the data interpretation process as: 1) extreme values; 2) values which would otherwise normally track the values of other variables in a time series; and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern.

- Level I validation flags and comments are included with each data record in the data base and are defined by Chow et al. (1994a). Level II validation tests and results are described in the following subsections.

Level II tests evaluate the chemical data for internal consistency. In this study, Level II data validations were made for: 1) comparison of collocated $PM_{2.5}$ mass precisions, 2) sum of chemical species versus $PM_{2.5}$ mass, and 3) physical consistency. Correlations and linear regression statistics were computed and scatter plots prepared to examine the data. Suspect data were flagged and reexamined to determine the cause of the discrepancy.

3.3.1 Collocated Precision and Comparison with PM_{10} Concentrations

Linear regression can be used to infer equivalence between the X and Y samplers as well as predictability of one sampler's measurement from that of another sampler (King, 1977). Regression slope and intercept, along with their standard errors, are given in Table 3-3. When the slope equals unity to within three standard errors, the intercept is equal to zero within three standard errors, and the correlation coefficient is greater than 0.9, the

Table 3-3. Collocated comparisons of $PM_{2.5}$ mass measurements during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.

Site	Species	Sampler Y[a]	Sampler X[a]	Slope[b]	Intercept[c] (µg/m³)	Correlation Coefficient[d]	No. of Pairs	Average Ratio[e]	Percent Distribution[f] <1σ	1-2σ	2-3σ	>3σ	Average Difference[g]	Precision Collocated[h]	RMS[i]	P>|T|[j]
H3	$PM_{2.5}$ Mass	H3	H3-CO	0.882 ± 0.036	1.326 ± 0.658	0.98	21	0.97 ± 0.06	76	24	0	0	0.632	1.428	1.37	0.0561
HC	$PM_{2.5}$ Mass	HC	HC-CO	1.015 ± 0.054	0.046 ± 0.986	0.97	21	1.02 ± 0.08	71	24	5	8	-0.304	1.641	1.48	0.4063
HT	$PM_{2.5}$ Mass	HT	HT-CO	0.966 ± 0.054	-0.343 ± 0.823	0.98	16	0.93 ± 0.13	38	38	19	0	0.813	1.447	1.17	0.0401

[a] X=primary sampler. Y=collocated.

[b] Regression slope with standard error.

[c] Regression intercept with standard error.

[d] Correlation coefficient.

[e] Average of Y/X and standard deviation of this ratio.

[f] Percentage of data pairs falling into the specified precision intervals, where each precision is equal to the root mean square (RMS) of the sum of the squared precisions of the X and Y samplers.

[g] Average of X minus Y.

[h] Collocated precision or standard deviation of X minus Y.

[i] RMS precision of the difference between X and Y, the root mean square (RMS) of the sum of the squared precisions of X and Y.

[j] Probability of a greater absolute value for Student's T under the hypothesis that the difference between X and Y is zero.

selection of independent and dependent variables is often considered to be equivalent (Berkson, 1950; Madansky, 1959; Kendall, 1951; 1952). If the correlation coefficient is greater than 0.9 but the slope and intercept criteria are not met, the compared measurements are said to be predictable from the independent variable. As seen in Table 3-3, the primary and collocated samplers at sites HC and HT meet all of the criteria for equivalence. The comparison at site H3 exhibits a slope that is slightly too low to meet the equivalence criteria, but the comparison does meet the intercept and correlation coefficient criteria, therefore this comparison is predictable by the above criteria. The indoor-outdoor comparison at Shell Westhollow has a slope much lower than unity, which was expected. It meets the criteria for predictability.

HS, P2-1 Not in Table 3-3.

Table 3-3 also presents the average ratios and standard deviation of "sampler Y to X" and the percent distribution of the data pairs whose difference (X minus Y) is less than 1σ, between 1σ and 2σ, between 2σ and 3σ, and greater than 3σ. Here, σ is the measurement uncertainty of "X-Y", which is the square root of the sum of the squared uncertainties ($\sigma^2_x+\sigma^2_y$), where σ_x and σ_y are the $PM_{2.5}$ measurement uncertainties for the X and Y samplers, respectively. Table 3-3 shows that for outdoor mass measurements over 90% of all the pair comparisons lie within a $\pm 3\sigma$ interval.

The average ratios and standard deviations of "sampler Y to X" in Table 3-3 show that the average Y/X ratio for outdoor mass measurements is equal to unity within one standard deviation of the average.

Table 3-3 gives the average of the paired differences (X-Y) between the X and Y samplers; the collocated precision, which is the standard deviation of the paired differences; and the root mean squared (RMS) precision (the square root of the mean squared precisions), which is essentially the average measurement uncertainty of "X-Y". The average differences and collocated precisions can be used to test the statistical hypothesis that the difference between samplers X and Y is zero.

A parametric test (Student's T-test) is performed for each pair of samplers to illustrate the paired differences. Table 3-3 gives the probability (P) for a greater absolute value of Student's T statistic. If P is less than 0.05, one can infer that one of the samplers gives a concentration which is greater or smaller than the other, depending on the sign of the average difference. Table 3-3 shows that $PM_{2.5}$ mass data is systematically higher at the collocated site when compared to the primary sampler at the HT site. The comparisons at the H3 and HC sites meet the criteria of equivalence based on the parametric test.

Because measurement uncertainty should be considered when making these comparisons, there is no rigorous statistical test or standard by which two samplers can be considered equivalent. However, the combined weight of the indices shown in Table 3-3 and the near one-to-one relationships in the regression analysis support the general conclusion that primary and collocated samplers measured the same mass concentrations (within measurement precisions) of $PM_{2.5}$ during this study.

Figure 3-3 shows the relationship between $PM_{2.5}$ mass measured by the roving collocated sampler and the three primary samplers. The collocated sampler was located at 3 sites (HG, HT, and H3), each operated by a different organization in the Houston area. With a slope of 0.96 ± 0.03, intercept of 0.26 ± 0.51 and correlation coefficient = 0.98, collocated mass data meet the criteria for equivalence. Figure 3-4 further illustrates the temporal equivalence of the mass measurements between the roving collocated sampler and the primary sampler during the study period from 03/11/97 to 03/12/98. With the associated measurement uncertainties, the collocated measurement resulted in identical measurement with the primary sampler.

Figure 3-5 shows the indoor versus outdoor relationship between $PM_{2.5}$ mass measured at the Shell Westhollow Technology Center both in an unused office indoors (site HS) and outdoors (site HW), using the same type of sampler. Good correlation ($r = 0.90$) is seen with the data from the indoor sampler being consistently lower. The Westhollow Technology Center has a single pass system to provide air to its offices, laboratories and ancillary facilities. Figure 3-6 shows that the two data sets exhibit the same concentration pattern, with the indoor samples being consistently about half of the outdoor concentration.

As an additional validation check, $PM_{2.5}$ values at each site were compared to PM_{10} values at the same sites. In cases where the $PM_{2.5}/PM_{10}$ ratio was greater than 1.0, the $PM_{2.5}$ value was invalidated. Table 3-4 summarizes $PM_{2.5}$ mass, PM_{10} mass, as well as the $PM_{2.5}/PM_{10}$ ratio for all days when both PM_{10} and $PM_{2.5}$ concentrations were obtained. These generally corresponded to the regularly scheduled sampling days except at El Paso, where both PM_{10} and $PM_{2.5}$ concentrations were obtained on additional days.

3.3.2 Sum of Chemical Species versus Mass

The sum of the individual chemical concentrations for $PM_{2.5}$ should be less than or equal to the corresponding gravimetrically measured mass concentrations. This sum includes chemicals quantified on the Teflon-membrane filters and on the quartz-fiber filters. Total sulfur (S), chloride (Cl^-) and soluble potassium (K^+) were excluded from the sum to avoid double counting. Since this sum is being used as a validation tool only, measured concentrations do not account for unmeasured metal oxides in crustal material, cations, or hydrogen in organic carbon.

Figure 3-7 shows a scatter plot of the $PM_{2.5}$ sum of species versus mass at all of the sites. This plot contains a solid line indicating the slope with a nonzero intercept and a dashed line indicating a one to one relationship. The correlation coefficient is generally lower with regression line forcing zero. Measurement uncertainties associated with the X- and Y-axes are shown for comparison. Regression statistics with mass as the independent variable (X) and sum of species as the dependent variable (Y) are also calculated. The slope with the intercept forced through zero is also shown for comparison. As intercepts are low compared to the measured concentrations, the slope closely represents the ratio of Y over X. Suspect data were examined and removed from future statistical analyses if sampling or analytical anomalies were identified.

Figure 3-7 shows that the sum of species is almost always less than the corresponding $PM_{2.5}$ mass within the measurement uncertainties. A good relationship is found between the sum of species and $PM_{2.5}$ mass with a correlation coefficient of 0.95. The three outliers are explainable by field flags indicating damaged quartz-fiber filters. Approximately 70% of the $PM_{2.5}$ mass can be explained by the chemical species measured during the study.

Figure 3-3. Scatter plot of collocated comparison of $PM_{2.5}$ mass measurements taken during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.

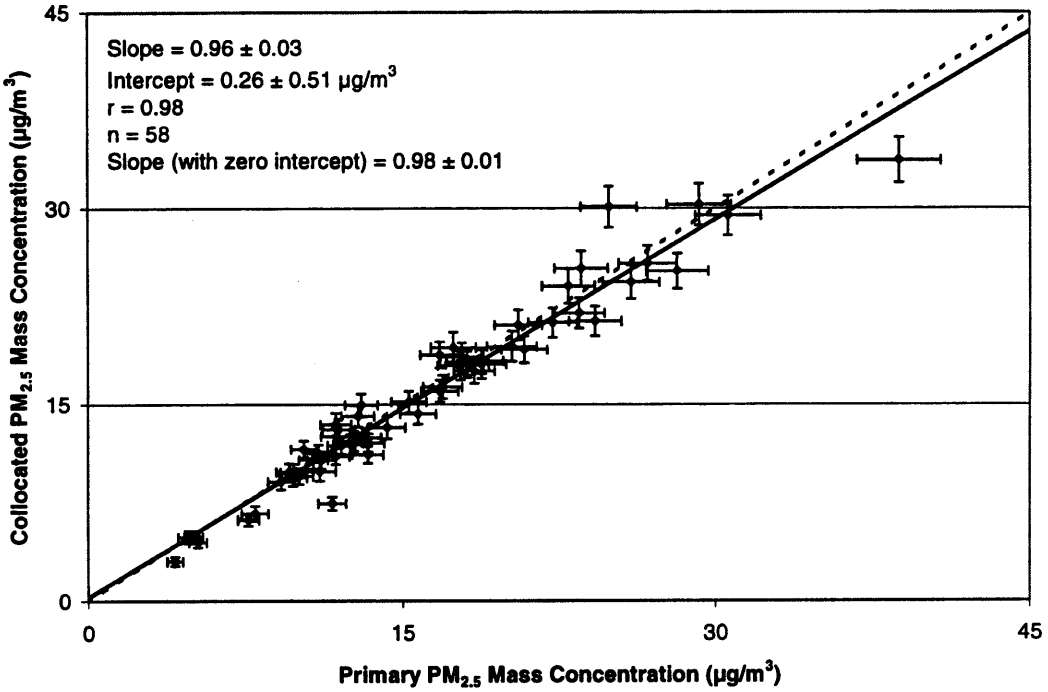


Figure 3-4. Collocated comparison of $PM_{2.5}$ mass measurements taken during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.

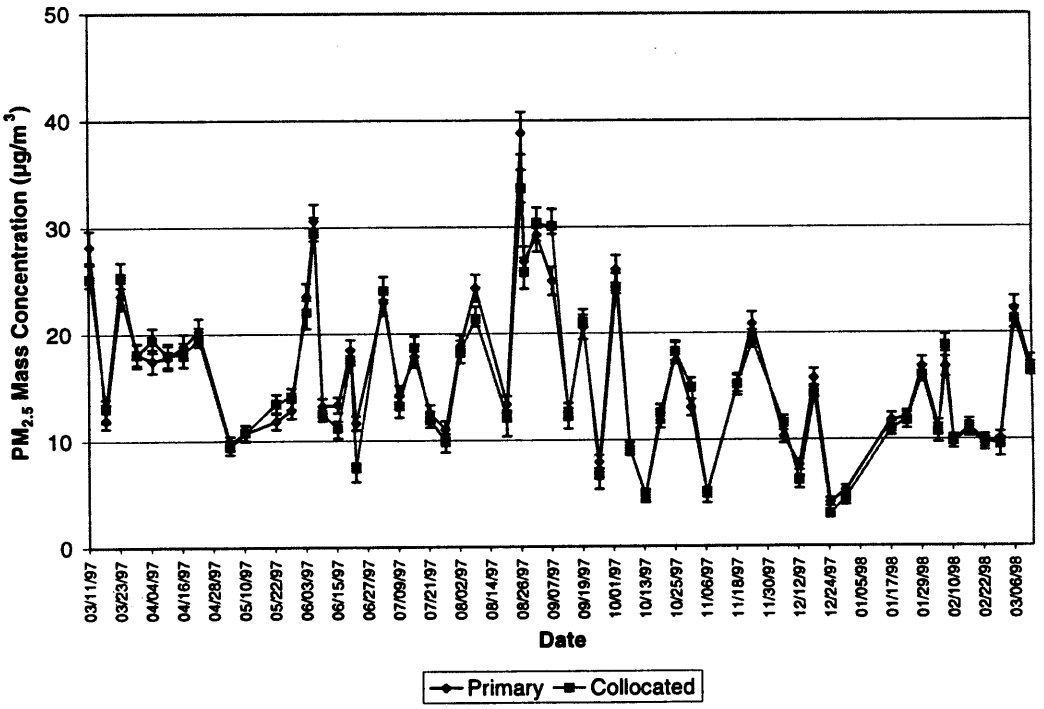


Figure 3-5. Scatter plot of indoor versus outdoor $PM_{2.5}$ mass measurements taken at the Shell Westhollow Technology Center site during the Texas $PM_{2.5}$ Sampling and Analysis Study between 09/13/97 and 03/12/98.

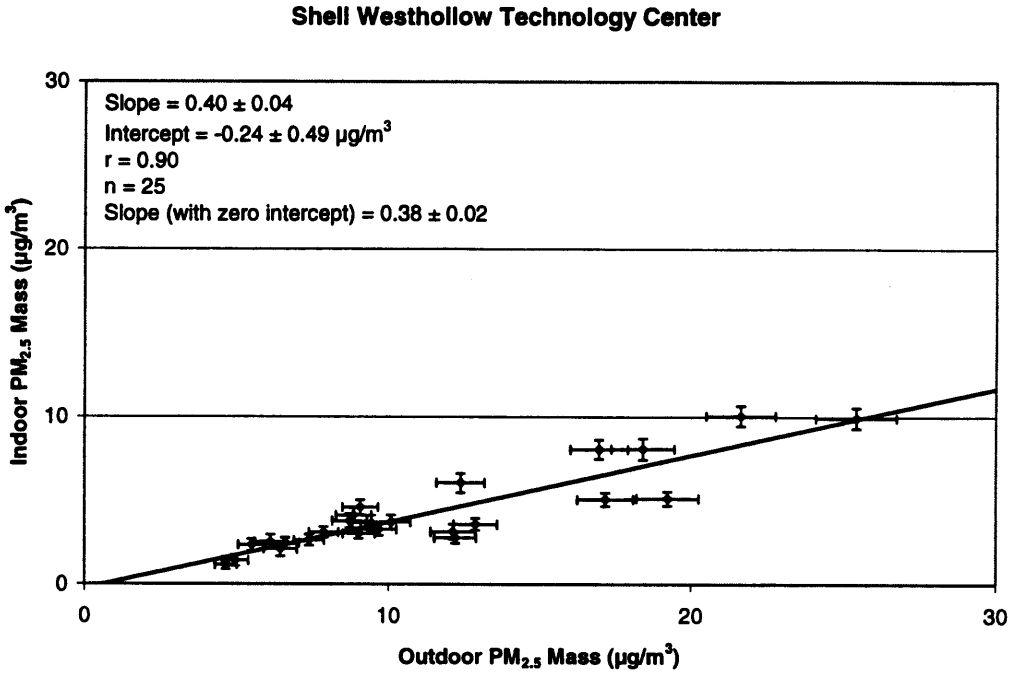


Figure 3-6. Collocated comparison of $PM_{2.5}$ mass measurements taken at the Shell Westhollow Technology Center site during the Texas $PM_{2.5}$ Sampling and Analysis Study between 09/13/97 and 03/12/98.

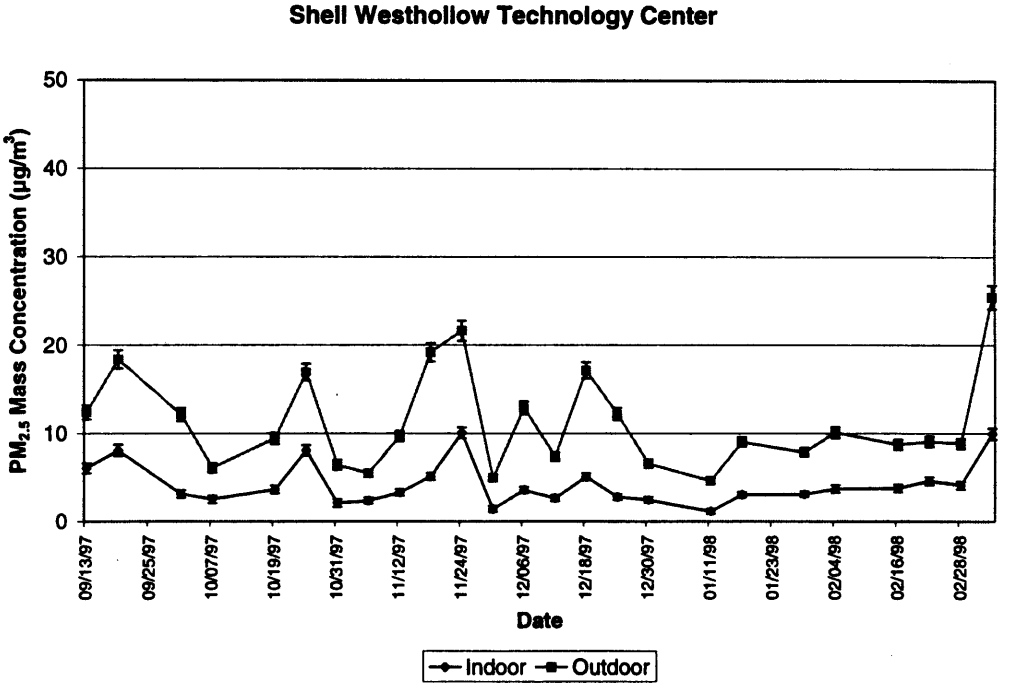


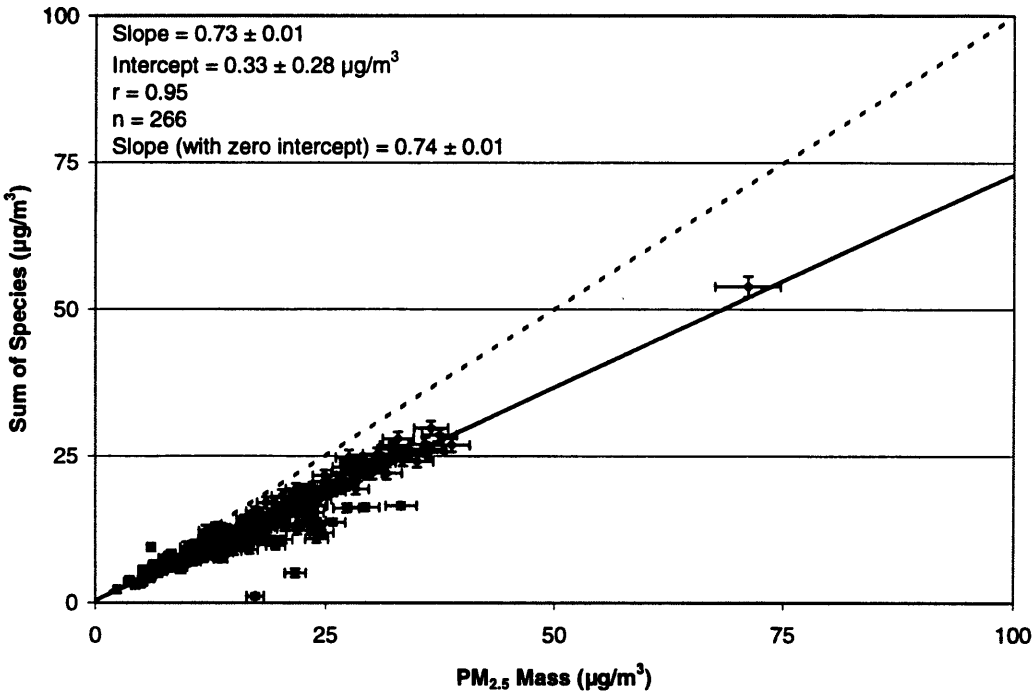
Table 3-4. Summary of scheduled days' $PM_{2.5}$ mass, PM_{10} mass, and $PM_{2.5}/PM_{10}$ ratio for all outdoor sites during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.

		Sites															
Parameter	Statistic	CC	DA	SA	EP[a]	H3	H7	HB	HC	HG	HM	HT	HW	HC-CO	HT-CO	H3-CO	SM
$PM_{2.5}$	N_{act}	53	57	53	51	56	57	50	57	24	58	58	56	20	14	19	25
	N_{exp}	62	62	62	62	62	62	62	62	32	62	62	62	22	18	22	32
	%Compl	85.5	91.9	85.5	82.3	90.3	91.9	80.6	91.9	75.0	93.5	93.5	90.3	90.9	77.8	86.4	78.1
	Mean	10.6	14.6	10.4	14.3	15.9	13.5	14.3	16.3	10.3	13.6	12.9	12.6	16.8	11.8	15.3	12.7
	StdDev	4.6	6.4	4.9	10.7	6.4	6.3	7.2	7.1	5.4	6.3	6.7	6.0	7.2	5.7	6.3	4.9
	CV	43.7	44.1	47.3	75.0	40.0	46.4	50.2	43.4	52.6	46.7	52.0	47.7	42.9	48.7	41.4	38.2
	Min	3.5	3.1	3.7	4.1	5.5	6.0	4.4	4.8	4.3	4.0	3.8	3.8	4.9	3.0	9.5	5.7
	Max	20.6	32.9	21.8	71.2	38.8	35.9	36.3	36.6	22.6	32.3	31.0	33.5	30.3	23.5	33.7	23.0
PM_{10}[a]	N_{act}	58	59	60	56	61	59	51	58	25	59	57	51	58	57	61	30
	N_{exp}	62	62	62	62	62	62	62	62	32	62	62	62	62	62	62	32
	%Compl	93.5	95.2	96.8	90.3	98.4	95.2	82.3	93.5	78.1	95.2	91.9	82.3	93.5	91.9	98.4	93.8
	Mean	32.9	30.1	21.9	29.0	32.3	28.1	29.1	48.8	26.2	29.9	23.6	22.6	48.8	23.6	32.3	23.6
	StdDev	17.3	11.6	10.3	8.9	15.5	12.1	14.3	25.2	23.1	16.7	10.8	12.7	25.2	10.8	15.5	13.9
	CV	52.4	38.7	47.0	30.7	48.0	43.0	49.1	51.6	88.2	55.6	46.0	56.4	51.6	46.0	48.0	59.0
	Min	14	14	10	16	16	12	13.4	16	10	12	12	11	16	12	16	11
	Max	78	64	58	144	82	73	74	137	90	84	57	62	137	57	82	65
$PM_{2.5}/PM_{10}$ Ratio	Nact	50	54	52	55	55	55	44	54	18	55	51	45	19	13	19	24
	Nexp	62	62	62	77	62	62	62	62	32	62	62	62	22	18	22	32
	%Compl	80.6	87.1	83.9	71.4	88.7	88.7	71.0	87.1	56.3	88.7	82.3	72.6	86.4	72.2	86.4	75.0
	Mean	0.37	0.54	0.51	0.45	0.62	0.63	0.61	0.43	0.56	0.54	0.68	0.65	0.47	0.67	0.60	0.70
	StdDev	0.14	0.14	0.14	0.11	0.15	0.16	0.18	0.18	0.21	0.18	0.17	0.17	0.17	0.16	0.18	0.15
	CV	36.6	25.8	28.1	24.9	24.0	24.6	28.7	41.7	37.8	32.2	24.9	25.6	37.1	23.2	29.4	21.4
	Min	0.14	0.23	0.24	0.22	0.23	0.30	0.24	0.18	0.23	0.20	0.33	0.29	0.21	0.45	0.29	0.31
	Max	0.66	0.92	0.80	0.76	0.90	0.91	0.96	0.94	0.99	0.93	1.00	0.98	0.86	0.95	0.90	0.93

Does this apply to the data as well?

[a] PM_{10} values for El Paso are reported in $\mu g/m^3$ at standard conditions for calendar years 1997 and 1998. For all other sites, PM_{10} values are reported in $\mu g/m^3$ at standard conditions for 1997 and at ambient conditions for 1998. The change in reporting conditions for PM_{10} in 1998 was a result of changes to the PM_{10} NAAQS in 1997. The difference for standard versus actual conditions at all sites except El Paso was found to be less than the measurement uncertainty. For El Paso, the difference was sometimes greater than measurement uncertainty, and thus, standard conditions were used for 1998 to be consistent with the units used in 1997.

Figure 3-7. Scatter plots of sum of species versus mass for $PM_{2.5}$ measurements acquired at all sites during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.



3.3.3 Physical Consistency

The composition of chemical species concentrations measured by different chemical analysis methods can be examined. Physical consistency was tested for: 1) sulfate versus total sulfur, 2) soluble potassium versus total potassium, 3) ammonium balance, and 4) anion and cation balance.

3.3.3.1 Sulfate versus Total Sulfur

Sulfate ($SO_4^=$) was acquired by ion chromatography (IC) analysis on quartz-fiber filters, and total sulfur (S) was obtained by x-ray fluorescence (XRF) analysis on Teflon-membrane filters. The ratio of sulfate to total sulfur should equal "three" if all of the sulfur were present as soluble sulfate. Figure 3-8 shows scatter plots of sulfate versus sulfur of the $PM_{2.5}$ measurements. Good correlation (r = 0.97) and an average ratio of 2.8 was found for these measurements, which indicates that the majority of the $PM_{2.5}$ sulfur was present as sulfate.

Two outliers were found – one at the San Antonio (SA) site on 08/26/97 and the other at the H7 site on 09/13/97. Analyses of these samples were verified, and the filters were correctly labeled and the IC and XRF spectra showed no anomalies. Both outliers had field flags indicating damaged quartz filters, which could explain the low relative sulfate concentrations.

Figure 3-8. Scatter plots of sulfate versus total sulfur for $PM_{2.5}$ measurements acquired at all sites during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.

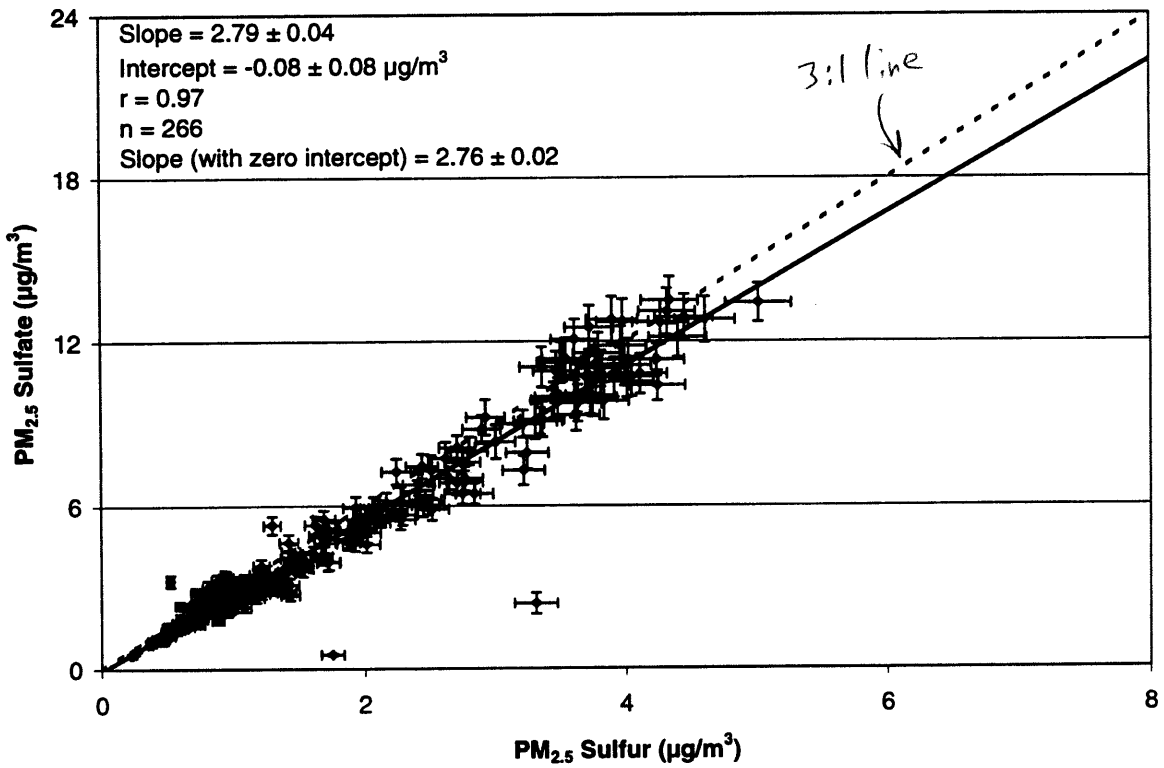


Fig. 3-9 shows a bimodal process. What is the reason?

3.3.3.2 Soluble Potassium versus Total Potassium

Soluble potassium (K^+) was acquired by atomic absorption spectrophotometry (AAS) analysis on quartz-fiber filters, and total potassium (K) was acquired by XRF analysis on Teflon-membrane filters. Since potassium concentrations are often used as an indicator of vegetative burning, it is important to assure the validity of the K^+ measurement.

Figure 3-9 shows that the data pairs are scattered, but they are well within the measurement uncertainties. The regression statistics reported a moderate correlation coefficient ($r = 0.80$) and insignificant intercept ($b < 0.01$ µg/m^3). Forcing zero intercepts gives a K^+/K ratio of 0.63. This analysis shows that K^+ concentrations are quite low in the study area, even though an average of 60% of the total potassium is in its soluble state.

3.3.3.3 Ammonium Balance

Ammonium nitrate (NH_4NO_3), ammonium sulfate ($[NH_4]_2SO_4$), and ammonium bisulfate (NH_4HSO_4), are the most likely nitrate and sulfate compounds to be found in Texas.

Figure 3-9. Scatter plots of soluble potassium versus total potassium for $PM_{2.5}$ measurements acquired at all sites during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.

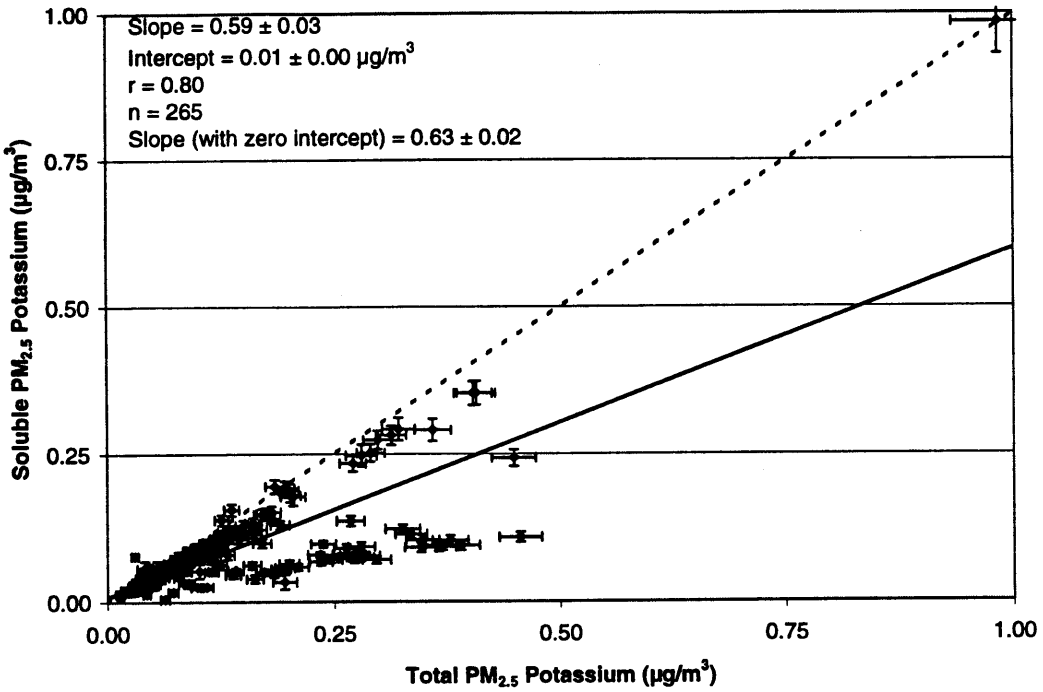
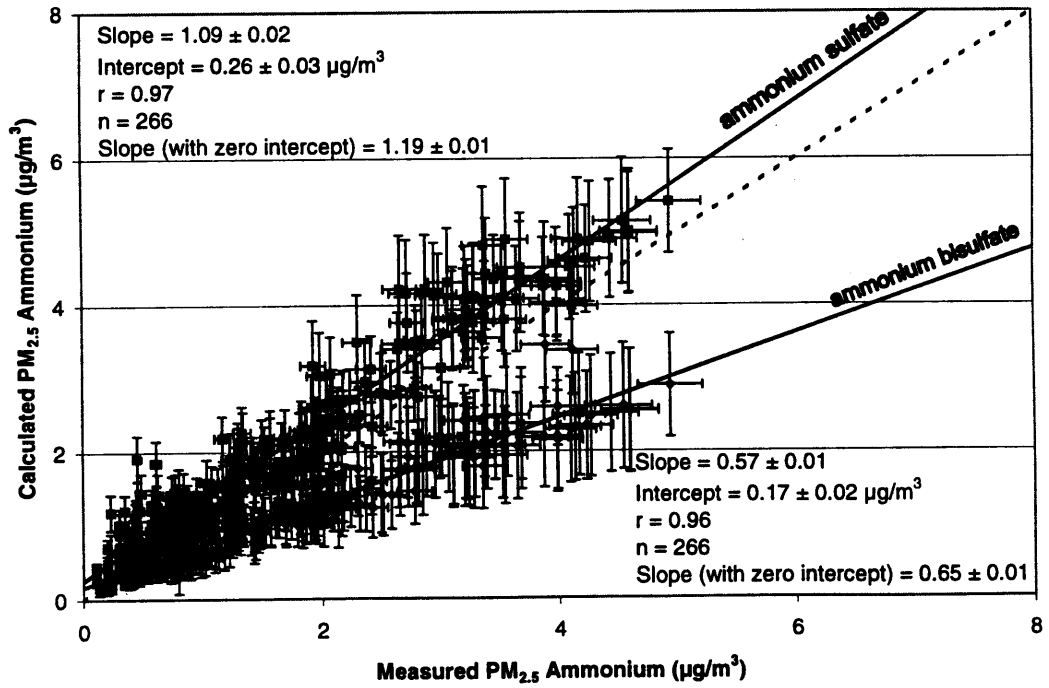


Figure 3-10. Scatter plots of calculated ammonium versus measured ammonium for $PM_{2.5}$ measurements acquired at all sites during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.



Some sodium nitrate ($NaNO_3$) and/or sodium sulfate (Na_2SO_4) may also be present at the coastal sites (HG, CC, and SM). Ammonium (NH_4^+) can be calculated based on the stoichiometric ratios of the different compounds and compared with that which was measured. In Figure 3-10, ammonium is calculated from nitrate and sulfate, assuming that all nitrate was in the form of ammonium nitrate and all sulfate was in the form of either ammonium sulfate (i.e., calculated ammonium = [0.38 × sulfate] + [0.29 × nitrate]) or ammonium bisulfate (i.e., calculated ammonium = [0.192 × sulfate] + [0.29 × nitrate]). These calculated values were compared with the measured values for ammonium.

With a few exceptions during the study period, Figure 3-10 shows excellent agreement for $PM_{2.5}$ ammonium with a correlation coefficient exceeding of 0.97 when ammonium sulfate was assumed, and exceeding 0.96 when ammonium bisulfate was assumed. The slopes in Figure 3-10 were 1.09 assuming ammonium sulfate, and 0.57 assuming ammonium bisulfate. These data imply that a majority of the sulfate was neutralized and in the form of ammonium sulfate during the study period between 03/11/97 and 03/12/98.

3.3.3.4 Anion and Cation Balance

During the study, anions were acquired for chloride, nitrate, and sulfate by IC analysis. Cations were acquired for soluble sodium and soluble potassium by AAS, and for ammonium by AC. All of the anion and cation samples were collected on quartz-fiber filters. The anion and cation balance in Figure 3-11 demonstrates that these ionic measurements are highly correlated ($r > 0.94$) with a slope of ≥ 0.98. As shown in Figure 3-11, most of the data points fell within one standard deviation of the one-to-one line. Forcing zero intercepts shows that most of the cations can be balanced with anions on a molar equivalent basis within ±13% of unity.

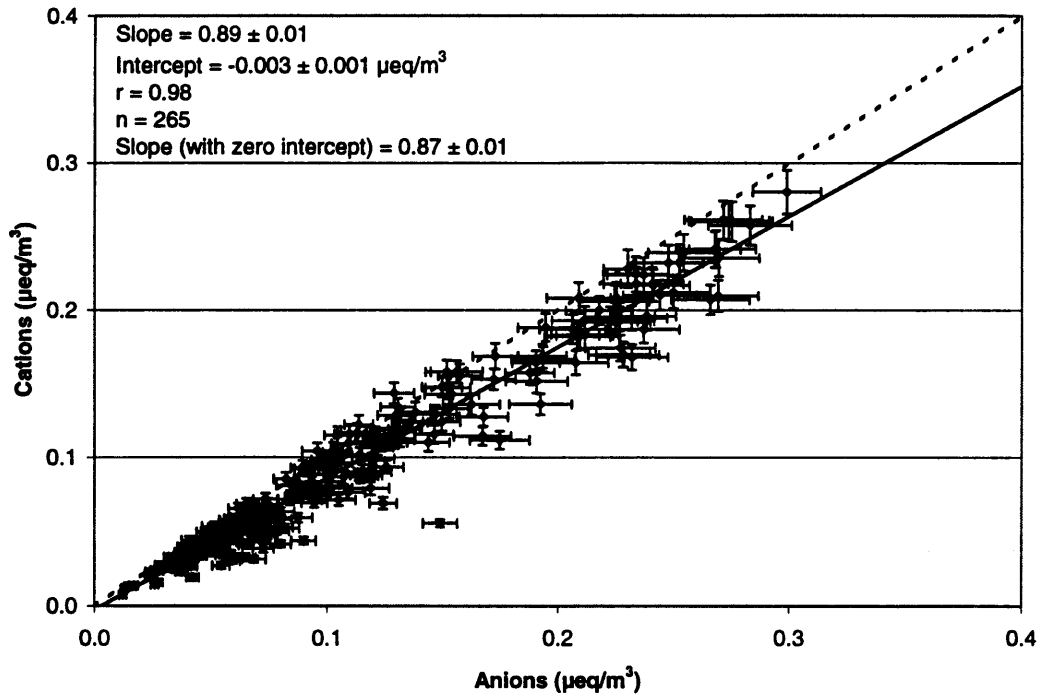



Figure 3-11. Scatter plots of cations versus anions for $PM_{2.5}$ measurements acquired at all sites during the Texas $PM_{2.5}$ Sampling and Analysis Study between 03/11/97 and 03/12/98.