Nicole P. Hyslop
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# UC Davis IMPROVE Measurements Quality Assurance Status Report Volume I

## 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. CIRA produced quarterly QA reports in 2003 and 2004 (http://vista.cira.colostate.edu/improve/Data/QA_QC/QAQC_nps.htm) documenting trends and problems with the data deliveries. This report series is intended to take over where those reports left off. The QA program entails several aspects, and this report will evolve to document more of those aspects over time.

The IMPROVE group at UC-Davis is undergoing several changes to the data handling, processing, and validation systems. Also, the standard operating procedures (SOPs) are being updated and developed. The status of these projects will be briefly described in this report.

## 2. DATA MANAGEMENT

We are working towards integrating the data management and processing tasks into SQL Server. Several data tables have been migrated to SQL Server: ions analysis results, carbon analysis results, HIPS analysis results, sampler flashcard data, and 15-minute and 24-hr average flow rates. The SQL Server database allows us to track, and when necessary, rollback changes to the data. We are in the process of developing the capabilities to acquire the balance readings and input the log sheet information directly into SQL Server. We will be testing and implementing those capabilities in the coming months. The next priority is to migrate the computer code required to calculate concentrations and create delivery files from FoxPro to SQL Server; this project will also involve a redesign of the delivery file format. The XRF data acquisition and processing will continue to occur on the VAX system and will not be migrated to SQL Server.

## 3. DOCUMENTATION

### 3.1 STANDARD OPERATING PROCEDURES

Most of the official standard operating procedures (SOPs) have not been updated since they were first written in 1996-1997. In 2006, we began to revise the SOPs with the help of a part-time editor. Table 1 summarizes the status of the SOP revisions.

Table 3-1. Status of SOP revisions, July 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 | 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

Starting with the 2005 data, the UC-Davis QA Engineer will review the data receipt, delivery, and validation process. The data are scheduled to be delivered to CIRA in blocks of multiple months so the data validation procedure is conducted on roughly a quarterly basis depending on when the data are received. This first report covers 14 months of data, but most subsequent reports will each cover a seasonal quarter. 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:** January 2005 through February 2006
**Reviewed in relation to:** 2003-2004
**Retrieved from the VIEWS Database on:** April 16-25, 2007

There was a significant change in the XRF analyses; the new vacuum Cu-anode XRF system was first used for the January 2005 data and the calibration procedure for the S measurements was changed. 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 (http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm).

At a few sites, large blocks (> 10 days) of data from the recent delivery were withheld (i.e., data were flagged as "QA" and -999 was substituted for all data values); the withheld data are listed in Table 1. Additionally a handful of sites require redelivery due to flag use violations and flow calculation problems, these sites and the details of the problems are also listed in Table 1.

Table 4-1. Unresolved problems in the 2005 data set.

| **Dates Impacted** | **Site** | **Problem Description** | **Date/Delivery Discovered** | **Temporary Resolution** | **Permanent Resolution** |
|---|---|---|---|---|---|
| Jan & Feb 2006 | CABA1 | Flow problem | March 2007 | QA flags on all data | Flows OK, set to NM |
| Jan 2005 – Feb 2006 | FLAT1 | Electrical interference | January 2007 | QA flags on all data | Cable shielding gives reliable flows |
| July 2005 – Feb 2006 | WASH1 | Calibration problem | January 2007 | QA flags on all data | Calibration updated, set to NM |
| 1/17/06 – 2/25/06 | WHPE1 | Sampled on wrong days | March 2007 | QA flags on all data | Flags set to EP, SW, or NM as appropriate |
| 1/26/06 – Feb 2006 | THRO1 | Flow problems | March 2007 | QA flags on all data | Used logs, set to NM |
| March – Nov 2005 | DOME1 | Major power problems | March 2005 | PO flags on all data | USFS installed new power supply |
| 9/13/05 – 11/21/05 | EVERX | Frog in cyclone | Nov 2005 | QA flags on all data | Changed to EP |
| 9/10/05 – 10/31/05 | HOOV1, HOOVX | Calibration problem | March 2007 | QA flags on all data | Calibration entered, reset to NM |
| 7/27/05 – 10/31/05 | SHMI1 | Calibration problem | March 2007 | QA flags on all data | Calibration entered, reset to NM |
| 9/28/05 – 10/19/05 | MEVEX | Needs XRF reanalysis | March 2007 | QA flags on all data | Remains QA, needs XRF |
| Oct 2005 | HOOV1 | C module data needs further review | March 2007 | QA flags on all C module data | Remains QA, awaiting DRI data from sample rerun |

## 4.2 FILE INTEGRITY CHECKS

### 4.2.1 XRF Data Files

A few records in the initial data deliveries were missing individual analyses. The Mo-XRF values were all zero for EVER1 on 1/20/06 and SAGU1 on 1/14/06. These records were restored and redelivered on April 27, 2007. The Cu-XRF values were all zeros for CACR1 on 12/21/05 and 12/24/05. These samples are to be reanalyzed and concentrations will be provided in the next data resubmittal. There were also several cases where the PESA H values were all zero. Currently, these records are labeled as valid because there is only one flag per module. Analysis-level flags must be implemented to properly flag these records.

The initial XRF delivery file was missing the zirconium (Zr) data. This resulted from a change in the RACE data processing routine. The missing data were discovered prior to the final data delivery, and the latest data delivery (April 27, 2007) contains the Zr data.

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 system.

Starting in October 2005, two Cu-anode XRF systems are used to analyze the filters. The current protocol is to analyze an entire month of samples on a single system. Different parameter names are used within the XRF data files to identify which system was used to analyze the samples.

### 4.2.2 Carbon Data Files

DRI added a new field to identify the specific instrument used to analyze each filter. In the first few data file deliveries, this field was incorrectly populated for the replicate analyses. For the replicate analyses, the same instrument number that was used for the initial analysis is also listed for the replicate. DRI has fixed the problem and submitted revised files.

### 4.2.3 Ions Data Files

There were a few duplicate ion records and corresponding missing ions records as a result of a UCD data processing error. The problem happened after the software that generated the analysis queue files failed to work on the upgraded computer operating system. For several months, the contractor files were generated manually and mistakes were made in this manual process. The errors were identified and the problems corrected before the data were submitted to CIRA.

The $NH_4^+$ analyses were discontinued in January 2005.

### 4.2.4 Weights Data Files

No irregularities were found in the weights files.

### 4.2.5 HIPS Data Files

No HIPS data were delivered for January 2006. No irregularities were found in the HIPS files.

### 4.2.6 Flow Rate Calibration Records

The flow rate calibrations have been entered into the database through February 2006. Some flow rates in the preliminary deliveries for spring 2006 are incorrect.

We have requested that the maintenance crews include a time with the calibration data (currently only a date is recorded); the time will be used to 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 or XRF data but have valid flags. Most of these instances resulted from collocated X-module filters that had been removed from standard processing to be used as reanalysis filters. They have subsequently undergone XRF analysis and the elemental data will be included in a future data resubmittal. PESA will not be performed so that these filters can remain undamaged for repeated reanalysis.
**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.

## 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).

For the dataset discussed herein, these checks identified some pattern shifts but nothing that triggered concern about the quality of a particular analysis. The pattern shifts were primarily in the Cu-XRF elements and likely result from changes to the XRF system discussed in Section 4.1. The following observations were made based on review of the network metric checks.

- Several of the Cu-XRF elements (Al, Ca, Cl, Fe, K, Si, and V) have very low median or $90^{th}$ percentile values (with Si being the most different) compared to previous years. These shifts result from improvements in the background in converting the Cu-anode XRF system from a helium to a vacuum environment.
- 90th percentiles of Cl are lower than previous years but Cl is still detected at the coast sites.
- Several soil elements (Ca, Fe, K, Si) in 2005 are lower than prior years, particularly Si.
- Zinc is still erratic from month to month.

Note: Need to add the overlapping elements from the XRF systems to the network-level checks (e.g., S, Ca).

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

There were noticeable differences in the Al and Si data in this delivery. These results are consistent with the expectation that the vacuum chamber on the Cu-anode XRF system would remove most of the Ar peak interference and thus improve the measurements of the lightest elements. The Ca and Ti concentrations did not have any noticeable differences from prior years.

Al was detected more frequently in the 2005 data set compared to prior years. Despite the fact that Al was detected more often, it appears to be detected at lower concentrations than in previous years, this shift is most obvious in the Al/Fe enrichment factor (EF) plots. The Al/Fe EF decreased at most sites in 2005. Figure 4-1 shows an example of this behavior at CACR1.

There were also observable differences in the Si/Fe ratios. The ratios were more consistent over time and slightly lower than in previous years. Figure 4-2 shows an example of this behavior at GRSM1. Measured Si concentrations appeared to be somewhat lower beginning in 2005, and the ratios were more consistent, particularly at sites with low Si concentrations. The ratios appear to be improved as a result of lower detection limits for Si with the new vacuum copper-anode XRF systems.

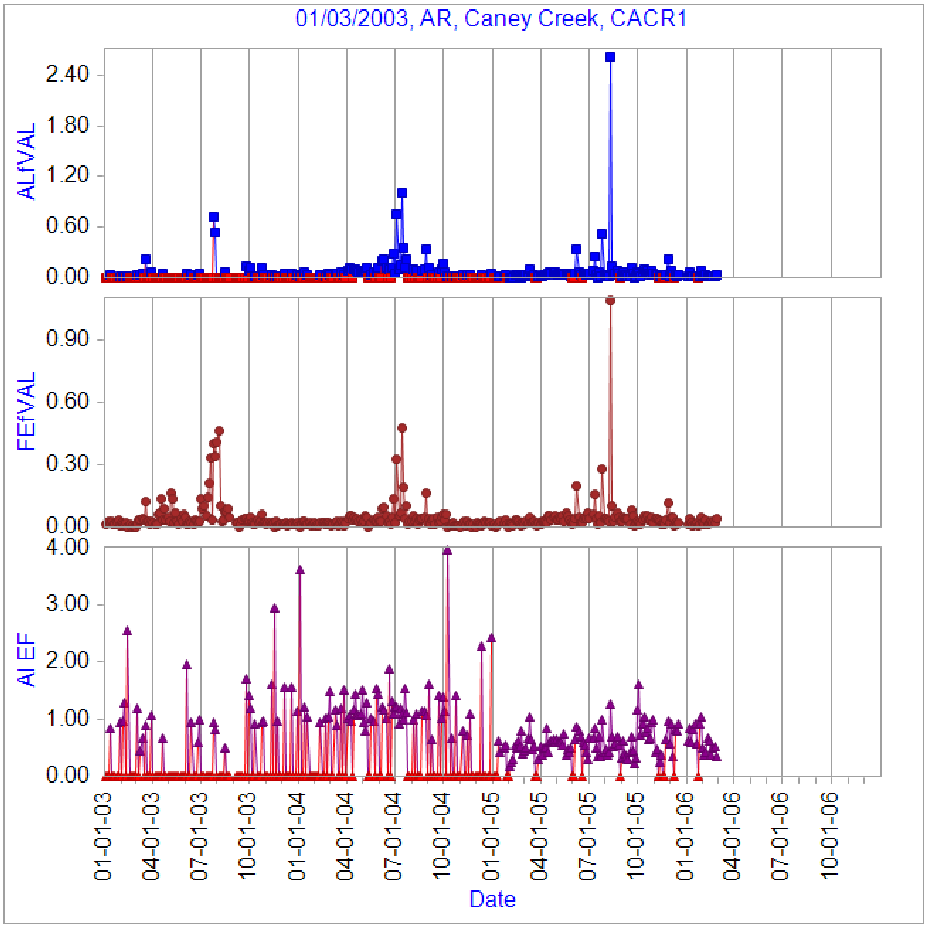


Figure 4-1. The first two graphs plot the Al and Fe concentrations over time, and the last graph plots the Al/Fe soil enrichment factor, which is the Al/Fe ratio divided by the Al/Fe ratio expected from soil.

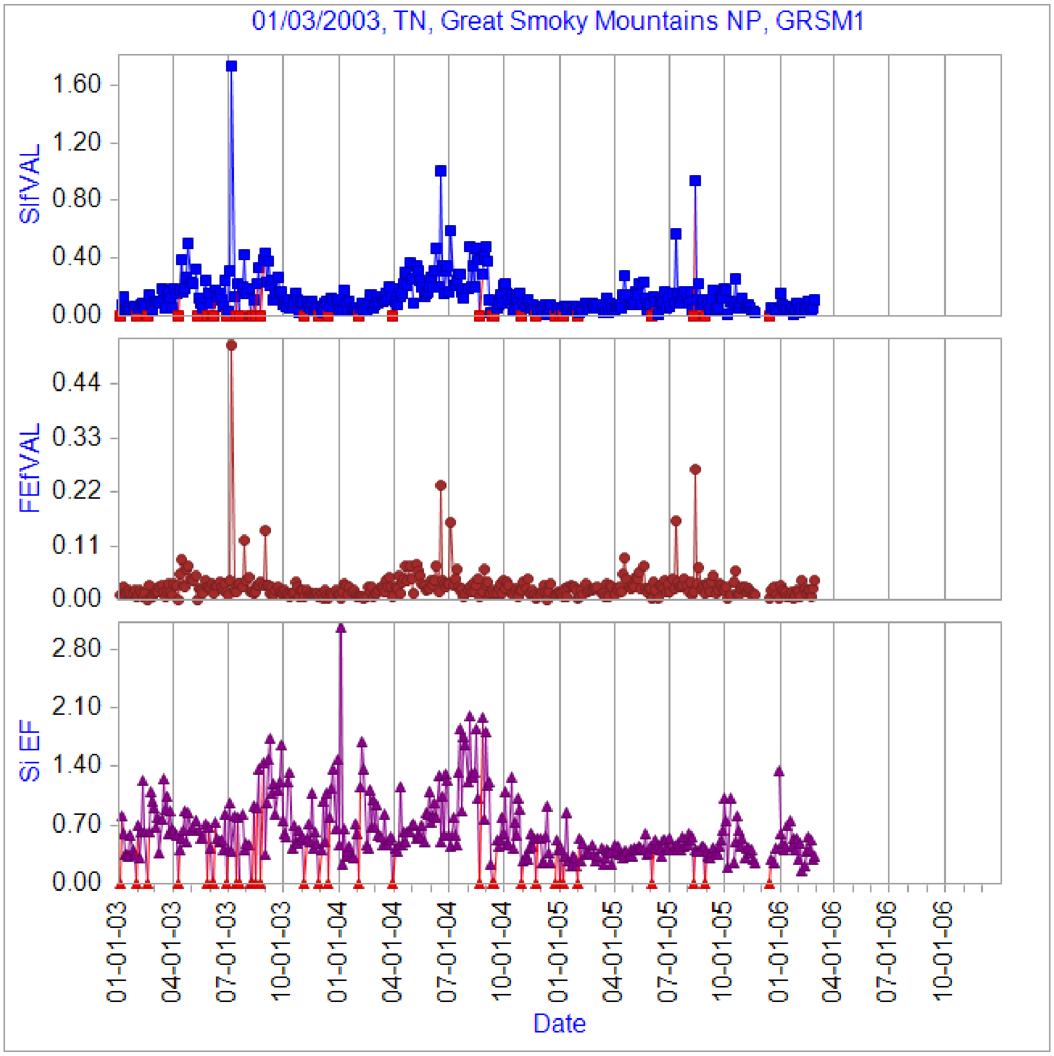


Figure 4-2. The first two graphs plot the Si and Fe concentrations over time, and the last graph plots the Si/Fe soil enrichment factor.

### 4.4.2 Flow Rate/Cutpoint

Time series of the A, B, and C module cut points for each site were examined for significant and persistent deviations from nominal conditions. The cutpoint equation used to create the following figures is incorrect and has been updated since these graphs were created. The actual changes in cutpoint are much less than indicated in these graphs. Nevertheless, the graphs provide an indication of changes in flow rate. There was only one site, MAVI1, that may have had increased soil concentrations as a result of persistent flow rate problems. Figure 4-3 shows the soil concentrations along with the A module cutpoint and ratio of soil to reconstructed fine mass (RCFM) over time at MAVI1; from June to October 2005 the cut points shifted to above 3 µm and the soil concentrations also increase during this period, possibly resulting from the higher cutpoint.  (Note: Using the John and Reichl cutpoint equation recommended by Jay Turner, the cutpoint never exceeded 2.8 µm during the period in question.)

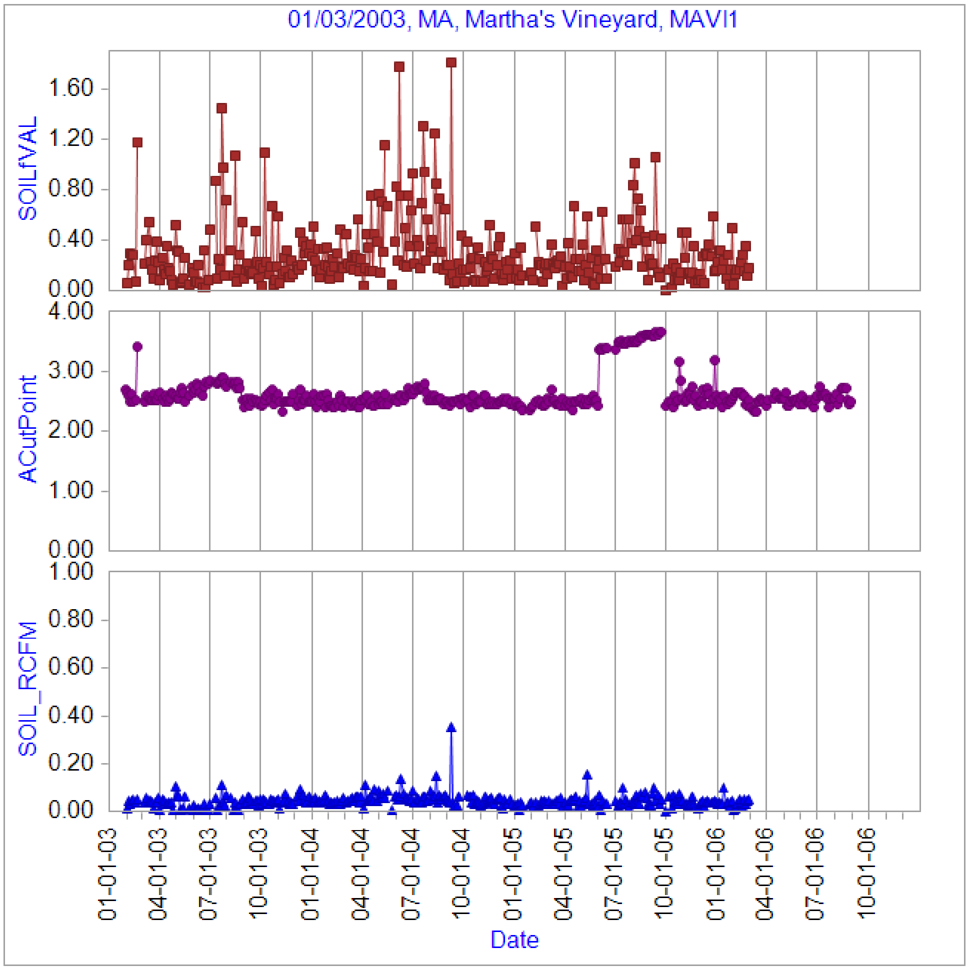


Figure 4-3.   The first graph shows the soil concentrations, second graph shows the cut point, and the third graph shows the ratio of soil to reconstructed fine mass (RCFM) over time.

Several sites show significant step changes in flow rate over time.  The steps often coincide with routine annual calibrations or emergency repairs (e.g., controller or e-box replacement).  Figure 4-4 and 4-5 show the cut points (from the old equation) over time at COHU1 and MELA1, respectively; both routine maintenance visits and emergency repairs are marked on the graphs with arrows.  Often the shifts in flowrate correspond to these events.  Significant shifts in flow rate as a result of annual maintenance or emergency repairs suggest that flow rate calibrations should be performed when flowrates are observed to shift abruptly or to differ significantly from nominal values.

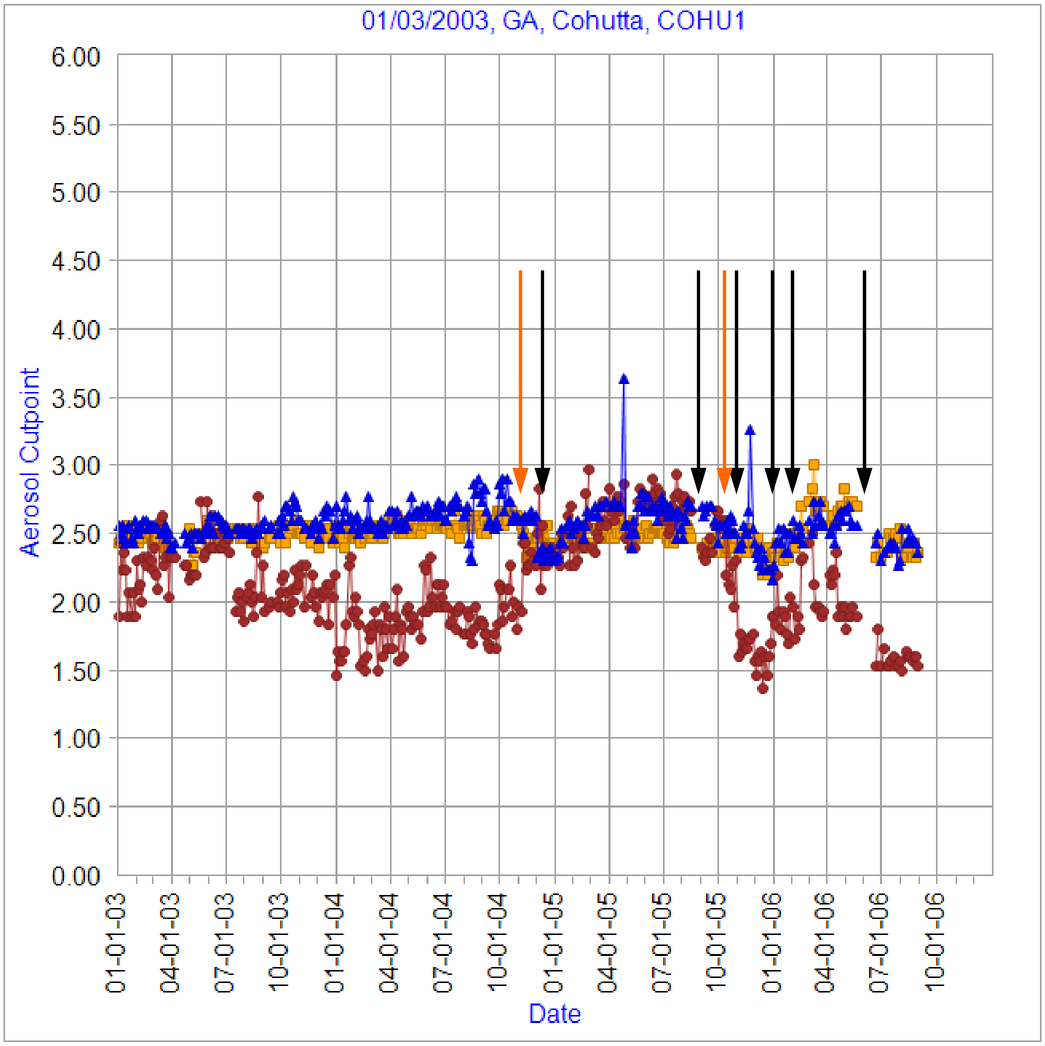


Figure 4-4. A (yellow), B (red), and C (blue) module cut points over time. The black arrows indicate controller changes and the orange arrows indicate annual maintenance visits.

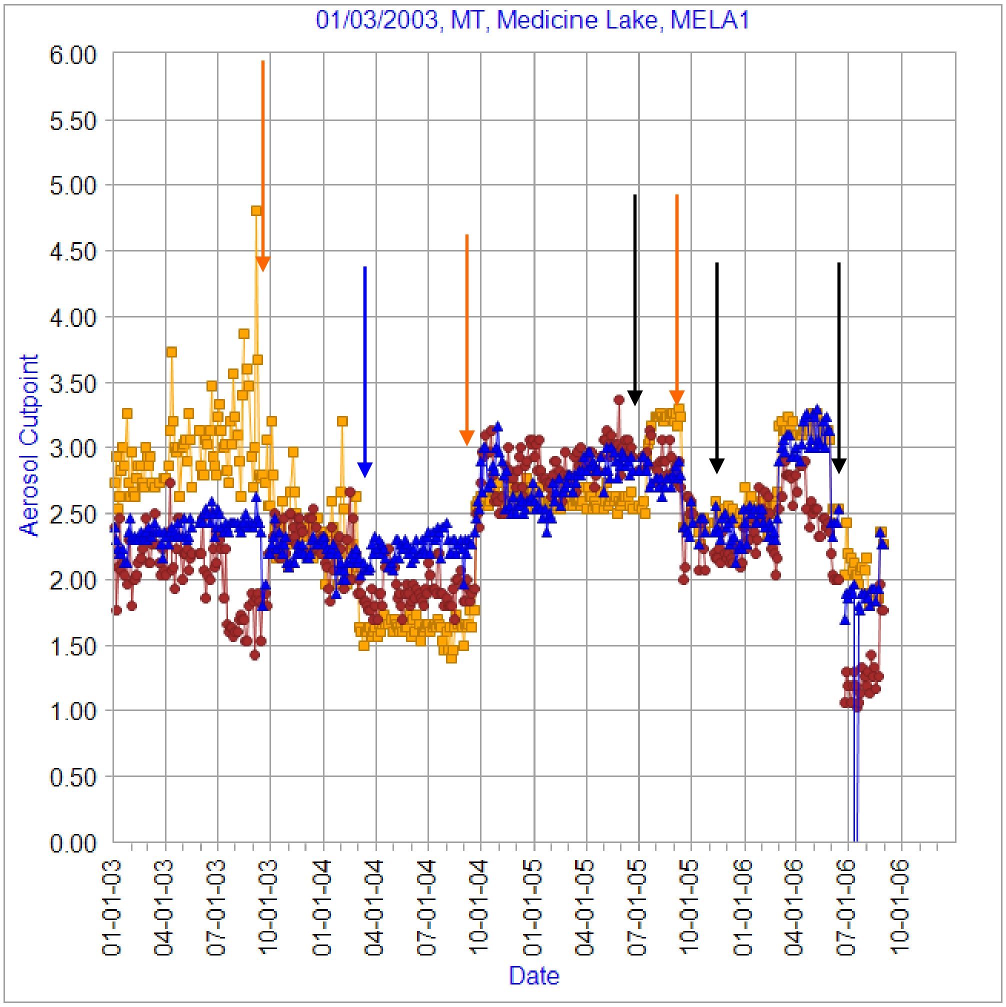


Figure 4-5. A (yellow), B (red), and C (blue) module cut points over time. The black arrows indicate controller changes, the orange arrows indicate annual maintenance visits, and the single blue arrow indicates a change from masked to unmasked A module cassettes.

Preliminary, un-validated data were delivered for March through August 2006, and some sites had dramatic jumps (10 to 20%) in flow rates during this period. Figure 4-6 shows an example of the shift in flow rate at Petrified Forest, AZ. The jumps occurred at sites for which calibrations were performed but had not been entered into the database.

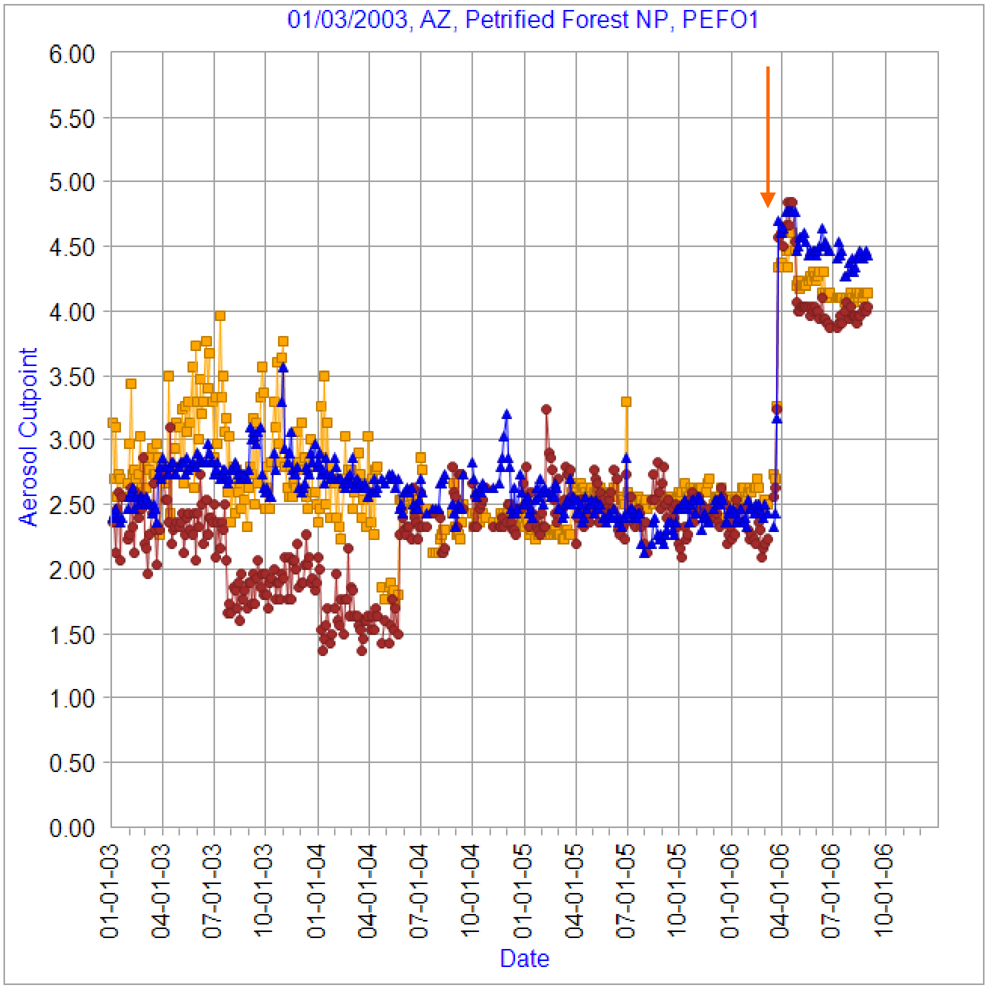


Figure 4-6. A (yellow), B (red), and C (blue) module cut points over time. The orange arrow points out the 2006 annual maintenance visit.

One additional observation is that day-to-day flowrate variations are higher at some sites than at others. Figure 4-7 shows an example of the flowrate variations at OLYM1, a site with considerable variability. Also, at some sites, the variations used to be large but have decreased, such as PEFO1 in Figure 4-6.

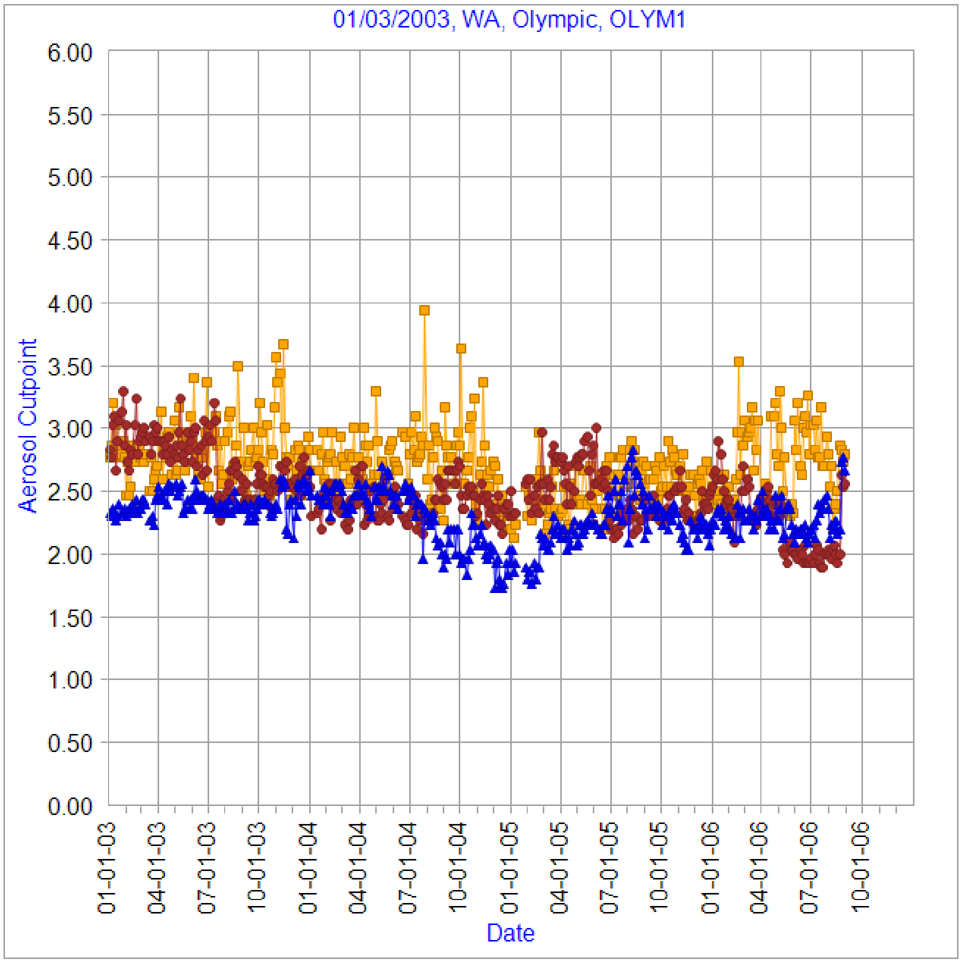


Figure 4-7. A (yellow), B (red), and C (blue) module cut points over time.

### 4.4.3 OC and EC

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

### 4.4.4 $NO_3$

There were no obvious network-wide or site-specific problems with $NO_3$.

### 4.4.5 $SO_4$ and S

Assuming all aerosol sulfur (S) is in the form of sulfate ($SO_4$), the $SO_4$/S ratio is expected to equal three. The disagreement between $SO_4$ and S became very pronounced at the beginning of 2005. S concentrations significantly increased as a result of a change in the calibration standards; this topic is discussed in more detail in a data advisory (http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0009/da0009_S_reporti ng.pdf). 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.

We will be re-implementing the quantitative checks of the S/$SO_4$ agreement included in the previous QA reports produced by CIRA but don't have those tools at this time. Figures 4-8 and 4-9 show the $SO_4$, S, and $SO_4$/S ratios over time at MKGO1 and WIMO1.

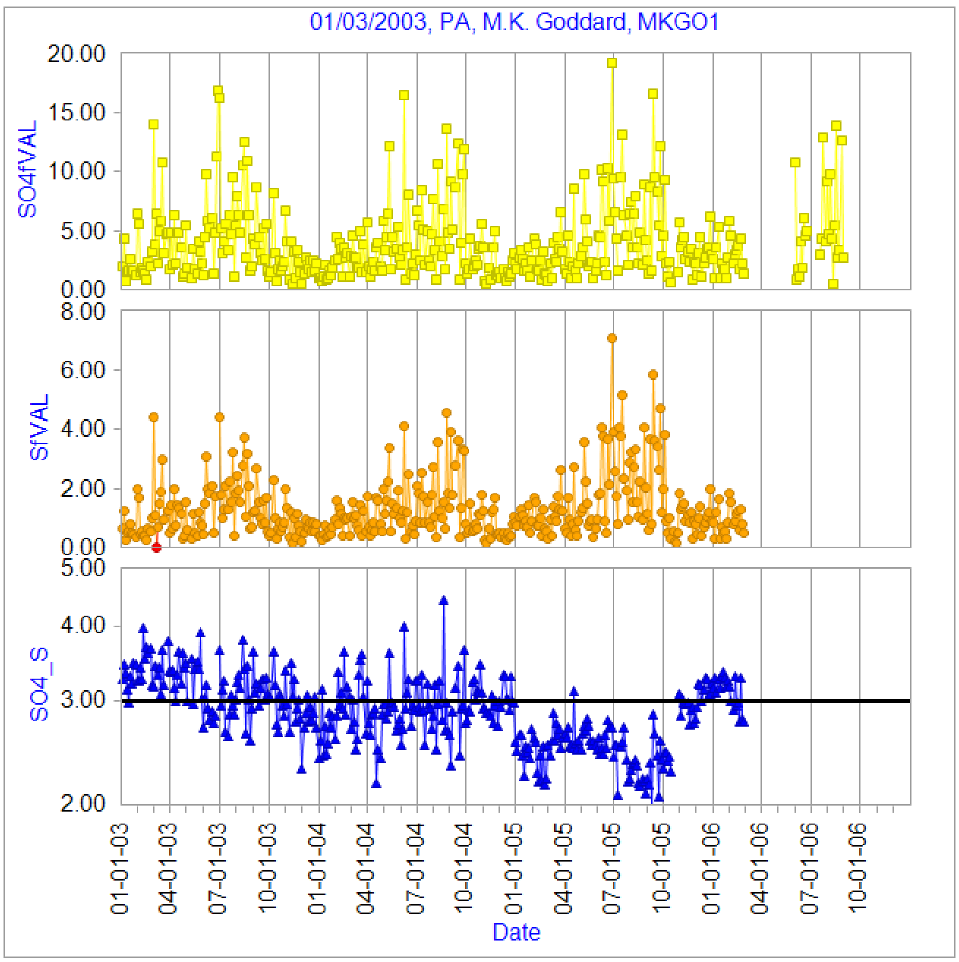


Figure 4-8. $SO_4$, S, and $SO_4$/S ratios over time at MKGO1.

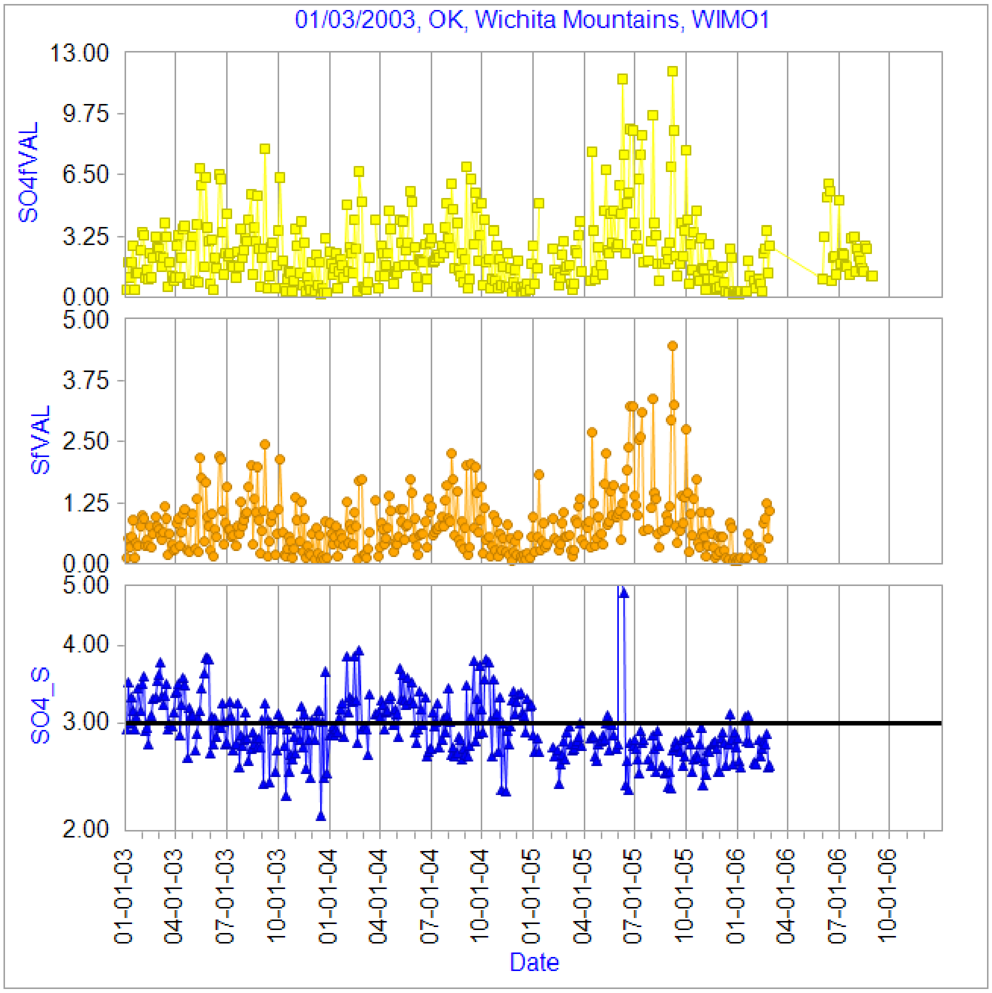


Figure 4-9. $SO_4$, S, and $SO_4$/S ratios over time at WIMO1.

### 4.4.6 Mass

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