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Office of Air Quality
Planning and Standards
Research Triangle Park, NC 27711

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# Final Report
# Evaluation of $PM_{2.5}$ Speciation Sampler Performance and Related Sample Collection and Stability Issues

# FINAL REPORT

# Evaluation of $PM_{2.5}$ Speciation Sampler Performance and Related Sample Collection and Stability Issues

for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Emissions, Monitoring, and Analysis Division (MD-14)
Research Triangle Park, North Carolina 27711

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# EXECUTIVE SUMMARY

$PM_{2.5}$ chemical speciation sampling is included in the monitoring requirements promulgated as part of the $PM_{2.5}$ National Ambient Air Quality Standards. Under this requirement EPA will establish a $PM_{2.5}$ chemical speciation network of approximately 50 core NAMS for routine speciation monitoring. This network will be used to provide a nationally consistent set of data for the assessment of trends and provide long term characterization of PM constituents. This network will also be used as a model for up to 250 additional speciation sites established by the States for information that may aid the development of State Implementation Plans. A vital consideration for these PM speciation monitoring sites is data comparability. EPA initially chose three samplers for consideration under the National Sampler Contract. The data under consideration in this study were collected from February 2000 through July 2000 at 13 sites across the nation with co-located samplers, in an effort to evaluate the consistency of these three samplers. Further data were collected in August 2000 to examine some special issues.

The analysis results detailed in this report are the end result of three important efforts. First, the data underwent a careful screening for outliers, or unusual data, so that results would not be skewed by these values. Next, considerable effort was put into graphical analysis of the data to determine what factors should be considered in the assessment of data comparability. (The results of these first two efforts are detailed in the appendices.) The third effort detailed in this report was statistical modeling based on the outcomes of the first two efforts.

The following are some of the major findings:

- Within a site the data show fairly consistent biases between co-located samplers on a log scale.

- There are significant site to site differences in: the number of days with outliers, the variability of parameters, the relationship between samplers, etc. These first two points are assumed in the remaining items.

- The measured PM2.5 mass was compared with co-located FRM measurements. Seventeen out of 24 of the samplers met the Expert Panel data objective of an $R^2$ value of at least 0.9 in a linear regression of the mass values against the FRM measurement. Deviations from this criteria appear to be caused by site influences that affect all the monitors at a site, rather than differences among sampler types.

- Only half of the samplers met the Expert Panel data objective that the ratio of the FRM mass mean to the speciation sampler mass mean be at least 0.9 and at most 1.1. The ratios tested strongly dependent on both site and sampler type. In all cases with co-located FRMs, the means for the mass followed the following ordering: URG $\leq$ Andersen $\leq$ MetOne. Six of the seven URG means were less than the corresponding FRM mean, all eight MetOne means were greater than the corresponding FRM mean, and six of the nine Andersen means were greater than the corresponding FRM mean.

- The concentration ordering noted for the mass applies to most of the species, namely URG $\leq$ Andersen $\leq$ MetOne. Moreover, while parameter specific, the percent of the time that this relation holds is consistent across sites. The exceptions to this ordering are chlorine, zinc, ammonium, and sulfate. For each of these exceptions, the percent of the time that the sampler types have one relationship or another varies by site. Of the species that do follow the general ordering above, only the nitrate data showed site to site differences in the percent of the time one sampler type is above another.

- For all species the magnitude of the biases between sampler types is strongly site dependent from a statistical point of view. The magnitudes are summarized in the appendix by site and species so that the practical significance can be assessed.

- The variability found in the sampling precision across sampler types is probably due to site influences, but is probably not generally of any practical concern.

- The blanks generally do not show site to site differences. The trip blanks and field blanks are generally about the same. The URG blanks tend to be the cleanest except for nitrate. Nearly all of the “dirtiest” 25 percent of the blanks were from the URG samplers. The practical difference among the sampler types needs to be assessed separately.

- The five special experiments all suffer from a lack of data. As such, modeling results are not robust against the inclusion or exclusion of outliers. Assuming that the outliers have been properly identified, then there is little or no significant effect on sulfate, nitrate, elemental carbon, or organic carbon concentrations found with leaving filters in the sampler for an extended period either before or after sampling. The only statistically significant difference found was that blanks left for a week in the sampler collected on average an extra 3.25 micrograms of organic carbon (before sampling).

- Qualitatively, both the face velocity experiment and the sampler to sampler comparisons suggest that measurements of carbon from low volume sampling yield higher concentrations than high volume sampling. The data from the sampler to sampler comparisons showed more consistency than the data from the face velocity experiment. (Carbon is measured from the Quartz filter. In the sampler to sampler comparisons the quartz filter flow rates were 16.7 lpm for the URG, 7.3 lpm for the Andersen, and 6.7

lpm for the MetOne. The face velocity experiment used Andersen samplers with flow rates of 7.3 lpm and 16.7 lpm.)

# 1.0 INTRODUCTION

Chemical speciation of $PM_{2.5}$ is included in the monitoring requirements set forth in the ***Federal Register*** (62 FR 38763). As a result EPA will establish a $PM_{2.5}$ chemical speciation network of approximately 50 NAMS, the "Trends" network, for routine speciation monitoring to provide nationally consistent data for the assessment of trends and long-term characterization of the metals, ions, and carbon constituents of $PM_{2.5}$. This network will be a model for the chemical speciation efforts of the States, up to 250 SLAMS, to be used for State Implementation Plans (SIPS).

Data comparability is a primary concern for the Trends network. A multi-sampler field evaluation study of co-located samplers was conducted from February 2000 through July 2000, with additional special studies in August of 2000, to evaluate consistency (referred to as the mini-Trends network). This report details the analyses to assess comparability of the various methods. The work was divided into three tasks corresponding to the data involved.

The first task worked with the routine monitoring data collected from February 2000 through July 2000 at 13 sites with co-located speciation samplers. Table 1.1 shows the site locations and the number of each sampler type at those locations. Table 1.2 shows the 14 species examined in the study.

## Table 1.1 Tasks 1 and 2 Sampling Sites and Samplers

| Region | State | Site | Number of Samplers | | | Start Date |
|---|---|---|---|---|---|---|
| | | | MetOne | Andersen | URG | |
| 1 | MA | Boston (Roxbury) | | 2 | 1 | 2/9/2000 |
| 2 | NY | Bronx Garden | 2 | 1 | | 2/9/2000 |
| 3 | PA | Philadelphia | | 1 | 1 | 2/9/2000 |
| 4 | FL | Tampa-St. Petersburg | 1 | | 1 | 2/9/2000 |
| 5 | IL | Chicago | | 1 | 1 | 2/9/2000 |
| 6 | TX | Houston | | 1 | 1 | 2/9/2000 |
| 7 | MO | St. Louis (Blair St.) | 1 | 1 | | 2/9/2000 |
| 8 | ND | Bismarck | 1 | | 1 | 2/9/2000 |
| | UT | Salt Lake City | 1 | 1 | | 2/9/2000 |
| 9 | AZ | Phoenix | 1 | | 2 | 2/9/2000 |
| | CA | Fresno | 1 | 1 | | 2/9/2000 |
| 10 | OR | Portland-Vancouver | 1 | 1 | | 2/9/2000 |
| | WA | Seattle (Beacon Hill) | 1 | | 1 | 2/9/2000 |

## Table 1.2 Task 1 and 2 Study Parameters

| Study Parameters | | | |
|---|---|---|---|
| 1. | $PM_{2.5}$ Mass | 2. | Silicon |
| 3. | Aluminum | 4. | Zinc |
| 5. | Calcium | 6. | Ammonium |
| 7. | Chlorine | 8. | Organic Carbon |
| 9. | Iron | 10. | Nitrate |
| 11. | Lead | 12. | Elemental Carbon |
| 13. | Tin | 14. | Sulfate |

The second task examined the field and trip blanks associated with these data and was also restricted to the parameters listed in Table 1.2.

Finally, the third task examined the results from five experiments run in August 2000 to investigate issues related to sequential sampling and sample collection methods. These special studies were restricted to either organic and elemental carbon or sulfate and nitrate.

The analyses generally followed three phases: data validation and outlier detection, mostly graphical exploratory analyses, and statistical modeling and testing. The methods and results of the first two phases as applied to Tasks 1 and 2 are briefly discussed in Section 2.0, with additional details given in the appendices. (See the accompanying CD for the collection of the main graphical output.) Section 3 examines the results of the modeling phase for Task 1 data, the routine data from the 13 sites. Section 4 examines the modeling results from the Task 2 data, the field and trip blanks collected with the routine data. Section 5 examines each of the five special experiments and ends with an overall assessment based on those experiments. Section 6 gives some guidance toward combining all of the results into a coherent picture.

# 2.0 OVERVIEW OF THE DATA VALIDATION AND EXPLORATORY ANALYSES

The first two phases of the analysis involved data validation and exploratory analysis. The primary output from this activity was to update the database with a series of flags that indicated unusual or questionable data and guided the modeling phase. A list of the flagged data has already been provided to EPA in electronic form, so that information is not duplicated here. Rather, procedures used to flag the data are described here.

## 2.1 DATA VALIDATION AND FLAGGING

While Battelle was carrying out this analysis, Research Triangle Institute (RTI managed the data collection) was also completing a review and flagging of the data. They also produced a list of data that they felt should not be included in any analysis. These data were removed before any modeling, but were included in most of the exploratory analyses. Their flagging was based on the historical record of the data. They flagged data with extremely low mass values (approximately the bottom 1 percent), data with inconsistent reconstructed mass balance, and data with an extreme anion to cation ratio (approximately the top and bottom 1 percent). The RTI flagged data is intended for flagging as “null” in AIRS.

Battelle flags were based on either a self consistency check of the data from a given sampler on a given day, or on a consistency check between co-located samplers. The self consistency checks were based on comparisons of the species mass or a partial reconstructed mass to the measured mass. If either a species mass or the partial reconstructed mass were significantly larger than the measured mass then a flag was generated (and applied to all the data for the particular sampler and day). Initially another flag was generated based on the ratio of a parameter mass to the measured mass that was extreme in terms of the number of inter quartile ranges from the median. This flag always coincided with one or more of the others and was not included in the final list of flags.

The sampler to sampler consistency flags were based on comparing the difference between the high and low value for co-located measurements of a parameter (including FRM mass). For each site these differences might all be very small or large with considerable variation. The flags indicate the extremes for the site. Hence, a difference that was flagged at one site may not be flagged at another. The flags were combined into an alphanumeric code that indicated which parameter(s) caused the flag. As in the above, if a flag was generated, then all the associated data for that day was flagged. After the RTI flagged data was removed, there were 45 out of 1,072 site-day combinations with data that were flagged with discrepancies in at least two species.

In most of the modeling analyses the modeling was done both with and without the flagged data. Some modeling was also done with certain sites removed, since the outliers tended to cluster by site. For the most part there was not an appreciable difference in the outcomes, because there is generally enough data to average out the outliers. All of the results and summaries referenced in this report are based on using data from all sites. As noted, the results and summaries are either based all non RTI flagged data (i.e., all valid data) or data that were not flagged by either Battelle or RTI.

## 2.2 EXPLORATORY ANALYSES

Many of the graphs generated during the exploratory analysis for Tasks 1 and 2 served multiple purposes. The main examples are in the appendix. The primary criteria for including the specific examples chosen for Appendix A was either to demonstrate outliers or trends within the data. In the latter case, the main concern was influences on the differences in the measured concentrations of the 14 study parameters. So while temperature certainly is a factor related to the magnitude of several of the species, it was not found to have any appreciable relationship to the difference between one sampler reading and another. Nor was the difference between temperatures reported for co-located samplers related to the difference in the concentrations. See the appendix for a list of examples and descriptions for how the graphs were generated.

One of the key outcomes of the exploratory analysis was the decision to do the main modeling on the logarithms of the concentrations rather than the raw concentrations. There are two reasons for using a log-scale. The primary reason is that for many of the parameters and sites the biases between co-located samplers are constant on the log-scale. Hence, the log-scale is more appropriate for describing the typical differences observed. The second reason for using the log-scale is that deviations from the mean are more symmetric on this scale. The statistical tests of significance are derived from normality assumptions. The tests are more robust to deviations from the normality assumptions when the random errors are symmetrically distributed.

# 3.0 ANALYSES OF THE ROUTINE DATA

There were three main types of analyses performed on the routine data. (Additional techniques were applied to the measured mass. See Section 3.1.) First, the concentrations for each parameter were studied with analysis of variance (ANOVA) models. The ANOVA models were applied to log transformed data, so deviations from the mean indicate multiplicative differences. The results of this investigation were site dependent. The second set of analyses examined an indicator of which sampler type gave the higher value. The results from this investigation were generally independent of the site, with the same qualitative result for most parameters. The third set of analyses examined the relative amounts of constituent parameters with an ANOVA model. The results of these analyses show that generally there are statistically significant differences in the relative composition among the sampler types.

The first ANOVA model started with modeling the concentration value for a parameter at a given site and day from a particular sampler as having an overall mean with deviations from the mean, which could be attributed to random daily shifts, either of the MET variables, temperature and barometric pressure, or the sampler's deviations from the daily means in temperature or pressure. As expected from the exploratory analyses, these were statistically insignificant. In the further analyses the MET variables were dropped from the model.

The next set of ANOVA analyses modeled the concentration value for a parameter at a given site and day from a particular sampler as having an overall mean with deviations from the mean, which could be attributed to site dependent random daily shifts, an overall site mean, a sampler type bias, and sampler type-site interaction. The sampler type-site interaction allows the model to assume that the bias of the sampler type is dependent on the site. These were modeled both assuming a common variance for all three sampler types, and assuming that the residual error (measurement error) for the three sampler types could be different.

While the statistical test for any difference between the relative sizes of the residual errors was significant (i.e., the statistical tests indicate that there is a difference in the CVs among the sampler types), this should be tempered with two observations. First, the differences in the CVs may not be of any practical significance, but, more importantly, the difference from site to site is generally much greater than that of sampler to sampler. The difference in the precision may be more of a reflection of the differences among the sites than that of the samplers, where a given sampler type may have by chance been more frequently situated at more variable sites. Unfortunately, the statistical models assuming different error variances by site did not converge, so it was not possible to test which was the more important factor in the precision estimates.

The model(s) described above was run using all valid data (data not flagged by RTI) above the MDL, using all the valid data except the data from Boston and Phoenix[1], and finally with all of the valid data excluding the Boston and Phoenix data and any data that were flagged in the outlier analysis. The results for each case were similar, only the results from the first case are reported.

The sampler type-site interactions were statistically significant. This indicates, for example, that how a URG compares to a MetOne depends on the site. The exploratory analysis and a close look at the estimates from the models indicates a strong pattern in how the sampler types compared with each other. While the scale of the deviations was strongly site dependent, the qualitative direction was quite uniform. To investigate the strength of this observation without comparing the size of any relative bias, the concentrations were modeled in a different manner in addition to the ANOVA analyses.

For each pair of data points, an indicator function was modeled. This yielded estimates of how often a URG measurement will be less than an Andersen measurement in a side by side comparison. To do this for each site with two samplers, the samplers were labeled A or B. If the site had a MetOne sampler, the MetOne was labeled A and the other was labeled B. If the site only had an Andersen and

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[1] These two sites had more data with multiple flags for large sampler to sampler inconsistencies than the other sites.

a URG sampler, then the Andersen was labeled A and the URG was labeled B. (So the URGs are always labeled B.) The indicator used was 1 if sampler B had a concentration value greater than the value from A. If there was no bias between the samplers, then on average the indicator should be 1 about half of the time. The probability that the indicator is 1 was modeled to have a different probability for each site (with logistic regression and the standard link for the binomial relationship), and this model was compared with a model that had separate probabilities for each sampler type pair (the three possibilities were MetOne-Andersen, MetOne-URG, and Andersen-URG). The statistical test for the fit of the more general model (site dependent probabilities) versus the sampler type specific probabilities shows that for most parameters, the same probabilities for sampler type pair are observed across sites. However, the probabilities associated with a sampler type pair are usually not 0.5.

Together, these analyses indicate that there is a clear relative bias between the sampler types, with URG < Andersen < MetOne for most parameters. They also indicate that the precision of the samplers is more dependent on site than sampler type. (If not, then the sites with a greater mean difference between the samplers would have had significantly different probabilities for concentration A < concentration B. Since this was not the case, it must be that the variability increases with the relative bias.) Hence, the results in Section 3.4 should be taken as being an indication of the expected site to site variability in precision rather than differences in sampler precision due to sampler type.

## 3.1 THE MEASURED $PM_{2.5}$ MASS CONCENTRATION

In the case of mass, there are co-located Federal Reference Method (FRM) measurements to compare with the speciation sampler measurements. This section has comparisons of the speciation sampler measurements to the FRM measurements based on the Expert Panel recommendations. Section 3.2 has the results for the analyses that were done for each of the parameters in this study.

The Expert Panel for the EPA Speciation Network set performance criteria for the mass concentration based on a linear regression with co-located FRM measurements. The criteria for a candidate method was: (1) the linear regression should have an $R^2$ value at least 0.9 and (2) the ratio of the candidate sampler concentration mean to the FRM mean should be between 0.9 and 1.1. Moreover, these criteria should be based on at least twenty 24-hour samples. Table 3.1 shows the results for the linear regression and the ratio of the sample means for each of the twenty-four samplers studied. In each case, at least twenty-one 24-hour samples were used to obtain the results. The results are not independent from each other in that the same set of FRM values are used for all the samplers at a site. The table shows that essentially all but seven of the samplers met the $R^2$ criteria (in one case the $R^2$ rounds up to 0.9). It also shows that the Andersen samplers faired both the best and the worst, and that the ratio for all of the URG samplers is strictly less than the ratio for all of the MetOne samplers.

The ratio and the $R^2$ values were tested for statistically significant site differences, sampler type differences, and differences that depend jointly on the site and sampler type. To better meet statistical assumptions the $R^2$ values were transformed[2] into the value $Y = ½ \ln((1+R)/(1-R))$. For both the ratio of the site means and the Ys, any differences due to the site and sampler type tested independent of each other.

The $R^2$ values have a significant site dependency (p-value = 0.0190) and a marginally significant sampler type dependancy (p-value = 0.0769). The site dependancy is certainly due in part to the fact that the same FRM results are used for all of the sampler comparisons at a site. If the FRM values are incorrect, then one expects the correlation to degrade. This may be part of the problem at the Boston site. Consider Figure 3.4, note that there are pairs of values for which the two Andersen samplers have the same mass value, but are different from the FRM value for the day. However, this would have the same effect on all of the samplers at a site and does not explain the discrepancies seen.

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[2] Hogg, R., and Tanis, E. (1977). Probability and Statistical Inference, Macmillan Publishing Company, Inc., New York, New York.

Hence, there must be other site effects that generally impact all of the samplers at a site. (See Figure 3.3.)

The ratio of the mean mass measured by the sampler versus the mean FRM mass is strongly dependent on both the site and the sampler type. Again, the common FRM values for a site contribute to the site effect, but there may be other site related effects as well. In this case, there is a very clear sampler type effect as well. All of the MetOne samplers have a ratio above 1. All except one of the URG samplers have ratios less than 1. Both of the above statements are somewhat confounded by the site effect. However, at all sites the URG means are less than the Andersen means, which in turn are less than the MetOne means. (See Figure 3.1.)

## Table 3.1 FRM to Speciation Sampler Regression Results, Sorted by the Ratio of the Mean Mass to the Mean FRM Mass.

| Site | POC | n | Intercept | Slope | R-squared | Ratio | Sampler |
|---|---|---|---|---|---|---|---|
| Boston | 7 | 24 | 0.228(.056) | 0.854(.056) | 0.914 | 0.874 | URG |
| Boston | 5 | 21 | 1.712(.109) | 0.750(.109) | 0.713 | 0.890 | Andersen |
| Bismark | 6 | 25 | 0.226(.046) | 0.862(.046) | 0.938 | 0.904 | URG |
| Chicago | 6 | 37 | -0.150(.035) | 0.928(.035) | 0.953 | 0.920 | URG |
| Boston | 6 | 23 | 3.896(.115) | 0.594(.115) | 0.559 | 0.927 | Andersen |
| Chicago | 5 | 37 | -0.272(.020) | 0.969(.020) | 0.986 | 0.953 | Andersen |
| Philadelphia | 6 | 24 | 0.907(.031) | 0.916(.031) | 0.975 | 0.984 | URG |
| Seattle | 6 | 39 | 0.314(.022) | 0.944(.022) | 0.981 | 0.987 | URG |
| Tampa | 6 | 32 | -1.668(.067) | 1.116(.067) | 0.903 | 0.990 | URG |
| Fresno | 6 | 26 | 0.463(.052) | 0.957(.052) | 0.934 | 1.010 | Andersen |
| Houston | 6 | 23 | 0.845(.034) | 0.959(.034) | 0.975 | 1.027 | URG |
| New York | 5 | 26 | 0.707(.024) | 0.984(.024) | 0.985 | 1.047 | Andersen |
| Tampa | 5 | 32 | 1.163(.061) | 0.973(.061) | 0.895 | 1.061 | MetOne |
| Philadelphia | 5 | 24 | 1.074(.028) | 0.990(.028) | 0.983 | 1.071 | Andersen |
| New York | 6 | 36 | 1.368(.023) | 1.014(.023) | 0.983 | 1.130 | MetOne |
| St.Louis | 6 | 37 | 2.927(.071) | 0.923(.071) | 0.830 | 1.137 | Andersen |
| St.Louis | 5 | 37 | 3.582(.091) | 0.878(.091) | 0.727 | 1.139 | MetOne |
| Fresno | 5 | 26 | 2.052(.102) | 0.916(.102) | 0.769 | 1.146 | MetOne |
| Houston | 5 | 23 | 3.248(.115) | 0.891(.115) | 0.742 | 1.150 | Andersen |
| Bismark | 5 | 25 | 1.700(.080) | 0.838(.080) | 0.826 | 1.154 | MetOne |
| Salt Lake | 6 | 23 | 1.025(.030) | 1.014(.030) | 0.982 | 1.156 | Andersen |
| New York | 7 | 37 | 1.539(.027) | 1.062(.027) | 0.978 | 1.186 | MetOne |
| Seattle | 5 | 39 | 1.329(.050) | 1.042(.050) | 0.920 | 1.223 | MetOne |
| Salt Lake | 5 | 23 | 1.916(.066) | 0.963(.066) | 0.910 | 1.229 | MetOne |

## Table 3.2 FRM to Speciation Sampler Regression Results, Sorted by the R-Squared Value.

| Site | POC | n | Intercept | Slope | R-squared | Ratio | Sampler |
|---|---|---|---|---|---|---|---|
| Boston | 6 | 23 | 3.896(.115) | 0.594(.115) | 0.559 | 0.927 | Andersen |
| Boston | 5 | 21 | 1.712(.109) | 0.750(.109) | 0.713 | 0.890 | Andersen |
| St.Louis | 5 | 37 | 3.582(.091) | 0.878(.091) | 0.727 | 1.139 | MetOne |
| Houston | 5 | 23 | 3.248(.115) | 0.891(.115) | 0.742 | 1.150 | Andersen |
| Fresno | 5 | 26 | 2.052(.102) | 0.916(.102) | 0.769 | 1.146 | MetOne |
| Bismark | 5 | 25 | 1.700(.080) | 0.838(.080) | 0.826 | 1.154 | MetOne |
| St.Louis | 6 | 37 | 2.927(.071) | 0.923(.071) | 0.830 | 1.137 | Andersen |
| Tampa | 5 | 32 | 1.163(.061) | 0.973(.061) | 0.895 | 1.061 | MetOne |
| Tampa | 6 | 32 | -1.668(.067) | 1.116(.067) | 0.903 | 0.990 | URG |
| Salt Lake | 5 | 23 | 1.916(.066) | 0.963(.066) | 0.910 | 1.229 | MetOne |
| Boston | 7 | 24 | 0.228(.056) | 0.854(.056) | 0.914 | 0.874 | URG |
| Seattle | 5 | 39 | 1.329(.050) | 1.042(.050) | 0.920 | 1.223 | MetOne |
| Fresno | 6 | 26 | 0.463(.052) | 0.957(.052) | 0.934 | 1.010 | Andersen |
| Bismark | 6 | 25 | 0.226(.046) | 0.862(.046) | 0.938 | 0.904 | URG |
| Chicago | 6 | 37 | -0.150(.035) | 0.928(.035) | 0.953 | 0.920 | URG |
| Houston | 6 | 23 | 0.845(.034) | 0.959(.034) | 0.975 | 1.027 | URG |
| Philadelphia | 6 | 24 | 0.907(.031) | 0.916(.031) | 0.975 | 0.984 | URG |
| New York | 7 | 37 | 1.539(.027) | 1.062(.027) | 0.978 | 1.186 | MetOne |
| Seattle | 6 | 39 | 0.314(.022) | 0.944(.022) | 0.981 | 0.987 | URG |
| Salt Lake | 6 | 23 | 1.025(.030) | 1.014(.030) | 0.982 | 1.156 | Andersen |
| New York | 6 | 36 | 1.368(.023) | 1.014(.023) | 0.983 | 1.130 | MetOne |
| Philadelphia | 5 | 24 | 1.074(.028) | 0.990(.028) | 0.983 | 1.071 | Andersen |
| New York | 5 | 26 | 0.707(.024) | 0.984(.024) | 0.985 | 1.047 | Andersen |
| Chicago | 5 | 37 | -0.272(.020) | 0.969(.020) | 0.986 | 0.953 | Andersen |

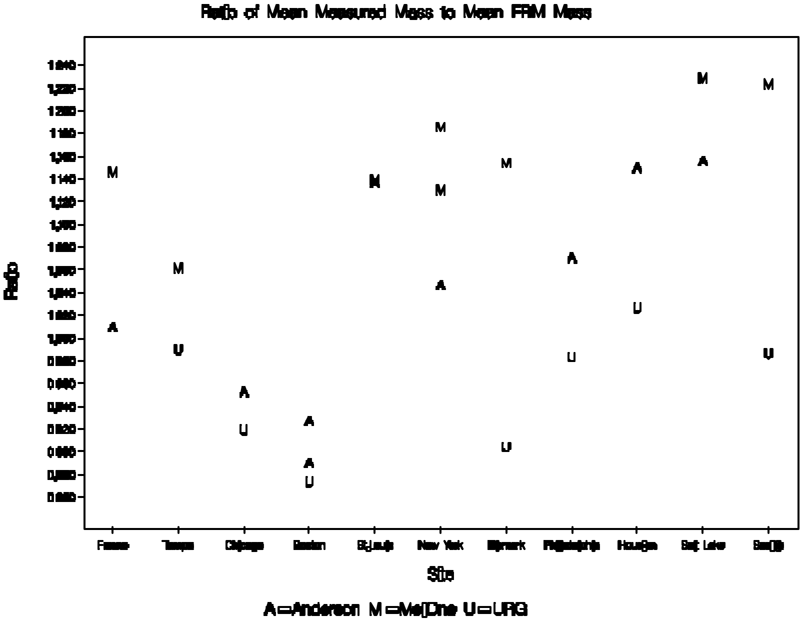


**Figure 3.1** Ratio of Mean Measured Mass to Mean Mass From a Co-located FRM.

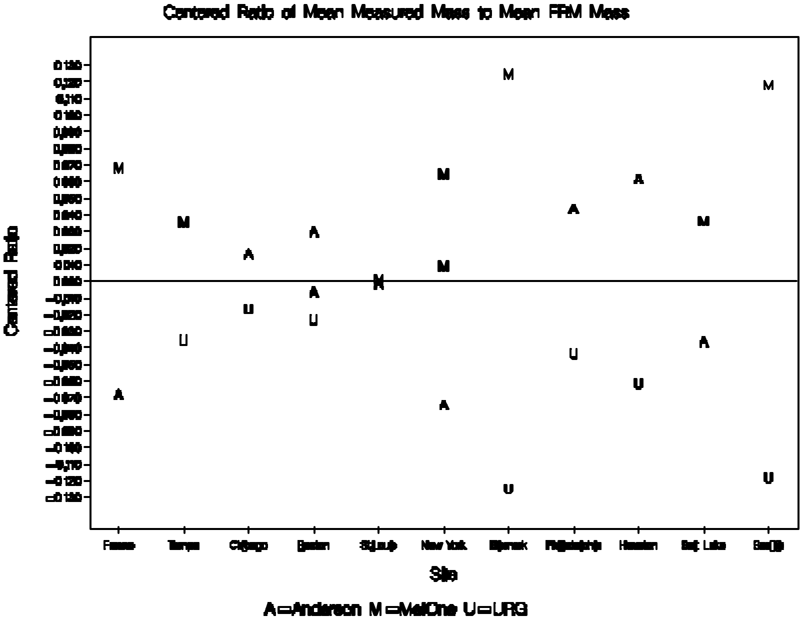


**Figure 3.2** The Relative Deviations of the Ratio of the Measured Mass to the Mean FRM Mass (the plotted values show the ratios minus the site mean).*

*Note that all of the MetOne values are above 0 and all of the URG values are below 0.

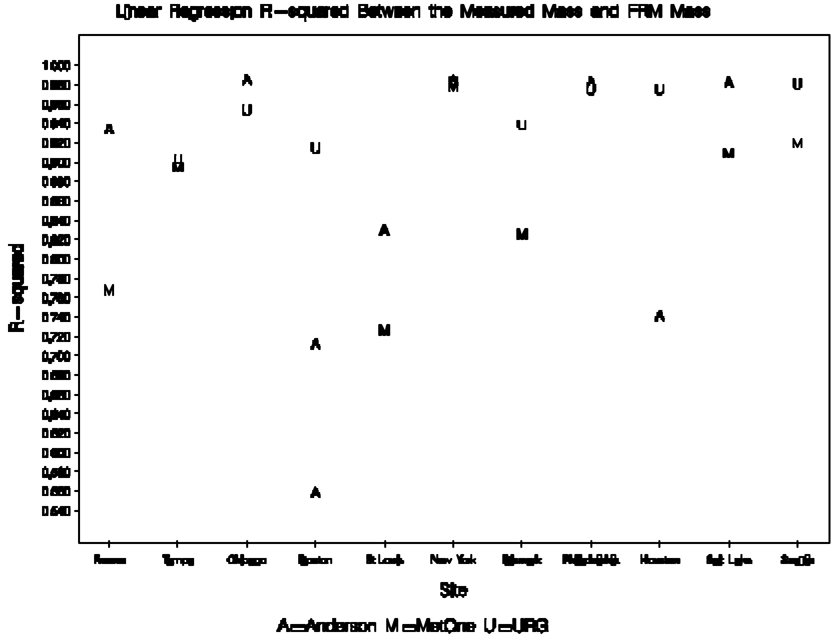


**Figure 3.3** **The Linear Regression R-squared with the Co-located FRM.**

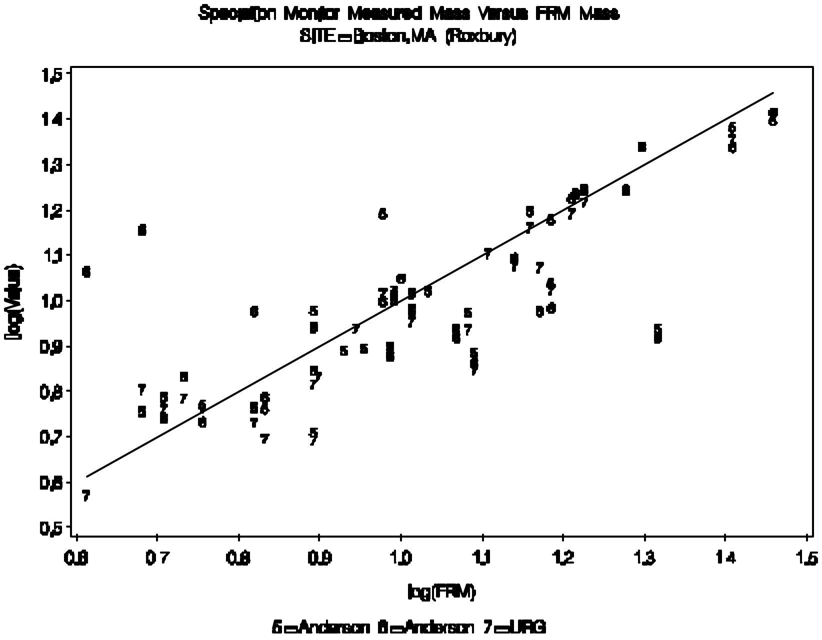


**Figure 3.4** **Speciation Sampler Measured Mass Versus a Co-located FRM Measurement.**

## 3.2 ROUTINE PARAMETER MEASUREMENTS

For each parameter the log-concentrations were modeled as follows. An individual value was treated as the sum of an overall mean, deviations from that mean based on the site, site specific deviations from the (site) mean due to the vendor, random site specific day-to-day variations from the site mean, and random measurement error. The site specific deviations due to a sampler type were tested to see if these were the same across all sites. The "average" sampler type and site deviations were tested to see if they were statistically different from zero.

Table 3.3 shows the p-values for these tests. A p-value less than 0.05 is generally considered significant. This general rule of thumb is often modified when many tests are being considered so that the overall error rate stays at 5 percent. In this case it does not matter, almost everything is highly significant. The conclusion of these tests is that individual samplers have statistically different relative biases among them and these biases are not consistent across sites or sampler types.

These results only indicate statistically significant differences. Hence, the differences are too large to be attributed to random chance alone. They do not indicate whether or not the differences are of practical significance. That requires expert judgement, typically in the form of DQOs . In the case of mass, the Expert Panel Recommendations can be used as a guide for assessing the practical significance of the differences. More generally, there are several tables given in Appendix B that summarize the findings from different points of view that should be used to evaluate the practical differences among the sampler types.

## Table 3.3 P-values for Tests of Significant Differences Among Sites, Sampler Types, and All Site-Sampler Type Combinations.

| Parameter | Estimated p-value* | | |
|---|---|---|---|
| | Site | Vendor | Site*Vendor |
| PM2.5 Mass | <.0001 | <.0001 | 0.0001 |
| Aluminum | <.0001 | <.0001 | <.0001 |
| Calcium | <.0001 | <.0001 | <.0001 |
| Chlorine | <.0001 | <.0001 | <.0001 |
| Iron | <.0001 | <.0001 | <.0001 |
| Lead | <.0001 | <.0001 | 0.0002 |
| Tin | 0.0031 | <.0001 | 0.3095 |
| Silicon | <.0001 | <.0001 | 0.0005 |
| Zinc | <.0001 | <.0001 | <.0001 |
| Ammonium | <.0001 | <.0001 | <.0001 |
| Organic Carbon | <.0001 | <.0001 | 0.0037 |
| Nitrate | <.0001 | <.0001 | 0.0087 |
| Elemental Carbon | <.0001 | <.0001 | 0.0596 |
| Sulfate | <.0001 | <.0001 | <.0001 |

* Results are shown using the all valid data.

Individual pairs of samplers are consistent (on a log scale), see Figures 3.5 and 3.6. However, at the Bismark site a typical difference (on the natural log scale) is for the MetOne to be 0.3 higher than the URG. At the Tampa site the difference typically is about 0.15 in the same direction. Figure 3.7 shows boxplots of the daily differences for organic carbon measurements for all sites on the log base 10 scale. The medians are clearly different from site to site, even between sites with samplers of the same type. (There is no visual difference between using the natural log versus base 10, only the units change.)

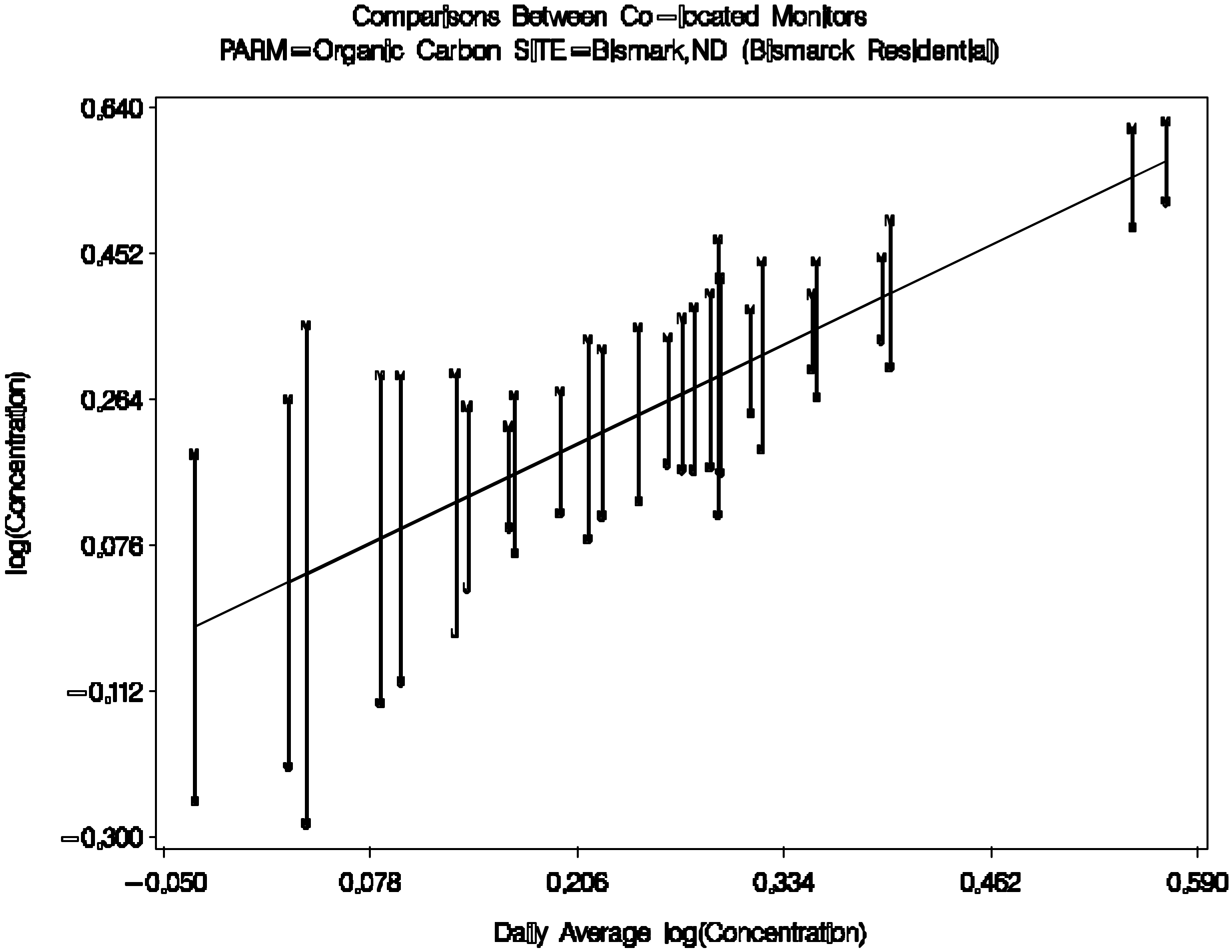


**Figure 3.5** Log OC Concentrations at Bismarck, ND Plotted Against the Mean of the Logs of the Concentration.

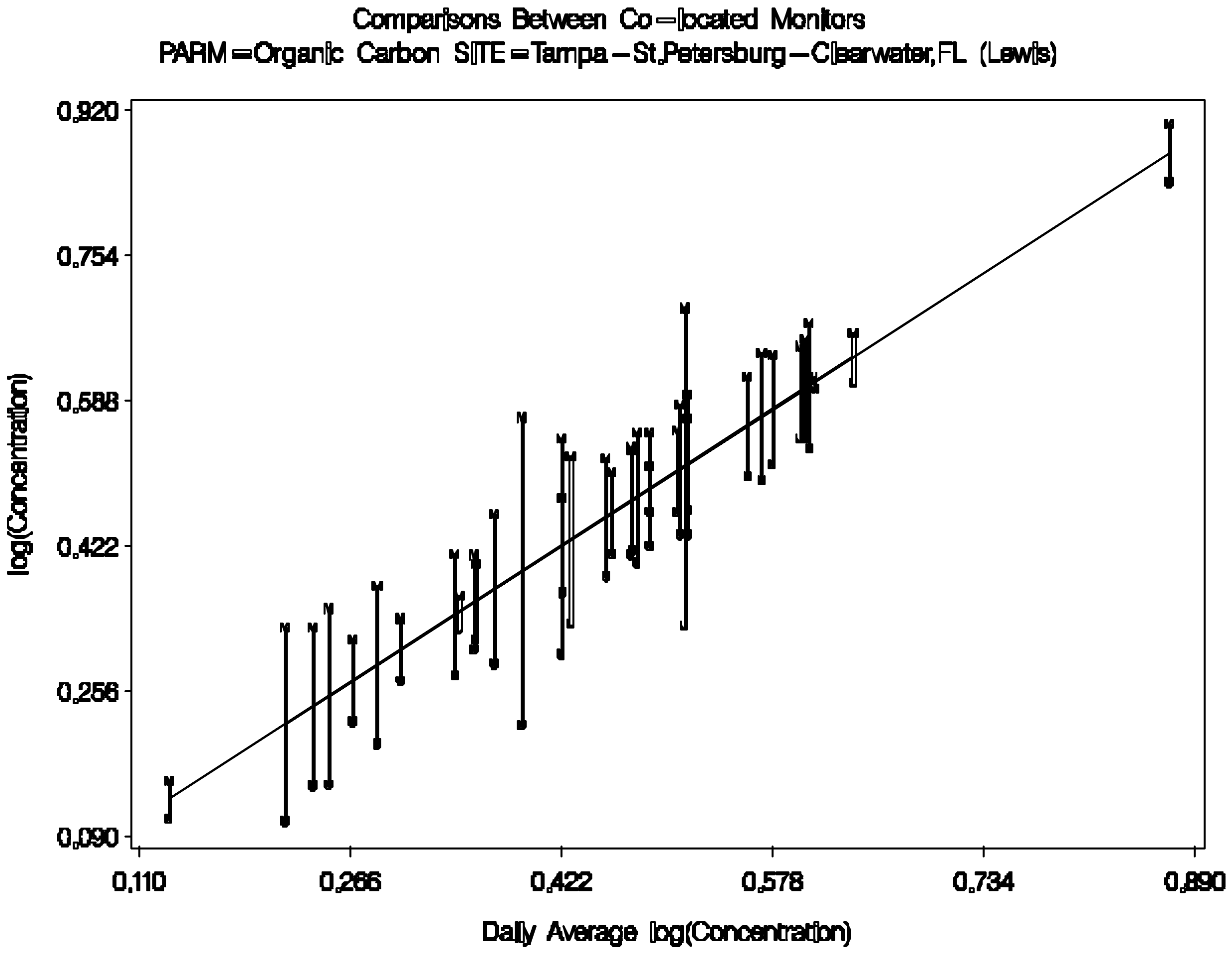


**Figure 3.6 Log OC Concentrations at Tampa, FL Plotted Against the Mean of the Logs of the Concentrations.**

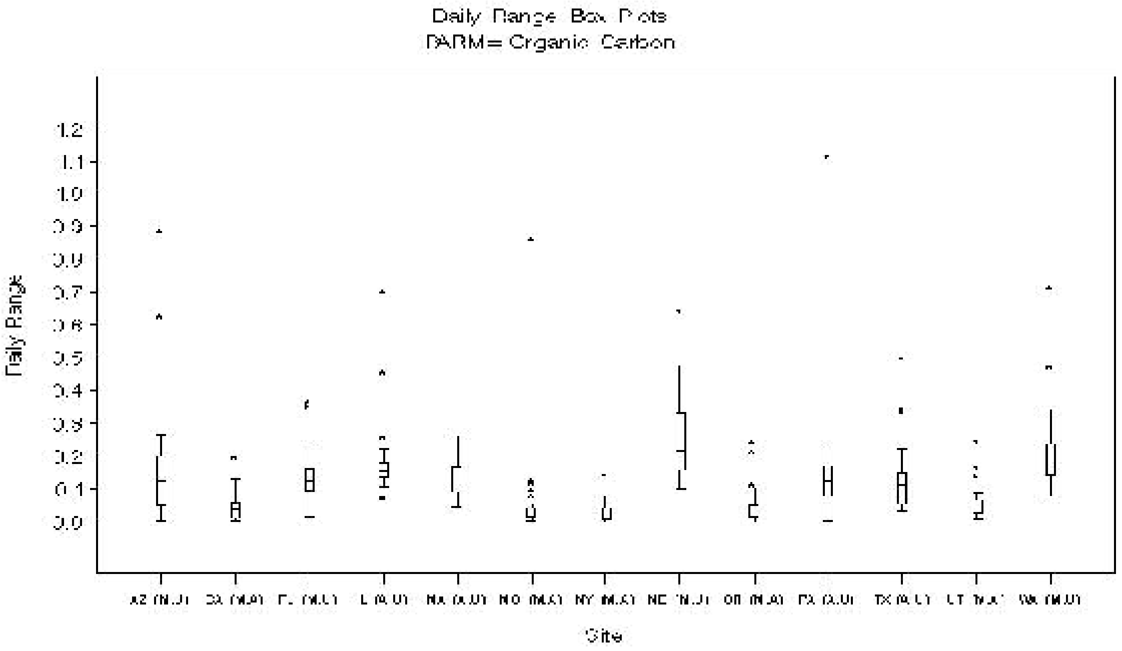


**Figure 3.7** **Box Plots of the Daily Range in the Logs of the OC Concentrations.**

There is a consistency across sites (and even species). As seen with the mass data, the directions of the relative biases are frequently the same. To further explore this the sites with two sampler types were tested as follows. All the MetOne samplers were labeled A and all of the URG samplers were labeled B. If an Andersen was paired with a MetOne, then the Andersen was labeled B. If an Andersen was paired with a URG, then the Andersen was labeled A. In this way there are three different pairings, and the order is always fixed. Then, for each pair of data points an indicator was created. If the concentration value from an “A” sampler was higher than the concentration from “B”, then the indicator was 1. Otherwise the indicator was 0. The percentage of the time that the indicator is 1 (for a given parameter) can be tested (using a technique called logistic regression) to see if this is a function of the site, or of just the sampler type, or if it is independent of both.

Table 3.4 shows the results for the tests of the null hypothesis that the probabilities are dependent on both site and sampler type versus the alternative that they depend only on sampler type. In most cases this test indicates that the probabilities are not dependent on the site. The exceptions are chlorine, ammonium, nitrate and sulfate. Since most species showed no site dependence the model was refit with only a sampler type pair dependency, and this was tested against no sampler type dependence. The p-values for these tests are strongly significant. Hence, generally there is a significant difference between the sampler types. However, since sampler pair and site are confounded the p-value for the significance of the sampler pair should be ignored whenever the site effect is significant. The overall conclusion is that there are significant vendor specific relative biases and the percent of the time that one vendor type is greater than another is not dependent on the site for most species. These results mimic the findings noted in the comparisons with the FRM mass measurements (Section 3.1). In fact, the ordering is the same for most parameters. See Table 3.4.

## Table 3.4 Probabilities of Sampler Type A Yielding Values Greater than Sampler Type B P-values for the Significance of Sampler Type and Site.

| Parameter | Estimated Probability of Vendor A > Vendor B | | | Estimated p-value | | Implied ordering to the vendor measurements* |
|---|---|---|---|---|---|---|
| | Andersen-URG | MetOne-Andersen | MetOne-URG | Pair | Site | |
| PM2.5 Mass | 0.90 | 0.72 | 0.96 | <.0001 | 0.0659 | U < A < M |
| Aluminum | 0.73 | 0.56 | 0.94 | <.0001 | 0.3519 | U < A = M |
| Calcium | 0.96 | 0.50 | 0.94 | <.0001 | 0.5119 | U < A = M |
| Chlorine | 0.70 | 0.29 | 0.81 | <.0001 | 0.0005 | U < M < A |
| Iron | 0.96 | 0.42 | 0.96 | <.0001 | 0.1192 | U < A = M |
| Lead | 0.63 | 0.75 | 0.94 | 0.0011 | 0.2697 | U < A < M |
| Tin | 0.48 | 0.98 | 1.00 | <.0001 | 0.8930 | U = A < M |
| Silicon | 0.93 | 0.48 | 0.90 | <.0001 | 0.3871 | U < A = M |
| Zinc | 0.76 | 0.12 | 0.27 | <.0001 | 0.0878 | M < U < A |
| Ammonium | 0.23 | 0.61 | 0.05 | <.0001 | 0.0008 | A < M < U |
| Organic Carbon | 0.95 | 0.70 | 0.99 | <.0001 | 0.0988 | U < A < M |
| Nitrate | 0.79 | 0.75 | 0.82 | 0.4360 | 0.0026 | U < A < M |
| Elemental Carbon | 0.85 | 0.54 | 0.80 | <.0001 | 0.8722 | U < A = M |
| Sulfate | 0.29 | 0.70 | 0.47 | <.0001 | 0.0004 | A < U = M |

* If the 95 percent confidence interval (not shown) for the estimated probability included 0.5, then the implied ordering is shown as "=" for "not significantly different."

The findings here also indicate that the differences in precision noted by sampler type is more likely site related rather than sampler type differences (Section 3.4). Here is how that conclusion is obtained. Consider the cases where site is not significant above. Suppose that the differences in the precision were not site related, but instead were truly vendor specific as the ANOVA model seems to indicate. We know that the magnitude of the relative biases changes from site to site. Assume that the variance does not change with site. Where the bias is small, the probability of the indicator being 1 should be closer to 0.5 than at a site where the bias is large (unless both are indistinguishable from 1). This does not happen. So the variability must change with the size of the relative bias.

## 3.3 ROUTINE PARAMETER MEASUREMENTS RELATIVE THE MEASURED MASS

Given that there are differences among the samplers that show a consistent ordering with the ordering for the measured mass, a logical next question is whether or not the samplers yield the same relative compositions. To test this for each parameter a new variable was created that was equal to the logarithm of the ratio of the parameter concentration to the concentration of the measured mass. This was modeled to have a random mean for site and day with fixed mean deviations for each site and sampler type within site.

For each parameter, there are significant deviations in the relative compositions between co-located samplers. Table 3.5 shows the significance of difference in relative composition of organic carbon at each site. Among the sites with Andersen and MetOne samplers, three of the five show no significant difference in the relative composition while relative amounts at Fresno and Portland are significantly different. Table B.4 has the complete list for all constituent parameters studied. Also see Tables B.1 and B.2 for the magnitude of the differences.

**Table 3.5 Significance of the differences in the relative amounts of Organic Carbon at each site.**

| Sampler Pair Type | Site | Significance of Sampler Differences for the Site |
|---|---|---|
| And-Met1 | Fresno | 0.0113 |
| And-Met1 | St. Louis | 0.4731 |
| And-Met1 | New York | 0.7536 |
| And-Met1 | Portland | 0.004 |
| And-Met1 | Salt Lake | 0.5642 |
| And-URG | Chicago | <.0001 |
| And-URG | Boston | <.0001 |
| And-URG | Philadelphia | <.0001 |
| And-URG | Houston | 0.0136 |
| Met1-URG | Phoenix | 0.2732 |
| Met1-URG | Tampa | <.0001 |
| Met1-URG | Bismarck | 0.0004 |
| Met1-URG | Seattle | <.0001 |

## 3.4 RELATIVE PRECISIONS OF THE SAMPLER TYPES

In addition to looking for relative biases among the sampler types, the precisions were also studied. The estimates of the variability were obtained by modeling two different sources of variability, temporal variability and measurement error, along with the estimates of mean behavior (all done on the log scale). The estimates in Table 3.6 are based on two different types of models with the data for each parameter modeled separately. The temporal and the aggregate measurement error estimates are based on models that assumed that the measurement error was independent of the sampler type. The sampler specific measurement errors come from statistical models for the data that assumed a temporal component to the variability and three distinct measurement errors. For both cases Table 3.6 shows the results using all non-RTI flagged data.

Generally, the statistical test for the significance of using three distinct measurement errors rather than a single aggregate measurement error was positive. Hence, the data showed that the precisions are generally distinct. An inspection of Table 3.6 shows that for many parameters, the MetOne precision was lower than the other two. However, there is a strong possibility that the differences noted here are in fact due to site to site differences, not sampler to sampler differences. To test this directly, more complex statistical models were tried, but the models failed to converge. The modeling based on indicators of which sampler had the higher concentration for a given site and day gives indirect evidence that the differences in precision noted here are due more to site differences, rather than the sampler type (See Section 3.2).

Where the models converged they show that the temporal component of the variability was often two to three times higher than the measurement error and many times larger than any difference among the samplers. Hence, for the purpose of establishing long term averages or annual trends, sampling frequency would be more important than measurement error and much more important than sampler type. Hence, from a practical point of view, there is extremely little difference in the precisions.

### Table 3.6 Estimated Variance Components for Each Parameter

| Parameter | Temporal Variation (CV) | Aggregate Measurement Error (CV) | Andersen Precision (CV) | MetOne Precision (CV) | URG Precision (CV) |
|---|---|---|---|---|---|
| PM2.5 Mass | 0.470 | 0.134 | 0.152 | 0.140 | 0.099 |
| Aluminum | 0.979 | 0.440 | 0.622 | 0.226 | 0.414 |
| Calcium | 0.540 | 0.302 | 0.379 | 0.195 | 0.297 |
| Chlorine | 1.673 | 0.547 | 0.739 | 0.263 | 0.578 |
| Iron | 0.615 | 0.263 | 0.302 | 0.147 | 0.304 |
| Lead | 0.477 | 0.266 | 0.344 | 0.208 | 0.231 |
| Tin [1] | 0.000 [1] | 0.187 [1] | 0.206 [1] | 0.167 [1] | 0.184 [1] |
| Silicon | 0.706 | 0.323 | 0.409 | 0.149 | 0.335 |
| Zinc | 0.794 | 0.269 | 0.254 | 0.349 | 0.180 |
| Ammonium | 0.862 | 0.267 | 0.278 | 0.138 | 0.355 |
| Organic Carbon | 0.381 | 0.181 | 0.111 | 0.077 | 0.291 |
| Nitrate | 0.862 | 0.221 | 0.219 | 0.059 | 0.318 |
| Elemental Carbon | 0.499 | 0.250 | 0.218 | 0.266 | 0.253 |
| Sulfate | 0.652 | 0.141 | 0.150 | 0.063 | 0.187 |

[1] The statistical model did not converge to a self-consistent state.

# 4.0 ANALYSIS OF THE BLANKS

In addition to the monitoring, filters are stepped through part or all of the sampling process except for the drawing of air through them. Ordinarily, analyzing these filters is used as a check for any contamination on the filter due to the handling. The purpose here is slightly different. In this case the blanks, both trip blanks and filter blanks, were used to test whether or not there is any tendency for one sampler type's filters to be contaminated significantly more than another. As usual this question is first asked in a statistical sense, and then if there are differences, there is a different question of whether there is a practical difference. However, the second question is further complicated by the fact that different volumes of air are drawn through the routine filters. For some this may change the point of view of what is a practical difference. For others it may not since any evidence of contamination casts some doubt on the measurements. For the purpose of this study, the masses found on the filters were not "corrected" for an average volume.

The statistical analysis of the blanks is complicated by the fact that many of the measurements are below the MDL, and frequently 0. Unlike the routine data there is not a transformation of scale that is suitable for ANOVA-like techniques. Instead, the data was converted to a binary form. This can be thought of as treating the individual values as either "negligible" contamination or "non-negligible." The goal was to use a practical definition that would separate the data by sampler type if there is any "difference". However, this a difficult item to quantify in a satisfactory manner. The MDL is not a good cutoff. For some compounds, essentially all of the data are on one side of the MDL or the other, so there is no basis for deciding whether one sampler type is "cleaner" than another. Further, the quantities labeled as the MDLs may or may not be the true detection limits. It was decided to use the data themselves as the basis for a practical cutoff, namely the parameter specific third quartile of all the blanks. (The third quartile is denoted Q3, and equals the value such that it is greater than or equal to 75 percent of the data and less than or equal to 25 percent of the data.) This assures that there will be sufficient data both above and below the cutoff to be useful (unless as in the case of zinc nearly 100 percent of the data is equal to 0). Also by its very nature Q3 is a practical (achievable) bound for the contamination levels with the current technology.

Using an indicator function treats very large values the same as values just over the cutoff. For instance, there were three cases where the mass was over 100 micrograms. Such extremes may or may not be real and certainly would influence an analysis that considered the scale. It was decided not to keep such extreme cases in the analysis even though they would not have an undue influence on the analysis. It should also be pointed out that such values appear to be "replicatable." That is, the experiments discussed in Section 5 included multiple blanks, and there were cases where unusually high values were replicated (See Sections 5.1 and 5.4).

Table 4.1 summarizes the data as used in the analysis. For each compound the MDL, the overall median, and overall Q3 is listed. These give an indication for the spread of the data and the relationship between typical values and the MDL. Also shown in Table 4.1 is the percent of the time that data from a given sampler type is above the overall Q3. For mass, the typical values are many times greater than the MDL. All of the actual proportions are less than 25 percent. This is possible when there are many values that are equal to Q3. Still there is a clear difference in percentages with Andersen > MetOne > URG. The modeling of the data checks to see if this is more likely due to site effects or if it is a true difference between the sampler types.

## Table 4.1 Summary of the Blank Data.

| Parameter | avg MDL (µg) | Median (µg) | Q3 (µg) | Actual Proportion > Q3 | | |
|---|---|---|---|---|---|---|
| | | | | Andersen (out of 93), % | MetOne (out of 83), % | URG (out of 81), % |
| PM2.5 Mass | 0.976 | 13.000 | 18.000 | 23.7 | 16.9 | 9.9 |
| Aluminum | 0.105 | 0.003 | 0.052 | 20.4 | 20.5 | 11.1 |
| Calcium | 0.033 | 0.041 | 0.056 | 14.0 | 21.7 | 17.3 |
| Chlorine | 0.056 | 0.000 | 0.018 | 16.1 | 22.9 | 12.3 |
| Iron | 0.019 | 0.031 | 0.045 | 17.2 | 19.3 | 13.6 |
| Lead | 0.053 | 0.026 | 0.041 | 14.0 | 16.9 | 18.5 |
| Tin | 0.172 | 0.184 | 0.227 | 9.7 | 20.5 | 22.2 |
| Silicon | 0.073 | 0.015 | 0.042 | 17.2 | 20.5 | 13.6 |
| Zinc | 0.014 | 0.000 | 0.000 | 4.3 | 2.4 | 0 |
| Ammonium | 0.163 | 0.000 | 0.000 | 10.8 | 0 | 3.7 |
| Organic Carbon | 1.412 | 12.199 | 15.380 | 20.4 | 28.9 | 3.7 |
| Nitrate | 0.078 | 0.739 | 1.124 | 4.3[1] | 8.4 | 42.5[2] |
| Elemental Carbon | 1.412 | 0.689 | 0.984 | 17.2 | 20.5 | 11.1 |
| Sulfate | 0.117 | 0.864 | 1.534 | 21.5 | 27.7 | 3.7 |

[1] 92 obs

[2] 80 obs

Table 4.2 shows the modeling results. In each case, the cutoff Q3 is listed for reference. The next three columns are p-values for the three tests of interest. The last three columns give confidence intervals for the probability of observing a value greater than Q3. These estimates are based on a model without a site effect and are “averaged” over blank type.

The column “Type” is for a test of any significant difference between field blanks and trip blanks. Trip blanks are taken and opened at the site, and then resealed for analysis. Field blanks are additionally placed in the sampler for a moment or two (sometimes with the sampler turned on to “shake loose” anything in the sampler). It would be natural to assume that for nonvolatile compounds the field blanks would naturally be higher than the trip blanks. However, field blanks and trip blanks are equally likely to have values greater than Q3. Lead is a notable exception to this observation with about 10 percent of the trip blanks greater than Q3 versus 28 percent of the field blanks. Ammonium, nitrate, and sulfate also show differences, but in the opposite direction since trip blanks are higher. For ammonium 5 percent of the field blanks are greater than 0 versus 12.5 percent of the trip blanks. For nitrate and sulfate, approximately 21-22 percent of the field blanks are above Q3 versus 33-35 percent of the trip blanks.

The “Sampler” column in Table 4.2 is a test of whether or not there are significant differences among the sampler types. The effects are averaged over blank type (see below). The effect of sampler type appears generally insignificant for the mass and the metals except tin. There are significant differences between the sampler types for ammonium, OC, nitrate, and sulfate.

The “site” column is a test of site dependent effects. The models with a site effect did not always converge because there were insufficient non-zero data to test. Where the models did converge, the site effect is negligible overall.

**Table 4.2 Modeling Results for the Blank Data.**

| Parameter | Q3 | Significance of | | | Estimated Probability of Being > Q3 | | |
|---|---|---|---|---|---|---|---|
| | | Type | Sampler | Site | Andersen | MetOne | URG |
| PM2.5 Mass | 18.000 | 0.3030 | 0.1374 | 0.5849 | (0.23,0.47) | (0.15,0.39) | (0.09,0.31) |
| Aluminum | 0.052 | 0.3690 | 0.2560 | 0.1507 | (0.19,0.42) | (0.19,0.44) | (0.09,0.31) |
| Calcium | 0.056 | 0.4442 | 0.1924 | 0.4446 | (0.09,0.28) | (0.19,0.44) | (0.15,0.38) |
| Chlorine | 0.018 | 0.4371 | 0.1583 | 0.3644 | (0.13,0.34) | (0.21,0.46) | (0.09,0.30) |
| Iron | 0.045 | 0.3270 | 0.5867 | 0.0403 | (0.12,0.33) | (0.16,0.40) | (0.10,0.32) |
| Lead | 0.041 | 0.0065 | 0.5573 | 0.2500 | (0.07,0.26) | (0.10,0.32) | (0.12,0.35) |
| Tin | 0.227 | 0.9602 | 0.0160 | 0.3586 | (0.07,0.24) | (0.19,0.44) | (0.22,0.48) |
| Silicon | 0.042 | 0.2784 | 0.4483 | 0.1528 | (0.12,0.33) | (0.17,0.42) | (0.10,0.32) |
| Zinc | 0.000 | 0.8938 | 0.2156 | * | (0.01,0.13) | (0.01,0.14) | ** |
| Ammonium | 0.000 | 0.0558 | 0.0044 | * | (0.07,0.27) | ** | (0.02,0.18) |
| Organic Carbon | 15.380 | 0.6974 | <.0001 | 0.0599 | (0.17,0.40) | (0.28,0.54) | (0.02,0.16) |
| Nitrate | 1.124 | 0.0441 | <.0001 | 0.5491 | (0.01,0.13) | (0.07,0.27) | (0.54,0.80) |
| Elemental Carbon | 0.984 | 0.4932 | 0.2379 | 0.1929 | (0.13,0.35) | (0.20,0.46) | (0.09,0.31) |
| Sulfate | 1.534 | 0.0138 | <.0001 | 0.1843 | (0.21,0.46) | (0.31,0.59) | (0.02,0.18) |

* Model does not converge
** Estimate not reliable

The above analysis is misleading for chlorine and silicon because the effect of sampler type is blank type specific. As a result, grouping the data by either factor tends to obscure the effects and leads to null conclusions. For these two compounds statistically significant sampler type-blank type differences were noted. See Figures 4.1 and 4.2. For all other compounds, a model with a sampler type-blank type interaction tested insignificant.

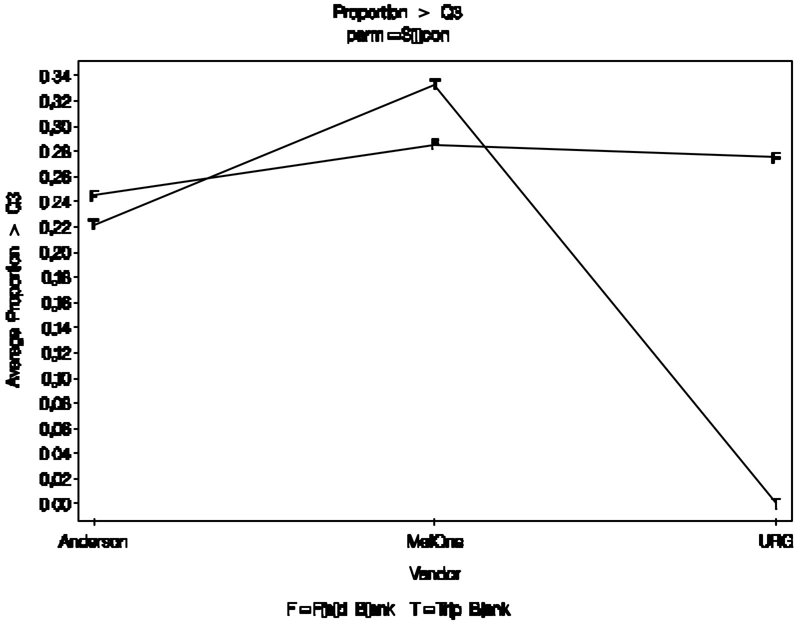


**Figure 4.1** The Proportion of Field and Trip Blanks with Silicon Measurements Greater than Q3 by Sampler Type.

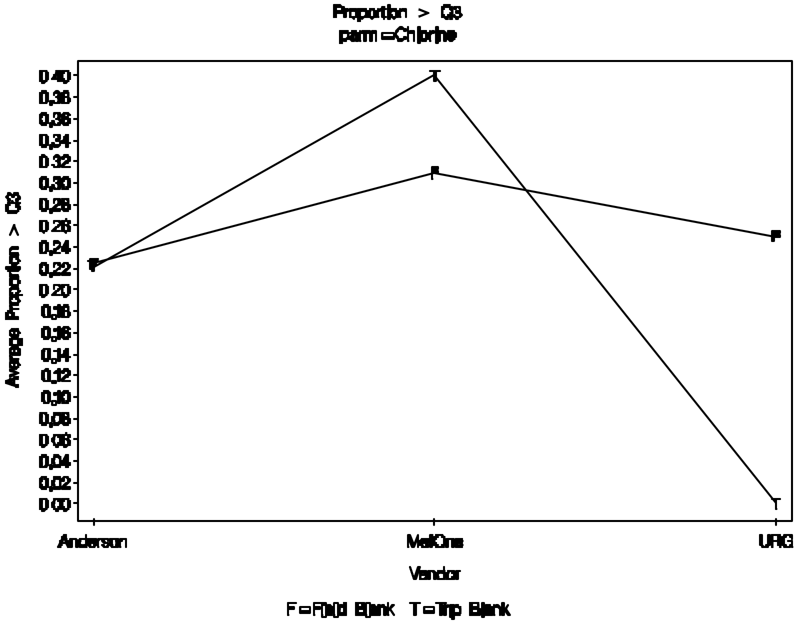


**Figure 4.2** The Proportion of Field and Trip Blanks with Chlorine Measurements Greater than Q3 by Sampler Type.

# 5.0 EXPERIMENTS TO SIMULATE AND TEST POTENTIAL SAMPLE INTEGRITY ISSUES WHEN USING SEQUENTIAL SPECIATION SAMPLERS

Five experiments were undertaken to test various issues that are associated with sequential samplers and sampling integrity. Four of the experiments are directly concerned with the fact that, in a sequential sampler the filters can collect material by passive sampling while sitting unsealed in the sampler. Also, if the filters have already collected material as part of a sample, then there is the possibility that some of the sample material may volatilize.
Sections 5.1 and 5.2 examine the results of two experiments that simulate the sequential sampling, specifically looking at organic and elemental carbon. Sections 5.4 and 5.5 examine the results for corresponding experiments that look at the effects on nitrate and sulfate. Section 5.3 examines the results of an additional experiment targeting a concern about the collection or loss of carbon compounds due to the face velocity at the quartz filter.

The experimental design called for the collection of more data than was collected for these five experiments. All of the available (and directly relevant) data is at least plotted in each of the following sections. The lack of data can affect the ability to detect small differences. This is especially true for data that have a relatively high variability. As will be seen, the results of the face velocity test are not quantitatively consistent from the results with the routine samples. The problem may be the lack of data.

## 5.1 COLLECTION OF VOLATILE ORGANIC COMPOUNDS ON BLANK QUARTZ FILTERS

In this experiment, a MetOne sampler was loaded with five quartz modules. The five modules were then left in the MetOne sampler for six to nine days while leaving the sampler idle. In this way the filters were exposed to ambient air for a week and the effects of filters sitting in the sampler for an extended period before sampling were simulated.

Figures 5.1 and 5.2 show scatter plots of the raw data for the experiment.

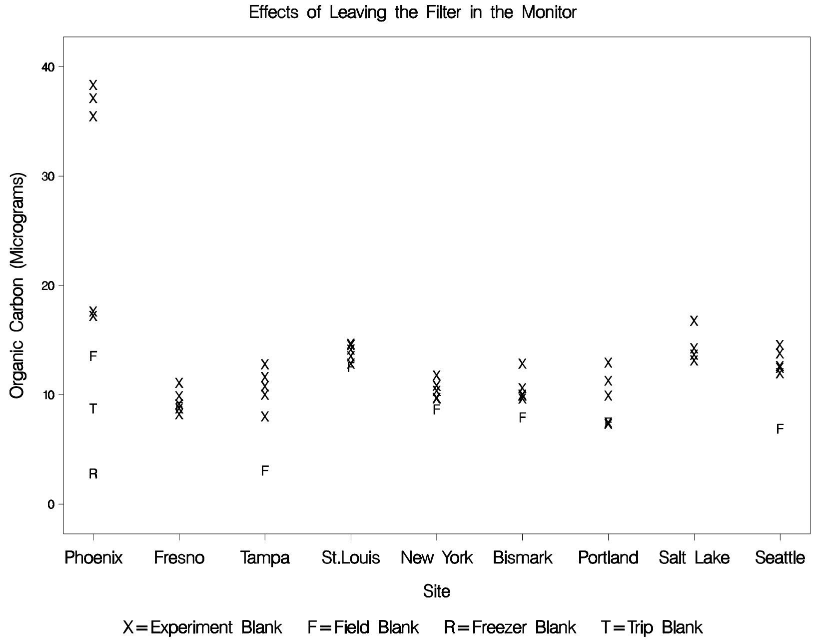


Figure 5.1 Effects of Leaving Blank Filters in the Sampler for a Week on the Measured OC.

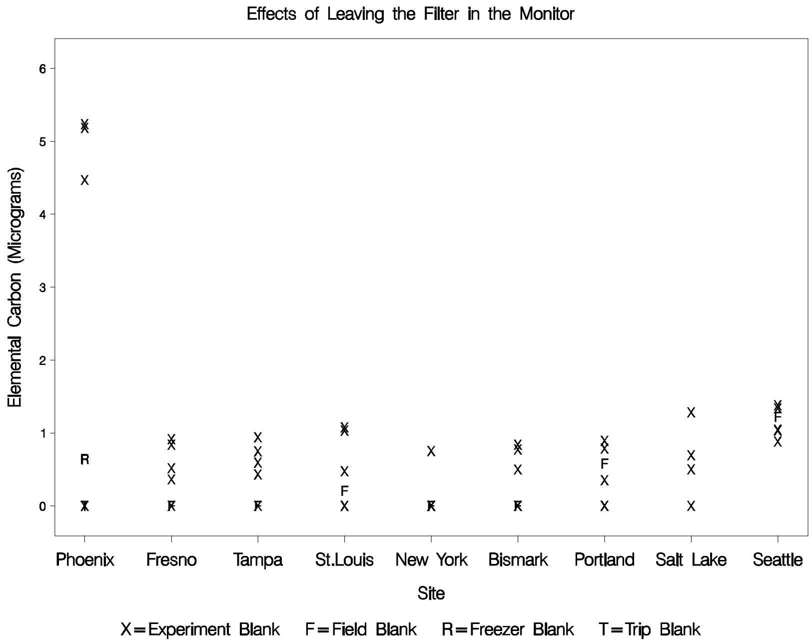


Figure 5.2 Effects of Leaving Blank Filters in the Sampler for a Week on the Measured EC.

Clearly the Phoenix data in this experiment has a different nature than the other sites. (See Section 5.6.) Hence, to begin with, the Phoenix data are treated as outliers and only the other data points are modeled. The mean response was modeled as an overall mean for each blank type with random variations due to the site. For OC the overall mean for the experiment blanks was estimated to be 11.53 micrograms with a standard error of 0.685 micrograms while the field blanks had an overall mean of 8.26 micrograms with a standard error of 0.894 micrograms. The p-value for the test of whether the true means are statistically different is <0.0001. Hence, with respect to OC, there is a significant statistical difference between the field blanks and the blanks that are left in the sampler for at least a week.

The EC data were modeled similarly (with the Phoenix data removed). For EC the overall mean for the experiment blanks was estimated to be 0.541 micrograms with a standard error of 0.108 micrograms while the field blanks had an overall mean of 0.295 micrograms with a standard error of 0.171 micrograms. The p-value for the test of whether the true means are statistically different is 0.129. Hence, with respect to EC, there is no significant statistical difference between the field blanks and the blanks that are left in the sampler for at least a week.

## 5.2 COLLECTION OF VOLATILE ORGANIC COMPOUNDS ON EXPOSED QUARTZ FILTERS

In this experiment five modules were loaded with quartz filters for a MetOne sampler. Two of these were recovered according to standard procedures (within 48 hours of sampling). The remaining filters were recovered at least six days after sampling. This simulated the condition of a sequential sampler where a sample is left in the sampler for an extended period. Figures 5.3 and 5.4 show scatter plots of the raw data for the experiment. Figure 5.5 shows the ratio of the EC concentration to the OC concentration.

Both Figures 5.3 and 5.4 show unusual values in opposite directions. The Phoenix data may not seem to matter because there were not any standard recovery measurements in the data. However, it could be useful in estimating the sampling error size, if this represents real data. To help decide, the ratio of the concentrations is also plotted in Figure 5.5.

The modeling was based on removing the Salt Lake and Phoenix data. The values were assumed to have a different mean for each site and day. The effect of leaving the filter in the sampler was modeled as producing a shift in the site mean (where the same shift is used for all sites). Table 5.1 shows the mean difference between the samples that were collected within 48 hours and those that were left in the sampler for at least 6 days and the associated p-value. In both cases there is no significant difference between the collection methods.

**Table 5.1 Mean Difference Between Standard Collection of Samples and Those Left in the Sampler.**

| Compound | Mean difference | Standard error | p-value |
|---|---|---|---|
| Organic carbon | 0.234 | 0.330 | 0.4841 |
| Elemental carbon | 0.039 | 0.042 | 0.3565 |

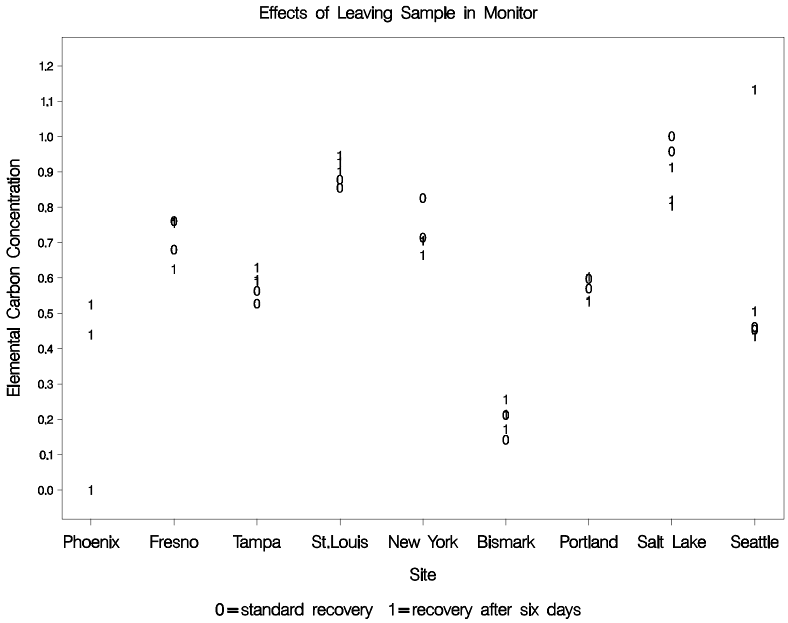


Figure 5.3 The Effects of Leaving a Filter in a Sampler for a Week on the Observed EC Concentration. Note That the Two Unusual Values Are in Opposite Directions.

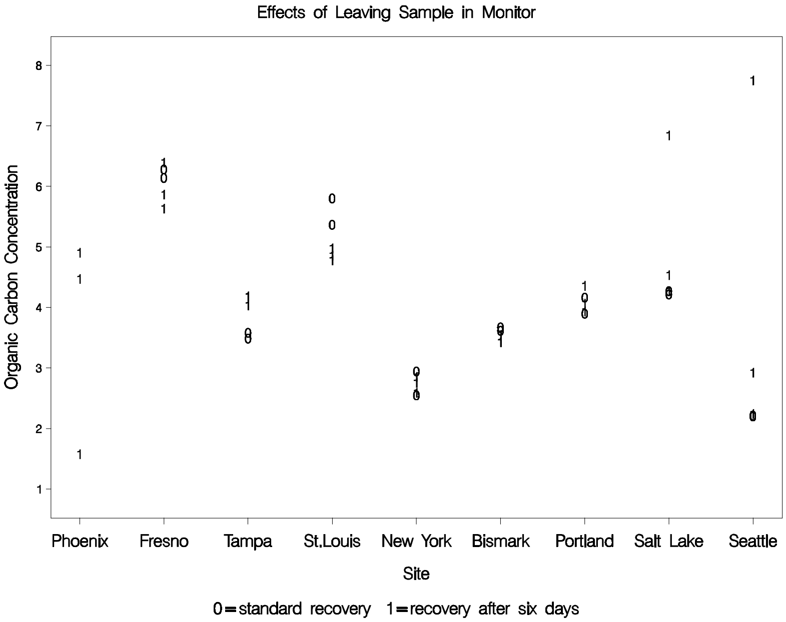


Figure 5.4 The Effects of Leaving a Filter in a Sampler for a Week on the Observed OC Concentration.

**Note That There Are Unusual Values in Opposite Directions.**

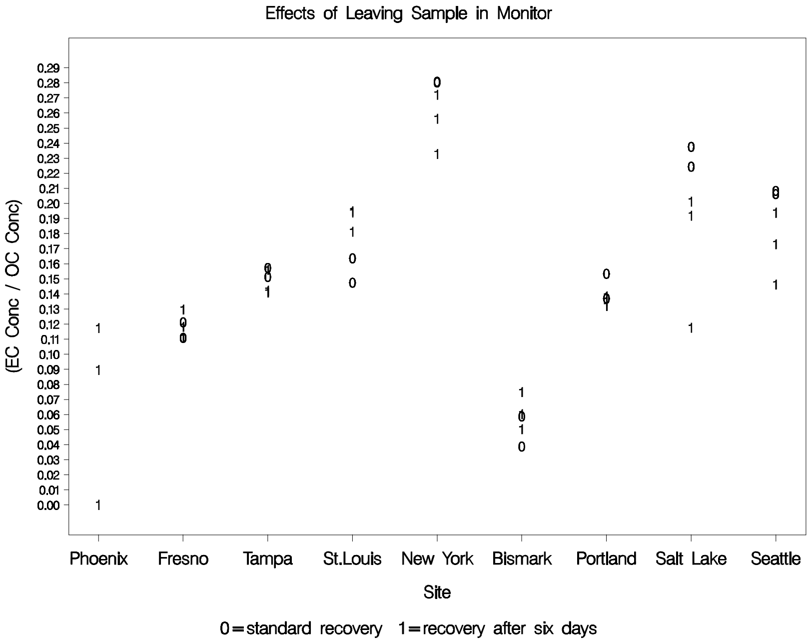


Figure 5.5 The Effects of Leaving a Filter in a Sampler for a Week on the Observed Ratio of the EC Concentration to the OC Concentration.

* *Note that the Seattle ratios now all appear "normal." The two unusual points, one in Phoenix and one in Salt Lake, are both low compared to the other values.

## 5.3 TESTING THE EFFECTS OF FACE VELOCITY ON THE COLLECTION OF VOLATILE ORGANIC COMPOUNDS ON QUARTZ FILTERS

In this experiment, channels 1 and 2 of Andersen samplers were loaded with a quartz filter. The two channels have flow rates of 7.3 lpm and 16.7 lpm under normal operations. In this way simultaneous samples were collected under the two different conditions on two separate quartz filters (with fewer differences between the sampling methods compared to using two different samplers from different vendors). Figures 5.6 and 5.7 below show the raw data with the concentration from the high volume channel plotted against the concentration from the low volume channel.

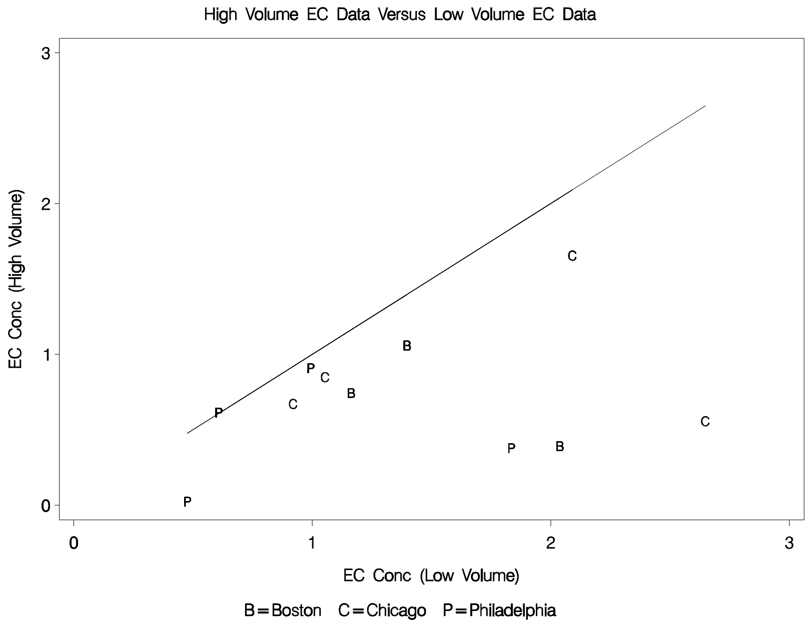


Figure 5.6 High Volume Elemental Carbon Concentrations Versus Low Volume Elemental Carbon Concentrations with a 1-1 line.

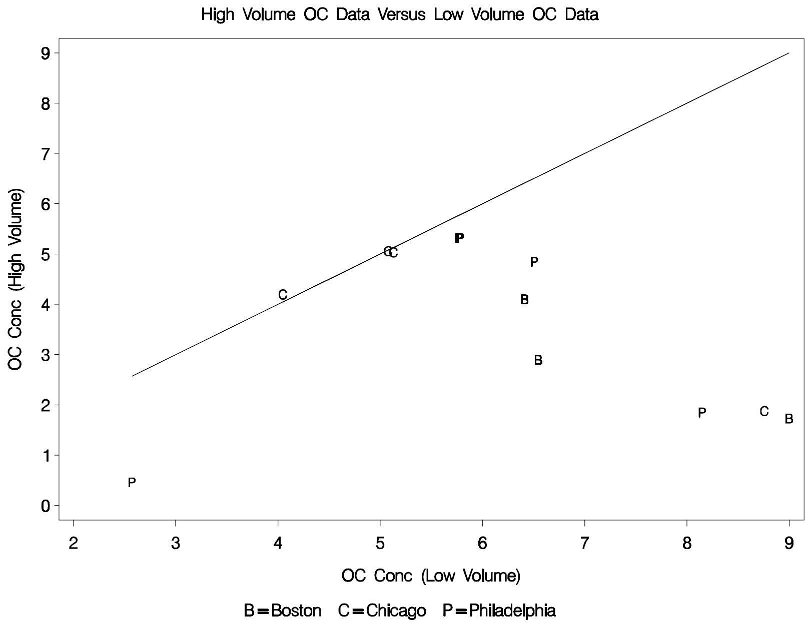


Figure 5.7 High Volume Organic Carbon Concentrations Versus Low Volume Organic Carbon Concentrations with a 1-1 line.

For both cases, the high volume concentrations were regressed against the low volume concentrations (the standard for an Andersen quartz filter). The regression results are shown below in Table 5.2. The regression procedure treats the low volume measurements as error free.

**Table 5.2 Regression Results for Modeling the High Volume Concentrations Against the Low Volume Concentrations.**

| Compound | Intercept (SE) | Slope (SE) | $R^2$ |
|---|---|---|---|
| Elemental Carbon | 0.451 (0.280) | 0.252 (0.184) | 0.136 |
| Organic Carbon | 4.809 (1.534) | -0.194 (0.244) | 0.050 |

To be more comparable with the results shown in Chapter 3, the above was repeated on the log scale. They seem to show much more disagreement than would be expected. (Compare Figure 5.10 with Figures 3.5 and 3.6. These compare the OC concentrations from co-located pairs of a URG sampler and a MetOne sampler. The flow rate for the MetOne is 6.7 lpm and the flow rate for the URG is 16.7 lpm.)

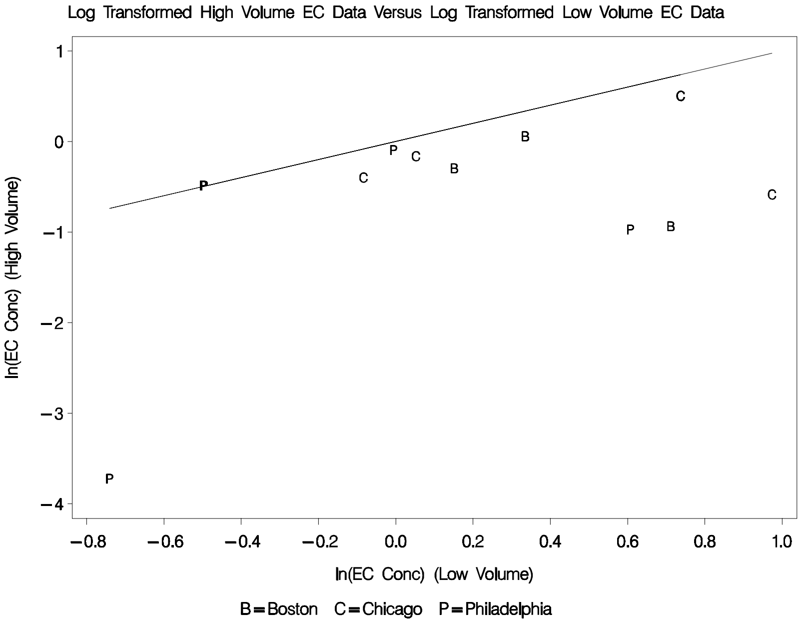


Figure 5.8 High Volume EC Data Versus Low Volume EC Data on the Log Scale.

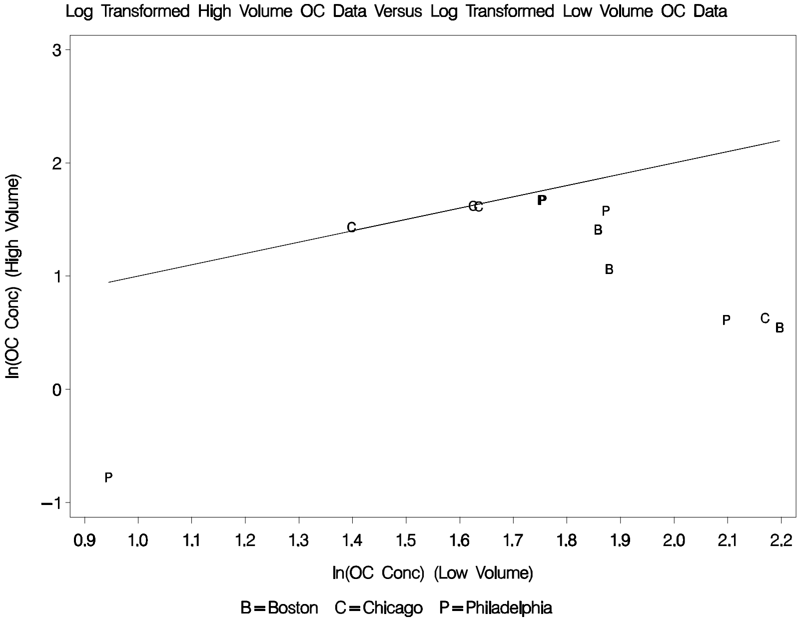


Figure 5.9 High Volume OC Data Versus Low Volume OC Data on the Log Scale.

**Table 5.3 Regression Results for Modeling the High Volume Concentrations Against the Low Volume Concentrations on the Log Scale.**

| Compound | Intercept (SE) | Slope (SE) | $R^2$ |
|---|---|---|---|
| Elemental Carbon | -0.700 (0.265) | 0.985 (0.484) | 0.257 |
| Organic Carbon | 0.350 (1.0158) | 0.451 (0.572) | 0.049 |

While there are less data for this experiment than was planned, there should be enough to detect some trend or correlation between the two sets of concentrations. On both scales there are three points with high low volume concentrations and low high-volume concentrations. As a result in both cases the slope is not significantly different from 0. (Hence, from a statistical perspective the low volume concentration provides no information about the high volume concentration.)

The routine data may have showed a bias between vendors, but at least they correlated well with each other. These data show no significant correlation. This inconsistency should be considered before drawing any conclusions based on these data.

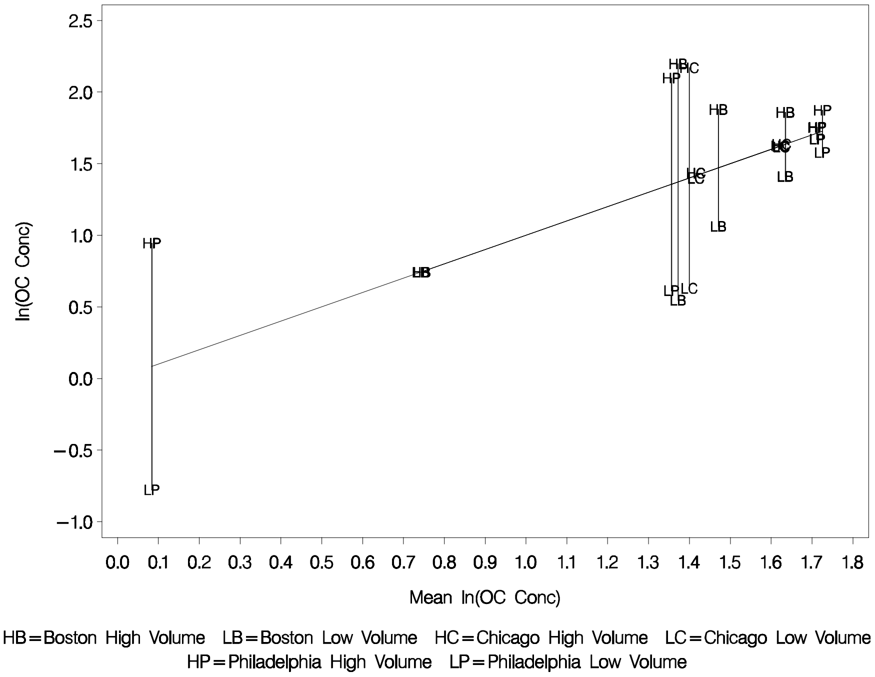


Figure 5.10 Log OC Concentrations from High and Low Volume Samples Plotted Against the Mean of the Logs of the Concentrations.

## 5.4 COLLECTION OF AMBIENT NITRATE AND SULFATE ON BLANK NYLON FILTERS

In this experiment in addition to field, trip, and “freezer” blanks (blanks stored in a freezer in the field), a MetOne sampler was loaded with 5 nylon modules. The five modules were then left in the MetOne sampler for six to nine days while leaving the sampler idle. In this way the filters were exposed to ambient air for a week and the effects of filters sitting in the sampler for an extended period before sampling was simulated.

Figures 5.11 and 5.12 show scatter plots of the raw data for the experiment.

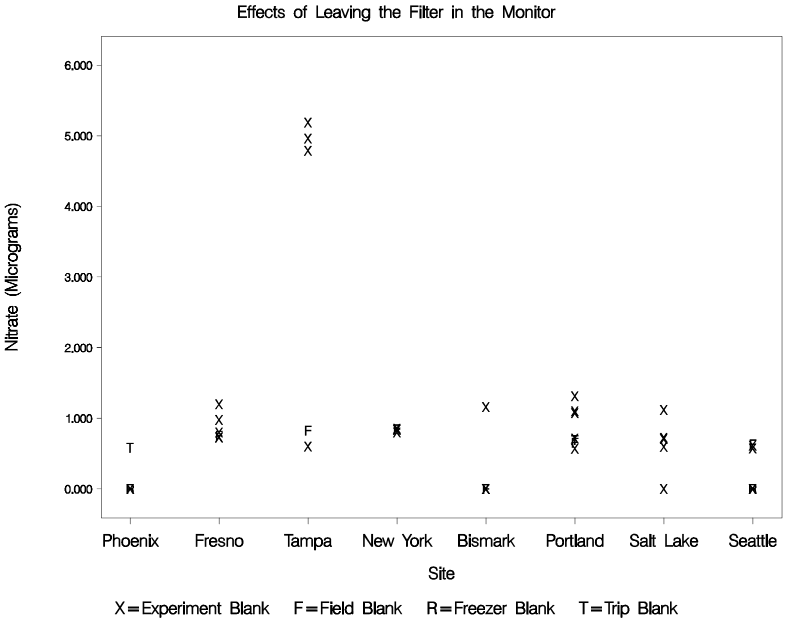


**Figure 5.11** Effects of Leaving Blank Filters in the Sampler for a Week on the Measured Nitrate.

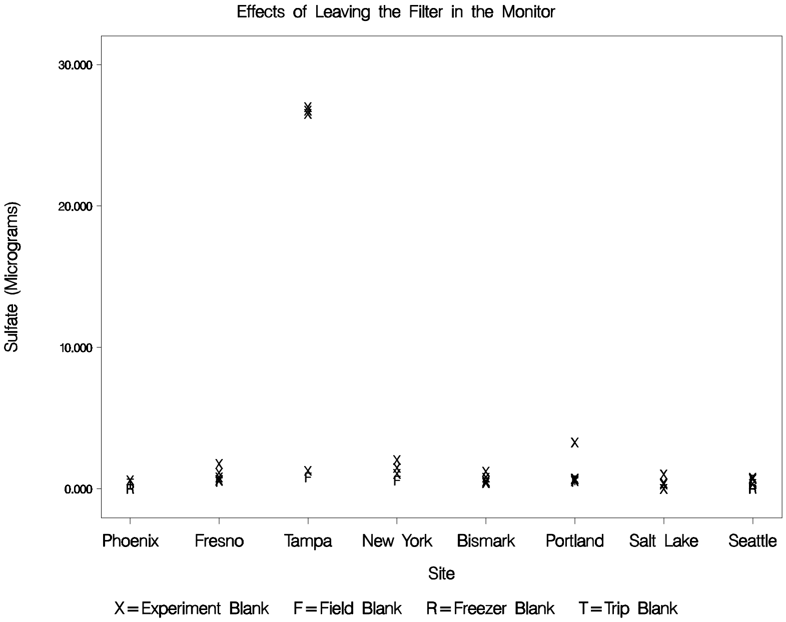


**Figure 5.12** Effects of Leaving Blank Filters in the Sampler for a Week on the Measured Sulfate.

Clearly the Tampa data in this experiment has a different nature than the other sites. (See Section 5.6.) Hence, to begin with, the Tampa data are treated as outliers and only the other data points are modeled. The mean response was modeled as an overall mean for each blank type with random variations due to the site. The means and standard errors for the various blank types are provided in Table 5.4.

### Table 5.4 Mean Nitrate and Sulfate on the Experiment Blanks.

| Blank type | Nitrate Mean (micrograms) | Nitrate Standard error | Sulfate Mean (micrograms) | Sulfate Standard error |
|---|---|---|---|---|
| Experiment blank | 0.5962 | 0.1163 | 0.8497 | 0.1351 |
| Field blank | 0.5490 | 0.1804 | 0.4862 | 0.2687 |
| Freezer blank | 0.1653 | 0.2696 | 0.04528 | 0.4214 |
| Trip blank | 0.6063 | 0.2690 | 0.4524 | 0.4210 |

Two statistical tests were conducted for both the nitrate data and the sulfate data. The first test was a combined test that the freezer blanks were 0 and that the field and trip blanks were the same. This is consistent with the data in both cases with p-values of 0.82 for the nitrate data and 0.99 for the sulfate data. The second test was a test of whether or not the experiment blanks differed significantly from the mean of the field and trip blanks. Again, this is consistent with the data (i.e., there is no significant difference). The p-values for these tests were 0.91 and 0.17 for the nitrate data and sulfate data, respectively.

## 5.5 COLLECTION OF AMBIENT NITRATE AND SULFATE ON EXPOSED NYLON FILTERS

In this experiment five modules were loaded with quartz filters for a MetOne sampler. Two of these were recovered according to standard procedures (within 48 hours of sampling). The remaining filters were recovered at least six days after sampling. This simulated the condition of a sequential sampler where a sample is left in the sampler for an extended period.

Figures 5.13 and 5.14 show scatter plots of the raw data for the experiment. Figure 5.15 shows the ratio of the nitrate concentration to the sulfate concentration.

The modeling was based on all the data in this case since there are only four sites. (The only unusual point was from one of the filters that was collected within 48 hours.) As in experiment 1B, the values were assumed to have a different mean for each site and day. The effect of leaving the filter in the sampler was modeled as producing a shift in the site mean (where the same shift is used for all sites). Table 5.5 shows the mean difference between the samples that were collected within 48 hours and those that were left in the sampler for at least six days, and the associated p-value. In both cases, there is no significant difference between the collection methods. However, note that the negative values in Table 5.5 indicate that the samples tended to lose mass over time. The lack of statistical significance may be due to the lack of data for this experiment.

**Table 5.5 Mean Difference Between Standard Collection of Samples and Those Left in the Sampler.**

| Species | Mean difference | Standard error | p-value |
|---|---|---|---|
| Nitrate | -1.347 | 0.653 | 0.0568 |
| Sulfate | -0.153 | 0.176 | 0.9320 |

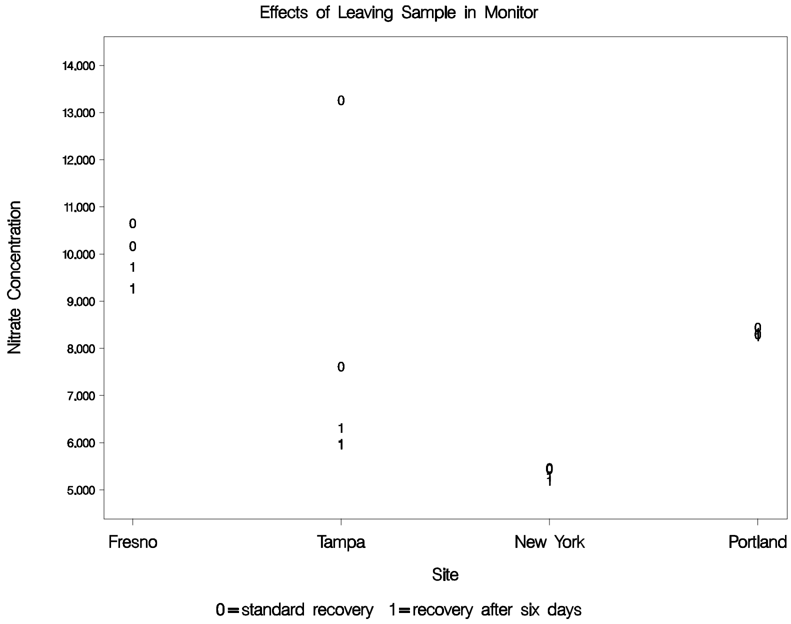


Figure 5.13 The Effects of Leaving a Filter in a Sampler for a Week on the Observed Nitrate Concentration.

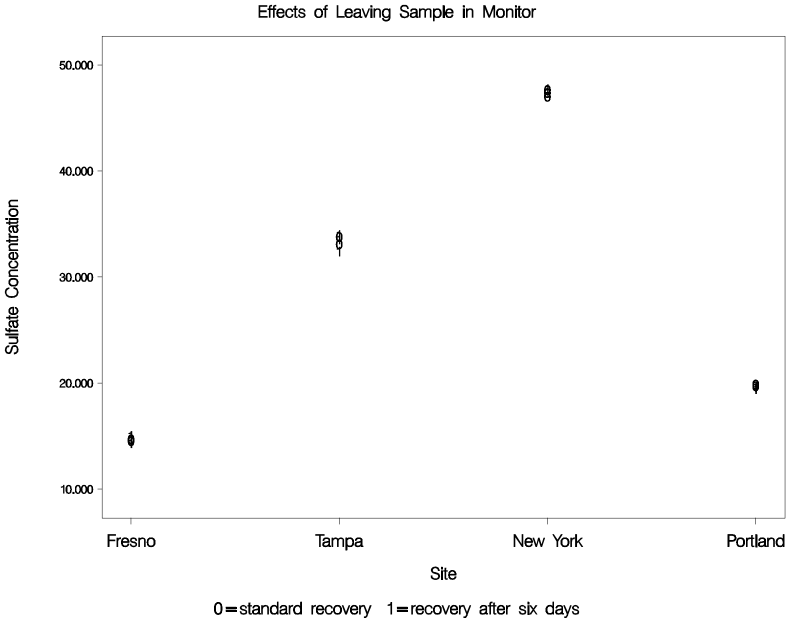


Figure 5.14 The Effects of Leaving a Filter in a Sampler for a Week on the Observed Sulfate Concentration.

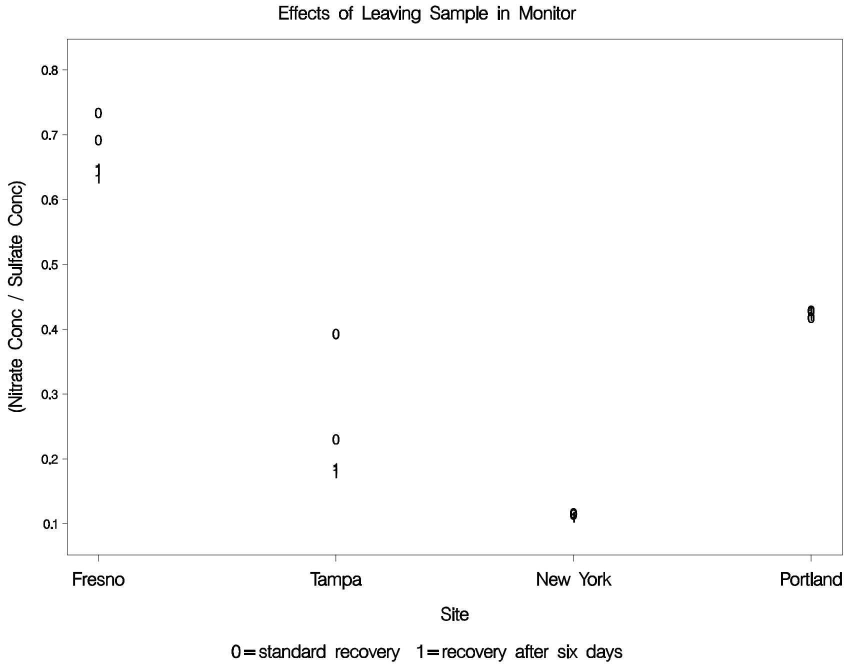


**Figure 5.15** **The Effects of Leaving a Filter in a Sampler for a Week on the Observed Ratio of the Nitrate Concentration to Sulfate Concentration.**

## 5.6 DISCUSSION

Consider Figure 5.11. Generally speaking, the spread and the magnitude of the experiment blanks (the ones left in the sampler for a week) are consistent with the spread and magnitude associated with the other blanks. (Keep in mind the 0s are really non-detects and could be anything up to the MDL or even slightly larger.) There is a notable exception. There are three experiment blanks for Tampa with approximately five micrograms of nitrate compared to a value of about one microgram for all of the other blanks.

Is this an anomalous result (i.e., an outlier) that should be thrown out before modeling? There are two arguments against this. First, the result appears to be replicated three times here. Moreover, both the nitrate and sulfate values are high. In fact, similar results occur in each of the four experiments that mimic sequential sampling conditions. Also, there a few data points in the blanks from the Task 2 data that have unusually high data. Hence, it would seem that, although rare, these represent real values. The second argument is that the whole point of this experiment is to guard against significant amounts of contamination.

Also, a note of caution is needed about the apparent replication. A true replicate would ideally have been from a filter loaded in a separate sampler. In this case, there are five filters all loaded into a common sampler. Since they are physically isolated from each other, then there is not as much of a problem treating these as true replicates. The usual problem with this is that the statistical model will end up estimating analytical error instead of sampling error. Since the analytical can be much less than sampling error, the statistical basis for trying to determine what represents a significant difference is drastically under estimated. Looking at the data for both Sections 5.1 and 5.4 it would appear that the measurements can be used as replicates, because not all of the experiment blanks from the associated site and day are unusually high.

As a result of the problems noted above, the measurements were modeled in several ways. First, they were modeled with all of the data, treating everything as true replicates. Next, they were modeled with all of the data, but with first replacing the experiment blanks from a site and day with their average. (So instead of having five measurements, there is only one experiment blank data point per site and day.) The third and fourth models are just as above with the anomalous sites removed. (The model version that excluded the sites with extreme data and treated the values as replicates was reported in the earlier sections.) The results are essentially the same, and are exactly as you would expect from looking at the plots. If the large values are removed, then there is little or no significant difference between the trip blanks, field blanks, and the experiment blanks. (The freezer blanks are usually significantly less.) Otherwise the experiment blanks can be significantly higher.

The blanks associated with the routine data showed only extremely rare occurrences of these high values. Yet unusual values occurred more than once within the five experiments. Hence ,it would seem that the correct answer is not to treat the unusual values here as outliers. The correct conclusion should be that there is significantly more sampling variability than would be indicated by the modeling results because these “outliers” should be included. (The results in

Section 3.3 include these values.) This leads to the same answers that there is little or no significant difference in the mean response, except for OC.

# 6.0 SYNTHESIS

We begin by summarizing the major findings. First, there are significant site to site differences that affect all parts of the assessment. At the Phoenix site, 13 of the 45 dates with data were flagged for inconsistency, while at the Fresno site only 3 of the 48 days with data were flagged. The evidence points to site-to-site differences that do not depend on the combination of samplers. Any of the results that show a significant site-to-site dependence need to be taken with caution because the sampler types are not distributed evenly across sites. Second, not all parameters behave the same. They do, however, frequently group as one would expect: soil components tend to be similar; sulfate, nitrate, and ammonium sometimes show similar results; and EC and OC frequently have similar results.

Given that there are fairly consistent biases between co-located samplers (on a log scale) the most important findings are:

- The measured PM2.5 mass was compared with co-located FRM measurements. Seventeen out of 24 of the samplers met the Expert Panel data objective of an $R^2$ value of at least 0.9 in a linear regression of the mass values against the FRM measurement. Deviations from this criteria appear to be caused by site influences that affect all the monitors at a site, rather than differences among sampler types.

- Only half of the samplers met the Expert Panel data objective that the ratio of the FRM mass mean to the speciation sampler mass mean be at least 0.9 and at most 1.1. The ratios tested strongly dependent on both site and sampler type. In all cases with co-located FRMs, the means for the mass followed the following ordering: URG $\leq$ Andersen $\leq$ MetOne. Six of the seven URG means were less than the corresponding

FRM mean, all eight MetOne means were greater than the corresponding FRM mean, and six of the nine Andersen means were greater than the corresponding FRM mean.

- The concentration ordering noted for the mass applies to most of the species, namely URG $\leq$ Andersen $\leq$ MetOne. Moreover, while parameter specific, the percent of the time that this relation holds is consistent across sites. The exceptions to this ordering are chlorine, zinc, ammonium, and sulfate. For each of these exceptions, the percent of the time that the sampler types have one relationship or another varies by site. Of the species that do follow the general ordering above, only the nitrate data showed site to site differences in the percent of the time one sampler type is above another.

- For all species, the magnitude of the biases between sampler types is strongly site dependent from a statistical point of view. The magnitudes are summarized in the appendix by site and species so that the practical significance can be assessed.

- The variability found in the sampling precision across sampler types is probably due to site influences, but is probably not generally of any practical concern.

- The blanks generally do not show site to site differences. The trip blanks and field blanks are generally about the same. The URG blanks tend to be the cleanest except for nitrate. Nearly all of the “dirtiest” 25 percent of the blanks were from the URG samplers. The practical difference among the sampler types needs to be assessed separately.

- The five special experiments all suffer from a lack of data. As such, modeling results are not robust against the inclusion or exclusion of outliers. Assuming that the outliers have been properly identified, then there is little or no significant effect on sulfate, nitrate, elemental carbon, or organic carbon concentrations found with leaving filters in the sampler for an extended period either before or after sampling. The only statistically significant difference found was that blanks left for a week in the sampler collected on average an extra 3.25 micrograms of organic carbon.

- Qualitatively, both the face velocity experiment and the sampler to sampler comparisons suggest that measurements of carbon from low volume sampling yield higher concentrations than high volume sampling. The data from the sampler to sampler comparisons showed more consistency than the data from the face velocity experiment.

All of these findings need to be assessed for their practical significance. The tables in Appendix B provide estimates that show the magnitude of the differences observed. It may be that because there were over 1,000 days worth of data to work with the differences detected by the statistical techniques are not of practical significance. The standard errors shown indicate the level of sensitivity for the statistical tests. If the standard errors are an order of magnitude less than "practical" differences, then the declared differences may not have any practical meaning. On the other hand, if the standard errors are approximately equal to or greater than what is considered a significant practical difference, then the findings above have practical implications.

Both absolute and relative differences should be considered. However, it may be easier to eliminate the cases where the site medians (Table B.1) are less than about one-tenth of the MDLs, or some other nominal value, so that only relative differences need to be considered. For example, the differences noted for aluminum, lead, and tin probably do not have any practical implications, since the data are all very close to or below the MDL. On the other hand, the sulfate data are well above the MDL. However, the relative differences are mostly below 10 percent, so these may not be of practical significance either.

Finally, it may also be helpful to rank the species by data user needs. The species have very different impacts on visibility and very different relative risks. Such characteristics may guide the level of acceptable differences between samplers.

# APPENDIX A:

# GUIDE TO THE GRAPHICAL OUTPUT FROM TASKS 1 AND 2

April 27, 2001

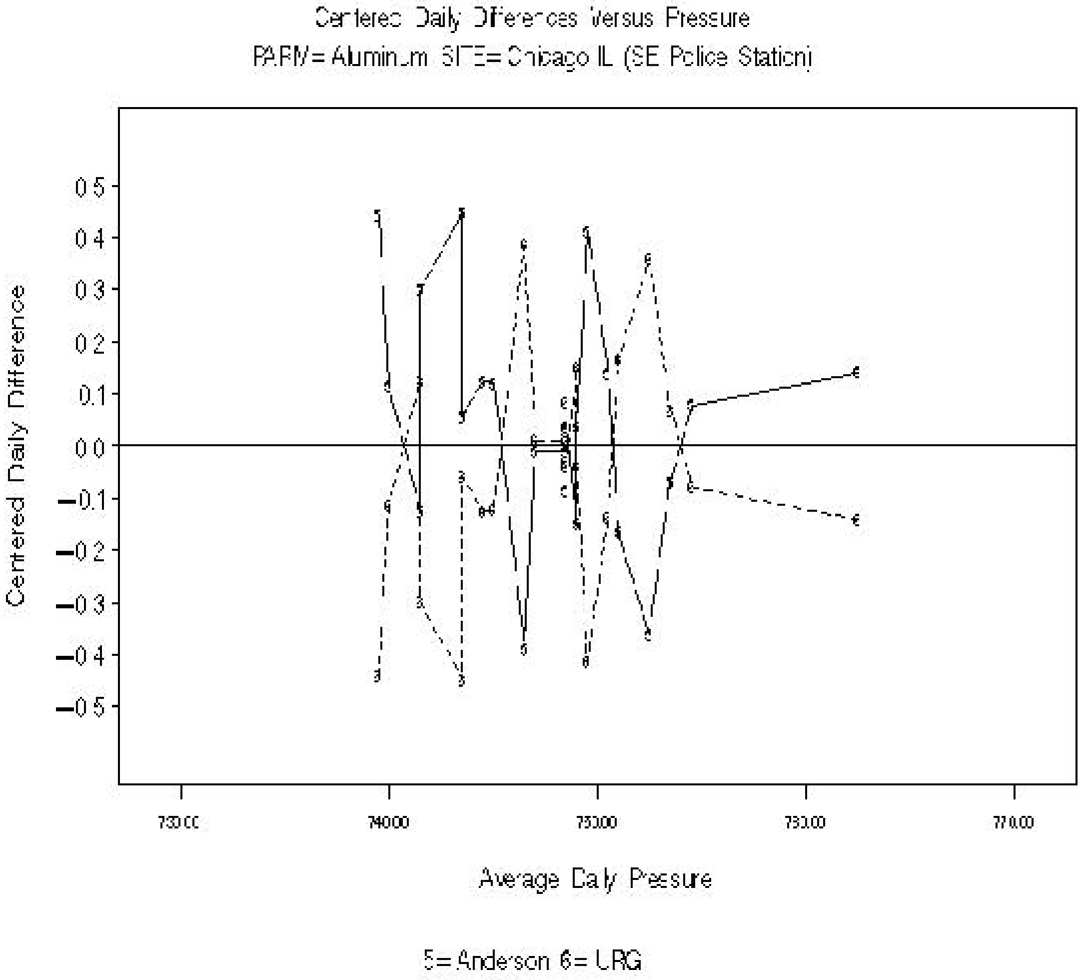
# Table of Contents

## List of Figures

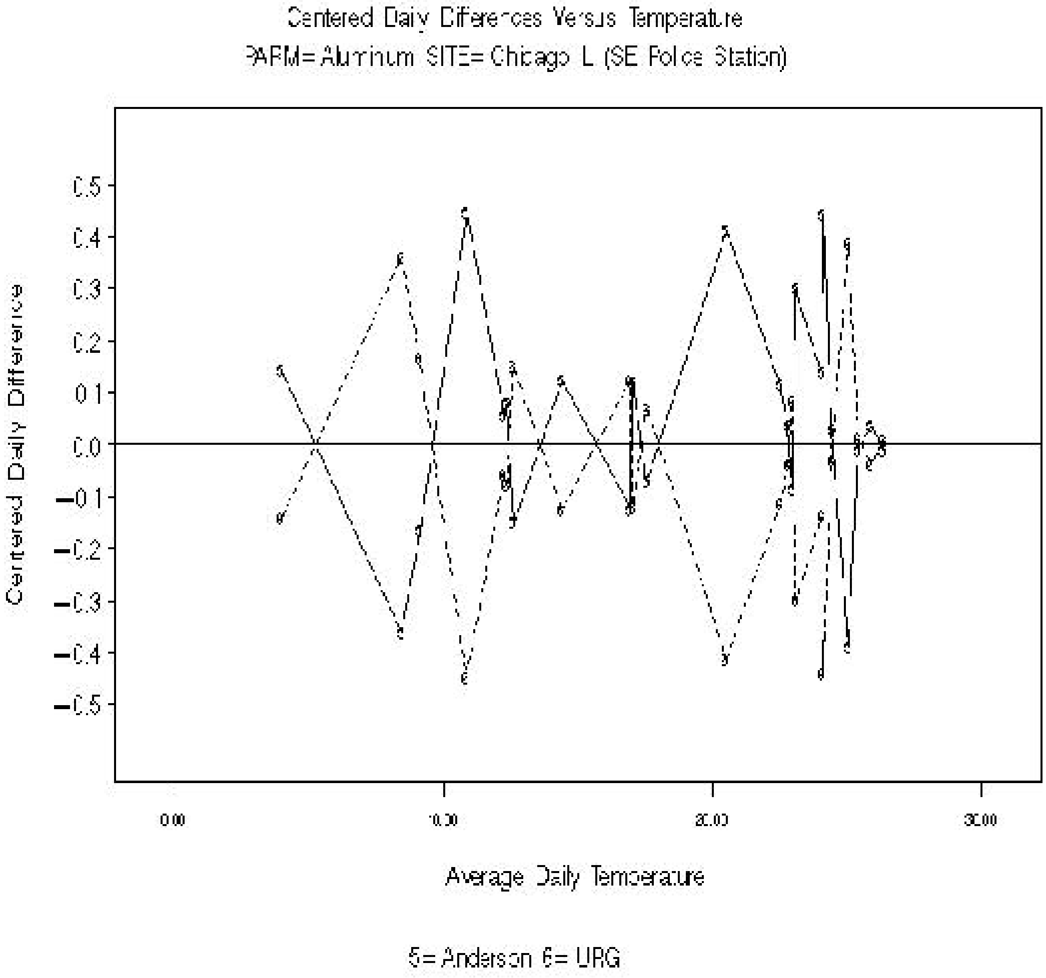
# APPENDIX A: GUIDE TO THE GRAPHICAL OUTPUT FROM TASKS 1 AND 2

This appendix contains examples of the major graphs considered throughout the project to assess the comparability of the sampler types. The three sections are the exploratory plots (the examples), a data dictionary, and the steps taken to produce the graphs. The graphs described will accompany the final report on CD. Until then, they are available at the Mini Trends website, www.sdas.battelle.org/minitrends.

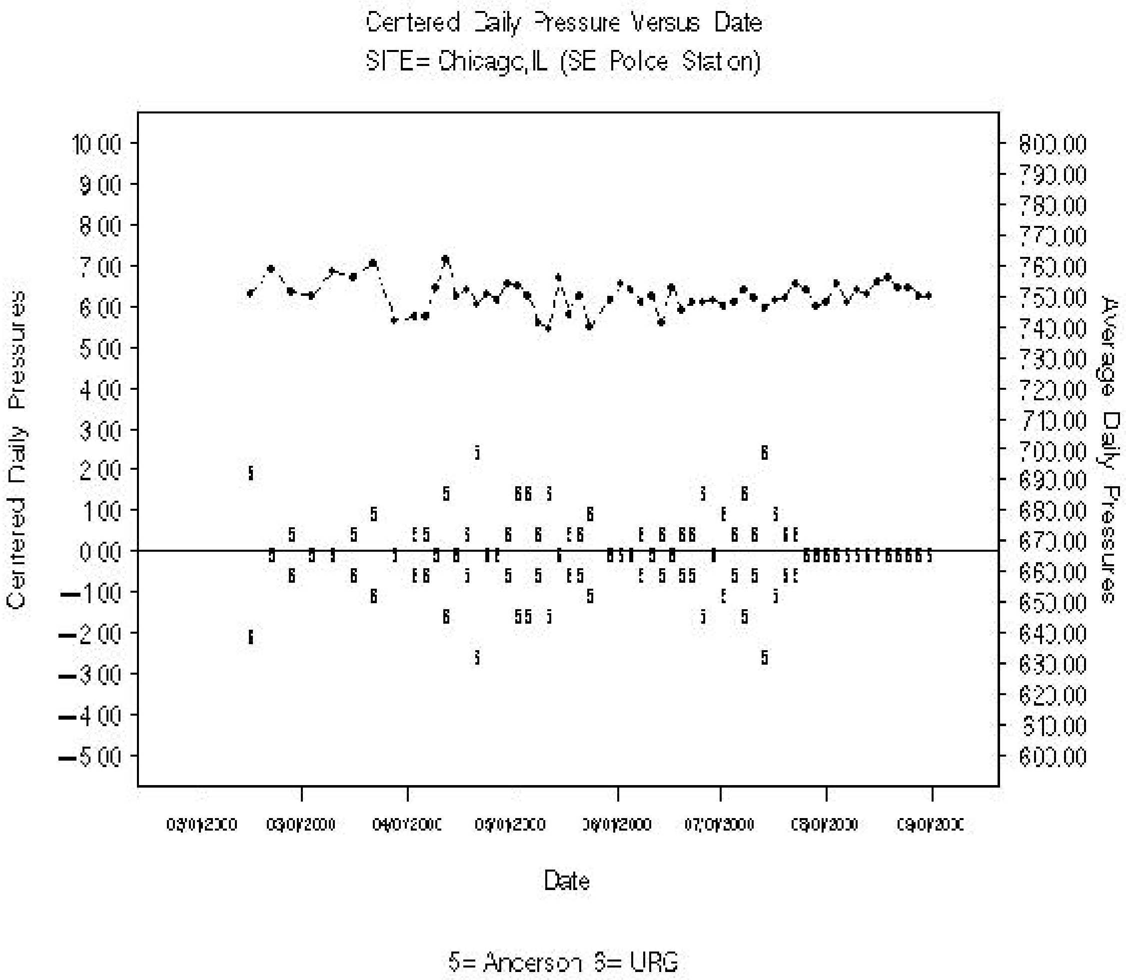
## A.1 EXPLORATORY PLOTS



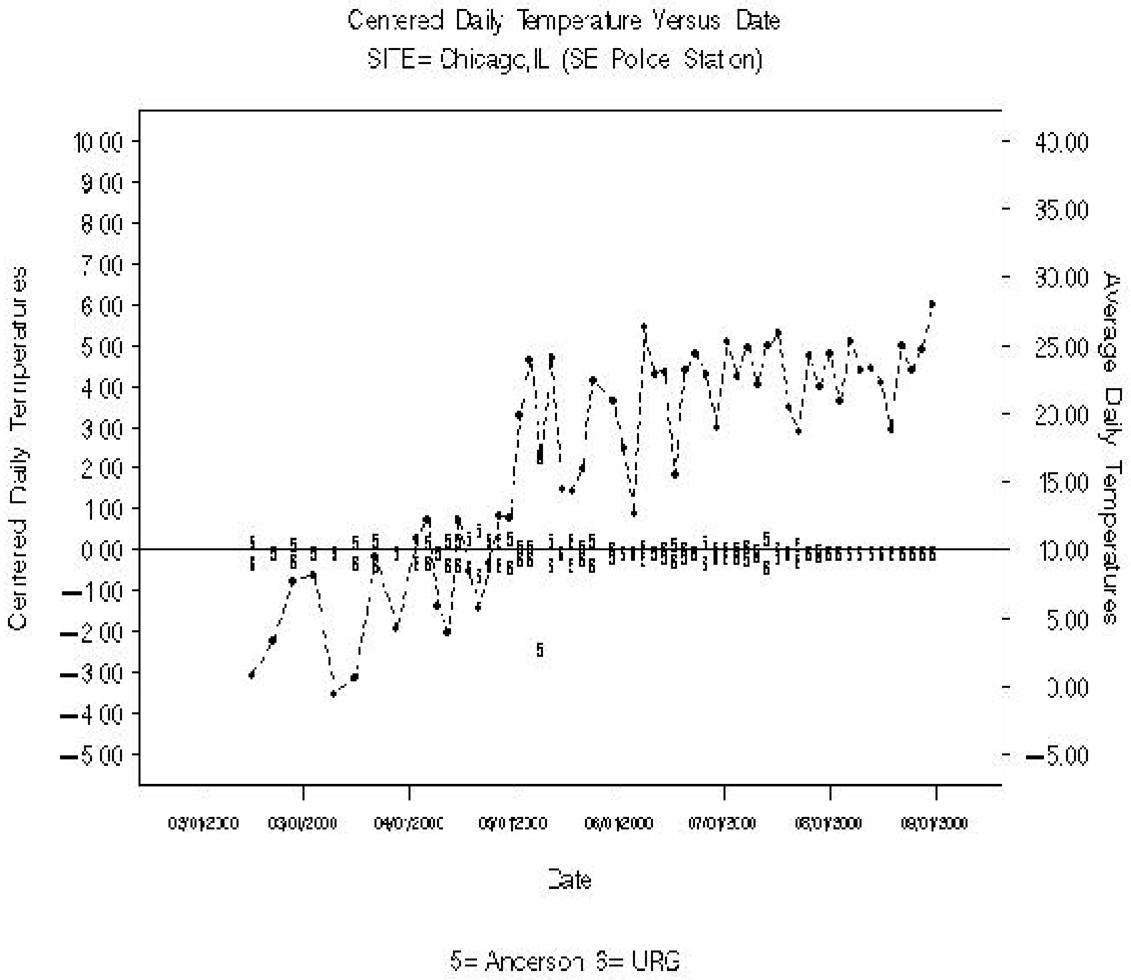
**Graph 1:** **Centered Daily Differences Versus Pressure. These plot the deviation from the daily mean of a monitor's parameter value versus the average pressure from all the monitors at the site.**



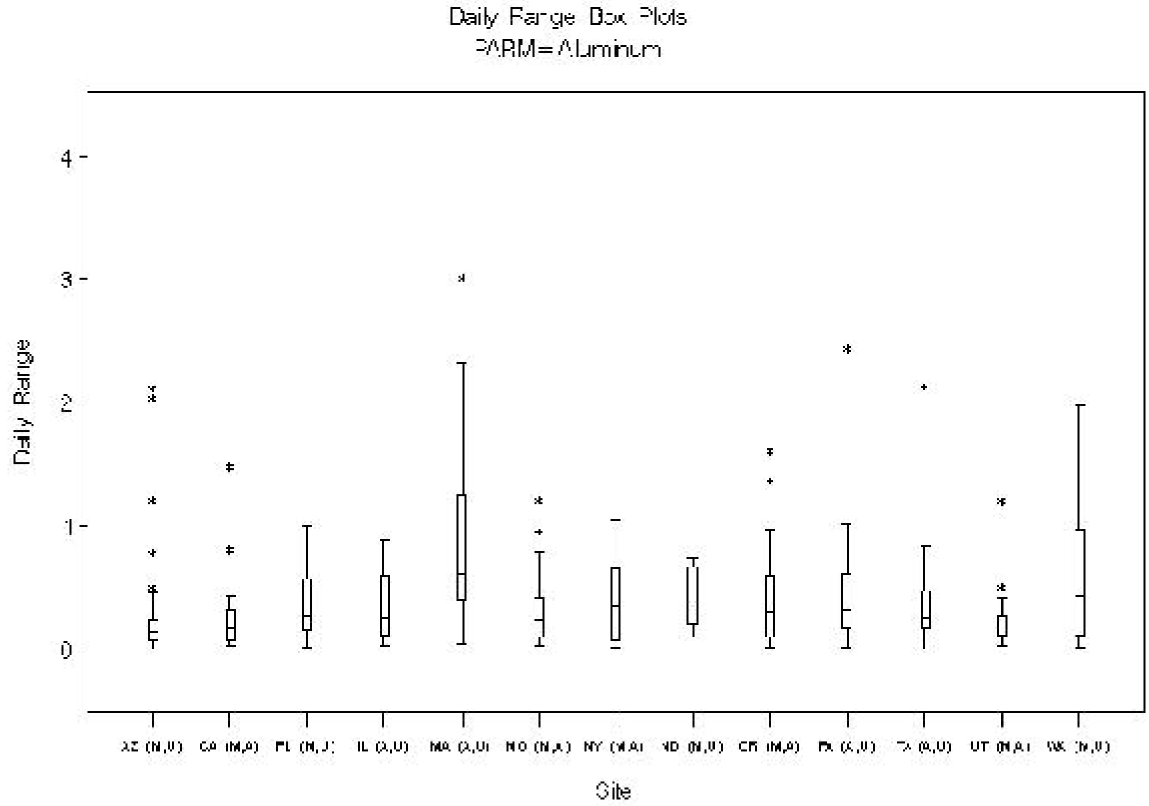
**Graph 2:** **Centered Daily Differences Versus Temperature. These plot the deviation from the daily mean of a monitor's parameter value versus the average temperature from all the monitors at the site.**



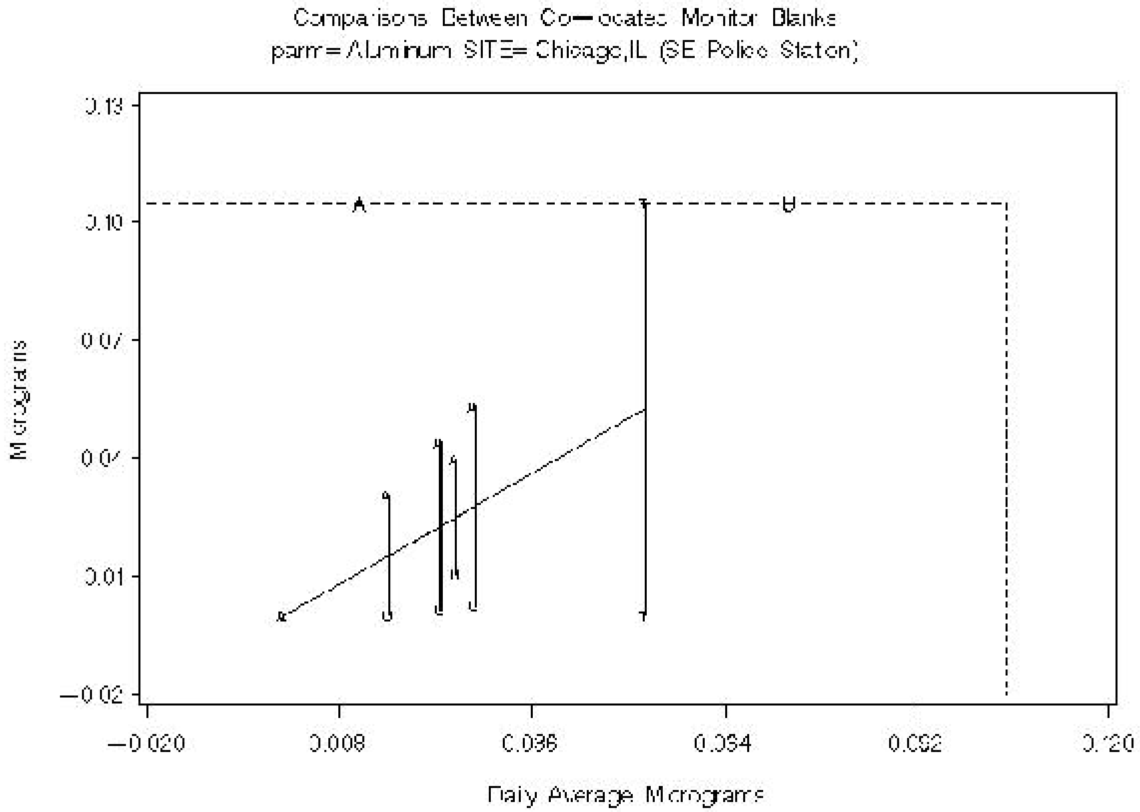
**Graph 3.** **Centered Daily Pressure Versus Date. These show a time series of the daily average pressure and the deviations from the mean by each monitor.**



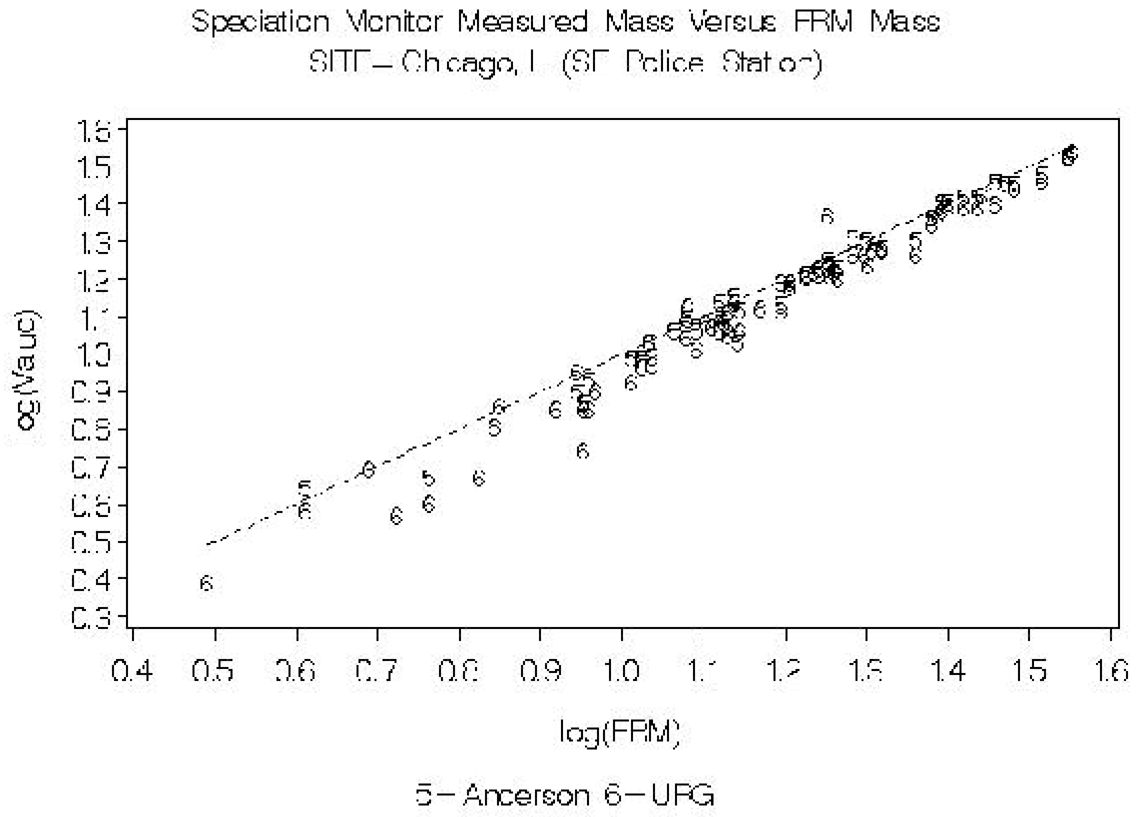
**Graph 4.** **Centered Daily Temperature Versus Date. These show a time series of the daily average temperature and the deviations from the mean by each monitor.**



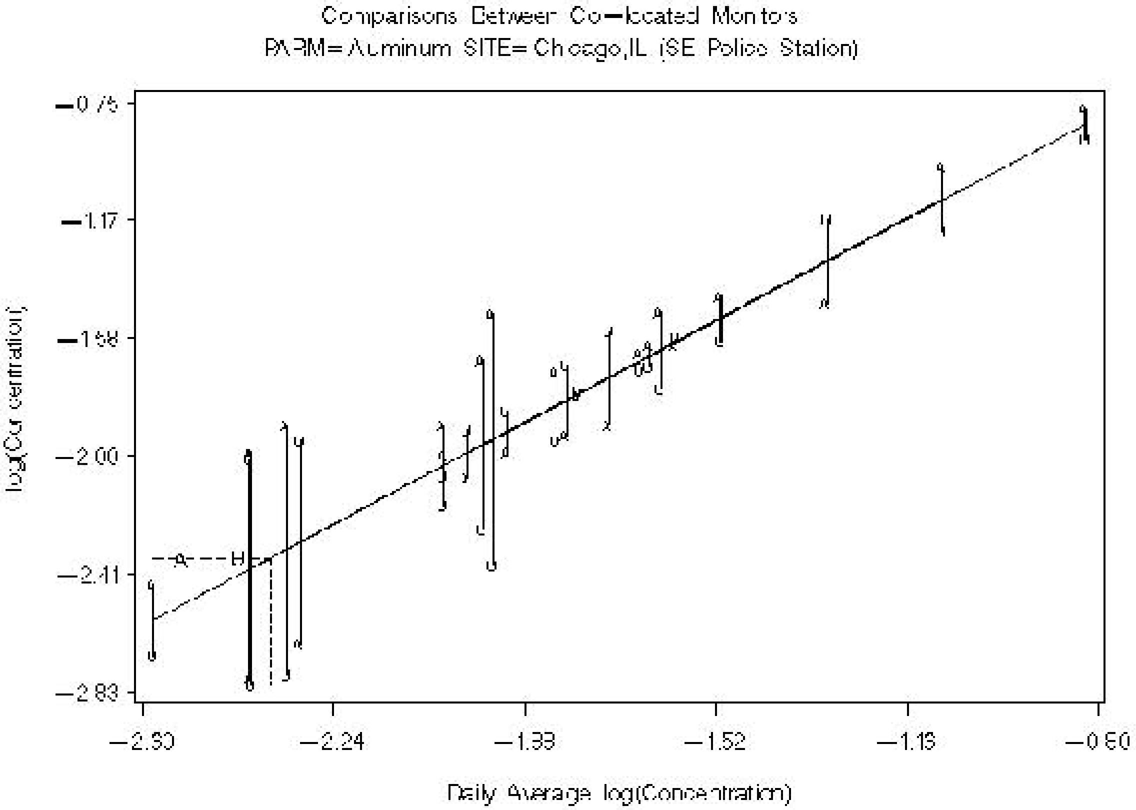
**Graph 5.** Daily Range Boxplots. Boxplots of the difference between the daily maximums and the minimums of a parameter for each site.



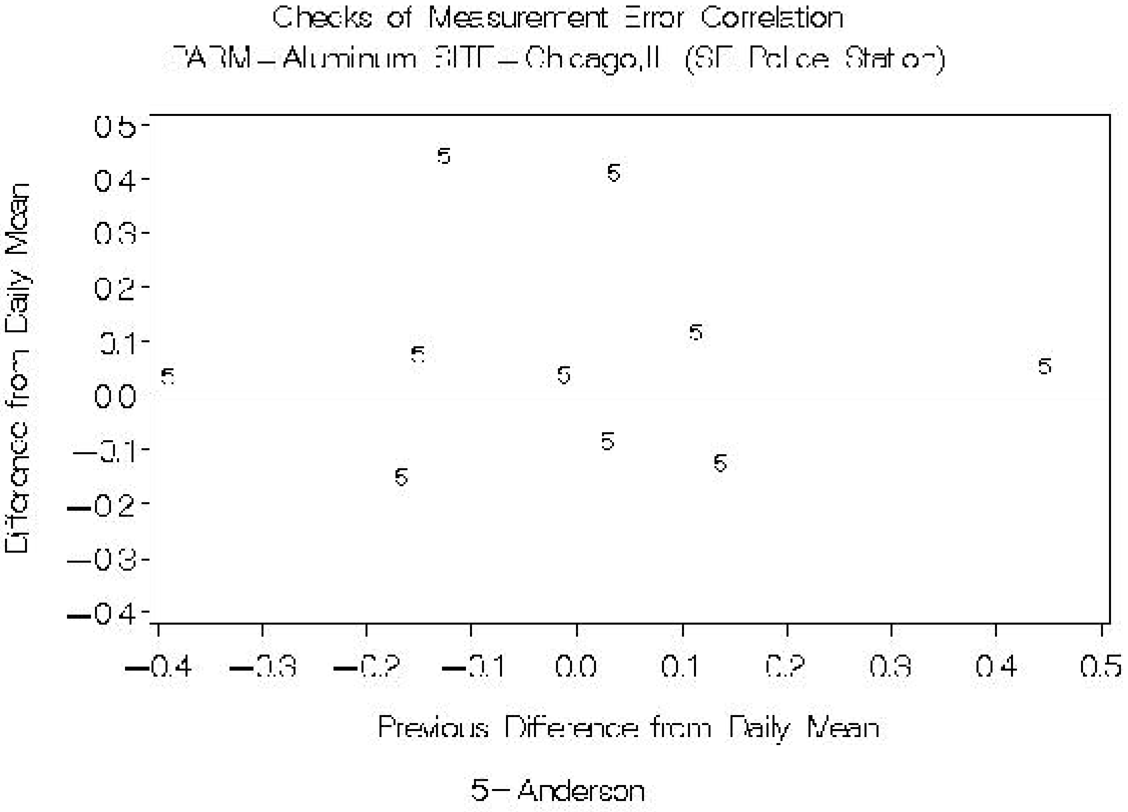
**Graph 6.** **Comparisons Between Co-located Monitor Blanks. These plot the daily average parameter mass of the blanks against the minimum and maximum values observed (connected by a vertical line). The letter indicates either the first letter of the vendor or a "T" for a trip blank. The daily means are connected by the diagonal line. The MDL is indicated with dashed rectangular boxes.**



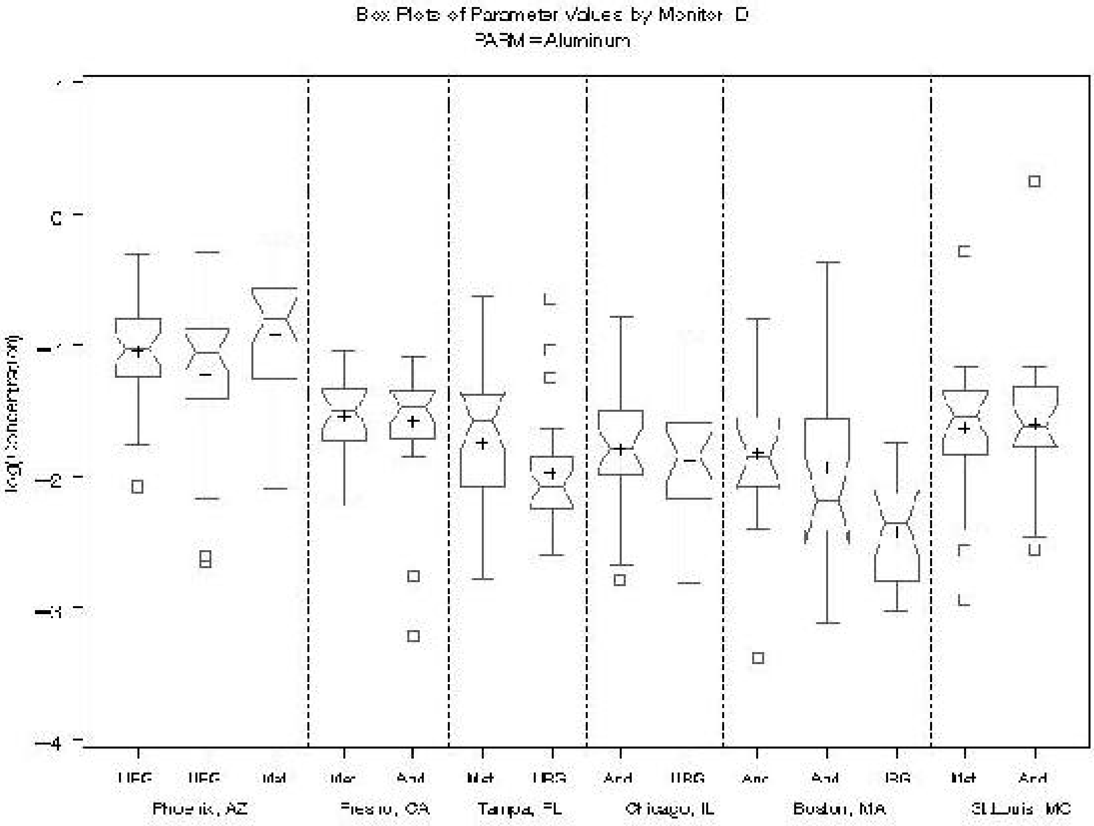
**Graph 7.** **Speciation Monitor Measured Mass Versus FRM mass. These are scatter plots of the total mass as measured by a monitor versus the co-located FRM measurement. The POC number is indicated on the graph.**



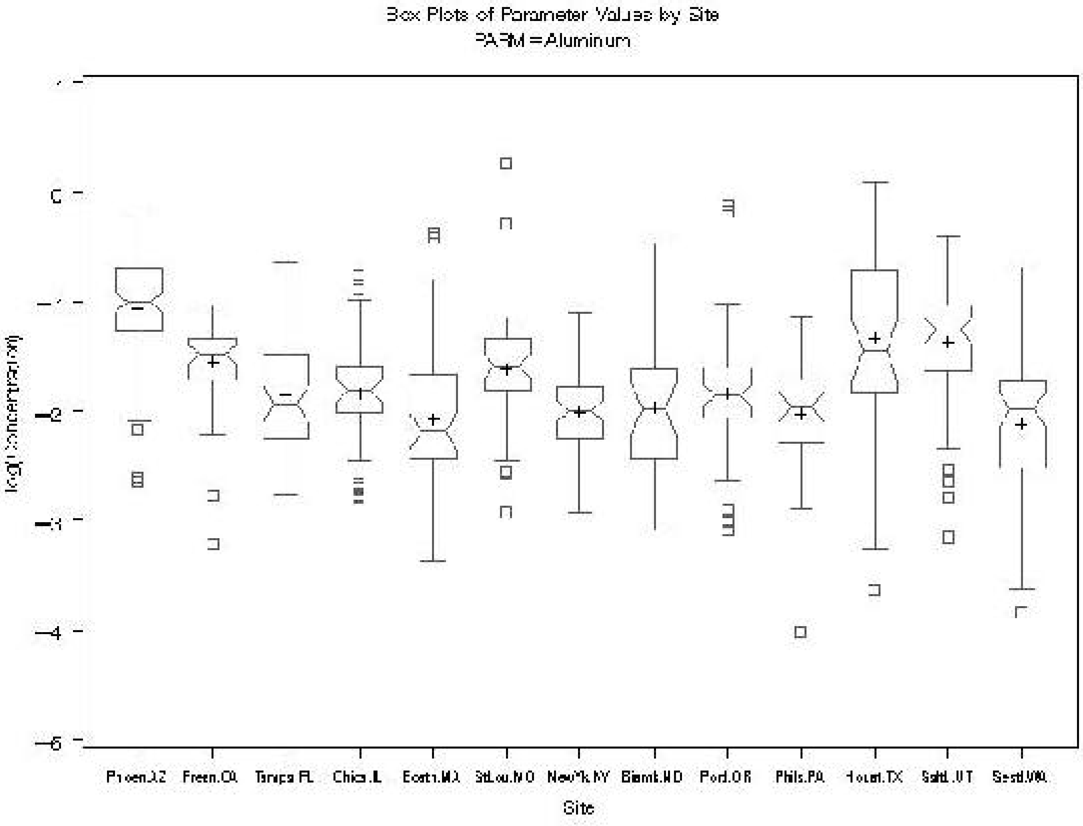
**Graph 8.** **Comparisons Between Co-located Monitor Blanks. These plot the daily average parameter mass of the routine data against the minimum and maximum values observed (connected by a vertical line). The daily means are connected by the diagonal line. The letter indicates the first letter of the vendor. The MDL is indicated with dashed rectangular boxes.**



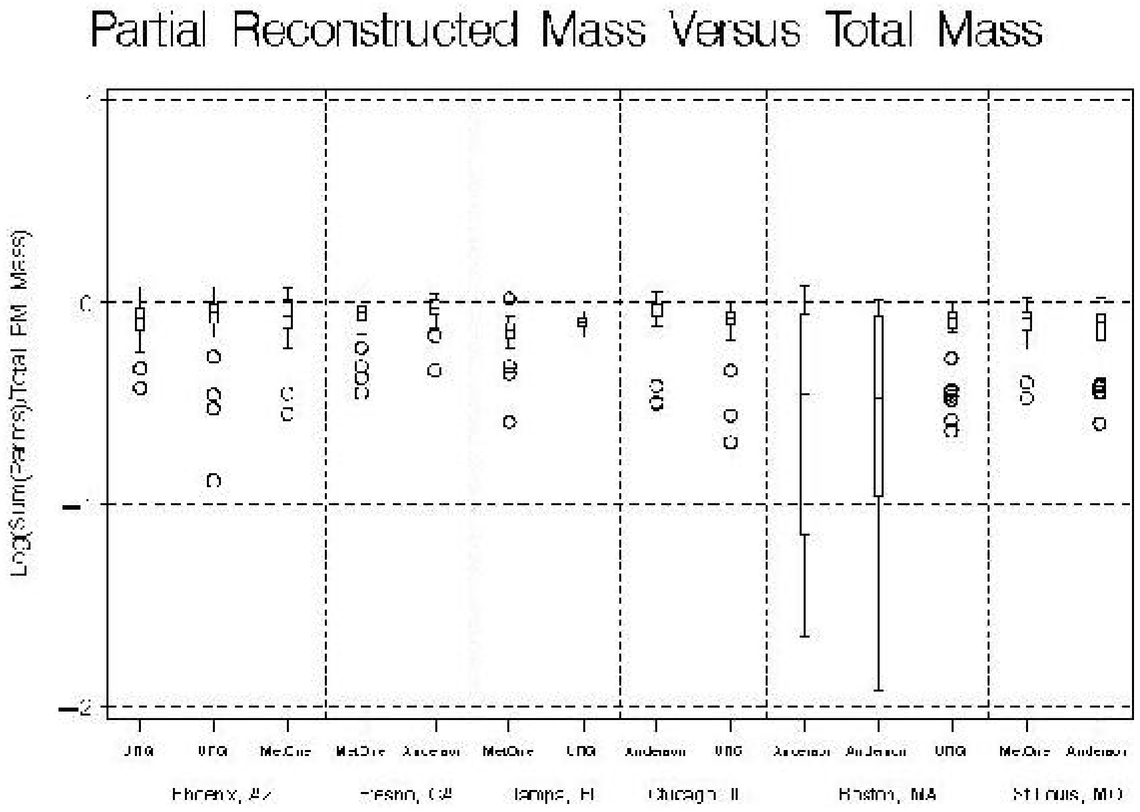
**Graph 9.** Checks of Measurement Error Correlation. These are scatter plots of a monitor's deviation from the site mean on one day versus the difference measured 3 days later.



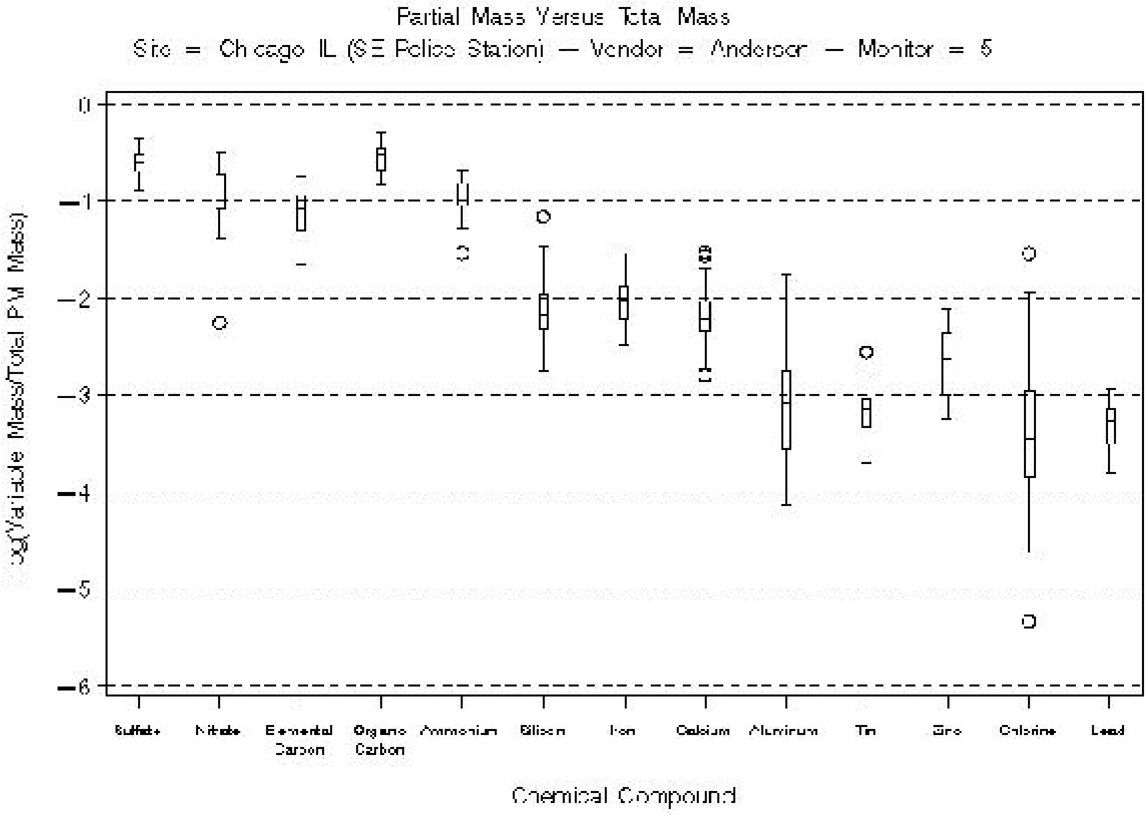
**Graph 10. Boxplots of Parameter Values by Monitor ID. These are side-by-side notched boxplots of the log-concentration for a parameter. The notch is an approximate 95 Percent confidence interval for the median. (In the example shown, the notches for two monitors at the Tampa site do not overlap. Hence, these have significantly different medians.)**



**Graph 11.** **Boxplots of Parameter Values by Site. These are side-by-side notched boxplots of the log-concentration for a parameter. The notch is an approximate 95 Percent confidence interval for the median. (In the example shown, the notches for Seattle and Salt Lake City do not overlap. Hence, these have significantly different medians.)**



**Graph 12. Partial Reconstructed Mass Versus Total Mass. These are boxplots of the log of the partial reconstructed mass (based on the 13 study parameters) over the measured mass for each monitor and site.**



**Graph 13.** **Partial Mass Versus Total Mass. These are boxplots of the log of the parameter mass over the measured mass for each site.**

## A.2 DATABASE DICTIONARY

**Database Dictionary**

| Variable Name | Brief Description of Variable Contents |
|---|---|
| **Type** | Measurement Type<br>C Routine or FRM |
| **Parm** | 5-digit AIRS Parameter Code<br>C Total of 66 different parameters |
| **Site** | 9-digit AIRS Site ID<br>C (ST-CTY-SITE#)<br>C Recorded within the database without hyphens<br>C Total of 13 sites<br>o Each site has co-located monitors |
| **Zdate** | Actual Sample Date<br>C Formatted mm/dd/yyyy |
| **Meth** | 3-digit Collection/Analysis Method Code<br>C Distinct AIRS method code for each of the collection/analysis methods<br>C Total of 16 methods |
| **Vendor** | Speciation Sampler Design<br>C Andersen<br>C URG<br>C MetOne |
| **POC** | 1-digit Parameter Occurrence Code<br>C Distinguishes co-located instruments<br>C 5, 6, or 7 |
| **Value** | Sample Values |
| **Units** | Units of measure |
| **MDL** | Minimum Detection Limits for each target analyte<br>C Specific to species/vendor<br>C Total of 60 parameters with an associated MDL<br>o Parameter 88309 and 88310 only have an associated URG MDL<br>o Total of 6 temperature and pressure parameters do not have an MDL |

| Variable Name | Brief Description of Variable Contents |
|---|---|
| **BATTELLE_FLAG1** | Indicates monitor to monitor inconsistency<br>C If a specific site, date, POC, and parameter was flagged, then all corresponding observations were also flagged<br>o The alphanumeric flag contains letters corresponding to each parameter that was responsible for causing the site and date to be flagged<br>C Alphanumeric flag that represents parameters:<br>A = PM2.5 Mass (88101)<br>B = Aluminum (88104)<br>C = Ammonium (88301)<br>D = Calcium (88111)<br>E = Chlorine (88115)<br>F = Elemental Carbon (88307)<br>G = Iron (88126)<br>H = Lead (88128)<br>I = Nitrate (88306)<br>J = Organic Carbon (88305)<br>K = Silicon (88165)<br>L = Sulfate (88403)<br>M = Tin (88160)<br>N = Zinc (88167) |
| **BATTELLE_FLAG2*** | Indicates that the reported mass concentration of one of the species was significantly greater than the mass concentration of the sample<br>C If a specific site, date, POC, and parameter were flagged, then all corresponding observations were also flagged<br>o The alphanumeric flag contains letters corresponding to each parameter that was responsible for causing the site, date, and POC to be flagged<br>o (the same alphanumeric parameter associations as for BATTELLE_FLAG1) |
| **BATTELLE_FLAG3*** | Indicates that the sum of the masses of the 13 components that we were considering was significantly greater than the total reported mass<br>C Takes on a value of 1 or @ (missing) |

* Care needs to be taken in using these flags in areas that have high nitrate concentrations (e.g. in the Southwest). The reconstructed mass is based on multiple filters that can account for the volatilization of the nitrate.

## A.3 STEPS TAKEN TO PRODUCE GRAPHS

### Outline for the m2mc graphs containing the Routine and FRM data
### (title: Comparisons Between Co-located Monitors)

**General Overview:** plots of *each day's* observations where the y axis corresponds to the $\log_{10}$ transformation of value and the x axis corresponds to the day's mean $\log_{10}$ transformation of value; on any given day there will be either 2 or 3 points observed (depending on how many pocs were recording at that site) and labeled with the corresponding vendor's initial; a vertical line connects the min and max values for the day and a 45 degree line connects the means across all days; MDL lines are represented on each graph as a vertical and a horizontal line that meet at a point on the 45 degree line – each MDL line is also labeled with the corresponding vendor's initial.

**Step 1.**

- Read in Routine and FRM data from the original dataset while eliminating all null observations (which are obvious outliers), keeping only the 14 parms of interest, keeping only days/sites with at least two vendors present, and only keeping observations where value>0
    - Eliminated all RTI flagged observations (known outliers)

    - Assigned a vendor name and an MDL value to each observation depending on the site and poc #

    - Get only the parm*site*zdate combinations where there were more than one vendor (thus to compare vendors) – 13 sites remain

    - Transformed the concentration value to the $\log_{10}$ scale; the resulting variable: $\log_{10}$_value

**<u>Step 2.</u>**

C Find specific parm*site mins, maxs, and means (of log$_{10}$_value) to get:

1. Range for plot axes
    C The y axis for each parm*site differs
        i. The axis goes from the minimum log$_{10}$_value over all days to the maximum log$_{10}$_value over all days (for that particular parm*site combination)

    C The x axis for each parm*site differs

        i. First, the mean log$_{10}$ value was found for each parm*site*zdate (i.e., within a given parm*site combination, the mean value was computed for each day)

        ii. Of these daily means, the minimum mean value and the maximum mean value were found and used as the axis boundaries

2. Reference lines for daily means
    C Creates a straight 45 degree reference line on the graph connecting the daily means (i.e.,where y=x)

3. Vertical bars for the daily range
    C Connects the daily minimum and maximum values with a straight vertical line

4. MDL vertical and horizontal lines
    C The MDL lines for each vendor*parm differs
        i. Plots the MDL line vertically from the x axis and horizontally from the

y axis and connects at the reference line

ii. Each MDL line is labeled with its corresponding vendor's initial

**<u>Step 3.</u>**

- Each y*x=group is plotted and labeled with the corresponding vendor
  - The variable y is the $\log_{10}$ transformation of the original value while the variable x is the mean $\log_{10}$_value, or the mean of all $\log_{10}$_values for a particular day
  - Each vertical connecting line represents one day of recording – a "summary" of each days' observations

**Outline for the m2mc graphs containing the FIELD and TRI P BLANK data**
**(title: Comparisons Between Co-located Monitor Blanks)**

**<u>General Overview:</u>** Basically the same plots as for the m2mc with Routine and FRM data, but with a few minor changes

Changes:

- Changed the MDL value to the MDL_blank value with the formula:
  MDL_blank = (conc. MDL)(flow rate in L/min)(1.44 to convert to micrograms) = MDL in micrograms

- Trip blanks were labeled as their own "group" in the plots, similar to the vendor labeling except with a "T"

- The axes were set on the plot to extend above or below the minimum and maximum points, whether they be the MDL lines or the actual values

**Outline for the boxplots containing the Routine and FRM data**
**(title: Daily Range Boxplots)**

**<u>General Overview:</u>** Daily range boxplots were created for each parm to see site-to-site comparisons of the (maximum $\log_{10}$ value – minimum $\log_{10}$ value) differences.

Using the dataset (d) that only contains observations for the 14 parms of interest, only days/sites with at least two vendors present, observations where value>0, no null observations, the $\log_{10}$ transformation of the original value, and only non-RTI flagged data:

- Found the minimum and maximum observations of $\log_{10}$ value (using the proc means procedure) for each parm*site*zdate combination

- From these, a new variable called ‘diff’ was created by taking the maximum $\log_{10}$_value and subtracting the minimum $\log_{10}$_value

- For each parm separately, ‘diff’ was plotted against site

    - Boxplots with whiskers and endlines were created for each set of points (parm*site specific); observations more than 1.5 iqr away from this box were represented by a star

    - Sites were labeled with the site’s state abbreviation, as well as the first initial of the vendors that were present at that site

## Outline for the log_FRM plots containing the Routine and FRM data (title: Speciation Monitor Measured Mass Versus FRM Mass)

**General Overview:** Scatter plots of daily values for each site's $\log_{10}$ transformed speciation mass vs $\log_{10}$ transformed frm mass.

Using the dataset (d) that only contains observations for the 14 parms of interest, only days/sites with at least two vendors present, observations where value>0, no null observations, the $\log_{10}$ transformation of the original value, and only the non-RTI flagged data:

- Plotted the $\log_{10}$ transformed speciation mass against $\log_{10}$ transformed frm mass
- Added a 45° line to the graph
    - Found the minimum and maximum $\log_{10}$ transformed FRM values, by site
    - In order to plot these two points, set the x variable ($\log_{10}$ FRM) was set to equal the minimum $\log_{10}$ FRM value and then set the y variable ($\log_{10}$ value) equal the minimum $\log_{10}$ FRM value and designated it as a different poc number to allow for connecting the points later with Interpol=join; this was repeated similarly for the maximum $\log_{10}$ FRM value
    - Each plotted point on the graph was labeled with its corresponding poc number
    - The footnote denoted the vendor-to-poc mapping information for that particular site

## Outline for the cddvspress and cddvstemp plots containing the Routine and FRM data (title: Centered Daily Differences Versus Pressure/ Centered Daily Differences Versus Temperature)

**<u>General Overview:</u>** Plot, by parm and site, the centered daily differences for a given parm versus the average daily pressure or temperature.

- Read in Routine and FRM data from the original dataset while eliminating all null observations (which are obvious outliers), keeping only the 14 parms of interest, keeping only days/sites with at least two vendors present, and only keeping observations where value>0
    - Eliminated all RTI flagged observations (known outliers)
    - Assigned a vendor name and an MDL value to each observation depending on the site and poc #
    - Get only the parm*site*zdate combinations where there were more than one vendor (thus to compare vendors) – 13 sites remain
    - Transformed the concentration value to the log$_{10}$ scale; the resulting variable: log$_{10}$_value
    - Created a separate dataset with only 2 parms, daily temperature and barometric pressure
- With the temp/press dataset, found average temperature and pressure by site and date; created separate datasets for temp and pressure

- Found daily mean (by parm and site) for the concentration values and created the centered daily values (i.e., log$_{10}$_value -log$_{10}$_value_mean)

- Merged the centered daily values data with the mean temp and pressure data (separately)

- Plot, by parm and site, the centered daily differences vs the average daily temp or pressure

    - Labeled each point with its poc number and then connected each point

    - The footnote denoted the vendor-to-poc mapping information

### Outline for the cdpress and cdtemp plots containing the Routine and FRM data

**(title: Centered Daily Pressure Versus Date / Centered Daily Temperature Versus Date)**

**General Overview:** Plot, by site, the centered daily pressure or temperature values versus date.

- Read in Routine and FRM data from the original dataset while eliminating all null observations (which are obvious outliers), keeping only sites with at least two vendors present, and keeping only the 2 parms of interest

    - Eliminated all RTI flagged observations (known outliers)

- Found the mean temp or pressure for each parm*site*zdate*poc

- Found the daily mean temp or pressure for each parm*site*zdate

- Merged these two datasets together and calculated the centered daily difference for temp and pressure separately

- Plotted the centered value versus the date

  - Labeled each point with the poc number

  - The footnote denoted the vendor-to-poc mapping information

- Plotted, on the same graph, the daily average temp or pressure versus the date and connected the points

  - This allowed us to see how the centered values were behaving while having an idea of what the actual averages were doing

## Outline for the parmbp and parmbps plots containing the Routine and FRM data (title: Boxplots of Parameter Values by Monitor ID/ Boxplots of Parameter Values by Site)

**General Overview:** Boxplots were created for each parameter, of the concentration values, by either monitor id or site.

Using the dataset (d) that only contains observations for the 14 parms of interest, only days/sites with at least two vendors present, observations where value>0, no null observations, the $\log_{10}$ transformation of the original value, and only the non-RTI flagged data:

- Created a monitor id number for each observation using the formula mon_id=(site*10)+poc2

  - Monitor id is a unique number specifying a specific site and poc

  - With this monitor id, an index was created to more simply specify the monitor id number, thus assigning it a number 1 -- 40

- Boxplots were created for each parameter by plotting the $\log_{10}$ transformation of value against the index (or monitor id)

  - Note that the plot for each parm spanned two pages (i.e., two separate jpegs) since there were numerous index values

- Boxplots were also created for each parameter by plotting the $\log_{10}$ transformation of value against the site (i.e., over all monitors at a given site)

## Outline for the mec plots containing the Routine and FRM data
## (title: Checks of Measurement Error Correlation)

**<u>General Overview:</u>** Scatter plots of measurement error for a given parm*site*poc2; looking at the day's centered $\log_{10}$ transformed value versus the centered $\log_{10}$ transformed value from three days ago; there is logically a correlation between the values from day to day since it will take more than a day to increase or decrease a concentration, but there should not be a correlation between the centered values

Using the dataset (d) that only contains observations for the 14 parms of interest, only days/sites with at least two vendors present, observations where value>0, no null observations, the $\log_{10}$ transformation of the original value, and only the non-RTI flagged data:

- Found the daily mean $\log_{10}$ transformed value for each parm*site*zdate

- Merged these two datasets together (d and the daily mean dataset) and calculated the centered daily difference

- From this merged dataset, each observation was set into a separate data set according to POC type (i.e., all POC=5, POC=6, POC=7, and POC=9 (FRM))

    - Looking at each parm*site*zdate separately, the zdate was compared to the previous observed date; if this observed date was 3 days previous, then the centered difference for that day was labeled 'pre_val'; thus for each observation, there is a centered value and a 'pre_val' if the previous date is only 3 days earlier (else, there is no pre_val associated with this observation)

    - These four separate datasets were then set back together to form one complete dataset

- Plotted the centered value versus the previous centered value (if there was one) for each parm*site*poc

    - Labeled each point with the poc number

    - The footnote denoted the vendor-to-poc mapping information

## Outline for the vmvstmc plots containing the Routine and FRM data
## (title: Partial Mass Versus Total Mass)

**General Overview:** Boxplots were created of the variable mass divided by total PM mass for each parameter by site, date, and monitor

Read in Routine data from the original dataset while eliminating all null observations (which are obvious outliers), keeping only the 14 parms of interest, and only keeping observations where value>0

- Eliminated all RTI flagged observations (known outliers)

- Assigned a vendor name and an MDL value to each observation depending on the site and monitor

- While looking at PM mass separately, found each site and date combination where there was more than one monitor present (i.e., for a given site and date, at least two monitors were recording) and only kept those sites and dates

    - These observations were merged with the remaining 13 variables by site, zdate, and monitor

        - The variable Log_Val was created by dividing each parameter's value by the PM mass value and taking the $\log_{10}$ transformation of the quotient; this was done for each site*zdate*monitor separately

- Plotted this variable, Log_Val, versus the associated parameter, for each parameter*site*vendor*monitor combination

### Outline for the smvstmc plots containing the Routine and FRM data (title: Partial Reconstructed Mass Versus Total Mass)

**<u>General Overview:</u>** Boxplots were created of the summed parameter values divided by the total PM mass, by site and vendor

Took the dataset previously created for the vmvstmc plots which had site*zdate*monitor combinations with more than one monitor observed

- The variable Sum_Val was created by summing the values of all parameters for a given site*zdate*monitor combination

- Another variable, Log_CM, was created by dividing the summed value by the PM mass value and taking the $\log_{10}$ transformation of the quotient; this was done for each site*monitor separately

- Plotted this variable, Log_CM, versus a variable called Count (a number unique to a particular site*vendor*monitor)

# APPENDIX B:

# TABLES OF SUMMARY STATISTICS

April 27, 2001

# Table of Contents

# APPENDIX B: TABLES OF SUMMARY STATISTICS

This appendix consists of four tables. Table B.1 shows the site median concentrations and maximum sampler MDL for each parameter. This is followed by the median relative differences between the samplers. This is defined as the median difference in concentration divided by the median for the site. Table B.2 shows mean differences calculated for the statistical models (for this table, all flagged data was removed). Table B.3 has the site means for each sampler type. Finally, Table B.4 extends Table 3.5 to all parameters.

## Table B.1 Median Relative Differences between Samplers for each Site and Parameter

| | | | Sampler type for | | | Site | Maximum | Relative median difference between samplers | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| PM2.5 Mass | Fresno | And-Met1 | MetOne | Andersen | | 10.7749 | 0.1040 | 12.3% | . | . | 9.3% | -1.7% | . |
| PM2.5 Mass | St.Louis | And-Met1 | MetOne | Andersen | | 15.2749 | 0.1040 | 1.6% | . | . | 11.3% | 2.7% | . |
| PM2.5 Mass | New York | And-Met1 | Andersen | MetOne | MetOne | 11.9236 | 0.1040 | -8.0% | -13.1% | -2.3% | 2.1% | 11.6% | 17.1% |
| PM2.5 Mass | Portland | And-Met1 | Andersen | MetOne | | 9.1515 | 0.1040 | -9.7% | . | . | . | . | . |
| PM2.5 Mass | Salt Lake | And-Met1 | MetOne | Andersen | | 6.4351 | 0.1040 | 4.6% | . | . | 21.6% | 12.9% | . |
| PM2.5 Mass | Chicago | And-URG | Andersen | URG | | 14.0000 | 0.1040 | 4.6% | . | . | -6.2% | -9.3% | . |
| PM2.5 Mass | Boston | And-URG | Andersen | Andersen | URG | 9.7000 | 0.1040 | 3.1% | 3.8% | 3.8% | -8.3% | -3.2% | -12.0% |
| PM2.5 Mass | Philadelphia | And-URG | Andersen | URG | | 12.5083 | 0.1040 | 11.1% | . | . | 8.0% | 0.7% | . |
| PM2.5 Mass | Houston | And-URG | Andersen | URG | | 12.3024 | 0.1040 | 10.6% | . | . | 14.1% | 0.7% | . |
| PM2.5 Mass | Phoenix | Met1-URG | URG | URG | MetOne | 8.0869 | 0.1040 | -1.0% | -24.5% | -20.8% | . | . | . |
| PM2.5 Mass | Tampa | Met1-URG | MetOne | URG | | 12.0103 | 0.1040 | 10.4% | . | . | 9.5% | -1.0% | . |
| PM2.5 Mass | Bismarck | Met1-URG | MetOne | URG | | 5.5000 | 0.1040 | 22.9% | . | . | 12.0% | -8.9% | . |
| PM2.5 Mass | Seattle | Met1-URG | MetOne | URG | | 7.2000 | 0.1040 | 24.6% | . | . | 19.6% | -3.4% | . |
| Aluminum | Fresno | And-Met1 | MetOne | Andersen | | 0.0328 | 0.0109 | -8.4% | . | . | . | . | . |
| Aluminum | St.Louis | And-Met1 | MetOne | Andersen | | 0.0258 | 0.0109 | -10.7% | . | . | . | . | . |
| Aluminum | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0100 | 0.0109 | -21.6% | -36.7% | -2.7% | . | . | . |
| Aluminum | Portland | And-Met1 | Andersen | MetOne | | 0.0139 | 0.0109 | -6.9% | . | . | . | . | . |
| Aluminum | Salt Lake | And-Met1 | MetOne | Andersen | | 0.0546 | 0.0109 | 11.7% | . | . | . | . | . |
| Aluminum | Chicago | And-URG | Andersen | URG | | 0.0153 | 0.0109 | 19.6% | . | . | . | . | . |
| Aluminum | Boston | And-URG | Andersen | Andersen | URG | 0.0065 | 0.0109 | 54.9% | 207.9% | 78.1% | . | . | . |
| Aluminum | Philadelphia | And-URG | Andersen | URG | | 0.0109 | 0.0109 | 70.0% | . | . | . | . | . |
| Aluminum | Houston | And-URG | Andersen | URG | | 0.0357 | 0.0109 | 68.9% | . | . | . | . | . |
| Aluminum | Phoenix | Met1-URG | URG | URG | MetOne | 0.0977 | 0.0109 | -9.4% | -55.3% | -18.2% | . | . | . |
| Aluminum | Tampa | Met1-URG | MetOne | URG | | 0.0117 | 0.0109 | 67.6% | . | . | . | . | . |
| Aluminum | Bismarck | Met1-URG | MetOne | URG | | 0.0104 | 0.0109 | 83.6% | . | . | . | . | . |
| Aluminum | Seattle | Met1-URG | MetOne | URG | | 0.0104 | 0.0109 | 28.9% | . | . | . | . | . |
| Calcium | Fresno | And-Met1 | MetOne | Andersen | | 0.0526 | 0.0035 | -0.8% | . | . | . | . | . |

|  |  |  | Sampler type for |  |  | Site | Maximum | Relative median difference between samplers |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| Calcium | St.Louis | And-Met1 | MetOne | Andersen |  | 0.1127 | 0.0035 | -4.7% | . | . | . | . | . |
| Calcium | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0382 | 0.0035 | -10.0% | -12.0% | -0.4% | . | . | . |
| Calcium | Portland | And-Met1 | Andersen | MetOne |  | 0.0311 | 0.0035 | -2.7% | . | . | . | . | . |
| Calcium | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.1461 | 0.0035 | 4.8% | . | . | . | . | . |
| Calcium | Chicago | And-URG | Andersen | URG |  | 0.0801 | 0.0035 | 19.5% | . | . | . | . | . |
| Calcium | Boston | And-URG | Andersen | Andersen | URG | 0.0327 | 0.0035 | -4.1% | 32.9% | 28.4% | . | . | . |
| Calcium | Philadelphia | And-URG | Andersen | URG |  | 0.0359 | 0.0035 | 45.5% | . | . | . | . | . |
| Calcium | Houston | And-URG | Andersen | URG |  | 0.0620 | 0.0035 | 50.5% | . | . | . | . | . |
| Calcium | Phoenix | Met1-URG | URG | URG | MetOne | 0.1310 | 0.0035 | -3.0% | -38.1% | -31.6% | . | . | . |
| Calcium | Tampa | Met1-URG | MetOne | URG |  | 0.0581 | 0.0035 | 29.2% | . | . | . | . | . |
| Calcium | Bismarck | Met1-URG | MetOne | URG |  | 0.0283 | 0.0035 | 60.0% | . | . | . | . | . |
| Calcium | Seattle | Met1-URG | MetOne | URG |  | 0.0340 | 0.0035 | 27.9% | . | . | . | . | . |
| Chlorine | Fresno | And-Met1 | MetOne | Andersen |  | 0.0038 | 0.0058 | 30.7% | . | . | . | . | . |
| Chlorine | St.Louis | And-Met1 | MetOne | Andersen |  | 0.0077 | 0.0058 | -51.3% | . | . | . | . | . |
| Chlorine | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0044 | 0.0058 | -6.4% | 30.5% | 21.5% | . | . | . |
| Chlorine | Portland | And-Met1 | Andersen | MetOne |  | 0.0113 | 0.0058 | 30.1% | . | . | . | . | . |
| Chlorine | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.0100 | 0.0058 | -45.5% | . | . | . | . | . |
| Chlorine | Chicago | And-URG | Andersen | URG |  | 0.0087 | 0.0058 | 7.5% | . | . | . | . | . |
| Chlorine | Boston | And-URG | Andersen | Andersen | URG | 0.0072 | 0.0058 | -1.4% | 48.5% | 51.1% | . | . | . |
| Chlorine | Philadelphia | And-URG | Andersen | URG |  | 0.0047 | 0.0058 | 37.3% | . | . | . | . | . |
| Chlorine | Houston | And-URG | Andersen | URG |  | 0.0397 | 0.0058 | 38.4% | . | . | . | . | . |
| Chlorine | Phoenix | Met1-URG | URG | URG | MetOne | 0.0449 | 0.0058 | -1.0% | -10.3% | -6.4% | . | . | . |
| Chlorine | Tampa | Met1-URG | MetOne | URG |  | 0.0087 | 0.0058 | 141.0% | . | . | . | . | . |
| Chlorine | Bismarck | Met1-URG | MetOne | URG |  | 0.0007 | 0.0058 | 259.8% | . | . | . | . | . |
| Chlorine | Seattle | Met1-URG | MetOne | URG |  | 0.0111 | 0.0058 | 46.2% | . | . | . | . | . |
| Iron | Fresno | And-Met1 | MetOne | Andersen |  | 0.0885 | 0.0020 | -1.6% | . | . | . | . | . |
| Iron | St.Louis | And-Met1 | MetOne | Andersen |  | 0.1336 | 0.0020 | -9.7% | . | . | . | . | . |
| Iron | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0834 | 0.0020 | -9.4% | -4.6% | 1.2% | . | . | . |
| Iron | Portland | And-Met1 | Andersen | MetOne |  | 0.0519 | 0.0020 | 2.5% | . | . | . | . | . |

|  |  |  | Sampler type for |  |  | Site | Maximum | Relative median difference between samplers |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| Iron | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.1204 | 0.0020 | 3.8% | . | . | . | . | . |
| Iron | Chicago | And-URG | Andersen | URG |  | 0.1257 | 0.0020 | 12.8% | . | . | . | . | . |
| Iron | Boston | And-URG | Andersen | Andersen | URG | 0.0580 | 0.0020 | -3.5% | 24.6% | 40.4% | . | . | . |
| Iron | Philadelphia | And-URG | Andersen | URG |  | 0.0740 | 0.0020 | 38.8% | . | . | . | . | . |
| Iron | Houston | And-URG | Andersen | URG |  | 0.0536 | 0.0020 | 31.4% | . | . | . | . | . |
| Iron | Phoenix | Met1-URG | URG | URG | MetOne | 0.1335 | 0.0020 | -3.5% | -33.1% | -25.9% | . | . | . |
| Iron | Tampa | Met1-URG | MetOne | URG |  | 0.0469 | 0.0020 | 18.2% | . | . | . | . | . |
| Iron | Bismarck | Met1-URG | MetOne | URG |  | 0.0304 | 0.0020 | 43.3% | . | . | . | . | . |
| Iron | Seattle | Met1-URG | MetOne | URG |  | 0.0498 | 0.0020 | 23.2% | . | . | . | . | . |
| Lead | Fresno | And-Met1 | MetOne | Andersen |  | 0.0030 | 0.0055 | 35.2% | . | . | . | . | . |
| Lead | St.Louis | And-Met1 | MetOne | Andersen |  | 0.0119 | 0.0055 | 5.9% | . | . | . | . | . |
| Lead | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0049 | 0.0055 | -34.1% | -36.8% | -13.9% | . | . | . |
| Lead | Portland | And-Met1 | Andersen | MetOne |  | 0.0057 | 0.0055 | -35.6% | . | . | . | . | . |
| Lead | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.0046 | 0.0055 | 35.9% | . | . | . | . | . |
| Lead | Chicago | And-URG | Andersen | URG |  | 0.0070 | 0.0055 | 6.4% | . | . | . | . | . |
| Lead | Boston | And-URG | Andersen | Andersen | URG | 0.0033 | 0.0055 | 4.4% | 13.5% | 5.2% | . | . | . |
| Lead | Philadelphia | And-URG | Andersen | URG |  | 0.0050 | 0.0055 | 7.2% | . | . | . | . | . |
| Lead | Houston | And-URG | Andersen | URG |  | 0.0026 | 0.0055 | -0.3% | . | . | . | . | . |
| Lead | Phoenix | Met1-URG | URG | URG | MetOne | 0.0034 | 0.0055 | -15.1% | -40.8% | -48.1% | . | . | . |
| Lead | Tampa | Met1-URG | MetOne | URG |  | 0.0041 | 0.0055 | 29.5% | . | . | . | . | . |
| Lead | Bismarck | Met1-URG | MetOne | URG |  | 0.0027 | 0.0055 | 63.6% | . | . | . | . | . |
| Lead | Seattle | Met1-URG | MetOne | URG |  | 0.0046 | 0.0055 | 17.4% | . | . | . | . | . |
| Tin | Fresno | And-Met1 | MetOne | Andersen |  | 0.0134 | 0.0179 | 87.7% | . | . | . | . | . |
| Tin | St.Louis | And-Met1 | MetOne | Andersen |  | 0.0131 | 0.0179 | 74.0% | . | . | . | . | . |
| Tin | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0174 | 0.0179 | -61.2% | -83.8% | -23.6% | . | . | . |
| Tin | Portland | And-Met1 | Andersen | MetOne |  | 0.0117 | 0.0179 | -94.2% | . | . | . | . | . |
| Tin | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.0122 | 0.0179 | 85.6% | . | . | . | . | . |
| Tin | Chicago | And-URG | Andersen | URG |  | 0.0093 | 0.0179 | -4.6% | . | . | . | . | . |
| Tin | Boston | And-URG | Andersen | Andersen | URG | 0.0076 | 0.0179 | -9.4% | -3.0% | 11.8% | . | . | . |

|  |  |  | Sampler type for |  |  | Site | Maximum | Relative median difference between samplers |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| Tin | Philadelphia | And-URG | Andersen | URG |  | 0.0087 | 0.0179 | -1.1% | . | . | . | . | . |
| Tin | Houston | And-URG | Andersen | URG |  | 0.0079 | 0.0179 | 7.7% | . | . | . | . | . |
| Tin | Phoenix | Met1-URG | URG | URG | MetOne | 0.0087 | 0.0179 | -14.3% | -111.9% | -103.2% | . | . | . |
| Tin | Tampa | Met1-URG | MetOne | URG |  | 0.0115 | 0.0179 | 88.3% | . | . | . | . | . |
| Tin | Bismarck | Met1-URG | MetOne | URG |  | 0.0124 | 0.0179 | 80.2% | . | . | . | . | . |
| Tin | Seattle | Met1-URG | MetOne | URG |  | 0.0129 | 0.0179 | 102.7% | . | . | . | . | . |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Silicon | Fresno | And-Met1 | MetOne | Andersen |  | 0.1723 | 0.0075 | -1.1% | . | . | . | . | . |
| Silicon | St.Louis | And-Met1 | MetOne | Andersen |  | 0.1230 | 0.0075 | -11.2% | . | . | . | . | . |
| Silicon | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0645 | 0.0075 | -6.5% | -13.2% | -1.4% | . | . | . |
| Silicon | Portland | And-Met1 | Andersen | MetOne |  | 0.0562 | 0.0075 | -0.4% | . | . | . | . | . |
| Silicon | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.1888 | 0.0075 | 3.5% | . | . | . | . | . |
| Silicon | Chicago | And-URG | Andersen | URG |  | 0.0990 | 0.0075 | 18.0% | . | . | . | . | . |
| Silicon | Boston | And-URG | Andersen | Andersen | URG | 0.0547 | 0.0075 | 3.3% | 27.9% | 31.0% | . | . | . |
| Silicon | Philadelphia | And-URG | Andersen | URG |  | 0.0727 | 0.0075 | 38.2% | . | . | . | . | . |
| Silicon | Houston | And-URG | Andersen | URG |  | 0.1407 | 0.0075 | 22.1% | . | . | . | . | . |
| Silicon | Phoenix | Met1-URG | URG | URG | MetOne | 0.2859 | 0.0075 | -6.5% | -46.5% | -18.9% | . | . | . |
| Silicon | Tampa | Met1-URG | MetOne | URG |  | 0.1191 | 0.0075 | 18.1% | . | . | . | . | . |
| Silicon | Bismarck | Met1-URG | MetOne | URG |  | 0.0699 | 0.0075 | 35.5% | . | . | . | . | . |
| Silicon | Seattle | Met1-URG | MetOne | URG |  | 0.0451 | 0.0075 | 30.5% | . | . | . | . | . |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Zinc | Fresno | And-Met1 | MetOne | Andersen |  | 0.0112 | 0.0014 | -166.8% | . | . | . | . | . |
| Zinc | St.Louis | And-Met1 | MetOne | Andersen |  | 0.0244 | 0.0014 | -36.7% | . | . | . | . | . |
| Zinc | New York | And-Met1 | Andersen | MetOne | MetOne | 0.0197 | 0.0014 | 8.2% | 7.7% | 1.0% | . | . | . |
| Zinc | Portland | And-Met1 | Andersen | MetOne |  | 0.0062 | 0.0014 | 36.3% | . | . | . | . | . |
| Zinc | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.0061 | 0.0014 | -24.3% | . | . | . | . | . |
| Zinc | Chicago | And-URG | Andersen | URG |  | 0.0366 | 0.0014 | 2.4% | . | . | . | . | . |
| Zinc | Boston | And-URG | Andersen | Andersen | URG | 0.0089 | 0.0014 | -1.2% | 2.9% | 5.2% | . | . | . |
| Zinc | Philadelphia | And-URG | Andersen | URG |  | 0.0124 | 0.0014 | 8.0% | . | . | . | . | . |
| Zinc | Houston | And-URG | Andersen | URG |  | 0.0054 | 0.0014 | 16.6% | . | . | . | . | . |
| Zinc | Phoenix | Met1-URG | URG | URG | MetOne | 0.0047 | 0.0014 | -6.0% | 18.8% | 27.4% | . | . | . |

|  |  |  |  | Sampler type for |  | Site | Maximum | Relative median difference between samplers |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| Zinc | Tampa | Met1-URG | MetOne | URG |  | 0.0053 | 0.0014 | -14.3% | . | . | . | . | . |
| Zinc | Bismarck | Met1-URG | MetOne | URG |  | 0.0021 | 0.0014 | -23.1% | . | . | . | . | . |
| Zinc | Seattle | Met1-URG | MetOne | URG |  | 0.0060 | 0.0014 | -14.1% | . | . | . | . | . |
| Ammonium | Fresno | And-Met1 | MetOne | Andersen |  | 0.6452 | 0.0170 | 20.4% | . | . | . | . | . |
| Ammonium | St.Louis | And-Met1 | MetOne | Andersen |  | 1.6273 | 0.0170 | -2.3% | . | . | . | . | . |
| Ammonium | New York | And-Met1 | Andersen | MetOne | MetOne | 1.1238 | 0.0170 | -5.0% | 1.5% | 1.5% | . | . | . |
| Ammonium | Portland | And-Met1 | Andersen | MetOne |  | 0.3066 | 0.0170 | -1.3% | . | . | . | . | . |
| Ammonium | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.2622 | 0.0170 | 6.0% | . | . | . | . | . |
| Ammonium | Chicago | And-URG | Andersen | URG |  | 1.2792 | 0.0170 | -2.8% | . | . | . | . | . |
| Ammonium | Boston | And-URG | Andersen | Andersen | URG | 0.6538 | 0.0170 | 9.2% | -48.5% | -42.6% | . | . | . |
| Ammonium | Philadelphia | And-URG | Andersen | URG |  | 1.4074 | 0.0170 | -15.7% | . | . | . | . | . |
| Ammonium | Houston | And-URG | Andersen | URG |  | 0.9261 | 0.0170 | -70.2% | . | . | . | . | . |
| Ammonium | Phoenix | Met1-URG | URG | URG | MetOne | 0.3603 | 0.0170 | 0.2% | -3.1% | -1.7% | . | . | . |
| Ammonium | Tampa | Met1-URG | MetOne | URG |  | 1.2229 | 0.0170 | -55.9% | . | . | . | . | . |
| Ammonium | Bismarck | Met1-URG | MetOne | URG |  | 0.4721 | 0.0170 | -32.1% | . | . | . | . | . |
| Ammonium | Seattle | Met1-URG | MetOne | URG |  | 0.4806 | 0.0170 | -25.5% | . | . | . | . | . |
| Organic Carbon | Fresno | And-Met1 | MetOne | Andersen |  | 4.3780 | 0.1460 | 1.6% | . | . | . | . | . |
| Organic Carbon | St.Louis | And-Met1 | MetOne | Andersen |  | 4.3132 | 0.1460 | 4.3% | . | . | . | . | . |
| Organic Carbon | New York | And-Met1 | Andersen | MetOne | MetOne | 3.6228 | 0.1460 | 2.4% | -3.2% | 0.3% | . | . | . |
| Organic Carbon | Portland | And-Met1 | Andersen | MetOne |  | 4.0846 | 0.1460 | -4.3% | . | . | . | . | . |
| Organic Carbon | Salt Lake | And-Met1 | MetOne | Andersen |  | 4.0413 | 0.1460 | 9.4% | . | . | . | . | . |
| Organic Carbon | Chicago | And-URG | Andersen | URG |  | 3.4811 | 0.1460 | 33.8% | . | . | . | . | . |
| Organic Carbon | Boston | And-URG | Andersen | Andersen | URG | 4.0557 | 0.1460 | 2.7% | 23.2% | 27.3% | . | . | . |
| Organic Carbon | Philadelphia | And-URG | Andersen | URG |  | 3.3165 | 0.1460 | 30.7% | . | . | . | . | . |
| Organic Carbon | Houston | And-URG | Andersen | URG |  | 2.1605 | 0.1460 | 18.7% | . | . | . | . | . |
| Organic Carbon | Phoenix | Met1-URG | URG | URG | MetOne | 3.4351 | 0.1460 | -8.0% | -43.7% | -28.2% | . | . | . |
| Organic Carbon | Tampa | Met1-URG | MetOne | URG |  | 2.8770 | 0.1460 | 29.3% | . | . | . | . | . |
| Organic Carbon | Bismarck | Met1-URG | MetOne | URG |  | 1.8676 | 0.1460 | 49.8% | . | . | . | . | . |
| Organic Carbon | Seattle | Met1-URG | MetOne | URG |  | 2.8822 | 0.1460 | 41.1% | . | . | . | . | . |

| | | | | Sampler type for | | Site | Maximum | | Relative median difference between samplers | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| Nitrate | Fresno | And-Met1 | MetOne | Andersen | | 1.1004 | 0.0080 | 10.1% | . | . | . | . | . |
| Nitrate | St.Louis | And-Met1 | MetOne | Andersen | | 1.0490 | 0.0080 | -0.2% | . | . | . | . | . |
| Nitrate | New York | And-Met1 | Andersen | MetOne | MetOne | 0.7440 | 0.0080 | -1.9% | -5.3% | -1.3% | . | . | . |
| Nitrate | Portland | And-Met1 | Andersen | MetOne | | 0.6488 | 0.0080 | -6.0% | . | . | . | . | . |
| Nitrate | Salt Lake | And-Met1 | MetOne | Andersen | | 0.3669 | 0.0080 | 11.0% | . | . | . | . | . |
| Nitrate | Chicago | And-URG | Andersen | URG | | 1.2154 | 0.0080 | 15.5% | . | . | . | . | . |
| Nitrate | Boston | And-URG | Andersen | Andersen | URG | 0.5088 | 0.0080 | 3.7% | 8.9% | 6.2% | . | . | . |
| Nitrate | Philadelphia | And-URG | Andersen | URG | | 1.3094 | 0.0080 | 12.2% | . | . | . | . | . |
| Nitrate | Houston | And-URG | Andersen | URG | | 0.6023 | 0.0080 | 23.4% | . | . | . | . | . |
| Nitrate | Phoenix | Met1-URG | URG | URG | MetOne | 0.3847 | 0.0080 | 4.6% | -20.2% | -20.6% | . | . | . |
| Nitrate | Tampa | Met1-URG | MetOne | URG | | 0.5128 | 0.0080 | 7.9% | . | . | . | . | . |
| Nitrate | Bismarck | Met1-URG | MetOne | URG | | 0.2734 | 0.0080 | 33.5% | . | . | . | . | . |
| Nitrate | Seattle | Met1-URG | MetOne | URG | | 0.6071 | 0.0080 | 16.2% | . | . | . | . | . |
| Elemental Carbon | Fresno | And-Met1 | MetOne | Andersen | | 0.4945 | 0.1460 | -9.1% | . | . | . | . | . |
| Elemental Carbon | St.Louis | And-Met1 | MetOne | Andersen | | 0.7649 | 0.1460 | 2.0% | . | . | . | . | . |
| Elemental Carbon | New York | And-Met1 | Andersen | MetOne | MetOne | 1.1654 | 0.1460 | 3.2% | 8.1% | -1.5% | . | . | . |
| Elemental Carbon | Portland | And-Met1 | Andersen | MetOne | | 0.6413 | 0.1460 | -5.3% | . | . | . | . | . |
| Elemental Carbon | Salt Lake | And-Met1 | MetOne | Andersen | | 0.6382 | 0.1460 | 5.4% | . | . | . | . | . |
| Elemental Carbon | Chicago | And-URG | Andersen | URG | | 0.9903 | 0.1460 | 22.9% | . | . | . | . | . |
| Elemental Carbon | Boston | And-URG | Andersen | Andersen | URG | 0.9590 | 0.1460 | 19.5% | -9.0% | -2.7% | . | . | . |
| Elemental Carbon | Philadelphia | And-URG | Andersen | URG | | 0.6573 | 0.1460 | 21.9% | . | . | . | . | . |
| Elemental Carbon | Houston | And-URG | Andersen | URG | | 0.3397 | 0.1460 | 12.6% | . | . | . | . | . |
| Elemental Carbon | Phoenix | Met1-URG | URG | URG | MetOne | 0.6048 | 0.1460 | -2.5% | -10.8% | -15.3% | . | . | . |
| Elemental Carbon | Tampa | Met1-URG | MetOne | URG | | 0.4757 | 0.1460 | 22.1% | . | . | . | . | . |
| Elemental Carbon | Bismarck | Met1-URG | MetOne | URG | | 0.1959 | 0.1460 | -15.3% | . | . | . | . | . |
| Elemental Carbon | Seattle | Met1-URG | MetOne | URG | | 0.6486 | 0.1460 | 34.8% | . | . | . | . | . |
| Sulfate | Fresno | And-Met1 | MetOne | Andersen | | 1.6899 | 0.0120 | 12.5% | . | . | . | . | . |
| Sulfate | St.Louis | And-Met1 | MetOne | Andersen | | 3.5810 | 0.0120 | -1.1% | . | . | . | . | . |

|  |  |  | Sampler type for |  |  | Site | Maximum | Relative median difference between samplers |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Site | Pair | Sampler 5 | Sampler 6 | Sampler 7 | Median | MDL | 5 to 6 | 5 to 7 | 6 to 7 | 5 to FRM | 6 to FRM | 7 to FRM |
| Sulfate | New York | And-Met1 | Andersen | MetOne | MetOne | 2.9367 | 0.0120 | -1.7% | 3.9% | 0.5% | . | . | . |
| Sulfate | Portland | And-Met1 | Andersen | MetOne |  | 1.1490 | 0.0120 | -3.9% | . | . | . | . | . |
| Sulfate | Salt Lake | And-Met1 | MetOne | Andersen |  | 0.8744 | 0.0120 | 6.5% | . | . | . | . | . |
| Sulfate | Chicago | And-URG | Andersen | URG |  | 3.0957 | 0.0120 | -2.3% | . | . | . | . | . |
| Sulfate | Boston | And-URG | Andersen | Andersen | URG | 2.1997 | 0.0120 | 0.5% | -15.7% | -10.4% | . | . | . |
| Sulfate | Philadelphia | And-URG | Andersen | URG |  | 3.1937 | 0.0120 | -2.0% | . | . | . | . | . |
| Sulfate | Houston | And-URG | Andersen | URG |  | 3.6743 | 0.0120 | -9.0% | . | . | . | . | . |
| Sulfate | Phoenix | Met1-URG | URG | URG | MetOne | 1.0603 | 0.0120 | -1.5% | -8.5% | -8.0% | . | . | . |
| Sulfate | Tampa | Met1-URG | MetOne | URG |  | 3.9425 | 0.0120 | -4.8% | . | . | . | . | . |
| Sulfate | Bismarck | Met1-URG | MetOne | URG |  | 1.2935 | 0.0120 | 0.4% | . | . | . | . | . |
| Sulfate | Seattle | Met1-URG | MetOne | URG |  | 1.4512 | 0.0120 | 3.1% | . | . | . | . | . |

## Table B.2 Mean Differences Between Sampler Types for Each Site and Parameter

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| PM2.5 Mass | And-Met1 | Fresno | -1.3052 | 0.3441 | -12.7% | 2.7% |
| PM2.5 Mass | And-Met1 | St. Louis | -0.5698 | 0.3090 | -2.8% | 2.7% |
| PM2.5 Mass | And-Met1 | New York | -1.4748 | 0.2696 | -10.6% | 2.2% |
| PM2.5 Mass | And-Met1 | Portland | -1.2551 | 0.3023 | -15.1% | 2.3% |
| PM2.5 Mass | And-Met1 | Salt Lake | -0.7965 | 0.2733 | -9.9% | 2.2% |
| PM2.5 Mass | And-URG | Chicago | 0.4394 | 0.3027 | 3.0% | 2.8% |
| PM2.5 Mass | And-URG | Boston | 0.3000 | 0.3198 | 2.7% | 3.0% |
| PM2.5 Mass | And-URG | Philadelphia | 1.3219 | 0.2837 | 9.5% | 2.8% |
| PM2.5 Mass | And-URG | Houston | 1.9952 | 0.3030 | 16.9% | 3.2% |
| PM2.5 Mass | Met1-URG | Phoenix | 1.8153 | 0.2621 | 23.6% | 2.9% |
| PM2.5 Mass | Met1-URG | Tampa | 1.1467 | 0.3250 | 9.3% | 3.2% |
| PM2.5 Mass | Met1-URG | Bismarck | 1.2272 | 0.4092 | 25.6% | 4.6% |
| PM2.5 Mass | Met1-URG | Seattle | 1.8529 | 0.2434 | 27.0% | 2.8% |
| Aluminum | And-Met1 | Fresno | 0.0055 | 0.0101 | 19.3% | 13.7% |
| Aluminum | And-Met1 | St. Louis | -0.0001 | 0.0150 | -12.8% | 14.7% |
| Aluminum | And-Met1 | New York | -0.0059 | 0.0137 | -34.2% | 10.2% |
| Aluminum | And-Met1 | Portland | -0.0005 | 0.0115 | -19.6% | 10.5% |
| Aluminum | And-Met1 | Salt Lake | -0.0133 | 0.0079 | -12.7% | 8.0% |
| Aluminum | And-URG | Chicago | 0.0043 | 0.0121 | 22.5% | 17.0% |
| Aluminum | And-URG | Boston | 0.0104 | 0.0193 | 116.9% | 47.7% |
| Aluminum | And-URG | Philadelphia | 0.0140 | 0.0134 | 54.9% | 23.6% |
| Aluminum | And-URG | Houston | 0.0833 | 0.0108 | 78.1% | 22.1% |
| Aluminum | Met1-URG | Phoenix | 0.0471 | 0.0075 | 44.8% | 12.4% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Aluminum | Met1-URG | Tampa | 0.0166 | 0.0141 | 164.5% | 42.2% |
| Aluminum | Met1-URG | Bismarck | 0.0268 | 0.0231 | 122.8% | 58.5% |
| Aluminum | Met1-URG | Seattle | 0.0089 | 0.0126 | 62.2% | 23.1% |
| Calcium | And-Met1 | Fresno | -0.0006 | 0.0075 | 0.4% | 5.7% |
| Calcium | And-Met1 | St. Louis | 0.0162 | 0.0067 | 9.8% | 5.6% |
| Calcium | And-Met1 | New York | -0.0068 | 0.0059 | -14.4% | 3.8% |
| Calcium | And-Met1 | Portland | -0.0002 | 0.0066 | -4.4% | 4.7% |
| Calcium | And-Met1 | Salt Lake | -0.0185 | 0.0060 | -4.5% | 4.3% |
| Calcium | And-URG | Chicago | 0.0254 | 0.0066 | 22.1% | 6.1% |
| Calcium | And-URG | Boston | 0.0114 | 0.0069 | 31.9% | 6.9% |
| Calcium | And-URG | Philadelphia | 0.0210 | 0.0062 | 57.2% | 7.3% |
| Calcium | And-URG | Houston | 0.0402 | 0.0066 | 55.9% | 7.8% |
| Calcium | Met1-URG | Phoenix | 0.0551 | 0.0057 | 45.4% | 6.3% |
| Calcium | Met1-URG | Tampa | 0.0266 | 0.0070 | 49.2% | 7.9% |
| Calcium | Met1-URG | Bismarck | 0.0231 | 0.0089 | 76.7% | 11.9% |
| Calcium | Met1-URG | Seattle | 0.0105 | 0.0053 | 34.0% | 5.4% |
| Chlorine | And-Met1 | Fresno | -0.0030 | 0.0403 | -34.5% | 27.0% |
| Chlorine | And-Met1 | St. Louis | 0.0108 | 0.0273 | 41.7% | 39.2% |
| Chlorine | And-Met1 | New York | 0.0102 | 0.0266 | -2.2% | 26.5% |
| Chlorine | And-Met1 | Portland | 0.0152 | 0.0172 | 59.1% | 27.7% |
| Chlorine | And-Met1 | Salt Lake | 0.0097 | 0.0150 | 28.2% | 19.5% |
| Chlorine | And-URG | Chicago | -0.0054 | 0.0188 | -4.2% | 18.2% |
| Chlorine | And-URG | Boston | 0.0079 | 0.0190 | 64.4% | 31.5% |
| Chlorine | And-URG | Philadelphia | 0.0006 | 0.0297 | 26.8% | 38.3% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Chlorine | And-URG | Houston | 0.0906 | 0.0149 | 73.0% | 25.9% |
| Chlorine | Met1-URG | Phoenix | 0.0052 | 0.0125 | 16.8% | 14.8% |
| Chlorine | Met1-URG | Tampa | 0.0666 | 0.0293 | 465.6% | 169.0% |
| Chlorine | Met1-URG | Seattle | 0.0038 | 0.0148 | 35.5% | 20.3% |
| | | | | | | |
| Iron | And-Met1 | Fresno | 0.0001 | 0.0064 | 2.2% | 4.3% |
| Iron | And-Met1 | St. Louis | 0.0074 | 0.0058 | 5.7% | 4.0% |
| Iron | And-Met1 | New York | -0.0065 | 0.0050 | -7.5% | 3.1% |
| Iron | And-Met1 | Portland | 0.0032 | 0.0057 | 5.3% | 3.9% |
| Iron | And-Met1 | Salt Lake | -0.0127 | 0.0051 | -6.8% | 3.1% |
| Iron | And-URG | Chicago | 0.0194 | 0.0057 | 13.4% | 4.2% |
| Iron | And-URG | Boston | 0.0212 | 0.0060 | 39.9% | 5.5% |
| Iron | And-URG | Philadelphia | 0.0312 | 0.0053 | 44.0% | 5.0% |
| Iron | And-URG | Houston | 0.0415 | 0.0057 | 41.4% | 5.3% |
| Iron | Met1-URG | Phoenix | 0.0464 | 0.0049 | 36.6% | 4.4% |
| Iron | Met1-URG | Tampa | 0.0093 | 0.0061 | 21.5% | 4.9% |
| Iron | Met1-URG | Bismarck | 0.0172 | 0.0076 | 64.9% | 8.3% |
| Iron | Met1-URG | Seattle | 0.0142 | 0.0046 | 29.8% | 3.9% |
| | | | | | | |
| Lead | And-Met1 | Fresno | -0.0040 | 0.0011 | -57.8% | 6.2% |
| Lead | And-Met1 | St. Louis | -0.0016 | 0.0005 | -12.2% | 6.0% |
| Lead | And-Met1 | New York | -0.0031 | 0.0005 | -40.4% | 4.4% |
| Lead | And-Met1 | Portland | -0.0041 | 0.0006 | -39.7% | 5.1% |
| Lead | And-Met1 | Salt Lake | -0.0019 | 0.0006 | -34.9% | 5.4% |
| Lead | And-URG | Chicago | 0.0006 | 0.0005 | 7.2% | 7.1% |
| Lead | And-URG | Boston | 0.0004 | 0.0006 | 9.6% | 8.7% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Lead | And-URG | Philadelphia | 0.0003 | 0.0005 | 4.7% | 7.0% |
| Lead | And-URG | Houston | -0.0001 | 0.0006 | -6.8% | 8.3% |
| Lead | Met1-URG | Phoenix | 0.0033 | 0.0009 | 74.1% | 21.6% |
| Lead | Met1-URG | Tampa | 0.0025 | 0.0007 | 68.4% | 15.8% |
| Lead | Met1-URG | Bismarck | 0.0038 | 0.0020 | 136.8% | 58.9% |
| Lead | Met1-URG | Seattle | 0.0032 | 0.0006 | 76.8% | 14.9% |
| Tin | And-Met1 | Fresno | -0.0130 | 0.0012 | -55.7% | 3.2% |
| Tin | And-Met1 | St. Louis | -0.0136 | 0.0010 | -54.4% | 2.9% |
| Tin | And-Met1 | New York | -0.0149 | 0.0010 | -61.2% | 2.4% |
| Tin | And-Met1 | Portland | -0.0130 | 0.0010 | -56.8% | 2.8% |
| Tin | And-Met1 | Salt Lake | -0.0151 | 0.0010 | -61.1% | 2.4% |
| Tin | And-URG | Chicago | 0.0002 | 0.0010 | 1.0% | 6.2% |
| Tin | And-URG | Boston | -0.0005 | 0.0011 | -4.8% | 6.6% |
| Tin | And-URG | Philadelphia | 0.0009 | 0.0009 | 7.4% | 5.9% |
| Tin | And-URG | Houston | 0.0003 | 0.0012 | 3.0% | 7.7% |
| Tin | Met1-URG | Phoenix | 0.0141 | 0.0011 | 153.4% | 17.2% |
| Tin | Met1-URG | Tampa | 0.0125 | 0.0011 | 129.0% | 16.1% |
| Tin | Met1-URG | Bismarck | 0.0143 | 0.0015 | 163.3% | 24.1% |
| Tin | Met1-URG | Seattle | 0.0151 | 0.0009 | 154.6% | 14.2% |
| Silicon | And-Met1 | Fresno | -0.0015 | 0.0159 | 1.3% | 5.1% |
| Silicon | And-Met1 | St. Louis | 0.0153 | 0.0143 | 6.7% | 4.8% |
| Silicon | And-Met1 | New York | -0.0089 | 0.0125 | -11.8% | 3.5% |
| Silicon | And-Met1 | Portland | 0.0049 | 0.0140 | 5.2% | 4.7% |
| Silicon | And-Met1 | Salt Lake | -0.0201 | 0.0127 | -3.6% | 3.9% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Silicon | And-URG | Chicago | 0.0228 | 0.0140 | 18.8% | 5.3% |
| Silicon | And-URG | Boston | 0.0215 | 0.0148 | 33.8% | 6.3% |
| Silicon | And-URG | Philadelphia | 0.0373 | 0.0131 | 39.3% | 5.8% |
| Silicon | And-URG | Houston | 0.1137 | 0.0140 | 35.2% | 6.0% |
| Silicon | Met1-URG | Phoenix | 0.1249 | 0.0121 | 37.1% | 5.3% |
| Silicon | Met1-URG | Tampa | 0.0284 | 0.0150 | 27.8% | 6.1% |
| Silicon | Met1-URG | Bismarck | 0.0510 | 0.0189 | 67.2% | 10.0% |
| Silicon | Met1-URG | Seattle | 0.0149 | 0.0113 | 31.3% | 4.7% |
| Zinc | And-Met1 | Fresno | 0.0202 | 0.0010 | 512.6% | 52.0% |
| Zinc | And-Met1 | St. Louis | 0.0107 | 0.0008 | 60.9% | 10.6% |
| Zinc | And-Met1 | New York | 0.0013 | 0.0007 | 6.7% | 6.0% |
| Zinc | And-Met1 | Portland | 0.0016 | 0.0008 | 27.5% | 8.6% |
| Zinc | And-Met1 | Salt Lake | 0.0016 | 0.0007 | 29.5% | 7.4% |
| Zinc | And-URG | Chicago | 0.0016 | 0.0008 | -0.7% | 6.3% |
| Zinc | And-URG | Boston | 0.0007 | 0.0008 | 11.0% | 7.4% |
| Zinc | And-URG | Philadelphia | 0.0016 | 0.0007 | 12.2% | 6.6% |
| Zinc | And-URG | Houston | 0.0008 | 0.0008 | 23.2% | 8.2% |
| Zinc | Met1-URG | Phoenix | -0.0008 | 0.0007 | -13.5% | 5.2% |
| Zinc | Met1-URG | Tampa | -0.0008 | 0.0009 | -15.1% | 6.1% |
| Zinc | Met1-URG | Bismarck | -0.0012 | 0.0020 | -24.0% | 12.6% |
| Zinc | Met1-URG | Seattle | -0.0008 | 0.0007 | -15.4% | 4.6% |
| Ammonium | And-Met1 | Fresno | -0.1561 | 0.0624 | -18.1% | 7.0% |
| Ammonium | And-Met1 | St. Louis | -0.1150 | 0.0544 | -3.8% | 7.1% |
| Ammonium | And-Met1 | New York | -0.0802 | 0.0474 | -3.6% | 6.2% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Ammonium | And-Met1 | Portland | 0.0229 | 0.0588 | 15.1% | 9.3% |
| Ammonium | And-Met1 | Salt Lake | -0.0240 | 0.0521 | -3.3% | 6.9% |
| Ammonium | And-URG | Chicago | -0.1300 | 0.0532 | -4.8% | 7.0% |
| Ammonium | And-URG | Boston | -0.3268 | 0.0572 | -40.7% | 4.6% |
| Ammonium | And-URG | Philadelphia | -0.2749 | 0.0499 | -13.8% | 5.9% |
| Ammonium | And-URG | Houston | -0.5601 | 0.0559 | -50.7% | 3.8% |
| Ammonium | Met1-URG | Phoenix | 0.0044 | 0.0461 | 1.1% | 6.4% |
| Ammonium | Met1-URG | Tampa | -0.7566 | 0.0571 | -53.2% | 3.6% |
| Ammonium | Met1-URG | Bismarck | -0.1448 | 0.0720 | -23.7% | 7.5% |
| Ammonium | Met1-URG | Seattle | -0.1648 | 0.0490 | -43.2% | 3.8% |
| | | | | | | |
| Organic Carbon | And-Met1 | Fresno | -0.1283 | 0.1248 | -2.6% | 3.4% |
| Organic Carbon | And-Met1 | St. Louis | -0.2487 | 0.1245 | -5.4% | 3.3% |
| Organic Carbon | And-Met1 | New York | 0.0078 | 0.2075 | -1.5% | 5.6% |
| Organic Carbon | And-Met1 | Portland | -0.2105 | 0.1123 | -4.7% | 3.0% |
| Organic Carbon | And-Met1 | Salt Lake | -0.4120 | 0.1126 | -9.7% | 2.8% |
| Organic Carbon | And-URG | Chicago | 1.1204 | 0.1099 | 36.0% | 4.1% |
| Organic Carbon | And-URG | Boston | 0.9913 | 0.1716 | 28.8% | 6.1% |
| Organic Carbon | And-URG | Philadelphia | 0.8070 | 0.1029 | 27.5% | 3.6% |
| Organic Carbon | And-URG | Houston | 0.5445 | 0.1332 | 35.3% | 5.0% |
| Organic Carbon | Met1-URG | Phoenix | 0.9815 | 0.0961 | 28.2% | 3.4% |
| Organic Carbon | Met1-URG | Tampa | 0.7263 | 0.1179 | 29.3% | 4.2% |
| Organic Carbon | Met1-URG | Bismarck | 0.7600 | 0.1481 | 53.4% | 6.3% |
| Organic Carbon | Met1-URG | Seattle | 1.2147 | 0.0884 | 52.2% | 3.7% |
| | | | | | | |
| Nitrate | And-Met1 | Fresno | -0.1386 | 0.0526 | -7.2% | 5.0% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Nitrate | And-Met1 | St. Louis | 0.0001 | 0.0459 | 1.5% | 4.7% |
| Nitrate | And-Met1 | New York | -0.0544 | 0.0400 | -6.6% | 3.8% |
| Nitrate | And-Met1 | Portland | -0.0363 | 0.0459 | -5.2% | 4.4% |
| Nitrate | And-Met1 | Salt Lake | -0.0802 | 0.0430 | -11.0% | 3.9% |
| Nitrate | And-URG | Chicago | 0.1894 | 0.0449 | 12.4% | 5.1% |
| Nitrate | And-URG | Boston | 0.1442 | 0.0483 | 21.3% | 5.9% |
| Nitrate | And-URG | Philadelphia | 0.1810 | 0.0421 | 18.2% | 5.1% |
| Nitrate | And-URG | Houston | 0.1657 | 0.0471 | 40.1% | 6.7% |
| Nitrate | Met1-URG | Phoenix | 0.0824 | 0.0389 | 26.2% | 5.0% |
| Nitrate | Met1-URG | Tampa | 0.0770 | 0.0482 | 19.4% | 5.8% |
| Nitrate | Met1-URG | Bismarck | 0.0998 | 0.0607 | 30.7% | 8.1% |
| Nitrate | Met1-URG | Seattle | 0.1508 | 0.0367 | 27.8% | 4.8% |
| Elemental Carbon | And-Met1 | Fresno | 0.0029 | 0.0463 | -3.3% | 7.4% |
| Elemental Carbon | And-Met1 | St. Louis | 0.0474 | 0.0460 | 7.0% | 8.1% |
| Elemental Carbon | And-Met1 | New York | 0.0636 | 0.0760 | 7.6% | 13.3% |
| Elemental Carbon | And-Met1 | Portland | -0.0599 | 0.0425 | -4.6% | 6.7% |
| Elemental Carbon | And-Met1 | Salt Lake | -0.0196 | 0.0418 | -4.4% | 6.6% |
| Elemental Carbon | And-URG | Chicago | 0.2406 | 0.0408 | 23.8% | 8.4% |
| Elemental Carbon | And-URG | Boston | 0.0109 | 0.0635 | -1.3% | 10.4% |
| Elemental Carbon | And-URG | Philadelphia | 0.1637 | 0.0381 | 22.0% | 7.7% |
| Elemental Carbon | And-URG | Houston | 0.1042 | 0.0511 | 29.7% | 11.0% |
| Elemental Carbon | Met1-URG | Phoenix | 0.0965 | 0.0362 | 16.7% | 7.0% |
| Elemental Carbon | Met1-URG | Tampa | 0.0984 | 0.0436 | 23.1% | 8.8% |
| Elemental Carbon | Met1-URG | Bismarck | 0.0766 | 0.0628 | 36.5% | 14.1% |
| Elemental Carbon | Met1-URG | Seattle | 0.2762 | 0.0332 | 47.4% | 8.1% |

| Parameter | Sampler Pair Type | Site | Mean Difference Between Sampler Types (migrograms/m$^3$) | Standard Error | Relative Difference | Standard Error |
|---|---|---|---|---|---|---|
| Sulfate | And-Met1 | Fresno | -0.1848 | 0.0779 | -10.7% | 2.7% |
| Sulfate | And-Met1 | St. Louis | -0.0316 | 0.0679 | 0.2% | 2.6% |
| Sulfate | And-Met1 | New York | -0.0209 | 0.0592 | -0.3% | 2.3% |
| Sulfate | And-Met1 | Portland | -0.0637 | 0.0680 | -4.5% | 2.5% |
| Sulfate | And-Met1 | Salt Lake | -0.0440 | 0.0636 | -5.2% | 2.3% |
| Sulfate | And-URG | Chicago | -0.2514 | 0.0664 | -5.3% | 2.4% |
| Sulfate | And-URG | Boston | -0.3957 | 0.0715 | -14.0% | 2.4% |
| Sulfate | And-URG | Philadelphia | -0.1281 | 0.0623 | -4.2% | 2.3% |
| Sulfate | And-URG | Houston | -0.2489 | 0.0697 | -6.9% | 2.5% |
| Sulfate | Met1-URG | Phoenix | 0.1026 | 0.0575 | 9.2% | 2.4% |
| Sulfate | Met1-URG | Tampa | -0.3445 | 0.0714 | -9.0% | 2.5% |
| Sulfate | Met1-URG | Bismarck | -0.0275 | 0.0899 | -1.7% | 3.4% |
| Sulfate | Met1-URG | Seattle | 0.0051 | 0.0542 | 2.5% | 2.1% |

## Table B.3 Sampler Type Means for all Sites and Parameters

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| PM2.5 Mass | And-Met1 | Fresno | Andersen | 9.027 | 1.271 |
| PM2.5 Mass | And-Met1 | Fresno | MetOne | 10.332 | 1.267 |
| PM2.5 Mass | And-Met1 | St. Louis | Andersen | 15.451 | 1.049 |
| PM2.5 Mass | And-Met1 | St. Louis | MetOne | 16.020 | 1.046 |
| PM2.5 Mass | And-Met1 | New York | Andersen | 14.093 | 0.992 |
| PM2.5 Mass | And-Met1 | New York | MetOne | 15.568 | 0.975 |
| PM2.5 Mass | And-Met1 | Portland | Andersen | 8.468 | 1.100 |
| PM2.5 Mass | And-Met1 | Portland | MetOne | 9.724 | 1.100 |
| PM2.5 Mass | And-Met1 | Salt Lake | Andersen | 8.004 | 1.078 |
| PM2.5 Mass | And-Met1 | Salt Lake | MetOne | 8.800 | 1.078 |
| PM2.5 Mass | And-URG | Chicago | Andersen | 17.518 | 1.162 |
| PM2.5 Mass | And-URG | Chicago | URG | 17.079 | 1.161 |
| PM2.5 Mass | And-URG | Boston | Andersen | 11.993 | 1.208 |
| PM2.5 Mass | And-URG | Boston | URG | 11.693 | 1.213 |
| PM2.5 Mass | And-URG | Philadelphia | Andersen | 14.991 | 1.032 |
| PM2.5 Mass | And-URG | Philadelphia | URG | 13.669 | 1.026 |
| PM2.5 Mass | And-URG | Houston | Andersen | 14.333 | 1.236 |
| PM2.5 Mass | And-URG | Houston | URG | 12.338 | 1.236 |
| PM2.5 Mass | Met1-URG | Phoenix | MetOne | 9.659 | 1.018 |
| PM2.5 Mass | Met1-URG | Phoenix | URG | 7.844 | 1.004 |
| PM2.5 Mass | Met1-URG | Tampa | MetOne | 15.024 | 1.123 |
| PM2.5 Mass | Met1-URG | Tampa | URG | 13.878 | 1.120 |
| PM2.5 Mass | Met1-URG | Bismarck | MetOne | 6.777 | 1.456 |
| PM2.5 Mass | Met1-URG | Bismarck | URG | 5.550 | 1.456 |
| PM2.5 Mass | Met1-URG | Seattle | MetOne | 9.482 | 0.930 |
| PM2.5 Mass | Met1-URG | Seattle | URG | 7.629 | 0.931 |
| | | | | | |
| Aluminum | And-Met1 | Fresno | Andersen | 0.042 | 0.022 |
| Aluminum | And-Met1 | Fresno | MetOne | 0.037 | 0.022 |
| Aluminum | And-Met1 | St. Louis | Andersen | 0.037 | 0.027 |
| Aluminum | And-Met1 | St. Louis | MetOne | 0.037 | 0.027 |
| Aluminum | And-Met1 | New York | Andersen | 0.015 | 0.025 |
| Aluminum | And-Met1 | New York | MetOne | 0.021 | 0.024 |
| Aluminum | And-Met1 | Portland | Andersen | 0.019 | 0.021 |
| Aluminum | And-Met1 | Portland | MetOne | 0.020 | 0.022 |
| Aluminum | And-Met1 | Salt Lake | Andersen | 0.076 | 0.019 |
| Aluminum | And-Met1 | Salt Lake | MetOne | 0.089 | 0.019 |
| Aluminum | And-URG | Chicago | Andersen | 0.026 | 0.026 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Aluminum | And-URG | Chicago | URG | 0.022 | 0.026 |
| Aluminum | And-URG | Boston | Andersen | 0.017 | 0.034 |
| Aluminum | And-URG | Boston | URG | 0.006 | 0.037 |
| Aluminum | And-URG | Philadelphia | Andersen | 0.025 | 0.027 |
| Aluminum | And-URG | Philadelphia | URG | 0.011 | 0.028 |
| Aluminum | And-URG | Houston | Andersen | 0.256 | 0.026 |
| Aluminum | And-URG | Houston | URG | 0.173 | 0.026 |
| Aluminum | Met1-URG | Phoenix | MetOne | 0.173 | 0.018 |
| Aluminum | Met1-URG | Phoenix | URG | 0.126 | 0.017 |
| Aluminum | Met1-URG | Tampa | MetOne | 0.035 | 0.027 |
| Aluminum | Met1-URG | Tampa | URG | 0.018 | 0.026 |
| Aluminum | Met1-URG | Bismarck | MetOne | 0.101 | 0.046 |
| Aluminum | Met1-URG | Bismarck | URG | 0.075 | 0.046 |
| Aluminum | Met1-URG | Seattle | MetOne | 0.035 | 0.024 |
| Aluminum | Met1-URG | Seattle | URG | 0.026 | 0.023 |
| | | | | | |
| Calcium | And-Met1 | Fresno | Andersen | 0.054 | 0.012 |
| Calcium | And-Met1 | Fresno | MetOne | 0.054 | 0.012 |
| Calcium | And-Met1 | St. Louis | Andersen | 0.128 | 0.010 |
| Calcium | And-Met1 | St. Louis | MetOne | 0.112 | 0.010 |
| Calcium | And-Met1 | New York | Andersen | 0.044 | 0.010 |
| Calcium | And-Met1 | New York | MetOne | 0.050 | 0.009 |
| Calcium | And-Met1 | Portland | Andersen | 0.036 | 0.010 |
| Calcium | And-Met1 | Portland | MetOne | 0.036 | 0.010 |
| Calcium | And-Met1 | Salt Lake | Andersen | 0.163 | 0.010 |
| Calcium | And-Met1 | Salt Lake | MetOne | 0.181 | 0.010 |
| Calcium | And-URG | Chicago | Andersen | 0.123 | 0.011 |
| Calcium | And-URG | Chicago | URG | 0.098 | 0.011 |
| Calcium | And-URG | Boston | Andersen | 0.044 | 0.011 |
| Calcium | And-URG | Boston | URG | 0.033 | 0.011 |
| Calcium | And-URG | Philadelphia | Andersen | 0.057 | 0.010 |
| Calcium | And-URG | Philadelphia | URG | 0.036 | 0.009 |
| Calcium | And-URG | Houston | Andersen | 0.109 | 0.011 |
| Calcium | And-URG | Houston | URG | 0.069 | 0.011 |
| Calcium | Met1-URG | Phoenix | MetOne | 0.188 | 0.010 |
| Calcium | Met1-URG | Phoenix | URG | 0.133 | 0.009 |
| Calcium | Met1-URG | Tampa | MetOne | 0.078 | 0.011 |
| Calcium | Met1-URG | Tampa | URG | 0.052 | 0.010 |
| Calcium | Met1-URG | Bismarck | MetOne | 0.063 | 0.014 |
| Calcium | Met1-URG | Bismarck | URG | 0.040 | 0.014 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Calcium | Met1-URG | Seattle | MetOne | 0.044 | 0.009 |
| Calcium | Met1-URG | Seattle | URG | 0.033 | 0.009 |
| | | | | | |
| Chlorine | And-Met1 | Fresno | Andersen | 0.018 | 0.042 |
| Chlorine | And-Met1 | Fresno | MetOne | 0.021 | 0.045 |
| Chlorine | And-Met1 | St. Louis | Andersen | 0.024 | 0.035 |
| Chlorine | And-Met1 | St. Louis | MetOne | 0.013 | 0.038 |
| Chlorine | And-Met1 | New York | Andersen | 0.023 | 0.034 |
| Chlorine | And-Met1 | New York | MetOne | 0.012 | 0.029 |
| Chlorine | And-Met1 | Portland | Andersen | 0.044 | 0.025 |
| Chlorine | And-Met1 | Portland | MetOne | 0.028 | 0.026 |
| Chlorine | And-Met1 | Salt Lake | Andersen | 0.019 | 0.020 |
| Chlorine | And-Met1 | Salt Lake | MetOne | 0.009 | 0.022 |
| Chlorine | And-URG | Chicago | Andersen | 0.042 | 0.028 |
| Chlorine | And-URG | Chicago | URG | 0.047 | 0.029 |
| Chlorine | And-URG | Boston | Andersen | 0.020 | 0.027 |
| Chlorine | And-URG | Boston | URG | 0.012 | 0.028 |
| Chlorine | And-URG | Philadelphia | Andersen | 0.008 | 0.037 |
| Chlorine | And-URG | Philadelphia | URG | 0.008 | 0.034 |
| Chlorine | And-URG | Houston | Andersen | 0.200 | 0.024 |
| Chlorine | And-URG | Houston | URG | 0.109 | 0.024 |
| Chlorine | Met1-URG | Phoenix | MetOne | 0.065 | 0.020 |
| Chlorine | Met1-URG | Phoenix | URG | 0.060 | 0.018 |
| Chlorine | Met1-URG | Tampa | MetOne | 0.085 | 0.035 |
| Chlorine | Met1-URG | Tampa | URG | 0.019 | 0.034 |
| Chlorine | Met1-URG | Seattle | MetOne | 0.061 | 0.020 |
| Chlorine | Met1-URG | Seattle | URG | 0.057 | 0.020 |
| | | | | | |
| Iron | And-Met1 | Fresno | Andersen | 0.088 | 0.016 |
| Iron | And-Met1 | Fresno | MetOne | 0.088 | 0.016 |
| Iron | And-Met1 | St. Louis | Andersen | 0.170 | 0.014 |
| Iron | And-Met1 | St. Louis | MetOne | 0.162 | 0.014 |
| Iron | And-Met1 | New York | Andersen | 0.103 | 0.013 |
| Iron | And-Met1 | New York | MetOne | 0.109 | 0.012 |
| Iron | And-Met1 | Portland | Andersen | 0.061 | 0.014 |
| Iron | And-Met1 | Portland | MetOne | 0.058 | 0.014 |
| Iron | And-Met1 | Salt Lake | Andersen | 0.140 | 0.014 |
| Iron | And-Met1 | Salt Lake | MetOne | 0.153 | 0.014 |
| Iron | And-URG | Chicago | Andersen | 0.180 | 0.015 |
| Iron | And-URG | Chicago | URG | 0.161 | 0.015 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Iron | And-URG | Boston | Andersen | 0.073 | 0.016 |
| Iron | And-URG | Boston | URG | 0.052 | 0.016 |
| Iron | And-URG | Philadelphia | Andersen | 0.101 | 0.013 |
| Iron | And-URG | Philadelphia | URG | 0.070 | 0.013 |
| Iron | And-URG | Houston | Andersen | 0.133 | 0.016 |
| Iron | And-URG | Houston | URG | 0.091 | 0.016 |
| Iron | Met1-URG | Phoenix | MetOne | 0.184 | 0.013 |
| Iron | Met1-URG | Phoenix | URG | 0.138 | 0.013 |
| Iron | Met1-URG | Tampa | MetOne | 0.055 | 0.015 |
| Iron | Met1-URG | Tampa | URG | 0.045 | 0.014 |
| Iron | Met1-URG | Bismarck | MetOne | 0.060 | 0.019 |
| Iron | Met1-URG | Bismarck | URG | 0.043 | 0.019 |
| Iron | Met1-URG | Seattle | MetOne | 0.073 | 0.012 |
| Iron | Met1-URG | Seattle | URG | 0.059 | 0.012 |
| | | | | | |
| Lead | And-Met1 | Fresno | Andersen | 0.003 | 0.002 |
| Lead | And-Met1 | Fresno | MetOne | 0.007 | 0.002 |
| Lead | And-Met1 | St. Louis | Andersen | 0.015 | 0.001 |
| Lead | And-Met1 | St. Louis | MetOne | 0.016 | 0.001 |
| Lead | And-Met1 | New York | Andersen | 0.005 | 0.001 |
| Lead | And-Met1 | New York | MetOne | 0.008 | 0.001 |
| Lead | And-Met1 | Portland | Andersen | 0.005 | 0.001 |
| Lead | And-Met1 | Portland | MetOne | 0.009 | 0.001 |
| Lead | And-Met1 | Salt Lake | Andersen | 0.005 | 0.001 |
| Lead | And-Met1 | Salt Lake | MetOne | 0.007 | 0.001 |
| Lead | And-URG | Chicago | Andersen | 0.010 | 0.001 |
| Lead | And-URG | Chicago | URG | 0.009 | 0.001 |
| Lead | And-URG | Boston | Andersen | 0.004 | 0.001 |
| Lead | And-URG | Boston | URG | 0.004 | 0.001 |
| Lead | And-URG | Philadelphia | Andersen | 0.006 | 0.001 |
| Lead | And-URG | Philadelphia | URG | 0.005 | 0.001 |
| Lead | And-URG | Houston | Andersen | 0.004 | 0.002 |
| Lead | And-URG | Houston | URG | 0.004 | 0.002 |
| Lead | Met1-URG | Phoenix | MetOne | 0.007 | 0.001 |
| Lead | Met1-URG | Phoenix | URG | 0.004 | 0.001 |
| Lead | Met1-URG | Tampa | MetOne | 0.007 | 0.001 |
| Lead | Met1-URG | Tampa | URG | 0.005 | 0.001 |
| Lead | Met1-URG | Bismarck | MetOne | 0.008 | 0.003 |
| Lead | Met1-URG | Bismarck | URG | 0.004 | 0.003 |
| Lead | Met1-URG | Seattle | MetOne | 0.010 | 0.001 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Lead | Met1-URG | Seattle | URG | 0.007 | 0.001 |
| | | | | | |
| Tin | And-Met1 | Fresno | Andersen | 0.010 | 0.001 |
| Tin | And-Met1 | Fresno | MetOne | 0.024 | 0.001 |
| Tin | And-Met1 | St. Louis | Andersen | 0.012 | 0.001 |
| Tin | And-Met1 | St. Louis | MetOne | 0.025 | 0.001 |
| Tin | And-Met1 | New York | Andersen | 0.009 | 0.001 |
| Tin | And-Met1 | New York | MetOne | 0.024 | 0.000 |
| Tin | And-Met1 | Portland | Andersen | 0.010 | 0.001 |
| Tin | And-Met1 | Portland | MetOne | 0.023 | 0.001 |
| Tin | And-Met1 | Salt Lake | Andersen | 0.010 | 0.001 |
| Tin | And-Met1 | Salt Lake | MetOne | 0.025 | 0.001 |
| Tin | And-URG | Chicago | Andersen | 0.011 | 0.001 |
| Tin | And-URG | Chicago | URG | 0.011 | 0.001 |
| Tin | And-URG | Boston | Andersen | 0.009 | 0.001 |
| Tin | And-URG | Boston | URG | 0.010 | 0.001 |
| Tin | And-URG | Philadelphia | Andersen | 0.010 | 0.001 |
| Tin | And-URG | Philadelphia | URG | 0.010 | 0.001 |
| Tin | And-URG | Houston | Andersen | 0.010 | 0.001 |
| Tin | And-URG | Houston | URG | 0.009 | 0.001 |
| Tin | Met1-URG | Phoenix | MetOne | 0.023 | 0.001 |
| Tin | Met1-URG | Phoenix | URG | 0.009 | 0.001 |
| Tin | Met1-URG | Tampa | MetOne | 0.022 | 0.001 |
| Tin | Met1-URG | Tampa | URG | 0.010 | 0.001 |
| Tin | Met1-URG | Bismarck | MetOne | 0.023 | 0.001 |
| Tin | Met1-URG | Bismarck | URG | 0.009 | 0.001 |
| Tin | Met1-URG | Seattle | MetOne | 0.025 | 0.001 |
| Tin | Met1-URG | Seattle | URG | 0.010 | 0.001 |
| | | | | | |
| Silicon | And-Met1 | Fresno | Andersen | 0.181 | 0.038 |
| Silicon | And-Met1 | Fresno | MetOne | 0.183 | 0.038 |
| Silicon | And-Met1 | St. Louis | Andersen | 0.151 | 0.031 |
| Silicon | And-Met1 | St. Louis | MetOne | 0.136 | 0.031 |
| Silicon | And-Met1 | New York | Andersen | 0.093 | 0.030 |
| Silicon | And-Met1 | New York | MetOne | 0.102 | 0.029 |
| Silicon | And-Met1 | Portland | Andersen | 0.076 | 0.033 |
| Silicon | And-Met1 | Portland | MetOne | 0.071 | 0.033 |
| Silicon | And-Met1 | Salt Lake | Andersen | 0.237 | 0.032 |
| Silicon | And-Met1 | Salt Lake | MetOne | 0.257 | 0.032 |
| Silicon | And-URG | Chicago | Andersen | 0.134 | 0.035 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Silicon | And-URG | Chicago | URG | 0.111 | 0.035 |
| Silicon | And-URG | Boston | Andersen | 0.077 | 0.036 |
| Silicon | And-URG | Boston | URG | 0.056 | 0.036 |
| Silicon | And-URG | Philadelphia | Andersen | 0.121 | 0.031 |
| Silicon | And-URG | Philadelphia | URG | 0.084 | 0.031 |
| Silicon | And-URG | Houston | Andersen | 0.402 | 0.037 |
| Silicon | And-URG | Houston | URG | 0.289 | 0.037 |
| Silicon | Met1-URG | Phoenix | MetOne | 0.481 | 0.031 |
| Silicon | Met1-URG | Phoenix | URG | 0.356 | 0.030 |
| Silicon | Met1-URG | Tampa | MetOne | 0.136 | 0.034 |
| Silicon | Met1-URG | Tampa | URG | 0.107 | 0.033 |
| Silicon | Met1-URG | Bismarck | MetOne | 0.167 | 0.044 |
| Silicon | Met1-URG | Bismarck | URG | 0.116 | 0.044 |
| Silicon | Met1-URG | Seattle | MetOne | 0.066 | 0.028 |
| Silicon | Met1-URG | Seattle | URG | 0.051 | 0.028 |
| | | | | | |
| Zinc | And-Met1 | Fresno | Andersen | 0.022 | 0.003 |
| Zinc | And-Met1 | Fresno | MetOne | 0.002 | 0.003 |
| Zinc | And-Met1 | St. Louis | Andersen | 0.034 | 0.002 |
| Zinc | And-Met1 | St. Louis | MetOne | 0.024 | 0.002 |
| Zinc | And-Met1 | New York | Andersen | 0.024 | 0.002 |
| Zinc | And-Met1 | New York | MetOne | 0.023 | 0.002 |
| Zinc | And-Met1 | Portland | Andersen | 0.009 | 0.002 |
| Zinc | And-Met1 | Portland | MetOne | 0.007 | 0.002 |
| Zinc | And-Met1 | Salt Lake | Andersen | 0.008 | 0.002 |
| Zinc | And-Met1 | Salt Lake | MetOne | 0.007 | 0.002 |
| Zinc | And-URG | Chicago | Andersen | 0.051 | 0.003 |
| Zinc | And-URG | Chicago | URG | 0.049 | 0.003 |
| Zinc | And-URG | Boston | Andersen | 0.010 | 0.003 |
| Zinc | And-URG | Boston | URG | 0.009 | 0.003 |
| Zinc | And-URG | Philadelphia | Andersen | 0.016 | 0.002 |
| Zinc | And-URG | Philadelphia | URG | 0.015 | 0.002 |
| Zinc | And-URG | Houston | Andersen | 0.006 | 0.003 |
| Zinc | And-URG | Houston | URG | 0.006 | 0.003 |
| Zinc | Met1-URG | Phoenix | MetOne | 0.005 | 0.002 |
| Zinc | Met1-URG | Phoenix | URG | 0.006 | 0.002 |
| Zinc | Met1-URG | Tampa | MetOne | 0.006 | 0.003 |
| Zinc | Met1-URG | Tampa | URG | 0.007 | 0.002 |
| Zinc | Met1-URG | Bismarck | MetOne | 0.002 | 0.005 |
| Zinc | Met1-URG | Bismarck | URG | 0.004 | 0.005 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Zinc | Met1-URG | Seattle | MetOne | 0.007 | 0.002 |
| Zinc | Met1-URG | Seattle | URG | 0.008 | 0.002 |
| | | | | | |
| Ammonium | And-Met1 | Fresno | Andersen | 0.583 | 0.216 |
| Ammonium | And-Met1 | Fresno | MetOne | 0.739 | 0.215 |
| Ammonium | And-Met1 | St. Louis | Andersen | 1.664 | 0.172 |
| Ammonium | And-Met1 | St. Louis | MetOne | 1.779 | 0.172 |
| Ammonium | And-Met1 | New York | Andersen | 1.491 | 0.163 |
| Ammonium | And-Met1 | New York | MetOne | 1.572 | 0.160 |
| Ammonium | And-Met1 | Portland | Andersen | 0.414 | 0.200 |
| Ammonium | And-Met1 | Portland | MetOne | 0.391 | 0.200 |
| Ammonium | And-Met1 | Salt Lake | Andersen | 0.352 | 0.187 |
| Ammonium | And-Met1 | Salt Lake | MetOne | 0.376 | 0.187 |
| Ammonium | And-URG | Chicago | Andersen | 2.218 | 0.191 |
| Ammonium | And-URG | Chicago | URG | 2.348 | 0.191 |
| Ammonium | And-URG | Boston | Andersen | 1.055 | 0.195 |
| Ammonium | And-URG | Boston | URG | 1.382 | 0.196 |
| Ammonium | And-URG | Philadelphia | Andersen | 1.685 | 0.167 |
| Ammonium | And-URG | Philadelphia | URG | 1.960 | 0.166 |
| Ammonium | And-URG | Houston | Andersen | 0.806 | 0.209 |
| Ammonium | And-URG | Houston | URG | 1.366 | 0.209 |
| Ammonium | Met1-URG | Phoenix | MetOne | 0.396 | 0.165 |
| Ammonium | Met1-URG | Phoenix | URG | 0.391 | 0.162 |
| Ammonium | Met1-URG | Tampa | MetOne | 1.210 | 0.182 |
| Ammonium | Met1-URG | Tampa | URG | 1.967 | 0.181 |
| Ammonium | Met1-URG | Bismarck | MetOne | 0.463 | 0.235 |
| Ammonium | Met1-URG | Bismarck | URG | 0.608 | 0.235 |
| Ammonium | Met1-URG | Seattle | MetOne | 0.431 | 0.171 |
| Ammonium | Met1-URG | Seattle | URG | 0.596 | 0.172 |
| | | | | | |
| Organic Carbon | And-Met1 | Fresno | Andersen | 4.569 | 0.327 |
| Organic Carbon | And-Met1 | Fresno | MetOne | 4.698 | 0.323 |
| Organic Carbon | And-Met1 | St. Louis | Andersen | 4.209 | 0.310 |
| Organic Carbon | And-Met1 | St. Louis | MetOne | 4.458 | 0.311 |
| Organic Carbon | And-Met1 | New York | Andersen | 4.394 | 0.353 |
| Organic Carbon | And-Met1 | New York | MetOne | 4.386 | 0.305 |
| Organic Carbon | And-Met1 | Portland | Andersen | 4.293 | 0.290 |
| Organic Carbon | And-Met1 | Portland | MetOne | 4.503 | 0.292 |
| Organic Carbon | And-Met1 | Salt Lake | Andersen | 4.145 | 0.316 |
| Organic Carbon | And-Met1 | Salt Lake | MetOne | 4.557 | 0.316 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Organic Carbon | And-URG | Chicago | Andersen | 4.507 | 0.302 |
| Organic Carbon | And-URG | Chicago | URG | 3.387 | 0.302 |
| Organic Carbon | And-URG | Boston | Andersen | 4.632 | 0.482 |
| Organic Carbon | And-URG | Boston | URG | 3.640 | 0.482 |
| Organic Carbon | And-URG | Philadelphia | Andersen | 3.983 | 0.266 |
| Organic Carbon | And-URG | Philadelphia | URG | 3.176 | 0.264 |
| Organic Carbon | And-URG | Houston | Andersen | 2.494 | 0.373 |
| Organic Carbon | And-URG | Houston | URG | 1.949 | 0.373 |
| Organic Carbon | Met1-URG | Phoenix | MetOne | 4.306 | 0.260 |
| Organic Carbon | Met1-URG | Phoenix | URG | 3.325 | 0.253 |
| Organic Carbon | Met1-URG | Tampa | MetOne | 3.526 | 0.297 |
| Organic Carbon | Met1-URG | Tampa | URG | 2.799 | 0.298 |
| Organic Carbon | Met1-URG | Bismarck | MetOne | 2.360 | 0.365 |
| Organic Carbon | Met1-URG | Bismarck | URG | 1.600 | 0.365 |
| Organic Carbon | Met1-URG | Seattle | MetOne | 3.755 | 0.238 |
| Organic Carbon | Met1-URG | Seattle | URG | 2.540 | 0.238 |
| Nitrate | And-Met1 | Fresno | Andersen | 1.254 | 0.236 |
| Nitrate | And-Met1 | Fresno | MetOne | 1.392 | 0.236 |
| Nitrate | And-Met1 | St. Louis | Andersen | 1.560 | 0.189 |
| Nitrate | And-Met1 | St. Louis | MetOne | 1.560 | 0.188 |
| Nitrate | And-Met1 | New York | Andersen | 1.081 | 0.178 |
| Nitrate | And-Met1 | New York | MetOne | 1.135 | 0.176 |
| Nitrate | And-Met1 | Portland | Andersen | 0.775 | 0.198 |
| Nitrate | And-Met1 | Portland | MetOne | 0.811 | 0.198 |
| Nitrate | And-Met1 | Salt Lake | Andersen | 0.758 | 0.202 |
| Nitrate | And-Met1 | Salt Lake | MetOne | 0.838 | 0.202 |
| Nitrate | And-URG | Chicago | Andersen | 2.563 | 0.210 |
| Nitrate | And-URG | Chicago | URG | 2.374 | 0.210 |
| Nitrate | And-URG | Boston | Andersen | 1.102 | 0.214 |
| Nitrate | And-URG | Boston | URG | 0.958 | 0.215 |
| Nitrate | And-URG | Philadelphia | Andersen | 1.499 | 0.183 |
| Nitrate | And-URG | Philadelphia | URG | 1.318 | 0.182 |
| Nitrate | And-URG | Houston | Andersen | 0.868 | 0.230 |
| Nitrate | And-URG | Houston | URG | 0.702 | 0.230 |
| Nitrate | Met1-URG | Phoenix | MetOne | 0.542 | 0.180 |
| Nitrate | Met1-URG | Phoenix | URG | 0.459 | 0.178 |
| Nitrate | Met1-URG | Tampa | MetOne | 0.613 | 0.199 |
| Nitrate | Met1-URG | Tampa | URG | 0.536 | 0.198 |
| Nitrate | Met1-URG | Bismarck | MetOne | 0.589 | 0.258 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Nitrate | Met1-URG | Bismarck | URG | 0.489 | 0.258 |
| Nitrate | Met1-URG | Seattle | MetOne | 0.847 | 0.167 |
| Nitrate | Met1-URG | Seattle | URG | 0.697 | 0.167 |
| Elemental Carbon | And-Met1 | Fresno | Andersen | 0.560 | 0.091 |
| Elemental Carbon | And-Met1 | Fresno | MetOne | 0.557 | 0.090 |
| Elemental Carbon | And-Met1 | St. Louis | Andersen | 0.878 | 0.084 |
| Elemental Carbon | And-Met1 | St. Louis | MetOne | 0.831 | 0.085 |
| Elemental Carbon | And-Met1 | New York | Andersen | 1.398 | 0.104 |
| Elemental Carbon | And-Met1 | New York | MetOne | 1.334 | 0.082 |
| Elemental Carbon | And-Met1 | Portland | Andersen | 0.656 | 0.078 |
| Elemental Carbon | And-Met1 | Portland | MetOne | 0.716 | 0.080 |
| Elemental Carbon | And-Met1 | Salt Lake | Andersen | 0.688 | 0.085 |
| Elemental Carbon | And-Met1 | Salt Lake | MetOne | 0.708 | 0.085 |
| Elemental Carbon | And-URG | Chicago | Andersen | 1.301 | 0.082 |
| Elemental Carbon | And-URG | Chicago | URG | 1.061 | 0.081 |
| Elemental Carbon | And-URG | Boston | Andersen | 0.910 | 0.130 |
| Elemental Carbon | And-URG | Boston | URG | 0.899 | 0.130 |
| Elemental Carbon | And-URG | Philadelphia | Andersen | 0.823 | 0.073 |
| Elemental Carbon | And-URG | Philadelphia | URG | 0.659 | 0.072 |
| Elemental Carbon | And-URG | Houston | Andersen | 0.412 | 0.102 |
| Elemental Carbon | And-URG | Houston | URG | 0.307 | 0.101 |
| Elemental Carbon | Met1-URG | Phoenix | MetOne | 0.704 | 0.072 |
| Elemental Carbon | Met1-URG | Phoenix | URG | 0.608 | 0.068 |
| Elemental Carbon | Met1-URG | Tampa | MetOne | 0.553 | 0.081 |
| Elemental Carbon | Met1-URG | Tampa | URG | 0.454 | 0.081 |
| Elemental Carbon | Met1-URG | Bismarck | MetOne | 0.279 | 0.107 |
| Elemental Carbon | Met1-URG | Bismarck | URG | 0.202 | 0.102 |
| Elemental Carbon | Met1-URG | Seattle | MetOne | 0.890 | 0.065 |
| Elemental Carbon | Met1-URG | Seattle | URG | 0.614 | 0.065 |
| Sulfate | And-Met1 | Fresno | Andersen | 1.552 | 0.491 |
| Sulfate | And-Met1 | Fresno | MetOne | 1.737 | 0.491 |
| Sulfate | And-Met1 | St. Louis | Andersen | 4.334 | 0.392 |
| Sulfate | And-Met1 | St. Louis | MetOne | 4.366 | 0.391 |
| Sulfate | And-Met1 | New York | Andersen | 3.941 | 0.368 |
| Sulfate | And-Met1 | New York | MetOne | 3.962 | 0.366 |
| Sulfate | And-Met1 | Portland | Andersen | 1.308 | 0.412 |
| Sulfate | And-Met1 | Portland | MetOne | 1.372 | 0.412 |
| Sulfate | And-Met1 | Salt Lake | Andersen | 0.890 | 0.420 |

| Parameter | Sampler type pair | Site | Sampler Type | Mean (migrograms/m3) | Standard Error |
|---|---|---|---|---|---|
| Sulfate | And-Met1 | Salt Lake | MetOne | 0.934 | 0.420 |
| Sulfate | And-URG | Chicago | Andersen | 4.587 | 0.437 |
| Sulfate | And-URG | Chicago | URG | 4.839 | 0.437 |
| Sulfate | And-URG | Boston | Andersen | 3.062 | 0.446 |
| Sulfate | And-URG | Boston | URG | 3.458 | 0.446 |
| Sulfate | And-URG | Philadelphia | Andersen | 4.469 | 0.379 |
| Sulfate | And-URG | Philadelphia | URG | 4.597 | 0.378 |
| Sulfate | And-URG | Houston | Andersen | 3.803 | 0.478 |
| Sulfate | And-URG | Houston | URG | 4.052 | 0.478 |
| Sulfate | Met1-URG | Phoenix | MetOne | 1.280 | 0.374 |
| Sulfate | Met1-URG | Phoenix | URG | 1.177 | 0.372 |
| Sulfate | Met1-URG | Tampa | MetOne | 4.732 | 0.413 |
| Sulfate | Met1-URG | Tampa | URG | 5.076 | 0.412 |
| Sulfate | Met1-URG | Bismarck | MetOne | 1.388 | 0.535 |
| Sulfate | Met1-URG | Bismarck | URG | 1.415 | 0.535 |
| Sulfate | Met1-URG | Seattle | MetOne | 1.470 | 0.347 |
| Sulfate | Met1-URG | Seattle | URG | 1.465 | 0.347 |

## Table B.4 Significance of the Difference in Relative Composition of the Mass Constituents by Site

| Parameter | Sampler pair type | Site | Significance of the differences in relative composition |
|---|---|---|---|
| Aluminum | And-Met1 | Fresno | 0.0051 |
| Aluminum | And-Met1 | St. Louis | 0.5504 |
| Aluminum | And-Met1 | New York | 0.013 |
| Aluminum | And-Met1 | Portland | 0.4937 |
| Aluminum | And-Met1 | Salt Lake | 0.7091 |
| Aluminum | And-URG | Chicago | 0.1275 |
| Aluminum | And-URG | Boston | 0.0008 |
| Aluminum | And-URG | Philadelphia | 0.0123 |
| Aluminum | And-URG | Houston | 0.0017 |
| Aluminum | Met1-URG | Phoenix | 0.0584 |
| Aluminum | Met1-URG | Tampa | <.0001 |
| Aluminum | Met1-URG | Bismarck | 0.0136 |
| Aluminum | Met1-URG | Seattle | 0.0617 |
| | | | |
| Calcium | And-Met1 | Fresno | 0.0102 |
| Calcium | And-Met1 | St. Louis | 0.0127 |
| Calcium | And-Met1 | New York | 0.32 |
| Calcium | And-Met1 | Portland | 0.0118 |
| Calcium | And-Met1 | Salt Lake | 0.1777 |
| Calcium | And-URG | Chicago | 0.0004 |
| Calcium | And-URG | Boston | <.0001 |
| Calcium | And-URG | Philadelphia | <.0001 |
| Calcium | And-URG | Houston | <.0001 |
| Calcium | Met1-URG | Phoenix | 0.0001 |
| Calcium | Met1-URG | Tampa | <.0001 |
| Calcium | Met1-URG | Bismarck | <.0001 |
| Calcium | Met1-URG | Seattle | 0.1866 |
| | | | |
| Chlorine | And-Met1 | Fresno | 0.4513 |
| Chlorine | And-Met1 | St. Louis | 0.1245 |
| Chlorine | And-Met1 | New York | 0.8266 |
| Chlorine | And-Met1 | Portland | 0.0003 |
| Chlorine | And-Met1 | Salt Lake | 0.0146 |
| Chlorine | And-URG | Chicago | 0.6376 |
| Chlorine | And-URG | Boston | 0.0086 |
| Chlorine | And-URG | Philadelphia | 0.8171 |
| Chlorine | And-URG | Houston | 0.0085 |

| Parameter | Sampler pair type | Site | Significance of the differences in relative composition |
|---|---|---|---|
| Chlorine | Met1-URG | Phoenix | 0.4424 |
| Chlorine | Met1-URG | Tampa | <.0001 |
| Chlorine | Met1-URG | Seattle | 0.669 |
| | | | |
| Iron | And-Met1 | Fresno | 0.0005 |
| Iron | And-Met1 | St. Louis | 0.0337 |
| Iron | And-Met1 | New York | 0.3221 |
| Iron | And-Met1 | Portland | <.0001 |
| Iron | And-Met1 | Salt Lake | 0.3384 |
| Iron | And-URG | Chicago | 0.0144 |
| Iron | And-URG | Boston | <.0001 |
| Iron | And-URG | Philadelphia | <.0001 |
| Iron | And-URG | Houston | <.0001 |
| Iron | Met1-URG | Phoenix | 0.0035 |
| Iron | Met1-URG | Tampa | 0.0158 |
| Iron | Met1-URG | Bismarck | <.0001 |
| Iron | Met1-URG | Seattle | 0.4817 |
| | | | |
| Lead | And-Met1 | Fresno | <.0001 |
| Lead | And-Met1 | St. Louis | 0.2303 |
| Lead | And-Met1 | New York | <.0001 |
| Lead | And-Met1 | Portland | <.0001 |
| Lead | And-Met1 | Salt Lake | 0.0014 |
| Lead | And-URG | Chicago | 0.4892 |
| Lead | And-URG | Boston | 0.6344 |
| Lead | And-URG | Philadelphia | 0.3106 |
| Lead | And-URG | Houston | 0.045 |
| Lead | Met1-URG | Phoenix | 0.0108 |
| Lead | Met1-URG | Tampa | <.0001 |
| Lead | Met1-URG | Bismarck | 0.008 |
| Lead | Met1-URG | Seattle | 0.0011 |
| | | | |
| Tin | And-Met1 | Fresno | <.0001 |
| Tin | And-Met1 | St. Louis | <.0001 |
| Tin | And-Met1 | New York | <.0001 |
| Tin | And-Met1 | Portland | <.0001 |
| Tin | And-Met1 | Salt Lake | <.0001 |
| Tin | And-URG | Chicago | 0.4986 |
| Tin | And-URG | Boston | 0.1768 |
| Tin | And-URG | Philadelphia | 0.4493 |

| Parameter | Sampler pair type | Site | Significance of the differences in relative composition |
|---|---|---|---|
| Tin | And-URG | Houston | 0.0455 |
| Tin | Met1-URG | Phoenix | <.0001 |
| Tin | Met1-URG | Tampa | <.0001 |
| Tin | Met1-URG | Bismarck | <.0001 |
| Tin | Met1-URG | Seattle | <.0001 |
| | | | |
| Silicon | And-Met1 | Fresno | 0.0029 |
| Silicon | And-Met1 | St. Louis | 0.0383 |
| Silicon | And-Met1 | New York | 0.7213 |
| Silicon | And-Met1 | Portland | <.0001 |
| Silicon | And-Met1 | Salt Lake | 0.0862 |
| Silicon | And-URG | Chicago | 0.0012 |
| Silicon | And-URG | Boston | <.0001 |
| Silicon | And-URG | Philadelphia | <.0001 |
| Silicon | And-URG | Houston | 0.001 |
| Silicon | Met1-URG | Phoenix | 0.0061 |
| Silicon | Met1-URG | Tampa | 0.0009 |
| Silicon | Met1-URG | Bismarck | <.0001 |
| Silicon | Met1-URG | Seattle | 0.3542 |
| | | | |
| Zinc | And-Met1 | Fresno | <.0001 |
| Zinc | And-Met1 | St. Louis | <.0001 |
| Zinc | And-Met1 | New York | 0.0049 |
| Zinc | And-Met1 | Portland | <.0001 |
| Zinc | And-Met1 | Salt Lake | <.0001 |
| Zinc | And-URG | Chicago | 0.6211 |
| Zinc | And-URG | Boston | 0.3427 |
| Zinc | And-URG | Philadelphia | 0.6825 |
| Zinc | And-URG | Houston | 0.3348 |
| Zinc | Met1-URG | Phoenix | <.0001 |
| Zinc | Met1-URG | Tampa | 0.0018 |
| Zinc | Met1-URG | Bismarck | 0.0041 |
| Zinc | Met1-URG | Seattle | <.0001 |
| | | | |
| Ammonium | And-Met1 | Fresno | 0.5197 |
| Ammonium | And-Met1 | St. Louis | 0.9005 |
| Ammonium | And-Met1 | New York | 0.3157 |
| Ammonium | And-Met1 | Portland | 0.0009 |
| Ammonium | And-Met1 | Salt Lake | 0.5352 |
| Ammonium | And-URG | Chicago | 0.3109 |

| Parameter | Sampler pair type | Site | Significance of the differences in relative composition |
|---|---|---|---|
| Ammonium | And-URG | Boston | <.0001 |
| Ammonium | And-URG | Philadelphia | 0.0008 |
| Ammonium | And-URG | Houston | <.0001 |
| Ammonium | Met1-URG | Phoenix | 0.0022 |
| Ammonium | Met1-URG | Tampa | <.0001 |
| Ammonium | Met1-URG | Bismarck | <.0001 |
| Ammonium | Met1-URG | Seattle | <.0001 |
| | | | |
| Organic Carbon | And-Met1 | Fresno | 0.0113 |
| Organic Carbon | And-Met1 | St. Louis | 0.4731 |
| Organic Carbon | And-Met1 | New York | 0.7536 |
| Organic Carbon | And-Met1 | Portland | 0.004 |
| Organic Carbon | And-Met1 | Salt Lake | 0.5642 |
| Organic Carbon | And-URG | Chicago | <.0001 |
| Organic Carbon | And-URG | Boston | <.0001 |
| Organic Carbon | And-URG | Philadelphia | <.0001 |
| Organic Carbon | And-URG | Houston | 0.0136 |
| Organic Carbon | Met1-URG | Phoenix | 0.2732 |
| Organic Carbon | Met1-URG | Tampa | <.0001 |
| Organic Carbon | Met1-URG | Bismarck | 0.0004 |
| Organic Carbon | Met1-URG | Seattle | <.0001 |
| | | | |
| Nitrate | And-Met1 | Fresno | 0.3286 |
| Nitrate | And-Met1 | St. Louis | 0.3575 |
| Nitrate | And-Met1 | New York | 0.3184 |
| Nitrate | And-Met1 | Portland | 0.0282 |
| Nitrate | And-Met1 | Salt Lake | 0.3755 |
| Nitrate | And-URG | Chicago | 0.0762 |
| Nitrate | And-URG | Boston | 0.0019 |
| Nitrate | And-URG | Philadelphia | 0.0861 |
| Nitrate | And-URG | Houston | 0.0002 |
| Nitrate | Met1-URG | Phoenix | 0.6289 |
| Nitrate | Met1-URG | Tampa | 0.0789 |
| Nitrate | Met1-URG | Bismarck | 0.5923 |
| Nitrate | Met1-URG | Seattle | 0.7199 |
| | | | |
| Elemental Carbon | And-Met1 | Fresno | 0.1999 |
| Elemental Carbon | And-Met1 | St. Louis | 0.2362 |
| Elemental Carbon | And-Met1 | New York | 0.5705 |
| Elemental Carbon | And-Met1 | Portland | 0.0896 |

| Parameter | Sampler pair type | Site | Significance of the differences in relative composition |
|---|---|---|---|
| Elemental Carbon | And-Met1 | Salt Lake | 0.291 |
| Elemental Carbon | And-URG | Chicago | 0.0108 |
| Elemental Carbon | And-URG | Boston | 0.9003 |
| Elemental Carbon | And-URG | Philadelphia | 0.1773 |
| Elemental Carbon | And-URG | Houston | 0.399 |
| Elemental Carbon | Met1-URG | Phoenix | 0.4172 |
| Elemental Carbon | Met1-URG | Tampa | 0.1473 |
| Elemental Carbon | Met1-URG | Bismarck | 0.8575 |
| Elemental Carbon | Met1-URG | Seattle | 0.0112 |
| | | | |
| Sulfate | And-Met1 | Fresno | 0.6654 |
| Sulfate | And-Met1 | St. Louis | 0.4026 |
| Sulfate | And-Met1 | New York | 0.0006 |
| Sulfate | And-Met1 | Portland | 0.0008 |
| Sulfate | And-Met1 | Salt Lake | 0.4998 |
| Sulfate | And-URG | Chicago | 0.0164 |
| Sulfate | And-URG | Boston | <.0001 |
| Sulfate | And-URG | Philadelphia | <.0001 |
| Sulfate | And-URG | Houston | <.0001 |
| Sulfate | Met1-URG | Phoenix | <.0001 |
| Sulfate | Met1-URG | Tampa | <.0001 |
| Sulfate | Met1-URG | Bismarck | <.0001 |
| Sulfate | Met1-URG | Seattle | <.0001 |

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16. ABSTRACT

EPA has established a PM2.5 chemical speciation trends network of 54 monitoring sites for routine operation. This network is used to provide a nationally consistent set of data for the assessment of trends and provide long term characterization of PM constituents. A vital consideration for these sites is data comparability. EPA initially chose three samplers for potential use in this network. The samplers were operated between February and July, 2000, at thirteen sites as part of an comparative assessment study. Further data were collected in August, 2000, to examine some special issues dealing with sample collection media stability. The analysis results detailed in this report are the end result of three important efforts. First, data underwent a careful screening for outliers, or unusual data, so that results would not be skewed by these values. Next, considerable effort was put into graphical analysis of the data to determine what factors should be considered in the assessment of data comparability. The third effort detailed in theis report was statistical modeling based on the outcomes of the first two efforts. The measured PM2.5 mass was compared with co-located Federal Reference Method sampler measurements. Seventeen out of 24 of the samplers met study data objectives of an $R^2$ value of at least 0.9 in a linear regression of the mass values against the FRM measurement. Deviations from this criteria appear to be caused by site influences that affect all the monitors at a site, rather than differences among sampler types. There are significant site to site differences in: the number of days with outliers, the variability of parameters, the relationship between samplers, etc. The variability found in the sampling precision across sampler types is probably due to site influences, but is probably not generally of any practical concern.

| | | |
|---|---|---|
| 17. KEY WORDS AND DOCUMENT ANALYSIS | | |
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