UCD IMPROVE Standard Operating Procedure #351

Data Processing and Validation

Interagency Monitoring of Protected Visual Environments
Air Quality Research Center
University of California, Davis

June 15, 2021
Version 5.1

Prepared By: DocuSigned by: Indu Thekkemeppilly Sivakumar 19F6B63B1B17443... Date: 6/7/2021

Reviewed By: DocuSigned by: Dominique Young BB55DBA34BAB407... Date: 6/7/2021

Approved By: DocuSigned by: C4452D4B4E1D400... Date: 6/8/2021

UCDAVIS
AIR QUALITY RESEARCH CENTER

DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
04/24/21	SRS	All	Reformatted to fit document guidelines.

TABLE OF CONTENTS

1. Purpose and Applicability 6
2. Summary of the Method 6
3. Definitions 7
4. Health and Safety Warnings 8
5. Cautions 8
6. Interferences 8
7. Personnel Qualifications 8
   7.1 Data & Reporting Group Manager 8
   7.2 Lead Quality Assurance Officer 8
   7.3 Quality Assurance Officer 8
8. Equipment and Supplies 9
9. Procedural Steps 10
   9.1 Data Ingestion 10
      9.1.1 Carbon Results 11
      9.1.2 Ion Results 13
      9.1.3 Element and Optical Absorption Results 14
      9.1.4 Re-ingesting 14
      9.1.5 Issue Tracking 14
   9.2 Data Processing 15
      9.2.1 Units 16
      9.2.2 Artifacts 17
      9.2.3 Volume 18
      9.2.4 Concentration, Uncertainty, and Method Detection Limit 20
      9.2.5 Equations of Composite Variables 32
   9.3 Data Validation 36
      9.3.1 Definition of Status Flags 38
      9.3.2 Level 1 Validation Procedures 39
      9.3.3 Level 2 Validation Procedures 48
   9.4 Data Delivery 78
      9.4.1 Submission to CIRA 78
      9.4.2 Submission to AQS 79

9.4.3 Submission to UCD CIA 83
9.5 Quarterly Field Status Report 84
9.6 Adding AQS Site Information 87
9.6.1 Updating UCD Database 87
9.6.2 Adding Site and Monitors to AQS 90
9.6.3 Updating NPS 94
9.6.4 Updating UCD-CIA Database 95
9.7 Miscellaneous Tasks 95
9.7.1 Box Creation 95
9.7.2 Changing Current Lab Station ID and Assigning UF 98
10. Data and Records Management 99
10.1 Disaster Recovery Plan 100
10.1.1 Facility Recovery 100
10.1.2 Hardware Recovery Plan 100
10.1.3 Software and Data Recovery Plan 100
10.1.4 Data Security 100
11. Quality Assurance and Quality Control 101
11.1 Code Development 101
11.2 Bug Reporting 101
11.3 Data Validation 101
12. References 101

LIST OF FIGURES

Figure 1. Carbon analysis results upload page 12
Figure 2. Ions analysis results upload page. 13
Figure 3. Data processing flow chart. 15
Figure 4. Screen shot of the IMPROVE Data website Field Blanks tab. 46
Figure 5. S3/SO4 comparison plot for the GRGU1 site 49
Figure 6. Comparison plot of light absorption coefficient measurements 53
Figure 7. Time series plot of PM_{10} and $PM_{2.5}$ masses and their ratio at BOWA1 site. 55
Figure 8. Time series plot of $PM_{2.5}$ gravimetric mass 56
Figure 9. Time series for RCMN versus Fine mass at EVER1 site. 56
Figure 10. Scatter plot of sulfur (×3) versus sulfate for the entire IMPROVE network. 58
Figure 11. Scatter plot of chlorine versus chloride for the entire IMPROVE network. 58
Figure 12. Scatter plot of fAbs versus EC the whole network 59
Figure 13. Scatter plot of fAbs versus EC the whole network 59

Figure 14. Scatter plot of OC versus EC the whole network. 60
Figure 15. Scatter plot of ECTR versus other wavelengths for the whole network. 60
Figure 16. Ratio of $PM_{2.5}$ mass (1A) over PM_{10} mass (4D) at ACAD1 site 61
Figure 17. Multi-year monthly 61
Figure 18. Filter swap page. 63
Figure 19. Analysis swap page. 65
Figure 20. Cartridge swap page. 67
Figure 21. Box swap page. 69
Figure 22. Box swap page after clicking the 'Update' button 70
Figure 23. Login screen for the EPA's Exchange Network Services Center website. 81
Figure 24. Home screen of the Exchange Network Services Center website. 81
Figure 25. Type AQS into the search bar. 82
Figure 26. Select the service named AQS Submit. 82
Figure 27. AQS data submission form. 83
Figure 28. UCD CIA submission website home page. 83
Figure 29. UCD CIA data submission details page. 84
Figure 30. AQS screen after logging into the application; select the Read Only User option. 88
Figure 31. AQS screen after selecting Monitor from the Maintain option. 89
Figure 32. AQS screen after logging into the application 91
Figure 33. AQS screen after selecting Site from the Maintain option. 91
Figure 34. AQS screen when searching for Owning Agency details. 93
Figure 35. Box creation page. 96
Figure 36. Cartridge creation page. 96
Figure 37. Box creation page; after addition of filter. 98

LIST OF TABLES

Table 1. Automated validity checks performed during carbon data upload. 12
Table 2. Automated validity checks performed during the ions data upload. 13
Table 3. Units for data delivered to the CIRA, AQS and UCD CIA databases 17
Table 4. Universal flow constants for the V4 controllers. 19
Table 5. Fractional uncertainty for the mass. 22
Table 6. Analytical method detection limits (MDL) in µg/filter for the ions species. 23
Table 7. Fractional uncertainty for ions. 24
Table 8. Analytical method detection limits (MDL) in µg/filter for the carbon species. 26
Table 9. Fractional uncertainty for the carbon species. 27
Table 10. Analytical method detection limits (MDL) in µg/cm2 for the elemental species. 28
Table 11. Fractional uncertainty for the elemental species 29
Table 12. Fractional uncertainty for the laser absorption data 32
Table 13. Status flags and their definitions. 38
Table 14. Definitions and application criteria of automatic flow flags for $PM_{2.5}$ 40
Table 15. Definitions and application criteria of automatic flow flags for PM_{10}. 41
Table 16. Qualitative checks and criteria for carbon (OC, EC, and TC) validation. 51

1. PURPOSE AND APPLICABILITY

This standard operating procedure (SOP) provides an overview of the procedures for processing and validating the sampling and analytical laboratory data for the IMPROVE network. Data processing and data validation are performed in parallel.

2. SUMMARY OF THE METHOD

Filter samples are collected routinely every third day throughout the year in the IMPROVE network, resulting in approximately 20,000 annual samples per module and approximately 80,000 total filters collected per year. Each site has four routine modules collecting deposit on PTFE, nylon, or quartz filters; PTFE filters are used in two of the modules, nylon and quartz filters are used in each of the other two modules. In addition, one site has a full suite of collocated modules and 13 sites have one additional collocated module.

Filter boxes are prepared by the Sample Handling Lab at the University of California, Davis (UCD) and sent to the field, where field sampling is conducted by local operators. Once the samples are received back at the UCD Sample Handling Lab after sampling, the exposed filters are sent to the laboratories at UCD, RTI International (RTI), and Desert Research Institute (DRI), along with associated operational sampling data such as sampling dates and site information.

PTFE samples are analyzed at UCD for $PM_{2.5}$ and PM_{10} gravimetric mass, elements by energy dispersive X-ray fluorescence (EDXRF), and optical absorption by Hybrid Integrating Plate/Sphere (HIPS). Nylon samples are analyzed at RTI for ions by ion chromatography (IC) and quartz samples are analyzed at DRI by thermal optical analysis (TOA). Following laboratory analysis, all analytical results are assembled by UCD for processing and initial validation. Ion analysis results from RTI and carbon analysis results from DRI are received in data files, typically delivered as .csv files for ions data and .xml files from DRI, and ingested into the UCD IMPROVE database using the UCD IMPROVE Data Management website. Gravimetric mass, elemental, carbon, and optical absorption analysis results from UCD are automatically ingested.

Data processing involves calculating sample volume from field data on flow rates and sampling duration and subsequently calculating ambient concentration, uncertainty, and method detection limit (MDL) for each analyte using the laboratory result plus the sample volume. The UCD analyst will use functions in the *crocker* software package to calculate final results and post them to the UCD IMPROVE database. The analyst will also review any output messages for errors. The calculated concentrations undergo validation for technical acceptability and reasonableness based on information such as routine quality control (QC) sample results, data quality indicator calculations, performance evaluation samples, internal and external audits, statistical screening, internal consistency checks, and range checks. The analyst uses the UCD IMPROVE Data Management website along with custom software in the R language to perform validation; the primary review tools are summary data tables and comparison figures.

Once the data have been processed and validated, the analyst prepares delivery files of the validated data sets using custom tools in the *crocker* R package. The final data files are checked

for correctness and then submitted to the Environmental Protection Agency's (EPA) AQS Database, the Cooperative Institute for Research in the Atmosphere (CIRA) Database (FED), and ingested into the CIA Database.

3. DEFINITIONS

- **AQRC:** Air Quality Research Center.
- **AQS:** EPA's Air Quality System database.
- **CSN and IMPROVE Archive (CIA) Database:** A database of the complete record of CSN and IMPROVE data coupled with a web-based visualization and analysis tool.
- **Chemical Speciation Network (CSN)**: EPA's $PM_{2.5}$ sampling network, with sites located principally in urban areas.
- **CIRA:** Cooperative Institute for Research in the Atmosphere.
- **crocker:** A custom software package in the R language that contains the data processing code used to produce, check, and post the final results.
- **CSV:** a comma-separated value file that is the common format for delivery files.
- **datvalIMPROVE:** A custom software package in the R language that contains the data validation code used to collect, compare, and flag the final results.
- **DRI:** Desert Research Institute.
- **Energy Dispersive X-Ray Fluorescence (EDXRF):** An analytical technique used to determine the concentration of elements.
- **Federal Land Manager Environmental Database (FED):** a database of environmental data managed by Cooperative Institute for Research in the Atmosphere (CIRA)
- **Hybrid Integrating Plate/Sphere (HIPS):** An analytical technique for optical absorption.
- **Ion Chromatography (IC):** An analytical technique used to determine the concentration of ions.
- **Interagency Monitoring of Protected Visual Environments (IMPROVE):** Federal $PM_{2.5}$ and PM_{10} sampling network directed by the National Park Service, with sites located principally in remote rural areas.
- **IMPROVE database:** A SQL Server database that is the central warehouse of IMPROVE preliminary and final data at UCD.
- **Method Detection Limit (MDL):** A lower limit of detection specific to method of analysis and reported parameter.
- **NPS:** National Park Service.
- **PM:** Particulate Matter. $PM_{2.5}$ is particulate matter with diameters 2.5 micrometers (μm) and smaller. PM_{10} is particulate matter with diameters 10 μm or smaller.
- **RTI:** Research Triangle Institute, International.
- **SQL:** database management system used by AQRC.
- **Thermal Optical Analysis (TOA):** An analytical technique used to determine the concentration of carbon.
- **UCD:** University of CA—Davis.

- **Extensible Markup Language (XML):** a markup language defining a set of rules for encoding documents in a particular format; used for IMPROVE carbon files.

4. HEALTH AND SAFETY WARNINGS

Not applicable.

5. CAUTIONS

Not applicable.

6. INTERFERENCES

Not applicable.

7. PERSONNEL QUALIFICATIONS

This section describes the responsibilities of the individuals involved in data processing and validation.

7.1 Data & Reporting Group Manager

The Data & Reporting Group Manager oversees all aspects of data ingestion, processing, validation, and reporting.

7.2 Lead Quality Assurance Officer

The lead quality assurance officer:

- devises techniques that improve the efficiency, traceability, and accuracy of the data management;
- develops validation criteria, automated and manual checks, and visualization tools for assessing data quality and consistency;
- reviews method detection limit (MDL) and uncertainty;
- identifies sampling or measurement deficiencies and proposes solutions/improvements;
- critically evaluates the data using knowledge of air quality and atmospheric chemistry to better understand trends and biases in the data at program level scale.

7.3 Quality Assurance Officer

The quality assurance officer:

- receives and ingests the analytical data to the University of California, Davis (UCD) IMPROVE database;
- reviews operational and analytical data for errors or incompleteness;
- processes species concentrations and posts monthly dataset to the UCD IMPROVE database;

- performs automated and manual validation checks on concentration data and determines the validity of samples;
- analyzes time-series and spatial trends in network data to assess data consistency due to sampling, measurement, or procedural changes;
- identifies sampling or measurement deficiencies and proposes solutions/improvements;
- communicates with laboratories regarding analytical issues and/or reanalysis requests;
- submits Level 2 validated data to project sponsors, Cooperative Institute for Research in the Atmosphere (CIRA), the EPA Air Quality System (AQS), and UCD CSN & IMPROVE Archive (CIA) databases.

8. EQUIPMENT AND SUPPLIES

The data processing and validation requires all operational and analytical data be loaded into the UCD IMPROVE database (Improve_2.1). The types of data include:

- Basic filter information such as sample date, site, purpose, and status. These data are recorded during filter preparation and handling and are stored in the *filter.Filters* table.
- Flow rates a raw flow readings are either acquired from sampler flashcards and stored in the *sampler.FlowSourceData* table (for V2 controllers) or uploaded daily by the controller and stored in the sampler.FlowSourceDataV2 table (for V4 controllers). In addition, handwritten log sheets that contain flow readings and other sampling information recorded by the operator are stored in the *filter.Filters* and *filter.SampleCartridges* tables.
- Average flow rates (24-hour average) are calculated using a SQL procedure called *sampler.spFilterAverageFlowRates* for each filter based on the raw flow readings or log sheet data. These are stored in the *sampler.AverageFlows* table.
- Pre- and post-sampling filter mass values are acquired in the UCD Sample Handling Laboratory and stored in the *analysis.Mass* table.
- Carbon analysis results are acquired from files generated by Desert Research Institute (DRI; Reno, NV) TOA Laboratory and are stored in the *analysis.Carbon*, *analysis.CarbonLaser*, and *analysis.CarbonRun* tables.
- Ions analysis results are acquired from files generated by RTI International (Research Triangle Park, NC) IC Laboratory and are stored in the *analysis.Ions* table.
- Elements analysis results are acquired from the UCD XRF Laboratory through a custom ingestion process and are stored in two tables in the database: *XRF.SampleAnalysis* and *XRF.DeviceCounts*. These are the main tables with mass loading results, reported as raw areal densities from the XRF instruments (ug/cm2). The *DeviceCounts* table contains the XRF results for each element. The *SampleAnalysis* table contains information about the filter analyzed, the instrument used for analysis, and the date and time of analysis.
- Optical absorption analysis results are acquired from the UCD Hybrid Integrating Plate/Sphere (HIPS) Laboratory through a custom ingestion process and are stored in the *hips.SampleAnalysis* table.

UCD has developed several custom tools for data processing and validation:

crocker: This program (a package in the R programming language) provides functions for processing raw filter weights, mass loadings, and flow rates into concentrations, uncertainties, and MDLs. *crocker* also provides utility functions that are used in the online data validation tools (see Section 6).

datvalIMPROVE: This R package provides functions for performing routine validation and quality control (QC) (see section 9.3.3).

IMPROVE Management Website (https://improve.aqrc.ucdavis.edu/): This web application provides all UCD laboratory staff with viewing access to relevant tables within the UCD IMPROVE database. Functions within the application pertinent to data processing and validation include:

- The Filter Section (https://improve.aqrc.ucdavis.edu/Filters) consists of web pages for searching for specific filters, reviewing operational and analytical data associated with a filter, or applying flags and comments.
- The Samplers Section (https://improve.aqrc.ucdavis.edu/Samplers) provides details of all IMPROVE samplers, both active and inactive sites, with options to edit information as well as options to add new samplers.
- The XRF Section (https://improve.aqrc.ucdavis.edu/Xrf/Home) is an interface for processing XRF elemental mass loadings, managing processed sets, and applying flags.
- The Analysis Data Section (https://improve.aqrc.ucdavis.edu/AnalysisData/Home) consists of web pages for importing and viewing carbon and ions data viewing mass and optical absorption data, and reviewing information on analysis pathways. Under this home page are the following subsections:
- The Operations Section (https://improve.aqrc.ucdavis.edu/Operations/Home) is a live display of the sampler status for the sites equipped with the V4 controllers. This section also consists of web pages for scheduling boxes and reviewing box details.
- The Reports Section (https://improve.aqrc.ucdavis.edu/Home/Reports) has links for IMPROVE status pages (https://shiny.aqrc.ucdavis.edu/ImproveStatus/) and IMPROVE data exploration pages (https://shiny.aqrc.ucdavis.edu/ImproveData/).

Flow Graphs (https://shiny.aqrc.ucdavis.edu/FlowRates/): This web application provides interactive visualizations of the raw 15-minute flow rates and temperatures as well as the processed 24-hr average flow rate in the UCD IMPROVE database.

IMPROVE Data Site (https://shiny.aqrc.ucdavis.edu/ImproveData/): This web application provides interactive visualizations of processed concentrations, uncertainties, and MDLs, plus custom tools for validation as described in Section 9.3.

9. PROCEDURAL STEPS

9.1 Data Ingestion

Prior to data processing and validation, data are ingested for each of the analysis pathways: (1) carbon results from DRI, (2) ions results from RTI, and (3) elemental and optical absorption results from UCD.

9.1.1 Carbon Results

Carbon analysis results are sent from DRI to UCD via email in .xml format, including three files:

1. CarbonData.xml
2. CarbonInformation.xml
3. CarbonLaser.xml

All three files are ingested using the UCD IMPROVE Management website. Figure 1 shows a screenshot of the carbon data upload page, which is accessed via the Analysis Data Section as described in section 8, selecting the **Carbons** tab, and clicking the **Ingest Data** button. To ingest the files from the data upload page, select the relevant files, create a name for the import batch under *Batch Label*, and click **Submit**. *CarbonInformation*, *CarbonLaser*, and *CarbonData* are ingested simultaneously, and an automated validity check is performed (Table 1). Results from the validity check will indicate upload failures. The Quality Assurance Officer will review the upload results and notify the Lead Quality Assurance Officer if there are upload failures from validation errors. After ingest, the source files are stored on the file server at U:\IMPROVE\RawDataReceived\Carbon DRI\Imported, within a folder which is named in accordance with the sample period covered by the source files. After successfully ingesting the results, the Quality Assurance Officer will save a copy of the Carbon Data Ingestion summary page by printing the page to a PDF and saving to U:\IMPROVE\RawDataReceived\Carbon DRI\IngestRecord\. Further details of the ingest file are recorded in a log file located at U:\IMPROVE\RawDataReceived\Carbon DRI\Carbon_Ingest_log.xlsx.

Figure 1. Carbon analysis results upload page.

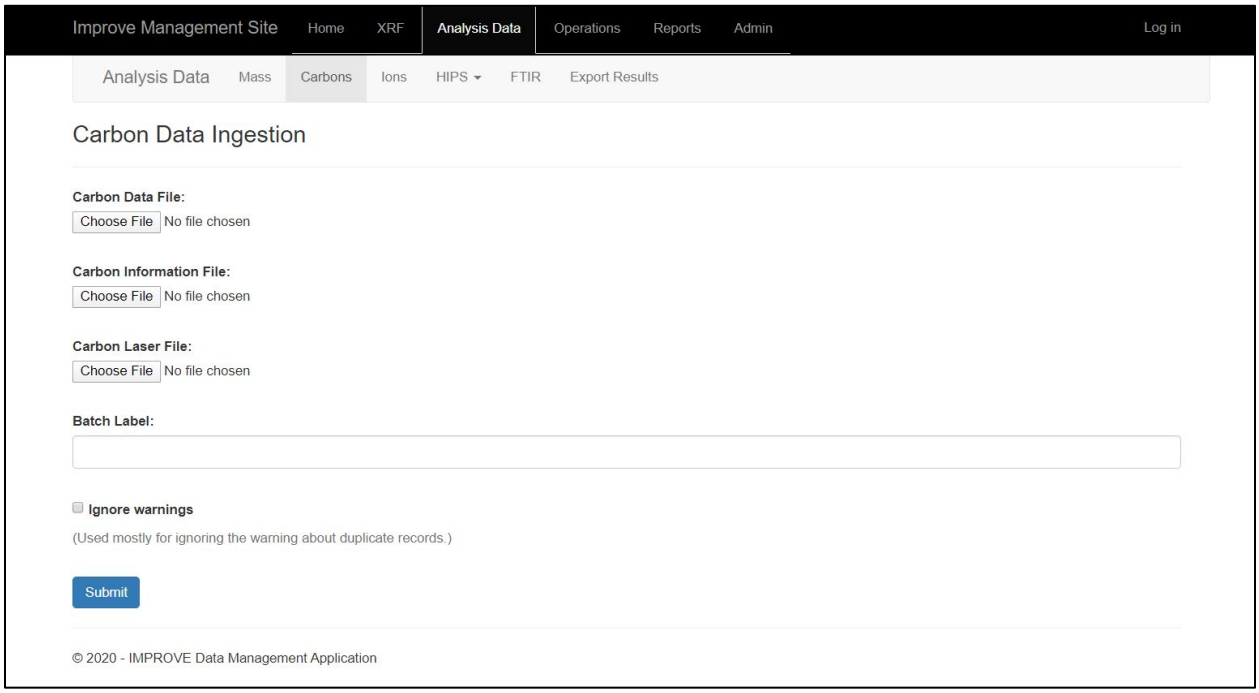


Table 1. Automated validity checks performed during carbon data upload.

Check	**Action**
Basic schema validation on xml files	Error
No filter found for record	Warning
Filter.Module doesn't match record Site field	Warning
Record is marked as re-analysis	Warning
Carbon Laser file has records missing wavelength	Warning
Found more parameter records than expected for an analysis	Warning
Parameter missing for an analysis	Warning
Comment from DRI on analysis	Note
Parameter/record already recorded in database	Warning
Incomplete analysis record (missing entries in either Carbon/Carbon Laser/Carbon Info file)	Warning

9.1.2 Ion Results

Ions analysis results are sent as one file from RTI to UCD via email in .csv format. The naming convention of the ions data includes the year followed by the ions data set number (e.g. '2020 1 2 3 data export to UCD').

The ion analysis records are ingested using the UCD IMPROVE Management website. Figure 2 shows a screenshot of the ions data upload page, accessed via the Analysis Data Section as described in section 8, selecting the Ions tab, and click the **Upload Data** button. To ingest a file from the data upload page, select the relevant file and click **submit**. An automated validity check is performed, and the validity check results will indicate if there are upload failures (Table 2). The Quality Assurance Officer will review the upload results and notify the Lead Quality Assurance Officer if there are upload failures from validation errors. After ingest, the source files are stored on the file server at U:\IMPROVE\RawDataReceived\Ions RTI\Ingested. After successfully ingesting the results, the Quality Assurance Officer will save a copy of the Ions Data Ingestion Status summary page by printing the page to a PDF and saving to U:\IMPROVE\RawDataReceived\Ions RTI\Ingest_record\. Further details of the ingest file are recorded in a log file located at U:\IMPROVE\RawDataReceived\Ions RTI\Ions_DataIngest_Log.xlsx.

Figure 2. Ions analysis results upload page.

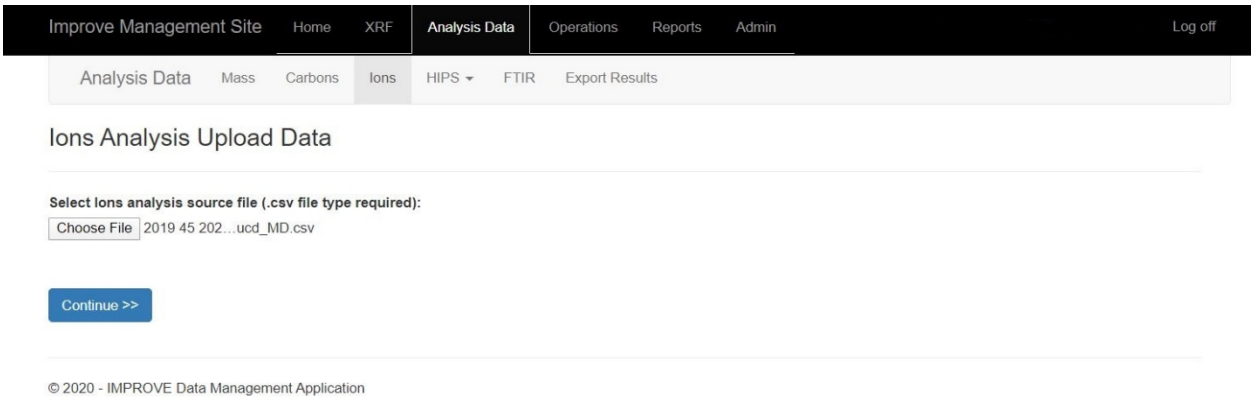


Table 2. Automated validity checks performed during the ions data upload.

Check	**Action**
Basic schema validation on csv files	Error message
No filter is found for record	Error message
Data already exists for filter record	Warning message
Parameter missing for a filter	None
Parameter already recorded in database	Warning

9.1.3 Element and Optical Absorption Results

Elemental analysis is performed at UCD. The PANalytical XRF software generates results files, which are automatically ingested. The results files are transmitted to a directory on the PANalytical XRF PC (C:\PANalytical\Transmission), and a Windows service (internally named *XRF Data Transfer*) monitors a transmission directory, checking hourly for new files. The XRF results files are standard text files with the extension *.qan*. The file name includes XRF analysis dates and times in the format *YYYYMMDDHHMMSS.qan*. The results files and contents are automatically parsed and ingested into tables in the UCD IMPROVE database.

Optical absorption analysis is performed at UCD. The HIPS instrument generates results which are then verified by the operator to be complete and then written to the database. The data are then available on the UCD IMPROVE database.

9.1.4 Re-ingesting

If errors are identified in the source files from DRI or RTI that cause the import to fail, or if results are updated as part of the validation and reanalysis process, new files must be requested and provided for ingestion. Upload the new files using the process described in sections 9.1.1 and 9.1.2.

For carbon, whether the files contain new batches of data or reanalysis results, take care to ingest with the *ignore warnings* box unchecked. Scrutinize the messages and warnings to check for errors and take note of further actions that may be required after the data is ingested (e.g., changing analysis QC codes). The import process indicates if there are matching existing records, if existing records are not updated, or if only new records are added (including cases with different analysis results from the sample filter). Once the messages have been reviewed and addressed, re-run the ingest process with the *ignore warnings* box checked. For carbon, if the reanalysis results are used, the analysis QC code can be updated using the tool available at https://improve.aqrc.ucdavis.edu/AnalysisData/Carbons/CarbonsQcReview.

For ions, the data are ingested without any changes to the original process; the QC code is updated using the tool available at https://improve.aqrc.ucdavis.edu/AnalysisData/Ions/IonsQcReview.

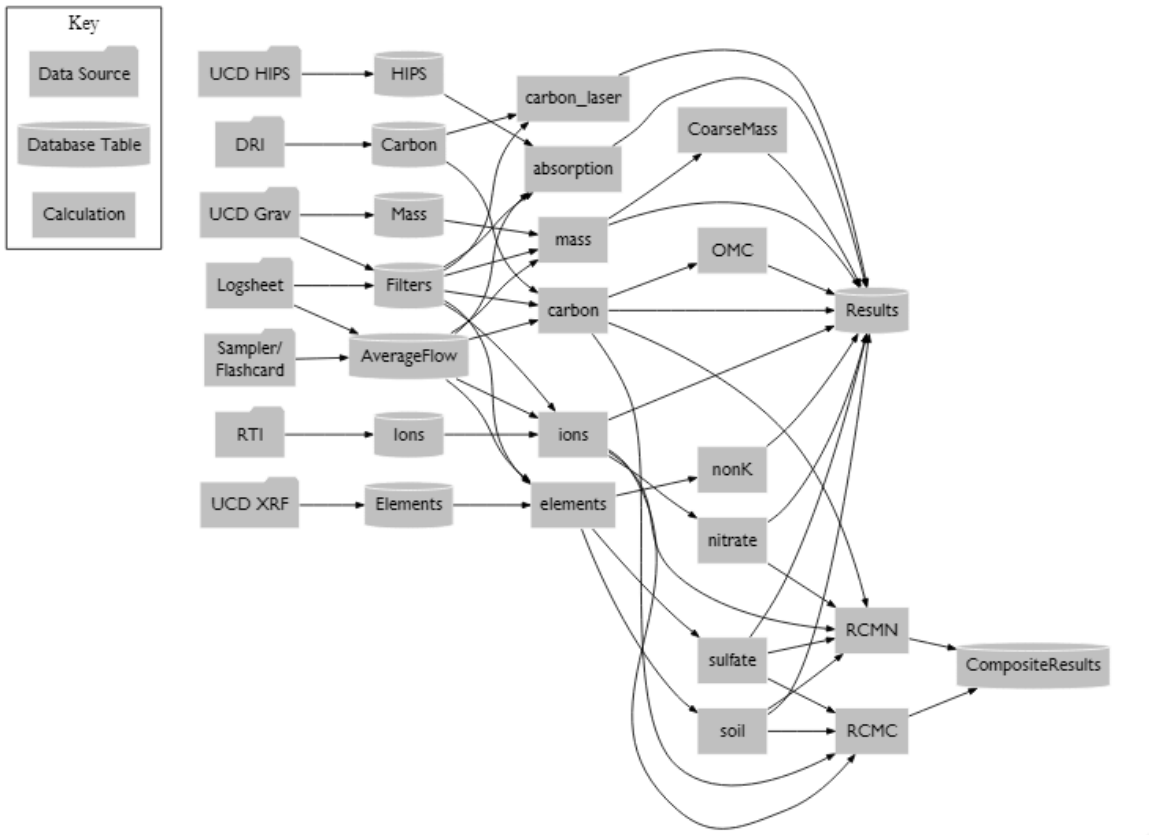
9.1.5 Issue Tracking

Software bugs and data management issues are tracked through JIRA tracking software. All users have access to the internal UCD JIRA website and can submit, track, and comment on issues. Users requesting new tools, modifications to existing tools, or to report bugs specific to the IMPROVE data should add JIRA tickets to the IMPROVE Data Management Software project at https://improve.atlassian.net/jira/software/c/projects/IMPSW/issues/

9.2 Data Processing

Data processing for IMPROVE consists of reducing and combining data from the sampling and analytical laboratories to calculate concentrations, uncertainty estimates, and method detection limits (MDLs). Figure 3 shows a flow chart for the IMPROVE data processing.

Figure 3. Data processing flow chart.



Calculation of concentrations and associated uncertainties and MDLs are performed within the *crocker* R package, while flow rate calculations are performed in the UCD IMPROVE database. Flow rate calculations are performed before calculating concentrations to ensure the most up-to-date flow data are used.

Flow data are processed in SQL using a stored procedure to derive the daily average flow rate and elapsed time (ET). The flow processing code automatically assigns non-normal flow status flags to the samples with flow rates that deviate from the nominal values.

The first six lines of the SQL query below state the variables to process flows with. In general, the start and end dates are declared to cover the month(s) of data being processed, and the sampler name is left blank to process flow data for the entire network. The flow processing can be performed on a single site, date, or even filter ID by declaring the appropriate values.

```
DECLARE @RC int
DECLARE @iStartDate datetime = 'mm/dd/yyyy'
DECLARE @iEndDate datetime = 'mm/dd/yyyy'
DECLARE @iSamplerName NVARCHAR(50) = NULL
DECLARE @iFilterId BIGINT = NULL
DECLARE @Debug bit = 1

EXECUTE @RC = [Improve_2.1].[sampler].[spFilterAverageFlowRates]
@iStartDate
,@iEndDate
,@iSamplerName
,@iFilterId
,@Debug
GO
```

If the execution code fails, evaluate the warning message and work with the Software & Analysis Group and/or Sample Handling Laboratory to identify the issue and resolve.

To calculate values for all measured and derived parameters, the following command is run in an R environment:

[month_data] <- crocker::improve_calculate_and_post([YYYY], [MM], server, AnalysisQcCode = 1, comment = "", replacingId = NULL, replacingQcCode = NULL)

This command will calculate concentrations, uncertainties, and MDLs for all measured and derived parameters for the year (*[YYYY]*) and month (*[MM]*) and upload the results to the UCD IMPROVE database (*server*, e.g., "production") specified in the command in preparation for validation. The processed concentration data are appended to the analysis.Results and analysis.CompositeResults table in the UCD IMPROVE database (Improve_2.1). A record that contains summary information for the data set, including the comment and the AnalysisQcCode, is inserted into the analysis.Sets table. An AnalysisQcCode of 1 is used for valid routine data.

9.2.1 Units

Table 3 lists the data types, parameters, and units for all data delivered to the CIRA, AQS, and UCD CIA databases (see section 9.4). For mass, ions, carbon, elements, and light absorption, the units listed are also used for uncertainty and MDL. NA indicates that the data type is not reported to the corresponding database.

Table 3. Units for data delivered to the CIRA, AQS and UCD CIA databases.

Data type	Parameter	CIRA unit	AQS unit	UCD CIA unit
Flow Rate	Flow	L/min	NA	NA
Elapsed Time	ET	min	NA	NA
Gravimetric mass	PM2.5, PM10	ng/m^3	$\mu g/m^3$	$\mu g/m^3$
Ions	Cld, NO_2, NO_3, SO_4	ng/m^3	$\mu g/m^3$	$\mu g/m^3$
Carbon	OC1, OC2, OC3, OC4, OC, OPTR, EC1, EC2, EC3, EC	ng/m^3	$\mu g/m^3$	$\mu g/m^3$
	TC, OPTT, OPTR at other wavelength, OPTT at other wavelength	ng/m^3	NA	NA
Carbon_laser	RefF_wavelength, Refl_wavelength, RefM_wavelength, TransF_wavelength, Transl_wavelength, TransM_wavelength	reading	NA	NA
Elements	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Se, Br, Rb, Sr, Zr	ng/m^3	$\mu g/m^3$	$\mu g/m^3$
Light absorption	fAbs	Mm^{-1}	NA	NA
Composite species	OMC, NHNO, NHSO, PM_{10}-$PM_{2.5}$, Soil	NA	$\mu g/m^3$	$\mu g/m^3$

9.2.2 Artifacts

An artifact is defined as any increase or decrease of material on the filter that positively or negatively biases the measurement of ambient concentration. Artifact corrections are applied to the ions, carbon, and element measurements. Artifact examples include:

(1) Contamination of the filter medium (positive).
(2) Contamination acquired by contact with the cassettes or in handling (positive).
(3) Adsorption of gases during collection that are erroneously measured as particles (positive).
(4) Volatilization of particles during collection and in handling (negative).
(5) Fall-off of particles during handling after collection (negative).

For the ion measurements, the artifact correction method attempts to account for the first two types of artifacts and is estimated using data from field blanks. Field blanks are handled as normal filters (loaded into cassettes and cartridges, shipped to and from the field, and left in the sampler for a week) except that no air is drawn through them. The field blanks are collected randomly at all sites on a periodic basis. When there are ≥ 50 field blanks in a month, the artifact correction is calculated for each species as the median loading measured on the field blanks. Otherwise, values from the previous month(s) are included until at least 50 field blanks are available. Artifact corrections are subtracted from each ambient concentration for the corresponding month.

For the carbon measurements, the artifact correction method attempts to account for the first three types of artifacts and is estimated using data from field blanks. The field blanks are handled as normal filters (loaded into cassettes and cartridges, shipped to and from

the field, and left in the sampler for a week) except that no air is drawn through them. The field blanks are collected randomly at all sites on a periodic basis. When there are ≥ 50 field blanks in a month, the artifact correction is calculated for each species as the median loading measured on the field blanks; otherwise, values from the previous month(s) are included until at least 50 field blanks are available. Artifact corrections are subtracted from each ambient concentration for the corresponding month. For further background information and detail regarding past use of stacked filters for artifact correction and subsequent application of a correction factor, see data advisories:

http://vista.cira.colostate.edu/Improve/wp-content/uploads/2016/04/Dillner_OCArtifactAdjustmentIMPROVEOct2012.pdf and http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0032/da0032_OC_artifact.pdf

Measurements are not corrected for the two negative artifact types (volatilization and fall-off). The measured mass loadings for the higher-volatility organics may be much less than those in the atmosphere because of volatilization of particles during the remainder of the sampling or during transportation. Volatilization of nitrate and chloride from the nylon filters is assumed to be insignificant. Depending on the environmental conditions, some ammonium nitrate collected on polytetrafluoroethylene (PTFE) filters may volatilize. In those cases, fine mass on the PTFE filter may underestimate the ambient $PM_{2.5}$ mass concentrations.

For discussion of artifact correction for element measurements, see section 9.2.5.4.

9.2.3 Volume

The sample volume is a product of the flow rate and the sampling duration. The sampling duration is determined using elapsed time (ET) as recorded by the sampler controller.

For the $PM_{2.5}$ modules (1A, 2B, and 3C modules), the flow rate is determined from measurement of static pressure across the cyclone using a pressure transducer (referred to as the CYC value). Since the pressure is measured before the filter, a decrease in measured flow rate could correspond with a lightly loaded filter since a smaller volume of air is being sampled. Prior to 2016, the 15-minute pressure measurements were averaged over the whole sampling period (nominally 24 hours) for calculating the average flow rate. Beginning data for samples collected in January 2016, the average flow rate is an elapsed time-weighted average, calculated from the individual 15-minute pressure measurement. The sampler flow rate for 1A, 2B, and 3C modules is calculated using equation 351-1.

$$Q = 10^{a} M^{b} * F(elev) * \sqrt{\frac{T + 273.15}{293.15}} \qquad (351\text{-}1)$$

Q = volumetric flow rate (using site-specific temperature and pressure, not STP)

a, b = calibration coefficients

M = cyclone transducer reading. If the transducer readings are taken from the controller screen, they can be used in equation 351-1 directly. If the transducer readings are taken from the flashcard file, they must be divided by 100.

F(elev) = elevation factor to account for pressure difference between sea level and site.

T = ambient temperature in degrees Celsius at time of sampling.

For the PM_{10} module (4D module), the flow rate is determined from measurement of absolute pressure downstream of the filters near the critical orifice using a pressure transducer (referred to as the ORI value); the CYC value is not available for the 4D module. Since the pressure is measured after the filter, a decrease in measured flow rate could be indicative of a heavily loaded filter or filter clogging that is restricting the flow. The sampler flow rate is calculated using equation 351-2.

$$Q = (c + d * G) * F(elev)^2 * \sqrt{\frac{T + 273.15}{293.15}} \quad (351\text{-}2)$$

Q = volumetric flow rate

c, d = calibration coefficients

G = critical orifice transducer reading. If the transducer readings are taken from the controller screen, they can be used in equation 351-2 directly. If the transducer readings are taken from the flashcard file, they must be divided by 100.

F(elev) = elevation factor to account for pressure difference between sea level and the site.

T = ambient temperature in degrees Celsius at time of sampling.

The calibration coefficients (a, b, c, and d) in equations (351-1) and (351-2) have historically been site-specific. Staring with data from samples collected January 2018, a set of universal flow constants for the V4 controller cyclone (CYC; equation 351-1) and orifice (ORI; equation 351-2). The constants are reviewed annually and updated as needed; the values are expected to vary minimally from year to year (Table 4).

Table 4. Universal flow constants for the V4 controllers.

Module	**Intercept (a, c)***	**Slope (b, d)***
$PM_{2.5}$	1.4891	0.3797
PM_{10}	1.320	1.325

* Applied to data from 1/1/2018 onward.

9.2.4 Concentration, Uncertainty, and Method Detection Limit

The calculations described in this section are performed in R using the R function listed at the beginning of section 9.2.

The concentration is calculated using equation 351-3, where the mass of material on the filter is equal to the difference between the mass measured on the sample and the mass on the unused filter. For gravimetric analysis, the mass on the unused filter is determined from the pre-weight of individual PTFE filters. For measurement of ions and carbon, the mass on the unused filter is determined from the median of field blank loadings. For calculation of element concentrations, see section 9.2.4.4.

$$C = \frac{\mathrm{A - B}}{\mathrm{V}} \tag{351-3}$$

C = ambient concentration (ng/m^3)

A = mass measured on sample (ng/filter or ng/cm^2)

B = artifact mass (ng/filter or ng/cm^2) = pre-weight or monthly median of ion or carbon field blank mass loading

V = sample air volume (m^3) = Q * Elapsed Time

Q = volumetric flow rate

The uncertainty is reported with each concentration. The general model for the uncertainty is a quadratic sum of two components of uncertainty as shown in Equation 351-4.

$$\sigma(c) = \sqrt{\left[fC\right]^2 + \left[\frac{\sigma_a}{V}\right]^2} \tag{351-4}$$

σ_a = analytical uncertainty. This is a constant term from additive sources of uncertainty, such as those related to background contamination of the filters. Analytical uncertainty is determined and reported by the laboratories. For large concentrations, this is small compared to the fractional term.

V = sample air volume (m^3)

C = ambient concentration (ng/m^3)

f = fractional uncertainty. This term results from various sources of proportional uncertainties, such as analytical calibration and flow rate measurements. Beginning with data from samples collected January 2018, fractional uncertainties (f) are determined using the most recent two years of data from collocated measurements (351-5 and 351-6). If the count of collocated pairs over the two-year period is less than 60, a value of 0.25 is adopted as f.

$$srd = \frac{(Collo - Routine)/\sqrt{2}}{(Collo + Routine)/2} \quad (351\text{-}5)$$

$$f = \frac{(84th\ percentile\ of\ srd) - (16th\ percentile\ of\ srd)}{2} \quad (351\text{-}6)$$

The *improve_fracUnc* function is run using the *crocker* R package to calculate and post a new set of fractional uncertainties as well as to replace older sets, when necessary. The date range specified must be for a two-year period prior to the current year of data to be processed. The function can also be used for other purposes where the user can specify any time period of interest.

improve_fracUnc(startdate, enddate, effectivedate, server = "production", AnalysisQcCode = 1, comment = "", replacingId = NULL, replacingQcCode = NULL)

For example, processing the 2019 concentration data should use the fractional uncertainties (f) calculated from 1/1/2017 through 12/31/2018 data. The function *improve_fracUnc* calculates and directly imports fractional uncertainty into database tables, Improve_2.1.analysis. UncertaintySets and Improve_2.1.analysis.Uncertainties.

improve_fracUnc(startdate = "2017-01-01", enddate = "2018-12-31", effectivedate = "2019-01-01", server = 'production', comment = "New set to be applied beginning with 2019 data")

For further details, refer to the function help file in R.

The MDLs are also reported with each concentration. Beginning with data from samples collected January 2018, MDLs for ions, carbon, and elements are calculated as 95th percentile minus median of field blanks.

9.2.4.1 $PM_{2.5}$ and PM_{10} Mass (1A and 4D Modules)

$PM_{2.5}$ mass is measured gravimetrically on the PTFE filter from the 1A Module. PM_{10} mass is measured gravimetrically on the PTFE filter from the 4D Module. The pre- and post-weights (as micrograms per filter) are stored in the *analysis.Mass* table in the UCD IMPROVE database.

The constant analytical uncertainty, σ_a, in equation 351-4 is equal to 5 μg for all filters. The mass concentration (C_{Mass}), uncertainty (σ_{Mass}), and MDL (mdl_{Mass}) in nanograms per cubic meter are calculated using the following equations:

$$C_{Mass} = 10^6\ ng/mg * \left(\frac{Postweight - preweight}{V}\right) \quad (351\text{-}7)$$

$$\sigma_{Mass} = 1000\frac{ng}{\mu g} * \frac{\sqrt{(0.608 * Max(P95,\ mdl_{analy\ tical}))^2 + (f * (postweight\text{-}preweight))^2}}{V} \quad (351\text{-}8)$$

$$mdl_{Mass} = 1000\frac{ng}{\mu g} * \frac{Max(P95, mdl_{analytical})}{V} \quad (351\text{-}9)$$

Where,

V = A-Module sample air volume (m^3)

P95 = 95th percentile of field blank measurements in µg/filter

$mdl_{analytical}$ = analytical MDL reported from the analytical laboratory (10 µg/filter for $PM_{2.5}$ and PM_{10}). The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL.

postweight = mass of filter after sampling

preweight = mass of filter before sampling

f = fractional uncertainty (Table 5).

Table 5. Fractional uncertainty for the mass.

Species	**f reported for data 2/28/1995 – 12/31/2006**	**f reported for data 1/1/2017 – 12/31/2017**	**f reported for data 1/1/2018 – 12/31/2018**	**f reported for data 1/1/2019 – 12/31/2019**	**f reported for data 1/1/2020 – current**
$PM_{2.5}$	0.03	0.03	0.04	0.04	0.04
PM_{10}	0.03	0.07	0.07	0.08	0.07

9.2.4.2 Ions (2B Module)

Ions are measured by ion chromatography using the nylon filter from the 2B Module. Ions data (as micrograms per filter) are stored in the *analysis.Ions* table in the UCD IMPROVE database.

The concentration (C_{ion}), uncertainty (σ_{ion}), and MDL (mdl_{ion}) in nanograms per cubic meter are calculated for the ion species using the following equations; however, for nitrite, when the concentration is less than or equal to zero, uncertainty is reported as zero:

$$C_{ion} = 1000\frac{ng}{\mu g} * \frac{\left(A_{ion} - B_{ion}\right)}{V_{B\,module}} \quad (351\text{-}10)$$

$$\sigma_{ion} = 1000\frac{ng}{\mu g} * \frac{\sqrt{(0.608 * Max(P95 - B_{ion}, mdl_{analytical}))^2 + (f * (A_{ion} - B_{ion}))^2}}{V_{B\ Module}} \quad (351\text{-}11)$$

$$mdl_{ion} = 1000\frac{ng}{\mu g} * \frac{Max(P95 - B_{ion}, mdl_{analytical})}{V_{B\ Module}} \quad (351\text{-}12)$$

Where,

A_{ion} = ambient mass loading in µg/filter

B_{ion} = median of the field blank mass loading in µg/filter when there are ≥ 50 field blanks in a month; otherwise, values from the previous month are used.

$V_{B\ module}$ = B-Module sample air volume (m^3)

P95 = 95th percentile of field blank measurements in µg/filter

$mdl_{analytical}$ = analytical MDL in µg/filter reported from the analytical laboratory (Table 6). The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL.

f = fractional uncertainty (Table 7).

Table 6. Analytical method detection limits (MDL) in µg/filter for the ions species.

Species	**Analytical MDLs used for data 1/1/2006 – 12/31/2019**	**Analytical MDLs used for data 1/1/2020 – current**
Chloride (Cl^-)	0.03	0.1
Nitrite (NO_2^-)	0.01	0.2
Nitrate (NO_3^-)	0.05	0.16
Sulfate ($SO_4^=$)	0.07	0.22

Table 7. Fractional uncertainty for ions.

Species	**f reported for data 1/1/2005 – 12/31/2016**	**f reported for data 1/1/2017 – 12/31/2017**	**f reported for data 1/1/2018 – 12/31/2018**	**f reported for data 1/1/2019 – 12/31/2019**	**f reported for data 1/1/2020 – current**
Chloride (Cl^-)	0.08	0.08	0.08	0.09	0.10
Nitrite (NO_2^-)	0.22	0.25	0.25	0.25	0.25
Nitrate (NO_3^-)	0.04	0.03	0.04	0.04	0.04
Sulfate ($SO_4^=$)	0.02	0.02	0.02	0.03	0.02

9.2.4.3 Carbon (3C Module)

Carbon is measured by thermal optical reflectance (TOR) and thermal optical transmittance (TOT) using the quartz filter from the 3C Module. The seven carbon fractions (OC1-OC4, EC1-EC3) and organic pyrolyzed carbon (OP) are recorded in micrograms per filter and stored in the analysis.Carbon table in the UCD IMPROVE database. For the carbon fractions, the primary factors that determine the fractional uncertainty are the homogeneity of the sample deposit and the accuracy of the temperature set point in each stage. For OP, the primary factors that determine the fractional uncertainty are the laser signal stability and the accuracy of the split point placement.

The TOR elemental carbon (ECTR) component is assumed to be all carbon evolved at 580 °C and above, after the laser indicates that reflectance has returned to the initial value. The TOR organic carbon (OCTR) component is assumed to be all carbon evolved at 580 °C and below, in a pure helium environment, plus the OP fraction. The total carbon (TC) is sum of OCTR and ECTR. Only the TOR OC and EC are calculated and reported.

The concentration, uncertainty, and MDL in nanograms per cubic meter for the carbon species (OC1, OC2, OC3, OC4, OPTR, OPTT, EC1, EC2, EC3, as well as OCTR, ECTR, TC) are calculated using the following equations:

$$C = 1000\frac{ng}{\mu g} * \frac{\left(A - B\right)}{V_{C\,module}} \tag{351-13}$$

$$\sigma_{Carbon} = 1000\frac{ng}{\mu g} * \frac{\sqrt{(0.608 * Max\left(P95 - B_{carbon}, mdl_{analytical}\right))^2 + (f * (A_{carbon} - B_{carbon}))^2}}{V_{C\ Module}} \tag{351-14}$$

$$mdl_{Carbon} = 1000\frac{ng}{\mu g} * \frac{Max(P95 - B_{carbon}, mdl_{analytical})}{V_{C\ Module}} \quad (351\text{-}15)$$

Where,

A_{carbon} = ambient mass loading in µg/filter

B_{carbon} = median of the field blank mass loading in µg/filter when there are ≥ 50 field blanks in that month, otherwise the number from the previous month is used.

$V_{C\ Module}$ = C-Module sample air volume (m^3)

P95 = 95th percentile of field blank measurements in µg/filter

$mdl_{analytical}$ = analytical MDL in µg/filter reported from the analytical laboratory (Table 8). The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL

f = fractional uncertainty (Table 9).

Table 8. Analytical method detection limits (MDL) in µg/filter for the carbon species.

Species	**Analytical MDLs used for data 1/1/2006 – 12/31/2019**	**Analytical MDLs used for data 1/1/2020 – current**
OC1	0.51	0.03
OC2	0.51	0.06
OC3	0.51	0.18
OC4	0.51	0.12
OPTR	0.15	0.12
OPTR at 405 nm	0.15	0.03
OPTR at 445 nm	0.15	0.06
OPTR at 532 nm	0.15	0.08
OPTR at 780 nm	0.15	0.08
OPTR at 808 nm	0.15	0.06
OPTR at 980 nm	0.15	0.12
OPTT	0.15	0.22
OPTT at 405 nm	0.15	0.18
OPTT at 445 nm	0.15	0.21
OPTT at 532 nm	0.15	0.19
OPTT at 780 nm	0.15	0.2
OPTT at 808 nm	0.15	0.19
OPTT at 980 nm	0.15	0.15
EC1	0.15	0.07
EC2	0.15	0.22
EC3	0.15	0.01
ECTR	0.15	0.23
OCTR	0.51	0.31
TC	0.57	0.43

* Prior to 2017, data for OP at different wavelengths were not reported.

Table 9. Fractional uncertainty for the carbon species.

Species	f reported for data 1/1/2005 – 12/31/2016*	f reported for data 1/1/2017 – 12/31/2017	f reported for data 1/1/2018 – 12/31/2018	f reported for data 1/1/2019 – 12/31/2019	f reported for data 1/1/2020 – current
OC1	0.23	0.27	0.23	0.24	0.21
OC2	0.15	0.13	0.11	0.10	0.09
OC3	0.13	0.13	0.13	0.11	0.09
OC4	0.15	0.13	0.13	0.14	0.16
OPTR	0.13	0.16	0.20	0.21	0.20
OPTR at 405 nm	N/A	0.18	0.18	0.19	0.19
OPTR at 445 nm	N/A	0.17	0.17	0.18	0.18
OPTR at 532 nm	N/A	0.20	0.21	0.21	0.21
OPTR at 780 nm	N/A	0.19	0.21	0.22	0.22
OPTR at 808 nm	N/A	0.19	0.20	0.21	0.22
OPTR at 980 nm	N/A	0.21	0.23	0.25	0.25
OPTT	0.13	0.12	0.14	0.15	0.14
OPTT at 405 nm	N/A	0.13	0.13	0.14	0.13
OPTT at 445 nm	N/A	0.13	0.13	0.15	0.14
OPTT at 532 nm	N/A	0.13	0.14	0.15	0.14
OPTT at 780 nm	N/A	0.13	0.14	0.16	0.14
OPTT at 808 nm	N/A	0.13	0.15	0.16	0.15
OPTT at 980 nm	N/A	0.14	0.16	0.17	0.15
EC1	0.10	0.10	0.11	0.11	0.11
EC2	0.17	0.18	0.19	0.21	0.22
EC3	0.42	0.25	0.25	0.25	0.25
ECTR	0.12	0.14	0.14	0.13	0.13
OCTR	0.08	0.09	0.08	0.07	0.07
TC	0.08	0.08	0.07	0.07	0.06

9.2.4.4 Elements (1A Module)

Elements are measured using X-ray fluorescence (XRF; PANalytical Epsilon 5) using the PTFE filters from the 1A Module.

The PANalytical XRF instruments report the elements in terms of counts per mV per second, which is converted into areal densities using element calibration factors (stored in the UCD IMPROVE database). Blank subtraction is performed on the XRF measurements by subtracting the median field blank count from the same filter lot as that of the sample filters. The field blank correction is specific to each filter lot and since the number of field

blanks from a filter lot used in a given month may not be statistically sufficient, a minimum of 35 field blanks are required before the median can be calculated. Field blank selection is therefore expanded to include field blanks from previous month(s) until at least 35 field blanks are found. The selected 35 field blanks are used to calculate batch and filter lot-specific blank correction. Areal uncertainty ($U_{element}$) is calculated as,

$$U_{element} = 1000\frac{ng}{\mu g} * \sqrt{(0.608 * Max\left((P95 - B_e), mdl_{analytical}\right))^2 + (f * (A_e - B_e))^2} \quad (351\text{-}18)$$

A_e = areal density calculated for the element measured by XRF.

B_e = median areal density of the field blank measured by XRF; ≥ 35 field blanks from before the determination date.

P95 = 95th percentile of field blank measured by XRF.

$mdl_{analytical}$ = analytical MDL in µg/cm^2 reported from the analytical laboratory (Table 10). The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL.

f = fractional uncertainty (Table 11).

0.608 = 1 / 1.645; used to estimate the one-sigma uncertainty at zero concentration from the MDL that is set at the 95th percentile, where 1.645 is the critical value for sigma in a one-tailed test for 5% significance.

Table 10. Analytical method detection limits (MDL) in µg/cm2 for the elemental species.

Species	**Analytical MDLs used for data 1/1/2006 – 12/31/2019**	**Analytical MDLs used for data 1/1/2020 – current**
Al	0.011	0.011
As	0.002	0.002
Br	0.001	0.001
Ca	0.021	0.003
Cl	0.002	0.002
Cr	0.001	0.001
Cu	0.002	0.001
Fe	0.012	0.003
K	0.005	0.001
Mg	0.021	0.02

Mn	0.003	0.002
Na	0.037	0.046
Ni	0.001	0.001
P	0.002	0.002
Pb	0.006	0.003
Rb	0.002	0.002
S	0.003	0.001
Se	0.002	0.001
Si	0.013	0.005
Sr	0.002	0.001
Ti	0.003	0.001
V	0.001	0.001
Zn	0.002	0.002
Zr	0.012	0.007

Table 11. Fractional uncertainty for the elemental species.

Species	**f reported for data 1/1/2005 – 12/31/2016**	**f reported for data 1/1/2017 – 12/31/2017**	**f reported for data 1/1/2018 – 12/31/2018**	**f reported for data 1/1/2019 – 12/31/2019**	**f reported for data 1/1/2020 - current**
Al	0.09	0.08	0.08	0.09	0.10
As	0.25	0.21	0.25	0.25	0.25
Br	0.10	0.11	0.10	0.09	0.09
Ca	0.06	0.07	0.06	0.07	0.09
Cl	0.14	0.18	0.14	0.14	0.16
Cr	0.22	0.17	0.15	0.17	0.16
Cu	0.12	0.11	0.13	0.10	0.10
Fe	0.06	0.06	0.05	0.06	0.08
K	0.03	0.05	0.03	0.04	0.05
Mg	0.15	0.16	0.15	0.15	0.17
Mn	0.13	0.13	0.14	0.13	0.13
Na	0.14	0.15	0.14	0.14	0.15

Ni	0.16	0.16	0.13	0.14	0.18
P	0.25	0.33	0.27	0.30	0.30
Pb	0.13	0.13	0.14	0.15	0.25
Rb	0.25	0.25	0.25	0.25	0.25
S	0.03	0.03	0.02	0.03	0.03
Se	0.25	0.12	0.25	0.25	0.25
Si	0.10	0.07	0.06	0.07	0.09
Sr	0.16	0.14	0.13	0.14	0.14
Ti	0.11	0.09	0.09	0.09	0.11
V	0.12	0.14	0.17	0.17	0.12
Zn	0.06	0.08	0.08	0.08	0.08
Zr	0.25	0.25	0.25	0.25	0.25

Areal densities, areal uncertainty, and areal MDL (in units of mass/area) are calculated during processing of XRF results. The concentration ($C_{element}$), uncertainty ($\sigma_{element}$), and MDL ($mdl_{element}$) in nanograms per cubic meter for the element species are calculated using the following equations:

$$C_{element} = 1000\frac{ng}{\mu g} * \frac{(A_e - B_e) * (Deposit\ area)}{V} \quad (351\text{-}19)$$

$$\sigma_{element} = \frac{(U_e) * (Deposit\ area)}{V} \quad (351\text{-}20)$$

$$mdl_{element} = 1000\frac{ng}{\mu g} * \frac{Max\left((P95 - B_e), mdl_{analytical}\right) * (Deposit\ area)}{V} \quad (351\text{-}21)$$

Where,

A_e = areal density calculated for the element measured by XRF.

B_e = median areal density of the field blank measured by XRF; ≥ 35 field blanks from before the determination date

Deposit area = area of sample deposit on the filter (cm^2), determined from the filter holder or mask size (approximately 20 mm).

U_e = areal uncertainty reported for the element measured by XRF.

P95 = 95th percentile of field blank measured by XRF.

$mdl_{analytical}$ = analytical MDL reported from the analytical laboratory. The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL.

V = 1A Module sample air volume (m^3).

9.2.4.5 Laser Absorption (1A Module)

Optical absorption is measured by a hybrid integrating plate and sphere (HIPS) system using the PTFE filter from the 1A Module. The laser absorption measurements are stored as reflectance (R) and transmittance (T) values in *hips.SampleAnalysis* table in the UCD IMPROVE database.

Results from the HIPS measurement are reported as filter absorption coefficient (fAbs) in units of Mm^{-1}, calculated from R and T. The concentration (fAbs), uncertainty (σ_{fAbs}), and MDL (mdl_{fAbs}) are calculated using the following equations:

$$fAbs = 100 * \frac{\tau_{633} * (Deposit\ Area)}{V_{A\ Module}} \quad (351\text{-}22)$$

Where,

$V_{A\ Module}$ = 1A Module sample air volume (m^3)

Deposit area = area of sample deposit on the filter (cm^2), determined from the filter holder or mask size (approximately 20 mm).

$$\tau_{633} = \frac{\log\left(Max\left(\frac{intercept + (slope\ *\ refelctance)}{transmittance}, 0.1\right)\right)}{}$$

$$\sigma fAbs = 100 * \frac{\sqrt{\left(\frac{1}{1.65} * Max\left(P95, mdl_{analytical}\right)\right)^2 + (f_{unitless}\ *\ \tau_{633})^2 * (Deposit\ Area)}}{V_{A\ Module}} \quad (351\text{-}23)$$

Where,

P95 = 95th percentile of field blank measurements.

$mdl_{analytical}$ = analytical MDL reported from the analytical laboratory (τ_{633} = 0.009, unitless). The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL.

$V_{A\ Module}$ = 1A Module sample air volume (m^3)

Deposit area = area of sample deposit on the filter (cm^2), determined from the filter holder or mask size (approximately 20 mm).

$$\tau_{633} = \log\left(Max\left(\frac{intercept + (slope * refelctance)}{transmittance}, 0.1\right)\right)$$

$f_{unitless}$ = unitless fractional uncertainty calculated from fractional uncertainty (Table 12) and nominal sample volume.

$$mdl_{fAbs} = 100 * \frac{Max\left(P95, mdl_{analytical}\right) * (Deposit\ Area)}{V_{A\ Module}} \quad (351\text{-}24)$$

Where,

P95 = 95th percentile of field blank measurements.

mdl $_{analytical}$ = analytical MDL reported from the analytical laboratory (τ_{633} = 0.009, unitless). The analytical MDL is considered the 'floor value' and is used as the reported MDL in the event that the median value of the field blanks is lower than the respective analytical MDL.

$V_{A\ Module}$ = 1A Module sample air volume (m^3)

Deposit area = area of sample deposit on the filter (cm^2), determined from the filter holder or mask size (approximately 20 mm).

Table 12. Fractional uncertainty for the laser absorption data.

Species	**f reported for data 2/28/1995 – 12/31/2006**	**f reported for data 1/1/2017 – 12/31/2017**	**f reported for data 1/1/2018 – 12/31/2018**	**f reported for data 1/1/2019 – 12/31/2019**	**f reported for data 1/1/2020 - current**
fAbs	0.03	0.06	0.06	0.05	0.06

9.2.5 Equations of Composite Variables

The following composite variables are combinations of the measured concentrations and are used in the Level 2 validation procedures described in section 9.3.3. For the composite variables, concentration is determined along with the uncertainty and MDL. The uncertainty calculations assume that the component concentrations are independent and the multiplicative factors have no uncertainty. The independence assumption is not strictly valid for many composites because of common factors, such as volume. However, the effect on the overall uncertainty is too small to warrant more complicated calculations.

9.2.5.1 Sulfate (3× sulfur from XRF) and Ammonium Sulfate (NHSO)

Sulfur is predominantly present as sulfate in the atmosphere. To compare the sulfur by XRF and the sulfate by ion chromatography, the XRF concentration is multiplied by the ratio of

sulfate to sulfur atomic mass (96.06/32.06 = 3.0). This composite is labeled S3 in the data validation plots.

The sulfate is generally present as ammonium sulfate, $(NH_4)_2SO_4$, although it can be present as ammonium bisulfate, $(NH_4)HSO_4$, sulfuric acid, H_2SO_4, gypsum, $CaSO_4 \cdot 2H_2O$, and, in marine areas, as sodium sulfate, Na_2SO_4. In many cases, the particle will include associated water, this is omitted from the calculation. In order to simplify the calculation, all sulfur is assumed to be present as ammonium sulfate. The concentrations (NHSO and S3), uncertainties (σ_{NHSO} and σ_{S3}), and MDLs (mdl_{NHSO} and mdl_{S3}) for ammonium sulfate (NHSO) and sulfate calculated from XRF sulfur (S3) are calculated using the following equations:

$$NHSO = 4.125 * S$$

$$S3 = 3 * S \quad (351\text{-}25)$$

$$\sigma_{NHSO} = 4.125 * \sigma(S)$$

$$\sigma_{S3} = 3 * \sigma(S) \quad (351\text{-}26)$$

$$mdl(NHSO) = 4.125 * mdl(S)$$

$$mdl(S3) = 3 * mdl(S) \quad (351\text{-}27)$$

For ammonium bisulfate, sulfuric acid, and sodium sulfate the factors are 3.59, 3.06, and 4.43, respectively. In the first two cases, the actual dry mass associated with sulfate is less than NHSO, and in the third case, more.

9.2.5.2 Ammonium Nitrate (NHNO)

This composite is the total dry concentration associated with nitrate, assuming 100% neutralization by ammonium. The concentrations (NHNO), uncertainties σ_{NHNO}), and MDLs (mdl_{NHNO}) are calculated using the following equations:

$$NHNO = 1.29 * NO_3^- \quad (351\text{-}28)$$

$$\sigma_{NHNO} = 1.29 * \sigma(NO_3^-) \quad (351\text{-}29)$$

$$mdl(NHNO) = 1.29 * mdl(NO_3^-) \quad (351\text{-}30)$$

9.2.5.3 Soil

The soil component consists of the sum of the predominantly soil elements measured by XRF, multiplied by a coefficient to account for oxygen for the normal oxide forms (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, TiO_2), and augmented by a factor to account for other compounds not included in the calculation, such as MgO, Na_2O, water, and CO_2. The following assumptions are made:

- Fe is split equally between FeO (oxide factor of 1.29) and Fe_2O_3 (oxide factor of 1.43), giving an overall Fe oxide factor of 1.36.
- Fine K has a non-soil component from smoke. Based on the K/Fe ratio for average sediment (*Handbook of Chemistry and Physics*), 0.6*Fe is used as a surrogate for soil K. The oxide factor for K $\left(K_2O, \frac{39.1*2+16.0\ \text{g/mol}}{39.1*2\ \text{g/mol}} = 1.2 \right)$ is added for a total Fe factor of 0.72*Fe (0.6*1.2) for the potassium oxide in soil. This increases the factor for Fe from 1.36 to 2.08.
- The oxide forms of the soil elements account for 86% of average sediment; in order to obtain the total mass associated with soil, the final factors are divided by 0.86 (*Handbook of Chemistry and Physics*). The concentrations, uncertainties, and MDLs are calculated using the following equations:

$$SOIL = 2.2*\max(Al,0) + 2.49*\max(Si,0) + 1.63*\max(Ca,0) + 2.42*\max(Fe,0) + 1.94*\max(Ti,0) \quad (351\text{-}31)$$

$$\sigma(SOIL) = \sqrt{(2.2*\max(\sigma(Al),0))^2 + (2.49*\max(\sigma(Si),0))^2 + (1.63*\max(\sigma(Ca),0))^2 + (2.42*\max(\sigma(Fe),0))^2 + (1.94*\max(\sigma(Ti),0))^2} \quad (351\text{-}32)$$

$$mdl(SOIL) = 0 \quad (351\text{-}33)$$

The soil variable is calculated for all valid XRF analyses.

9.2.5.4 Non-Soil Potassium (KNON)

Non-soil potassium is the measured fine potassium minus the soil potassium estimated from iron. Non-soil potassium is a qualitative tracer of smoke. However, the ratio of potassium/smoke mass may change as the aerosol ages. Particulate smoke potassium may be produced by the transformation of volatilized potassium, and appears to be in a smaller size range than most smoke mass. Close to the smoke source, the particulate potassium may not have time to form. For long-range transport, most other smoke mass may settle out more than potassium mass. The concentrations, uncertainties, and MDLs are calculated using the following equations:

$$KNON = (K - 0.6*Fe) \quad (351\text{-}34)$$

$$\sigma(KNON) = \sqrt{\sigma^2(K) + [0.6*\sigma(Fe)]^2} \quad (351\text{-}35)$$

$$mdl(KNON) = 0 \quad (351\text{-}36)$$

The soil factor of 0.6 may vary slightly with the site; this will produce a small positive or negative offset for baseline values when no smoke is present. Therefore, negative values are retained. KNON is calculated for all valid XRF analyses. If a concentration is less than the MDL, the concentration and uncertainty are assumed to be equal to the MDL.

9.2.5.5 Organic Carbon by Mass (OMC)

To determine the total amount of organic mass associated with the organic carbon, the ratio of organic mass to organic carbon is assumed to be 1.8. The concentrations, uncertainties, and MDLs are calculated using the following equations:

$$OMC = 1.8 \times OC = 1.8 \times (O1 + O2 + O3 + O4 + OP) \quad (351\text{-}37)$$

$$\sigma_{OMC} = 1.8 \times \sigma_{OC} \quad (351\text{-}38)$$

See equation of 351-14 for σ_{OC}.

$$mdl_{OMC} = 1.8 \times mdl_{OC} \quad (351\text{-}39)$$

See equation 351-15 for mdl_{OC}.

9.2.5.6 Black Carbon

Black carbon is estimated from the initial and final laser readings from the 3C Module quartz filter analysis. For cross-module validation, black carbon is compared to light absorption coefficient (fAbs) measured by HIPS from the 1A Module PTFE filter.

$$BC = \frac{ln\,(transfinal - transinitial)}{MAC} \quad (351\text{-}40)$$

TransFinal = Final laser transmittance value of the sample

TransInitial = Initial laser transmittance value of the sample

MAC = Black carbon mass absorption cross-section and it is a constant of 23 m^2/g at 632.8 nm wavelength.

9.2.5.7 Reconstructed Mass Using Carbon Measurements (RCMC)

Reconstructed mass is the sum of sulfate, soil, salt, elemental carbon, and organic mass. The only components not included are water and nitrate. The concentrations and uncertainties are calculated using the following equations; negative values are substituted with zero. RCMC concentration is always positive. Uncertainty is calculated as the combination of the individual uncertainties. The MDL for RCMC is zero.

$$RCMC = NHSO + Soil + 1.8 \times Chloride + ECTR + OMC \quad (351\text{-}41)$$

Where,

NHSO = ammonium sulfate concentration

Soil = soil concentration

Chloride = chloride concentration as measured by IC

ECTR = elemental carbon concentration by TOR

OMC = concentration of organic mass by carbon

$$\sigma_{RCMC} = \sqrt{\sigma_{NHSO}^2 + \sigma_{Soil}^2 + (1.8\sigma_{Chloride})^2 + \sigma_{ECTR}^2 + \sigma_{OMC}^2} \quad (351\text{-}42)$$

$$\text{mdl}_{RCMC} = 0 \quad (351\text{-}43)$$

RCMC is more relevant at sites where the neutralization of sulfate may be less than 100%, at sites with high nitrate, and at marine sites.

9.2.5.8 Reconstructed Fine Mass (RCMN)

At sites where ammonium nitrate (NHNO) is present, adding ammonium nitrate to the RCMC can make the reconstructed mass very close to the measured value. The concentrations and uncertainties are calculated using the following equations; negative values are substituted with zero. RCMN concentration is always positive. Uncertainty is calculated as the combination of the individual uncertainties. The MDL for RCMN is zero.

$$RCMN = NHSO + NHNO + Soil + 1.8 \times Chloride + ECTR + OMC \quad (351\text{-}44)$$

Where,

NHSO = ammonium sulfate concentration

NHNO = ammonium nitrate concentration

Soil = soil concentration

Chloride = chloride concentration as measured by IC

ECTR = elemental carbon concentration by TOR

OMC = concentration of organic mass by carbon

$$\sigma_{RCMN} = \sqrt{\sigma_{NHSO}^2 + \sigma_{NHSO}^2 + \sigma_{Soil}^2 + (1.8\sigma_{Chloride})^2 + \sigma_{ECTR}^2 + \sigma_{OMC}^2} \quad (351\text{-}45)$$

$$\text{mdl}_{RCMN} = 0 \quad (351\text{-}46)$$

9.3 Data Validation

Data validation performed at UCD involves assessing the quality, reliability, and integrity of the data. Watson et al. (1995) define a three-level data validation process for environmental measurement studies. The levels are only intended as general guidelines. The IMPROVE data delivered to CIRA and AQS databases are considered to be a mixture of Level 1B and Level 2 validated data. The levels are applied to IMPROVE as follows:

Level 0: Data at this level are, in essence, raw data obtained directly from the data acquiring instruments. These data can be reduced or reformatted but are unedited and unreviewed, without any adjustments for known biases or problems that might have been identified during preventative maintenance checks or audits. These data may monitor instrument operations on a frequent basis. Averaging times represent the minimum intervals recorded, and these data may

need to be aggregated to obtain averages for the sampling periods. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline shifts, span changes, or known problems been applied. IMPROVE Level 0 data includes:

- Raw pressure transducer and temperature data from the sampler flashcards or the V4 controllers before automated validity tests.
- Filter weight measurements before automated validity tests.
- XRF raw spectra.

Level 1A: Data at this level have passed several qualitative reviews for accuracy and completeness. The focus of Level 1A validation is to obtain as complete a data set as possible. IMPROVE Level 1A data validation includes:

- Reviewing operator log sheets to verify operation of the sampler.
- Verifying operator log sheet entries against sampler flashcard data.
- Assigning correct flow and temperature source codes.
- Assigning status flags to invalid or questionable samples to reflect sampler malfunctions, site or laboratory operator errors, or power outages.
- Identifying, investigating, and flagging data that are beyond reasonable bounds or are unrepresentative of the variable being measured (e.g., flow rate measurements that change significantly over the sampling period).

Level 1B: Data at this level have passed additional automated quantitative and qualitative reviews for accuracy and internal consistency. Discrepancies that cannot be resolved are reported to the measurement laboratories for investigation. Data that deviate from consistency objectives are individually examined for errors. Obvious outliers (e.g., -85 °C temperature) are invalidated by applying a status flag. Changes to the data (e.g., swapping dates on consecutive samples) are recorded and documented by applying status flags and providing comments. Level 1B data review is carried out using custom software developed for this purpose. IMPROVE level 1B data validation includes:

- Verifying filter weight measurements to ensure that
    - the range is within specified limits;
    - the post-weight is greater than the pre-weight.
- Examining daily flow rates based on a report that identifies flow rates with significant variations over 24 hours.
- Setting status flags when deviations from nominal operational settings have occurred (e.g., flow rates outside quantitative tolerances).
- Examining the ion, carbon, and elemental field blank data for evidence of sample swaps.
- Examining individual data points identified as potential sample swaps between two adjacent dates.
- Comparing the analytical data to expectations based on historical data.

Level 2: Level 2 data validation occurs after data from various measurement methods have been assembled in the UCD IMPROVE database. Level 2 validation involves cross-module

comparisons of various species. Data submitted to CIRA and AQS databases are considered to be validated at Level 1B and Level 2. Additional Level 2 data validation is performed at CIRA.

IMPROVE Level 2 data validation consists of site-by-site and network-wide examination of time series and scatter plot of data, including:

- Comparing sulfur and sulfate concentrations.
- Comparing elemental carbon, black carbon, and light absorption coefficients.
- Examining PM_{10} mass and $PM_{2.5}$ mass for cases where $PM_{2.5}$ is greater than PM_{10} and where $PM_{2.5}$ and/or PM_{10} are zero or negative.
- Comparing $PM_{2.5}$ gravimetric mass and reconstructed mass.
- Comparing organic carbon and elemental carbon.

Level 3: This level of data review is applied after data delivery and is beyond the scope of data validation performed by UCD. At this level, the data are reconciled with other research findings, such as modeling results or theoretical predictions. Level 3 validation continues for as long as the CIRA and AQS databases are maintained.

Data validation is not a linear process. A significant amount of data validation (including Level 0) is performed by the analytical laboratories before the data are delivered to the quality assurance officer. The SOPs for the analytical laboratories describe their data validation procedures in detail. The following sections discuss the Level 1 and Level 2 validation processes that occur once the data are received from the field and laboratories.

9.3.1 Definition of Status Flags

Status flags are used as standardized abbreviations describing the status of individual sample results, and are assigned during the Level 1 and 2 validation processes (Table 13). Samples associated with “Terminal” flag are invalidated for a variety of reasons, and no concentration, uncertainty, or MDL values are reported, whereas those associated with “Informational” flag are still valid samples and concentrations, uncertainties, and MDLs are reported. The “Temporary” flags are assigned for a variety of reasons to aid data validation; they are replaced before final data reporting.

Table 13. Status flags and their definitions.

Status Flag	**Description**	**Flag Type**	**AQS code**
BI	Bad Installation of Sample Cartridge or Filter	Terminal	BJ
CG	Sample Flow Rate Out of Spec.	Informational	W
CL	Sample Flow Rate Out of Limits	Terminal	AH
DA	Sample not analyzed	Terminal	AM
DE	Reported value is an estimate	Informational	LJ
EP	Equipment Problem	Terminal	AN
LF	Sample Flow Rate Out of Spec.	Informational	W
NF	No Flow	Temporary	

NM	Normal	Informational	
NS	No Sample Collected/Late Sample Change	Terminal	AF
OL	Site Off Line	Terminal	AD
PO	Power Outage	Terminal	AV
QD	Questionable Data	Temporary	4
SA	Sampling Anomaly	Informational	1
SO	Still out	Temporary	
SP	Same-day Field Blank/Sample Swap	Informational	
SW	Sampling Dates Swap	Informational	
TO	Timing Outside normal bounds	Informational	Y
TU	Incorrect Time (with time shift >= 6hrs)	Informational	3
UN	Undetermined Weight	Informational	AM
XX	Sample Destroyed, Damaged or Contaminated	Terminal	AJ
PM	Undefined but allowed by SWAP as informational	No longer used	
NR	Not Reanalyzed by DRI	No longer used	
NA	Not Applicable	No longer used	AM
QA	Quality Assurance	No longer used	4
QC	Quality Control	No longer used	
RF	Really High Flow Rate	No longer used	W
PC	Possible Contamination	No longer used	4

9.3.2 Level 1 Validation Procedures

Level 1 validation is conducted throughout the sample handling and analysis processes. Validation for the gravimetric $PM_{2.5}$ and PM_{10} masses, $PM_{2.5}$ elements, optical absorption, ions, and carbon data is conducted by the laboratory technicians performing the analyses. The following Technical Information (TI) documents are available for mass validation and XRF data validation:

Mass validation: *Sample Handling TI 251Q: General Laboratory Procedures*, section 5.8

XRF validation: *XRF TI 130E: Level I Validation*

HIPS validation: *HIPS SOP 276: Optical Absorption Analysis of $PM_{2.5}$ Samples*

Level 1 flow rate validation is performed as a four-step process. Additional Level 1B validation checks are performed on data completeness and field blank validity before processing the concentration data. The following sections discuss the flow validation and Level 1B checks in detail.

9.3.2.1 Flow Validation

Flow data from the V4 controllers is automatically transmitted daily to the UCD IMPROVE database for near real-time review by the Sample Handling Laboratory (SHL) and Field Group. Field log sheets and flashcards (with raw pressure transducer readings) are also available as backup flow data and are shipped with the physical sampled filters from the field sites to the UCD SHL. The SHL receives flow data from the V2 controllers by flashcard and log sheet; only one IMPROVE site has the older V2 controller (BYIS). As part of the Level 1A validation process, flow data are reviewed for inconsistency resulting from sampling anomaly and/or sampler malfunction. In these cases, the sample status is changed from NM to a terminal or temporary flag, and filter/sample event comments are provided. When automatically transmitted flow data are not available, the flashcard, log sheet, or nominal value can be used instead. The Flow Source Code (FlwSrc) for the affected sample is changed from the default (MC) to log sheet (LC/LO) or nominal value (NF) to ensure accurate calculation of the average flow rate. Detailed procedures on flow data ingestion and Level 1A validation can be found in the *Sample Handling TI 251E Entering Log Sheets and Simple Problem Diagnosis*.

Prior to checking flow data, the quality assurance officer processes flow data using the SQL query described in section 9.2 to derive the daily average flow rate and elapsed time (ET). The flow processing code automatically assigns non-normal flow status flags to the samples with flow rates that deviate from the nominal values. Table 14 and 15 list the types of flow flags and the associated criteria for applying them to $PM_{2.5}$ and PM_{10} samples, respectively.

Table 14. Definitions and application criteria of automatic flow flags for $PM_{2.5}$.

Automatic Flow Flag	**Definition**	**Type**	**Criteria for Application for $PM_{2.5}$ Samples**
CL	Clogged Filter	Terminal	Flow rate < 15 L/min for more than 6 hours if flashcard data are used Average flow rate < 15 L/min if log sheet values are used
CG	Clogging Filter	Informational	Flow rate < 18 L/min for more than 6 hours if flashcard data used Average flow rate < 18 L/min if log sheet values are used
LF	Low/high flow rate	Informational	Average flow rate < 19.7 L/min or > 24.1 L/min
PO	Power Outage	Terminal	Elapsed time < 1080 minutes (18 hours)
EP	Equipment Problem	Terminal	Elapsed time > 1800 minutes (30 hours) or is missing
TO	Timing Outside normal bounds	Informational	Elapsed time between 1080 minutes (18 hours) - 1380 minutes (23 hours) or 1500 minutes (25 hours) – 1800 minutes (30 hours)

The 2016 IMPROVE $PM_{2.5}$ cyclone characterization test yielded results consistent with the characterization performed by John and Reischl (1980). The particle size cut of the cyclone at any operating flow rate can be determined from the following equation:

$$D_{50} = 52.5 * Q^{-0.99} \quad (351\text{-}47)$$

Where,

D_{50} = 50% cutoff diameter (in µm)

Q = flow rate (in L/min)

Note that at the nominal flow rate of 23 L/min, the 50% cutoff diameter is 2.36 µm rather than 2.5 µm.

The criteria for the CL, CG, and LF flags are determined based on calculation limitations, performance testing, and particle size cut. If >24 15-minute (6 hours in total) flow rate readings are below 15 L/min, or if the average flow rate is below 15 L/min when log sheet data are used, the sample is flagged as CL and no concentration data are reported. The $PM_{2.5}$ cyclone cut point is 3.6 µm at 15 L/min.

The criteria for applying CG and LF flags are based primarily on cut point characterization of the $PM_{2.5}$ cyclone. The cut point is 3.0 µm, 2.75 µm, and 2.25 µm at 18 L/min, 19.7 L/min, and 24.1 L/min, respectively. The 2.25 - 2.75 µm range is considered a reasonable range of particle cut points for a data labeled as $PM_{2.5}$.

A similar set of flags is applied to the PM_{10} data (Table 15), but with several differences in the criteria, due principally to the lower flow rate at which the PM_{10} sampler operates. The relationship between the PM_{10} Sierra cyclone and particle size cut is not well characterized so the criteria are determined somewhat arbitrarily. It is important to note that under circumstance of a failing pump that produces less vacuum, equation (351-2) is no longer true and the calculated flow rates for the PM_{10} module are not valid.

Table 15. Definitions and application criteria of automatic flow flags for PM_{10}.

Validation Flag	**Definition**	**Type**	**Criteria for Application for PM_{10} Samples**
CL	Clogged Filter	Terminal	Flow rate < 10 L/min for more than 6 hours if flashcard data are used Average flow rate < 10 L/min if log sheet values are used
CG	Clogging Filter	Informational	Flow rate < 14 L/min for more than 6 hours if flashcard data are used; Average flow rate < 14 L/min if log sheet values are used
LF	Low/high flow rate	Informational	Average flow rate < 15 L/min or > 18 L/min
PO	Power Outage	Terminal	Elapsed time < 1080 minutes (18 hours)
EP	Equipment Problem	Terminal	Elapsed time > 1800 minutes (30 hours) or is missing

TO	Timing Outside normal bounds	Informational	Elapsed time between 1080 minutes (18 hours) - 1380 minutes (23 hours) or 1500 minutes (25 hours) – 1800 minutes (30 hours)

Several Level 1B checks on the 15-minute raw flow data are performed by running the *flow.check* function (for both the V2 and V4 controller data) in the *datvalIMPROVE* R package. To perform these checks, open an R environment (such as RStudio) and run the following command:

[month_flow] <- datvalIMPROVE::flow.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], site = ['%'], list_all = ['FALSE'], server = 'production')

When *list_all* is set to FALSE, the function returns a report that lists all the samples during the date period specified with abnormal flow variability, abnormal sampling temperature, and number of records for further investigation. If the *list_all* argument is set to TRUE, only the sample events with relative standard deviation out of range will be returned. The analyst can perform the checks for all active sites in the network by setting *site = '%'* or just for a particular site by specifying the site name. Several criteria are checked:

- Abnormal flow variability: > 8% during a 24-hour sampling period; can be caused by equipment installation problems or steady pressure drop from heavily loaded filter.
- Abnormal sampling temperature: relative standard deviation of temperature < 0.01% or > 10%; average temperature < 20 °C or > 40 °C.
- Abnormal number of records: number of 15-minute flow readings is < 72 rows (equivalent to 18 hours of run time) or > 104 rows (equivalent to 26 hours of run time).

Additional criteria implemented for the V4 controller include:

- The 15-minute raw pressure readings that are out of range (CYC pressure < -1.25 or > 1.25; ORI pressure < 0 or > 15) are registered as NULL and excluded from the 24-hour average flow calculation.
- The 15-minute raw cyclone pressure readings that are slightly below 0 (-1.25 ≤ CYC pressure ≤ 0) are treated as 0 in the 24-hour average flow calculation.

9.3.2.1.1 Flow Validation Report

The flow validation report is generated as an Excel spreadsheet and is populated using the data returned from running the *flow.check* function as described above. The spreadsheet has several tabs as described below:

- V2 Controller Flow Review: This sheet is populated with flow data from sites still using the V2 controller (e.g. BYIS1). Generate this data by running the following command in R:

  View([month_flow]$OldController)

  Copy/paste information into the spreadsheet and color code the modules (A = red, B = Yellow, C = Green, and D = Blue). Three asterisks (***) are used to indicate data issues.

- V4 Controller Flow Review: This sheet is populated using flow data from sites using the V4 controller. Generate this data by running the following command in R:

  View([month_flow]$NewController$MainCheck)

  Copy/paste information into the spreadsheet and color code the modules (A = red, B = Yellow, C = Green, and D = Blue). Three asterisks (***) are used to indicate data issues.

- V4 Controller Solenoid Check: This sheet is populated with flow source records for cases where the open solenoid position is not equal to the cartridge position. Generate this data by running the following command in R:

  View([month_flow]$NewController$SolenoidCheck)

- CG, CL, LF, PO: These sheets contain lists of samples where the flow status is flagged as CG, CL, LF, or PO and require confirmation of appropriate flagging (see Tables 12 and 13). Generate this data by running the following command in R:

  [month_flowflag] <- datvalIMPROVE::flow.status(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], flowflag = [('CG', 'CL', 'LF', 'PO')], server = 'production')

  To generate a list with only one of the flow flags, set the *flowflag* argument to equal one of the four flags. Copy/paste the results to the appropriately labelled sheet within flow validation report.

- No Flow Data: This sheet contains a list of samples that are not in alignment with average flow rates. Generate this data by running the following command in R:

  [month_missing] <- datvalIMPROVE::flow.completeness(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = 'production')

To further investigate the data returned from the flow checks and to validate flow data, flow plots are carefully reviewed (IMPROVE Flow Graphs; https://shiny.aqrc.ucdavis.edu/FlowRates/). The Flow Source Code is assigned if the primary source (MC; automatically transmitted flow data or flash card) is not reliable. Guidelines for validating flow data include:

- Review the flow charts to identify unstable flow readings. Evaluate to determine if there is an absence of pattern or if the flow is changing gradually during the sampling day. No pattern indicates a potential issue requiring further investigation. Gradual change throughout the sampling period may be caused by heavy loading.

- If automatically transmitted flow data and flashcard data are not available or reliable, use log sheet data which can be retrieved from the Filters page of IMPROVE Management Site.
- The Flow Source Code or Filter Status Code can be updated as needed from the Filters page of the IMPROVE Management Site.
- Utilize the Average Flow Plot in the Flow Graphing App to further evaluate flow data.
- Utilize the Early Review page in the IMPROVE Data App to view site-by-site analysis data, which can be used to help evaluate flow issues.

Finally, all samples flagged as terminal (i.e., CL and PO) by the flow processing code are manually reviewed for errors. In cases where valid samples are flagged as invalid (e.g., corrupt flash card files or faulty transducer readings), the flow source code is changed and average flow rate is reprocessed to correct the sample status.

9.3.2.2 Level 1B Checks

The analysis data reported by the measurement laboratories are ingested into the UCD IMPROVE database to their corresponding tables (e.g., analysis.Carbon, analysis.CarbonLaser, hips.SampleAnalysis, analysis.Ions, and analysis.Mass), as described in section 9.1. Several checks are performed using the *datvalIMPROVE* package in R, including:

- Data Completeness: the *completeness.check* function returns records with missing analytical data for each module. To perform these checks, run the following command in the R environment:

  [month_year_check] <- datvalIMPROVE::completeness.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], module_type = ["module"], data_type = ["analysis type"], server = "production")

  This command will perform the completeness check for data within the date range (*startdate* to *enddate*), for the specific module (*["module"]* can be A, B, C, or D), and data type (*["analysis type"]* can be xrf, Mass, hips, Ions, or Carbon). The last argument in the command specifies that the calculations will use the production database (i.e. the IMPROVE operational database).

  If any analyses are missing, confirm that data are missing and contact the appropriate analysis lab to confirm the status of the results.

- Field Blank Swap: the *ions_fb.check*, *elements fb.check*, and *carbon_fb.check* functions check for possible swap between same-day field blanks and samples for nylon, PTFE, and quartz filter samples. To perform these checks, run the following command in the R environment:

  [month_year_ion_check] <- datvalIMPROVE::ions_fb.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], by = ["ions species"], sameday_swap_only = ['FALSE'])

[month_year_ion_check] <- datvalIMPROVE::elements_fb.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], by = ["element species"], sameday_swap_only = ['FALSE'])

[month_year_carbon_check] <- datvalIMPROVE::carbon_fb.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], by = ["carbon species"], sameday_swap_only = ['FALSE'])

This command will perform the checks for data within the date range (*startdate* to *enddate*), and will provide a 'Yes' or 'No' response to indicate if the field blank mass loading of the specified species (*["ions species"]*, e.g. "Sulfate" or (*["elements species"]*, e.g. "S" or *["carbon species"]*, e.g. "ECTR") is higher than the associated sample mass loading. If *sameday_swap_only* is set to 'FALSE', all records will be returned. To return only the possible same-day swaps, set to 'TRUE'.

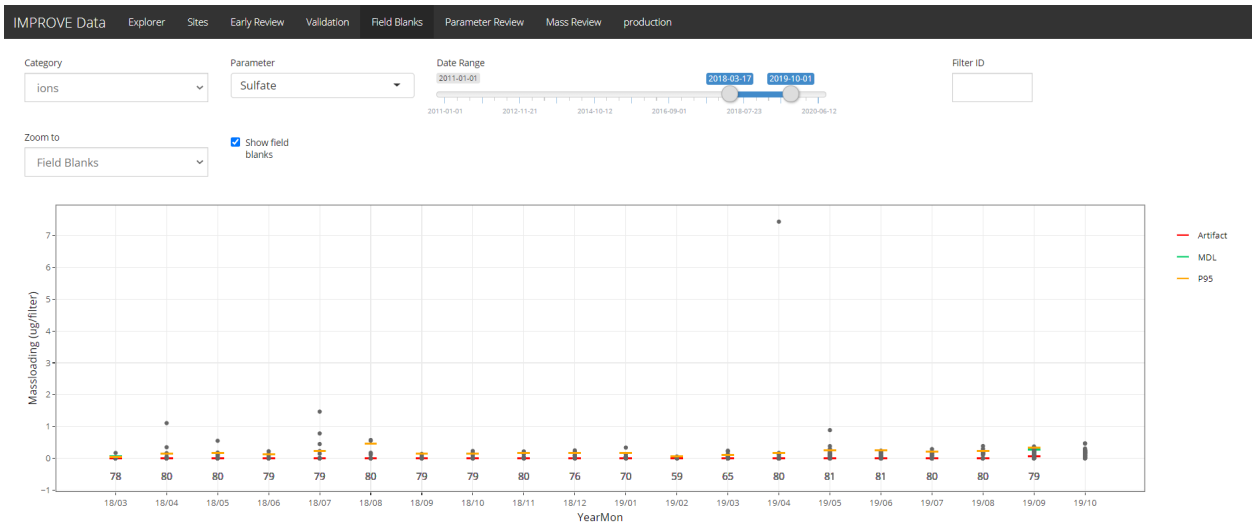
Review the results to determine if there are sample and/or the field blank issues. The field blank may have been used as a sample and have similar mass loadings to the sample, and/or the sample may have been used as a field blank and have mass loadings lower than expected. However, the sample should also be investigated for issues independent of a swap. In some instances, the sample may have actual low concentrations similar to the field blank. Field blank contamination is also possible, for example zinc contamination from XRF analysis or chloride contamination from IC analysis, in which case only certain field blank species would be elevated relative to the sample.

- Evaluate Field Blanks: Typically, for ions, sulfate is the primary species used for sample versus field blank comparison (followed by nitrate and then chloride). For elements sulfur (S) is the primary species (followed by sodium (Na) and then silicon (Si)). For carbon, ECTR, OCTR, OPTR, and TCTC are the primary species used for field blank comparison.

  For all analysis types (ions, carbon, elements, and mass), field blank data across the network can be compared using the Field Blanks tab in the IMPROVE Data website (https://shiny.aqrc.ucdavis.edu/ImproveData/; Figure 4). The mass loading of a specified parameter should be compared to field blank data from the same month as well as to the network history for both high and low cases (although the latter are rare). From the Field Blanks tab, if a point is selected, the mass loadings for all species measured on the field blank and sample filters are displayed for comparison. Plots on the Validation tab should also be reviewed to determine if a sample value is unusually low.

  Artifact and MDL values are calculated using field blank results and are expected to vary month-to-month; they are calculated for the entire network and can be impacted by shifts in field blank concentrations. As such, the artifact, MDL, and field blank 95^{th} percentile values are reviewed to identify processing issues as well as evaluate the results to determine if any field blank high mass loading cases are causing unexpected impacts. The artifact and MDL calculation methods are meant to be robust against occasional field blank outliers.

Figure 4. Screen shot of the IMPROVE Data website Field Blanks tab.



* For elements, carbon, and ions, since there's a minimum requirement on field blank count, the statistics (artifact, mdl, P95) are not necessarily calculated from the field blank individuals collected/shown in that month only. The field blanks from adjacent months may have been used too.

Following the checks, concentrations, MDLs, and uncertainties are processed and posted in the analysis.Results table using the *improve_calculate_and_post* function in the *crocker* package. To perform the processing, run the following command in the R environment:

[month_data] <- crocker::improve_calculate_and_post([YYYY], [MM], 'production', AnalysisQcCode = 1, comment = ['Initial Posting'], replacingId = NULL, replacingQcCode = NULL)

This command calculates concentrations, uncertainties, and MDLs for all measured and derived parameters for the year *([YYYY])* and month *([MM])*, using all data from the production database, and appends the processed data to the analysis.Results or analysis.CompositeResults table in the UCD IMPROVE production database as an analysis set. It also inserts a records into the analysis.ResultsSets table that provides summary information for this set, including the *comment* and *AnalysisQcCode*. Routine data uses *AnalysisQcCode = 1*. During Level 2 validation, the data may be modified and *improve_calculate_and_post* is run again and a new complete data set is posted to the database. When data is re-run/posted, the following actions need to be taken for version control and data integrity:

- Add comment to describe the new dataset;
- Change the analysis QC code of the previously posted dataset(s) by including the data set ID of the previous posting (*replacingId*) and the analysis QC code (*replacingQcCode*) that should be associated with that data set.

The following additional checks are performed:

- Elapsed Time and Sampling Days: Checks are performed by running the *etime.check* and *daycount* functions in *datvalIMPROVE*. These checks ensure there are no records with ET greater than 24 hours and no sites with less than 10 or more than 11 sampling

days (February is typically an exception). To perform these checks, run the following command in the R environment:

[month_time] <- datvalIMPROVE::etime.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production")

[month_days] <- datvalIMPROVE::daycount(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production")

- Questionable Data (QD): To guide the Level 2 validation, a list of filters with the QD flag (QD – questionable data) is generated. To generate the list, run the following command in the R environment:

  [month_QD] <- datvalIMPROVE::QD.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production")

  QD status is typically assigned by the sample handling lab technicians during initial inspection of the physical samples and the raw flow rate data. These cases are investigated by reviewing the data in the Validation plots and other tools, such as comparing results with neighboring sites. QD flags are resolved and removed by requesting further analysis and/or changing the status back to NM or assigning appropriate terminal or informational flags. There should be no records with QD in the status field in the delivery files.

- Concentration Range: The *Validsta_BadData* function in *datvalIMPROVE* uses a set of criteria listed in the R code to generate a list of results for cases where a valid sample has concentration data outside of defined normal ranges. To generate the list, run the following command in the R environment:

  [month_ValidSta] <- datvalIMPROVE::ValidSta_BadData(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production")

  The results are reviewed using techniques described in section 9.3.3 to investigate potential analysis issues, variations in uncertainty/MDL, and historical and nearby site comparisons. Reanalysis is requested when necessary/possible.

- Objective Code: The *ObjCode.check* function in *datvalIMPROVE* performs a check on the ObjectiveCode field in the data file. This field should only contain RT (routine) or CL (collocated). To perform this check, run the following command in the R environment:

  [month_Obj] <- datvalIMPROVE::ObjCode.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production")

Many of the functions described in this section (section 9.3.2) and section 9.3.3 can be performed simultaneously using the *datvalIMPROVE::improve_validate* function. This function should be run at the beginning of initial validation as well as prior to delivery. Perform this check using the following command in the R environment, and evaluate the output from the checks described below for initial validation:

[month_output] <- datvalIMPROVE::improve_validate(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'])

- **output$flow_completeness –** flow.completeness
- **output$flow_status -** flow.status
- **output$elapsed_time -** etime.check
- **output$day_count –** daycount
- **output$objective_code –** ObjCode.check
- **output$mass** - mf_mt.check
- **output$rcm -** mf_rcm.check
- **output$swap -** swap.check
- **output$QD -** QD.check
- **output$validatsta_bad -** Validsta_BadData

9.3.3 Level 2 Validation Procedures

Level 2 validation is performed by comparing site-by-site concentration data obtained from different modules as well as by assessing network-wide long-term trends using a variety of R scripts and data visualization tools.

9.3.3.1 Cross-Module Comparison

9.3.3.1.1 1A Module versus 2B Module

Quality assurance for the 1A and 2B Modules consists of comparing the measured concentrations of sulfur and sulfate. Sulfur concentrations are reported through elemental analysis of the PTFE filter from the 1A Module, while sulfate concentrations are determined by ion chromatography analysis of the nylon filter from the 2B Module. Discrepancies between 1A Module sulfur (times three, S3) and 2B Module sulfate (SO4) concentrations are investigated. If an analytical error is suspected, a request is sent to the corresponding laboratories for a reanalysis of the sample.

The *swap.check* function in the *datvalIMPROVE* package returns samples marked as "swap" and/or "outlier". To perform this check, run the following command in the R environment:

[month_swap] <- datvalIMPROVE::swap.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server ="production", type =["swap or outlier"])

The *type* argument specifies the records that should be shown in the output and can be "swap", "outlier", "swap and outlier", "swap or outlier", and "all".

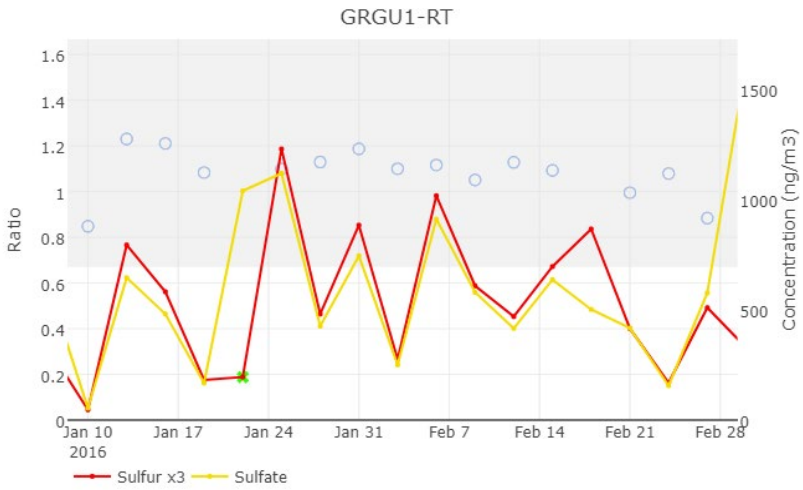
For checking possible sample swaps, successive pairs of data are examined using the algorithm outlined below. In equation (351-47), two indices for each pair of sulfur and sulfate data are calculated using data from the current and the next sampling days (referred to as subscript 1 and 2, respectively).

$$Index1 = \left(\frac{S3_1}{SO4_1} - 1\right) \times \left(\frac{S3_2}{SO4_2} - 1\right) \qquad Index2 = \left(\frac{S3_1}{SO4_2} - 1\right) \times \left(\frac{S3_2}{SO4_1} - 1\right) \qquad (351\text{-}48)$$

If $PM_{2.5}$ sulfur is in the form of sulfate, the S3/SO4 ratio is close to unity. If the samples are not subject to a swap, *Index1* would be close to zero and *Index2* would be large (and may be either positive or negative). The criterion for flagging a pair of samples as swap is when *Index1* < -0.03 and 0.05 < *Index2* < 0.05, which have been set empirically. The criterion for the "outlier" flag is when the S3/SO4 ratio < 0.667 or > 1.8.

The S3/SO4 plots in the Early Review and Validation tabs on the IMPROVE Data Site (https://shiny.aqrc.ucdavis.edu/ImproveData/) are used to further investigate samples flagged as swap and/or outlier. Figure 5 shows an example of an outlier pair at the GRGU1 site on 1/21/2016. On that day, the sulfate concentration is 1041.06 ng/m^3 while the S3 is 195.51 ng/m^3, yielding a S3/SO4 ratio of 0.19, well below the acceptable range. In cases like this, the flow rate and elapsed time are first examined to make sure the correct flow source code is assigned. If an analytical error is suspected, the XRF and/or IC laboratories perform a reanalysis. If the reanalysis results resolve the issue, the sample mass loadings are updated in the UCD IMPROVE database and the concentration data reprocessed. If the reanalysis results are the same as the original analysis, the samples may be flagged as terminal with XX (Sample Destroyed, Damaged, or Contaminated) status.

Figure 5. S3/SO4 comparison plot for the GRGU1 site showing the 1/21/2016 sample pair as an outlier (green x).



Similar to the sulfur and sulfate comparison, chlorine (from XRF analysis of the Module 1A filter) and chloride (from IC analysis of the Module 2B filter) concentrations can also be compared and can be used as supporting evidence for issues identified during the sulfur and sulfate comparison. It may also be possible to identify chloride contamination by comparing chlorine to chloride.

When reanalysis yields changes to results, further action is required:

- For elements from the 1A filter, the analysis laboratory will assign the appropriate analysis QC code to each of the result sets so that only one set is marked as valid. The updated results can be viewed in the Early Review S/SO4 plot to confirm that the issue(s) have been resolved. Appropriate comments should be added to the affected filter(s) to indicate that reanalysis was performed, briefly explaining the reasoning, and state which set of results (original or reanalysis) are reported.
- For ions from the 2B filter, the analysis lab sends updated data files, which must be ingested following the steps outlined in section 9.1.2. A list should be generated of filter IDs for which additional results have been ingested into the database. The comments from the analysis lab are reviewed to determine which set of analysis results to report, and the analysis QC code is changed using the QC review tool (https://improve.aqrc.ucdavis.edu/AnalysisData/Ions/IonsQcReview). For example, if the analysis lab indicates that the reanalysis results should be reported, the invalid analysis QC Code (= 0) should be assigned to the original results and the valid analysis QC Code (= 1) should be assigned the newly ingested reanalysis results. The updated results can be viewed in the Early Review plots to confirm that the issue(s) have been resolved. Appropriate comments should be added to the affected filter(s) to indicate that reanalysis was performed, briefly explaining the reasoning, and state which set of results (original or reanalysis) are reported.

9.3.3.1.2 1A Module versus 3C Module

The light absorption coefficient (fAbs) at 635 nm is measured by HIPS from the 1A Module PTFE filter and is compared qualitatively with the elemental carbon (EC) concentration measured by TOR from the 3C Module quartz filter as well as with the black carbon (BC) concentrations estimated from the initial and final laser readings from the 3C Module quartz filter analysis. Visual inspection of the data is performed to identify outliers using the fAbs, BC, and EC time series plot on the Validation page of the IMPROVE data website. Figure 6 shows an example comparison plot of fAbs (times 100), EC, and BC from the BOND1 site. Black carbon and fAbs are both optical measurements and are expected to compare well, whereas fAbs and EC are determined by different methods and may not be consistently comparable. If an analytical error in either measurement

is suspected, other measurement data from the same module is examined to determine validity of the sample.

The relationship between EC, BC, and fAbs is used to evaluate the carbon and HIPS results and select samples for carbon reanalysis. However, the relationships between these parameters vary across sites and seasons, making quantitative criteria ineffective for identification of outliers. As such, site-specific historical results and results from nearby sites are used to provide insight into anomalous samples. Issues identified during the comparison of EC, BC, and fAbs results can be further investigated using qualitative checks and criteria to evaluate 3C Module carbon results (OC, EC, and TC) independently of fAbs (Table 16).

Table 16. Qualitative checks and criteria for carbon (OC, EC, and TC) validation.

Analytical Issue	Considerations
OC/EC split point	Evaluate and compare OC, EC, and TC values.
Laser response	Evaluate EC 808 nm versus EC 635 nm (ECTR); dissimilar results indicate a laser issue.
Laser issue	Consider EC 635 nm (ECTR) versus all other EC wavelengths; if only EC 635 nm is zero, the issue is likely specific to the 635 nm laser.

In addition, the following points should also be considered:

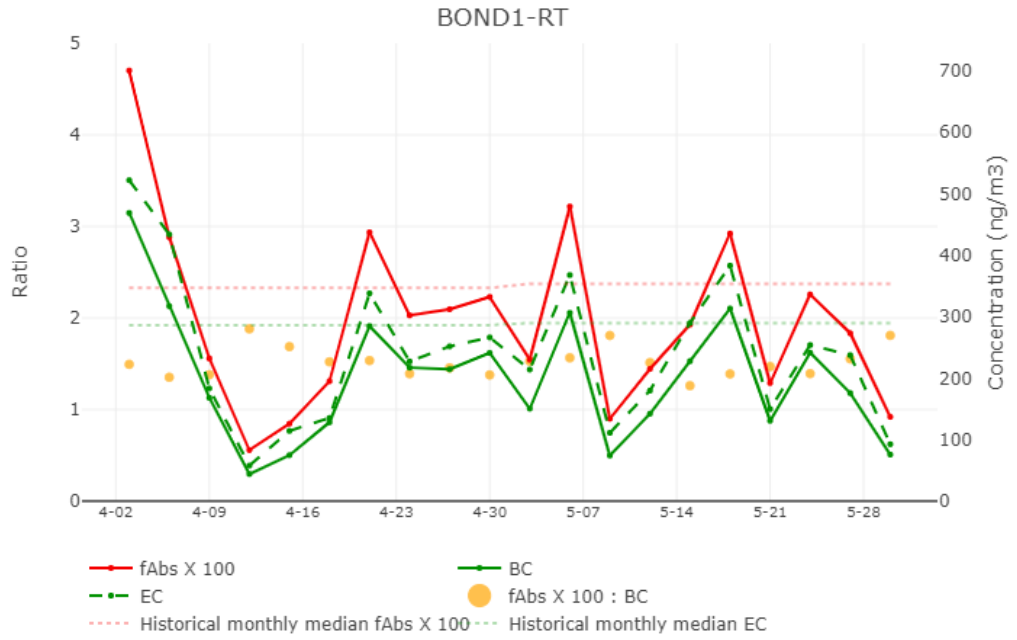
- Consider the trend of ECTR relative to fAbs and BC. If ECTR is low, investigate to determine if it is anomalous or if there have been other occurrences in recent months/years.
- Evaluate $PM_{2.5}$ relative to RCMN. If ECTR is unexpectedly high/low, then re-evaluate OCTR and ECTR. If OMC is unexpectedly high/low, then re-evaluate OCTR and ECTR.
- Compare ECTR and OCTR to nearby sites.
- Evaluate the OCTR/ECTR ratio at the site relative to recent days/months/years.
- Investigate ECTR values that are negative or zero. If values are negative, evaluate the original mass loading relative to the artifact correction. If the value is 0.00 but ECTT has a value, there may be a split point issue.
- Compare ECTR results at different wavelengths using the ECTR scatter plot available on the early review tab. For some sources, ECTR 635 nm should be close to ECTR 808 nm. For sources that emit brown carbon (e.g., fire), ECTR 405 nm is larger than ECTR 635 nm. If ECTR = 0 at 635 nm but ECTR at all other wavelengths are non-zero, there is likely an issue with the 635 nm laser.
- Inspect TC replicate and/or reanalysis results. If different is > 10%, request a third analysis. The maximum number of punches available for a quartz filter is three; there will be cases where reanalysis is not possible. In

such cases, proper documentation regarding filter/ sampling events leading to the use of extra punch should be documented.

When reanalysis yields changes to results, further action is required:

- For fAbs from the 1A filter, the analysis laboratory will assign the appropriate analysis QC code to each of the result sets so that only one set is marked as valid. The updated results can be viewed in the early review plots to confirm that the issue(s) have been resolved. Appropriate comments should be added to the affected filter(s) to indicate that reanalysis was performed, briefly explaining the reasoning, and state which set of results (original or reanalysis) are reported.
- For carbon from the 3C filter, reanalysis results received from the analysis laboratory must be ingested following the steps outlined in section 9.1.2. A list should be generated of filter IDs for which additional results have been ingested into the database. The comments from the analysis lab are reviewed to determine which set of analysis results to report, and the analysis QC code in the [IMPROVE_2.1].[analysis].[CarbonRun] production database table must be changed accordingly. This can be done using the QC review tool available at https://improve.aqrc.ucdavis.edu/AnalysisData/Carbons/CarbonsQcReview. For example, if the analysis lab indicates that the reanalysis results should be reported, the invalid analysis QC Code (= 0) should be assigned to the original results and the valid analysis QC Code (= 1) should be assigned the newly ingested reanalysis results. If the analysis laboratory indicates that the reanalysis results are within replicate criteria or if only one species was affected, the replicate or reanalysis analysis QC code (= 2) should be assigned to the relevant set of results and parameters that were unaffected by the issue. The updated results can be viewed in the early review plots to confirm that the issue(s) have been resolved. Further, the analyst should review the mass loadings for all sets of analysis results for a given filter. Appropriate comments should be added to the affected filter(s) to indicate that reanalysis was performed, briefly explaining the reasoning, and state which set of results (original or reanalysis) are reported.

Figure 6. Comparison plot of light absorption coefficient measurements (fAbs, times 100) from 1A Module and elemental carbon (EC) measurements and black carbon measurements from 3C Module at BOND1 site.



9.3.3.1.3 1A Module versus 4D Module

1A module $PM_{2.5}$ mass and 4D module PM_{10} mass are reviewed and compared (Figure 7). The *mf_mt.check* function in the *datvalIMPROVE* package is run using the following command in the R environment:

[month_PM] <- datvalIMPROVE::mf_mt.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production", problemonly = ["TRUE"])

The check returns a list of samples flagged as mass outliers if the *problemonly* argument is set to 'TRUE' and any of the following criteria are met:

- $PM_{2.5}$ or PM_{10} mass concentration is negative (negative value does not necessarily mean invalid).
- $PM_{2.5}$ mass is greater than PM_{10} mass and Z-score > 1.
- PM_{10} mass is abnormally high and Z-score > -43 (the number 43 is set empirically).

Where the Z-score is calculated using equation (351-48),

$$Z\_score = 1.41 \times \frac{PM_{2.5} - PM_{10}}{\sqrt{(unc_{PM2.5})^2 + (unc_{PM10})^2}} \qquad (351\text{-}49)$$

For samples that are flagged for one of the above cases, further investigation is required to identify the cause:

- Use the mass time-series plot on the Validation page;
- Investigate occurrence of a possible swap ($PM_{2.5}$ to PM_{10} swap, adjacent day swap, etc). If a swap may have occurred request further investigation from the Sample Handling Laboratory, and correct swapped data as needed.
- If the data appear abnormal, request confirmation of the post-weight from the Sample Handling Laboratory; the pre-weight cannot be re-determined after sampling;
- Samples with invalid mass concentrations are flagged as "UN" (Undetermined Weight).

After identifying filters with a mass discrepancy, create a reweigh list containing the following columns (in the following order); Filter ID, Sampler, Objective Code, Sample Date, Module, Issue Type, Validation comments, and Requested action. This list is then used to generate a reweigh request sheet with various information the weigh lab requires including pre- and post-weight data and information regarding the balance used for weighing. To generate the reweigh request sheet from the reweigh list, the following function is used:

datvalIMPROVE::reweigh_sheet(*inputpath = ['filepath.xlsx'], input_sheet =[NULL], output_path = ['filepath.xlsx'], output_sheet = ['Reweigh'], server = ['production'])*

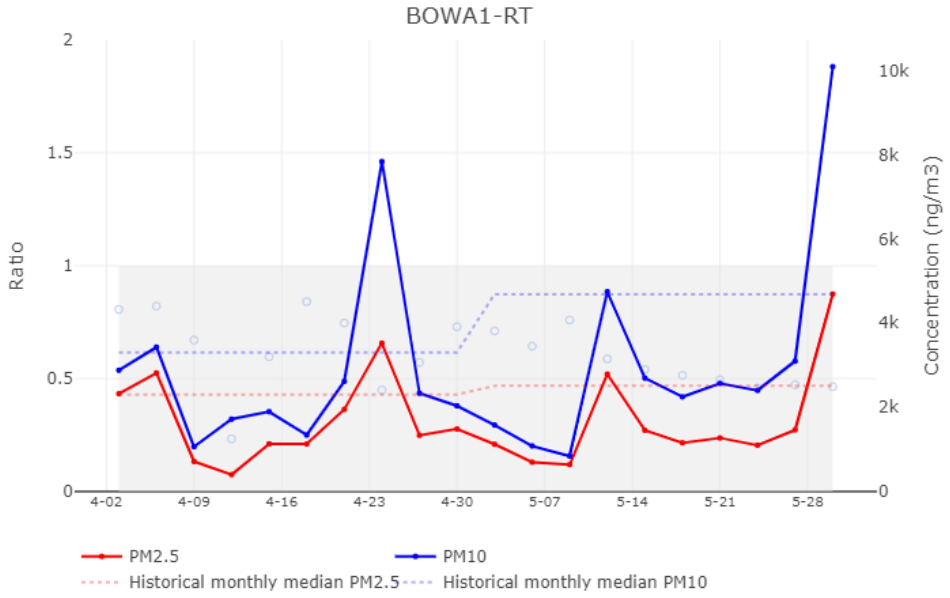
where *inputpath* is the file path and file name of the reweigh list and *input_sheet* denotes the relevant sheet within the reweigh list spreadsheet. The user can specify the name and location of the output file (*output_path*) as well as the sheet name (*output_sheet*), where the default sheet name is "Reweigh" if not specified. A typical command is shown below:

reweigh_sheet(input_path = "C:/IMPROVE_Reweigh_list_Feb2020.xlsx", input_sheet = "ReweighList", output_path = "C:/IMPROVE_Reweigh_list_Feb2020_final.xlsx", output_sheet = "Reweighlist_New", server = "production")

The generated reweigh request sheet is then sent to the weigh lab for cases to be assessed. When reweighing yields changes to results, the validation group reviews the reweigh results along with the weigh lab recommendations before requesting the weigh lab update the results, typically post-weight values, as necessary. Once the data are updated by the weigh lab, the validation group checks the early review plots to confirm the changes are as expected. In cases where results are either still questionable after reweighing or results did not change, due to

questionable pre-weights for example, the filter status is updated to UN (Undetermined weight).

Figure 7. Time series plot of PM_{10} and $PM_{2.5}$ masses and their ratio at BOWA1 site.



9.3.3.1.4 $PM_{2.5}$ Reconstructed Mass versus Gravimetric Mass

The $PM_{2.5}$ reconstructed masses, RCMC and RCMN, are calculated by equations 351-40 and 351-43, respectively. RCMC and RCMN are compared to the gravimetric mass (MF) as a check of measured components from the 1A, 2B, and 3C Modules (Figure 8). The *mf_rcm.check* function in the *datvalIMPROVE* package is run using the following command in the R environment:

[month_recon] <- datvalIMPROVE::mf_rcm.check(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], server = "production", problemonly = ["TRUE"])

The *mf_rcm.check* returns a list of samples flagged as outliers if the *problemonly* argument is set to 'TRUE' and any of the following criteria are met:

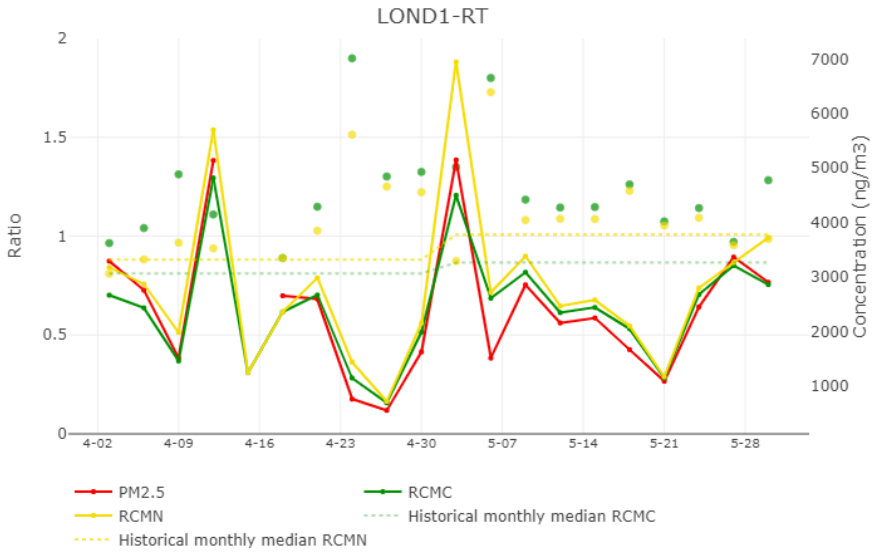
- RCMC is higher than two times MF, and the RCMC Z-score > 3; the number three is set empirically. These samples are accompanied with a comment "MF << RCMC".
- The RCMN Z-score < -22; the number 22 is set empirically. These samples are accompanied with a comment "MF >> RCMN".

Z scores are calculated as follows:

$$RCMC\_Z\_score = 1.41 \times \frac{RCMC - PM_{2.5}}{\sqrt{(unc_{PM2.5})^2 + (unc_{RCMC})^2}} \quad (351\text{-}50)$$

$$RCMN\_Z\_score = 1.41 \times \frac{\text{RCMN} - \text{PM}_{2.5}}{\sqrt{(unc_{PM2.5})^2 + (unc_{RCMN})^2}} \quad \text{(351-51)}$$

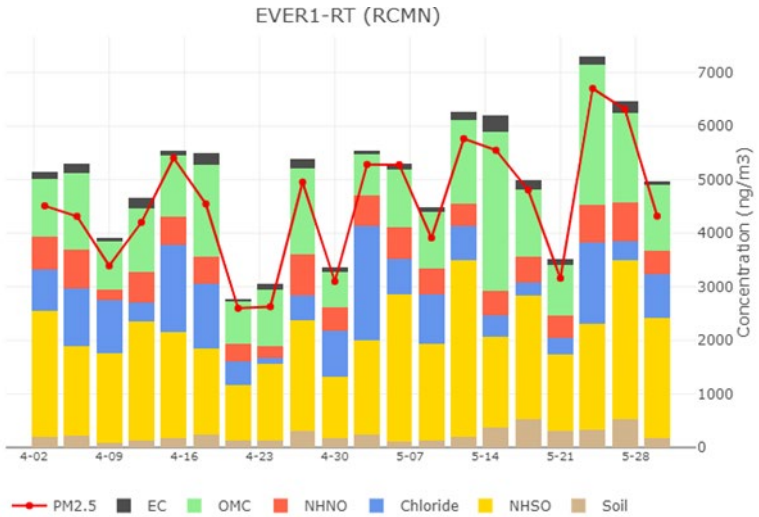
Figure 8. Time series plot of $PM_{2.5}$ gravimetric mass, reconstructed mass without nitrate (RCMC) and reconstructed mass with nitrate (RCMN) and their ratios at LOND1 site.



RCMN is also plotted as a bar plot (Figure 9), along with the $PM_{2.5}$ time series, for comparison of RCMN and $PM_{2.5}$ concentrations and to enable the contributions from the various species to be viewed and evaluated.

If $PM_{2.5}$ data is questionable, follow the steps outlined in section 9.3.3.1.3 to further investigate and identify the cause, including potentially requesting a reweigh.

Figure 9. Time series for RCMN versus Fine mass at EVER1 site.



9.3.3.2 Long-Term Network-Wide Checks

Several data visualization tools and control plots are used for long-term network-wide checks in addition to the site-by-site monthly data evaluation. These checks help reveal the long-term trends and seasonal patterns, if any, as well as any network-wide problems. Below are examples of the tools and plots that are routinely used and reviewed:

- Scatter plot of S3 versus SO4 mass loadings for the whole network (Figure 10). This plot is accessible from the IMPROVE Data site, "Early Review" tab.

- Scatter plot of chlorine versus chloride mass loadings for the whole network (Figure 11). This plot is accessible from the IMPROVE Data site, "Early Review" tab.

- Scatter plot of fAbs versus BC (converted from TOR absorption measurements) for the whole network (Figure 12). This plot is accessible from the IMPROVE Data site, "Early Review" tab.

- Scatter plot of fAbs versus EC for the whole network (Figure 13). This plot is accessible from the IMPROVE Data site, "Early Review" tab.

- Scatter plot of OC versus EC for the whole network, (Figure 14). This plot is accessible from the IMPROVE Data site, "Early Review" tab.

- Scatter plot of all EC wavelengths for the whole network. (Figure 15). This plot is accessible from the IMPROVE Data site, "Early Review" tab.

- Time series plot of the 1A to 4D mass loading ratio showing the long-term trend and historical data at a given site (Figure 16). This tool is accessible from the IMPROVE Data site, "Mass Review" tab.

- Monthly median, 90%, and 10% percentiles of the concentration data for all reported species. Figure 17 shows an example time-series plot for OC concentrations between 2011 and 2016. These plots are generated in R, and are typically included as part of the IMPROVE Quality Assurance Report.

Figure 10. Scatter plot of sulfur (×3) versus sulfate for the entire IMPROVE network.

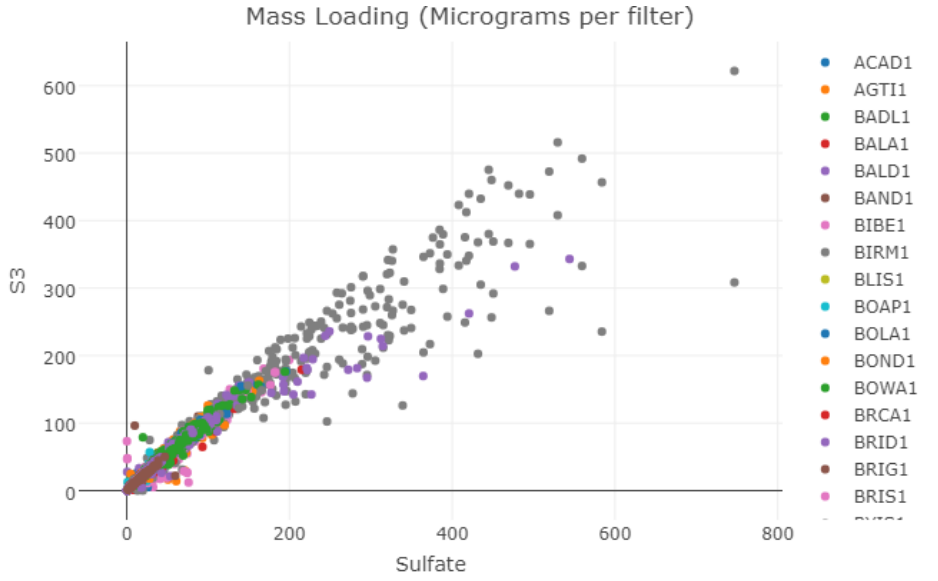


Figure 11. Scatter plot of chlorine versus chloride for the entire IMPROVE network.

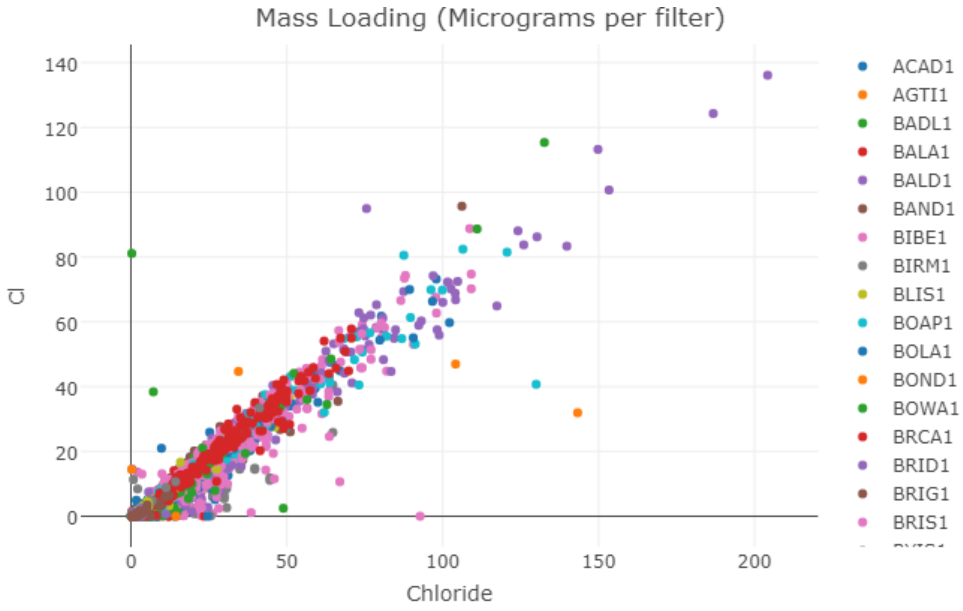


Figure 12. Scatter plot of fAbs versus EC for the whole network.

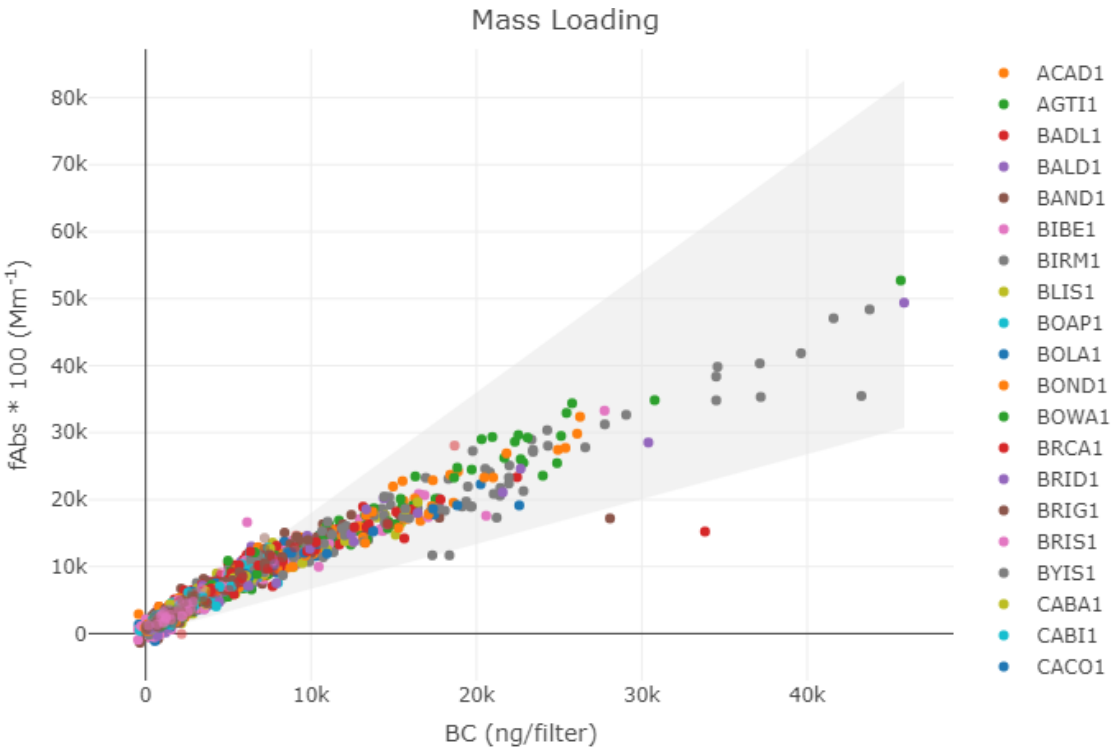


Figure 13. Scatter plot of fAbs versus EC for the whole network.

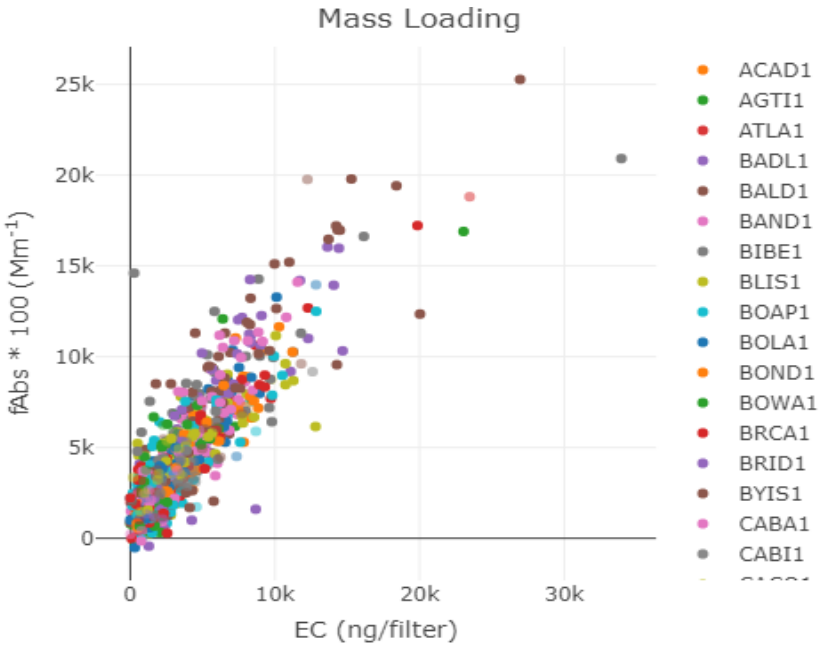


Figure 14. Scatter plot of OC versus EC for the whole network.

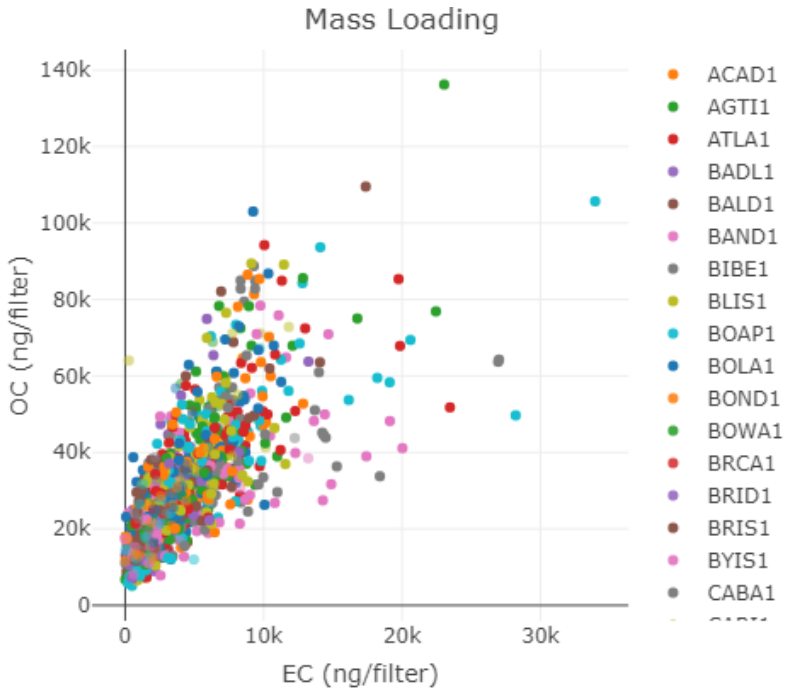


Figure 15. Scatter plot of ECTR versus other wavelengths for the whole network.

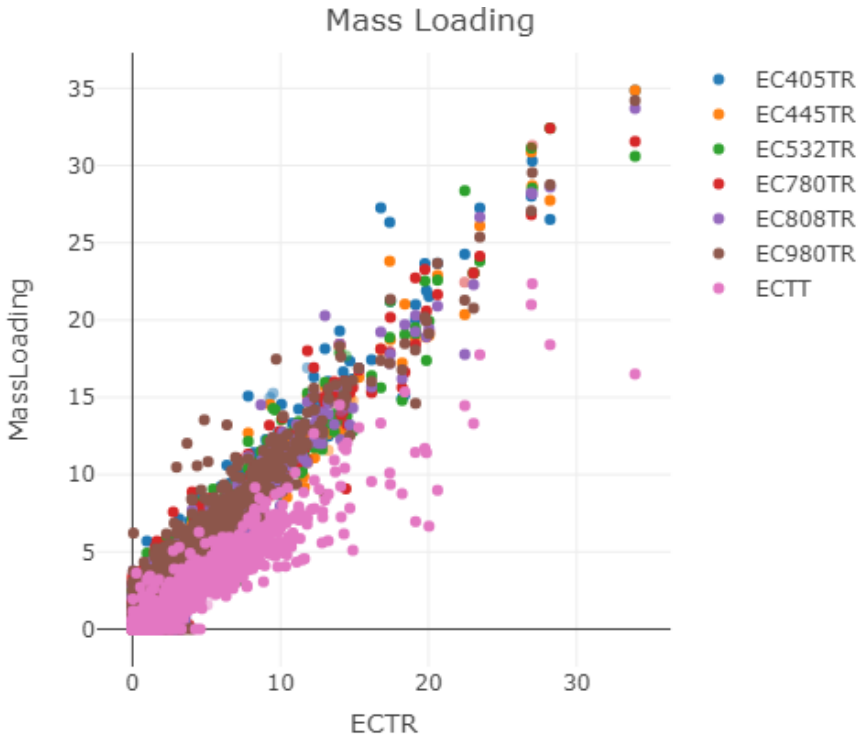


Figure 16. Ratio of $PM_{2.5}$ mass (1A) over PM_{10} mass (4D) at ACAD1 site, represented as raw measurements not adjusted for flow rates. Points are individual sample days (pink = Q1, green = Q2, blue = Q3, purple = Q4). Black line is the multi-year monthly mean. Blue line is the locally weighted average (LOESS).

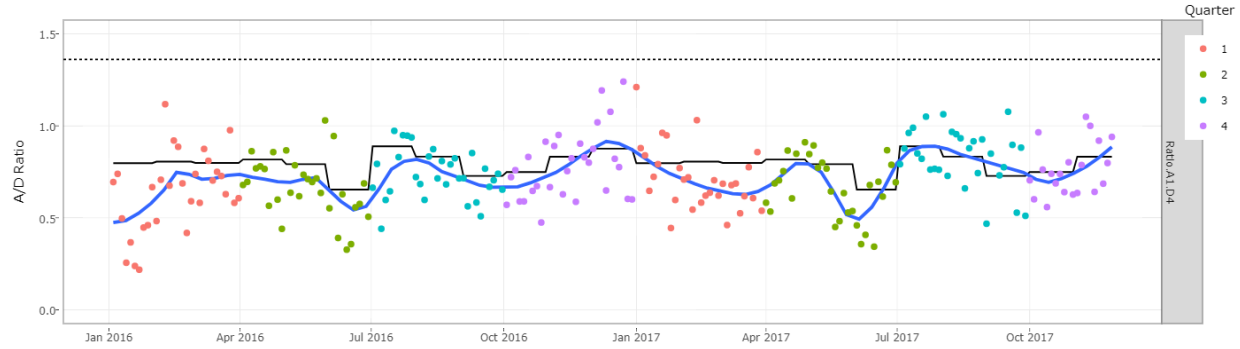
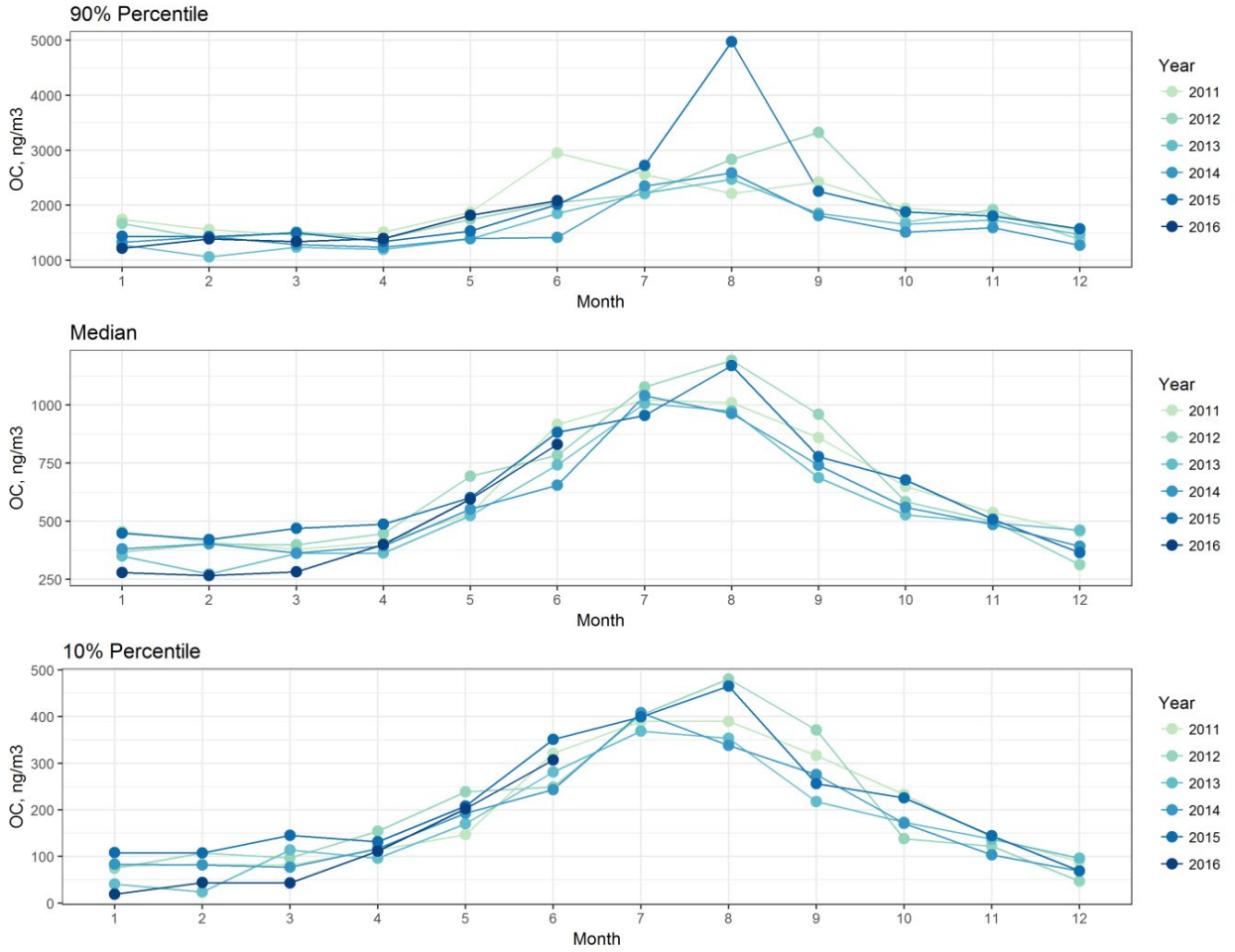


Figure 17. Multi-year monthly 10% percentile (top), median (middle) and 90% percentile (bottom) of organic carbon (OC) concentrations (in ng/m3) for the whole IMPROVE network from 2011 to 2016.



9.3.3.3 Common Validation Findings

Some validation findings tend to recur periodically, and effort is made to handle and resolve them consistently. Some examples of common findings are covered in this section, though those mentioned here are not inclusive of all scenarios or variations.

9.3.3.3.1 Filter & Analysis Data Swaps

There are several types of swaps in terms of the filter purposes involved and at what point in the process the swap occurred. Swaps are addressed using the swap tool in the web app (https://improve.aqrc.ucdavis.edu/Swap).

Filter Swaps

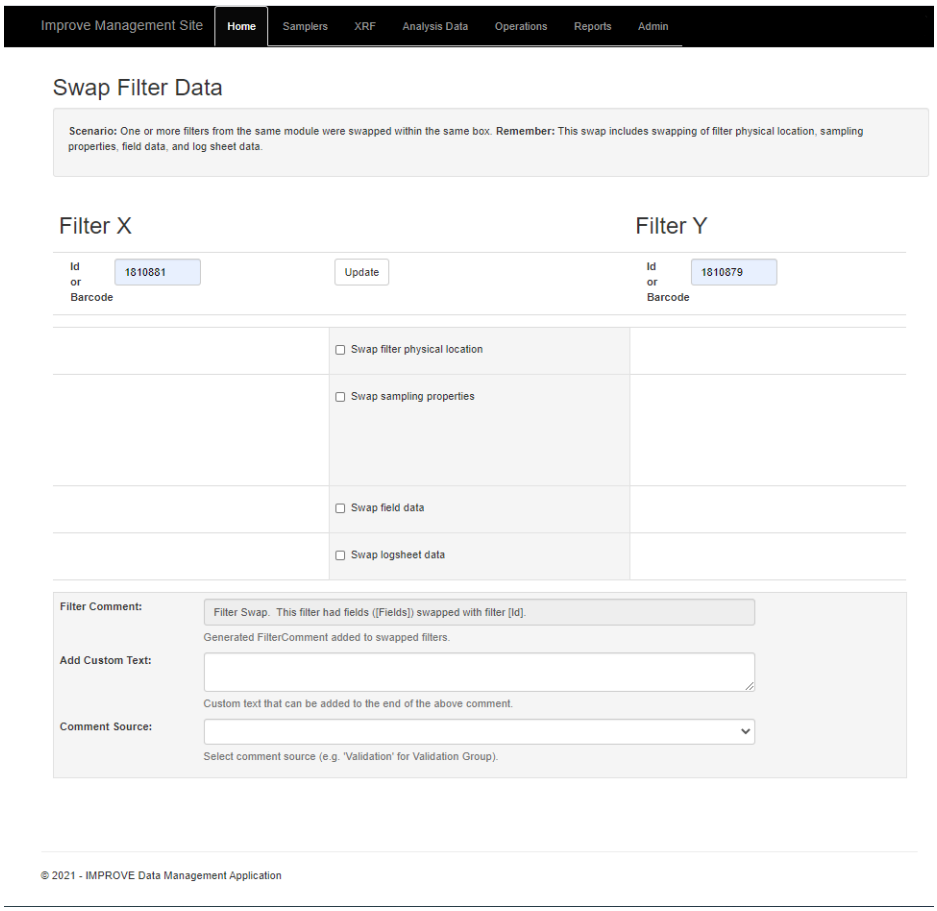
These types of swaps occurred before sampling (all downstream data are swapped, including flow data and all analysis associated with the filters); also referred to as cartridge position swap. Examples of filter swaps include:

- A routine sample filter was swapped with a field blank filter.
- A routine sample filter was swapped with a collocated sample filter.
- One or more of the same module filters were swapped within the same box (sample date swap).
- A 1A filter was swapped with a 4D filter (uncommon).
- The cartridge was installed incorrectly (rotated clockwise or counter clockwise), and one or more filters sampled on the incorrect day.

For these types of swaps, all data fields are to be swapped relating to the cartridge position between the relevant filters, including filter position properties (Cartridge Position) and log sheet records. Field data also needs to be swapped, specifically flow data. To perform the swap of all of these fields, use the Filter option in the swap tool and follow the steps below:

1. Access the filter swap tool found at https://improve.aqrc.ucdavis.edu/Swap/Filters. The resulting swap page has fields to enter the Filter Id/Barcode of the filters that need to be swapped, where only PTFE filters have barcodes. Enter the filter IDs/Barcode in Filter X and Filter Y fields (Figure 18) and click on the ‘Update’ button. Filter details such as Filter Properties, Physical location, Sampling Properties, Field data (e.g., flow), Log Sheet data, and Analysis data will then show under the relevant filters.
2. Review data shown is as expected.

Figure 18. Filter swap page.



3. There are four fields available for swapping; filter physical location, sampling properties (including filter purpose), field data, and logsheet data. In the case of a field blank-sample (FB-SA) swap, there is only one filter with flow information; the flow information is assigned to the wrong Filter ID. For all types of filter swaps, select all four fields to be swapped. A comment including the information of filter details swapped is added automatically when a swap is conducted and can be reviewed in the 'Filter Comment' section. Use the 'Add Custom Text' section to add more details on the nature of the swap. Select 'Validation' as the 'Comment Source'. Click 'Swap Data' to do the swap.
4. Check to ensure that the swap was performed by reviewing data in the Early Review tab. The Early Review tab shows data in mass loading from the analysis table; changes are reflected here without data needing to be reprocessed first. If the swap involved a FB filter, also review the Field Blank tab.
5. Using the filter details page in the web app (https://improve.aqrc.ucdavis.edu/Filters/Details), change the filter status to 'SP – Field Blank/Sample Swap' for both filters involved in a FB-SA swap

and to 'SW – Swapped Sample Dates' for all filters involved in sample-only swaps.

6. After all edits are performed and data is ready to be prepared for delivery, reprocess flows following the steps outlined in section 9.2.
7. Reprocess concentrations following the steps outlined in section 9.2.
8. Review the final data in the Validation plots and Field Blank tab.

Analysis Swaps

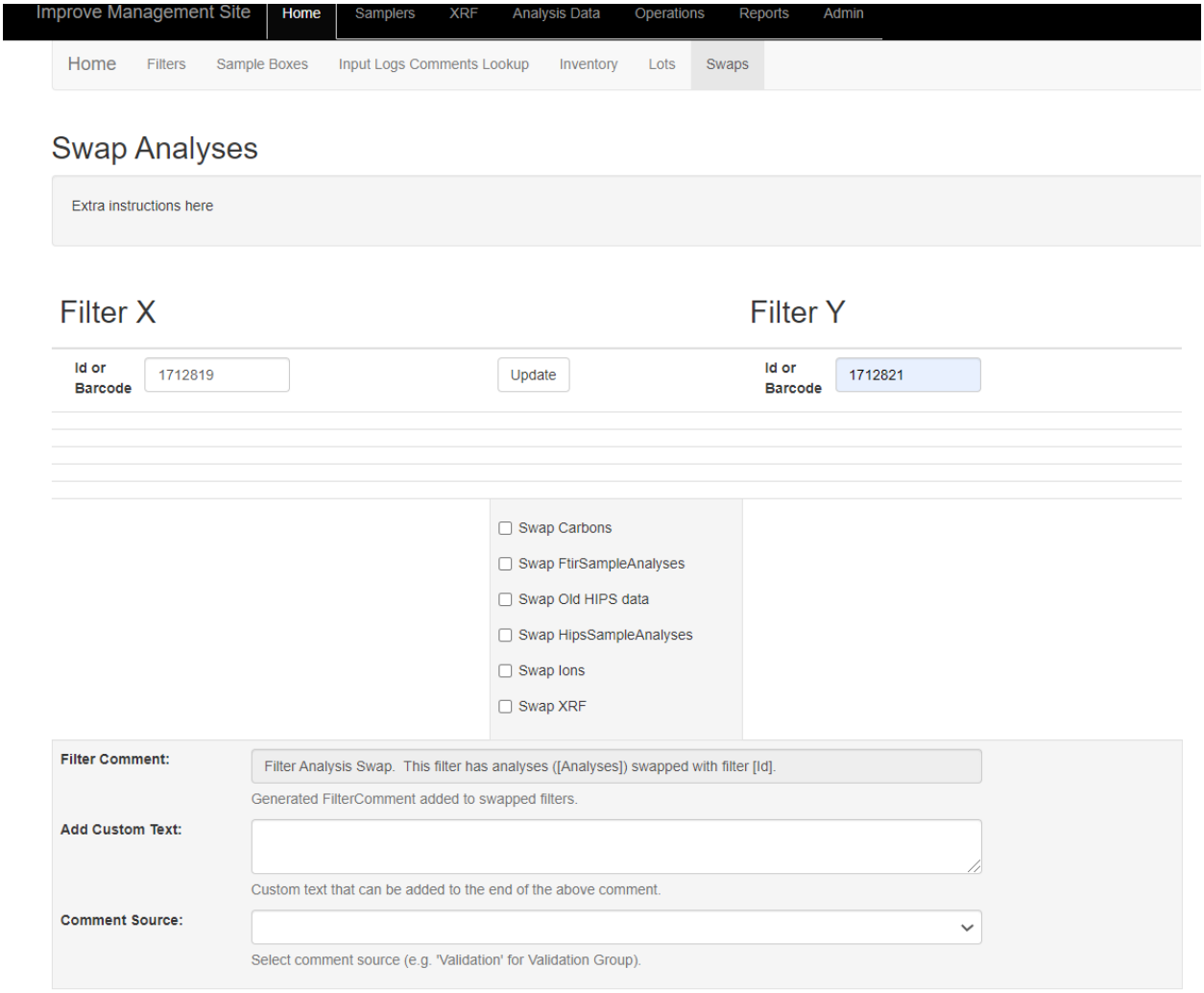
These swaps occurred after sampling, before all analyses are complete (flow data are OK, analysis data are swapped). Swaps can occur between sample-sample (SA-SA) filters or field blank-sample (FB-SA) filters.

To perform the swap, use the Analyses option in the swap tool and follow the steps below:

1. Confirm the swap happened for the same module and identify which analysis data are swapped; if multiple analyses are performed on that filter, which is the case for A module filters, identify which sets of analyses have been swapped. Usually, if the filters are swapped at a lab station, all downstream analyses will be swapped.
2. Access the analyses swap tool found at https://improve.aqrc.ucdavis.edu/Swap/Analyses. The resulting swap page has fields to enter the Filter Id/Barcode of the filters that need to be swapped, where only PTFE filters have barcodes. Enter the filter IDs/Barcode in Filter X and Filter Y fields (Figure 19) and click on the 'Update' button. Filter details such as Filter Properties, Physical location, Sampling Properties, Field data (e.g., flow), Log Sheet data, and Analysis data will then show under the relevant filters.
3. Review data shown is as expected.
4. The following fields are available for the swap: Carbons, FtirSampleAnalyses, Old HIPS data (for filters before database change in March 2020), HipsSampleAnalyses, Ions, and XRF. Depending on the filter type and swap point (in the case of A module filters), select the appropriate fields. This is particularly relevant for A module filters where multiple analyses are performed: gravimetric, FTIR, XRF, and HIPS analysis. Be sure to determine after which analysis the swap occurred and only swap the downstream data from that point. For example, if the sample was swapped after gravimetric analysis while placing the filter in a Petri dish, then the FTIR, XRF, and HIPS analysis data will need to be swapped. If the swap occurred after XRF analysis but before HIPS analysis, only HIPS data need to be swapped. The swap tool does not have the option to swap gravimetric mass data; such a swap is unlikely if the

filter was weighed in the automated weighing chamber. If the filter was swapped before gravimetric analysis and the filter was weighed on a manual balance, please ask the weigh lab to swap the relevant data. A comment including the information of filter details swapped is added automatically when a swap is conducted and can be reviewed in the 'Filter Comment' section. Use the 'Add Custom Text' section to add more details on the nature of the swap. Select 'Validation' as the 'Comment Source'. Click 'Swap Data' to do the swap.

Figure 19. Analysis swap page.



5. Inform the relevant analysis labs about the swaps performed.
6. Check to ensure that the swap was performed by reviewing data in the Early Review tab. The Early Review tab shows data in mass loading from the analysis table; changes are reflected here without data needing to be

reprocessed first. If the swap involved a FB filter, also review the Field Blank tab.

7. Using the filter details page in the web app (https://improve.aqrc.ucdavis.edu/Filters/Details), change the filter status to 'SP – Field Blank/Sample Swap' for both filters involved in a FB-SA swap and to 'SW – Swapped Sample Dates' for all filters involved in sample-only swaps.
8. After all edits are performed and data is ready to be prepared for delivery, reprocess flows following the steps outlined in section 9.2.
9. Reprocess concentrations following the steps outlined in section 9.2.
10. Review the final data in the Validation plots and Field Blank tab.

9.3.3.3.2 Cartridge Swaps

When a cartridge designated for a particular week is set up incorrectly to run in another week or another module, multiple cartridges are likely involved. Examples of cartridge swaps include:

1. A site came back online but does not have a new box:
    a. One or two weeks of an old unused box are used in place of the current box (most common scenario).
2. A site came back online, but did not have a new box at the moment. The old Week 3 unused filters were used in place of the current Week 1. A new box was generated and sent out. In the new box:
    a. Week 1 filters were never used
    b. Week 2 & Week 3 sampled correctly
3. Weeks are used in the incorrect order:
    a. Example: Cartridge in the Week 3 bag is used instead of that in the Week 1 bag.
4. Cartridges are input into any wrong module.
    a. This scenario is only possible when an A module cartridge is placed in a D module (as all are PTFE filters) and vice versa.

To perform the swap using the swap tool for cartridges, each cartridge pair swap will have to be performed one at a time. A cartridge swap can be performed only if both cartridges have the same number of filters, except for cartridges with field blanks.

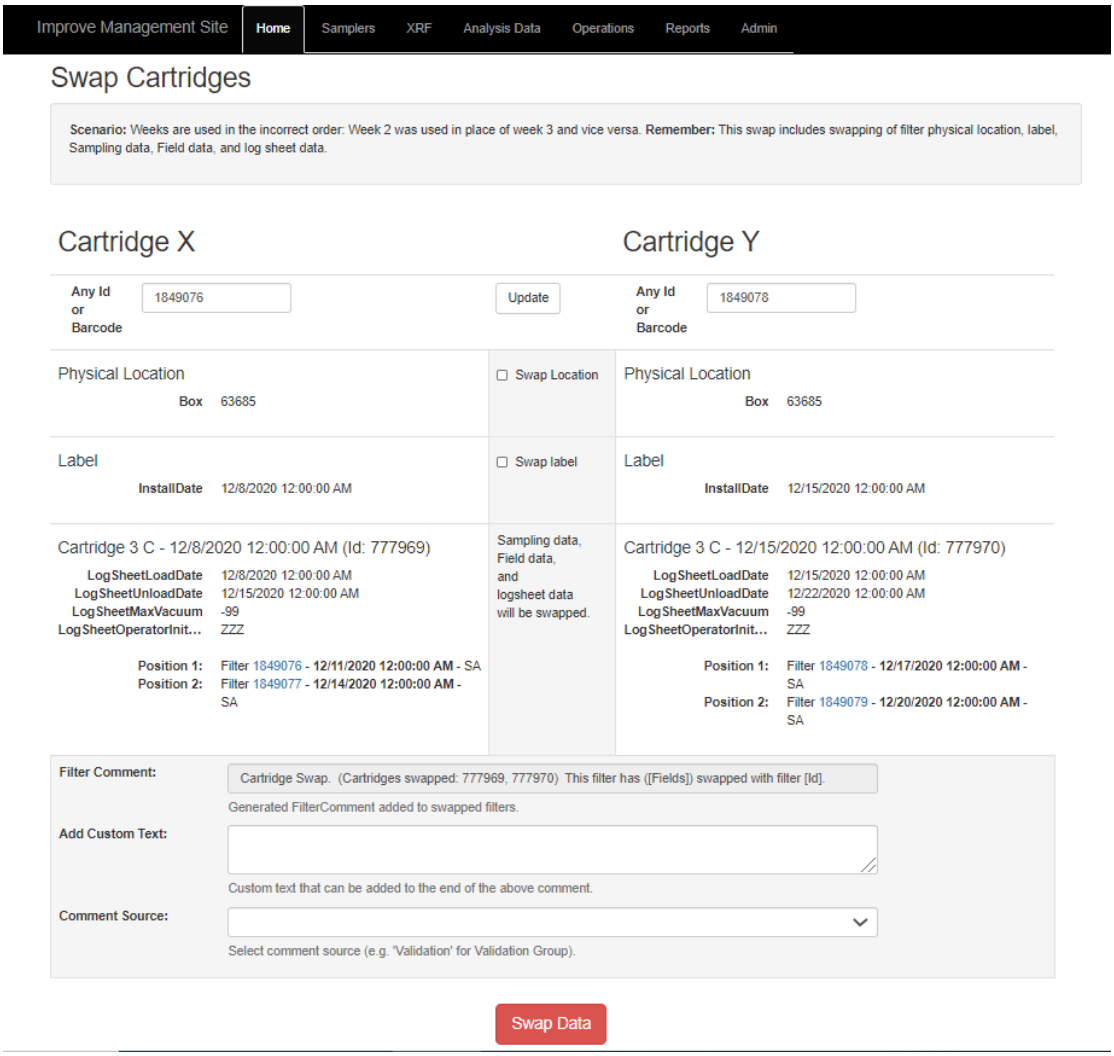
- **Cartridge Swaps:** Same module swap or A-D module swap. Resolve by following these steps:

    1. Access the cartridge swap tool found at https://improve.aqrc.ucdavis.edu/Swap/Cartridges. The resulting swap page has fields to add one filter Id/Barcode (only PTFE filters have barcodes) from each cartridge or the cartridge ID that needs to be swapped. Enter the relevant Ids/barcodes in the Cartridge X and Cartridge

Y fields and click on the 'Update' button. The filter details like Sampling data, Field data, and log sheet data will be shown under the relevant filters/cartridges (Figure 20).

2. Review data shown is as expected.
3. The following fields are available for the swap; Label and Location. Select both fields. A comment including information and details of the filter(s) and cartridge(s) swapped is added automatically when a swap is conducted and can be reviewed in the 'Filter Comment' section. Use the 'Add Custom Text' section to add more details on the nature of the swap. Select 'Validation' as the 'Comment Source'. Click 'Swap Data' to do the swap.

Figure 20. Cartridge swap page.



4. Check to ensure that the swap was performed by reviewing data in the Early Review tab. The Early Review tab shows data in mass loading from the analysis table; changes are reflected here without data needing to be reprocessed first.

5. Using the filter details page in the web app (https://improve.aqrc.ucdavis.edu/Filters/Details), change the filter status to 'SW – Swapped Sample Dates' for all filters involved in sample-only swaps.
6. After all edits are performed and data is ready to be prepared for delivery, reprocess flows following the steps outlined in section 9.2.
7. Reprocess concentrations following the steps outlined in section 9.2.
8. Review the final data in the Validation plots tab.

9.3.3.3.3 Box Swaps

Swapping filters from entire boxes is sometimes necessary. A box swap becomes necessary when:

a) Box X was lost/not delivered, so Box Y of a future cycle was used.
b) Box X was unused from an old cycle; it was used in place of Box Y of a future cycle.
c) Box X was lost/not delivered, so Box Y was assembled for the exact sampling dates but not processed through the Improve database.
d) Box X was assembled and processed through the database but never used/shipped out because the site was offline.
e) Box X was sent to the wrong site and sampled fully in the incorrect site. This usually happens with the same cycle of boxes, but an instance could occur where a 2-3-2 box samples in place of a 3-2-2 box and vice versa. In that case this procedure will not work.

Note that the cartridges have to line up for this to work i.e., if any other swaps occurred within the box, this procedure will not work. In those cases, the procedure is to do a cartridge swap for each pair of cartridges. For example, if week one from the original box was sampled and weeks two and three from the new box were sampled then using this box swap tool is not an option.

For all of the above examples, the swaps can be performed using the steps outlined below.

1. **Step 1:** Access the box swap tool found at https://improve.aqrc.ucdavis.edu/Swap/Boxes. The resulting swap page has fields to enter one filter Id/Barcode (only PTFE filters have barcodes) from each box or the Box Id that needs to be swapped. Only filter Ids/Barcodes or Box Ids are to be entered here; Cartridge Ids are not to be entered. Enter the relevant Ids/Barcodes in the Box X and Box Y fields (Figure 21) and click on the 'Update' button. All the box properties and cartridge/filter details will be displayed under the box Id fields (Figure 22).

2. **Step 2:** Review data shown is as expected for the boxes, cartridges, and filters. Also, compare and make sure all details match between the boxes (such as 2-3-2 vs. 2-3-2).
3. **Step 3:** Only the Box Label (Install Date) field is available for the swap. Select this field. A comment including the information of filter details swapped is added automatically when a swap is conducted and can be reviewed in the 'Filter Comment' section. Use the 'Add Custom Text' section to add more details on the nature of the swap. Select 'Validation' as the 'Comment Source'. Click 'Swap Data' to do the swap.
4. **Step 4:** Sometimes multiple box swaps need to be performed to address the issue; repeat steps 1-3 for each pair of boxes. In each case, the type of box swap scenario should be assessed to determine which box pairs, if any, are to be swapped.
5. **Step 5**: After a box swap is performed, the statuses of all filters in the boxes need to be addressed based on the swap situation. If the box is swapped in place of a lost or undelivered box (example 'a' in the above section), please refer to section 9.7.2 to update the filter purpose and current lab station Id of the lost/undelivered box. In cases where a box is swapped with another site (example 'e'), all filter statuses in both boxes need to be updated to 'SW – Swapped Sample Dates' using the filter details page in the web app (https://improve.aqrc.ucdavis.edu/Filters/Details).

Figure 21. Box swap page.

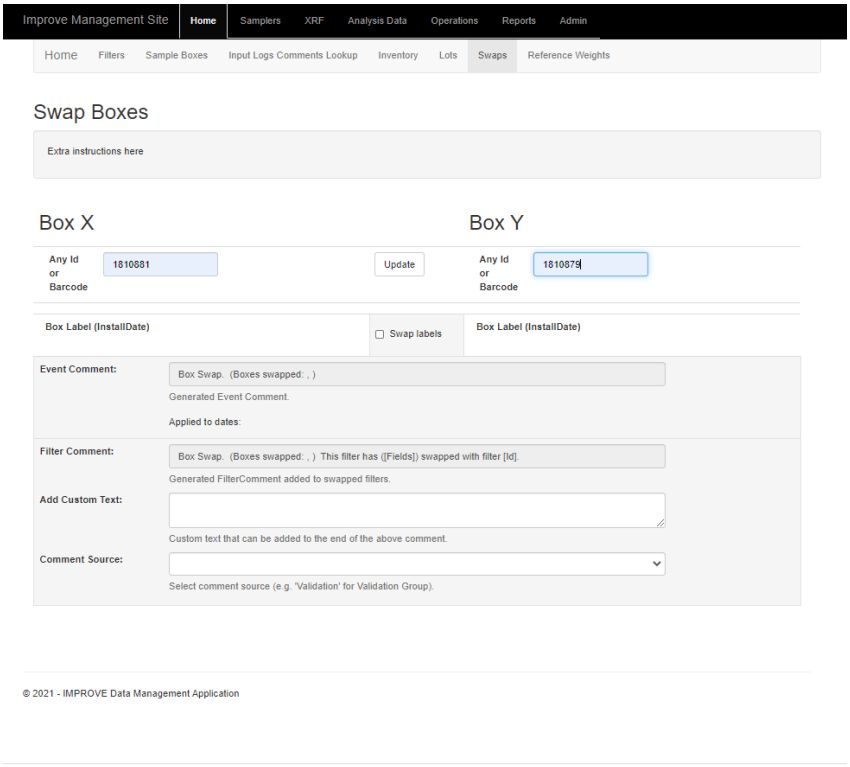
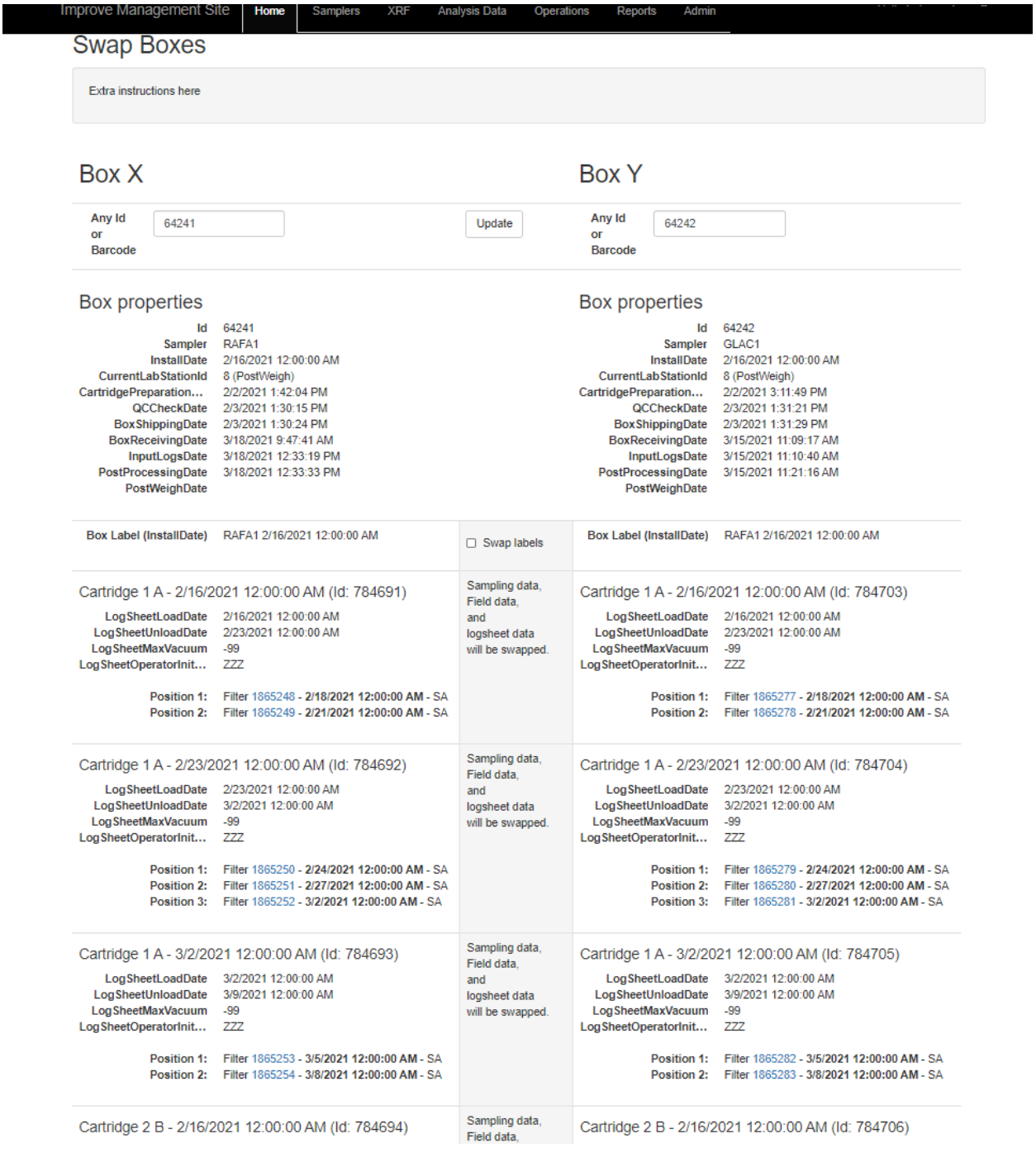


Figure 22. Box swap page after clicking the 'Update' button. Only A module filter details are displayed due to page length.



9.3.3.3.4 Sampling Anomalies and Questionable Data

There are several types of sampling anomalies and questionable data commonly observed during validation. Included here are guidelines for addressing and resolving these issues.

Note that the NPS treats the SA (sampling anomaly) flag as terminal for Regional Haze Rule purposes; consider the application of the SA flag carefully and apply alternative flags where appropriate. For cases where there is a non-standard sampling but no noticeable data bias a flag other than SA may be used. If a site audit finds any sampling issues, then the SA flag may be appropriate.

- **Module stack not fully inserted**
    - Typically flagged QD by the Sample Handling Laboratory with comment applied. Has previously occurred for the D-Module stack.
    - Review the data and JIRA notes to determine if this has previously been an issue or if it is a longer-term issue. Previous cases have been flagged SA (sampling anomaly) to indicate an operational deviation when the cross-module concentration data agreed.
    - For current cases, review the relevant concentration data and compare with results from other modules. If the cross-module results agree, consider changing the status to NM (normal) or apply the SA flag to indicate an operational deviation. If the cross-module results do not agree, consider other actions such as reanalysis or invalidation.
- **Module flow obstruction**
    - Typically flagged QD by the Sample Handling Laboratory with comment applied. Has previously occurred for the B and D Modules.
    - Review the data and JIRA notes to determine if this has previously been an issue or if it is a longer-term issue.
    - Notes from previously resolved issues are included here to provide context and framework for handling future similar cases:
        - D module flow obstruction example: The SA flag was applied because the impact to the data was not quantifiable and the PM_{10} and $PM_{2.5}$ masses compared relatively well. Some nearby sampling dates had flow rate flagged as low or clogging, but not on all days, and a null code was not applied. However, the SA flag will have been treated as invalid for Regional Haze Rule purposes.
        - B module flow obstruction example: The cross-module comparison ratios were evaluated, and since sulfur and sulfate trended reasonably well together, and there were no outliers, the SA flag was applied rather than invalidating. The final reported data will have been treated as invalid for Regional Haze Rule purposes, however.
- **Possible manifold open / cartridges not seated correctly**
    - Typically flagged QD by the Sample Handling Laboratory with comment applied. A typical comment is: *Module/filter CARTs, possible MANIFOLD open / CART not seated correctly, low FLOW*.

- Assess the concentration data and compare with other modules. Evaluate the flow and filter statuses.
- Review JIRA notes to determine if this has previously been an issue or if it is a longer-term issue.
- Notes from previously resolved issues are included here to provide context and framework for handling of future similar cases:
  - Scenario #1: Comment from Sample Handling Lab indicated, *3C CARTs, possible MANIFOLD open / CART not seated correctly, low FLOW*. The EC and BC data agreed with the fAbs, suggesting that the leak was not severe. The flow rate through the filter was lower than expected and the LF flow status flag was applied. The filter status was kept as NM rather than applying the SA flag. Since LF is a more severe status than NM, the LF flow status flag would have been reported to end users. If the flow status had been LF and the filter status was SA, the SA flag would have been reported to the end user.
  - Scenario #2: In some cases, the Sampling Handling Laboratory invalidates filters with the BI terminal flag (BI – bad install) prior to data validation. The Sample Handling Laboratory will invalidate the filter if there was no sample collected, which can be confirmed for 1A and 4D filters when the pre- and post-weight difference is zero. Filters may also be invalidated if the filter deposit is much lighter in appearance relative to the other three filters collected on the same day. If there is uncertainty, the Sample Handling Laboratory applies the QD flag (typical for 2B and 3C filters).

- **Double filter**
  - Typically flagged QD by the Sample Handling Laboratory with comment applied. Most commonly found for 3C filters. If the double filter issue is not identified until the filters are in the carbon analysis lab, the analysis lab analyzed the top filter and adds a comment noting the situation.
  - Previous cases may have been flagged SA (sampling anomaly) to indicate an operational deviation when the cross-module concentration data agreed. For current cases, review the relevant concentration data and compare with results from other modules. If the cross-module results agree, consider changing the status to NM (normal) or apply the SA flag to indicate an operational deviation. If the cross-module results do not agree, consider other actions such as reanalysis or invalidation.

- **Pre-weight unknown**
  - Only applies to 1A and 4D filters, samples and field blanks.
  - Typically flagged QD by the Sample Handling Laboratory with comment applied. For example, a typical comment is: *Module/filter FIL mass difference negative/high, POST weight confirmed, PRE weight unknown*. This can appear as pre- to post-weight difference of zero or negative, high PM_{10}, or $PM_{2.5}$>PM_{10}.

- Assess the severity of the situation by evaluating the $PM_{2.5}/PM_{10}$ ratio, $PM_{2.5}$ relative to RCMN, and regional mode comparisons.
- If the pre-weight is unknown, the filter status should have the UN terminal flag (UN – undetermined mass), which invalidates only the mass parameter from the affected filter. If the comment does not mention pre-weight, review the mass data, request re-weigh, and investigate other issues (such barcode assignments in the database).

- **Quartz contamination**
  - This typically applies to 1A and 4D filters only.
  - Typically flagged QD by the Sample Handling Laboratory with comment applied. Quartz contmation occurs on PTFE filters if a screen with quartz deposit is installed. The PTFE and quartz screens are kept apart in the Sample Handling Laboratory, but there is potential for contamination due to human error. White deposit or white specs on the PTFE filter are indications of quartz contamination.
  - Assess the severity of the situation by evaluating the concentration data and compare with results from other modules.
  - If the quartz contamination is deemed to not be significant enough to impact analysis, the filter status should be changed to NM.
- **Insects / large particles**
  - This typically applies to 4D filters.
  - Because of the D Module sampling design, it is not uncommon to see insects or other large particles such as seeds on the filters. In some cases the Sample Handling Laboratory is able to remove the debris and reweigh the filter. The QD flag and an appropriate comment are applied to the filter to indicate possible impact to the analysis results.
  - Review the data to determine if the results appear reasonable; if so, change the filter status to NM. Another visual check and/or reanlaysis could be reqeusted if the data appear questionable.
- **Dropped filters**
  - Filters can be dropped at any point during the sampling or analysis process. A comment is typically applied by the laboratory to indicate such. If the filter was dropped in the Sample Hanlding Laboratory, the QD flag is also applied.
  - The Sample Handling Laboratory distinguishes between dropping filters on the floor and on the counter, where heavy contamination is assumed for the former.
  - Assess the concentration data and compare with other modules. Evaluate ralative to historical data form the site and same day neighboring sites.
  - Review the data to determine if the results appear reasonable; if so, change the filter status to NM. Another visual check and/or reanlaysis could be reqeusted if

the data appear questionable. The nylon filter from the 2B module will not be available because it was extracted for analysis. Invalidate the filter if the contamination appears to be severe.

- **Wrinkled filter**
  - This is a common occurrence for 3C filters and is observed either at the Sample Handling Laboratory and/or the analysis lab.
  - A wrinkled filter can occur when loading the filter at the lab or in the field. The cartridge may have come lose causing the filter to shift and wrinkle. A wrinkled filter will likely have an uneven/low deposit.
- **Filter blown out / bulging filter**
  - The quartz filters from the 3C module are commonly suspected of being blown out when filter bulging is observed at the Sample Handling Laboratory and/or the analysis lab; 37 mm nylon filters from the 2B module are also sometimes observed to have crinkled edges.
  - For 25 mm quartz filters from the 3C module, it is possible to "suck out" part of the filter when (aggressively) taking off the red caps. While installed in the modules, the edges of the quartz filters are compressed between the screen and a flat lip on the cassette bottom, which weakens the outer edges; the edges will be relatively rough. Bulging filters can also suggest airflow in the wrong direction and can occur if quartz filters are loaded without screens or loaded upside down; for these cases there will be little or no sample deposit.
  - For 37 mm nylon filters from the 2B module, it is possible to crinkle the edges of the filter while loading. For these cases, the filter looks similar to a bulged filter but usually folds flat during sampling. Filter cassettes must be assembled with a press to ensure even pressure.
  - Reivew all data – including the flow data – to determine if and when the filter was disfigured. Flow issues may result in application of flow-related informational or terminal flags (see criteria in Table 14 and Table 15), and may explain concentration discrepancies such as poor sulfur to sulfate agreement. If the flow status is normal and the data appear reasonable, the filter status should be changed to NM.
- **Holes**
  - Holes can be observed for any filter type and range from pin holes to larger holes that destroy the filter. Holes can be introduced at various points during the sampling and analysis process; filters are flagged QD, invalidated, and/or have comments applied.
  - Analysis can be impacted by a hole of any size, and the extent of impact varies by analysis type. As such, all analysis results should be reviewed independently (for example, HIPS analysis may be impacted even though mass analysis is not). If concentration results are suspect, a visual check and reanalysis should be requested, if available. The nylon filter from the 2B module will not be

available because it was extracted for analysis. Review the flow data to evaluate potential sampling issues. If the results are determined to have been impacted by the hole, invalidate the filter; if the results are reasonable, change the status to NM.

- **Egregious sulfur/sulfate discrepancy and corresponding factors**
  - During data validation, the following observtaions may be made for a sample date at a site:
    - Large discrepancy between sulfur and sulfate concentrations, whereby sulfate is higher than sulfuar, the 3*sulfur/sulfate ratio is shown to be an outlier, and the respective uncertainties do not overlap;
    - RCMN is higher than $PM_{2.5}$;
    - total sample concentration (RCMN) is high; and
    - the nitrate component is large.
  - If such an observation is made a spot check reanalysis of both 'A' and 'B' filters is performed. If there are many sample dates at a single site and/or if there are many samples from many different sites that all meet this criteria, the analyst will identify a subset of the worst cases and request reanalysis of both 'A' and 'B' filters.
  - If the reanalysis results do not show any issues with analysis, the data is reviewed again to rule out other potential sampling issues.
  - If a collocated CSN site is available, the sulfur and sulfate concentrations should be compared between the two networks. If there are any discrepancies between the sulfur and/or sulfate concentrations from the IMPROVE samples with the CSN samples, the relevant IMPROVE filter should be invalidated using 'XX' (Sample Destroyed, Damaged, or Contaminated) status. If a collocated CSN site is not available and if there are no other issues than the above four criteria, the filter status can be changed to 'NM' (Normal).

For all cases identified, appropriate comments should be added to acknowledge the issue and detail any actions taken.

9.3.3.4 Recommended validation guidelines

The following section provides guidelines on the approach to validating data to determine if a sample is to be invalidated.

1) Unusual data observation made during validation, typically through reviewing plots on the ImproveData Validation page or from checks performed in R using the validation package e.g.:
   a. Sulfate concentration much higher than sulfur concentration;
   b. Sulfate concentration near zero but sulfur concentration is not;
   c. Negative EC concentration but BC and fAbs are positive and not near zero;

   d. $PM_{2.5}$ much higher than PM_{10}.

2) Review other data for the sample date and check composite variables calculated using the problem species, where available.
   a. E.g. if sulfate >> sulfur, review RCM vs. $PM_{2.5}$ as NHSO (= 4.125 *S) is used in calculating RCM. These relationships can be used to determine if the problem is with sulfur or sulfate, thus the 'A' or 'B' filter, respectively.
3) Review other anlaysis data from the problematic filter.
   a. E.g. if the problem filter is suspected to be 'B' as sulfate is near zero, check other ions species for similar observations. Is sulfate the only species with near zero concentration?
4) Review adjacent sample days for patterns and compare longer term with historical data.
   a. Use the plots on the Validation page as well as the Explorer page. If this pattern has been seen at the site at similar times in previous years, review the filters for comments and statuses to determine how the sample was handled previously. If the pattern is frequently observed, the current observation may be atmospherically real. If a similar pattern has not previously been observed, the data may still represent the air conditions but further investigation needs to be performed.
5) Review nearby sites for similar patterns.
   a. Local events may impact a subset of sites. Run the back trajectories, if available, in the Explorer page to determine which of the nearby sites may be expected to show similar trends and/or whether the air mass travelled over the ocean.
6) If there is no evidence for a particular issue to explain the observation, request reanlaysis of the the questionable filter(s) to rule out any anlaysis issues. Contact the sample handling lab to determine if there were any sampling or sample handling issues.
7) If no issues are found with the analysis, sampling, or sample handling, thus no changes are made to the data, the analyst should determine how egregious the issue is.
   a. For example, if the sulfate concentration is much higher than the sulfur concentration, the 3*S/SO4 ratio is an outlier, no similar cases have been observed previously, reanalysis results confirm the original anlaysis is valid, flow data does not indicate sampling issues, and surrounding sampling dates also do not show any issues, the analyst should consider invalidating the filter.

If the sulfate concentration is only slightly higher than the sulfur concentration, the 3*S/SO4 ratio is not an outlier and/or the resepctive uncertainties overlap, then perhaps the analyst will consider leaving the filters as valid.

9.3.3.5 Final Review

Several final checks are performed before submission of data delivery files to the CIRA (FED), EPA (AQS), and UCD CIA databases:

- The *QD.check* function in *datvalIMPROVE* (described in section 9.3.2.2) is run again after validation is complete to confirm that there are no remaining records with QD status. No records with QD in the status field should exist in the delivery files.
- The *ObjCode.check* function in *datvalIMPROVE* (described in section 9.3.2.2) is run again after validation is complete to confirm that only RT (routine) or CL (collocated) objective codes exist in the data file.
- The *ValidSta_BadData* function in *datvalIMPROVE* (described in section 9.3.2.2) is run again after validation is complete to confirm that there are no remaining records with a valid status with values outside of defined normal ranges.
- The *ValidSta_NullData* function in *datvalIMPROVE* checks to determine if there are cases where no value (-999) is reported but the filter is marked as valid. Perform this check using the following command in the R environment:

  [month_ValidNull] <- datvalIMPROVE::ValidSta_NullData(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'], "production")

  Confirm application of a terminal flag or locate the missing analysis results and follow the steps to reprocess the data for delivery.

- The *MDL_UNC* function in *datvalIMPROVE* checks to determine if calculated MDLs or uncertainties have negative values. To obtain a list of records that meet this criteria, run the following command in the R environment:

  [month_mdl_uncl] <- datvalIMPROVE::MDL_UNC(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'])

  Review records to determine why the uncertainty or MDL is negative and resolve as needed.

- The *sitecount* function in *datvalIMPROVE* is used to determine the site count for a specific delivery file to CIRA (FED). Perform this check using the following command in the R environment:

  [month_site] <- datvalIMPROVE::sitecount(filepath = ['filepath.csv'])

  The *filepath* argument is a character string containing the file path and file name of the wide-format file for delivery to CIRA, where the file itself is a .csv file format.

- The *deliverycheck* function in *datvalIMPROVE* checks to determine if there are cases in the delivery file to CIRA where the data are valid but marked with a terminal flag or the data are invalid but marked with a valid flag. Perform this check using the following command in the R environment:

  [month_delivery] <- datvalIMPROVE::deliverycheck(filepath = ['filepath.csv'])

  The *filepath* argument is a character string containing the file path and file name of the skinny-format file for delivery to CIRA, where the file itself is a .csv file format.

As noted in section 9.3.2, many of the functions described above can be performed simultaneously using the *datvalIMPROVE::improve_validate* function. Prior to delivery, some checks performed for initial validation are executed again and some additional final checks are performed. Using the following command in the R environment, evaluate the output from the checks described below for delivery:

[month_output] <- datvalIMPROVE::improve_validate(startdate = ['YYYY-MM-DD'], enddate = ['YYYY-MM-DD'])

- **output$objective_code –** ObjCode.check
- **output$QD -** QD.check
- **output$validsta_null -** ValidSta_NullData
- **output$validsta_bad -** ValidSta_BadData
- **output$mdl_unc -** MDL_UNC

9.4 Data Delivery

After Level 2 data validation is complete, the data files are submitted to CIRA, AQS, and UCD CIA databases.

9.4.1 Submission to CIRA

Export files for CIRA (FED) are created using the *improve_export_fed* and *improve_export_wide* functions in the *crocker* package, in which the year, month, and server for both functions are entered. The functions create "skinny" and "wide" versions of the dataset, and both are submitted. To generate the "skinny" format export file, run the following command in the R environment:

*crocker::improve_export_fed(*year = *[YYYY],* month = *[MM], server = 'production')*

To generate the "wide" format export file, run the following command in the R environment:

*crocker::improve_export_wide(*year = *[YYYY],* month = *[MM], server = 'production')*

The files are saved under *U:\IMPROVE\FED Export*, named 'IMPROVE_Data_YYYY_MM_server' and 'IMPROVE_WideData_YYYY_MM_server' (e.g., "IMPROVE_Data_2017_02_production'), respectively. These files are compressed into a zip folder and are emailed to the CIRA correspondent(s) as an attachment.

The following checks are performed on the skinny format files:

- Open the CSV file and make sure the following columns exist: Id, FilterId, Sampler, ObjectiveCode, SampleDate, Status, Parameter, Value, Uncertainty, MDL, Unit, POC, ModuleTypeCode.
- In the CSV file, filter the Status column to 'UN' and review the parameters listed in the Parameter column: only PM_{10} or $PM_{2.5}$ should be listed. If non-mass parameters are listed, inform the software group to fix the issue.

- For the BYIS1 site, a value for the fAbs parameter is not reported for the routine module. To check this, filter the data in the Sampler column to 'BYIS1' and 'RT' in the ObjectiveCcode column, and select 'fAbs in the Parameter field. Review the data in the Value field and confirm values are reported as -999.
- For filters with pending analysis results, use the filter option in the CSV to select the particular filter Id from the FilterId column and confirm the values for all parameters for that filter are reported as -999 and only the 'NS' status is listed in the Status column.

The following checks are performed on the wide format files:

- Make sure the 'UN' status is only applied to the mass. This can be done by opening the CSV file and using the find and search option for 'UN'. Review the results and confirm 'UN' is only listed under the columns named PM10_flag or PM2.5_flag.
- In the CSV file, spot check the number of rows per site equals the number of sample dates in that month. For example, for the month of February, nine rows are expected. Other months are expected to have 10 or 11 rows.

9.4.2 Submission to AQS

AQS data export files are created using the *improve_export_aqs* function in the *crocker* package. To generate the AQS delivery file, run the following command in the R environment:

crocker::improve_export_aqs([YYYY], [MM], server = "production", filename = [NULL], action = ["keep"], site = ['XXXXX'], param = [NULL], del_type = ["I"])

This command will generate a formatted text file suitable for AQS delivery containing all data for the year (*[YYYY]*) and month (*[MM]*) and save to the location specified in *filename*, with the default file name and path in the format of '[aqs_path]/AQSResultsOutput_[today]_[year]_[month]_[server].txt'. A typical command for routine monthly data delivery can be run as follows:

crocker::improve_export_aqs(2020, 04, 'production')

The function has the capability to generate an AQS delivery file down to the parameter level (*param*) and/or particular site(s) (*site*). If *action* is specified as "keep", only the specified records are retained in the delivery file whereas "drop" will remove the specified records. In addition to generating delivery files to add data to the AQS database, the function can also be used to create delivery files to update or delete data within AQS by specifying the *del_type*. To display the helper documentation for the function, the user can run *?improve_export_aqs* in the R Studio console.

Once the file has been generated, various checks should be performed by running the following commands in R Studio:

- Check for existence of duplicate records:

  duplicates <- find_duplicates(aqs, c('StateCode', 'CountyCode', 'SiteID', 'POC', 'SampleStartDate', 'AQSParameterCode', 'AQSMethodCode'))

- Check the number of unique parameters:

  if(count(unique(aqs[c("AQSParameterCode")])) == 45) {print('ok')}

- Check for existence of records with null values and no null code:

  noVal.null <- aqs%>% dplyr::filter(Value == "" & NullCode == "")

- Check for existence of records with non-null values and a null code:

  null.noData <- aqs%>% dplyr::filter(NullCode != "" & Value != "")

- Check for existence of records with a qualifier validity flag and a null code:

  null.noData <- aqs%>% dplyr::filter(NullCode != "" & Qualifier1 != "")

In addition to checking the data file for issues that would result in a failed AQS delivery, the validator also reviews the data further to obtain information on the data set as a whole. The validator can compare this with similar information from previous months of data to determine if the current month of data is reasonable or if there is an unexpectedly large increase in the number of invalid records, for example.

- Count the number of records with a null value and null code:

  noData <- aqs%>% dplyr::filter(NullCode != "" & Value == "")

- Count the number of invalid and valid records:

  no.Nulls <- aqs%>% dplyr::group_by(NullCode)%>% dplyr::summarise(n_nulls = n())%>% dplyr::arrange(n_nulls)

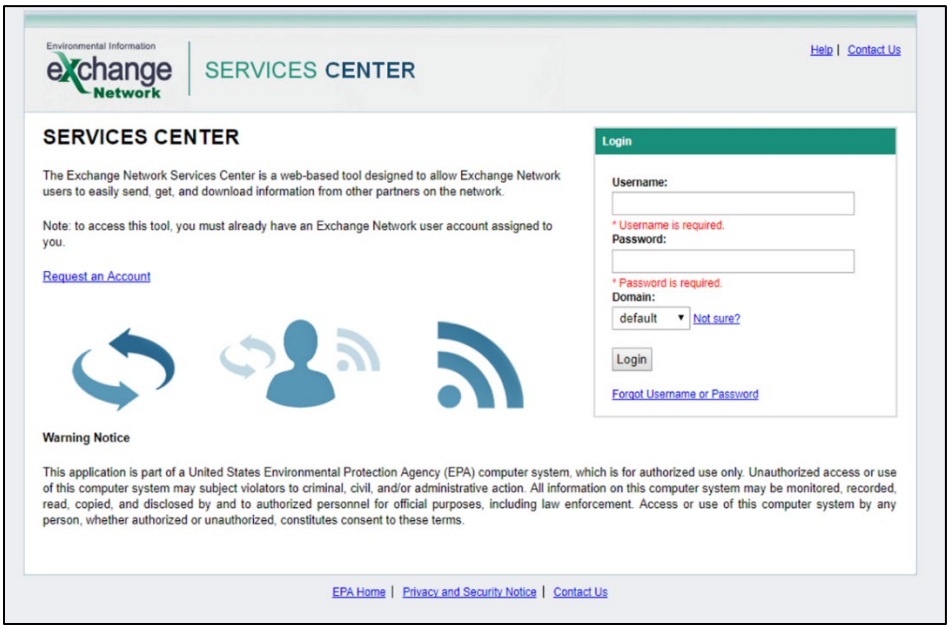
  For each dataset, the data validator keeps a record of the null codes reported and the number of records with each null code to put each month into context with previous months of data.

  - After running the command above, the validator can confirm the total number of invalid and valid records in the file matches the total number of records in the dataset by running the following command: *print(sum(no.Nulls$n_nulls))*
  - Further, the number of invalid records (those with a null code) can be counted and compared with the results from the check for existence of records with non-null values and a null code:

    no.Nulls.total <- no.Nulls%>% dplyr::filter(NullCode != "")
    print(sum(no.Nulls.total$n_nulls))

Once the checks have been completed, the data can be delivered to AQS. To submit batch data files to AQS, open a web browser and navigate to the EPA Exchange Network Services website, https://enservices.epa.gov/login.aspx (Figure 23). Use credentials to login.

Figure 23. Login screen for the EPA's Exchange Network Services Center website.

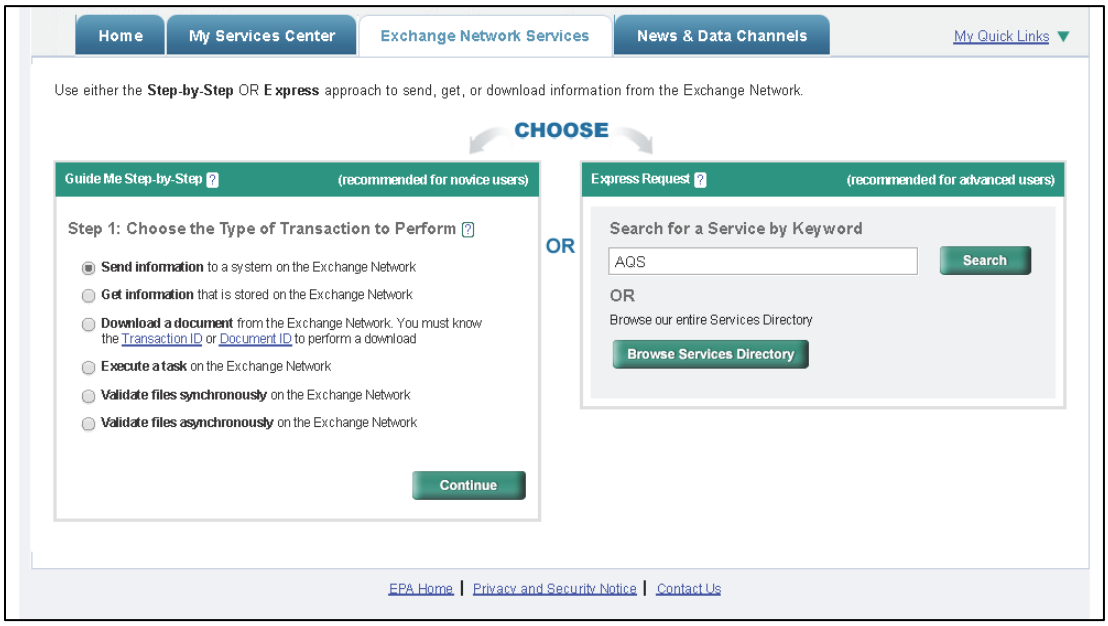


Following login, the home screen is accessed (Figure 24). For efficiency, add the AQS service to the home screen **My Quick Links** bar; however, it is also possible to search for the AQS submission form. To search, use the **Go** button of the **Exchange Network Services** bar.

Figure 24. Home screen of the Exchange Network Services Center website.

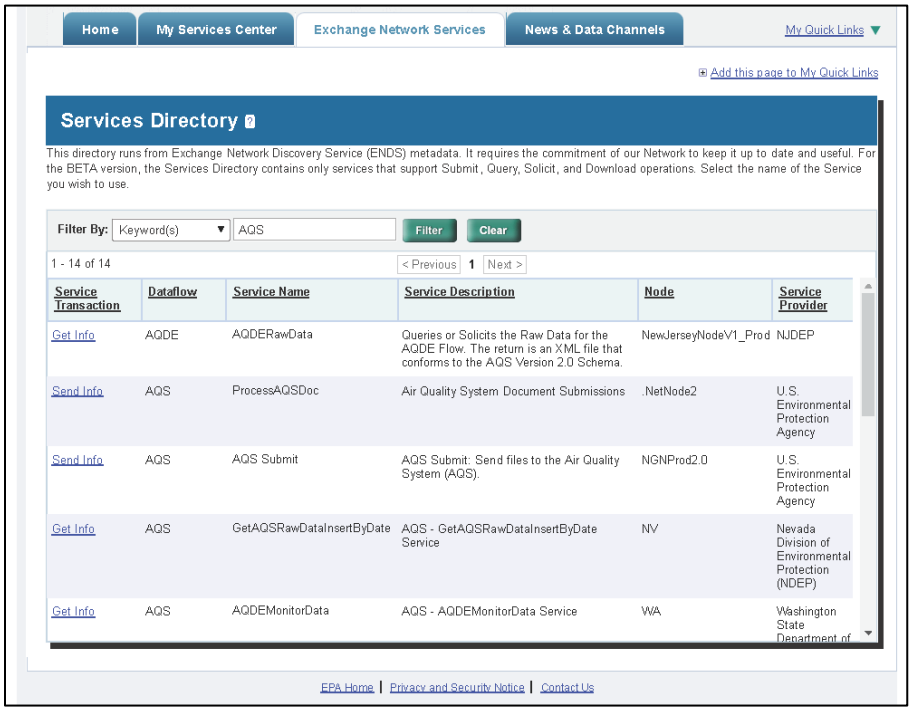
Next, the option for a step-by-step guide and a search bar presented (Figure 25); type **AQS** into the search bar.

Figure 25. Type AQS into the search bar.



The search results will show all available processes associated with the AQS system (Figure 26). To access the AQS submission form, choose the service that has **AQS Submit** specified in the **Service Name** field (usually the third option listed).

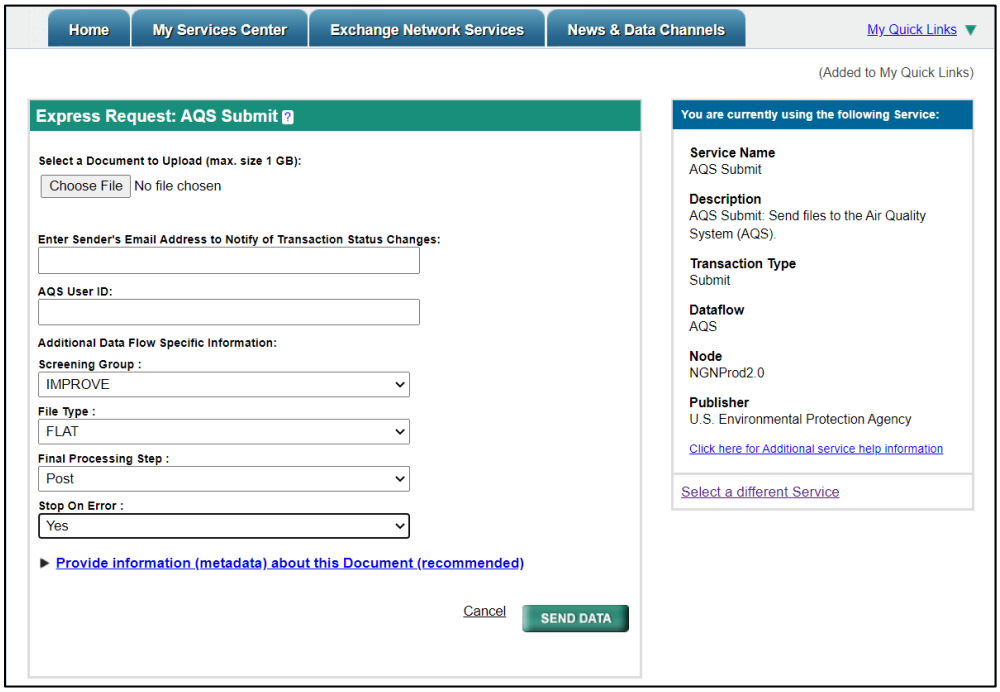
Figure 26. Select the service named **AQS Submit**.



Fill out the submission form, specifying email address, AQS user ID, screening group (IMPROVE), the file type (FLAT), the final processing step (POST), and whether to stop on

errors (YES). See Figure 27 for an example. Use the **Choose File** button to select the file generated from the previous step. Press the **SEND DATA** button to submit the form. Monitor progress of the data submission through the web portal.

Figure 27. AQS data submission form.

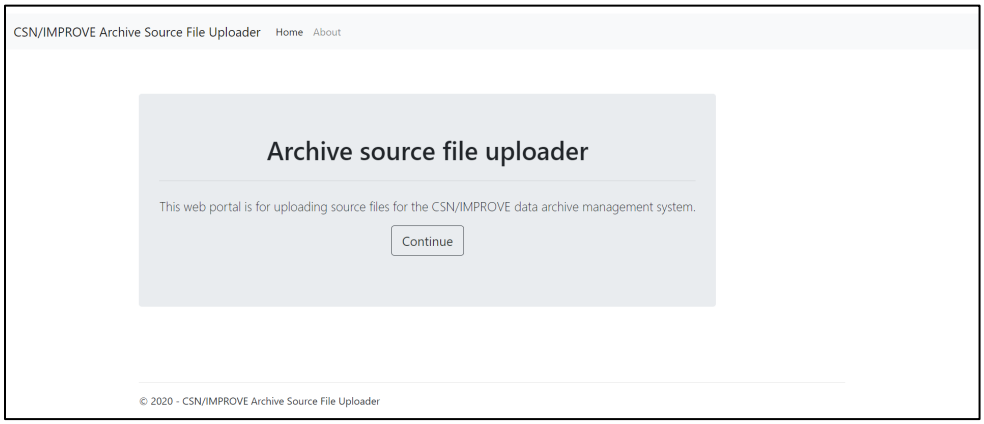


9.4.3 Submission to UCD CIA

The CSN/IMPROVE Archive (CIA) is a database of the complete record of CSN and IMPROVE data coupled with a web-based visualization and analysis tool.

1. Open a web browser and navigate to the UCD CIA submission website, https://cia-uploadportal.azurewebsites.net/ (Figure 28).

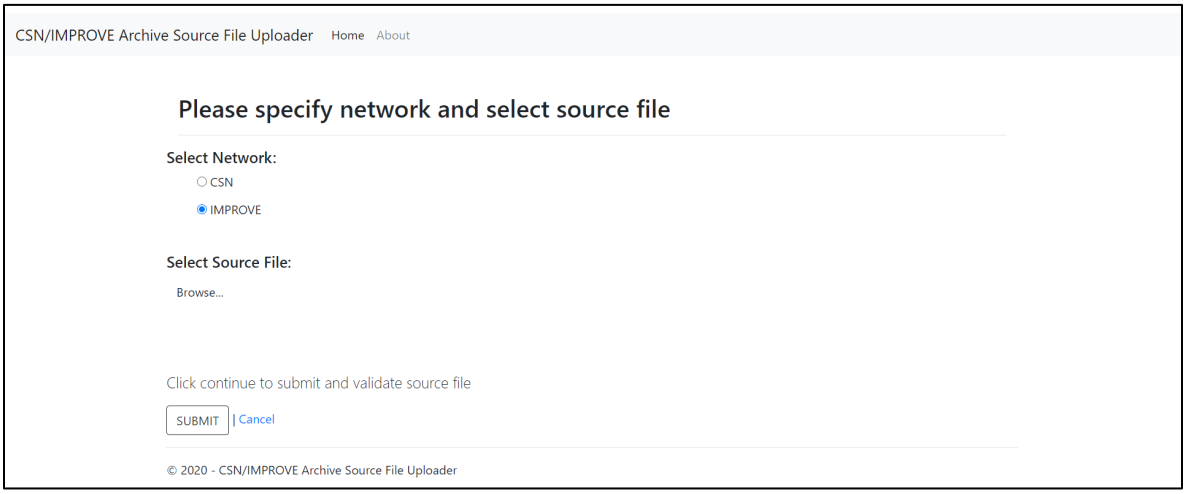
Figure 28. UCD CIA submission website home page.



2. Click the **Continue** button in the center of the page.

3. Specify the network of choice that you will be delivering the data for, which in this case is **IMPROVE**. See Figure 29 for an example.

Figure 29. UCD CIA data submission details page.



4. Click **Browse** and select the file generated/submitted successfully to AQS.
5. Once the file is selected, click **Submit**; the next page will indicate if the submission was successful.

9.5 Quarterly Field Status Report

A field status report is generated quarterly to report on the status of all samples collected across the network for the previous quarter. Site status is evaluated relative to the regional haze rule criteria. The following information outlines the steps to generate the report and the checks to perform before delivery.

1. First, process flow data. Use the SQL execution code detailed in section 9.2 and process flows for the relevant date range to be covered in the quarterly field status report by changing the Start Date and End Date fields. If successful, a date/time of completion will show in the window. If the execution code fails, evaluate the warning message and work with the Software & Analysis Group and/or Sample Handling Laboratory to identify the issue and resolve. Processing flows at this point ensures the most up-to-date flow data and subsequent statuses are reported.
2. Create the report spreadsheet:
   - For the first quarter of a new year, save a copy of the template report under another name, with the format of *IMPROVE Status Report YYYY Q#*. The template report is located at U:\IMPROVE\Status Reports\Status_Report_Template.xlsx.
   - For the second, third, or fourth quarter, find the last report and save it under a name indicating the relevant quarter number. Previous reports are located at U:\IMPROVE\Status Reports\Reports
   - In the report there are four tabs:
     - Site Status Report

- Status Flag Table
- Flag Definitions: available from the database,

  *SELECT **

  FROM [Improve_2.1].[filter].[Statuses]

- Sampler Locations: Determine if any sites are new, re-started, or have stopped during the relevant quarter by reviewing the date information in the *[Improve_2.1].[sampler].[Samplers]* and *[Improve_2.1].[module].[Modules]* tables in the production database. The *sampler.Samplers* table gives the site installation date, while the *module.*Modules table lists the first sampling date.

3. Populate the report:

- From the IMPROVE Status page (https://shiny.aqrc.ucdavis.edu/ImproveStatus/), access the Network Status and Network Timeline tabs
  - The Network Status tab provides a count of the different statuses used per site, the total number of terminal statuses, which quarter they occur in, the percent complete by quarter, and the number of consecutive invalid statuses.
    - Change the Year and Ending Quarter fields to align with the reporting period.
    - Download the full table by clicking on the 'Download' button. A .csv file is downloaded.
    - Compare the columns in the Site Status Report tab to the content of the downloaded spreadsheet; add new columns to the Site Status Report tab as needed.
    - Compare the sampler details in the Site Status Report tab to the content of the downloaded spreadsheet; add sampler details to or remove sampler details from the Site Status Report tab as needed.
    - Confirm that included flags are allowed (for example, the RF flag is no longer used). Investigate cases where unallowed flags are applied; work with the Sample Handling Laboratory to resolve.
    - Add the flag, definition, and result to the Flag Definitions tab of the report spreadsheet if not already listed.
    - Copy/paste content from the downloaded spreadsheet to the Site Status Report tab.
    - Color the relevant fields:
      - Percent Complete by Quarter:

        < 75%, yellow
        < 50%, red

      - Consecutive Terminal Samples:

        > 7, yellow
        > 10, red

      - Annual Completeness:

        < 75%, red

Note that the Annual Completeness column should only be colored for the fourth quarter (Q4) report. Report uncolored values for the first, second, and third quarter reports.

- Check formatting for consistency, including font style and type, coloring and shading.
- Consecutive Terminal Samples may require merged cells in order to report a single number per row. Select all the cells to be merged; navigate to the MS Office Home tab and select Merge Across (drop down menu by Merge and Center); click okay for each row for the cells highlighted.
- Update the date and quarter details at the top of the Site Status Report tab.

- The Network Timeline documents the most severe filter status for each site and date. For this report, exclude the flow status; flow validation often results in changes to status and is performed after this report is generated.
  - Change the Year to be relevant.
  - Do a search for NF statuses. If any NF statuses are found, process the flows again using the SQL execution code. If the NF statuses are for the most recent quarterly period, run the code in SQL, changing the Start Date and End Date fields accordingly; if successful, a date/time of completion will show in the window:

    If the NF statuses are for a small set of filters/sites/dates, confirm why this is the case and edit the above code above to run on the specified filter, date range, and/or site.

  - Do a search for no statuses. For sites with no statuses, determine if it is a new site or if there is a reason such as paused shipments or the site temporarily offline.
    If the site is new, there may be blank records prior to the start date; if so, leave as-is but make sure the site is not falsely reported as failing the Regional Haze Rule criteria.
    If shipments are paused, work with the Software & Analysis Group and Sample Handling Laboratory; records may need to be added and/or the OL status may need to be manually inserted.

  - If no NF or blank statuses are found, the data can be downloaded to be included in the report. There is a checkbox option defaulted to include the collocated module data on the network timeline page. As the Network Status page does not include statuses of filters from collocated modules, the data downloaded from the Network Timeline page should also only use filter statuses from routine modules. To do this, unselect the 'Include collocated modules' option and download the data by clicking on the 'Download' button. The default name of the downloaded .csv filter is 'IMPROVE_network_timeline.csv'. As the PHOE5 site is a collocated site with all four modules, it is considered an independent site in the Network Status table. To include the data from this site in the quarterly report, re-select the 'Include collocated modules' option and download the file by clicking on the 'Download' button. The file name is 'IMPROVE_network_timeline_cl.csv'. Copy the line containing the PHOE5

information from this file and paste/insert it into the IMPROVE_network_timeline.csv file in the row under PHOE1.
    - Compare the site list from the IMPROVE_network _timeline.csv with the sites listed in the Sampler Locations and Status Flag Table tabs in the Site Status Report tab. Update site and date information as needed after confirming with the Lead QA Officer; some sites are for special studies and are not included in this report.
    - Copy/paste all content from the IMPROVE_network_timeline.csv to the Status Flag Table tab.
    - Color the relevant fields:
        - QD flags, yellow
        - Null/terminal flags, red
4. Perform checks prior to delivery:
    - Verify that the color coding is correctly assigned.
    - Status Flag Table tab: Look for blocks of red (invalid) and SO flags. Investigate using JIRA and/or follow up with the Sample Handling Laboratory.
    - Status Flag Table tab: Spot check to ensure that the number of terminal flags is corresponding to those reported in the Site Status Report tab.
    - Status Flag Table tab: Confirm that the sites listed are also shown in the Site Status Report tab and the Sampler Locations tab.
    - Flag Definitions tab: Confirm that the formatting and color coding is correct.
    - Sampler Locations tab: Confirm that new sites have been added.
5. Send to the Data & Reporting Group Manager for review.
6. Once reviewed and approved, the Data & Reporting Group Manager will deliver to various personnel including IMPROVE site operators, NPS, and EPA staff via email. A summary of site losses is to be included in the body of the email.

9.6 Adding AQS Site Information

Whenever a new site starts within the network and the data will be delivered routinely to AQS, both the UCD database is to be updated with AQS related information and the AQS database is to be updated to add the new site and its associated monitors (where monitors are the AQS term for parameters). The site details should also be sent to NPS prior to data delivery when a new site starts sampling.

9.6.1 Updating UCD Database

9.6.1.1 AQS Site ID

An AqsSiteId needs to be assigned to the new site in the sampler.Samplers table in the UCD database (Improve_2.1), which consists of State Code, County Code, and Site Id. Further information can be found in sections 3.2.3-3.2.5 of the AQS Data Coding Manual (https://www.epa.gov/sites/production/files/2015-09/documents/aqs_data_coding_manual_0.pdf). If the state and county where the site is located are known, then the associated codes can be found by searching FIPS online (Federal Information Processing Standards/Series, e.g.

https://geonames.usgs.gov/apex/f?p=138:1:::NO:1:P1_SHOW_FIPS55,P1_SHOW_ADV,P1_SHOW_ANTAR:Y,,). The user should query the AQS database to determine if a site already exists at the same location. To do this, the user should follow these steps:

- Log into the AQS application
- Select the Read Only User option (Figure 30)
- Go to Maintain
- Select Monitor (Figure 31)
- Type in the State Code and County Code
- Click on the 'Execute Query' button.

Figure 30. AQS screen after logging into the application; select the Read Only User option.

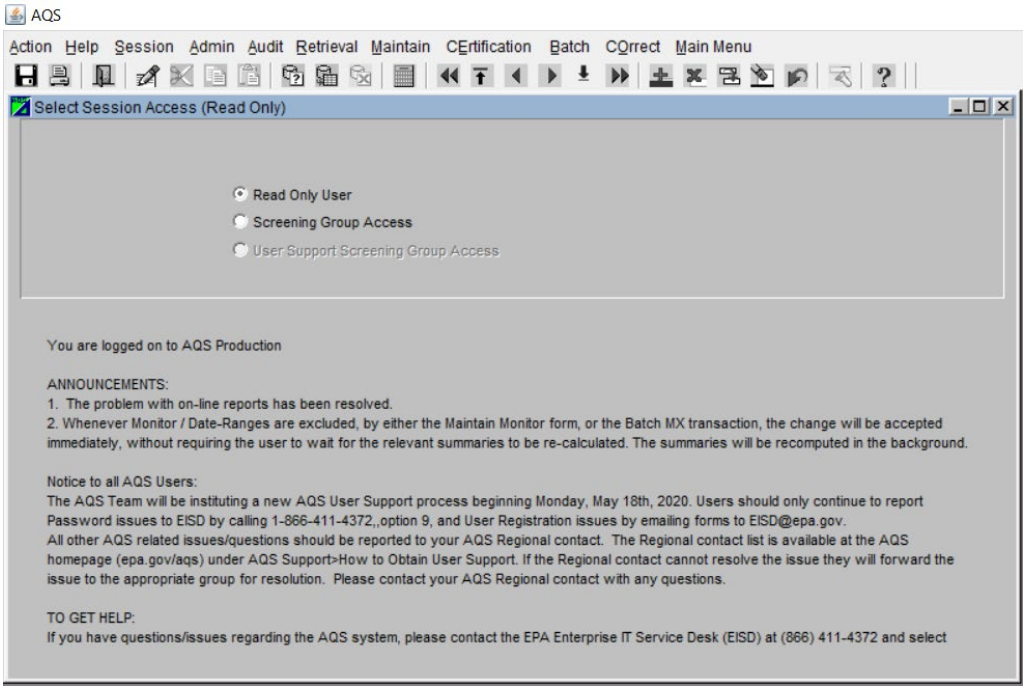
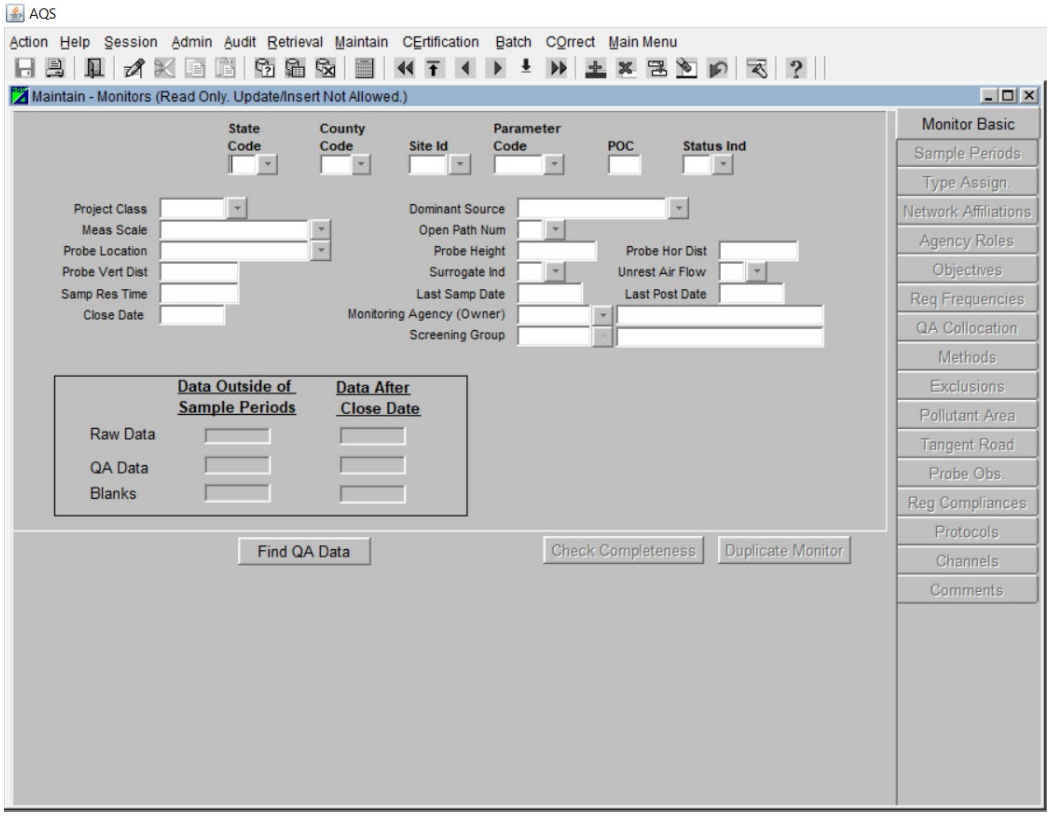


Figure 31. AQS screen after selecting **Monitor** from the Maintain option.



The site does not already exist in AQS if no results are returned. If any results are returned, the user should review the details to confirm if the parameter code and/or the POC is one that is reported as part of the IMPROVE network. By convention, if the site does not already exist in AQS, the Site Id assigned is '9000'. The user should repeat the steps above to include the Site Id of '9000' and executing the query again to confirm the site and/or monitors does not already exist.

Once the State Code, County Code, and Site Id are known, the UCD database can be updated as follows:

- Query the database using the following SQL query to find the relevant site record, where 'XXXX#' represents the four-character site name plus the number, typically 1.

  *SELECT **

  FROM [Improve_2.1].[sampler].[Samplers]

  WHERE Name = 'XXXX#'

- Update this site record with the newly generated AQS site ID, a nine-digit ID comprising the State Code, County Code, and Site ID, with no separation.

  UPDATE [Improve_2.1].[sampler].[Samplers]

  SET AqsSiteId = '#########'

  WHERE Name = 'XXXX#'

9.6.1.2 AQS Parameters and POCs

In addition to updating the Samplers table in the database with the AQS site ID, POCs (Parameter Occurrence Code) need to be added to the analysis.AqsPOCs table. In AQS, POCs are assigned per parameter. If there was no existing site in AQS, POC = 1 for all parameters, except for the coarse mass parameter (PM10-PM2.5), which is assigned POC = 5 by convention. If there are existing collocated sites in AQS, the next smallest different number is to be used, e.g. POC = 2.

To add the parameters and POCs to the database, specifically the *analysis.AqsPOCs* table, a SQL insert query can be written using the starting format below where each set of values is for a different parameter:

INSERT INTO [Improve_2.1].[analysis].[AqsPOCs] (SamplerName, ObjectiveCode, Parameter, POC)

Values (SamplerNameX, ObjectiveCodeX, ParameterX, POCX), (SamplerNameX, ObjectiveCodeX, ParameterY, POCX), …

Alternatively, to add to the database in bulk, an R script can be written and used, ensuring that the outputs from each step of the script is reviewing along the way.

9.6.2 Adding Site and Monitors to AQS

9.6.2.1 Adding a New Site to AQS

To add a new site to AQS the user should follow the steps below:

- Log into the AQS application
- Select the IMPROVE Screening Group Access option (Figure 32)
- Go to Maintain
- Select Site
- Click ‘Cancel Query’ (Figure 33).
  - This allows the user to click on the ‘Check Validity’ button at the bottom of the window once various details have been entered.

Figure 32. AQS screen after logging into the application; select the Screening Group Access option and then IMPROVE.

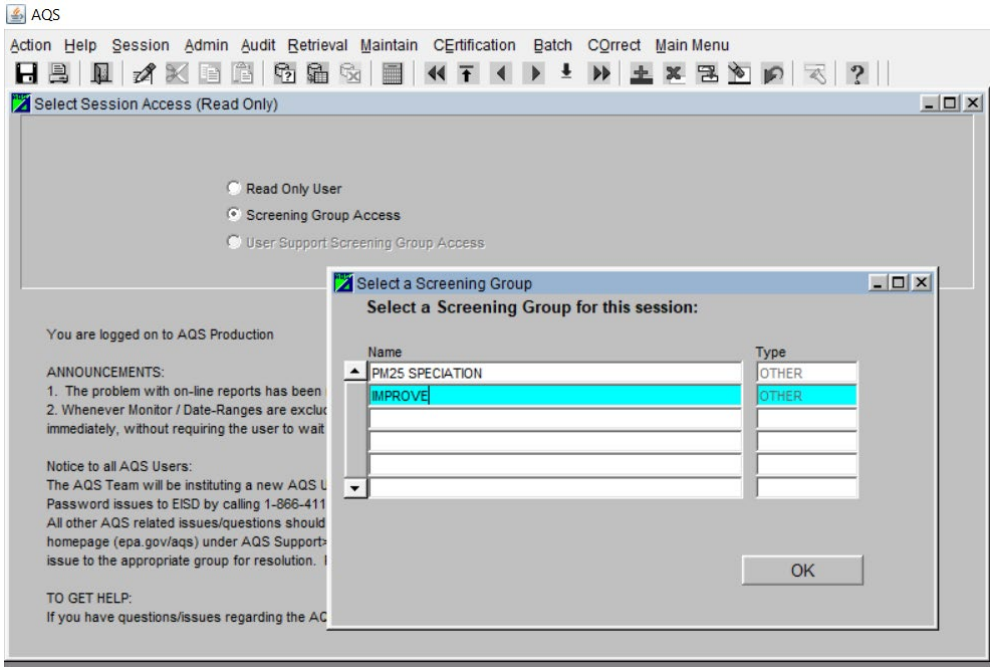
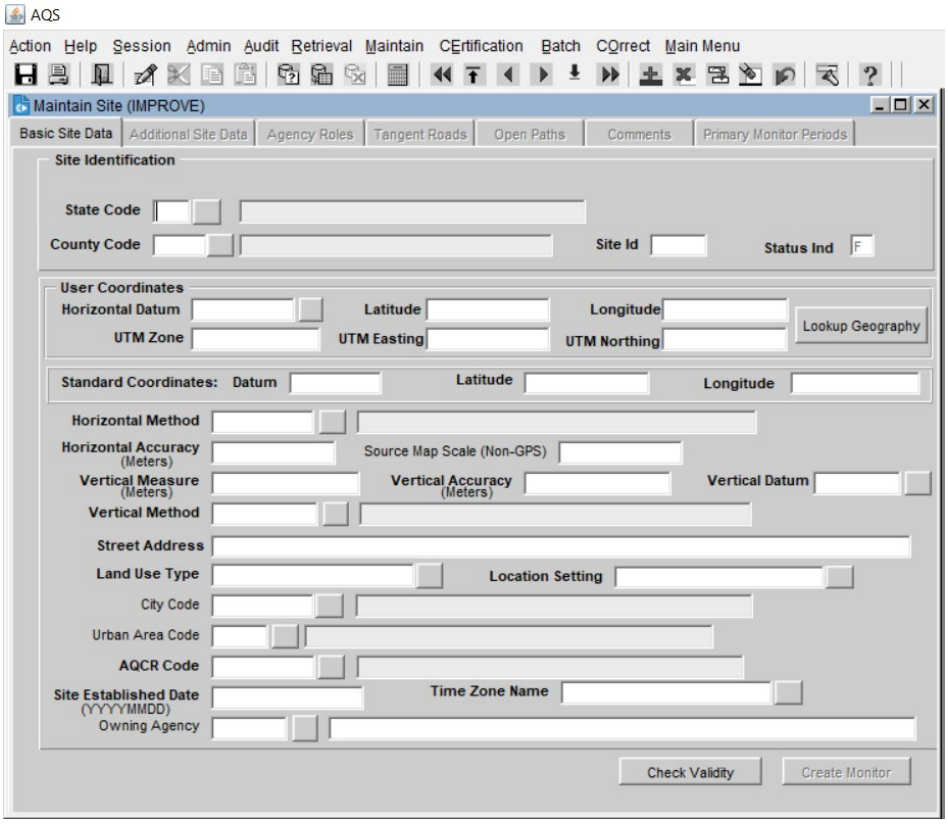


Figure 33. AQS screen after selecting **Site** from the Maintain option and clicking **Cancel Query**.

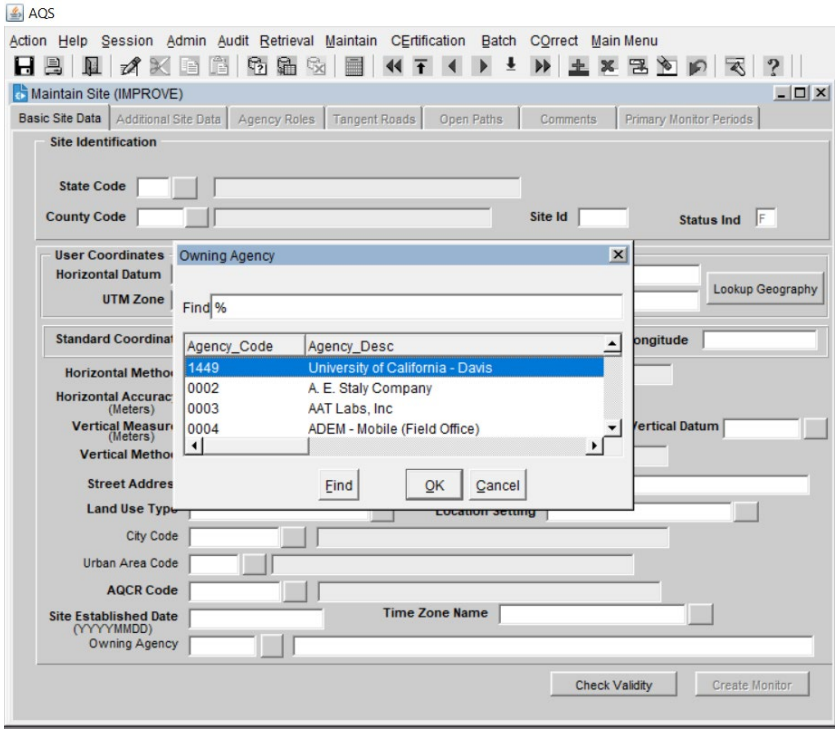


The fields to be completed are detailed below:

- Site Identification
    - The State Code, County Code and Site Id should all be known from the previous section. Enter the codes; the associated names will fill automatically.
- User Coordinates
    - Horizontal Datum: WGS84 (by convention).
    - Latitude and Longitude: find in the IMPROVE Data page, under Sites, select the relevant site.
    - Horizonal Method: 103 (by convention).
    - Horizontal Accuracy: 5 (by convention).
    - Source Map Scale (Non-GPS): 10000 (by convention)
    - Vertical Measures: Site elevation; find in the IMPROVE Data page, under Sites, select the relevant site.
    - Vertical Accuracy: 5 (by convention).
    - Vertical Datum: NAVD88 (by convention).
    - Vertical Method: 001 (by convention).
    - Street Address: If not already known, the site operator may have to be contacted to obtain this information.
    - Land Use Type: If not already known, the site operator may have to be contacted to obtain this information. Options for this field are: Residential, Commercial, Industrial, Agricultural, Forest, Desert, Mobile, Blighted Areas, Military Reservation.
    - Location Setting: If not already known, the site operator may have to be contacted to obtain this information. Options for this field are: Urban and center city, Suburban, Rural.
    - AQCR Code: Use the drop-down menu, select the code listed; there should only be one.
    - Site Established Date: Find in the sampler.Samplers table in the UCD database.
    - Time Zone Name: Use the drop-down menu, select the option listed.

Owning Agency: If not already known, the site operator may have to be contacted to obtain this information. To search for the agency and obtain the relevant agency code, use the drop-down menu and in the ‘Find’ box, type in the details of the agency (Figure 34) and select the appropriate affiliation from the returned results.

Figure 34. AQS screen when searching for Owning Agency details.



Once all the fields have been entered, the user should click 'Check Validity' at the bottom of the screen. A 'Row_Errors' window may appear with Error Descriptions left blank. If not blank, the user should return to the Site's window and correct the errors. Upon completion, the details are saved by clicking on the save button at the top right of the AQS window (under 'Action'). Follow any additional prompts, e.g. click 'Lookup Geography', and save again.

For confirmation the site is saved, the user should navigate to a fresh Maintain Site window, enter the State Code, County Code, and Site Id and execute query. The full site details should be displayed and the Status Ind should have changed from 'F' to 'P', meaning the site is now in production.

9.6.2.2 Adding Monitors to AQS

In addition to opening the parent site, the monitors (parameters) need to be opened. There are two methods for adding monitors: Batch processing (preferred because of high efficiency) and manually adding monitors, one at a time.

For batch processing, the user should follow these steps:

- Navigate to the template text file, monitor_template.txt, at U:\IMPROVE\AQS\AQS_Documentation.
- Save this as a new file, with a file name that indicates which site it is for.
- Update the State Code, County Code, Site Id, and POC, if necessary by performing a 'Find and Replace' in Notepad (or other application).

- If this is a new site, then the only date in the file should be updated to be the site start date. If the site is being closed, then an end date needs to be added as well (this field is currently blank in the template).
- Navigate to the Exchange Network website and submit the file in the same way that raw data is delivered as described in section 9.4.2.

To add monitors manually, one at a time, the user should follow these steps:

- After adding the site to AQS as detailed in section 9.6.2.1, the user should ensure they are in the IMPROVE Screening Group Access session and navigate to the Maintain Monitors window (Figure 31).

The following details the information that must be added to each specified tab to open a parameter (monitor):

- Monitor Basic: enter State Code, County Code, Site Id, Parameter Code, and POC for the parameter that is being opened.
- Sample Period: enter the date used for 'Site Established Date' when creating the site in the 'Begin Date' field.
- Type Assign: enter 'EPA' as the Monitor Type and Begin Date is the same date as the Site Established Date.
- Network Affiliations: enter 'IMPROVE' for the Monitor Network Code and the Begin Date.
- Agency Roles: enter a row each for Agency roles of ANALYZING, COLLECTING, REPORTING and PQAO, list the Agency Code as '0745', and the Begin Date. If the Site Established Date is before 2007-01-01, the Begin Date should be entered as '20070101'.
- Objectives: select 'GENERAL/BACKGROUND and enter '0000' for the UA Represented field.

The user should save the entry and confirm that the 'Status Ind' in the Monitor Basic tab is 'P'. To add more monitors for the same site, the user should click on the 'Duplicate Monitor' option at the bottom of the Monitor Basic tab and enter the appropriate parameter code details. The user should follow these steps until all relevant monitors are opened.

9.6.3 Updating NPS

The NPS needs to have the site details for any new site that starts sampling in advance of data delivery. The NPS requires the following information be sent:

- Site Name
- State
- County
- AQS Code
- Latitude
- Longitude
- Elevation

- Start Date
- End Date (assumed to be blank at present)
- Sponsor/Agency
- Location Description
- Rural or Urban (or other demographic code)
- Land Use code, if any
- Photos of the site.

9.6.4 Updating UCD-CIA Database

Whenever a new sampler is added, the sites table in the UCD-CIA database needs to be updated. The request should be directed to the software group. The software group uses the EPA's master AQS site list to add information to the database. If a new sampler is not added to the UCD-CIA database prior to data submission, the data will stage but will not migrate. Once the relevant sampler information is added to the database, the staged data will successfully be posted to the UCD-CIA database when the SQL query to migrate data is next run (typically every night).

9.7 Miscellaneous Tasks

9.7.1 Box Creation

Occasionally the box sent to the site by the sample handling lab is lost either before it reaches the site or after sampling and before being received back at the sample handling lab at UCD. For boxes that are lost prior to sampling, a replacement box is created and sent to the site as soon as the sample handling lab is alerted to the lost box. If the Data & Reporting group are requested to assist in the creation of a new/replacement box, the following tool can be used: https://improve.aqrc.ucdavis.edu/Operations/BoxSchedules, which can be accessed by going to the IMPROVE Management Site, selecting the 'Operations' tab and the sub-tab of 'Schedule'. To create a box the following steps should be taken:

1. Go to the Box Schedules page and select the site via the drop-down menu next to 'Sampler' for which the new box is needed. Click on the 'Go' button to the right (Figure 35).
2. Scroll to the bottom of the page and click on the 'Add New Box' (Figure 35) button on the left.
3. This will lead to a 'Create Box' page. Enter the relevant date in the 'InstallDate' option and click 'Create'.
4. Select 'Add New Cartridge' and on the 'Create Cartridge' page that is subsequently opened, various cartridge information can be added including Sampler Module ID (e.g., 1A, 2B, 3C, 4D), Install Date (this is the cartridge install date and can be found in the IMPROVE calendar), and Schedule Week (i.e., Week 1, Week2, or Week 3). An example of install dates and schedule weeks is as follows: next upcoming box install date is on 04/20. The week 1 installment is 04/20, week 2 is 04/27, and week 3 is 05/04. The cartridge installment is always on a Tuesday regardless of it being a 2-

3-2 or 3-2-2 box. Figure 36 shows an example of a Cartridge that is ready to be created. Once all relevant and required information is added, click on 'Create'.

Figure 35. Box creation page.

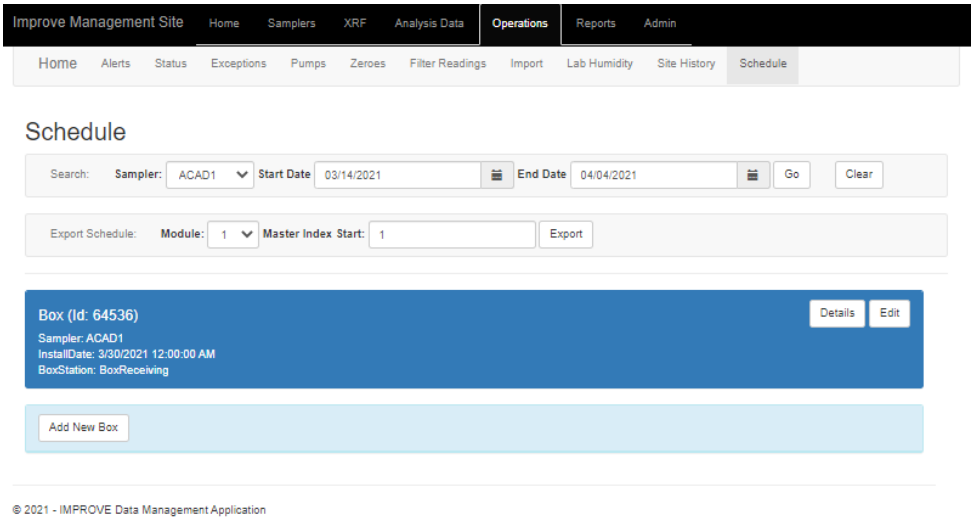
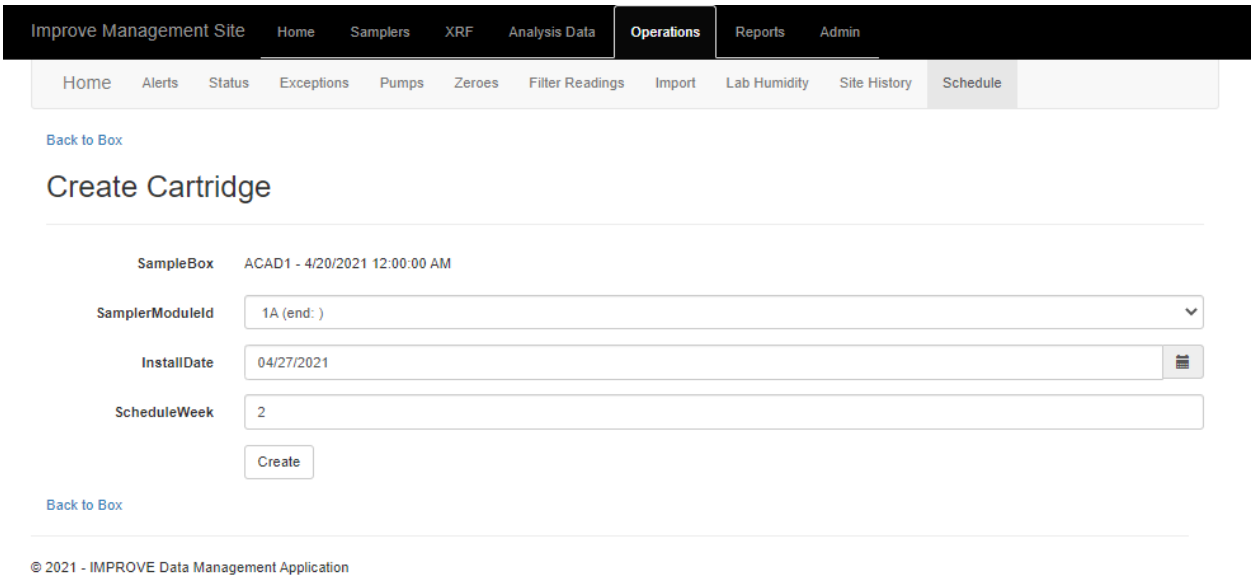


Figure 36. Cartridge creation page.



5. Once the cartridge is added, individual filters can then be added, one-by-one, using the Add Filter feature on the page loaded after creating the cartridge. After clicking on 'Add Filter', the 'Create Filter' page is loaded. Every filter added requires the following information to be added: Cartridge Position (1, 2, or 3), Sample Date, Quarter Position (which can be found from the details of the lost box), Lot ID, and an indicator for whether it is a Moveable Cassette ('o-ring'). For the 2-3-2 boxes the Moveable Cassette will always be the third position of the second week. For the 3-2-2

boxes the Moveable Cassette will always be the third position of the first week. All four modules will have the Moveable Cassette on the same date (position); as the cartridges are cloned, this information will automatically be transferred. Once all information for a single filter is filled, click on the 'Create' button at the bottom of the page. A summary of the added filter is then displayed (Figure 37).

6. To add more filters, click 'Add Filter' at the bottom of the summary information. Repeat the instruction from step 5 to add the filter information. The number of filters to be added depends on whether it is a three- or two-position week. The box schedule can be found under the Cartridge Id details (near Module details; Figure 37). For a three-position week, three filters will need to be added and for a two-position week, two filters will need to be added.

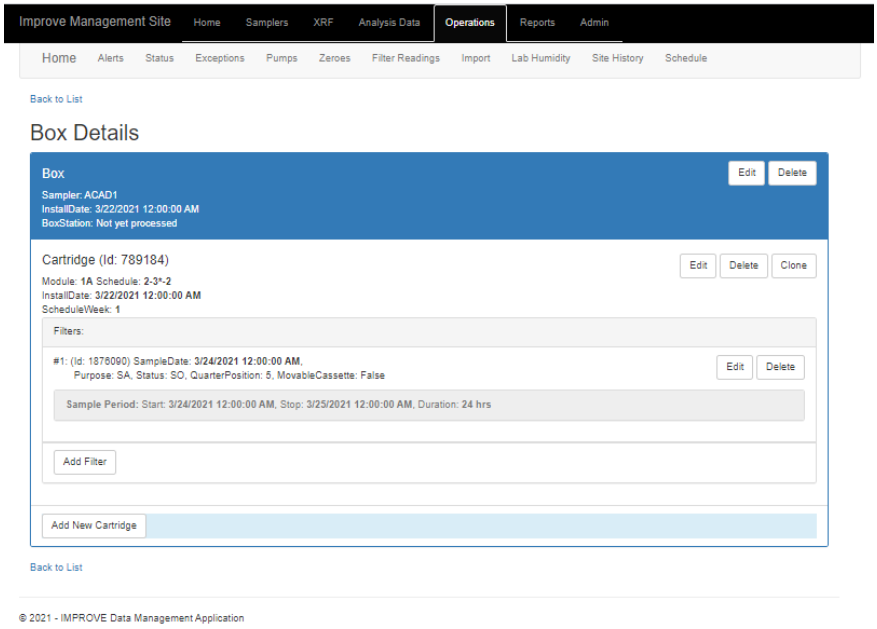
7. Once a cartridge is created and all relevant filters have been added, the cartridge can be cloned to create cartridges for other modules by clicking the 'Clone' button to the right of the cartridge information on the Box Details page (Figure 37). The user should select the relevant Destination Module and Destination Lot from the drop-down menus and click 'Create'.

8. Repeat steps 4-7 to create the cartridges for the second and third week.

9. Once the entire box has been created, the box details are to be send to the sample handling lab to add filter pre-weights and filter barcodes for the PTFE filters. Make sure the current lab station Id (as described in section 9.7.2) is set to 2 so the sample handling lab can assign the pre-weights accordingly. If the box was created in place of a lost box, please proceed to section 9.7.2 for further actions that need to be taken.

10. If an item needs editing or deleting at any point of the box creation, the edit/delete options on the right-hand side can be used accordingly (Figure 37). To delete a box, all cartridges must first be deleted. To delete a cartridge, all filters within the cartridge must first be deleted.

Figure 37. Box creation page; after addition of filter.



9.7.2 Changing Current Lab Station ID and Assigning UF

When a replacement box is created in the case when boxes are lost prior to sampling, there are several additional steps to be performed to correctly assign data and other information to both the new box and lost box.

- For the new box, the sample handling lab assigns filter pre-weights. The current lab station of the box needs to be PreWeigh (Station ID = 2) to enable the sample handling lab to assign the weights. If the current lab station is not PreWeigh, it can be changed by running the following SQL update query in the UCD database, where *NewBoxID* is the ID of the newly created box:

  UPDATE [Improve_2.1].[filter].[SampleBoxes]

  SET CurrentLabStationId = 2

  WHERE Id = NewBoxID

  Check the update was successful by performing a SQL select query e.g.:

  *SELECT **

  FROM [Improve_2.1].[filter].[SampleBoxes]

  WHERE Id = NewBoxID

- For the lost box, the current lab station needs to be updated to Finished (Station ID = 9). To do this, run the following SQL update query in the UCD database, where *LostBoxId* is the ID of the lost box:

  UPDATE [Improve_2.1].[filter].[SampleBoxes]

SET CurrentLabStationId = 9

WHERE Id = LostBoxId

To check the update was successful, perform a SQL select query e.g.:

*SELECT **

FROM [Improve_2.1].[filter].[SampleBoxes]

WHERE Id = LostBoxID

- For the filters in the lost box, the filter purposes are to be updated to UF (Unused/Lost Filter (Filter Purpose ID = 16) and can be updated using the following SQL update query, where *LostBoxId* is the ID of the lost box:

  UPDATE f

  SET f.FilterPurposeId = 16

  FROM [Improve_2.1].[filter].[Filters] f

  LEFT JOIN [Improve_2.1].[filter].[SampleCartridges] sc ON sc.Id = f.SampleCartridgeId

  WHERE sc.SampleBoxId = LostBoxID

  After updating the filter purpose, review and confirm the filter purpose Id for the whole box is correct by running the following query.

  *SELECT **

  FROM [Improve_2.1].[filter].[Filters] f

  LEFT JOIN [Improve_2.1].[filter].[SampleCartridges] sc ON sc.Id = f.SampleCartridgeId

  WHERE sc.SampleBoxId =BoxID

10. DATA AND RECORDS MANAGEMENT

The IMPROVE data are stored in Microsoft SQL Server Databases at UC Davis. The production database is run on a dedicated Windows Server with a RAID array for storage and with offsite backups. Our development and test database environments are virtual machines. To test back up recovery, our development and testing environments are regularly restored from the production backups.

Data management is handled through custom software that interfaces with the UCD IMPROVE database. The primary applications for data ingest and management were developed on the .NET platform. Data processing and calculations were developed as R software packages. In addition, to support data validation and operational monitoring, several interactive visualizations have been developed using the R Shiny platform.

10.1 Disaster Recovery Plan

The scope of recovery activities will depend on the nature of the disaster. Response to an actual disaster may require implementing multiple sections of this SOP.

10.1.1 Facility Recovery

Private security services patrol the laboratory building on a regular basis (including nights, weekends, and holidays). In addition, campus facilities and maintenance staff are on call at all times.

Databases, file servers, and web server virtual and dedicated machines operate primarily out of the Metro IT data center in Hoagland Hall on the UCD campus. Metro IT has a highly-available, disaster recoverable virtualization environment. Weekly backups of the virtual hard drives are taken offsite and stored in the Campus Data Center. In the event of a disaster in Hoagland, critical machines will be mounted at the Campus Data Center. The Drew Avenue laboratory is directly connected to the main campus internet. In the event that connection is disrupted (such as through a construction accident), connections will be switched to a local backup server until service can be restored.

10.1.2 Hardware Recovery Plan

The campus network of IT Administrator staff allows for rapid response to server failure and recovery issues.

10.1.3 Software and Data Recovery Plan

10.1.3.1 UCD Laboratories

Raw and processed analysis data produced with the UCD laboratories are saved and available for use at any time on the computers associated with each instrument, including the PANalytical Epsilon 5 EDXRF, MTL Automated Weighing System (gravimetric mass), Hybrid Integrating Plate and Sphere (HIPS).

Operational flow rate information from samplers in the field is automatically transferred nightly to a file processing server. As a backup, the flow data are stored on SD cards and delivered to the sample handling lab along with the exposed filters.

Data from all analyses, along with the flows, are scheduled to automatically transfer to a central Microsoft SQL Server database located at a data center on the UCD campus. Differential backups are performed daily, and full backups are performed weekly.

10.1.4 Data Security

UCD access policies: Access to databases and computers associated with this project is limited to authorized project personnel by use of access control lists for files, programs, and database access. Access to laboratory and office space is controlled by keycards.
Password policies: Unique passwords are issued to each employee by the UCD campus system administrator. Password integrity is monitored by the UCD campus system administrator.

Termination policies: System access is revoked for terminated personnel. The IT Administrator disables domain accounts and passwords upon termination of employment. **Virus protection:** Microsoft Endpoint Protection is used for virus scanning and protection. All staff are required to complete annual cyber security awareness training.

11. QUALITY ASSURANCE AND QUALITY CONTROL

11.1 Code Development

Software for data management, processing, and validation is developed in-house by professional software engineers. Source code is managed through a code repository. Development of code changes and new applications is conducted on a development environment that parallels the production environment. Prior to deployment in production, all code changes undergo testing within a separate test environment. The testing, which is conducted by developers, managers, and users, is targeted both at the identification of software bugs and the confirmation of valid data equivalent to the production system.

11.2 Bug Reporting

Software bugs and data management issues are tracked through JIRA tracking software. All UCD users have access to an internal JIRA website and can submit, track, and comment on bug reports.

11.3 Data Validation

Data integrity is enforced within the UCD IMPROVE database via unique primary keys and non-nullable records. Data completeness and data quality are thoroughly checked through the data validation process, as described elsewhere in this SOP.

12. REFERENCES

Hyslop, N.P. and White, W.H. (2008) Estimating Precision Using Duplicate Measurements. J. Air & Waste Manage. Assoc. 59:1032–1039.DOI:10.3155/1047-3289.59.9.1032.

John, W. and Reischl, G.P. (1980) A Cyclone for Size-Selective Sampling of Ambient Air, J. Air Pollut. Control Assoc., 30 (8), 872-876.

Watson, J.G.; Lioy, P.J.; Mueller, P.K. (1995). The measurement process: Precision, accuracy, and validity. In Air Sampling Instruments for Evaluation of Atmospheric Contaminants, 8th; Cohen, B. S., Hering, S. V., Eds.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 187-194.