APPENDIX 3D: Particulate Concentration Intercomparison

3D.1 IMPROVE and SCISAS (Page)

Overview of Comparisons

Most of the comparisons are between the IMPROVE and SCISAS samplers at Page. The Page SCISAS sampler was operated on the same 12 hour cycle beginning at 800 and 2000 as was the IMPROVE sampler. A SCISAS sampler was also operating at Hopi Point throughout the study but it only took 24-hour samples beginning at midnight.

Fine Mass Concentrations: IMPROVE and SCISAS

The comparison between the 12-hour SCISAS mass concentrations (WFPM) and the 12-hour IMPROVE mass concentrations (FFPM) is shown in Figure 3D.1. (See Appendix 3G for information on perpendicular regression.) The correlation is 0.95, and the slope is one standard deviation from one. The statistically insignificant intercept indicates that the mass artifact of 15 μm for the IMPROVE samples was reasonable. The average difference was 30% less than the difference predicted from the propagated precisions.

Fine Elemental Concentrations: IMPROVE and SCISAS

The comparison for sulfur, shown in Figure 3D.2, shows excellent agreement, with a correlation of 0.98, a slope within 1 standard deviation of unity, and an intercept which is 1 standard deviation from zero. Two of the points significantly deviate from the 1:1 line. In both cases, the sulfate value from IMPROVE filter B is approximately equal to the mean of the IMPROVE A and SCISAS W values. It is therefore probable that both A and W are incorrect for these two measurements. The average difference of 50 ng/m^3 was 40% larger than the 36 ng/m^3 difference predicted from the propagated precisions.

The comparisons for trace elements also show good agreement: Zn (Figure 3D.3), Pb (Figure 3D.4), and Se (Figure 3D.5). The average differences in all cases were 50% smaller thant the differences predicted from the propagated precisions. The common characteristic for all of these variables is that they are associated with particles that are predominantly smaller than 2.5 μm. The excellent agreement for selenium ($r^2 = 0.9$) indicates that the concentrations for this important trace metal at Page are reliable, despite the low ambient concentrations. However, there was a major disagreement in the concentration of copper (Figure 3D.6). The average concentrations were around 0.5 ng/m^3 for the IMPROVE sampler, around 7 ng/m^3 for the SCISAS fine, and around

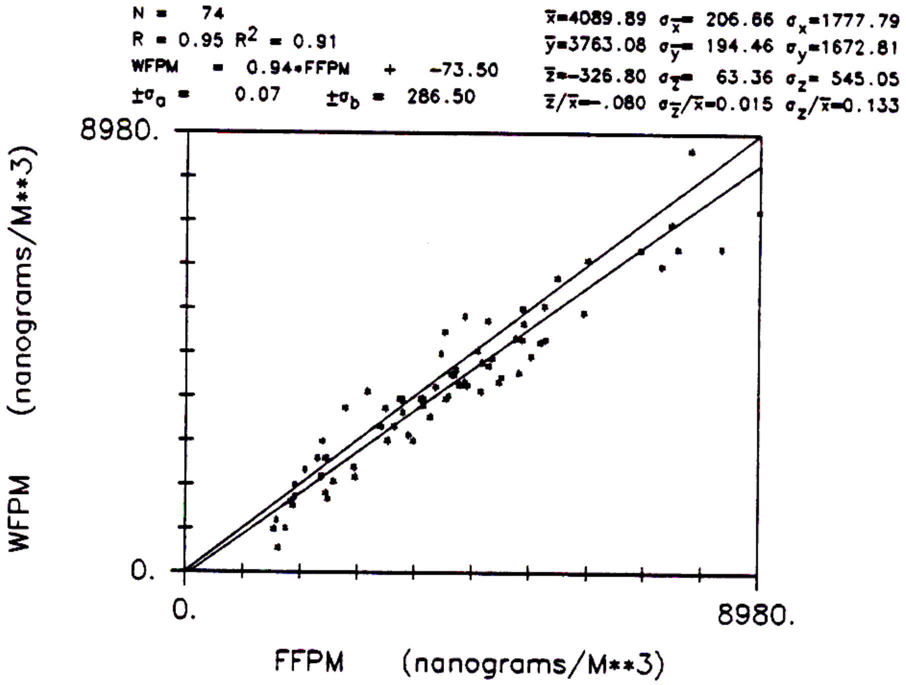

Figure 3D.1: Comparison of mass by SCISAS (WFPM) and by IMPROVE (FFPM) at Page.

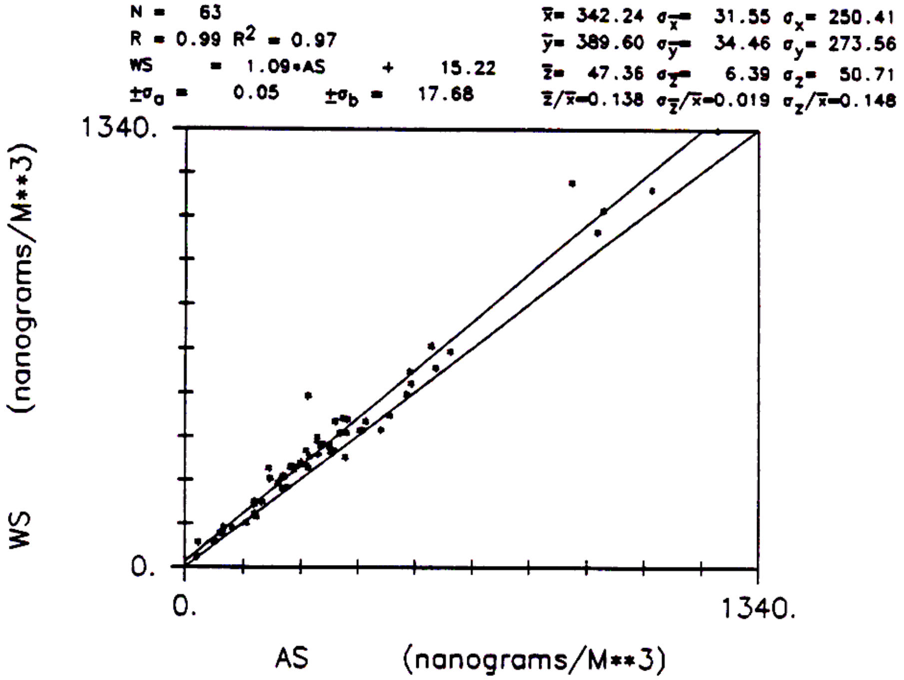

Figure 3D.2: Comparison of sulfur by SCISAS (WS) and by IMPROVE (AS) at Page.

10 ng/m^3 for the SCISAS total. In our previous experience of sampling in this region with the SFU sampler, average concentrations above 3 ng/m^3 were observed only in the vicinity of the copper smelters. There is no correlation between SCISAS copper and any of the other trace metals. It is probable that the SCISAS samples contained a copper artifact.

There are large disagreements for the soil elements. There are several possible reasons for poor intercomparisons of soil elements.

- A significant fraction of the soil mass is often associated with particles near 2.5 μm. If the samplers have different collection efficients, the resulting concentrations could differ slightly.
- Soils are sometimes generated locally, which can produce large spatial gradients in concentration. The SCISAS inlet was approximately 1 meter lower than the IMPROVE inlet and separated by 3 meters.
- Soils are ubiquitous and can contaminate the sample either during collection or handling.

Figures 3D.7 and 3D.8 show the comparisons for fine calcium and iron. The IMPROVE calcium values are the average of two 6-hour measurements, while the iron values are 12-hour measurements. The average differences were 3–4 times the differences predicted from the propagated precisions. For calcium, most ratios were between 1 and 2, although there were 16 cases in which the SCISAS Ca is twice the IMPROVE Ca. These 16 cases are indicated by circles and will be examined in detail. The disagreements here are much larger than for sulfur and the trace elements, so the differences were not caused by errors in flow rate. The differences were also too large to be explained by small differences in collection efficiency. Figure 3D.9 shows the variation in the ratio of SCISAS fine Ca/IMPROVE fine Ca for the WHITEX time period at Page. For most of the periods from 8 Jan to 27 Jan, the ratio was close to unity. Between 28 Jan and 11 Feb, the ratio increased, with a range of 1 to 2.7. Beginning with 12 Feb, the SCISAS fine was significantly larger than the IMPROVE fine. The ratio appears to follow patterns rather than being completely random. Thus the maximum difference on 12 Feb was preceeded by two periods when th difference was increasing. This figure cannot distinguish between excess SCISAS fine Ca and insufficient IMPROVE fine Ca.

The judgement of which sampler was correct can be made by comparing both fine calciums with the SCISAS total calcium. Figure 3D.10 shows the variation in both fine/total ratios over the WHITEX period. For the NPS/EPA networks using SFU samplers, we found that the $PM_{2.5}/PM_{15}$ ratio for Ca is approximately 0.12; similar ratios were obtained for DICHOT samples collected in 1980. The ratio of average IMPROVE fine Ca/average SCISAS total Ca for corresponding samples at Page in WHITEX was also 0.12. This ratio is shown on the figure as a solid line. In many cases, the ratio of SCISAS fine/SCISAS total was far larger than 0.12. In two cases, the ratio exceeded 1.0, indicating that the SCISAS fine Ca exceeded the SCISAS total Ca, which is not physically possible. A comparison of these two timeplots indicates that the periods of high ratio of SCISAS/IMPROVE were generally the same as those periods when the fine/total ratio for SCISAS was much larger than 0.12. The conclusion is that many of the SCISAS fine samples were contaminated with soil, either during sampling or in handling.

Soil contamination does not account for every case of disagreement. In 4 of the 16 cases of major disagreement for both calcium and iron, the SCISAS total and fine were consistent, while the two IMPROVE filters were consistent. Again, the SCISAS was larger than the IMPROVE. Three of the four cases occurred during periods of high winds, although not every period of high wind had disagreement. The most reasonable explanation is that there were large spatial gradients in the fine soil concentrations. In the final case of disagreement for calcium, there was excellent

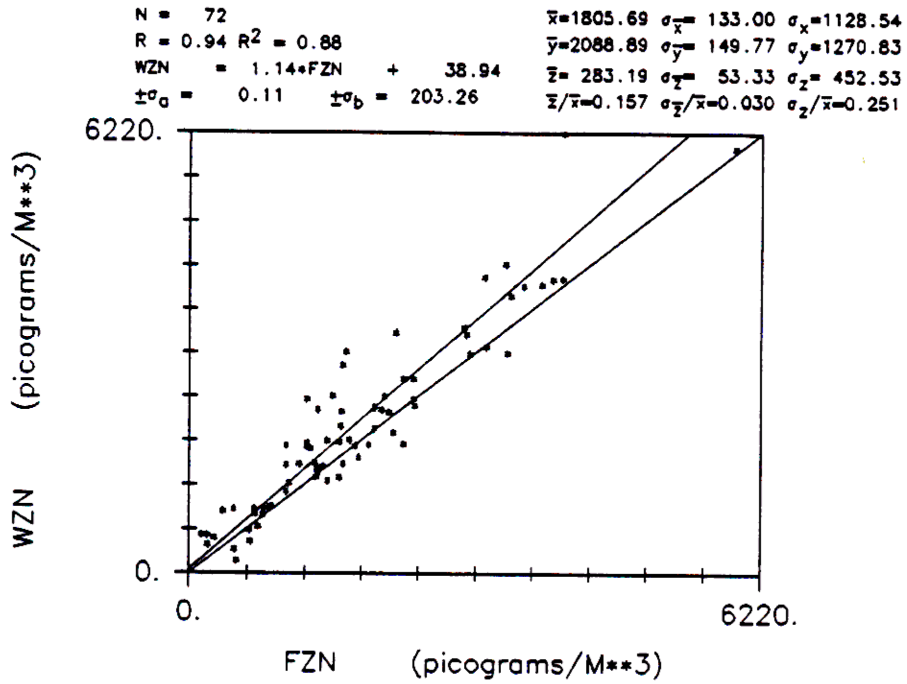

Figure 3D.3: Comparison of zinc by SCISAS (WZN) and by IMPROVE (FZN) at Page.

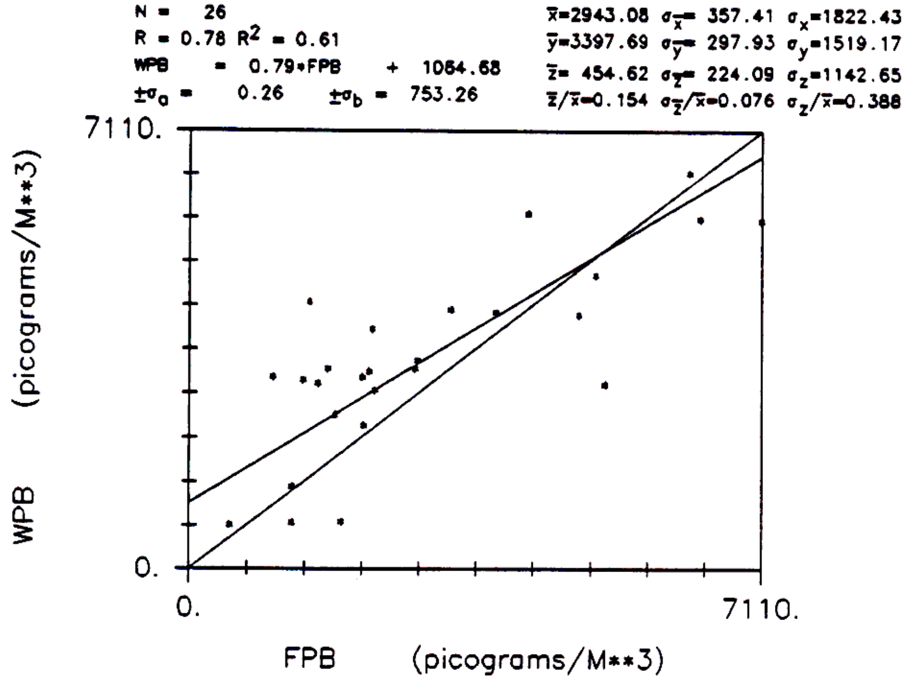

Figure 3D.4: Comparison of lead by SCISAS (WPB) and by IMPROVE (FPB) at Page.

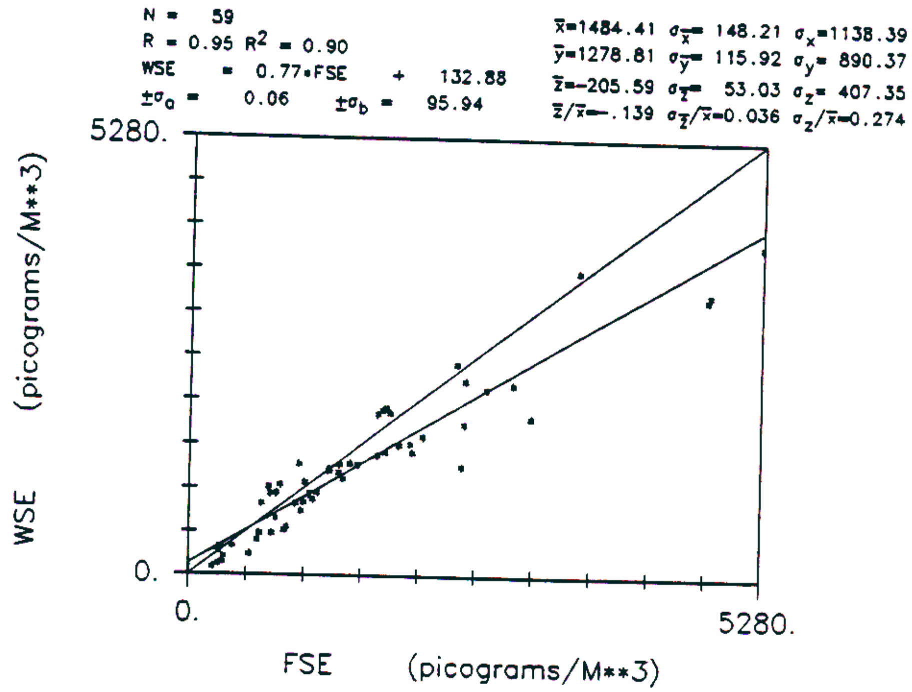

Figure 3D.5: Comparison of selenium by SCISAS (WSE) and by IMPROVE (FSE) at Page.

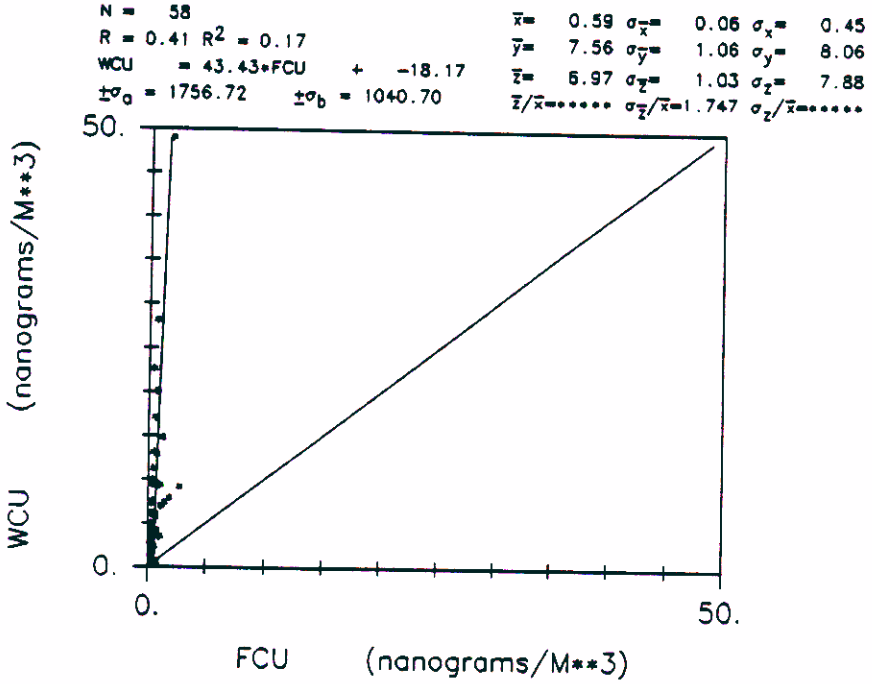

Figure 3D.6: Comparison of copper by SCISAS (WCU) and by IMPROVE (FCU) at Page.

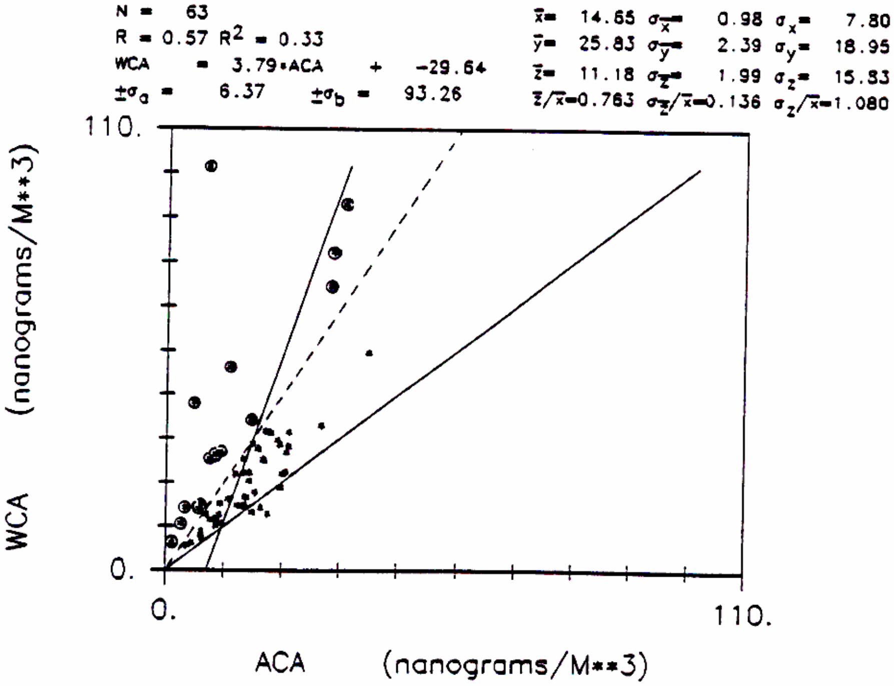

Figure 3D.7: Comparison of calcium by SCISAS (WCA) and by IMPROVE (ACA) at Page. The 6-hour IMPROVE concentrations were averaged to give 12-hour values. The circled points have a ratio exceeding 2.

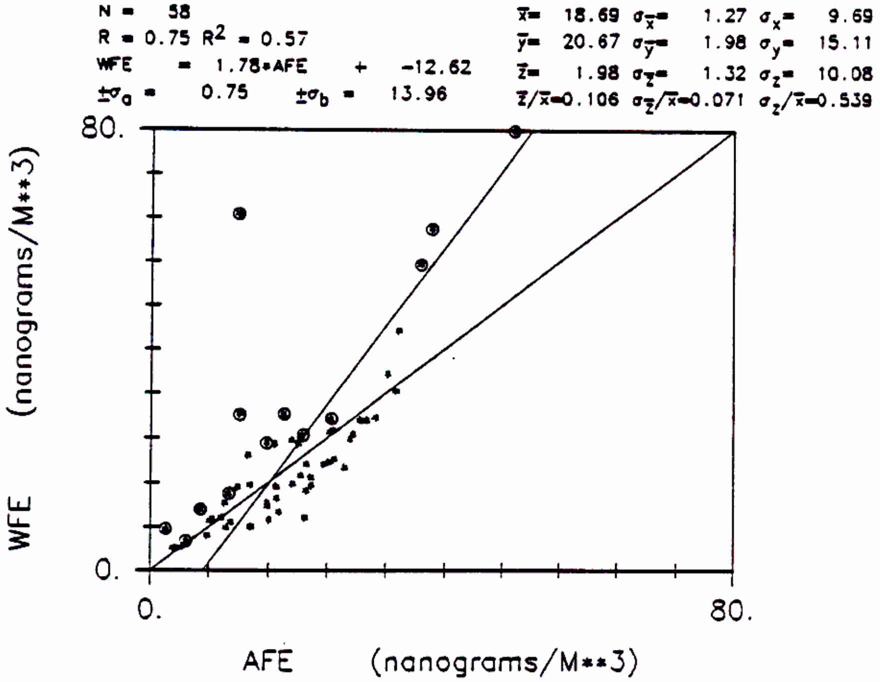

Figure 3D.8: Comparison of iron by SCISAS (WFE) and by IMPROVE (FFE) at Page.

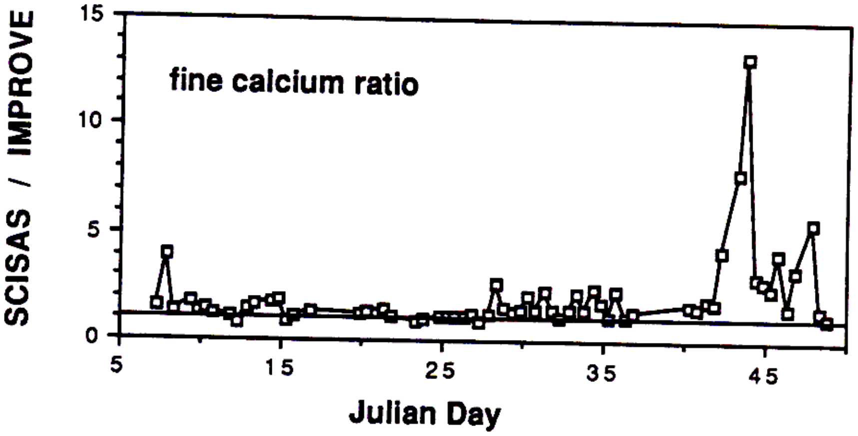

Figure 3D.9: Ratios of SCISAS fine Ca/IMPROVE fine Ca at Page.

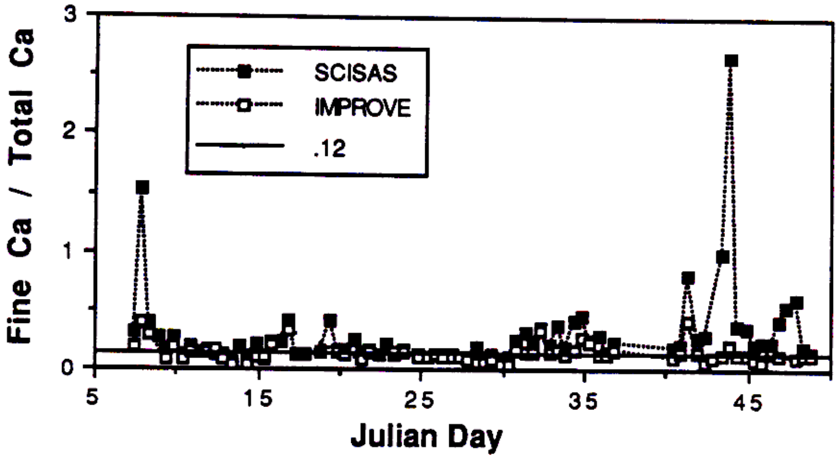

Figure 3D.10: Ratios of SCISAS fine Ca/SCISAS total Ca and IMPROVE fine Ca/SCISAS total Ca at Page. The straight line is a typical ratio for western aerosols.

agreement for all measurement for iron. Internal consistency does not favor either fine calcium measurement.

This comparison indicates that the SCISAS sampler had significant soil contamination during some of the periods of the study. There may have been smaller contamination during other periods. The cause of the contamination is not known. The comparison also shown that under certain conditions there may have been significant spatial variation of soil particles. Except for these few periods, the SCISAS total iron and calcium was consistent with the IMPROVE fine data. The most important conclusion is that the soil contamination of the Page fine samples did not affect correct the model analyses, which used only the iron concentrations measured by the IMPROVE sampler. The comparison does not suggest that there were any major problems with the IMPROVE soil concentrations.

Nitrate Concentration: IMPROVE and SCISAS

The SCISAS sampler included NO_x vapors and should be equivalent to the IMPROVE module D, without denuder. These two are compared in Figure 3D.11; the two IMPROVE nylon modules are compared in Figure 3D.12. The SCISAS filter (UNO3) has consistently higher readings than the nondenuder filter (DNO3), which has higher concentrations than the denuder filter (ENO3). It appears that there was some denuding in the D module.

Fine Carbon Concentrations: IMPROVE and SCISAS

The SCISAS sampler ran a 12-hour quartz filter (designated "V") that was analyzed by the TMO method, while the IMPROVE sampler ran a quartz filter (designated "C") that was analyzed by the TOR method. The organic concentrations (OC * 1.4) are compared in Figure 3D.13. The fit is not very good, but the mean values differ by only 18%, with COC being larger. The average difference of 270 ng/m^3 was equal to the difference predicted from the propagated precisions of 260 ng/m^3. Also shown in this figure is the comparison between the SCISAS-TMO results with IMPROVE teflon estimates of organic mass using hydrogen and sulfur. The comparison is much better than that for TMO *vs* TOR.

Figure 3D.14 shows very poor agreement between TOR and TMO in the measurement of elemental carbon at Page. Not only is the average concentration by TOR 5 times that by TMO, but the correlation is poor and the intercept significantly differs from zero. Previous studies have shown major disagreement when the source of elemental carbon is wood smoke.[1] In this case, the town of Page is the most likely source of the wood smoke. The correlation between the coefficient of optical absorption and elemental carbon by TOR, shown in Figure 3D.15 is also low, but the average values are approximately equal, it an absorption efficiency of 10 m^2/g is used. For this reason, we have chosen to label the elemental carbon by TOR as light-absorbing carbon, LAC

Reconstructed Mass: IMPROVE and SCISAS

The comparison of the reconstructed mass and the gravimetric mass for the 12-hour IMPROVE sampler was shown in Figure 3D.16. The reconstructed mass in that figure used hydrogen to estimate organics, absorption to estimate elemental carbon, and included ammonium nitrate, based on the nitrate measurements on Teflon. Since the SCISAS sampler does not measure nitrate on the Teflon, all reconstructed masses in this section will exclude ammonium nitrate. For the IMPROVE sampler, the inclusion of ammonium nitrate increases the slope by 2% without affecting the correlation coefficient. The procedure for reconstructing the SCISAS mass is the same as that for the IMPROVE sampler. The periods with soil contamination were included, since the extra

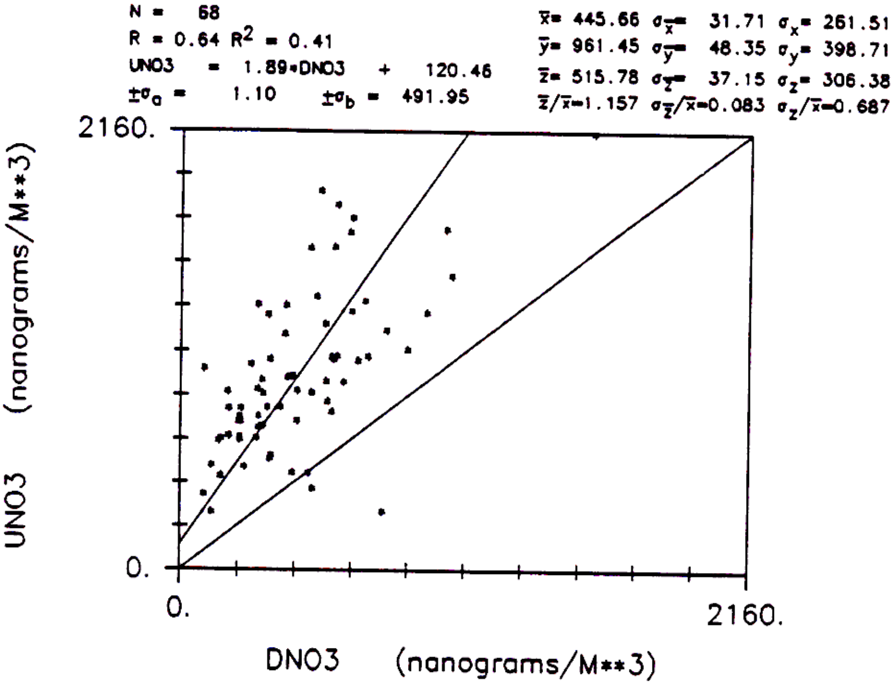

Figure 3D.11: Comparison of total nitrate by SCISAS (UNO3) and total nitrate by IMPROVE (DNO3) at Page.

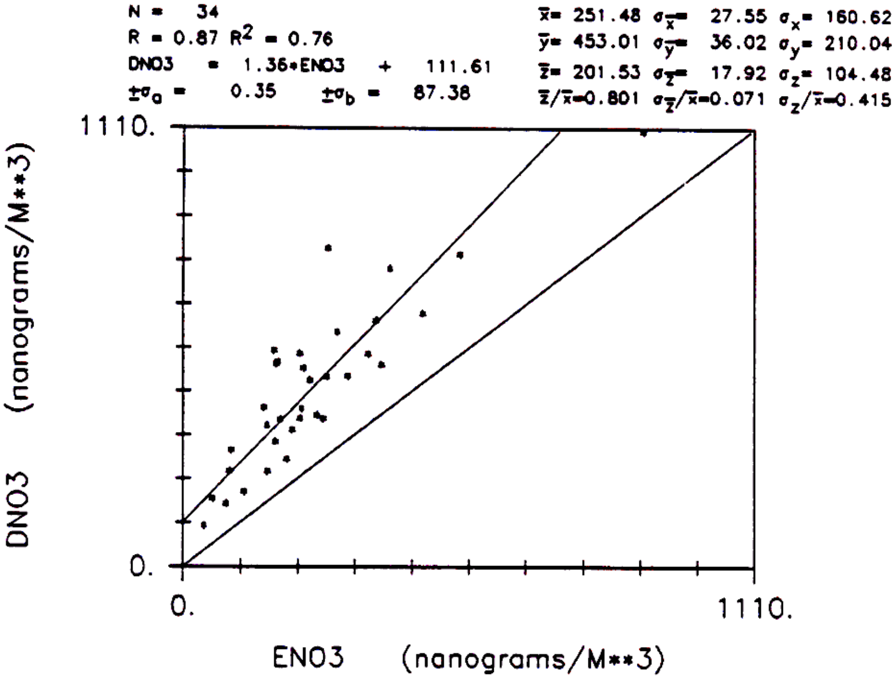

Figure 3D.12: Comparison of total nitrate by IMPROVE (DNO3) and particulate nitrate by IMPROVE (ENO3) at Page.

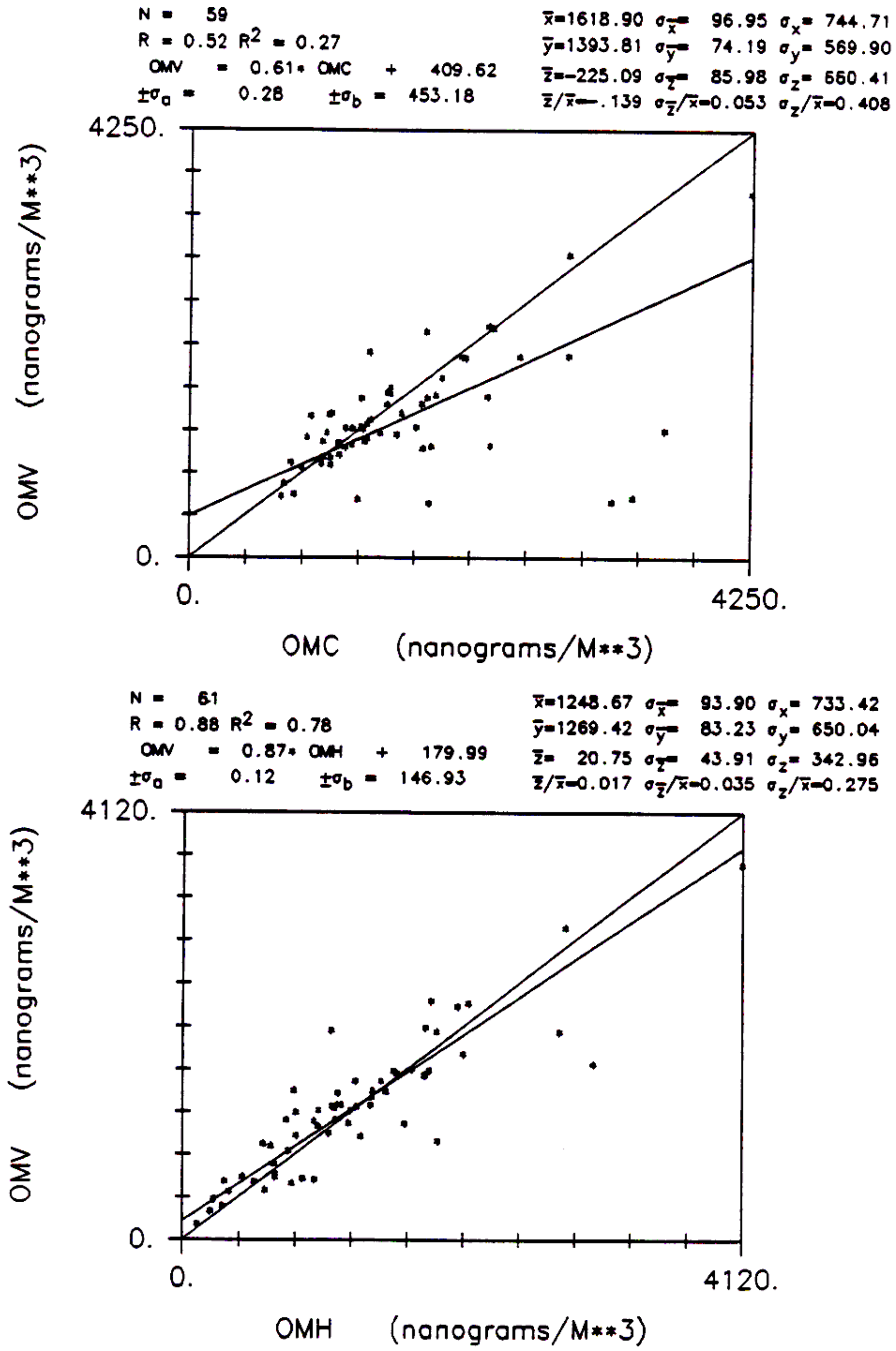

Figure 3D.13: Comparison of organic mass (OC*1.4) by SCISAS/TMO (OMV) with IMPROVE/TOR (OMC) and IMPROVE/hydrogen (OMH).

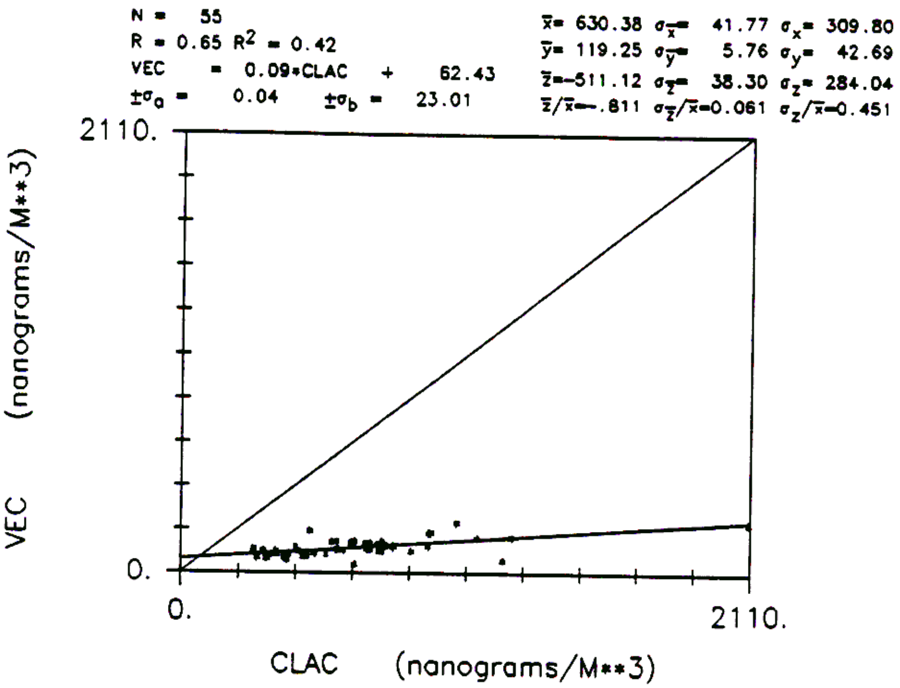

Figure 3D.14: Comparison of elemental carbon by SCISAS and TMO (VEC) and light-absorbing carbon by IMPROVE and TOR (CLAC) at Page.

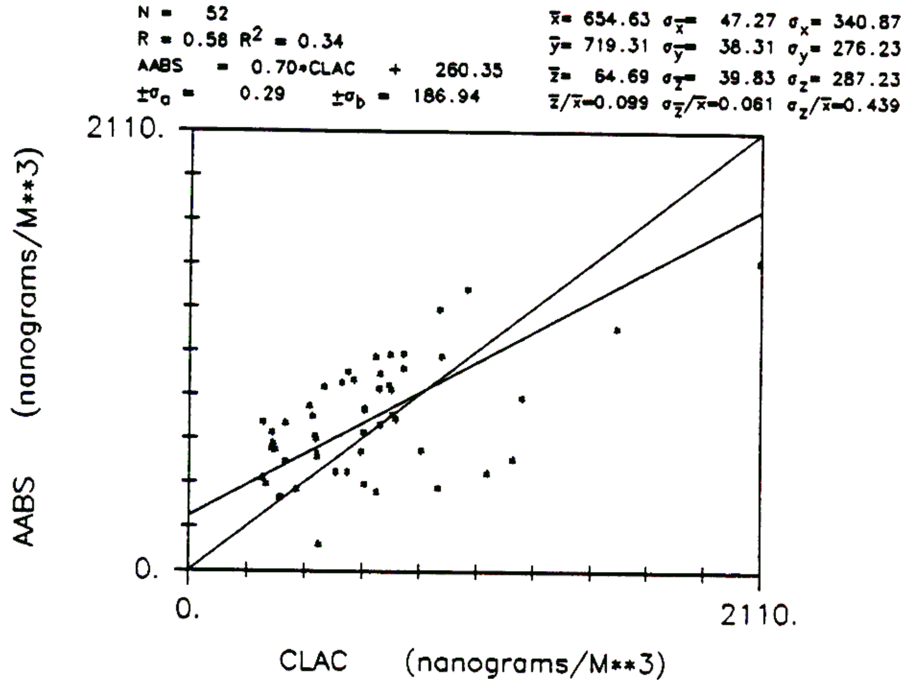

Figure 3D.15: Comparison of elemental carbon by TOR (CLAC) and the coefficient of absorption by LIPM (AABS) at Page. The coefficient is expressed as equivalent concentration of absorbing particles assuming an efficiency of 10 m^2/g.

mass involved was a small fraction of the gravimetric mass and should not affect the discussion. The comparison between the reconstructed masses and the gravimetric masses for both samplers are shown in Figure 3D.17. The reconstructed mass for the IMPROVE sampler uses the hydrogen concentration and the coefficient of absorption to estimate organic and elemental carbon. The fit assumes that the uncertainties are constant for all mass concentrations. The fit is somewhat better for the SCISAS sampler ($r^2 = 0.97$ *vs* $r^2 = 0.93$). The slope for the SCISAS sampler is slightly closer to 1.0 than that for the IMPROVE sampler (0.94 *vs* 0.93); however, if the uncertainty for each concentration is included in the fitting procedure, the slope for the IMPROVE sampler is slightly closer to 1.0 (0.92 *vs* 0.86). The residual mass, obtained by subtracting the reconstructed mass from the gravimetric mass, is approximately 8–10% of the mass. Approximately one-quarter of this residual mass would be ammonium nitrate, with the rest being other volatile particles and water that would be removed in the x-ray analysis. Figure 3D.18 compares the two reconstructed masses and Figure 3D.19 compares the IMPROVE reconstructed mass with the SCISAS gravimetric mass. The regression line for the two reconstructed masses goes through the origin and has a slope of 1.0. These comparison show that the two samplers gave equivalent results for reconstructed mass.

3D.2 IMPROVE and DRUM (All Primary)

Fine Sulfur Concentrations: IMPROVE and DRUM

Fine particles concentrations (smaller than 2.1 μm) were obtained for the DRUM sampler by summing the rotating stages 3 through 8 and the afterfilter. Figures 3D.20 through 3D.23 compare the fine sulfur concentrations by the DRUM to those by the IMPROVE at each site. The DRUM concentrations shown were not corrected for the 10.7% loss factor discussed in Appendix 3A.2 and should be multiplied by 1.12. After correction, the ratio of average concentrations (DRUM/IMPROVE) were 0.91, 1.08, 0.99, and 0.99. Thus, there appears to be no bias between the two samplers.

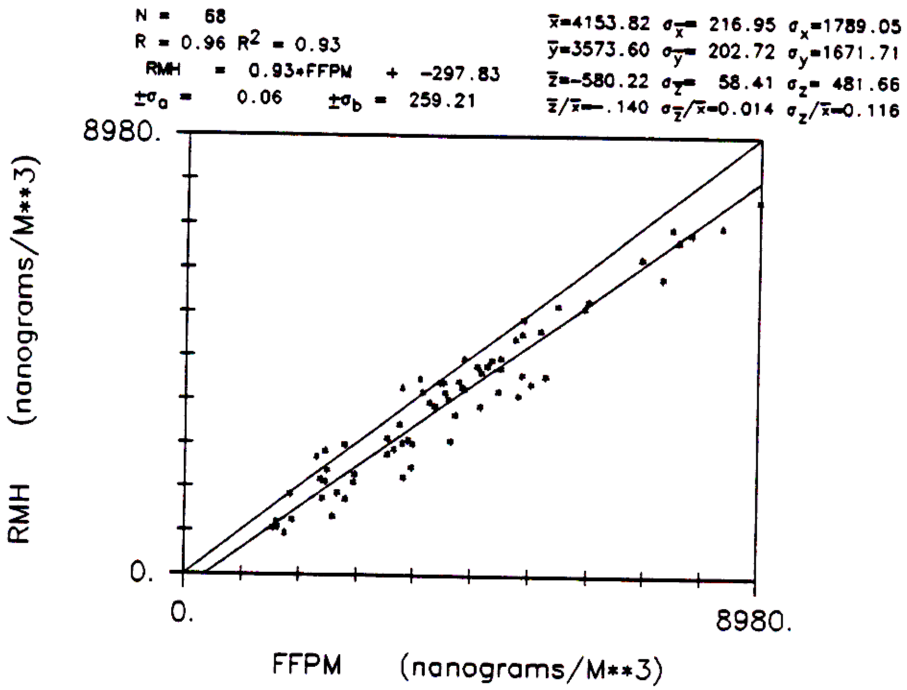

Figure 3D.16: Comparison of reconstructed mass (RMH) and gravimetric mass (FFPM) for IMPROVE at Page. RMH uses organic and elemental carbon from *H* and the coefficient of absorption. Nitrate is not included.

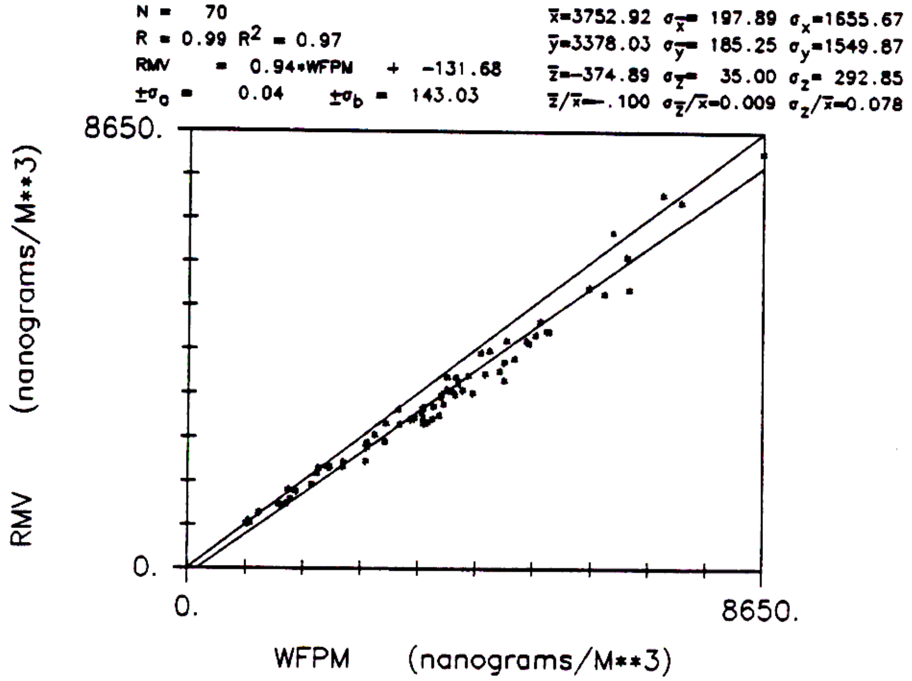

Figure 3D.17: Comparison of reconstructed mass (RMV) and gravimetric mass (WFPM) for SCISAS at Page. Nitrate is not included.

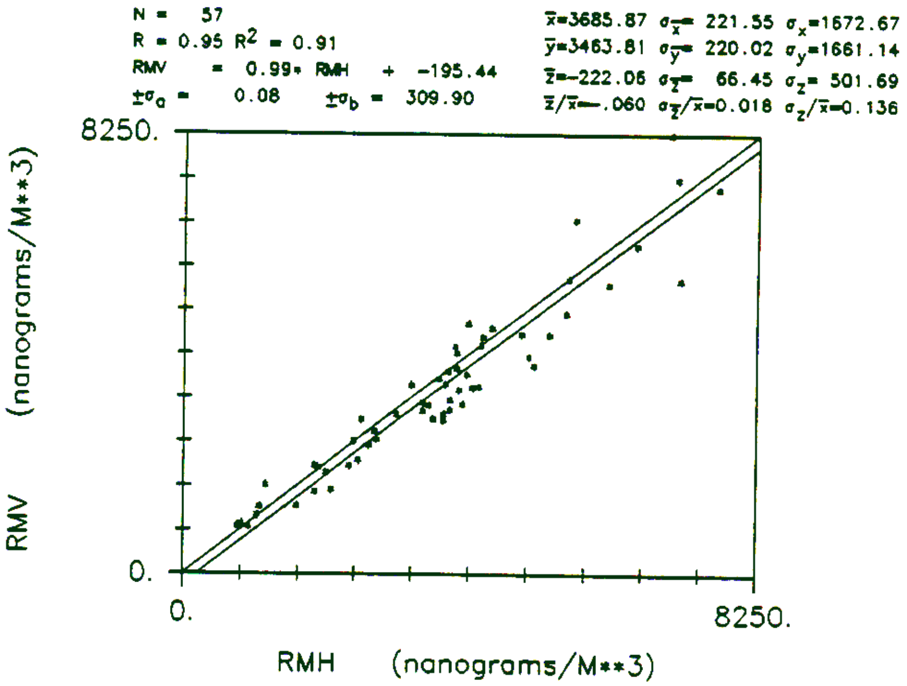

Figure 3D.18: Comparison of reconstructed mass for SCISAS (RMV) and reconstructed mass for IMPROVE (RMH) at Page. Nitrate is not included.

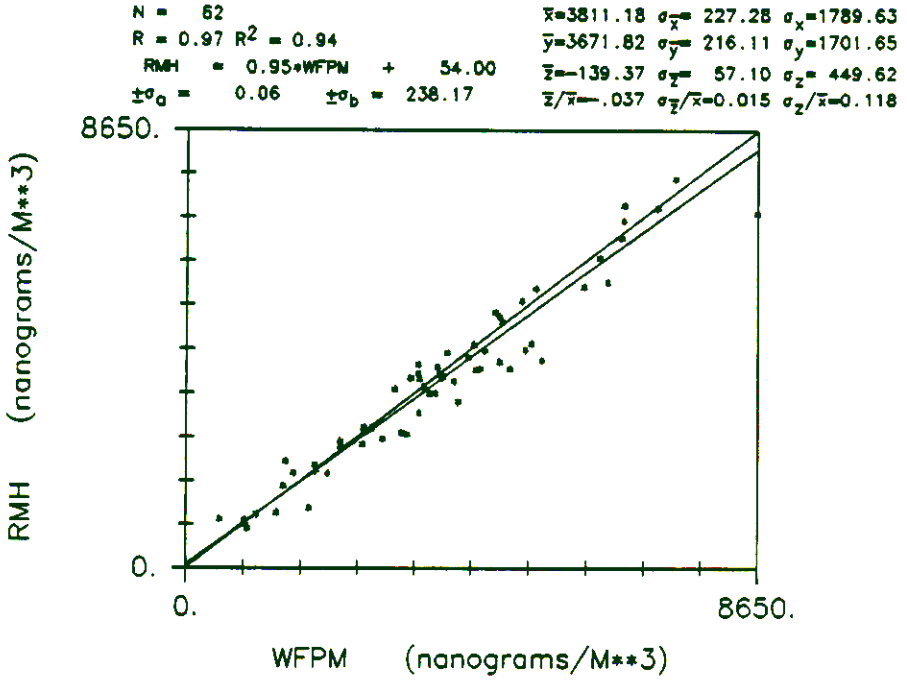

Figure 3D.19: Comparison of reconstructed mass for IMPROVE (RMH) and gravimetric mass for SCISAS (WFPM) at Page. Nitrate is not included.

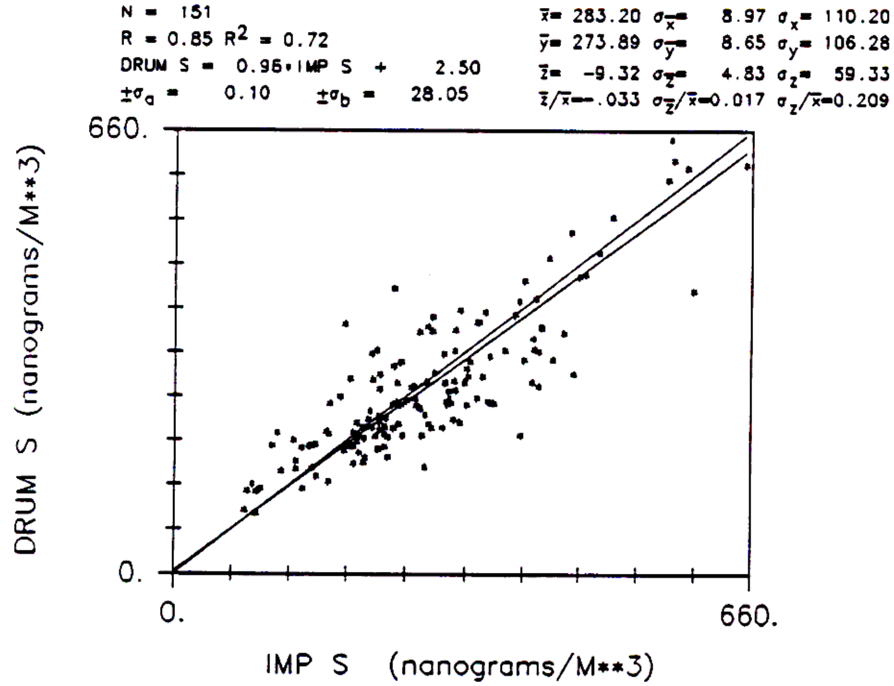

Figure 3D.20: Comparison of fine sulfur by DRUM (sum of stages 3 to AF) and by IMPROVE at Canyonlands.

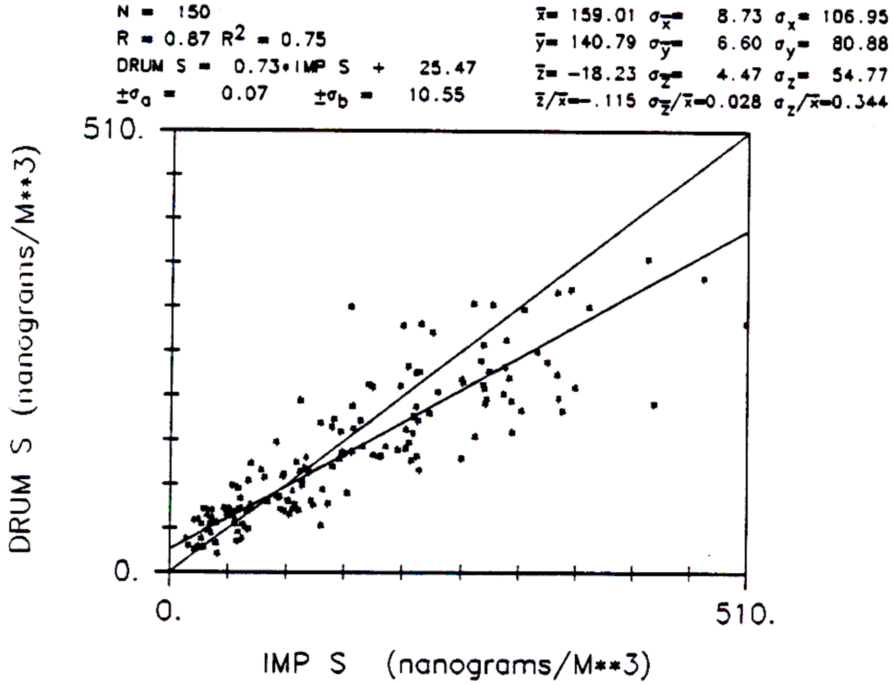

Figure 3D.21: Comparison of fine sulfur by DRUM (sum of stages 3 to AF) and IMPROVE at Hopi.

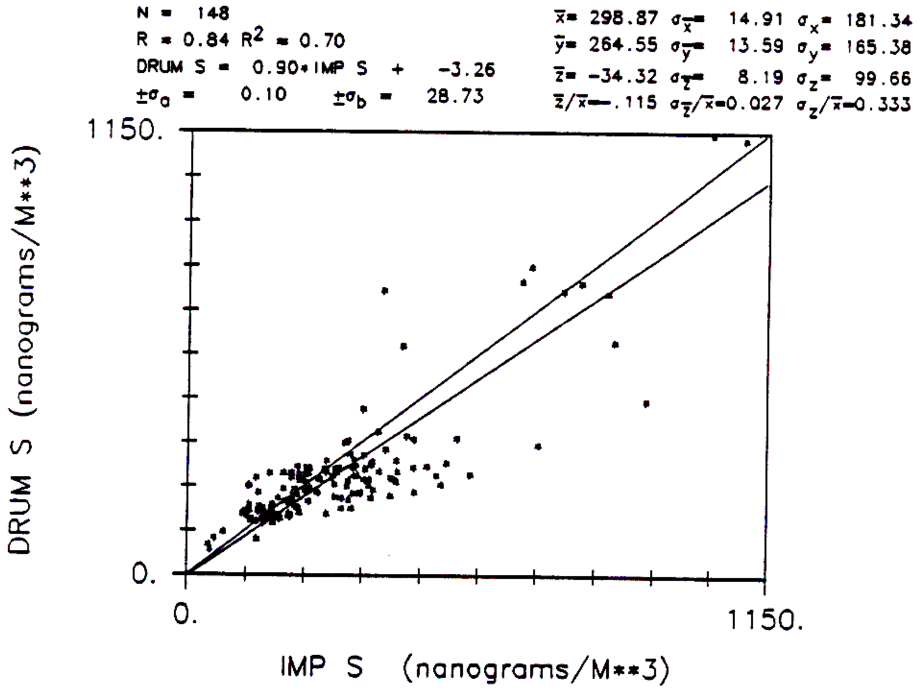

Figure 3D.22: Comparison of fine sulfur by DRUM (sum of stages 3 to AF) and by IMPROVE at Bullfrog.

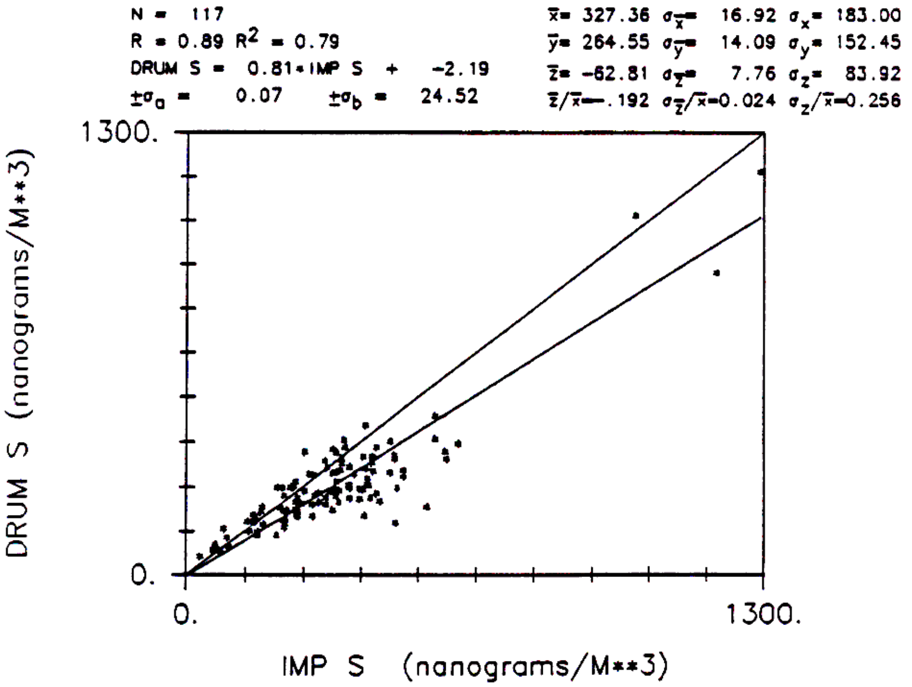

Figure 3D.23: Comparison of fine sulfur by DRUM (sum of stages 3 to AF) and by IMPROVE at Page.

References

[1] Countess, R.J., "Quality assurance audits of laboratories performing carbonaceous aerosol measurements," 1989 *Proceedings of the 81st Annual Meeting of APCA*, June 19–24, 1988, Dallas, TX, paper 88–53.6.