

UC Davis IMPROVE Measurements Quality Assurance Status Report Volume II

1. INTRODUCTION

This report is intended to summarize the current status of the QA program at UC-Davis including the recent data delivery, documentation, and program changes.

2. DATA MANAGEMENT

There is no significant progress to report on the data management redesign. The emphasis continues to be on ingesting the flashcard data from the samplers.

3. DOCUMENTATION

3.1 STANDARD OPERATING PROCEDURES

Table 1 summarizes the status of the SOP revisions.

Table 3-1. Status of SOP revisions, September 2007.

SOP #	Topic	Expected Completion Date	Status
101	Procurement	October 2007	In progress
126	Site Selection	September 2007	Revised SOP needs final approval
151	Site Installation	February 2008	To be written
201	Site Operators	Completed	Revised and posted on IMPROVE website 2004
226	Annual Maintenance	February 2008	In progress
251	Sample Handling	October 2007	In progress
276	HIPS	September 2007	Revised SOP needs final approval
301	XRF	December 2007	In progress
326	PIXE/PESA	September 2007	Revised SOP needs final approval
351	Data Processing/ Validation	September 2007	Draft prepared; needs final approval

3.2 METADATA

Metadata were last delivered to CIRA on June 27, 2006. The last delivery covered maintenance activities through May 2006.

4. DATA REVIEW AND VALIDATION

The data are scheduled to be delivered to CIRA six months after the filters are collected. Data delivery is currently 11 months behind collection; data are being delivered at a faster rate than normal to catch up on the backlog. Seven months of data have been delivered to CIRA since the previous QA report was published in May 2007. Therefore, this report covers seven months of data.

The validation tests involve some checks of data metrics and visual inspection of graphs. The tests will evolve over time to include more quantitative checks.

4.1 SUMMARY

Data Period: March 2006 through September 2006

Reviewed in relation to: 2004-2005

Retrieved from the VIEWS Database on: September 12-21, 2007

As mentioned in the previous report, there were significant changes in the XRF analyses recently; the new vacuum Cu-anode XRF system was first used for the January 2005 data and a second vacuum Cu-anode XRF system was introduced in October 2005. Distinct shifts in the S to SO₄ ratios are obvious during 2006, and these shifts appear to be related to the two different Cu-anode XRF instruments. Figure 4-1 shows the ratio of sulfur times three to sulfate for the entire network. The symbols mark the medians and the lines span the inner-quartile range (25th to 75th percentiles). Further discussions of the XRF systems can be found in the XRF QA reports (http://vista.cira.colostate.edu/improve/Data/QA_QC/QAQC_UCD.htm). In addition, the data advisories address various XRF issues including differences between the two Cu-anode instruments (http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm).

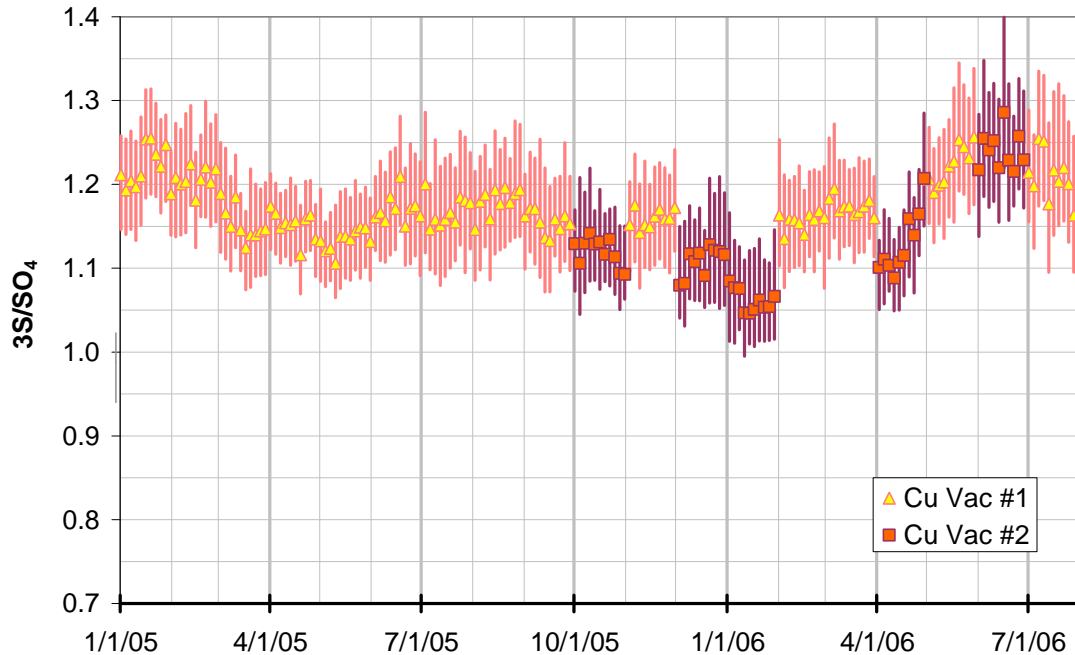


Figure 4-1. The ratio of sulfur times three divided by SO_4 for the entire network since the introduction of the vacuum Cu XRF systems in January 2005.

Shifts in some elements analyzed by the Mo-XRF instrument were noticed in the review of the March to May 2006 data. For example, Figure 4-2 shows the median network-wide Br loadings by year and month for the last few years; the median Br loadings in 2006 are lower than in the past. The XRF group explained that the shifts were caused by a change in the calibration procedure (see data advisory at http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0014/da0014_Mo_drop.pdf). Starting with September 2005 samples, a new set of standards were used to calibrate the Mo-anode XRF system. The calibration constants for several elements changed as a result of the new standards.

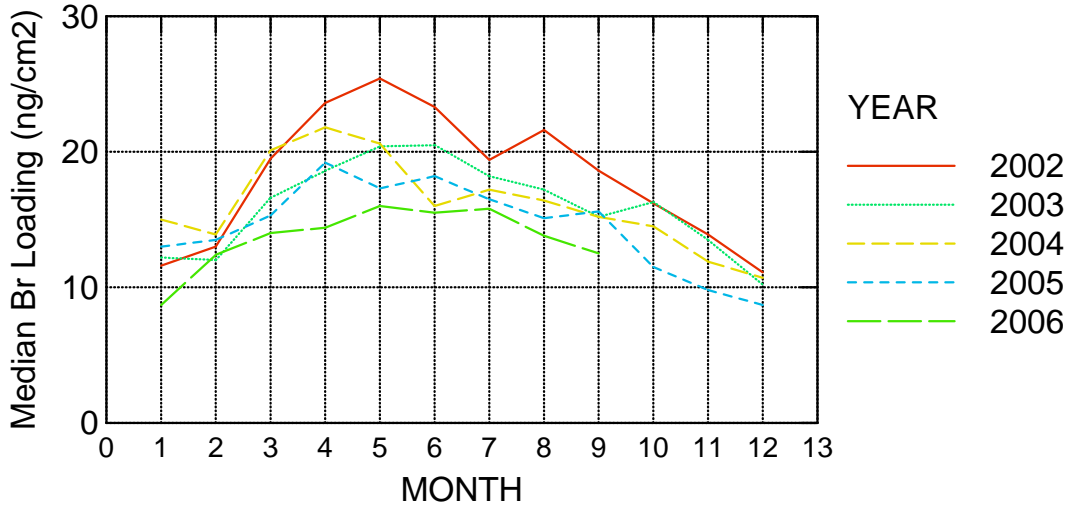


Figure 4-2. Median Br loadings in the entire routine network.

No sites had large blocks (> 10 days) of data withheld from the current data set; therefore, Table 1 is empty.

The OP MDLs in March and the EC3 MDLs in March and August reported to CIRA were all zero. The MDLs are calculated by UCD based on the standard deviation of the secondary (backup) filter concentrations. Zero MDL values are a reoccurring problem and can easily be rectified by setting minimum possible values for the MDLs. A similar solution has already been applied to avoid zeros in the ions MDLs, where the analytical MDLs reported by RTI are used as minimum values. DRI does not report analytical MDLs for the carbon fractions so a reasonable substitute is being investigated. This problem will be fixed in future deliveries.

Table 1. Unresolved problems in the data set.

Dates Impacted	Site	Problem Description	Date/Delivery Discovered	Temporary Resolution	Permanent Resolution

4.2 FILE INTEGRITY CHECKS

4.2.1 XRF Data Files

Several records in the initial XRF data files were missing individual analyses. PESA data are missing for 39 records because the filters were damaged by the vacuum Cu-anode instruments. All the damaged filters were analyzed on the first vacuum Cu-XRF system. The XRF group believes they have identified and fixed the problem, and the number of damaged filters decreased from 22 in May down to 4 in September.

Some missing records resulted from incomplete flags in the XRF data files. The XRF files have a status flag column for each analysis – PESA, Cu-XRF, and Mo-XRF – but these flags have not been utilized consistently. Requests have been made to utilize these flags if an analysis is missing or invalid but the flags continue to be inconsistently used. For future deliveries, the XRF group will be asked to review the data files one more time immediately before delivery to CIRA.

Routine analysis of Teflon field blanks began with the September 2005 samples on the Mo XRF system and with the December 2005 samples on the Cu XRF systems. A few months have been skipped on the Cu systems but the most recent months (July-Sept 2007) of field blanks have been analyzed. The XRF group plans to analyze the skipped field blanks at a later date.

Table 2. XRF field blank analysis inventory. The number in the Cu-anode row indicates which instrument was used to analyze the field blanks.

Instrument	March	April	May	June	July	Aug	Sept
Mo-anode	√	√	√	√	√	√	√
Cu-anode		#2			#1	#2	#1

4.2.2 Carbon Data Files

No irregularities were found in the carbon files.

4.2.3 Ions Data Files

No irregularities were found in the ions files.

4.2.4 Weights Data Files

No irregularities were found in the weights files.

4.2.5 HIPS Data Files

Samples collected in January, March, May, June, and July 2006 have not been analyzed on the HIPS instrument. No irregularities were found in the reported HIPS data.

4.2.6 Flow Rate Calibration Records

The flow rate calibrations have been entered into the database through December 2006. For quality control purposes, the calibrations should be reviewed and entered into the database within one to two months of the performance date.

The calibration times are still set to midnight in the latest entries. The maintenance group has been asked to include a time with the calibration data. The calibration time is necessary to properly calculate flow rates when a calibration is performed in the middle of a sampling day.

4.2.7 Delivery Data files

Duplicate records: None

Incomplete records: Several records are missing PESA analyses because the filters were damaged in the Cu-XRF analysis. In addition, several records from the collocated sites in September are missing PESA data but have valid flags. The collocated A-module filters from PMRF, SAFO, and SAMA were removed from standard processing prior to PESA analysis and used for special SO₄ analyses.

Flag use violations: Several records have valid data flags with invalid analyses. This problem cannot be solved until the delivery files use analysis- or parameter-specific validation flags.

Inadequate metadata: The clocks were set incorrectly for over a month at KAIS1 (3/15-4/29/06) and SULA1 (3/3-4/8/06). The corresponding data were labeled with the incorrect times and flagged as SA (Sampling Anomaly). The SA flag does not convey the necessary information for the data user. Clock problems should be remedied by correcting the sampling date/time and flagging them with a more specific flag. Unfortunately, the current database structure makes this fix cumbersome and error-prone. This problem will be resolved in the new data management system.

Undelivered data: Data from a few special sites have not been delivered for several months. These sites include MALO and the carbon-only urban sites (PITT, ATLA, and DETR). The MALO1 and MALO2 sites were removed from the routine operations in March 2005, and the C-only sites were removed from the routine operations in August 2005.

4.3 NETWORK-LEVEL DATA QUALITY CONTROL

The raw analytical data for the entire network are checked to help identify problems that may affect a particular analytical system. The carbon, ions, and elements data are checked by calculating percentiles, minimum values, and maximum values for the entire network and comparing these values for the current month to corresponding values from the same month in prior years. The raw loading data from the laboratory (in mass/area) are used for these checks (i.e., the loadings have not been divided by the sample volume to determine concentrations). As discussed in Section 4.1, the network-level checks revealed shifts in several of the Mo-XRF elements. The carbon fractions continue to exhibit distinct differences since the introduction of the new instruments in January 2005. Figure 4-3 shows the network-wide median OC3 loadings for the last few years.

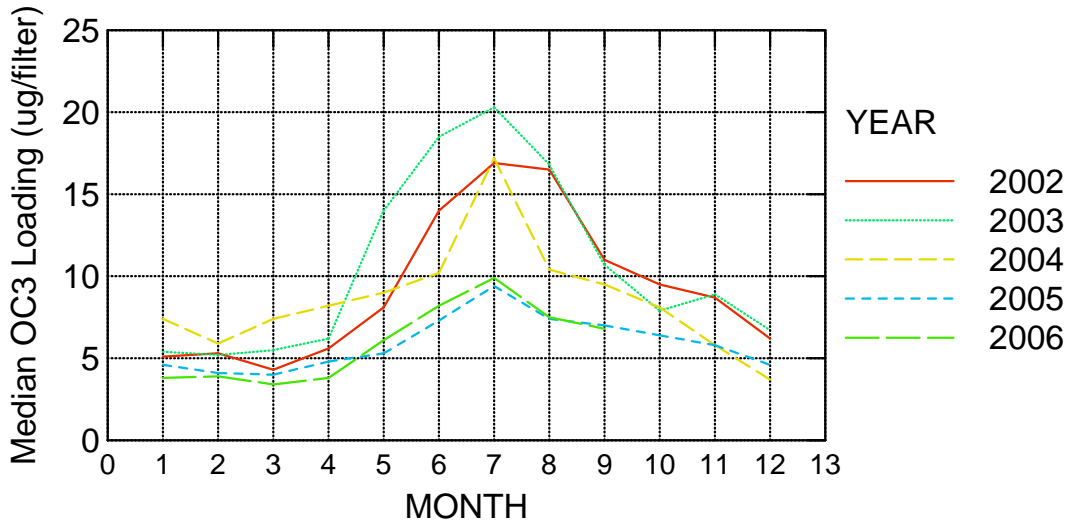


Figure 4-3. Median Br loadings in the entire routine network.

4.4 SITE-SPECIFIC DATA VALIDATION REVIEW

The site-specific data validation review consists of looking through a series of graphs for each site. The graphs are constructed using the CIRA web tools (<http://vista.cira.colostate.edu/idms/Tools/DataBrowser.aspx>) which access the VIEWS database.

4.4.1 Soil Elements

Plots of Al, Ca, Si, Ti, and Fe were inspected. The individual element concentrations were inspected along with the enrichment factors (EF) relative to Fe. The enrichment factor is the ratio of the element to Fe divided by the expected ratio in soil

(e.g., $\frac{\left(\frac{Al}{Fe}\right)_{sample}}{\left(\frac{Al}{Fe}\right)_{soil}}$).

Detection rates for Al and Si continue to be higher in 2006 compared to the years prior to 2005. The Al/Fe and Si/Fe ratios are more consistent over time and slightly lower than prior to 2005. The Al and Si measurements improved as a result of lower detection limits in the new vacuum Cu-anode XRF systems.

4.4.2 Flow Rate/Cutpoint

The cutpoint equation has been corrected since the previous report; the cutpoint equation used to create the following figures is based on the original equation developed

by John et al.¹ The change is described in more detail in a data advisory (http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0015/da0015_NewFlowFlags.pdf).

Time series graphs of the A module cutpoint, soil concentrations, and the ratios of soil to reconstructed fine mass were reviewed for all sites. Figure 4-4 shows an example of these plots for VIIS; variations in cutpoint are notable when the soil concentrations are the highest. This level of variation is unavoidable with passive flow control. Figure 4-5 shows a cyclical pattern in the MORA A module cutpoint. The source of the variation is unknown. The pattern is also seen in the B and C modules. NOAB and TRCR show similar patterns but not as pronounced.

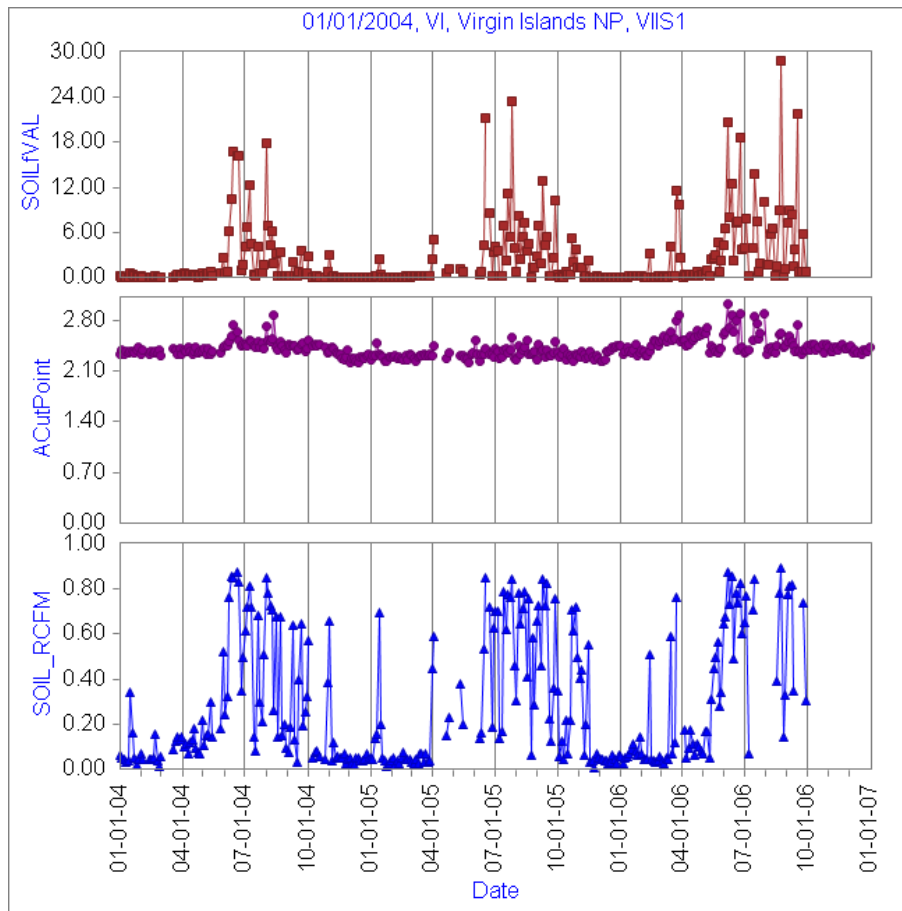


Figure 4-4. Soil concentrations in $\mu\text{g}/\text{m}^3$ (top), A module cutpoints in μm (middle), and ratios of soil to reconstructed fine mass at VIIS.

¹ [John, W., Reischl, G.](#), 1980. A cyclone for size-selective sampling of ambient air. *Journal of the Air Pollution Control Association* 30, 872-876.

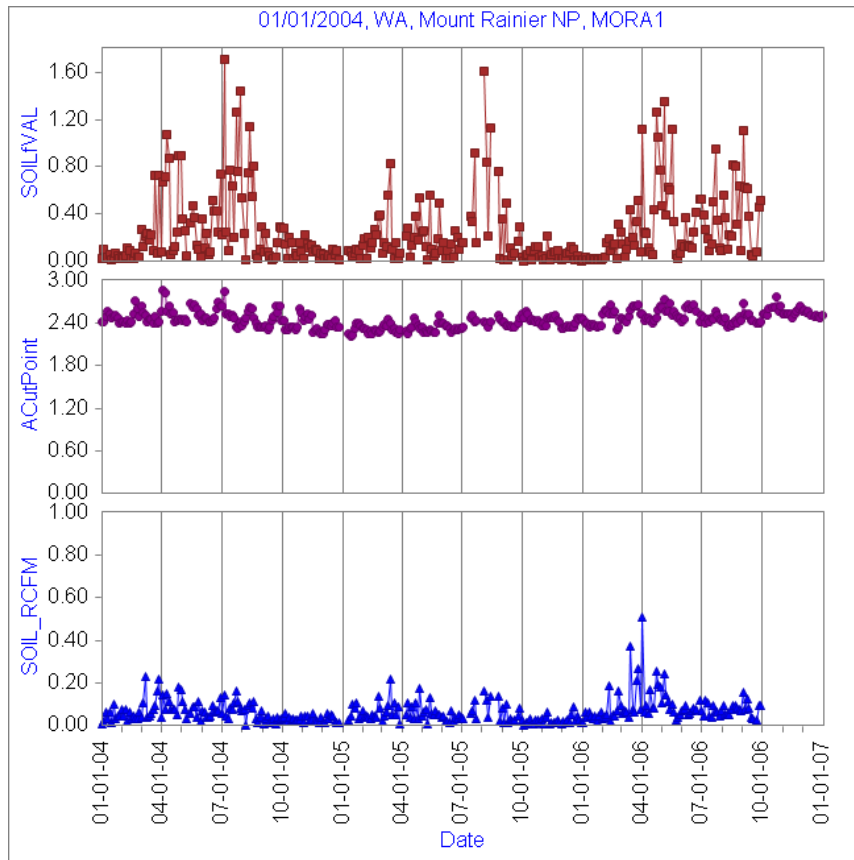


Figure 4-5. Soil concentrations in $\mu\text{g}/\text{m}^3$ (top), A module cutpoints in μm (middle), and ratios of soil to reconstructed fine mass at MORA.

Time series of the A, B, and C module cutpoints for each site were examined for significant and persistent deviations from nominal conditions. The B module cutpoints shifted at all sites around April 2006 as a result of a nylon filter lot change; the cutpoints were corrected during the annual maintenance visits, which were sometimes several months after the shift occurred. Figure 4-6 shows an example of the B module cutpoint shift at CRLA.

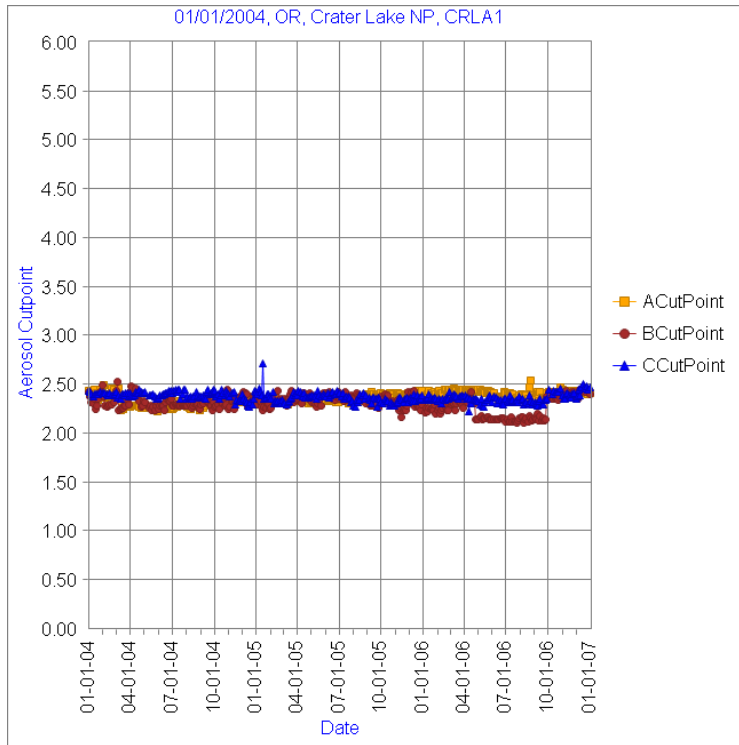


Figure 4-6. A, B, and C module cutpoints in μm at CRLA.

Controller changes continue to cause cutpoint problems at sites. Figure 4-7 shows the cutpoints at PORE1. A new controller was installed on 7/4/2006, and the A module cutpoints jumped up and then slowly decayed to their nominal values for unknown reasons. Anecdotally, several cases of unusual flowrates were observed and appear to be related to controller changes during this period. To methodically assess the effects of controller changes, the maintenance and calibration information need to be organized in a database.

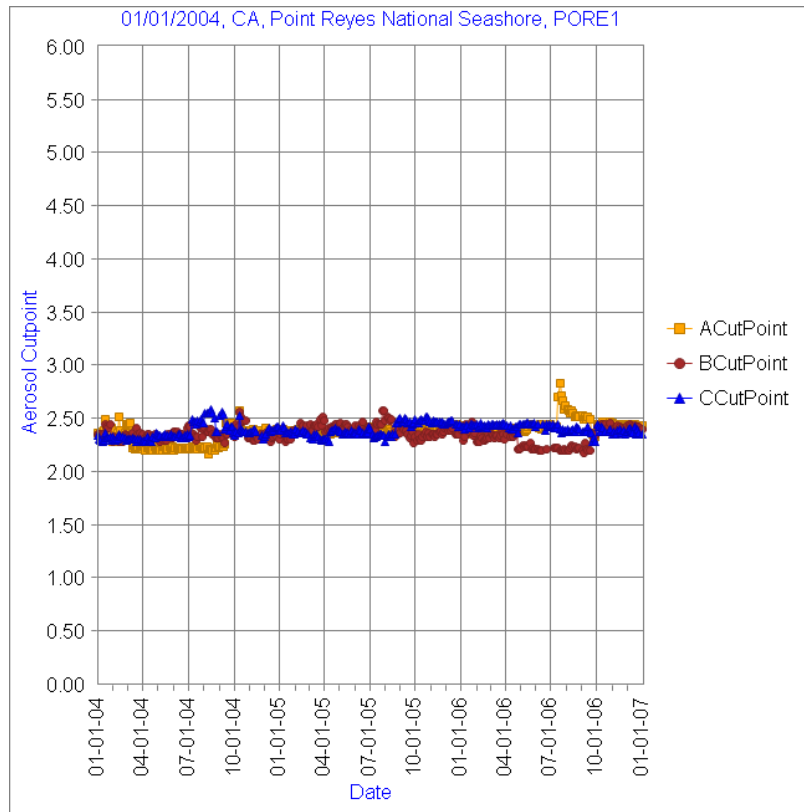


Figure 4-7. A, B, and C module cutpoints in μm at PORE1.

4.4.3 Organic Carbon

Organic mass concentrations estimated from the PESA hydrogen measurements (OMH) and TOR OC measurements (OMC) were compared at each site. Several sites show an increase in the ratio of these two estimates in the last two years. Figure 4-8 shows an example of this behavior at JARB1 (bottom graph). It is difficult to determine from these graphs which measurement is causing the increase in the ratios. Figure 4-9 shows the OC to TC ratios at all sites in the network; this figure suggests that the increase may be related to a decrease in the OC concentrations coinciding with the introduction of the new carbon analyzers in January 2005.

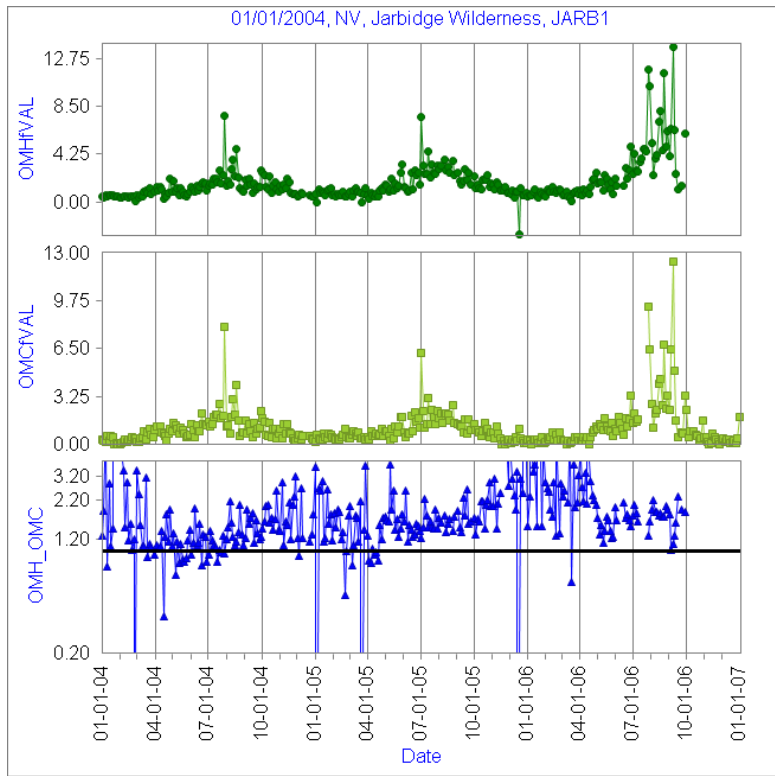


Figure 4-8. Organic mass estimated from hydrogen (top), organic mass estimated from OC (middle), and the ratio of these two estimates (bottom) at JARB1.

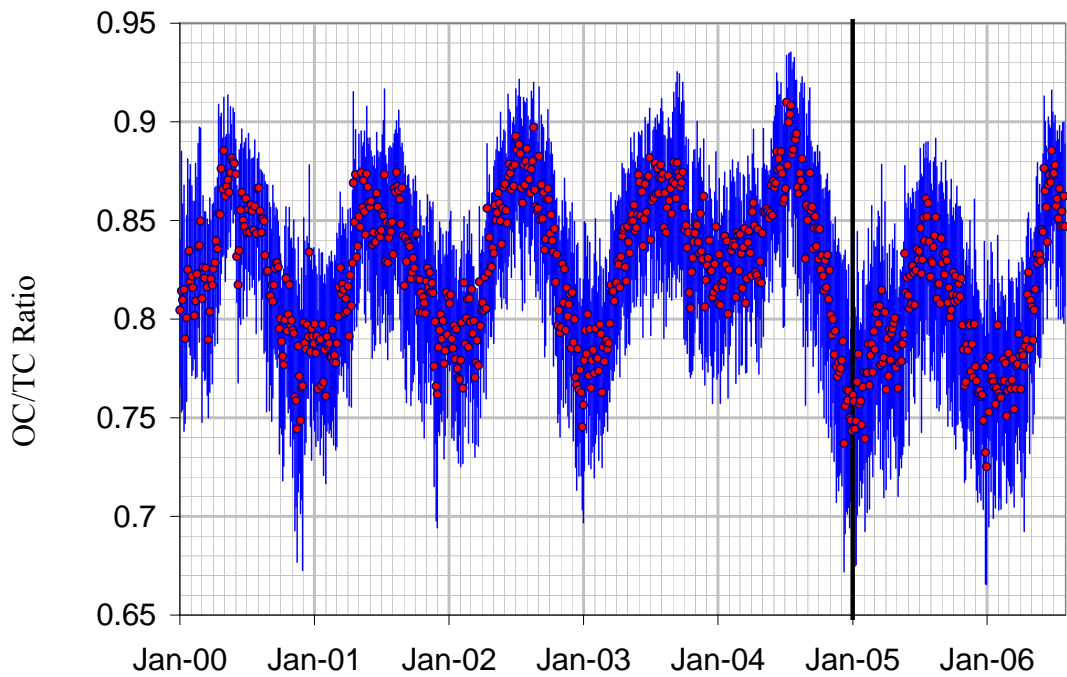


Figure 4-9. Ratio of organic carbon (OC) to total carbon (TC) at all the sites in the network. The line spans the inner-quartile range (25th to 75th percentiles) and the dot indicates the median value.

Figures 4-10 and 4-11 show the organic mass plots for IKBA and NEYO. Both sites show shifts in the OMH/OMC ratio near the end of the data record. Several sites showed this shift, and the NEYO site shows a definite increase in the H concentrations in July 2006. These shifts may simply be resulting from seasonal variations but they should be reevaluated in the next data validation cycle.

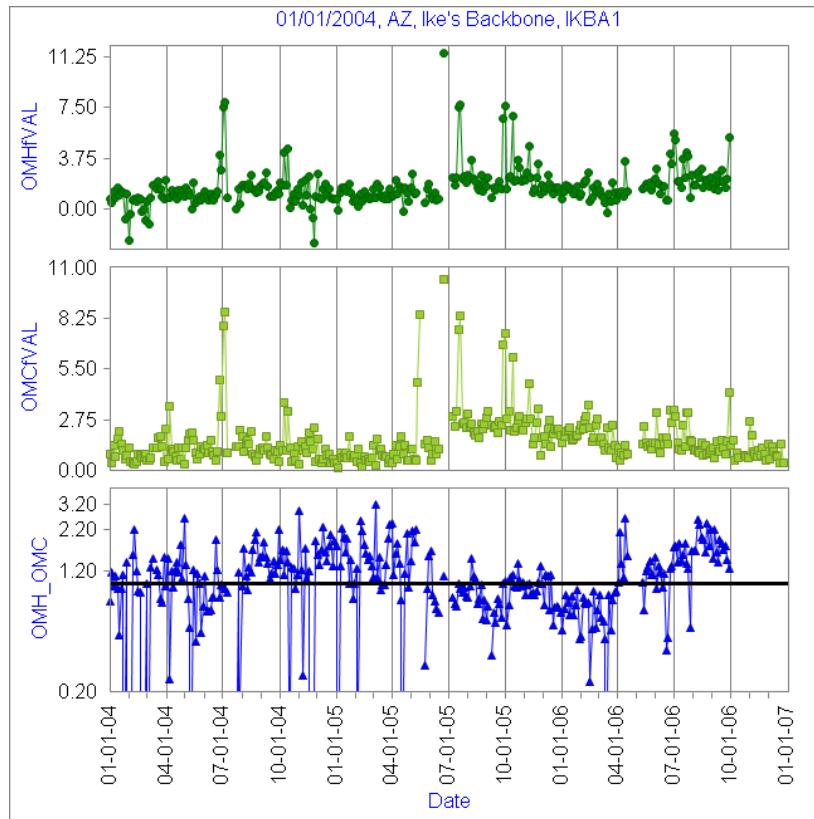


Figure 4-10. Organic mass estimated from hydrogen (top), organic mass estimated from OC (middle), and the ratio of these two estimates (bottom) at IKBA1.

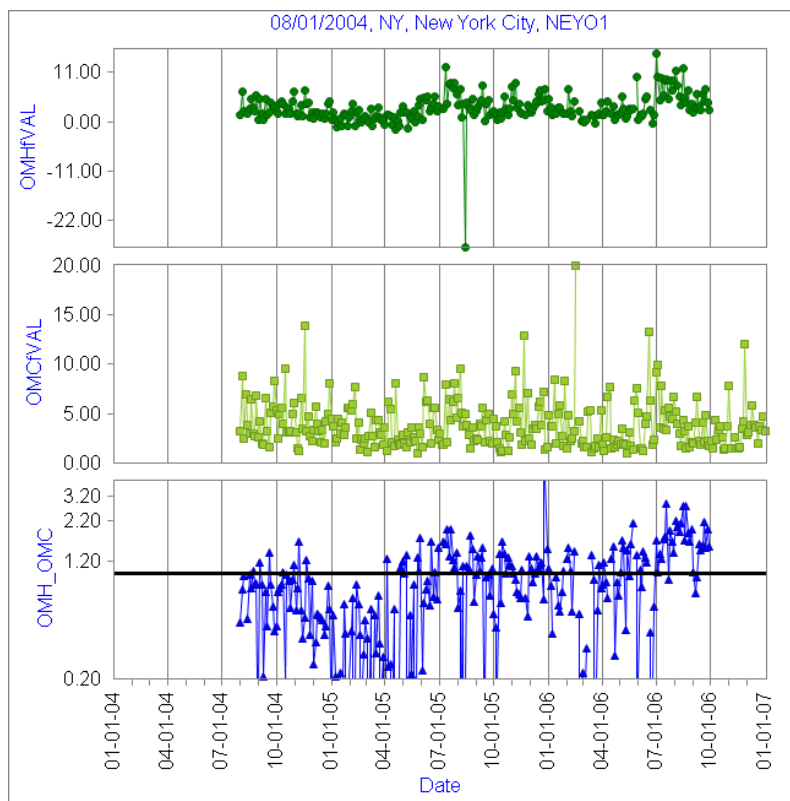


Figure 4-11. Organic mass estimated from hydrogen (top), organic mass estimated from OC (middle), and the ratio of these two estimates (bottom) at NEYO.

4.4.4 NO₃

There were no obvious network-wide or site-specific problems with NO₃.

4.4.5 SO₄ and S

Assuming all aerosol sulfur (S) is in the form of sulfate (SO₄), the SO₄/S ratio is expected to equal three. The disagreement between SO₄ and S continues to vary from month to month. We are taking steps to better understand our XRF measurements and their possible contributions to this bias. One project is designed to deposit laboratory aerosol of known sulfur concentration on clean Teflon filters. Also, we are participating in a round-robin XRF laboratory comparison in conjunction with EPA's Particulate Matter Center at UC Davis. Figures 4-12 and 4-13 show the SO₄, S, and SO₄/S ratios over time at SNPA1 and GRBA1.

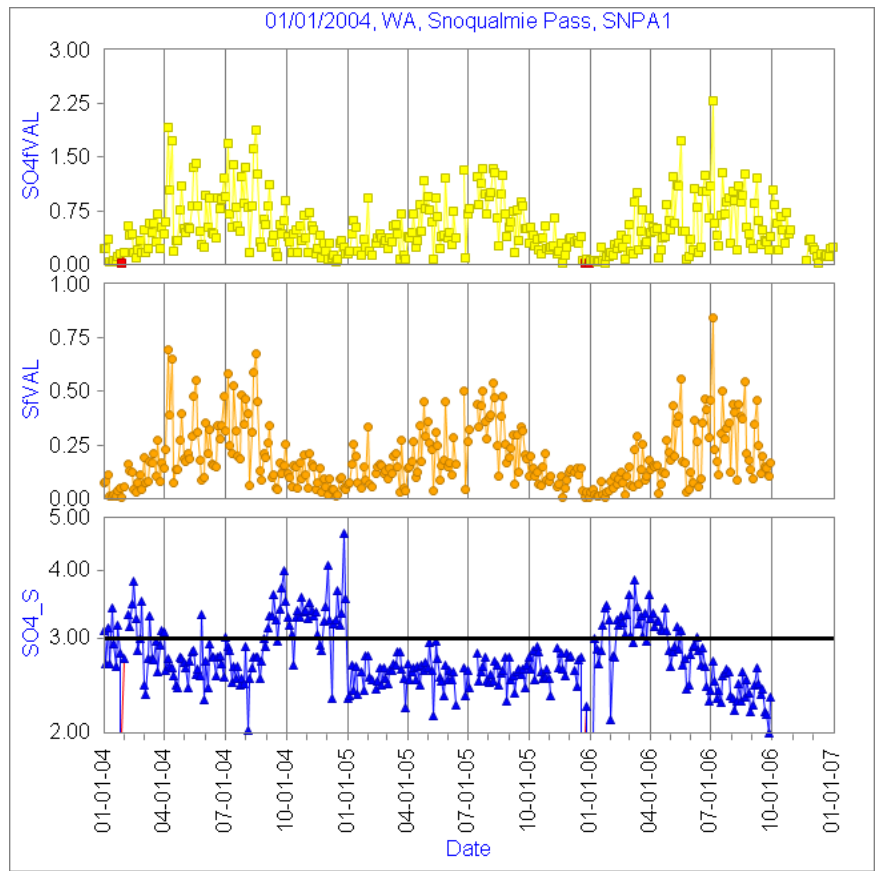


Figure 4-12. SO₄, S, and SO₄/S ratios over time at SNPA1.

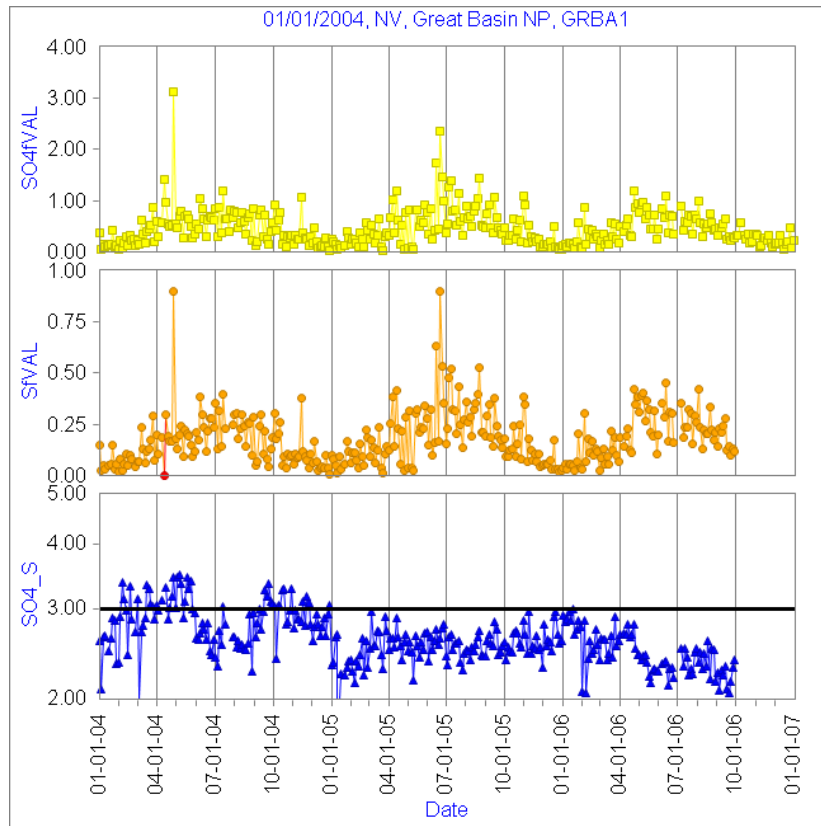


Figure 4-13. SO₄, S, and SO₄/S ratios over time at WIMO1.

4.4.6 Mass

There were no obvious significant problems identified examining the relationship between RCFM and FM.