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UC Davis IMPROVE Measurements Quality Assurance Status Report Volume III

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

The current emphasis in database development is on ingesting the flashcard data from the samplers. All sampler flowrate calibration data are now maintained in SQL database tables. Historical calibration coefficients are archived for each site, along with an audit record of any changes that have been made. Each set of calibration coefficients is accompanied by a designation to indicate whether they were obtained during a routine maintenance visit or through a special audit or recalibration.

3. DOCUMENTATION

3.1 STANDARD OPERATING PROCEDURES

Table 1 summarizes the status of the SOP revisions. The Expected Completion Dates have been updated since the last QA report. The Data Processing/Validation SOP and Site Selection SOP have been finalized and posted on the IMPROVE website since the last QA report.

Table 1. Status of SOP revisions, July 2008.

SOP #	Topic	Expected Completion Date	Status
101	Procurement	October 2008	In progress
126	Site Selection	Completed	Revised and posted on IMPROVE website in July 2008
151	Site Installation	October 2008	To be written
201	Site Operators	Completed	Revised and posted on IMPROVE website 2004
226	Annual Maintenance	February 2009	In progress
251	Sample Handling	October 2008	In progress
276	HIPS	September 2008	Revised SOP needs final approval
301	XRF	December 2008	In progress
326	PIXE/PESA	September 2008	Revised SOP needs final approval
351	Data Processing/ Validation	Completed	Revised and posted on IMPROVE website in July 2008

3.2 METADATA

Metadata were last delivered to CIRA on June 27, 2006. The last delivery covered maintenance activities through May 2006. Metadata deliveries are on hold until a more automated system for making the deliveries can be developed. This involves designing a system to input, store, and track metadata.

4. DATA REVIEW AND VALIDATION

Three months of data have been delivered to CIRA since the previous QA report was published in September 2007. The data are scheduled to be delivered to CIRA six months after the filters are collected. Data delivery is currently 17 months behind collection. This delay has occurred because the XRF group at UC Davis has been developing a new calibration procedure, to be based on a curve that will be fit through all the calibration standard data. The development of this calibration procedure is expected to be completed later this summer. Once the calibration is established, all the 2007 data will be delivered.

4.1 SUMMARY

Data Period: October 2006 through December 2006
Reviewed in relation to: 2004-2005
Data reviewed using VIEWS: June 12-20, 2008

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 SO_4 ratios are obvious during 2006, and these shifts appear to be related to the two different Cu-anode XRF instruments. Figure 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). This problem is still being investigated through several different approaches.

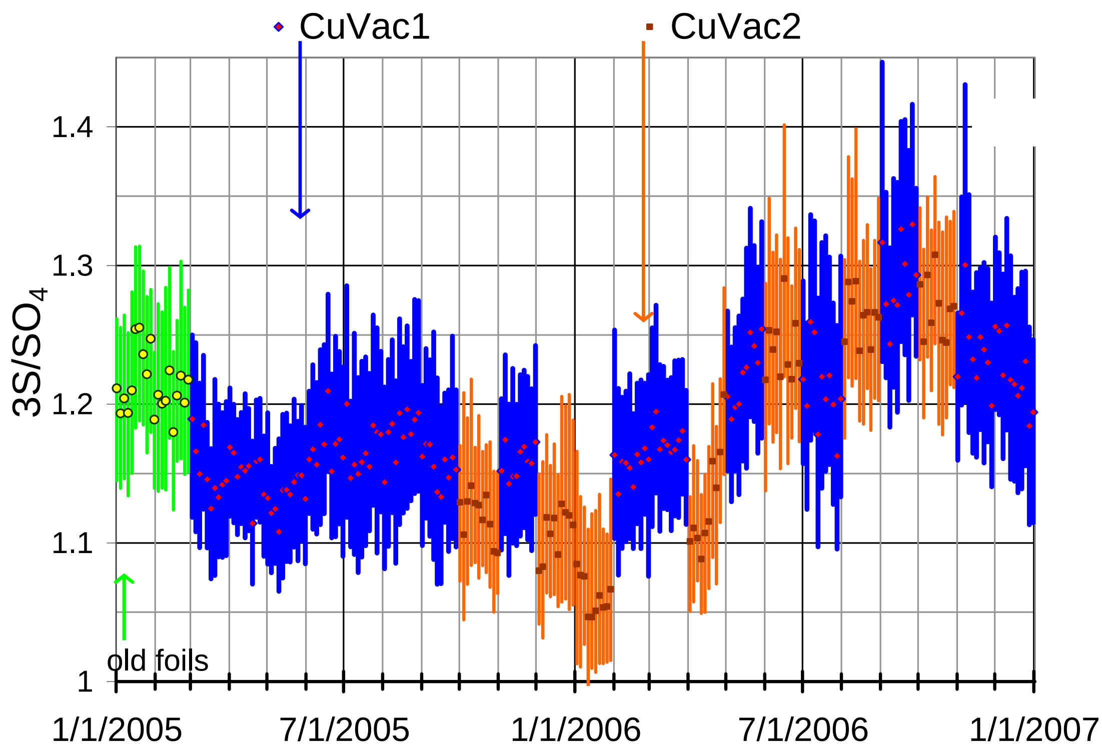

Figure 1. The ratio of sulfur times three divided by SO_4 for the entire network since the introduction of the vacuum Cu XRF systems in January 2005.

No sites had large blocks (> 10 days) of data withheld from the current data set. Table 1 lists two anomalies in the data set. The EC3 MDLs reported to CIRA in March and August and OP MDLs in March are all zero. This zero MDL problem was discussed in the previous data quality report. In that report, I stated that the reported MDLs would be assigned minimum values of analytical MDLs to avoid zero MDLs. Lowell plans to implement this approach beginning with the January 2007 data.

Table 1. Block of missing data or unresolved problems in the data set.

Dates Impacted	**Site**	**Problem Description**	**Date/Delivery Discovered**	**Temporary Resolution**	**Permanent Resolution**
11/1-11/28/2006	HOOV1	No site operator			
Mar, Aug 2006	All	Zero MDL values for EC3 and OP	Sept 2007		

4.2 FILE INTEGRITY CHECKS

4.2.1 XRF Data Files

In the last report, a problem involving holes in the Teflon filters caused by the Cu vacuum system was discussed. This problem appears to be fixed. The number of damaged filters was only two in October, four in November, and four in December. The PESA, Cu-XRF, and Mo-XRF status flags in the XRF data files are now properly assigned so the data are correctly reported as missing instead of zeros in the 2006 delivery. These flags have been set by Lowell Ashbaugh during his data validation effort for the 2006 data. Beginning with the 2007 data the XRF group plans to set the flags. They are the generators of the data and thus have first-hand knowledge of damaged filters. As part of the data management redesign, we will develop the capability to deliver parameter-level flags as opposed to module-level flags to CIRA. We will be discussing delivery options with CIRA to make sure the individual parameters receive the proper flags.

Routine analysis of Teflon field blanks continues as shown in Table 2. The field blank analysis results are similar to prior months in 2006.

Table 2. XRF 2006 field blank analysis inventory. The number in the Cu-anode row indicates which instrument was used to analyze the field blanks.

Instrument	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Mo-anode	√	√	√	√	√	√	√	√	√	√	√	√
Cu-anode		√		√			√	√	√	√	√	√
Cu system used for sample analysis	#2	#1	#1	#2	#1	#2	#1	#2	#1	#2	#1	#1

4.2.2 Carbon Data Files

DRI reported a few invalid carbon analyses. The carbon data file contained -99 values but no flag. Currently, these invalid records are identified manually. We need to work with DRI to establish a convention for reporting invalid/missing data, and we need to develop an automated way to change our flags to properly report the missing data.

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

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 May 2008. We have attained our goal of reviewing and entering the calibrations 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 on a sampling day.

Flow rate audit results were used to backdate a total of 90 $PM_{2.5}$ modules and 11 PM_{10} in 2006. There are a total of approximately 510 $PM_{2.5}$ modules in the network (170*3) so approximately 18% of the $PM_{2.5}$ modules and 6% of the PM_{10} modules required flow rate calibration adjustments.

4.2.7 Delivery Data files

Duplicate records: None
Incomplete records: None
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: Nothing new.
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 samples have not been analyzed by XRF recently so we can attempt to maintain our schedule for the core IMPROVE network. Once we get back on schedule in the laboratory we will analyze our backlog of MALO samples. The data from the C-only sites are available and we are working to devise a special data format so we can deliver them to CIRA. Lowell plans to complete this work later this summer.

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 air volume to determine concentrations).

There is a see-saw pattern in the light element loadings in mid-2006. Figures 2, 3, and 4 show this pattern in the 90th percentile loadings for Mg, Al, and Cr. The pattern is related to which of the two Cu-anode XRF systems was used to analyze the month of filters (Figure 1 and Table 1 show the system number used for each month). All the samples from March and May 2006 were reanalyzed by Cu anode XRF in an attempt to understand the irregularities observed in those months. After review of the data we concluded that there was no compelling evidence to consider the reanalysis data to be superior to the original analysis data. Thus, the original analysis data were submitted as the official data.

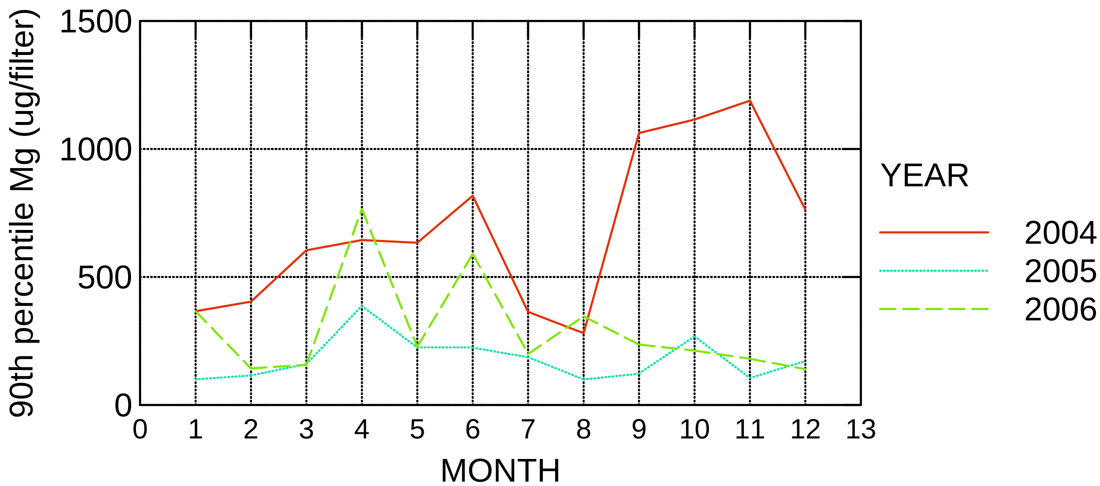

Figure 2. 90th percentile magnesium loadings in the entire routine network.

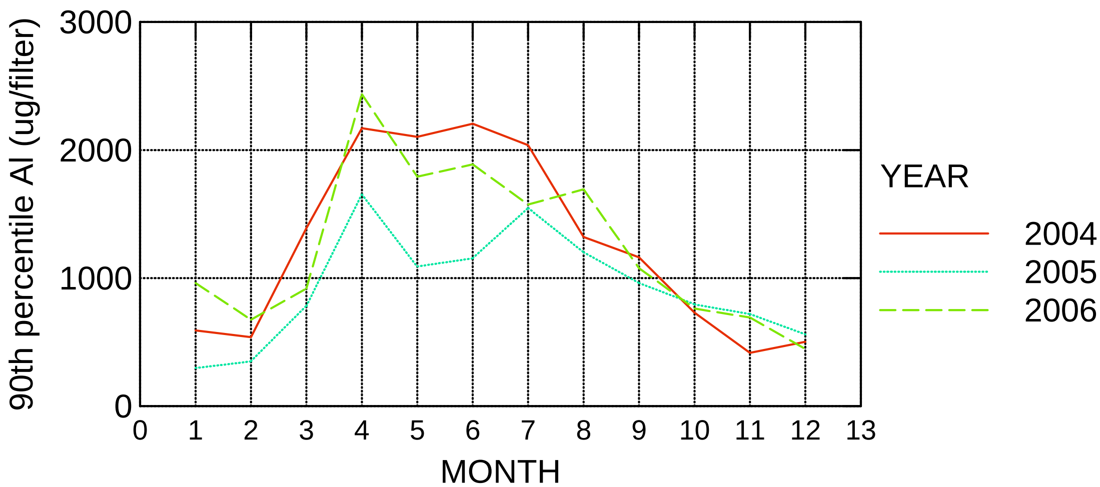

Figure 3. 90th percentile aluminum loadings in the entire routine network.

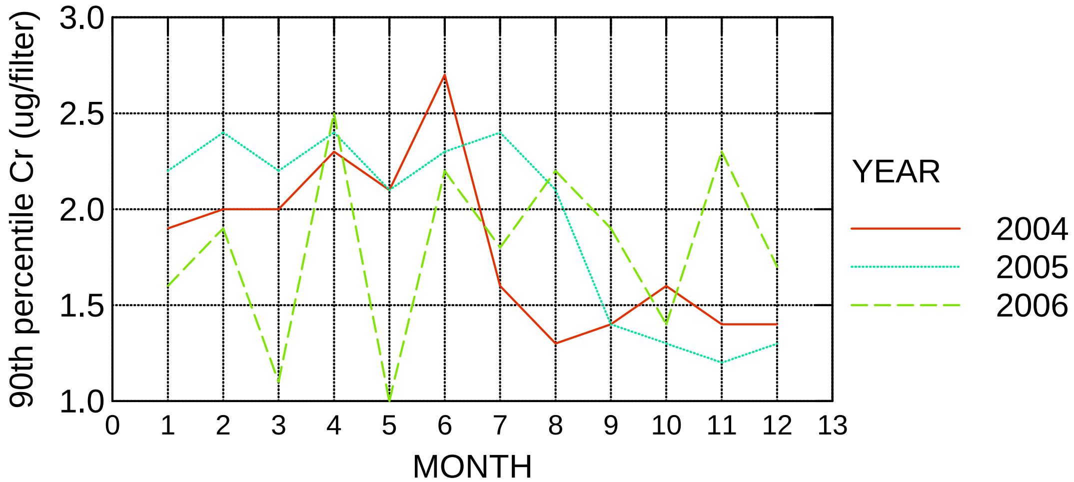

Figure 4. 90th percentile chromium loadings in the entire routine network.

Shifts in several of the Mo-XRF element loadings were reported in the previous report and a data advisory. Arsenic was one of the elements that showed a significant shift in loadings between August and September 2005, but the shift seems to have reversed between August and September 2006. Figure 5 shows the 90th percentile As loadings. According to the XRF QA report, the Mo-XRF system was recalibrated between August and September 2006, which explains the shift. Shifts were not evident in any of other Mo-XRF elements.

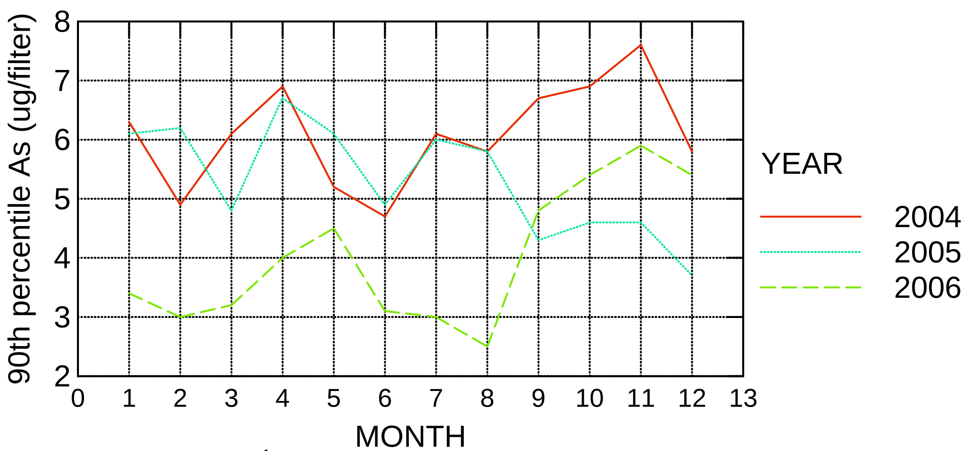

Figure 5. 90th percentile arsenic loadings in the entire routine network.

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

- No abnormalities were found in the review of these plots.

4.4.2 Flow Rate/Cutpoint

Time series of the A, B, and C module cutpoints for each site were examined for significant and persistent deviations from nominal conditions.

- At SIAN1 (Figure 6), the flowrates were all recalibrated during the annual maintenance trip on 3/26/06 but the recalibrated flowrates are very different from nominal. The maintenance group verified the calibration results.

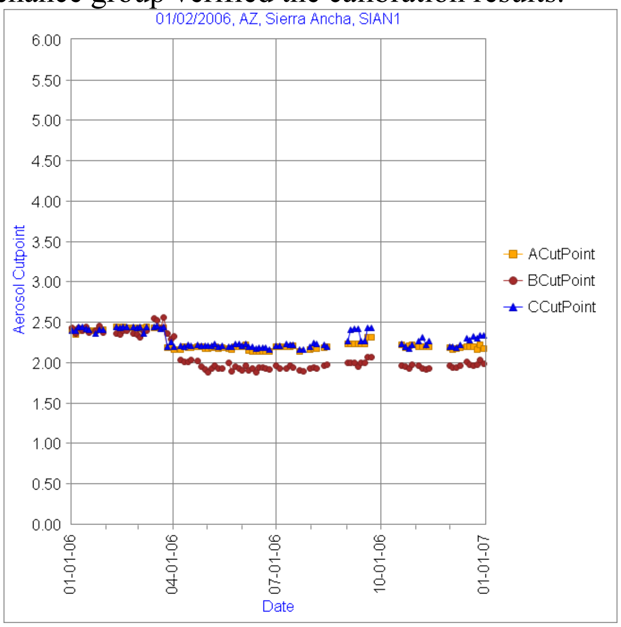

Figure 6. A, B, and C module cutpoints in µm at SIAN.

4.4.3 Organic Carbon

Estimates of organic mass (OM) based on PESA hydrogen measurements (OMH) and TOR OC measurements (OMC) were compared at each site.

- The shift in OC measurements discussed in the prior report is discussed in more detail in a new data advisory. The shift appears to be resulting from a combination of lower OC loadings and higher H loadings, as shown in Figures 7 and 8.

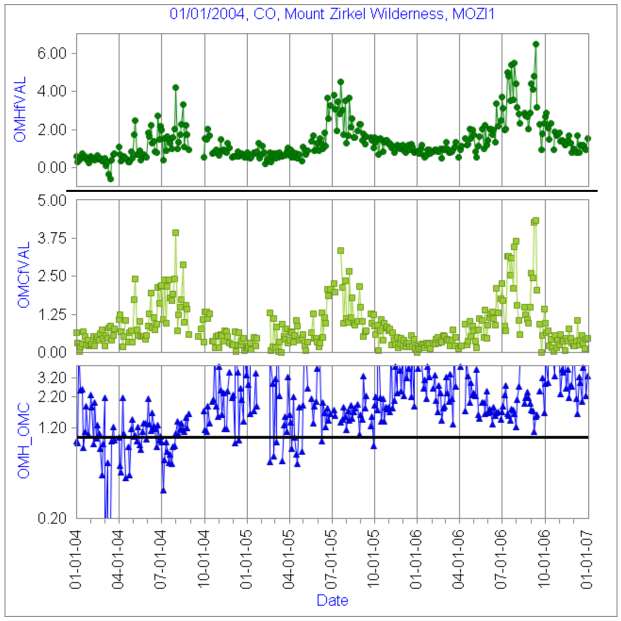

Figure 7. Organic mass estimated from hydrogen (top), organic mass estimated from OC (middle), and the ratio of these two estimates (bottom) at MOZI1.

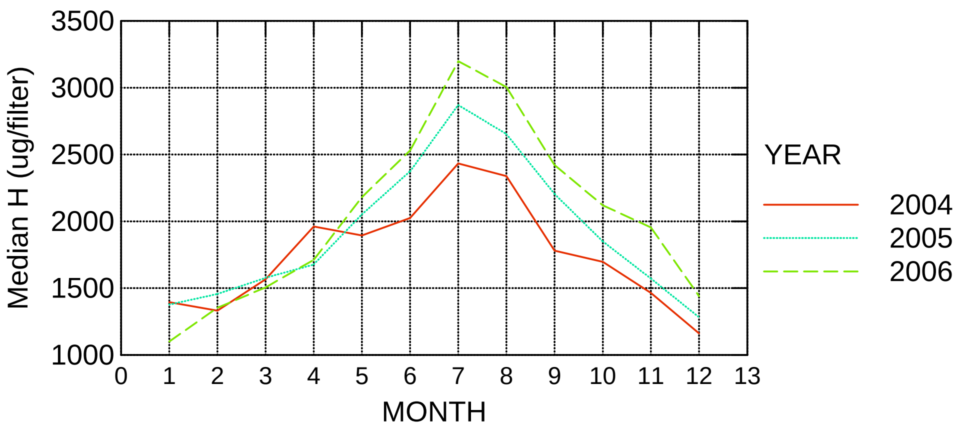

Figure 8. Network-wide median H loadings in 2004, 2005, and 2006. The median H loadings are noticeably higher in the later half of each of the three consecutive years.

4.4.4 NO_3

Nitrate concentrations are reviewed along with reconstructed mass estimates.

- 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 continues to vary from month to month as shown in Figure 1. None of the sites displayed unique behavior in terms of SO_4/S ratios.